

Crystallography of Transformation Mechanisms in Inorganic Compounds



by
Christopher Dean B.Sc.(Hons.)

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Department of Physical & Inorganic Chemistry
The University of Adelaide.
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Abstract

The objective of the project was to determine the mechanisms of solid state structural transformations in some inorganic compounds. Compounds which appeared to have potentially martensitic transformations were examined in order to test the applicability of the phenomenological theory of martensitic transformations. The techniques used were crystal growth, single crystal X-ray diffraction photography and diffractometry, optical and scanning electron microscopy and computing. The characteristic interface plane, shape change and lattice orientation relation of the transformations were studied and compared with the predictions of the phenomenological theory. Partly transformed crystals were used whenever possible as they yielded more accurate data. A computer program was written to enable the extensive comparisons between theory and experiment, and to assist with the experimental work. The lattice orientation relations determined by X-ray diffraction were a guide to the lattice correspondences and hence to the atomic movements.

The transformation in uranyl hydroxide was induced by cooling and by uniaxial stress. All crystals had essentially identical transformation characteristics and this led to a precise model for comparison with theory. Only a few of the martensitic solutions calculated for a large range of plausible slip systems agreed with the experimental results.

The wurtzite to sodium chloride type transformation in manganese sulphide was induced by heating. Analysis of the X-ray patterns revealed three mechanisms, one of which represented a new polymorph. One of the other two mechanisms proceeded by a slow-moving interface and the other by sudden steps.

The wurtzite to sodium chloride type transformation in silver iodide was performed under hydrostatic pressure. Orientation relations were found for the forward and reverse transformations including those for the intermediate phase. The structural changes were dominated by large atomic translations.

The room temperature crystal structures of rubidium and caesium nitrates were determined. The nitrate planes were found to be parallel to the faces of the pseudo-

cubes of metals. Larger reorientations of the nitrates were predicted for transformation under pressure than during heating.

Some collaborative, structural crystallography was undertaken which made use of available techniques. The crystal structures of three different anilinium-vermiculite intercalates were studied. The silicate layers were disordered to different extents and the interlayer electron density distribution was complicated by the presence of hydrated metal cations. Likely anilinium positions were located in the most ordered material.

"I have the best of evidence for this assertion -"

- H.G. Wells, *The Island of Dr. Moreau* (1896)

Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University and to the best of my knowledge contains no material previously published or written by another person, except where due reference is made. I consent to this thesis being made available for photocopying and loan if it is accepted for the award of the degree.

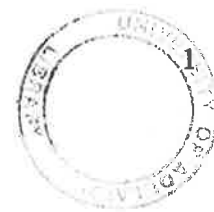
Signed....

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My supervisor Dr.S.W.Kennedy provided apparatus for the study of transformations and engaged in useful discussions on transformations. Dr.M.R.Snow provided expert guidance on general scientific procedure and crystal structure solving. Thanks are expressed to my colleagues P.K.Schultz, M.R.Snow, P.G.Slade, E.Horn, T.W.Hambley, J.R.Rodgers, to my postgraduate peers, and to my parents, for companionship. I am grateful to P.G.Slade and P.A.Stone of C.S.I.R.O. for an intriguing scientific collaboration and a view of the other half of Australian crystallography. The departmental workshops provided attentive and high quality service. I am grateful to the computing centre's system programmers and to my typist for their dedicated assistance. I was financially supported by a Commonwealth Postgraduate Research Award, by my parents, and by Dr.M.R.Snow, for services rendered.

Dedicated to the memory of

a faithful dog



CHAPTER 1

General Introduction

1.1 Introduction to Martensitic Transformations

The majority of crystalline compounds can incur a structural transformation under the influence of changes in temperature or pressure. Large dimensional changes of the structural parameters allow a distinct view of the atomic mechanisms which can readily be interpreted in terms of atomic movements. Putnis & McConnell (1980) described the study of mechanisms as:

“ ... the relationships between the parent and product phases: their spatial dimensions, distribution and crystallographic relationships.”

Martensitic transformations generally involve substantial changes in the structural parameters. These transformations have a rapid progression and each unit cell in the crystal has an identical, or at least symmetry equivalent, distortion. This feature helps to reduce the complexity of the atomic mechanisms compared with those in a diffusional change. There are also external macroscopic effects which are correlated with geometric changes in the unit cell dimensions and orientation. The following two definitions of martensitic transformations are according to Cohen, Olson & Clapp (1979) and Rao (1984) respectively:

“ ... a lattice-distortive, virtually diffusionless structural change having a dominant deviatoric component and associated shape change such that strain energy dominates the kinetics and morphology during the transformation.”

“ ... a structural change caused by atomic displacements (and not by diffusion) corresponding to a homogeneous deformation wherein the parent and product phases are related by a substitutional lattice correspondence, an irrational habit plane and a precise orientational relationship.”

The definitions quoted so far give a preliminary insight to the inclination of this thesis.

Martensitic transformations were first observed in metal alloys (Lucas, 1924, references cited therein) and were first found in inorganic non-metals in 1958 (Wolten, 1960), these being in CsCl, NiNO_2 and ZrO_2 . The number of reported comparisons between experimental observations of martensitic transformations and the theoretical predictions is still increasing although the phenomenological theories were developed in the 1950's (Bowles & MacKenzie, 1954, BM; Wechsler, Lieberman & Read, 1953, WLR). These two mathematical theories are equivalent and are called the phenomenological or the invariant plane strain (IPS) theories because they are based on the occurrence of such a strain. Many more compounds have joined the list of substances with martensitic transformations, which includes: organics (e.g. 1,20-eicosanedioic acid, Asahi et al., 1985), semiconductors (e.g. CdS, Turusbekov et al., 1977), minerals (e.g. KCl, Turusbekov et al., 1977) and intermetallics (e.g. V_3Si , Wayman, 1978).

Due to the shape and volume changes associated with martensitic transformations, they are of most importance to materials scientists. This is exemplified by the genesis of the subject being in steels. After metal alloys the next Mecca was zirconia (ZrO_2). The transformation in confined zirconia particles subdues cracking in ceramics (Kriven, 1984) and therefore analysis of the transformation is important to ceramic toughening. A transformation in polyethelene has characteristics agreeing with the IPS theory (Kriven, 1982), and dicalcium silicate which is a component of Portland cement clinker has shown evidence of a martensitic transformation (Kriven, 1982; Groves, 1983).

1.2 The Enigma

The phenomenological (IPS) theory of martensitic transformations has been shown to be applicable to some inorganic compounds, for example in NaCN (Gash, 1983) and NH_4Br (Fraser & Kennedy, 1974) but has been unsuccessful in explaining other martensitic transformations in inorganic compounds, for example in confined ZrO_2 particles (Kriven, 1984) and CsCl (Watanabe, Tokonami & Morimoto, 1977). Thus a problem arises because the IPS theory cannot account for the features of some martensitic transformations. As yet there are no guidelines as to which compounds,

under which conditions, the theory can be applied to, i.e. in which instances it gives a veritable ^cdescription of the geometric mechanism. Once this has been determined then steps can be taken to correct or reform the ^{eo}theory to make it generally applicable.

Steps to advance from the IPS theory are being made in the form of improvements (e.g. Choudhry & Crocker, 1983) and new theories (e.g. Zhang, 1984; Hyde & Anderson, 1986). From a more fundamental viewpoint, if the new theories are found to be at least partially applicable and they can be integrated with the IPS theory, then together they may lead to a universal description of martensitic transformations. Meanwhile many more potentially martensitic transformations in inorganic, non-metallic compounds must be studied in order to find when the phenomenological theory of martensitic transformations is applicable. The compounds studied should be ones which are known to undergo a martensitic transformation but more work is also needed to find more examples of these.

The most extensively studied transformation in inorganic compounds which appears martensitic is the sodium chloride $\rightarrow$ caesium chloride (B1 $\rightarrow$ B2) type transformation. Another change in structure type, which is similar but has been much less studied, is the wurtzite $\rightarrow$ sodium chloride (B4 $\rightarrow$ B1) transformation which is of interest because it can also proceed by two mechanisms. Transformations in more complex compounds provide an interesting aspect to the range of applicability of the IPS theory.

1.3 The Objective

The research of the S.W.Kennedy school of crystallography (e.g. NH_4Br , Fraser & Kennedy, 1974; RbNO_3 , Kennedy & Kriven, 1976; MnS , Kennedy & Summerville, 1981) has centred on determining which compounds accord with the BM and WLR theories and what are the atomic mechanisms. The work on transformations presented in this thesis will be along the same lines. The objective of the present work was to determine the mechanisms of structural transformations in some inorganic compounds. The compounds examined were those which appeared to have potentially martensitic transformations in order to test the applicability of the IPS theory. Some

investigations were also undertaken for the purpose of finding more examples of martensitic transformations.

1.4 The IPS Theory of Martensitic Transformations

The prominent characteristics of a martensitic transformation are a change in crystal shape, a reproducible orientation relation (angular relationship between the product and parent axes systems) and a planar interface between the product and parent portions of a partly transformed crystal. Fine scale surface structure is sometimes observed, indicative of slip or twinning (the lattice invariant shear). The BM and WLR theories rationalise these characteristics, both use matrix algebra but proceed on different paths to arrive at the same result. In the present work only the BM theory was used as the corresponding computer program was readily available (Ledbetter & Wayman, 1971).

The input data to the calculations are the unit cells' dimensions, the unit cell axes correspondence between the two phases (called the lattice correspondence) and possible lattice invariant shear systems in the parent cell. The cells' dimensions and lattice correspondence are used to calculate a pure lattice distortion of the parent's unit cell. The lattice invariant shear is difficult to detect and is therefore the most varied operand of the calculations.

The lattice invariant shear (abbreviated to LIS) occurs to relieve the stresses which build up during the lattice distortion. Therefore some of the likely slip systems are those that can operate in the product phase. These can be referred to the parent lattice using the lattice correspondence. As the slip occurs whilst the structure is still in its intermediate strained state, it is reasonable also to consider the slip systems of the parent material. This was done for the $\delta \rightarrow \alpha$ transformation in Pu by Choudhry & Crocker (1985) who found that some of the theoretical predictions agreed with the observations. Likely slip planes are cleavage planes or planes which facilitate mechanical slip.

Lattice invariant shear in the form of twinning requires the alternation of the

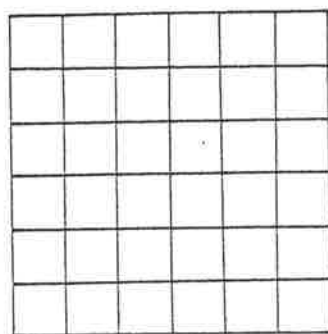
lattice distortion on a symmetry plane of the parent lattice for both Type I and Type II twins (Bowles & Wayman, 1972). Twin planes found for deformation twinning of the product phase are candidates (Bowles & Wayman, 1972; Choudhry & Crocker, 1985). In general for Type I twinning the twin plane must be a mirror plane of the parent and its normal must be a two-fold axis (Christian, 1965a). The corresponding plane in the product must not be a mirror plane (Christian, 1965b; Gash, 1983). This means that the possible twin planes are planes which lose their mirror symmetry during transformation. For Type II twinning the twin plane need not have rational indices although the twin direction must have them. The twin direction must be an axis of two-fold rotational symmetry in the parent structure and must lose its symmetry upon transformation. Type II twinning has been observed in the martensitic transformation in NiTi by Knowles & Smith (1981) and their theoretical predictions agreed with the experimental data. In this case the conjugate twin plane was a mirror plane in the parent phase and the twin direction was its normal. As the lattice distortion refers only to the lattice and not to the whole crystal structure, the symmetry of only the lattice need be taken into ^caccount when considering possible twinning systems (Christian, 1965a).

The phenomenological theory of martensitic transformations can be broken down into three mathematically distinct operations although they may occur simultaneously in the real crystal:

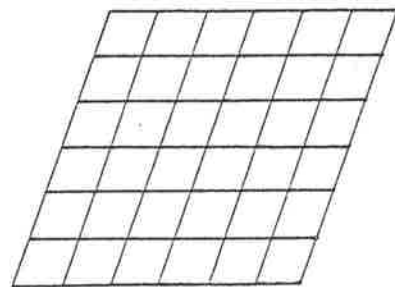
$$\begin{array}{ccccccc}
 \text{Macroscopic} & = & \text{Lattice invariant} & \times & \text{Lattice} & \times & \text{Pure lattice} \\
 \text{shear} & & \text{shear} & & \text{rotation} & & \text{strain} \\
 P1 & = & P2 & \times & R & \times & B
 \end{array}$$

The symbols P1, P2, R and B are the names commonly assigned in the BM theory to the respective 3×3 matrices representing each operation. The product RB represents an invariant line strain and is given the symbol S. The macroscopic shear is often termed the invariant plane strain.

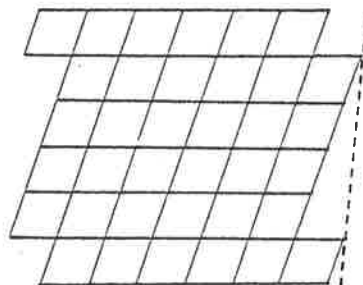
The planes and directions after transformation by the lattice distortion plus rotation (i.e. the invariant line strain, S) can be denoted by referring them to the



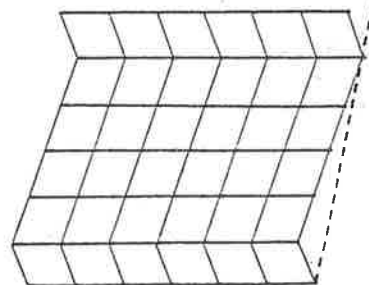
Parent lattice



Pure lattice distortion



Pure lattice distortion plus
LIS by slip



Pure lattice distortion plus
LIS by twinning

Figure 1.1 A two dimensional idealization of the pure lattice distortion and LIS components of a martensitic transformation. The dashed lines show the new crystal edges on a macroscopic scale. The lattice rotation has been omitted for simplicity.

product cell axes system (basis[†]). However, after transformation of crystal faces and edges by the macroscopic shear (invariant plane strain, P1) they cannot be readily indexed on the product's basis. The difference arises because the lattice invariant shear does not alter the orientation or dimensions of the unit cell but does act upon the external shape of the crystal (Fig. 1.1).

The output data from the theory are matrices and vectors representing the macroscopic shear, orientation relation and the lattice invariant shear. There is not always a solution for each set of input data because an invariant plane cannot always be found.

Each solution calculated using the phenomenological theory for a particular lattice distortion and lattice invariant shear consists of four modes of transformation called "martensite variants". Each variant is identifiable by its lattice invariant shear magnitude, lattice rotation (orientation relation) and macroscopic shear. The latter two characteristics can be readily measured and thereby facilitate a comparison between the theory and experiment.

1.5 Experimental Analysis of Martensitic Transformations

To observe the orientation relation between the two unit cells, one needs to observe the diffraction patterns before and after transformation. The compounds selected in the present work were examined by X-ray diffraction. The orientation relation also provides a guide to the lattice correspondence and hence to the atomic movements.

The macroscopic shear can be examined by microscopy and can be separated into the shear plane (called the interface or habit plane) and the direction vector of shear. This vector is manifested by changes in crystal morphology which can be measured in terms of angles between the new faces and edges. It is more easily recordable from a partly transformed crystal as the change of each face can be measured individually. Partly transformed crystals are also necessary for the evaluation of habit plane indices.

[†] The word "basis" is a mathematical term for axes system

1.6 Organic Intercalated Vermiculite

Vermiculite is a clay mineral usually formed by the weathering of magnesium micas. It has a layered structure with no covalent or ionic bonds holding adjacent layers together in its natural state. Each layer contains one central sheet of metal atoms octahedrally coordinated to oxygens, and two surrounding sheets of metal atoms tetrahedrally coordinated to oxygen atoms (Fig. 1.2). Each octahedron has hydroxyl groups and these are not bonded to a tetrahedron resulting in a "ditrigonal" cavity in the tetrahedral sheet. The octahedral cations are mainly magnesium and the tetrahedral cations are mainly silicon with a small fraction of aluminium. Due to the lower charge of aluminium than of silicon, the layers have an overall negative charge. In nature the negative charge is balanced by the presence of hydrated metallic cations such as Mg^{2+} or Cu^{2+} in the interlayer region. In the laboratory the cations may be replaced by others such as Na^+ and La^{3+} and the vermiculite behaves essentially like a cation exchange resin.

The hydrated metallic cations can also be replaced by a large variety of organic ions. The replacement process is called intercalation, the organic molecules are called intercalants and the whole product is called an intercalate. The intercalates have a range of applications (Barrer, 1978) such as paint thickeners and the stationary phase in gas-solid chromatography. The intercalants may be harmful compounds such as detergents (Slade, Raupach & Emerson, 1978) or industrial pollutants (Slade & Raupach, 1982). The intercalates also undergo a wide variety of organic reactions for which the silicate layers act as efficient acidic heterogeneous catalysts (Ballantine et al., 1985).

Knowledge of the structures of intercalates would allow one to understand the bonding and steric restrictions and therefore allow one to tailor the material and predict its behaviour. Due to the inherent disorder and defects in vermiculite intercalates, their three-dimensional crystal structures have previously evaded determination. However, recent collaborative work with P.G.Slade and P.A.Stone (C.S.I.R.O. Division of Soils) and with P.K.Schultz (P.& I. Chem. Dept., Univ., Adelaide), has shown that the three

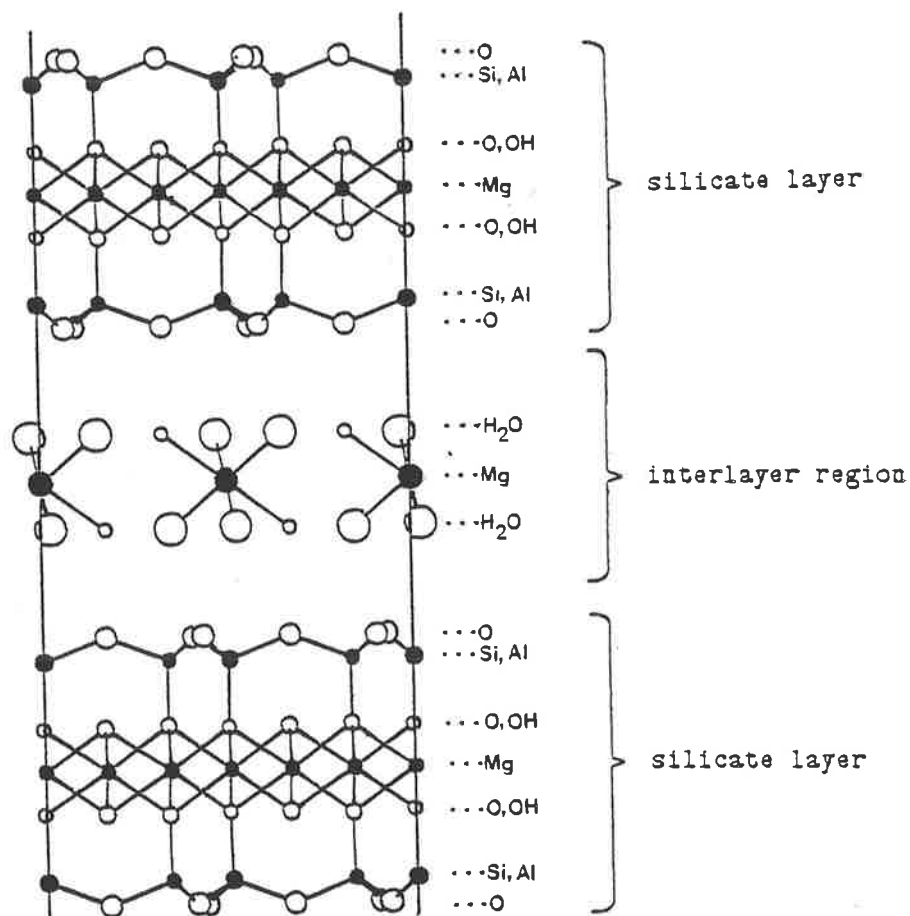


Figure 1.2 Projection of Mg-vermiculite down the a-axis (c vertical) showing atomic environments at different levels along c ($\parallel z$). Atomic coordinates from Shirozu & Bailey (1966). Drawn using ORTEP-II (Johnson, 1976).

dimensional crystal structure of anilinium-(intercalated) vermiculite can be determined by single crystal X-ray diffraction. For this work it was necessary to use a wide range of crystallographic techniques and the procedure is described in chapter 6.

1.7 Nomenclature, Notation and Format

The nomenclature, notation and format in this thesis follow, as far as possible, the instructions given in "Notes for Authors" (Int. Union Cryst., 1983) and "Guidelines on Higher Degrees by Research and Specifications for Thesis" (Adel. Univ., 1984). For different phases of a particular compound the Strukturbericht symbols rather than Roman numerals or Greek symbols were used where possible, in order to facilitate comparisons between different compounds. For hexagonal and trigonal structures, planes and directions were written in four index notation to indicate the symmetry of the lattice (Cheadle & Lane, 1968; Nicholas, 1970). The nomenclature for aspects of martensitic transformations follows the most prevalent usage except for the term "orientation relation" which was used in place of "orientation relationships" on the advice of S.W.Kennedy. During discussions on the movement of planar entities (e.g. for an atomic mechanism or a change in morphology), "tilt" will indicate turning of the plane about a line within the plane and "rotation" will refer to turning about its plane normal.

CHAPTER 2.

The Martensitic Transformation

$\beta \rightarrow \alpha$ -Uranyl Hydroxide ($\text{UO}_2(\text{OH})_2$)

2.1 Introduction

The $\beta \rightarrow \alpha$ - $\text{UO}_2(\text{OH})_2$ transformation is one of the few structure changes which are accompanied by large shape changes and an infinite hysteresis. These properties make it particularly suitable for crystallographic investigation. Crystals of the β -phase can be transformed under shearing forces (Harris & Taylor, 1962 (abbreviated to HT)) or by cooling (Taylor, 1971). Upon cooling, Taylor, Kelly & Downer (1972) (abbreviated to TKD), noted audible clicks, an infinite hysteresis and the existence of an orientation relation, which they concluded were analogous to a martensitic transformation. They also described a set of coordinated atomic rearrangements. Comparison of these observations with some definitions of martensitic transformation (e.g. Bilby & Christian, 1956; Rao, 1984) reveals that the $\beta \rightarrow \alpha$ - $\text{UO}_2(\text{OH})_2$ transformation is martensitic. The objective of this project was to determine the crystallographic features of the transformation and thereby decide if the transformation supports the phenomenological theory of martensitic transformation.

The structure of β - $\text{UO}_2(\text{OH})_2$ consists of corner bridged UO_6 octahedra in layers parallel to $\{001\}_\beta$. α - $\text{UO}_2(\text{OH})_2$ also consists of layers but with each uranium bonded to eight oxygens and with a larger interlayer separation than in the β -phase. The α -phase is a dehydrated modification of the mineral schoepite (Walker, 1923; Christ & Clark, 1960). Both α and β - $\text{UO}_2(\text{OH})_2$ can be grown from solution as platelets with the structural layers parallel to the plate faces (Bergstrom & Lundgren, 1956; Rundle, 1970). There also exists a γ -phase which behaves similarly to the β -phase (Seigel, Hoekstra & Gebert, 1972) but it has not been studied to the same extent.

The first proposal of a lattice correspondence between the β and α -phases was by HT on the basis of optical and X-ray evidence: $a_\beta \rightarrow a_\alpha, b_\beta \rightarrow c_\alpha, c_\beta \rightarrow b_\alpha$. This

correspondence was reaffirmed by Cordfunke & Debets (1964) and was used by Taylor (1971) to describe the atomic movements during the transformation. A different lattice correspondence was derived by TKD from observations of the morphologies of partly transformed crystals: $a_\beta \rightarrow c_\alpha$, $b_\beta \rightarrow a_\alpha$, $c_\beta \rightarrow b_\alpha$. This approach was made possible because the platelet face was virtually untilted by the transformation and the transformed crystals had morphologies similar to the chemically synthesised α -phase crystals.

As the hysteresis is infinite it was not necessary to examine the phenomenological features below the transformation temperature of 5.1°C (TKD). This allowed the use of relatively uncomplicated cooling apparatus for the transformations on the optical microscope and X-ray camera.

The shape change of a martensitic transformation can result in fallacious lattice orientation relation data if one or more crystal faces or corners are anchored to a support throughout the transformation. Due to the large shape change accompanying the $\beta \rightarrow \alpha\text{-UO}_2(\text{OH})_2$ transformation it was necessary to use partly transformed crystals for determination of the orientation relation.

The importance of using transformation temperature lattice parameters in the phenomenological calculations was noted by Kriven, Fraser & Kennedy (1981) and by Fraser & Kennedy (1974). Near the transformation temperature the lattice parameters may substantially deviate and consequently they were determined in the present investigation.

From optical evidence on transformations under pressure, HT reported that lines seen on the $\{001\}_\beta$ face after transformation were slip lines. However without additional experimental evidence on slip, one must consider for the phenomenological calculations a range of slip systems limited only by the condition that their planes and directions have low indices and thereby correspond to close packed entities.

Planes and directions of the β -phase after transformation by the macroscopic shear will be denoted by a superscript prime. For example the $\{001\}_\beta$ surface becomes $\{001\}'_\beta$ after transformation. Planes and directions after the action of the pure lattice strain

plus lattice rotation will be denoted by referring them to the α -basis. For example, $(001)_\beta$ becomes $(010)_\alpha$; (according to the correspondence of TKD).

2.2 Experimental

2.2.1 Crystal Growth

The reported methods of growing β - $\text{UO}_2(\text{OH})_2$ involve either thermal hydrolysis or alkaline precipitation and they are summarised in Table 2.1. The substance γ - UO_3 was not available for use as a reagent and apparatus was not available for the hydrothermal methods. The use of sealed glass tubes was prohibited (by law), and so to prevent evaporation of water a domestic pressure cooking vessel was used. The uranyl acetate and uranyl nitrate (plus lanthanum hydroxide/pyridine) mixtures were placed in unsealed flasks surrounded by deionised water in the pressure vessel and maintained at $114 \pm 4^\circ\text{C}$ for three days. The precipitates were filtered, washed with ethanol and carbon tetrachloride, then dried in a rotary pump vacuum. The transformation effects were only studied using the crystals from the lanthanum hydroxide reaction.

2.2.2 Optical Microscopy

Transmitted and reflected light techniques including dark field and Nomarski interference contrast were employed on a Reichert Zetopan microscope. Photographs were taken on 35mm black and white film for precise angle measurements of the macroscopic shear.

A cold stage was constructed (section 7.2.2.1) for in situ transformations. Crystals on glass slides were overlayed with a coverslip to prevent condensation damage and were cooled to $-10 \pm 5^\circ\text{C}$. Several hundred crystals were used in each cooling run as only a very small percentage partly transformed. Pressure transformations were effected by the method of HT but without immersion oil as this would have obscured the intended scanning electron microscopy. For observation of the thin sides of crystals a 2-circle goniometer (section 7.2.2.3) was used.

Reagents (aqueous)	Enviroment	Phases obtained	Literature source
Aged γ - UO_3	100°C, Hydrothermal	β, α	Cordfunke & Debets (1964)
γ - UO_3	240°C, Hydrothermal	β, α	Dawson et al. (1956)
$\text{UO}_2(\text{NO}_3)_2$, pyridine	97°C	?	Lindval' & Kuznetsova (1974)
$\text{UO}_2(\text{NO}_3)_2$, HNO_3	290°C, Hydrothermal	β, α	Bannister & Taylor (1970)
$\text{UO}_2(\text{NO}_3)_2$	115°C, Hydrothermal, H_2	β	Robins (1966)
$\text{UO}_2(\text{NO}_3)_2 \cdot \text{La}(\text{HO})_3$	85°C	β, α	Hoekstra & Siegel (1973)
$\text{UO}_2(\text{CH}_3\text{.COO})_2$	117°	β	Bergström & Lundgren (1956)

Table 2.1 Reported methods for growing crystals of uranyl hydroxide.

Forty partly transformed crystals including two transformed by pressure were examined. An additional ten partly transformed crystals were mounted on glass rods and inspected on the goniometer.

2.2.3 Scanning Electron Microscopy and Electron Microprobe Analysis

Both fully and partly transformed crystals were examined by scanning electron microscopy. S.E.M. samples were either supported on a standard X-ray diffraction type mount or laid on aluminium stubs. The E.M.P. samples were laid on a graphite disc. Specimens were coated with gold for the S.E.M. or with carbon for the E.M.P. analysis. The E.M.P. (section 7.3) was operated at 20KeV and 5nA. On the energy dispersive spectrometer the elements which were tested for and their detection limits in weight % are as follows: Na .5, Si .3, P .9, S .3, Cl .1, K .3, Ag .1. Wavelength dispersive spectrometer scans were also run to check for lanthanum, which was a reagent for crystal growth. In the S.E.M. (section 7.3) crystals were examined for evidence of slip and any other noteworthy surface features.

2.2.4 X-ray Diffraction

2.2.4.1 Orientation Relation

β -phase crystals from 50 to 100 μ m wide were chosen for transformation by cooling on the precession camera. Araldite was thinly smeared over the crystals to prevent condensation damage and material loss due to cracking and the subsequent fragmentation. Five crystals were transformed by cooling them to $-20 \pm 10^\circ\text{C}$ with the X-ray camera cooling apparatus (section 7.2.4.1). The orientations of the products were calculated from precession photographs.

Seven crystals which had been partly transformed on the optical microscope, including two transformed by uniaxial pressure were also analysed. The positions of diffraction spots on Laue photographs implied that $(001)_\beta$ was colinear with $(010)_\alpha$ but

the relative intensities of symmetry equivalent spots indicated otherwise. Consequently, the orientation relations were calculated from the lengths of white radiation streaks on precession photographs rather than from the positions of spots on Laue photographs.

2.2.4.2 Low Temperature Lattice Parameters

Two β -phase crystals which measured approximately $200 \times 100 \times 50 \mu\text{m}^3$ were selected from the precipitate of the $\text{La}(\text{OH})_3$ reaction. One α -phase crystal which measured $80 \times 90 \times 1 \mu\text{m}^3$ was selected from a portion of the above precipitate after cooling it to -10°C . Crystals were affixed to glass rods with a minimal amount of Araldite (epoxy resin adhesive), and sheathed in 0.5mm glass capillary tubes.

All crystals were oriented on the CAD4 diffractometer (section 7.4). The cell constants were refined from the setting angles of twenty-five reflections with 2θ between 18 and 50° . Due to the mosaic spread, higher angle reflections were too broad for more precise measurement. The calibration of the CAD4 cooling apparatus is described in section 7.4.3 Cooling was achieved by increasing the rate of cold gas production.

2.2.5 Martensite Calculations and Comparisons with the Experimental Observations

Program MRTNST (section 7.6) was used for calculating the primary characteristics of the theoretically possible slip systems. The lattice parameters and the principal strains adopted for the computations were those calculated for 5.1°C from the present work. Trial slip systems had planes in the range $(000)_\beta \rightarrow (112)_\beta$ and the slip directions in these planes were from the range $[\overline{221}]_\beta \rightarrow [221]_\beta$. The slip system $(110)[\overline{112}]_\beta$ was also tried as some lines on the transformed crystals (HT) were in the $\{110\}'_\beta$ plane. No twinning systems were tested due to the experimental evidence for their absence (HT). No dilatation of the habit plane was allowed for because the brittleness of the crystals and the absence of curvature of the habit plane indicated that very little elastic distortion would be tolerated (Christian, 1965c).

The principal axes' rotations and the macroscopic shears calculated for each variant were compared with the experimental results using program COATI (section 7.5). Theoretical orientation relations were calculated by applying the invariant line strain matrix and the theoretical shape changes were calculated from the invariant plane strain matrix.

Improbable theoretical martensite variants were eliminated by the following tests. A variant was considered acceptable if its orientation relation satisfied the criterion that $[001]_{\beta} \wedge [010]_{\alpha}$ was within 1.5° from 2.8° , and the deviation from the experimental values for the rotations of the other two axes were $\leq 2^{\circ}$. The experimental and theoretical habit planes and shape changes were compared by reading off angles from computer drawings of partly transformed crystals. The theoretical habit plane trace had to lie within 2° of the experimental trace on the $(001)_{\beta}$ face. No restriction was placed on the theoretical habit plane^e trace on the $\{110\}_{\beta}$ faces due to the large experimental uncertainty. The angles between the $\langle 110 \rangle_{\beta}$ type edges after transformation had to lie within the range $63(\pm 5)^{\circ}$ or the alternate angle $117(\pm 5)^{\circ}$. The $\{001\}_{\beta}$ surface was only allowed to tilt by up to 8° .

2.3 Results

2.3.1 Crystal Growth

The pyridine reaction yielded a yellow precipitate which was too fine for single crystal work and was not further studied. The other two reactions yielded bright yellow platelets of the β -phase between 10 and 100 μm wide. There was no γ -phase present but a small amount of α -phase was observed. β -phase crystals had $\{001\}$ and $\{11l\}$ faces (where $l=0,1,2$), but some had $\{100\}$ faces and resembled hexagonal platelets. Crystals from the uranyl acetate hydrolysis were more platy than those from the $\text{La}(\text{OH})_3$ reaction. The former crystals also showed some green impurities and were consequently discarded. No impurity elements were detected in the latter crystals

by the electron microprobe analysis. The predominant cleavage planes of the β -phase crystals were $\{001\}$ and $\{111\}$.

2.3.2 Optical Microscopy

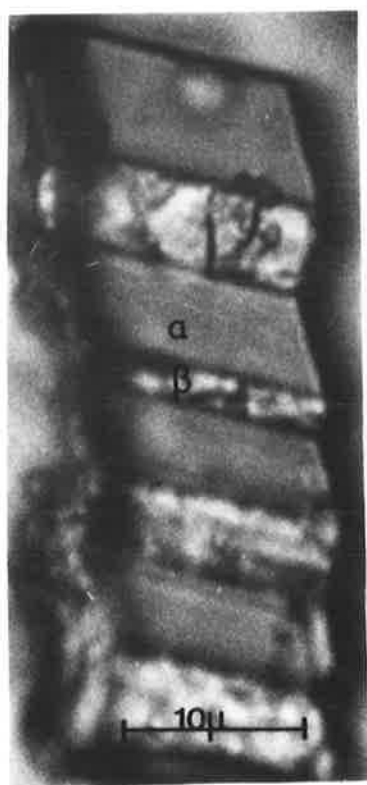
The measured angles associated with the macroscopic shear are shown in Fig. 2.2. The transformed crystals had symmetrical extinctions to within 1° , indicating that the edges on the platelets were close to $\langle 101 \rangle_\alpha$. Such crystals would be indistinguishable from chemically synthesised ones. Thus the shape change was very similar to the hypothetical effect of the pure lattice distortion alone. The habit plane was straight (Fig. 2.1) and was of the form $\{1\ 1.134\ 0\}$. There was no step or tilt at the habit plane trace on the $\{001\}$ face. The lines noted by HT on the $\{001\}'_\beta$ face were also observed in the present work (Fig. 2.1.c) and found to be parallel to the habit plane trace. There were no steps across these lines and their occurrence was very intermittent. There were growth layers parallel to $\{001\}_\beta$ on the $\{110\}_\beta$ faces and the interface showed small kinks where it crossed the layer boundaries (Fig. 2.1.g). Cleavage on $\{001\}_\beta$ during transformation was common. Crystals larger than $100\mu\text{m}$ wide always shattered into fragments upon transformation. Some partly transformed crystals would not transform further even when immersed in liquid nitrogen. Polyphase crystals (such as in Fig. 2.1.a) were occasionally found.

Transformation by uniaxial stress only eventuated if the pressure was applied along $\langle 010 \rangle_\beta$. Pressure along $\langle 100 \rangle_\beta$, $\langle 001 \rangle_\beta$ or parallel to the $\{110\}_\beta$ normals resulted in fracture without transformation. The observable characteristics of crystals partly transformed by uniaxial pressure were the same as for those partly transformed by cooling.

2.3.3 Scanning Electron Microscopy

There was no tilt, to within 3° , or a step at the junction of the $\{001\}_\beta$ and $\{001\}'_\beta$ faces. The interface traces were all straight lines (Fig. 2.3.a-c) thereby implying a planar interface. Lines parallel with the interface trace on the $\{001\}'_\beta$ face generally

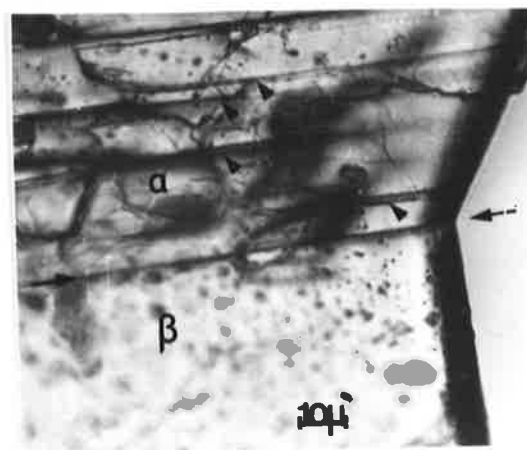
Figure 2.1 Optical micrographs of partly transformed crystals.
(a), (b) and (c) are viewed onto $\{001\}_{\beta}$. (d), (e), (f) and
(g) are viewed onto $\{110\}_{\beta}$. See section 2.3.2 for details.



a



b



c



d

e

f

g

Figure 2.1

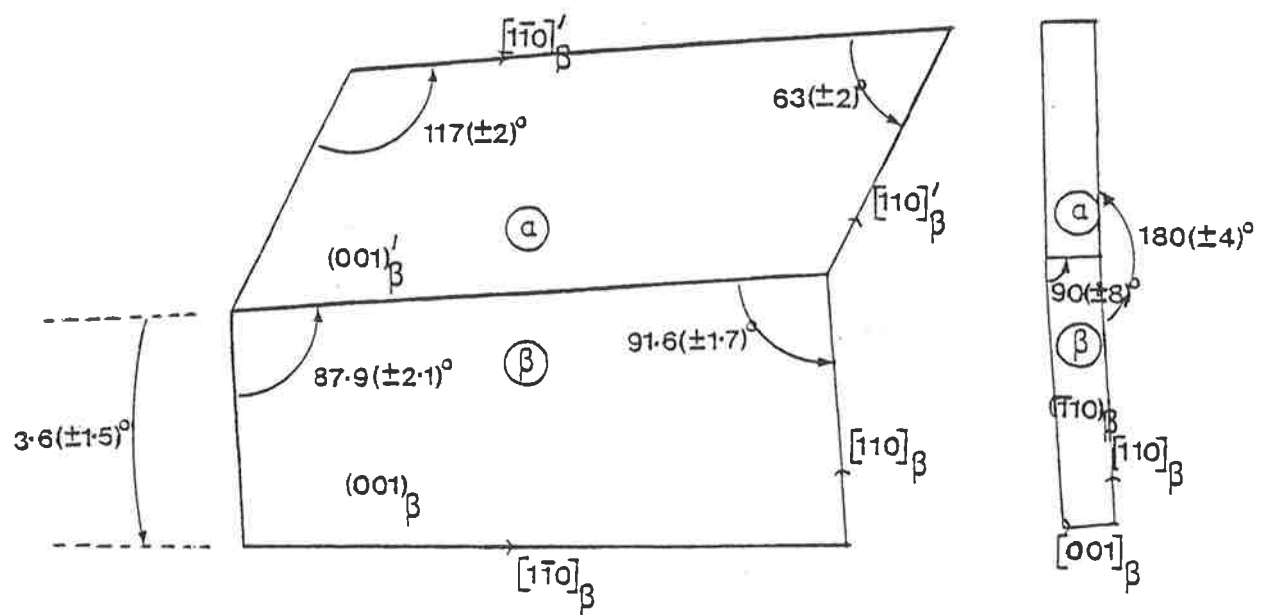
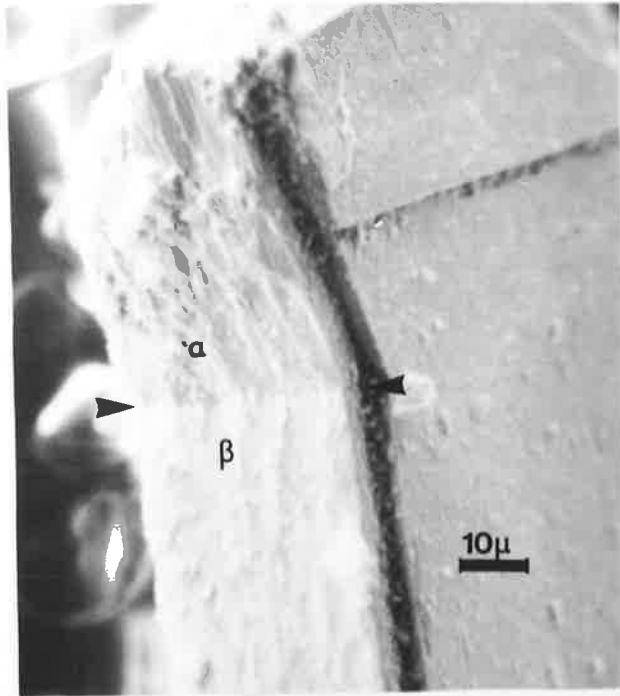
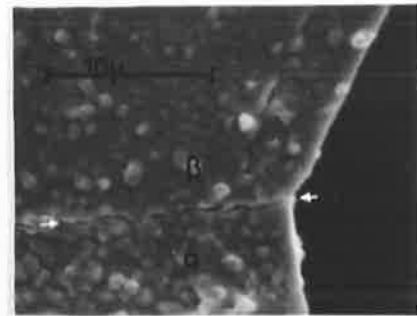


Figure 2.2 Angles corresponding to the experimentally observed macroscopic shear.

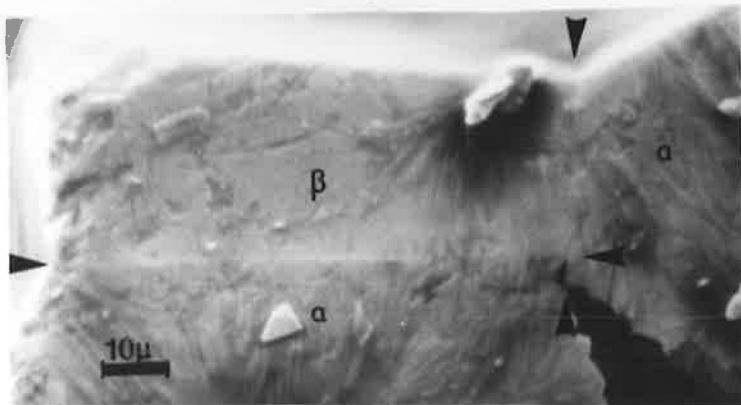
Figure 2.3 S.E.M. photographs of (a), (b) and (c) partly transformed crystals and (d) an α -phase crystal. (a) is a skew view with $\{001\}_\beta$ on the R.H.S. (b) and (c) are viewed onto $\{001\}_\beta$. (d) is viewed onto $\{001\}_\beta$. See section 2.3.3 for details.



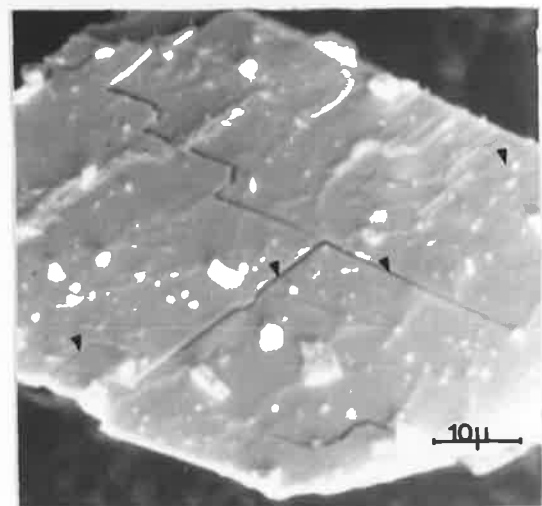
a



b



c



d

Figure 2.3

appeared as thin gaps without steps. Planes containing these lines were of the form $\{111\}'_{\beta}$ (where $l = 0, 1$ or 2), (Fig. 2.3.d). There were also lines at $15(\pm 10)^{\circ}$ from $\langle 001 \rangle_{\beta}$ on the $\{110\}'_{\beta}$ faces, which were most probably fine scale cleavage steps.

2.3.4 X-ray Diffraction

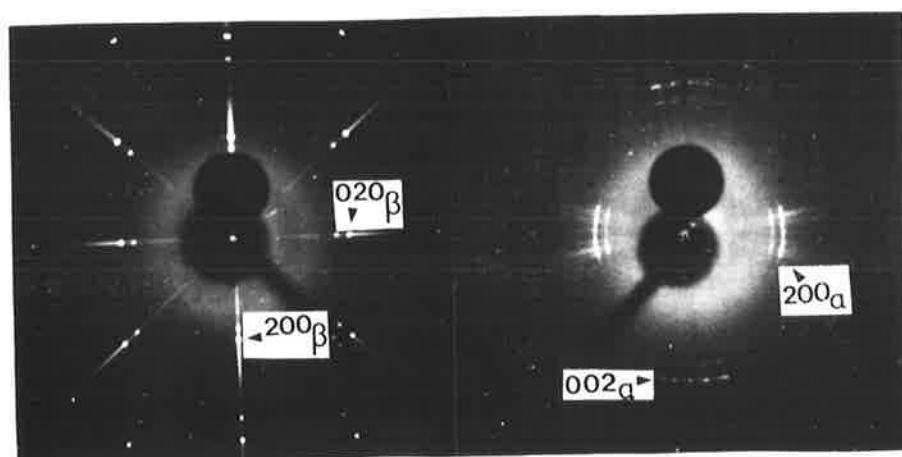
2.3.4.1 Orientation Relation

All the crystals which were cooled on the X-ray camera transformed fully. The unit cell axes after transformation were generally spread around their original positions by $\pm 10^{\circ}$ (Fig. 2.4.a-d). These orientation data were not considered to be definitive enough for comparison with the theoretical data due to the probable influence of the large shape change. Similarly, orientation relations from crystals partly transformed by uniaxial stress were not used as they had appreciable reflection spreading in some zones, although not nearly as severe as for the previously mentioned crystals. However, the results from the uniaxially stressed crystals agreed with those from the partial transformations effected by cooling on the microscope. The α -phase reflections from the latter type of crystals were only spread by $\pm 0.4^{\circ}$ and the corresponding average orientation relation is shown in Fig. 2.5. A typical precession photograph displaying the orientation relation is given in Fig. 2.4.e. The orientation relation essentially consisted of a rotation of $15.6(\pm 0.7)^{\circ}$ around $[001]_{\beta}$ as $[010]_{\alpha}$ only deviated from $[001]_{\beta}$ by $2.8(\pm 1.0)^{\circ}$. The proximity of the axes within each of the pairs (a_{β}, c_{α}) , (b_{β}, a_{α}) and (c_{β}, b_{α}) confirms that the lattice correspondence of TKD is correct. Neglecting the tilt of b_{α} from c_{β} , the orientation relation can be approximately stated as $[001]_{\beta} \parallel [010]_{\alpha}$, $(110)_{\beta} \parallel (101)_{\alpha}$. It can be more accurately represented by the pure lattice distortion plus a rotation of $15.9 (\pm 1.0)^{\circ}$ around $[\overline{.218} \overline{.262} 1]_{\beta}$.

2.3.4.2 Lattice Parameters

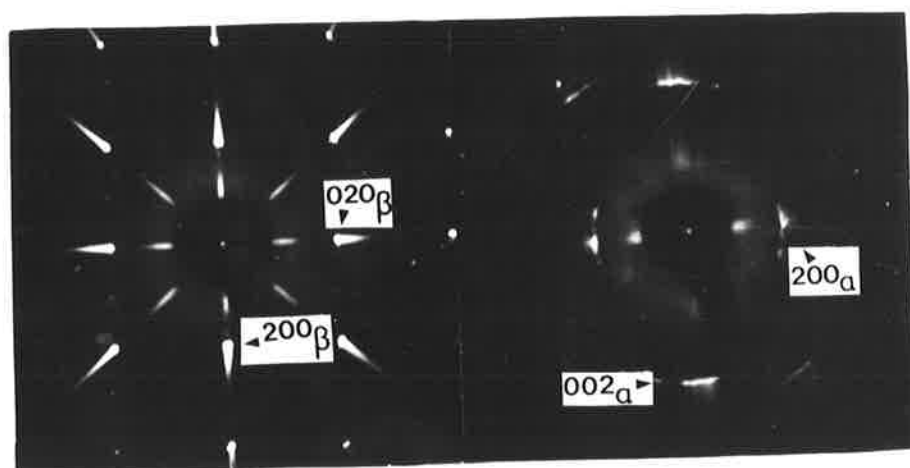
The change of lattice parameters with temperature is shown in Fig. 2.6. The straight lines of best-fit were determined by linear regression. The unit cell angles did

Figure 2.4 X-ray diffraction precession photographs from (a), (b), (c) and (d) a crystal which was transformed by cooling on the X-ray camera. (e) a crystal which was partly transformed on the optical microscope. See section 2.3.4.1 for details.



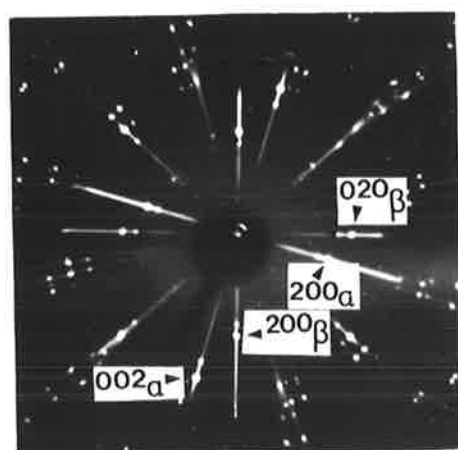
a

b



c

d



e

Figure 2.4

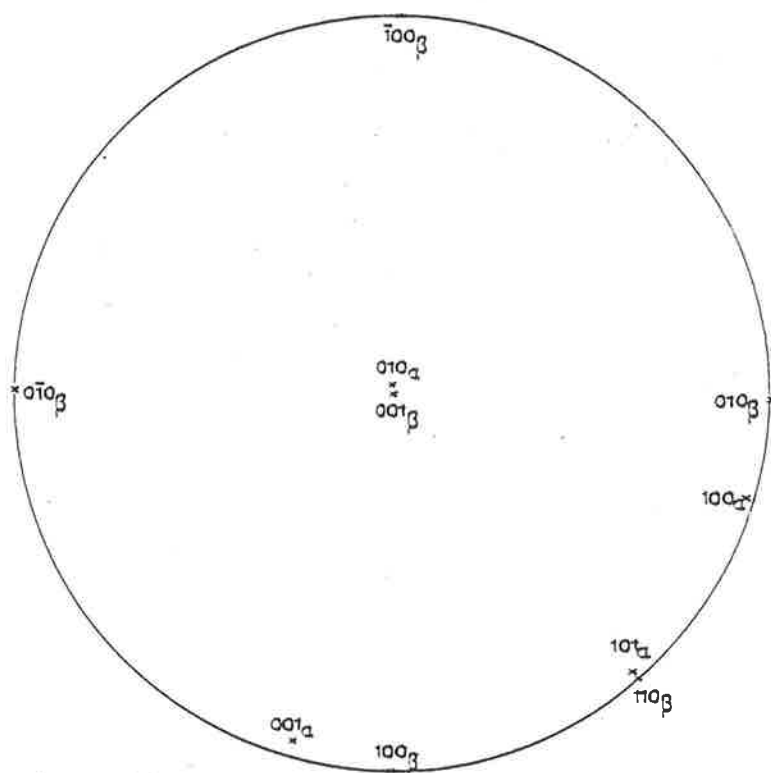


Figure 2.6 Average orientation relation observed in crystals partly transformed on the optical microscope. Stereogram of planes.

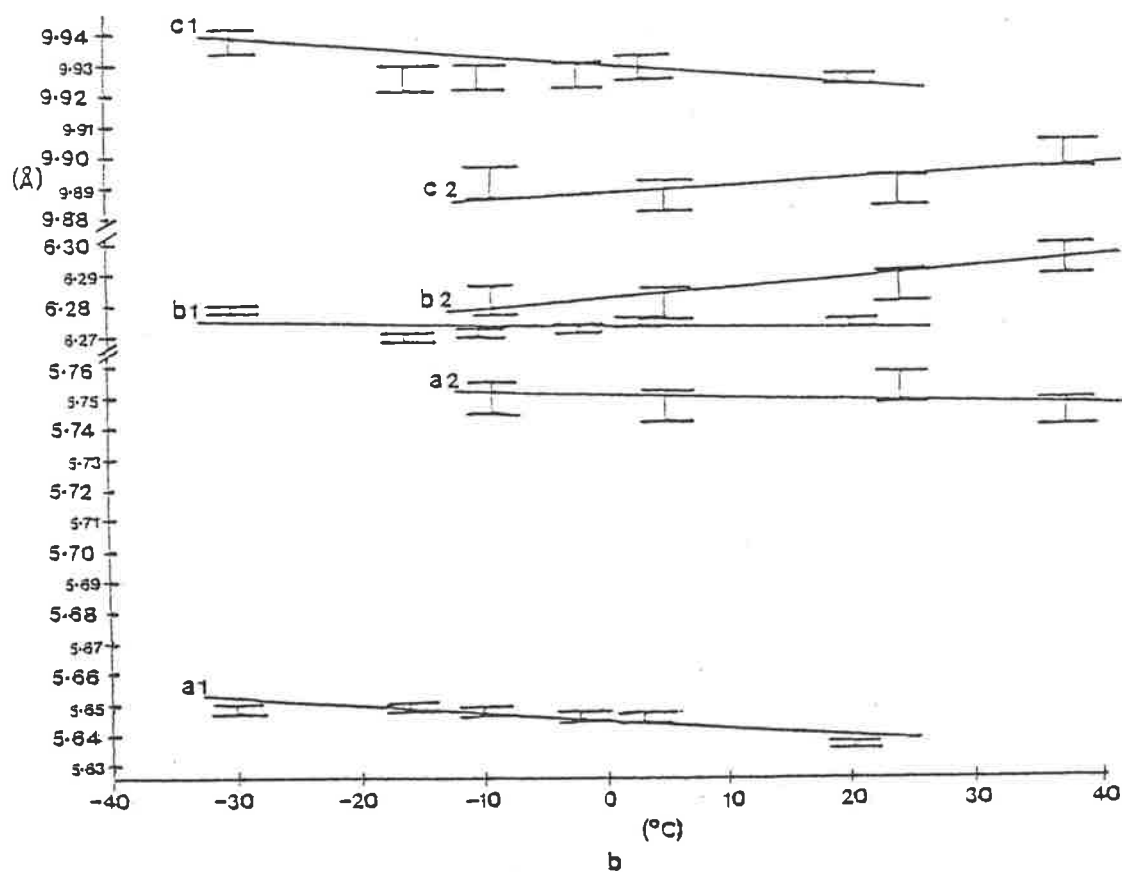
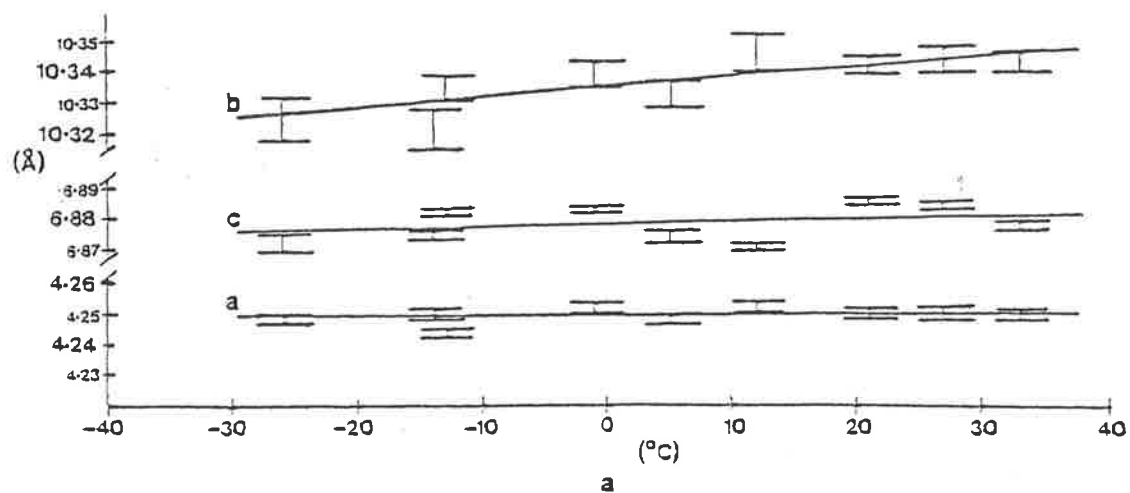


Figure 2.6 Thermal expansion of unit cell axes for:
(a) $\alpha\text{-UO}_2(\text{OH})_2$ and (b) $\beta\text{-UO}_2(\text{OH})_2$ (crystals 1 and 2).

not deviate from 90° . Both β -phase crystals supercooled to at least 15°C below the reported transformation temperature.

The unit cell axes lengths at 5.1°C (transformation temperature from TKD) were calculated for use in the phenomenological calculations and are given in Table 2.2.

Table 2.2 Axes lengths (in Å) of α - and β - $\text{UO}_2(\text{HO})_2$

		5.1°C	20°C
α	a	4.249(± 5)	4.250(± 5)
	b	10.345(± 1)	10.34(± 5)
	c	6.877(± 5)	6.880(± 5)
β	a	5.70(± 5)	5.69(± 5)
	b	6.278(± 6)	6.28(± 1)
	c	9.991(± 2)	9.91(± 2)

Using the lattice correspondence of TKD these axes gave principal distortions of 1.2065, 0.6768 and 1.0427 parallel to a_β , b_β and c_β respectively. The pure lattice strain matrix B, is then:

$$\begin{bmatrix} 1.2065 & 0 & 0 \\ 0 & .6768 & 0 \\ 0 & 0 & 1.0427 \end{bmatrix}.$$

The room temperature (20°C) lattice parameters, also in Table 2.2, agree with the literature values of HT and Taylor & Hurst (1971). The differences in lattice parameters between the two β -phase crystals are comparable with the variations due to temperature changes.

The a_β axis increases with decreasing temperature. The other two axes of the β -phase show a more complex behaviour by initially decreasing on cooling and then tending to increase at even lower temperatures. The parameters of the α -phase show a gradual decrease with decreasing temperature with a steeper gradient for the non-basal, $[010]_\alpha$ axis.

No.	Slip system	Variant No.	Tilt of $(001)_\beta$	$[110]_\beta \wedge [1\bar{1}0]_\beta^\dagger$	$[110]_\beta \wedge [\bar{1}10]_\beta^\dagger$	$[100]_\beta \wedge [001]_\alpha^\dagger$	$[010]_\beta \wedge [001]_\alpha^\dagger$	$[001]_\beta \wedge [010]_\alpha$	Habit plane trace $\wedge [1\bar{1}0]_\beta^\dagger$	Habit plane trace $\wedge [110]_\beta^\ddagger$	M2	M1	Habit plane (referred to β).
1	(011) [01 $\bar{1}$]	3	3.5	65.8	114.2	14.5	14.0	3.4	3.9	85	.099	.501	1 1.15 .218
2	(012) [12 $\bar{1}$]	4	1.8	65.6	114.4	15.0	15.0	1.5	2.5	88	.089	.503	1 1.09 .09
3	(012) [02 $\bar{1}$]	3	0.5	65.6	114.4	14.2	14.8	2.3	4.25	89	.086	.501	1 1.1 .03
4	(112) [02 $\bar{1}$]	3	1.8	65.5	114.5	15.5	15.5	1.4	5.4	88	.100	.504	1 1.21 .11
5	(112) [11 $\bar{1}$]	3	1.4	63.4	116.6	15.4	15.5	1.9	5.0	89	.085	.543	1 1.19 .07
Experimentally Observed.			0(± 4)	63(± 2)	117(± 2)	15.6(± 1)	15.6(± 1)	2.8(± 1)	3.6(± 1.5)	90(± 8)	—	—	1 1.13 0

Table 2.3 Characteristics of the five calculated martensitic variants which agreed with the experimental results. The experimentally observed values are given for comparison. Angles are given in degrees. M2 is the L.I.S. magnitude and M1 is the macroscopic shear magnitude.

† Angle projected onto $(001)_\beta$.

‡ Angle projected onto $(1\bar{1}0)_\beta$.

2.3.5 Comparisons Between Theoretical Calculations and Experimental Observations

From all the slip systems tested with MRTNST, 95 were theoretically possible, corresponding to 380 martensite variants. Only five of these variants were found to agree with the experimental results and their characteristics are listed in Table 2.3. Substituting the room temperature lattice parameters in place of those calculated for 5.1°C, gave approximately a 0.5° difference in the orientation relations and habit planes. Also, some slip systems became theoretically non-solvable but none of these were from the five matches mentioned above.

2.4 Discussion

2.4.1 Crystal Growth

The small size of the crystals from the pyridine reaction reveals that pyridine was too strong a base and caused too many crystal growth nuclei with a low solubility. A lower concentration of pyridine would be more successful. The small amount of α -phase found with the β -phase was a product of transformation at the low temperature reached during the evaporative drying. Hoekstra & Siegel (1973) suggested that the hydrothermally synthesised α -phase crystals of Taylor & Hurst (1971) were products of the $\beta \rightarrow \alpha$ transformation. Rundle (1970) reported hydrothermally grown α -phase crystals with parallel striations on their $\{001\}'_{\beta}$ faces. Those crystals were possibly also transformation products as similar lines appear after transformation.

2.4.2 Microscopy

The stability of some partly transformed crystals, down to liquid nitrogen temperature, indicates interface immobility due to defects (Christian, 1965d) or interface relaxation (Kennedy, 1980). The untransformed region of the crystal is stabilized by the strains set up at the interface. Polyphase crystals such as in Fig. 2.1.a give an indication

of the range of the effect. The thinnest untransformed band was $2\text{ }\mu\text{m}$ wide. Nucleation of different areas in a crystal can be simultaneous or consecutive. The crystal shown in Fig. 2.3.c must have undergone two crystallographically equivalent macroscopic shears simultaneously as the α -phase crystallites have split apart by irregular cracking rather than along one of the habit planes. The greater tendency for larger crystals to crack could be explained by the presence of such shears or by the more numerous destabilizing defects. The straightness of the interface and absence of a step implies that it is an undistorted plane. The lines parallel to the possible habit plane traces on the $\{001\}'_{\beta}$ surface (Figs. 2.1.c, 2.3.d) may correspond to discontinuities across either slip planes or fracture due to otherwise unresolved transformation stresses.

The fact that pressure induced transformation only eventuated when b_{β} was compressed is physically significant as this is the only axis which is shorter after transformation. The equivalence of the results from transformations initiated by cooling and pressure indicates that the same mechanism could be operative in both instances.

2.4.3 Orientation Relation

The basal unit cell axes of both phases bisect the corners of the two dimensional characteristic platelets (TKD). During transformation on the X-ray camera the glue immobilised the corners thus preventing shearing and thereby causing extensive fragmentation and resulting in a preferred orientation with colinearity of the axes. The effect on the orientation relation from anchoring only one crystal surface has been noted by Kennedy (1973). It would cause a more complicated preferred orientation effect due to the symmetry equivalent possibilities of the macroscopic shear. Corrections to the orientation relation, similar to those of Mnyukh et al. (1975), would have to be applied.

Due to the fragmentation resulting from the morphological restraints of the glue, the corresponding orientation results are only a representation of the lattice correspondence and not of the orientation relation.

2.4.4 Atomic Movements During the Transformation

The transformation proceeds by rotation of the UO_6 octahedra about the $\text{O}=\text{U}=\text{O}$ line, with oxygen atoms moving towards the bonded hydrogen atoms (TKD). The van der Vaal's bonds become longer, making the interlayer connections weaker, which explains the $\{001\}_\beta$ cleavage during transformation. Rotation of three dimensional atomic groups has been observed in LiKSO_4 (Bansal & Roy, 1984), ReO_3 (Axe et al., 1985) and in the alkali feldspars (Brown et al., 1984), but the $\beta \rightarrow \alpha\text{-UO}_2(\text{OH})_2$ transformation is the only one found to be martensitic. The change in coordination number of the uranium atoms from 6 to 8 introduces an additional aspect called "penetrative interaction", in the classification system of Lacy (1965).

TKD chose the lattice correspondence such that the position $[\frac{1}{2}, 0, \frac{1}{2}]$ of the α -phase cell was coincident with the origin of the β -phase cell. Due to the face centered array of uranium atoms in both phases, three other choices of the origin for the α -phase cell are possible. Hence there are four choices in total, namely those at $[0,0,0]$, $[\frac{1}{2}, \frac{1}{2}, 0]$, $[\frac{1}{2}, 0, \frac{1}{2}]$ and $[0, \frac{1}{2}, \frac{1}{2}]$. The first two choices are equivalent because the α -phase is C-centered, and similarly for the latter two. Therefore, the four choices pair into two unique ones. Choosing the relative cell positions of the two phases such that the origins are superimposed would require large tilts of the $\text{O}_2\text{-U-O}_2$ planes in addition to their rotations. Although the choice of TKD is clearly the energetically favourable one, the possibility of options should be noted.

The behaviour of the β -phase lattice parameters above 0°C follow the extrapolations from the work of Bannister & Taylor (1970) above 20°C . The suggestion of an increase of b_β at the lower temperatures implies that just prior to the transformation the uranium atoms are set apart by the translation of the oxygen atoms to their lower energy positions. The application of pressure along b_β would then seem to prevent the transformation. However, as the pressure was only applied to the corners of the crystal there would have been ample sites with b_β axes of lengths suitable for nucleation. The negative thermal expansion of a_β can be interpreted as a storage of potential energy at lower temperatures and therefore it permits instability in the structure. The hydrogen

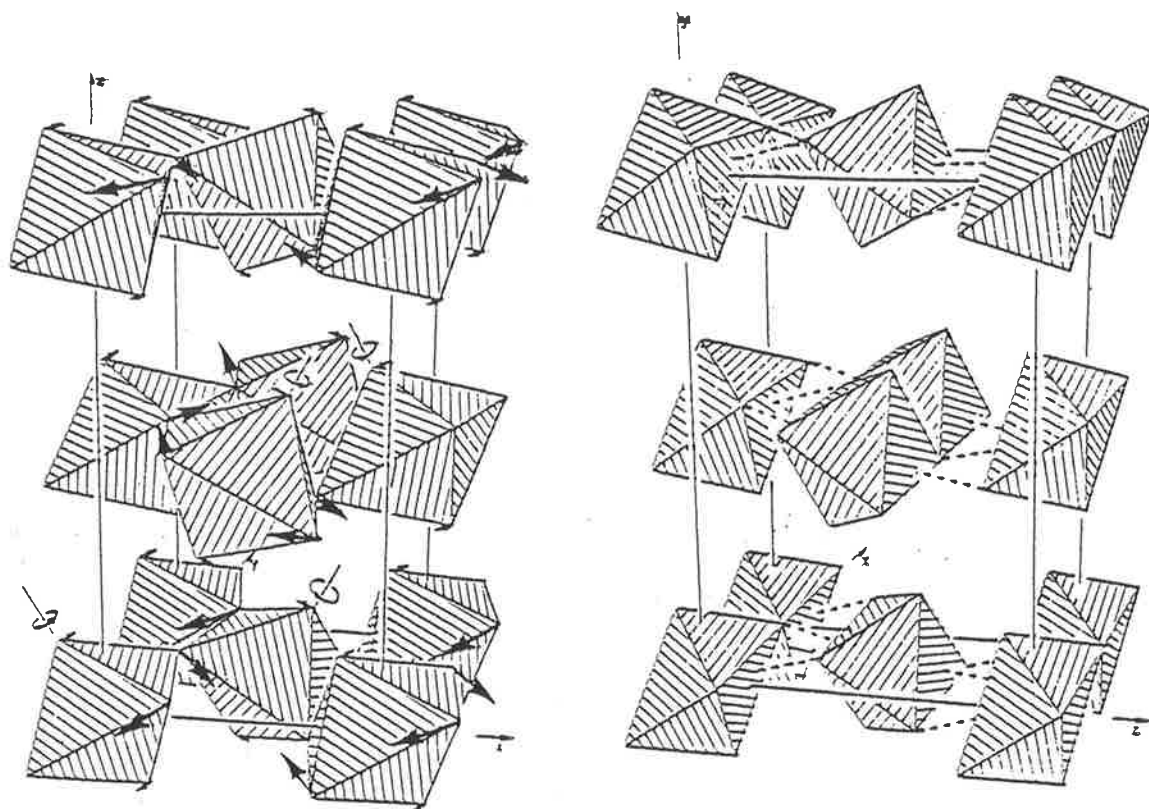


Figure 2.7 Movements of oxygen atom atoms (in terms of octahedral movements) for the transformation $\beta \rightarrow \alpha$ - $\text{UO}_2(\text{OH})_2$. The β -phase is on the L.H.S. Dashed lines in the α -phase represent longer U-O bonds. Axes directions are $x||a$, $y||b$, and $z||c$. (See section 2.4.4 for details). Drawn using a modified ORTEP-II (section 7.8).

bonding can then dominate the transformation as explained by TKD. The increase in the interlayer spacing after transformation is merely a consequential distortion.

Previous authors (Jaswon & Wheeler, 1948; Nishiyama, 1978a) have stated that the correct lattice correspondence for a martensitic transformation is the one with the minimum principal distortions, $\sum_{i=1,3} |\eta_i - 1|$. This would probably be the path of least atomic movement and therefore least bond disruption. In $\beta \rightarrow \alpha\text{-UO}_2(\text{OH})_2$ the lattice correspondence which has the minimum principal distortions is: $a_\beta \rightarrow a_\alpha$, $b_\beta \rightarrow c_\alpha$, $c_\beta \rightarrow b_\alpha$ with $\sum_{i=1,3} |\eta_i - 1| = 0.393$. This was not the observed correspondence which had $\sum_{i=1,3} |\eta_i - 1| = 0.572$. This represents an apparent breakdown of the above rule. However, the observed lattice correspondence is still governed by minimum atomic movements. Relatively few atoms are at the corners of the unit cell and so minimal movement of the corners does not imply a situation of overall minimum atomic movement. The lattice correspondence in this comparatively complex structure is governed by the proximity of the oxygen atoms in the β -phase to their final positions in the α -phase.

2.4.5 The Need for a Lattice Invariant Shear

The transformed crystals resemble the chemically synthesised α -phase so closely that the requirement of a lattice invariant shear appears questionable. The need can be verified by examination of the fit at the interface plane. The fit between the $\{001\}_\beta$ and $\{001\}'_\beta$ faces is the simplest to calculate. From the lattice orientation relation it was seen that $\langle 001 \rangle_\beta$ inclines by a maximum of 4.0° . Without lattice invariant shear, with a component along $\langle 001 \rangle_\beta$, this small tilt would cause a step of 3.4% at the habit plane due to expansion along $\langle 001 \rangle_\beta$. It is doubtful that this could be offset by elastic deformation. A partly transformed crystal of thickness $5 \mu\text{m}$ would have a $.18 \mu\text{m}$ step which is approximately twice the optical resolution of $.1 \mu\text{m}$ obtainable with Nomarski interference. The step would not show up on the thinnest crystals studied but would definitely appear on the larger $10 \mu\text{m}$ thick crystals. No such step was seen on these larger crystals with optical microscopy or by scanning electron microscopy.

Consequently a lattice invariant shear with a component parallel to $\langle 001 \rangle_\beta$ must be operative.

2.4.6 Martensite Calculations and Comparisons with the Experimental Observations

The process of elimination, from the large number of theoretical solutions possible, was greatly facilitated by COATI. The acceptable solutions are the third and/or fourth martensite variants for each slip system. The other variants have larger lattice invariant shears and did not match the experimental observations. The phenomenological theory coded in MRTNST does not imply that the third and fourth variants are those with the smallest L.I.S. They are the smallest in this instance because of the particular choice of crystallographically equivalent slip systems. For example, if the slip system $(012)[\bar{1}21]_\beta$ was selected instead of $(012)[12\bar{1}]_\beta$, the acceptable variants were 1 and 2 rather than 3 and 4.

The predominant cleavage planes are likely candidates for the lattice invariant shear plane. However, neither of the cleavage planes $\{001\}_\beta$ or $\{110\}_\beta$ yielded a theoretical solution which fitted the experimental observations. The slip magnitudes for the acceptable theoretical solutions are all similar and consequently one cannot choose which one is operative from magnitude alone. The type and number of bonds broken during slip must be taken into account. The slip system $(011)\{011\}_\beta$ would require more U-O bonds to be broken than the other four systems as it more frequently crosses the layers of corner-shared octahedra. The cleavage planes in the α -phase are derived from $\{001\}_\beta$ and $\{111\}_\beta$ of the β -phase. Consequently, besides cleavage between the layers the next most likely cleavage plane cuts diagonally across the basal plane. Therefore, out of the two remaining slip planes, $(112)_\beta$ should be more energetically favourable than $(012)_\beta$. Out of the five theoretical slip systems which matched the experimental data, the ones which are most energetically favourable are then $(112)[02\bar{1}]_\beta$ and $(112)[\bar{1}11]_\beta$. The calculated geometric characteristics of these two systems are very similar and consequently both remain as possibilities. Either of these

two systems could have produced some of the lines often seen parallel to $\langle 110 \rangle'_\beta$ on the $\{001\}'_\beta$ surface. In different crystals, with different defect distributions or external constraints, different slip systems may be chosen if their activation energies are similar.

The reduction in the number of possible slip systems to only one was prevented, partly by the imprecision in the lattice parameters, and by the analogous variations in habit plane^e between different crystals. Although Bannister & Taylor (1970) used powder samples for their thermal expansion experiments they still found notable differences in lattice parameters between different samples. These differences must be due to growth defects. For more accurate martensite calculations and comparisons lattice parameters would have to be determined on the same crystal from which the macroscopic shear and orientation relation were measured. The standard reflection search routine of the CAD4 diffractometer cannot cope with the presence of two lattices. Instead, one would have to hand-pick reflection positions from a Laue photograph and enter them into the computer and then have it refine their locations by the usual method. Simplification of the crystals' diffraction pattern by splitting the partly transformed crystal into its component phases would prevent the determination of the orientation relation. An accurate determination of the orientation relation near the transformation temperature may also be necessary due to the changes in thermal contraction of the b_β and c_β axes at the lowest temperatures. The error in the measurement of the habit plane at room temperature, due to the anisotropy of thermal contraction, would only be small compared with the errors involved with optical measurement. The transformation temperature of the particular crystal could be determined before the above measurements, by cooling a batch of the crystals in small decrements of temperature and removing the transformed crystals after each decrement.

During classical slip or shear (Anderson et al., 1974), two close packed planes remain untilted; these being the shear plane and a perpendicular plane containing the direction of shear. In the transformation of $\text{UO}_2(\text{OH})_2$, two perpendicular close packed planes; $\{110\}_\beta$ and $\{001\}_\beta$, remained unrotated to within 4° . This occurred despite the large rotations of the two basal unit cell axes (by approximately 16°). By comparing

the orientation relation with the photographs of partly transformed crystals, it can be demonstrated readily that the particular plane of the form $\{110\}_\beta$, which remained unrotated, was the one just a few degrees from the habit plane. Thus the transformation resembles a deformation shear on $\{110\}_\beta$.

If one placed a hypothetical restraint on the orientation relation such that $\{001\}_\beta$ and one of the planes of the form $\{110\}_\beta$ (namely $(110)_\beta$) remained untilted, then the rotation of the a_β and b_β axes in the $\{001\}_\beta$ plane was calculated to be 17.3° . This is approximately 2° away from the observed orientation relation. By overlapping drawings of α - and β -phase crystals in this orientation the habit plane trace was found to be 8.7° from $[1\bar{1}0]_\beta$ and approximately 5° from the experimental habit plane. When the above process was repeated, but with the empirical orientation relation, then the calculated habit plane was still 1.4° away from that observed experimentally.

Thus the action of a shear on $\{110\}_\beta$ alone cannot explain the observed transformation geometry although the predictions are appreciably close. The differences between these values and those seen in the experiment may be due to the orientation and habit plane adjustments which occur when a lattice invariant shear is incorporated to obtain an undistorted interface.

2.4.7 Minimization of Energy Expenditure by the Shears During Transformation

The shape change in $\text{UO}_2(\text{OH})_2$ appears to be governed by a pseudo deformation shear on $\{110\}_\beta$. If instead of shearing on this plane, the structure was sheared on $\{001\}_\beta$, then large distortions of $\{001\}_\beta$ by up to 32% would occur in the proximity of the interface. The maximum deformation in the interface when shearing on $\{110\}_\beta$ is only 4%. Such large distortions as 32% would require considerable movements of atoms in an area greater than two or three unit cells, for which the activation energy would be prohibitive. Relief by slip at such high frequency would also require a very large activation energy. Similar arguments apply to the next most closely packed planes; $\{101\}_\beta$ and $\{011\}_\beta$.

The five acceptable theoretical solutions all have L.I.S. magnitudes close to 0.09 which is small compared to the macroscopic shear magnitudes of approximately 0.51. This result, together with the fact that the observed shape change is similar to that for the pure lattice distortion, implies that a small L.I.S. is operative. Roitburd & Kurdjumov (1979) stated that a larger elastic distortion is necessary for compatibility between the two lattices when the invariant plane strain differs more from the pure lattice strain. The L.I.S. relieves the elastic distortion at the interface and so the statement of Roitburd & Kurdjomov (1979) implies that the L.I.S. will be smaller when the macroscopic shear simulates the pure lattice deformation. This explains the shape change seen in $\beta \rightarrow \alpha\text{-UO}_2(\text{OH})_2$.

CHAPTER 3

The Wurtzite $\rightarrow$ Sodium Chloride Type Transformation in Manganese Sulphide (MnS)

3.1 Introduction

Manganese sulphide with the wurtzite (B4) structure transforms to the sodium chloride (B1) structure when heated to about 300°C (Furuseth & Kjekshus, 1965) or when pressurised to 37kb (Rooymans, 1962). The coordination number changes from four to six. Two possible mechanisms, A and B, for the transformation upon heating have been described by Kennedy & Summerville (1981) (abbreviated to KS). Mechanism A was described as a basal layer $((0001)_{B4})$ translation and mechanism B as primarily distortive and martensitic. Orientation relations and optical microscopic analyses were given for both mechanisms. The zincblende (B3) $\rightarrow$ sodium chloride type transformation in MnS has similarly been described by Kennedy, Harris & Summerville (1980). The applicability of the Phenomenological theory of martensitic transformations to the structure change B4 $\rightarrow$ B1 would greatly widen the scope of the theory as it has not previously been tested on such a change in coordination number in inorganic compounds.

The B1, B3 and B4 polymorphs of MnS have the colours green, pink (or orange) and red respectively (Ford et al., 1963) and are often denoted by the symbols α , β and γ . The two tetrahedrally coordinated phases are metastable at standard temperature and pressure (STP) with respect to the B1-phase (Rao & Pisharody, 1976). The transformation B3 $\rightarrow$ B4 in MnS has also been observed under heating or physical stress (Kennedy, Harris & Summerville, 1980). The B1-phase is found with other metallic sulphides in vein deposits (Ford, 1932) and is called alabandite. Due to its comparatively large thermal contraction in steels it can reduce the embrittlement effects of alumina and silicate inclusions (Brooksbank & Andrews, 1968). All three polymorphs of MnS are p-type semiconductors (Widemeier & Sigai, 1969; CRC Handbook of

Chemistry & Physics, 1983a).

The reported temperature of the B3→B1 transformation is 200°C (Furusetth & Kjekshus, 1965; Rao & Pisharody, 1970). However the temperature of the B4→B1 transformation differs within the literature. Fureseth & Kjekshus (1965) reported 300°C. Schwartz, Tauber & Shappiro (1967) (abbreviated to STS) reported 264(±5)°C with a contamination of .03wt% of Si and 450°C with 2wt% of Si. A value of 200(±10)°C was reported by KS.

The objective of this project was to calculate the phenomenological martensite solutions for the mechanism B of KS and to compare these with the experimental observations of KS. However, some vital information was not reported by the latter authors and so it was necessary to undertake further experimental analysis as described in the next paragraph.

The habit plane provides a sensitive test between theoretical predictions and experimental observations as it can greatly vary between different theoretical solutions. KS unfortunately approximated their observed interface plane to the nearest, low index, rational plane. The two angles which they reported between the interface traces and the edges are insufficient to recalculate their observed habit plane. Consequently, in order to perform a comparison between theory and observation, the habit plane had to be remeasured. An angle of shape change, 12°, reported by KS was only measured in projection for one crystal edge and therefore it did not define the three-dimensional shape change. Kennedy (1985) also stated that this angle was only recorded from the one crystal shown in the paper by KS. It has been shown in chapter 2 that a large shape change can significantly reduce the accuracy and precision of the orientation relation determined when the crystal is glued during transformation. KS used this method for determining their orientation relations. Consequently, due to the large shape change they reported, it was desirable to undertake a redetermination of the orientation relations using crystals which had been partly transformed without physical constraints. Thus the experiments by KS served as qualitative groundwork for study of the transformation.

KS stated that the principal strains for the A mechanism each represented a contraction and consequently there was no invariant line and therefore no possibility of a martensitic mechanism. Nishiyama (1978b) demonstrated how the fcc lattice can distort into the hcp lattice assuming the same lattice correspondence as that found for the A mechanism in MnS. During the pure lattice strain the hexagonal c-axis tilts by approximately 19° with respect to the basal plane. KS assumed that one of the principal strains was along the hexagonal c-axis. Principal strains must remain unrotated during a pure lattice strain and therefore the premises of KS were incorrect. Thus the possibility of a martensitic transformation, with the lattice correspondence of the A mechanism, also had to be investigated.

Possible slip systems which must be considered have been discussed in section 1.4. The reported slip modes for the (NaCl) type structure are of the types $(001)[1\bar{1}0]$, $(001)[100]$, $(110)[001]$ and $(110)[1\bar{1}0]$ (Beurger, 1930). These can be referred to the B4-phase using the appropriate lattice correspondence. For the A and B mechanisms respectively, the correspondence matrices are:

$$\begin{bmatrix} 0 & -.5 & .5 \\ .5 & 0 & .5 \\ -.5 & .5 & 1 \end{bmatrix} \text{ and } \begin{bmatrix} .5 & -.5 & 0 \\ .5 & .5 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Das & Weinstein (1967) found the following slip systems in deformed B4-phase cadmium sulphide: $(0001)[11\bar{2}0]$, $(0001)[10\bar{1}0]$, $(10\bar{1}0)[1\bar{2}\bar{1}0]$, $(10\bar{1}0)[0001]$ and $(1\bar{2}10)[10\bar{1}0]$. The above mentioned B1 and B4-phase slip systems were possibilities for the lattice invariant shear.

For the A mechanism there are two planes which lose their mirror symmetry and therefore could be twin planes of a LIS by twinning. These planes are $(0001)_{B4}$ and $(1\bar{1}00)_{B4}$ which become $(111)_{B1}$ and $(11\bar{1})_{B1}$ respectively. The directions $[0001]_{B4}$ and $[1\bar{1}00]_{B4}$ lose their two fold rotational symmetry to become $[112]_{B1}$ and $[1\bar{1}\bar{2}]_{B1}$ respectively and could therefore be Type II twinning directions. For the B mechanism there is no loss of symmetry of the lattice and consequently no twinning possibilities.

The transformation temperature of MnS is high enough above room temperature to warrant the use of appropriate lattice parameters for the phenomenological calculations.

Thermal expansion data for the B4-phase were not available, most probably because of its metastability and consequent scarcity. The thermal expansion of wurtzite phase CdS and ZnS were available (Oskot-Skii, Kobayakov & Solodukhin, 1980; Skinner, 1962). CdS is a closer analogy than ZnS to MnS due to its similar polymorphism and therefore represents a model on which to base the thermal expansion of B4-phase MnS. The thermal expansion of B1-phase MnS was determined by Brooksbank & Andrews (1968).

3.2 Experimental

3.2.1 Crystal Selection

The crystals had been grown by J.Pockett (Adelaide Univ., 1977) at 30°C by the method used by STS and KS. Approximately 5% of the crystals showed B1-phase inclusions and consequently were not further studied. Most of the crystals used were hexagonal prisms, bevelled at one end, and with a length of approximately twice their diameter. Many of these were also slightly wider at the bevelled end (Fig. 3.1.a). The prisms were only translucent and so surface features on the undersides were not distinguishable. The most distinct cleavage was on the basal plane but subconchoidal fracture predominated. Approximately 10% of the crystals were hexagonal platelets, transparent due to their thinness. The average sizes of the prisms were $60 \times 30 \times 30 \mu\text{m}^3$ and the platelets were $10 \times 50 \times 50 \mu\text{m}^3$.

3.2.1 Optical Microscopy

The heating stage used is described in section 7.2.2.2. It was calibrated to a precision of $\pm 10^\circ\text{C}$. Three hexagonal platelets and about sixty hexagonal prisms were studied. The prisms were all laid on their $\{10\bar{1}0\}_{\text{B4}}$ faces and the platelets on their $\{0001\}_{\text{B4}}$ faces. Crystals were usually heated at $30^\circ\text{C}/\text{min.}$ but some were heated at $200^\circ\text{C}/\text{min.}$ to test for any effect of mild thermal shock. Only one crystal was heated at a time so as to allow detailed observation.

Transmitted and reflected light, dark field and Nomarski interference contrast were used for inspection. The latter technique was employed to detect small differences in surface relief. Photographs were taken for more precise measurements.

3.2.3 Electron Microprobe Analysis and Scanning Electron Microscopy

Four B4-phase crystals intended for E.M.P. analysis were mounted as described in section 7.3. Spot analyses were performed at three locations on the uppermost $\{10\bar{1}0\}$ face of each crystal. The elements tested for and their detection limits were as follows: Na .03, Mg .02, Al .03, Si .03, P .04, S .04, Cl .04, K .04, Ca .05, Ti .07, V .08, Cr .09, Mn .11, Fe .27, Ni .19.

Two B4-phase prisms were laid on aluminium stubs and gold coated. They were transformed in the S.E.M. using the heater made by P.Schultz (section 7.3). The heating rate was about $50^{\circ}\text{C}/\text{min.}$ with a maximum temperature of $600 \pm 50^{\circ}\text{C.}$ The crystals were slowly cooled to room temperature before exposing them to air.

3.2.4 Orientation Relations by X-ray Diffraction

Besides four crystals which were transformed on the X-ray camera, seven others had previously been transformed on the optical microscope and two in the S.E.M. before examination by X-ray diffraction. All crystals were glued onto thin glass fibres with a minimal amount of Araldite (epoxy resin adhesive). They were initially oriented with a surface facing the X-ray beam to within 3° using the Stoe telescope with reflected light. Partly transformed and untransformed crystals were further oriented so that for each crystal at least two of the planes $\{10\bar{1}0\}_{\text{B}_4}$, $\{11\bar{2}0\}_{\text{B}_4}$ and $\{0001\}_{\text{B}_4}$ could be turned to face the X-ray beam by rotating the spindle axis of the camera. For transformations on the X-ray camera the heater used was calibrated to $\pm 50^{\circ}\text{C}$ (section 7.2.4.2). Three previously untransformed crystals were heated to 250°C for five minutes and one at 340°C for one hour.

Although both precession and Laue photographs were recorded, the orientations of product crystallites were deduced from precession photographs only. Due to the large

number of product crystallites the Laue photographs were too complex to solve without prior knowledge of the results from the precession photographs.

3.2.5 Martensite Calculations and the Comparisons

The percentage increase in the unit cell axes lengths of wurtzite phase CdS from room temperature to the transformation temperature of MnS were calculated from the data of Oskot-Skii, Kobayakov & Solodukhin (1980) and applied to the room temperature axes of wurtzite (B4) phase MnS. The lattice parameter of the B1-phase at 330°C was deduced from the data of Brooksbank & Andrews (1968). These calculated lattice parameters were used for all the phenomenological calculations.

Program COATI (section 7.7) was used to calculate the principal distortions vectors for the A mechanism. Due to the orthogonal symmetry of the lattice correspondence for the B mechanism the directions of the principal distortions are evident from inspection and are parallel to $[11\bar{2}0]_{B4}$, $[\bar{1}100]_{B4}$ and $[0001]_{B4}$.

The phenomenological calculations were carried out by program MRTNST (section 7.6). The trial slip systems have been mentioned in section 3.1. From these slip systems, extra ones equivalent either by the symmetry of the B1-phase or by the symmetry of the B4-phase were also tested. Comparison with the experimental observations was performed using program COATI.

3.3 Results

3.3.1 Optical Microscopy

The majority of the transformations proceeded by successive sudden bursts and section 3.3.1.1 is devoted to their description. In two small hexagonal platelets there were slow-moving rounded interfaces and they are discussed separately.

3.3.1.1 Sudden Transformation Mode

Transformation began at the bevelled end of the prisms and spread along

Figure 3.1 Optical micrographs. All in reflected light. (c) and (e) are with dark-field illumination. (b), (d), (h) and (k) are with Nomarski interference contrast. All are viewed onto $\{10\bar{1}0\}_{B_4}$ except (g) and (l) which are viewed onto $\{0001\}_{B_4}$. See section 3.3.1 for details.

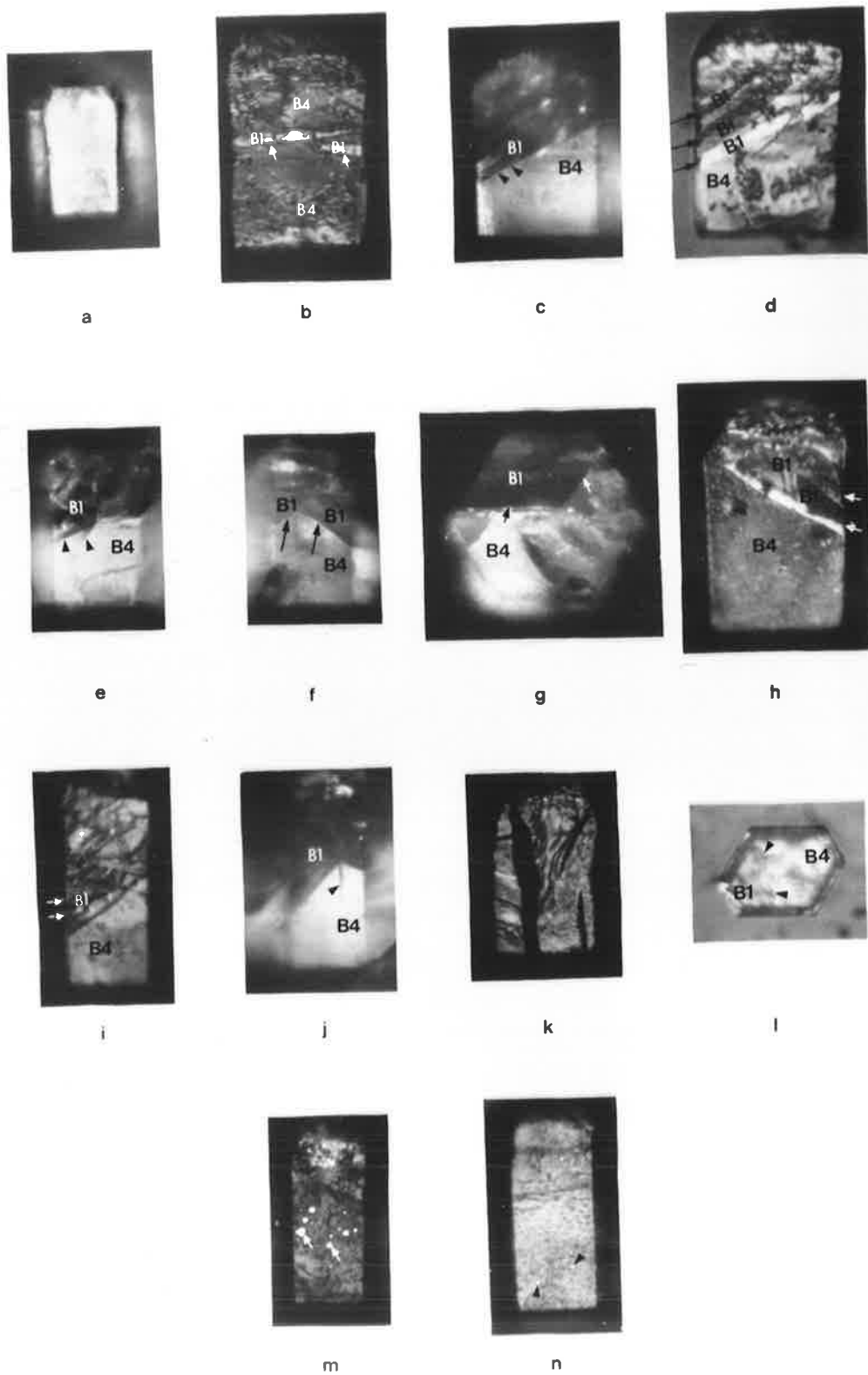


Figure 3.1

their length in discrete bursts. The average initial transformation temperature was $330(\pm 20)^{\circ}\text{C}$ with the minimum at 240°C and a maximum of 400°C . Further transformation occurred on increasing temperature and there were two to four different transformation temperatures for each crystal. The temperature span between successive transformations in any one crystal ranged from 30 to 150°C . About 5% of the crystals transformed again within a minute after transformation if the temperature was maintained at about 400°C . Complete transformation was very rarely detected as residual small pockets of B4 phase usually remained. After a few minutes at 430°C the surface became discoloured and rough, thereby preventing the observation of a maximum transformation temperature.

Each individual domain which transformed was about $1/20$ to $1/5$ of the crystal volume but above 370°C the domains were sometimes up to one half of the crystal volume. The shapes of the transformed domains were either large pyramidal sections or less commonly thin wedges (Fig. 3.1.b→d), the latter appearing as bands on one face. Occasionally there were thin wafers of the B1-phase (Fig. 3.1.e). Areas of untransformed crystal often gradually turned green (indicating transformation) over several minutes with no apparent interface.

The interface traces on the crystal surfaces were mostly straight (Fig. 3.1.c) but about one fifth of them were curved (Fig. 3.1.f). The occasional thin wedge shaped regions of B1-phase also implied a curved habit plane, commonly referred to as lenticular in metallurgical literature. The angles which the interface traces on $\{10\bar{1}0\}_{\text{B}_4}$ made with the $\langle 0001 \rangle_{\text{B}_4}$ edges varied greatly between different crystals and even within the same crystal. For interfaces in which the curvature was only slight (Fig. 3.1.d), the trace was approximated as the midrib. Alternatively, interfaces with a relatively small radius of curvature (Fig. 3.1.f) were disregarded. The interfaces on crystals which had $\langle 0001 \rangle_{\text{B}_4}$ type edges with an angular divergence of more than 3° were also disregarded due to indeterminate indices of the surface. Interfaces which contained blotches due to atmospheric effects were also quantitatively disregarded. A total of twenty three angles between interface traces and $\langle 0001 \rangle_{\text{B}_4}$ type edges were reliably measured with a

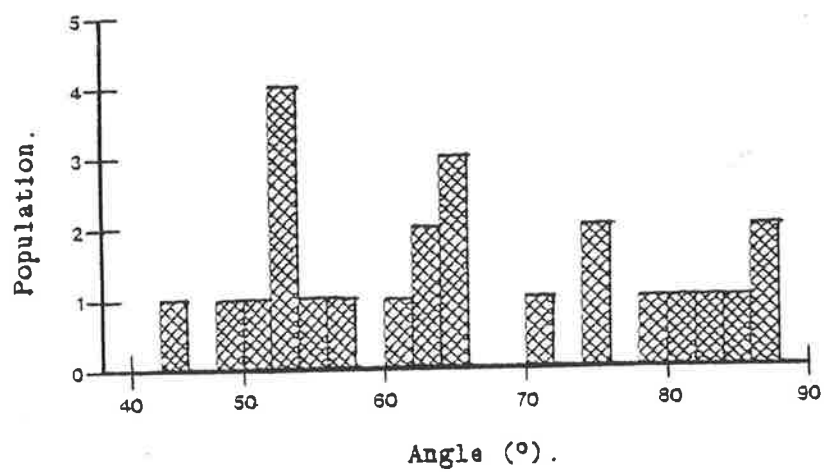


Figure 3.2 Bar graph of the population of habit plane angles at 2 degree intervals.

precision of $\pm 2^\circ$. They are shown diagrammatically in Fig. 3.2. Due to the 60° incline between neighbouring faces only inappreciable segments of the interface trace remained in focus on the sloping sides. However the interfaces were followed across edges of two prisms to give interface planes of $\{1\ 1.9\ \overline{2.9}\ 6.5\}_{B_4}$ and $\{1\ \overline{3.1}\ \overline{2.1}\ 9.7\}_{B_4}$. The interface traces on the $\{0001\}_{B_4}$ surface of one platelet (Fig. 3.1.g) were at 2.5° to the $\langle 10\overline{1}0 \rangle_{B_4}$ edges.

Volumes as large as one half of the crystal transformed without surface tilts. One small hexagonal platelet fully transformed in several regions simultaneously also without a change in shape. Although an absence of tilting was predominant, the surfaces adjoining the interface trace were often slightly bent thereby producing different surface relief between the two phases further from the interface. Sometimes the two surfaces were not bent, but there was a step between the two phases or between two individual B1-phase regions (Fig. 3.1.h) thereby implying a shape change. Approximately 5% of these latter products also tilted by up to 10° (Fig. 3.1.i).

While transforming, about one fifth of the crystals jerked sideways. When large fractions transformed on the lower sides of the crystals they even rolled over. The platelets only jerked without rolling over.

Cracking occurred in approximately 90% of the transformations. Crystals which had jumped were cracked but those which didn't move also frequently developed cracks. They were mainly located in the B1-phase but sometimes occurred in the B4-phase at the junction of two interface traces (Fig. 3.1.j). The larger cracks were more indiscriminate and appeared as gaps (Fig. 3.1.k) rather than as single lines.

3.3.1.2 Slow-moving Interface Mode

In two thin ($\approx 3\mu\text{m}$) hexagonal platelets at $300(\pm 20)^\circ\text{C}$ a rounded, slow-moving interface advanced across the crystal (Fig. 3.1.l). In its wake a green shade was left, indicative of a transformation. There was no shape change or crystal movement. The speed of progression was about $2\ \mu\text{m}/\text{sec}$. The first wave only produced a green tinge, but about seven further interfaces took the same path (as seen in projection) and

increased the green hue. One platelet which had transformed only by this mode was studied by X-ray diffraction. The other platelet finally transformed fully by the sudden mode in one step at 400°C.

3.3.1.3 Spots and Discolouration

Light grey, spherical spots often appeared on the crystal surface during heating. Their number and size increased with both time and temperature but more so with time. The spots first appeared after about ten minutes at 300($\pm$ 20)°C. They initially oscillated in girth at about 3Hz for 30 seconds, after which time they slowly grew without oscillation. At 400°C some which were about one fifth of the crystal width momentarily vanished but quickly regrew. Initial transformation usually precluded the appearance and growth of the spots. Spots which formed after transformation mainly congregated along the interface traces and cracks, thereby obscuring photography. More spots grew on the B1-phase than on the B4-phase. The spots coalesced into blotches and eventually covered the surface which became greyish brown. The surfaces of both phases became opaque and rough after ten to fifteen minutes at 400°C.

3.3.2 Scanning Electron Microscopy and Electron Microprobe Analysis

During heating there was no shape change. The only effects were small cracks. After removal from the S.E.M. the crystals were still shiny but were green under transmitted light in the optical microscope.

The E.M.P. analysis revealed no variation in atomic composition in different areas of the crystals' surfaces. The average amounts of impurities in weight % were as follows:

Na .48, Mg .10, Si .73.

3.3.3 Orientation Relations

3.3.3.1 Transformations on the X-ray Camera

The relative intensities of products and parent reflections of the three crystals

heated to 250°C indicated that they had transformed by between 25 and 50%. The fourth crystal had transformed by 80%. The parent phases remained unrotated and there were no increases in diffuseness of their diffraction spots, except for the crystal which had 80% transformed in which case the spreading was $\pm 0.5^\circ$. Room temperature lattice parameters are given in Table 3.1

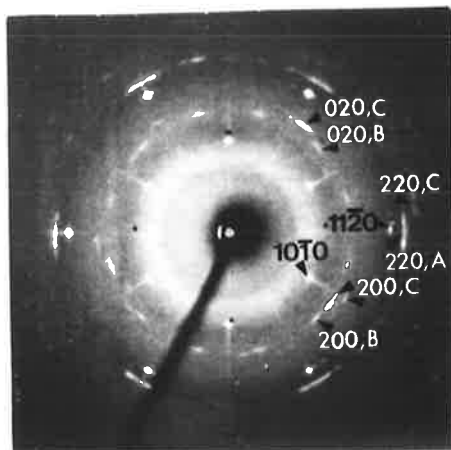
3.3.3.1.a View Onto $\{0001\}_{B4}$

After transformation the new reflections seen on a precession photograph had interplanar spacings of $1.83(\pm 0.03)$ and $2.61(\pm 0.03)\text{\AA}$, which were indexed on a lattice of the B1-phase as $\{220\}_{B1}$ and $\{200\}_{B1}$ respectively ($a_{B1} = 5.22\text{\AA}$). Neither of these reflections could be indexed on the zincblende (B3) phase.

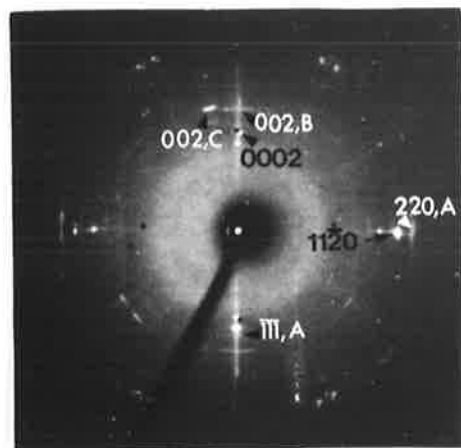
The $\{220\}_{B1}$ reflections were at $4(\pm 2)^\circ$ to the $\{11\bar{2}0\}_{B4}$ normals and also thinly spread across this 8° separation. These twelve reflections corresponded to two B1-phase crystals, each having one of $\langle 111 \rangle_{B1}$ approximately parallel to $\langle 0001 \rangle_{B4}$ but rotated around this latter direction by $\pm 4^\circ$. Orientations of this type will be called type "A" after the nomenclature of KS.

The $\{200\}_{B1}$ reflections were between 0 and $3(\pm 1.5)^\circ$ from a position at 15° to the $\{11\bar{2}0\}_{B4}$ normals. These $\{200\}_{B1}$ reflections were also at the same angles to the $\{11\bar{2}0\}_{B4}$ normals which are at 30° to the $\{10\bar{1}0\}_{B4}$ normals. For each parent crystal there were only a maximum of twelve $\{200\}_{B1}$ reflections. These could be grouped into three sets on the condition that in any one set the four reflections were 90° apart. For each set the angle of rotation from $\{11\bar{2}0\}_{B4}$ was independent from the rotation of the other two sets. Each set could therefore be assigned to a separate crystallite and its four reflections indexed cyclically as $(200)_{B1}$, $(020)_{B1}$, $(\bar{2}00)_{B1}$ and $(0\bar{2}0)_{B1}$. This implied that $[001]_{B1}$ was approximately parallel to $[0001]_{B4}$. The deviation for each set from the average position, $\{200\}_{B1}$ at 15° to $\{11\bar{2}0\}_{B1}$, appeared to be random but was not just a reflection spreading effect. For each parent crystal one of the three sets of $\{200\}_{B1}$ reflections was approximately 1.5 times as intense as the other two sets. This observation lent further support to the grouping scheme. These three sets

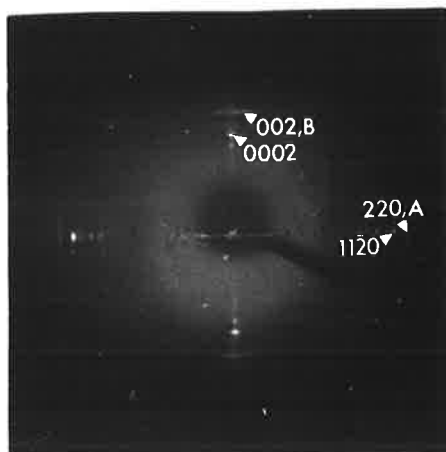
Figure 3.3 X-ray precession photographs of partly transformed crystals. (a), (d) and (e) are viewed onto $\{0001\}_{B4}$. (b) and (c) are viewed onto $\{10\bar{1}0\}_{B4}$. Crystals were transformed on (a), (b) the X-ray camera and (c), (d) and (e) the optical microscope. See section 3.3.3 for details.



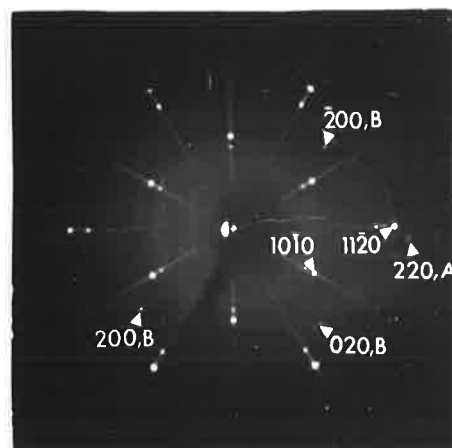
a



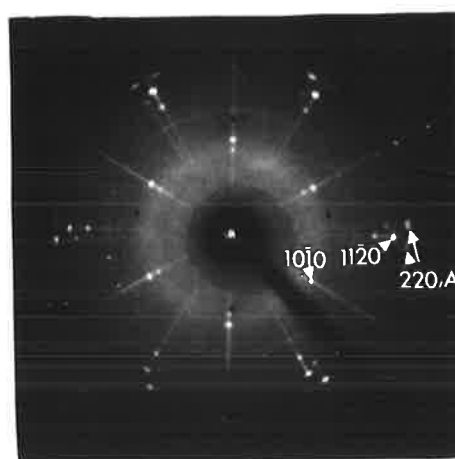
b



c



d



e

Figure 3.3

of orientations will be called type "B" after the nomenclature of KS.

For one crystal, which had at least half transformed (Fig. 3.3.a), a fourth set of the type B orientations existed with $(100)_{B1}$ at $+5(\pm 2.5)^\circ$ to $(10\bar{1}0)_{B4}$. This fourth set was twice as intense as any of the other three sets and its $\{220\}_{B1}$ reflections were visible. This indicated that it corresponded to a much larger crystallite. The interplanar spacings as shown by its $\{200\}_{B1}$ and $\{220\}_{B1}$ reflections were anomalously small. One of the $\langle 100 \rangle_{B1}$ axes was shorter than its perpendicular partner. The interplanar spacings were: $1.75\text{\AA}$ $(2\bar{2}0)_{B1}$; $2.44\text{\AA}$ $(200)_{B1}$; $1.72\text{\AA}$ $(220)_{B1}$ and $2.58\text{\AA}$ $(020)_{B1}$. These spacings do not correspond to the B3 phase. The variations indicate that if the structure was approximately of the B1 type then it was significantly distorted by as much as 8% along one axis. The reflections on one side of the origin were not clearly visible, thereby implying that $[001]_{B1}$ was tilted from $[0001]_{B4}$ by several degrees. Such a tilt produces some deviation in the interplanar spacing calculated from the precession photograph, but not significantly so for the precision used here. This orientation will be called type "C" and possible causes for the anomalies will be discussed in section 3.4.4.

For this same crystal, one reflection corresponding to an interplanar spacing of $2.38\text{\AA}$, was parallel to one of the $\{10\bar{1}0\}_{B4}$ normals. This reflection most likely represented a slightly rotated type C orientation, but there were no perpendicular planes for confirmation of this. The spread of the usual type C orientations brought some of them to within 2° from this orientation and consequently it will not be given a separate name.

3.3.3.1.b View Onto $\{10\bar{1}0\}_{B4}$

The $\{220\}_{B1}$, $\{111\}_{B1}$ and $\{222\}_{B1}$ reflections conformed with the type A orientations seen on the view onto $\{0001\}_{B1}$. Additionally, in the present view, they indicated that one of $\langle 111 \rangle_{B1}$ (for the type A orientations) was at $4.5(\pm 1.)^\circ$ to $\langle 0001 \rangle_{B4}$.

The $\{200\}_{B1}$ reflections conformed with the type B orientations and indicated that $[001]_{B1}$ deviated from $[0001]_{B4}$ by as much as 6° .

Each crystal showed very faint reflections from type C orientations and they

indicated that $[001]_{B1}$ deviated from $[0001]_{B4}$ by as much as 5° . Some of their corresponding faint reflections in the view onto $\{0001\}_{B1}$ were hidden by the large number of more intense reflections. For the crystal which had at least half transformed (Fig. 3.3.b) the deviation of $[001]_{B1}$ (for one of the type C orientations) from $[0001]_{B4}$ was $12(\pm 1.5)^\circ$ and the corresponding interplanar spacing was $2.49\text{\AA}$.

3.3.3.1.c View Onto $\{11\bar{2}0\}_{B4}$

The new reflections after transformation were only from the $\{200\}_{B1}$ form. There were two types, distinguishable by their spreading and intensity. The first type were consistent with type A orientations and were spread slightly more than the parent reflections. The second type, which were more spread and weaker than the first type, were consistent with type B orientations.

3.3.3.1.d Relative Proportions of Product in Type A, B and C Orientations

Judging from the relative intensities of the $\{200\}_{B1}$ reflections for the type A and B orientations on the various views, the amount of product in the type A orientations was about four times the amount in the type B orientations. The type C orientations represented about one quarter or less of the product volume represented by the type B orientations.

3.3.3.2 X-ray Analysis of Crystals Transformed on the Optical Microscope

The crystals had transformed by between 5 and 100% without an increase in diffuseness of the parents' reflections. The products' reflections were generally spread by $\pm 5^\circ$ except for the fully transformed crystal with a spread of $\pm 4^\circ$. These former crystals provided more precise type A, B and C orientation relations than those from crystals transformed on the X-ray camera. The type A orientations were again more dominant than the type B orientations. However the product phase in the crystal which had only transformed by 5% was a single crystallite with a type B orientation.

3.3.3.2.a Mechanism A

In the view onto $\{0001\}_{B4}$ the product (type A) was rotated by $\pm 4.5(\pm 0.5)^\circ$ from $\{220\}_{B1} \parallel \{11\bar{2}0\}_{B4}$ and was also very faintly spread between these two orientations. One of the two sets was often as intense as the other set. Within any one set the relative intensities of the six $\{220\}_{B1}$ reflections indicated that the crystallite was tilted about a $\{10\bar{1}0\}_{B4}$ normal. Comparison of the two sets indicated that they were tilted around different $\{10\bar{1}0\}_{B4}$ normals which were 60° apart. The views onto $\{10\bar{1}0\}_{B4}$ and $\{11\bar{2}0\}_{B4}$ indicated that the amount of this tilt was $\pm 4.3^\circ$. The product was also spread between these two orientations.

The thin platelet which had partially transformed by the slow-moving interface mode only, was half transformed and showed only type A orientations together with a faint ring of $\{200\}_{B1}$ reflections (Fig. 3.3.e).

In summary, the orientation relation for the A mechanism (deduced from these partly transformed crystals) is $(11\bar{2}0)_{B4} \parallel (\bar{1}10)_{B1}$, $(0001)_{B4} \parallel (111)_{B1}$ plus a 4.5° rotation around $[0001]_{B4}$ and a 4.3° rotation around $(10\bar{1}0)_{B4}$ (Fig. 3.4.a). Due to the symmetry of the two phases there are four possible orientations of the product which correspond to two pairs with different $\pm$ rotations.

3.3.3.2.b Mechanism B

In the view onto $\{0001\}_{B4}$ the type B orientations were rotated from the average ($\{200\}_{B1}$ at 15° to $\{11\bar{2}0\}_{B4}$) by up to $4.0(\pm 0.3)^\circ$ (e.g. Fig. 3.3.d). There was often a pronounced variation in intensity between the different type B sets and the number of visible sets (for different parent crystals) ranged from one to three. The views onto $\{10\bar{1}0\}_{B4}$ and $\{11\bar{2}0\}_{B4}$ indicated a range of tilts of $[001]_{B1}$ with respect to $[0001]_{B4}$ by up to 5° and without any localisation within this range. One of the three possible orientation relation ranges for mechanism B is shown in Fig. 3.4.b; the others are generated by $\pm 120^\circ$ rotations around $[0001]_{B4}$.

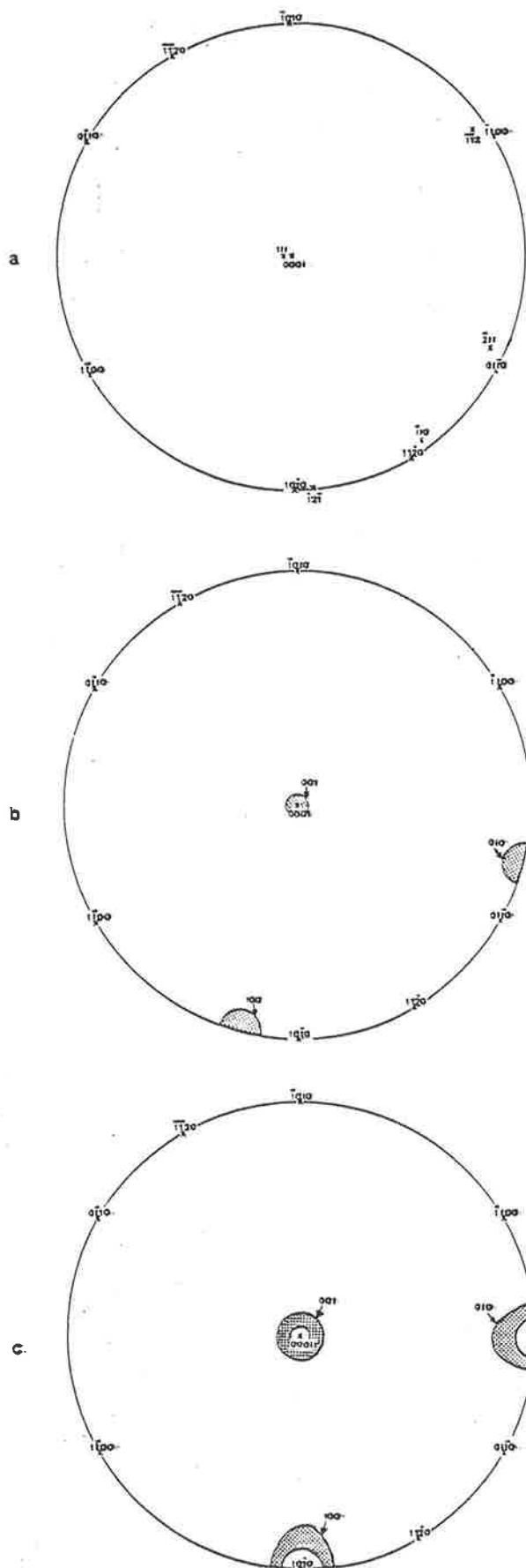


Figure 3.4 Stereographic representation of orientation relations seen for mechanisms (a) A, (b) B and (c) C. Four index notation refers only to the B4-phase. The dotted areas indicate ranges of possible orientations and not reflection spreading. See section 3.3.2 for details.

3.3.3.2.c Mechanism C

The orientation relation for this mechanism was obtained with only a little more precision than for that calculated from crystals transformed on the X-ray set. The $\{100\}_{B1}$ reflections were between 5 and 8° from $\{10\bar{1}0\}_{B4}$ in different crystals viewed onto $\{0001\}_{B4}$. One of the three possible orientation relation ranges for mechanism C is shown in Fig. 3.4.c; the others are generated by $\pm 120^\circ$ rotations around $[0001]_{B4}$.

3.3.3.3 X-ray Analysis of Crystals Transformed in the S.E.M

The A, B and C orientation relations seen for crystals transformed by other methods were also present in these crystals. Both crystals had transformed fully and their reflections were spread by approximately $\pm 4^\circ$. The average interplanar spacing for $\{200\}_{B1}$ for products with the type C orientation was $2.48(\pm 0.03)\text{\AA}$.

3.3.4 Martensitic Calculations and Comparisons

The percentage increase in the lengths of the B4-phase a- and c-axes due to thermal expansion (between room temperature and 330°C) were 0.183% and 0.162% respectively. The corresponding high temperature lattice parameters were $a_{B4}=3.983$ and $c_{B4}=6.44\text{\AA}$. Incidentally, the percentage increases for wurtzite phase ZnS were both .243%. The lattice parameter of the B1-phase at 330°C was $5.2478\text{\AA}$. The principal distortion vectors for the A and B mechanisms are given in Table 3.1.

In the A mechanism, for Type I twinning, the twinning directions in $(0001)_{B4}$ and $(1\bar{1}00)_{B4}$ were calculated to be $[1\bar{1}00]_{B4}$ and $[0001]_{B4}$ respectively. Therefore the proposed Type II twinning elements coincided with the Type I due to the lattice symmetry. There were no martensitic solutions for either of the two twin planes (and therefore none for the Type II twinning). From all the slip systems which were tested with the A mechanism, three gave martensitic solutions and only one of these had an orientation relation close to that observed. This slip system was $(10\bar{1}1)[01\bar{1}0]_{B4}$ which corresponds to the sodium chloride type slip system $(010)[\bar{1}01]_{B1}$ mentioned in section 3.1. The four variants of this slip system were different and only variant 1

a

	B4	B1
$\approx 25^\circ\text{C}$	$\dagger a = 3.976$ $c = 6.43$	$\dagger a = 5.2191$
330°C	$\dagger\dagger a = 3.983$ $c = 6.44$	$\dagger a = 5.2478$

b

	Mechanism A		Mechanism B	
	Direction	Magnitude	Direction	Magnitude
η_1	$1 \bar{1} 0 .87253$	0.78455	$1 \ 1 \ \bar{2} \ 0$	1.31755
η_2	$1 \ 1 \ \bar{2} \ 0$	0.93165	$\bar{1} \ 1 \ 0 \ 0$	0.76069
η_3	$\bar{1} \ 1 \ 0 \ 1.31518$	1.11735	$0 \ 0 \ 0 \ 1$	0.81488
B	$\begin{bmatrix} .92467 & .00718 & -.15212 \\ .00718 & .92447 & .15212 \\ -.08728 & .08728 & .98462 \end{bmatrix}$		$\begin{bmatrix} 1.03912 & .27843 & 0 \\ .27843 & 1.03912 & 0 \\ 0 & 0 & .81488 \end{bmatrix}$	

Table 3.1 (a) Lattice parameters of MnS in Å ($\dagger$ ASTM power file No. 3-1073; $\dagger\dagger$ Brooksbank & Andrews, 1968; $\dagger\dagger$ section 3.3.4) and (b) principle distortion vectors, η_1, η_2, η_3 (at 330°C), $\Delta V = -18.3\%$. The pure lattice strain matrices (B) are referred to the B4 unit cell.

$$P1 = \begin{bmatrix} .92339 & .02565 & -.24153 \\ .16672 & .94417 & .52564 \\ -.01613 & .00540 & .94914 \end{bmatrix} \quad P2 = \begin{bmatrix} 1 & 0 & 0 \\ -.20369 & 1 & -.20369 \\ 0 & 0 & 1 \end{bmatrix} \quad S = \begin{bmatrix} .91817 & .02565 & -.24676 \\ -.02560 & .94417 & .33332 \\ -.01723 & .00540 & .94804 \end{bmatrix}$$

Habit plane $(.3008 \quad \overline{.1007} \quad \overline{.2008} \quad .9484)_{B4}$

Slip magnitude .267

Shape change $(10\bar{1}0)_{B4} \wedge (10\bar{1}0)'_{B4} = 5.6^\circ$
 $(0001)_{B4} \wedge (0001)'_{B4} = 1.8^\circ$

Table 3.2 Theoretically predicted characteristics of the slip system $(10\bar{1}1)[01\bar{1}0]_{B4}$ for mechanism A, Variant No.1. Matrices are referred to the B4-phase unit cell.

(Table 3.2) was close to the observed orientation relation. The rotations from the ideal $(11\bar{2}0)_{B4} \parallel (110)_{B1}$ with $(0001)_{B4} \parallel (1\bar{1}1)_{B1}$ were in the same directions as those seen experimentally but were smaller in magnitude: namely 1.6° (Fig. 3.5) compared with 4.5° (Fig. 3.4.a). The agreement between the theoretical and experimental results was close but outside the region of experimental error. The predicted surface tilts ranged from approximately 2 to 6° and were compatible with some of the experimentally observed tilts.

For the B mechanism no martensitic solutions were found to agree with the experimental observations even though the requirements for a match were not strict. For example, any predicted orientation relations within 7° of that observed experimentally were considered acceptable; but none were in that region.

3.4 Discussion

3.4.1 General Comparison With Earlier Work

The B1 phase inclusions seen in some of the B4-phase crystals matches the observations of STS but is contrary to KS. The non-parallel edges on some of the prism faces ($\{10\bar{1}0\}_{B4}$) of the B4-phase crystals implies either that the l index was not exactly zero or that the crystals were slightly foliated. The semi concoidal fracture indicates that the former is more probable.

The observed transformation temperature agrees well with the literature values mentioned earlier, except with the value of $200(\pm 10)^\circ\text{C}$ (KS) which is anomalously low. STS correlated a lower transformation temperature with a lower Si content, and therefore the low temperature of KS may be due to a lower Si content in their crystals.

The range of transformation temperatures reported by STS matches that found in individual crystals in the present work and suggests a range of Si content within each crystal. An alternative reason for the observed temperature range could be that strains from previously transformed regions had partially stabilized the B4-phase. A similar effect was observed in $\beta \rightarrow \alpha\text{-UO}_2(\text{OH})_2$ (chapter 2).

The green colour of crystals transformed in the S.E.M. implies that the brownish discolouration of crystals heated in the optical microscope was due to reaction with the atmosphere. Auroux et al. (1973) stated that B4-phase oxidizes to Mn_2O_3 in air at ambient or high temperature. The shapes and locations of small spots seen on the surface are similar to the UO_3 nuclei on the heated $\beta\text{-UO}_2(\text{OH})_2$ crystals observed by Bannister (1974). Their oscillation is not explainable, but may represent an equilibrium reaction. The predominance of spots along interface traces and their higher population in the B1-phase, represents the higher dislocation density in these regions.

The operation of two mechanisms agrees with the work of KS. The A mechanism was seen to have a slow moving interface and the B mechanism is associated with a sudden transformation. The use of crystals which had been partly transformed, without external stresses, permitted the recording of more precise orientation relation data.

3.4.2 Mechanism A

The gradual change from orange to green seen in isolated regions of the hexagonal prisms could have been caused by successive type A (slow and rounded) transformation fronts moving along the basal plane, like those seen in the thin platelets. Similar interfaces have been observed in NH_4I (section 8.3), NH_4Br (Kennedy et al. (1974)) and in $\text{KNO}_3^\dagger$, but have not been previously observed in MnS . The absence of a shape change accompanying the slow rounded interfaces can be explained by the atomic layer translation occurring in different directions which are equivalent by symmetry. Such cancellation of a macroscopic distortion has been observed in the hcp-fcc transformation in Co (Nishiyama, 1978). The reason for the invariant offset of the type A orientations from the ideal $[11\bar{2}0]_{\text{B4}} \parallel [110]_{\text{B1}}$ is not obvious. One reason could be that a martensitic mechanism is operative for which the offset represents a rotation needed to counterpose a lattice invariant shear. However, the slow rounded interface is atypical of martensitic transformations and implies a diffusional mechanism. Another possible cause could be

[†] The transformation of KNO_3 under pressure was performed in a diamond-anvil pressure cell (section 7.2.4.3)

that the observed orientation relation permits the interface to be a plane of maximum structural coherence on a submicroscopic scale even though it is curved on a microscopic scale.

A view of the atomistic mechanism of the type A transformation is depicted in Fig. 3.5. The mechanism was described on a planar scale by KS. Some bonds are broken whilst some new ones are formed when the atoms move from tetrahedral to octahedral sites during translations of basal layers. Each basal layer only undergoes a comparatively small uniform contraction ($\approx 7\%$) and the atoms within each layer do not change their relative positions. Hence the approach of KS.

The possibility exists for two modes of execution of the type A mechanism. One could be a slow, thermally driven process and the other, a sudden shear type transformation (e.g. Kriven, 1981). The slow moving interface in the present work was linked to the type A mechanism. However, the agreement between the experimentally observed orientation relationship and that predicted by phenomenological martensite theory for $(10\bar{1}0)[01\bar{1}0]_{B_4}$ slip was close. The small difference may be due to a double shear mechanism or relaxation of the geometrical constraints. Support for the latter possibility comes from the observation of curved interface traces. Thus, although a slow moving interface mode is operative for the A mechanism, a martensitic mode may also be operative with the same orientation relation.

3.4.3 Mechanism B

For the sudden transformations, if a unique interface exists then Fig. 3.2 would show three distinct peaks corresponding to observations on the faces $(10\bar{1}0)_{B_4}$, $(1\bar{1}00)_{B_4}$ and $(0\bar{1}10)_{B_4}$. No such groupings occur and instead there is a wide range of interface planes. The curvature of some interface planes indicates that a variation of up to $\pm 7^\circ$ is permitted, whilst the range of different orientation relations observed was less than $\pm 4.0^\circ$. The difference in variation implies that either the orientation of the interface plane is less restricted than that of the lattice, or that the interface reflects more sensitivity to crystal imperfections than does the lattice orientation relation. A sample

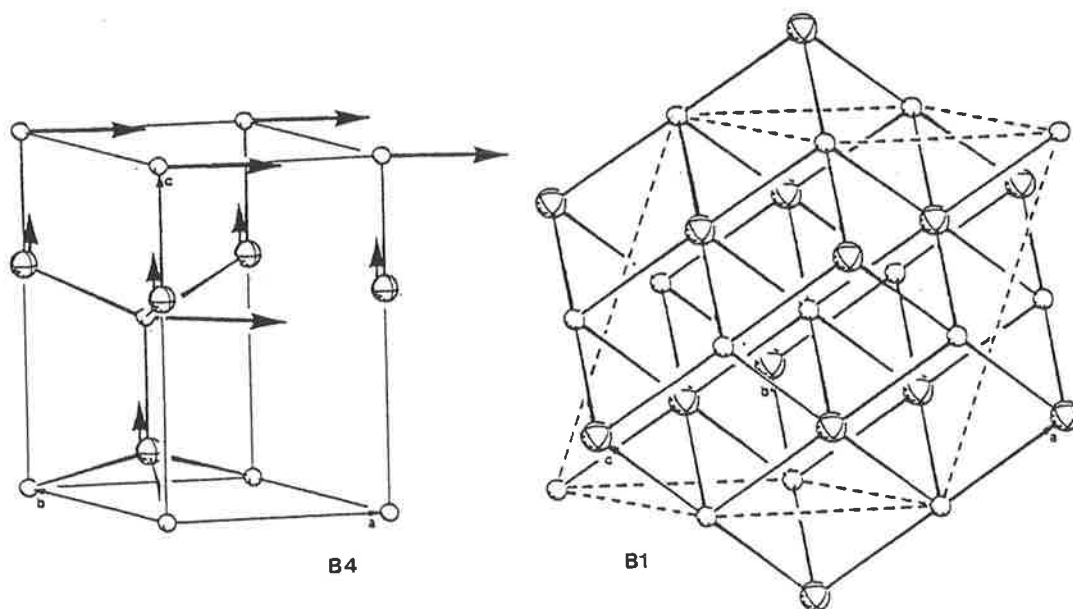


Figure 3.5 Atomic movements for mechanism A. The small circles represent cations and the larger circles with crosses represent the anions. (The same representations will be used in further structural illustrations of atomic movements).

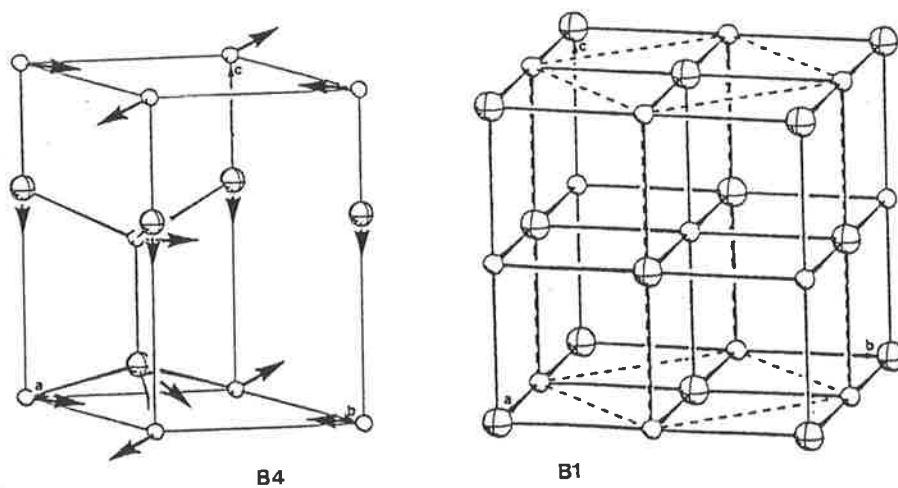


Figure 3.6 Atomic movements for mechanism B.

pool of one or two hundred precise interface trace measurements would yield statistics capable of revealing any restrictions on the indices of the interface plane. This would take many man-hours, as approximately eight hundred crystals would have to be studied due to the paucity of unambiguous, straight interface traces.

The small surface discontinuities noted in some instances implies that the interface was a plane of mismatch between the structures and therefore not a martensitic habit plane in these cases. Contraction of the B1-phase was noted by KS but was attributed to a slow propagation. The scarcity of tilted surfaces implies that tilting is not an integral part of the usual mechanism. Cracking could induce some surface tilting of up to 10° . Therefore the tilts can not be reliably compared with those calculated theoretically except in the absence of any cracks. The cracking was most likely due to the interaction of two or more transforming regions with incompatible shape changes. The crystal in Fig. 2 of KS shows a small bend on the untransformed edge opposite to the edge from which their shape change was measured. Some adjustment of their reported angle of tilt is therefore necessary. A shape change with a surface tilt of over 10° (as reported by KS) is more likely to cause crystal fragmentation rather than just cracking. Such fragmentation was seen in $\beta \rightarrow \alpha\text{-UO}_2(\text{OH})_2$ (TKD), but has never been observed in MnS. This supports the present optical evidence of very little shape change. The similarity in the orientation relations deduced from crystals transformed on the X-ray camera to those transformed on the optical microscope is due to the combined effects of the minor shape change and the fact that the surrounding parent phase was more restrictive than the adjacent adhesive.

The individuality of the three members of the type B orientations and the fact that in one crystal only one member occurred, implies that the three orientations are not vital members of a twinned product as suggested by KS. The twinning which they referred to may not have been intended to imply one of the formally defined Type I or Type II twins, but equivalent options of the lattice strain which are generated by the structural 3-fold screw axis of the parent phase. However such options could not have a common plane of fit (twin plane) except for $\{10\bar{1}0\}_{B4}$ in which case the product would

consist of a single orientation rather than twins as this plane becomes the mirror plane $\{110\}_{B1}$.

KS stated that in the basal plane the principal distortions were parallel to " $\langle a \rangle$ " and $\langle 1\bar{1}00 \rangle_{B4}$. The former of these directions was probably meant to be parallel to the symmetrically generated third basal axis rather than to the unit cell a-axis which their notation implies. It could have been written as $[\bar{1}\bar{1}20]_{B4}$ in which case their directions are equivalent to those in the present work. Also, the use of the angle bracket rather than the square bracket in the notation of KS does not necessitate the use of a right handed transformation as required. Consequently the directions were restated in section 3.2.5.

KS postulated that their "B3" mechanism was martensitic. Their orientation "B3" corresponds to the type B orientation of the present work, except that KS did not record the offsets from the average orientation. Their angles (calculated by the present author using the method of Lieberman, 1958) between the cones of unextended vectors were close to their experimentally observed angle $(100)_{B1} \wedge (10\bar{1}0)_{B4} = 15^\circ$ for the orientation "B3". From this they claimed that the angles represented a rotation of the lattice about the hexagonal c-axis in a martensitic mechanism. The martensitic solutions calculated in the present work, although not agreeing with the experimental observations, had a wide range of lattice rotations and not just 15° .

The fact that no matches were found between the phenomenological theory and the experimental observations is surprising but does not imply that the transformation is not martensitic. The most obvious characteristics of the transformation, such as its speed and lattice distortion, indicate that it is martensitic, but the more subtle features such as occasional misfit at the interface, varying orientation relations, interface planes and curved interface traces imply that it does not meet the formal, geometrical requirements of the IPS theory of martensitic transformations. Thus the transformation via the B mechanism appears to proceed with relaxed geometrical constraints. High resolution electron microscopic investigation (such as by Van Tendeloo, Van Landuyt & Amelinckx, 1981) of the transformation would probably yield further details. Such

a study would determine if any of the interface traces attributed to mechanism B in the present work should have been attributed to mechanism C or a martensitic mode of mechanism A.

The atomic movements associated with the B mechanism are illustrated in a three-dimensional (skew) view by Corl (1967) who proposed this mechanism for the transformation of cadmium sulphide (CdS) under pressure after considering its "rapid nature". The atomic movements are also shown in Fig. 3.6 for completeness within this thesis. KS wrongly stated that Corl (1967) did not specify the cation displacements. In contrast to the A mechanism, no bonds are broken in the B mechanism. The increase in coordination number is achieved by each atom forming two new bonds by the combination of a lattice distortion and minor atomic shuffles.

3.4.4 Mechanism C

The equivalence between type C orientations in different crystals indicates that they were not type B orientations fortuitously rotated by the shape change of a neighbouring region. The fact that type C was observed in crystals transformed in the S.E.M., which is an evacuated environment, implies that it was not the product of reaction with the atmosphere. The diffraction photographs showed that it was akin to the type B orientations but the inequality of interplanar spacings implied that the lattice had less symmetry than cubic.

Re-examination of the X-ray diffraction photographs of KS revealed that their orientation relation "B2" was identical to type C of the present work. The match was found from the orientation and interplanar spacings. Diffraction spots corresponding to their particular orientation were annotated as " α -phase with the wrong d-spacing" in the laboratory notes of E. Summerville (1979) although no discrepancy was mentioned in the report by KS. Also upon re-examination of those diffraction photographs of KS which were available, their orientation relation "B1" (i.e. $(100)_{B1} \parallel (10\bar{1}0)_{B4}, (001)_{B1} \parallel (0001)_{B4}$) could not be found. A type C product was found with this orientation in the present work, which suggests that their interplanar spac-

ings may also have deviated from the ideal B1-phase. However, without checking the remainder of their photographs one cannot be certain of this. The angular separation between the orientation "B1" of KS and the usual type C of the present work is within the limits of experimental error and is quite possibly produced by the same mechanism.

The possible influence of the Si impurity on the transformation must be considered. STS found a 1% contraction of the hexagonal c-axis for a Si content of 2 wt%. This was attributed to the substitution of two Mn^{2+} ions by one Si^{4+} ion. If the silicon was localised rather than uniformly scattered then the corresponding reduction in unit cell size could account for the interplanar spacings of the type C orientations. During examination by E.M.P. no variation in Si content was found in different areas of the surface. Localisation of the Si would cause a splitting of the B4 phase diffraction spots but this was not observed. Selected-area electron diffraction could provide a more accurate answer to this problem. Although localised Si appears to be an unlikely cause for the type C orientation, the possibility of an indirect effect of evenly spread cation vacancies can not be rejected. One possibility for the structure of the type C crystallites is that it is related to one of the intermediate phases which are common in the wurtzite to sodium chloride type structure changes. Such intermediate phases occur in AgI (Moore & Kasper, 1968), CdTe and InTe (Rooymans, 1969). The type C orientations do represent a new polymorph of MnS but further postulation as to its structure is only conjecture at this stage. Due to this uncertainty it was not considered worthwhile, without the use of an electron microscope, to obtain its orientation relation more precisely.

CHAPTER 4

The Wurtzite $\leftrightarrow$ Sodium Chloride Type and Related Transformations in Silver Iodide (AgI) Under Hydrostatic Pressure

4.1 Introduction

There are six polymorphs of AgI known to exist at different temperatures and pressures and with some overlap of stability fields. At standard temperature and pressure (STP) there is a stable wurtzite (B4) form and a metastable zincblende (B3) form (Bassett & Takahashi, 1965). The first high pressure phase was discovered by Tamman (1911) and found to have the sodium chloride (B1) structure type by Jacobs (1938). A phase-IV, intermediate between the B4- and B1-phases, was discovered by Van Valkenburg (1964). Its structure was deduced by Moore & Kasper (1968) (abbreviated to MK) to be tetragonal with a layering reminiscent of PbO. However, according to Mellander, Bowling & Baranowski (1980) the structure of phase IV is still in doubt. Meisalo & Kalliomäki (1979) stated that phase-IV can be bypassed under hydrostatic pressure. This should be easily verified as its black appearance (Duecker & Lippincott, 1964) should render it readily identifiable. A body centred cubic (b.c.c.) phase exists above 147°C and a possibly CsCl type phase exists above 100kbar (Bassett & Takahashi, 1965). Further details of the history are reviewed by Mellander, Bowling & Baranowski (1980).

The object of this project was to determine the mechanism of the B4 $\leftrightarrow$ B1 type transformation and of the transformations associated with the intermediate phase. No previous work has been done on the orientation relations under pressure. Silver iodide should provide an interesting comparison with manganese sulphide, due to the possible effects of the different elements present.

MK postulated a layer translation mechanism for the B3 $\rightarrow$ IV transformation in conjunction with the lattice correspondence $[110]_{B3} \rightarrow [100]_{IV}$, $[001]_{B3} \rightarrow [001]_{IV}$. Bas-

sett & Takahashi (1965) reported that on cycling across the $B4/B3 \leftrightarrow IV$ transformation the single crystal domains in their powder sample reappeared at the same places and termed this phenomenon the "memory effect". They said that the memory effect had not occurred in the $IV \leftrightarrow B1$ transformation and concluded that whereas this transformation was reconstructive the former was displacive. A memory effect was also noted for the transformation of wurtzite to the high temperature (b.c.c) phase by Burley (1967), which was later found to be martensitic by Mills, Perrott & Fletcher (1970). The presence of a martensitic transformation at high temperatures leads one to believe that the transformations under pressure, where less energy is available for diffusion, are possibly also martensitic.

Martensitic calculations were undertaken in this investigation in order to help decide whether or not a martensitic mechanism could operate during the wurtzite $\rightarrow$ sodium chloride type transformation in AgI.

Upon release of pressure from the B1-phase (Adams & Davis, 1965) or phase-IV (Bassett & Takahashi, 1965), the new phase has the B3 (zincblende) structure and not that of B4, even though the stable phase at STP had the B4 structure. The B3-phase may also be obtained by lengthy grinding of the B4-phase. This conversion can be reversed by heating to above 55°C (Bassett & Takahashi, 1965).

If the high pressure phase could be stabilized then one would be able to remove the crystal from the diamond anvil pressure cell and examine any morphological effects of the transformation. AgBr has the B1 structure at STP and therefore substitution of Br for I in AgI should help to stabilize the high pressure phase. Natajara & Rao (1970) found that up to 10 mole % of Br could be incorporated into the wurtzite lattice by crystal growth from solution. In Br substituted AgI Shahi & Wagner (1980) found a super conductivity effect similar to that induced by an increase in pressure. They attributed this to Ag^+ diffusion.

4.2 Experimental

4.2.1 Crystal Growth

The method used followed that of Natajara & Rao (1970) except that the inclusion of AgI as one of the reagents was bypassed.

An aqueous solution of 5 wt% AgNO_3 was added with constant stirring to a saturated solution of KI until a faint yellow colour persisted. The yellow precipitate was allowed to settle and the solution was decanted into a beaker and placed in a light-proof desiccator. In place of a desiccant there was water for slow dilution of the solution (Mills, Perrott & Fletcher, 1970). After three days the crystals were removed, washed in ethanol and dried under rotary pump vacuum.

In order to grow crystals of the solid solution $\text{AgI}_x\text{Br}_{1-x}$, substitution of 10→15 mole % of KI by KBr was carried out in the above procedure.

4.2.2 Application of Pressure and Subsequent X-ray Diffraction Analysis

Three hexagonal prisms and three hexagonal platelets were studied. The differently shaped crystals were used so that any effect on the orientation relation, due to the anchoring of a particular crystal face, could be detected. The platelets were $.2(\pm .1)\text{mm}$ across and $.03(\pm .02)\text{mm}$ high. The bipyramids were approximately $.1 \times .2 \times .1\text{mm}^3$. The platelets were laid onto the diamond anvils on their $\{0001\}_{\text{B}_4}$ faces and the bipyramids on their $\{10\bar{1}1\}_{\text{B}_4}$ faces. Phosphor-bronze gaskets were used with n-hexane as the pressure transmitting liquid (section 7.2.4.3.c). Effects due to the release of pressure were also studied. Optical effects were studied through a $15\times$ binocular microscope. The pressure cell was incompatible with a higher powered microscope and consequently no interface plane measurements were possible. Also, shape changes with edge rotations of less than about 10° were not discernable. The view of the crystal was tantamount to a two dimensional projection and therefore no three dimensional optical data were recorded.

As the gasket and guide pins, did not transmit X-rays it was only possible to obtain essentially one populous view of the diffraction pattern. Both Laue and precession photographs were recorded. The precession photographs had a much higher scattering component from the beryllium disc when the pressure cell was not perpendicular to the beam. Consequently the Laue photographs were predominantly used for the orientation determinations. Analysis of the Laue patterns of the bipyramids after transformation required the use of program COATI.

4.2.3 Martensitic Calculations for the B4→B1 Type Transformation

The principal distortion vectors were calculated by the same method as used for MnS (section 3.2.5). This included using the same lattice correspondence matrices. The lattice parameters used for the B4- and B1-phase were from the ASTM powder file (No. 9-374) and from MK respectively. The transformation pressure lattice parameters for the B4-phase were not available in the literature. However, due to the relatively low pressure needed for transformation, it was not considered necessary to undertake experiments for the determination of these lattice parameters.

The lattice invariant shear systems tested (using program MRTNST) were the same as those tested for MnS (section 3.1). The predicted orientation relations were compared with those observed experimentally, with the aid of program COATI.

4.3 Results

4.3.1 Crystal Growth

The crystals which were removed after three days of growth were pale yellow hexagonal platelets, pyramids and bipyramids. The B4 structure was verified by X-ray precession photography. The crystals were from .1 to .5 mm wide, and the platelets were approximately .05 mm thick. They all had strong $\{0001\}_{B4}$ cleavage and could be easily plastically deformed. The pyramidal faces and the faces on the sides of the

Figure 4.1 X-ray diffraction precession photograph of a B4-phase
 $\text{AgI}_x\text{Br}_{1-x}$ crystal viewed onto $(0001)_{\text{B4}}$. (Section 4.3.1)

Figure 4.2 X-ray diffraction precession photographs of a platelet viewed
onto $(0001)_{\text{B4}}$ in the diamond anvil cell (a) at STP (b) under pressure
(c) after return to STP.

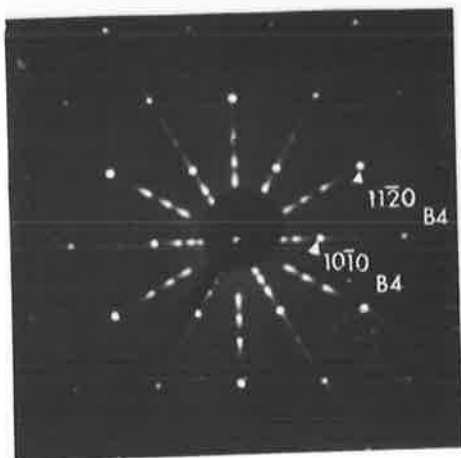


Figure 4.1

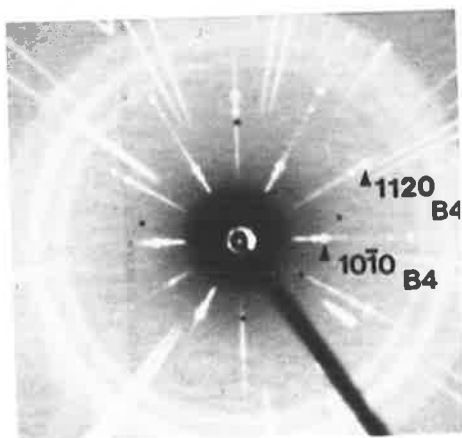
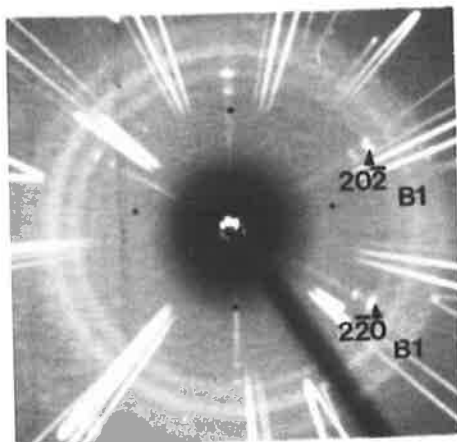
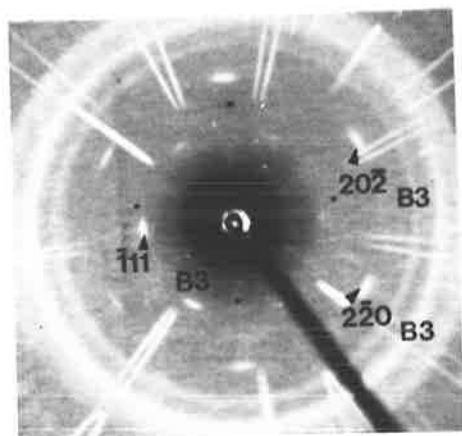


Figure 4.2

a



b



c

platelets were of the form $\{10\bar{1}1\}_{B4}$. Solutions which were left for a month in the desiccator yielded hexagonal pyramids up to 3mm wide.

The diffraction patterns of some of the AgI_xBr_{-x} crystals showed the presence of additional crystallites and others showed substantial asterism. These crystals were therefore not further studied. One of these solid solution crystals showed a superlattice and a precession photograph onto $\{0001\}_{B4}$ is shown in Fig. 4.1. The superlattice reflections indicated that the Br^- substitution was ordered.

4.3.2 Application of Pressure

4.3.2.1 Optical Microscopy

The duration of the transformations was less than one second and proceeded by one of two modes. Either the crystal became black (indicating phase-IV) or secondly, many straight parallel lines (striations) appeared and the crystal remained virtually clear (indicating the B1-phase). About 90% of one bipyramid transformed by the second mode but the remaining 10% transformed to phase-IV. In one platelet a small area of the crystal remained untransformed. In all the transformations of AgI seen in the pressure cell, no change in crystal shape was detected.

Additional pressure had no effect on the second mode, thereby confirming that the crystals were in the B1-phase. But for the first mode additional pressure caused the crystals to become transparent with striations and thereby resemble the crystals which had transformed straight to the B1-phase.

4.3.2.2 Orientation Relations from X-ray Diffraction

The spread of diffraction spots from the products of the initial transformation was $\pm 3^\circ$. Upon transformation from phase-IV the spreading increased to $\pm 4^\circ$. No reflections were significantly spread in 2θ .

Figure 4.3 X-ray diffraction photographs of a bipyramid viewed onto $(10\bar{1}1)_{B4}$ in the diamond anvil pressure cell (a) at STP (b) medium pressure (c) higher pressure (d) released to medium pressure (e) released to STP (f) two days after release to STP. The first member of each pair of photographs is a (front) Laue and second member is a precession photograph.

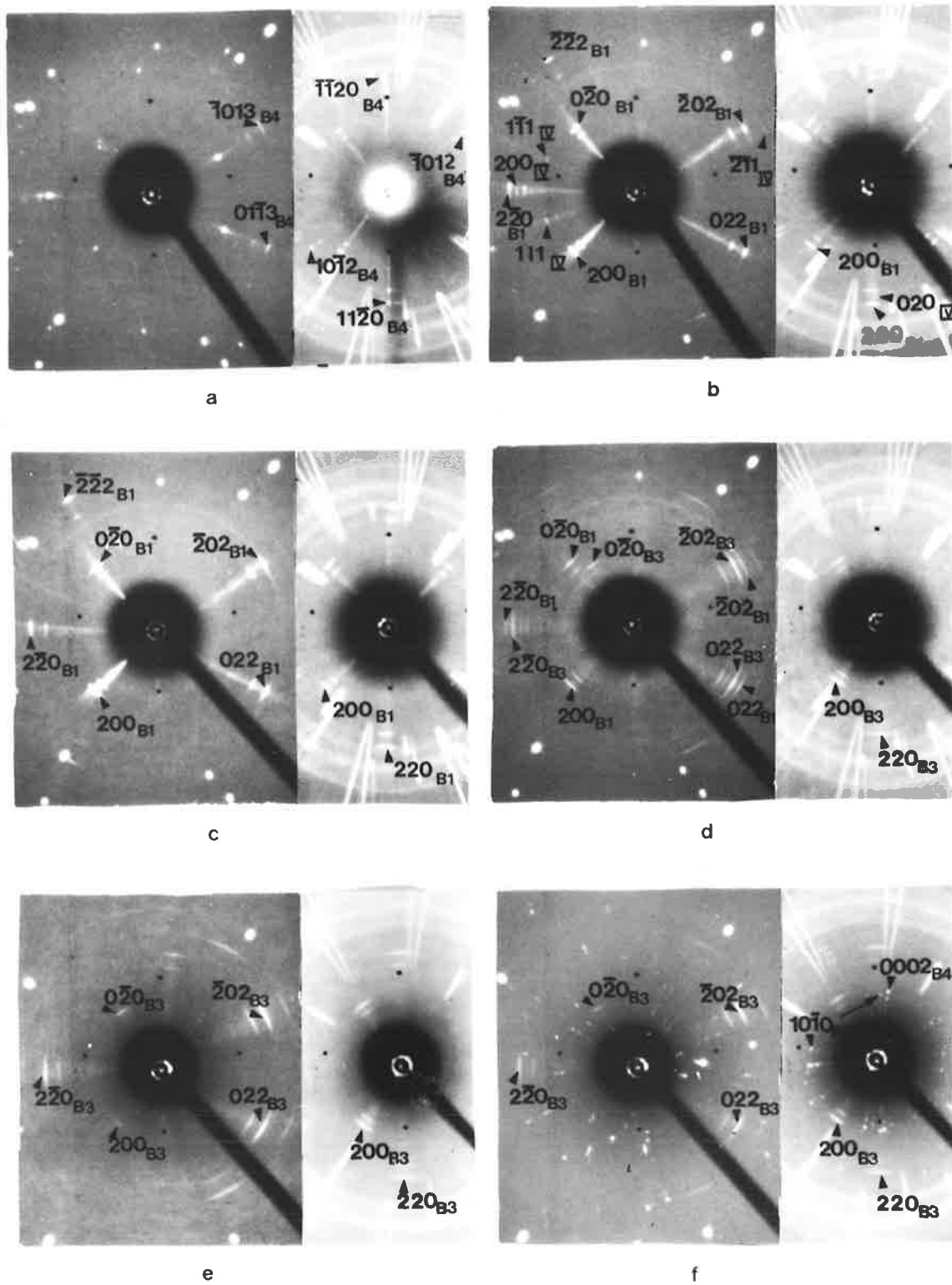


Figure 4.3

4.3.2.2.a Platelets

The Laue diffraction patterns contained an array of six major spots distributed with hexagonal symmetry. The spots were all doublets with the fainter partner closest to the centre of the photograph. This doubling corresponded to the separate MoK_α and MoK_β wavelengths. By assigning the MoK_α wavelength to the outermost member of each doublet, the interplanar spacing of these reflections was calculated to be $2.14\text{\AA}$, which implies reflections from either of $\{220\}_{\text{B1}}$ or $\{201\}_{\text{IV}}$. If the spots were from phase-IV then they must have been from different crystallites for which there were no other reflections present. Alternatively, if the reflections were from the B1-phase then they all originated from one crystal with the orientation relation: $(1\bar{1}1)_{\text{B1}} \parallel (0001)_{\text{B4}}$, $(110)_{\text{B1}} \parallel (11\bar{2}0)_{\text{B4}}$. This is approximately the same orientation relation as for the "A mechanism" in MnS (section 3.4). The reflections could have been assigned to different B1-phase crystallites but again there were no other supporting reflections for such crystallites. For one of the larger hexagonal platelets the $\{220\}_{\text{B1}}$ reflections were so intense that they also appeared on the precession photographs (Fig. 4.2). For a perfect crystal these $\{220\}_{\text{B1}}$ reflections could only show up on the precession and not on the Laue photographs. The situation observed is due to the appreciable asterism after transformation. An additional $15(\pm 7)$ kbar pressure did not alter any of the diffraction spots allocated to the B1-phase, thus confirming their assignment.

For the platelet in which a small area appeared optically not to transform the parent reflections were present at their original positions, thereby indicating that the crystal had not noticeably moved. The equivalence of the orientation relation for this crystal with that of the other platelets indicated that there was no shape change effect on the orientation relation.

4.3.2.2.b Bipyramids

No B4-phase remained after transformation. Two of the three bipyramids firstly transformed to phase-IV and then to the B1-phase. The diffraction patterns recorded in the presence of phase-IV were initially too complex to solve. After further transfor-

mation some of the diffraction spots disappeared, and therefore those which remained were assigned to the B1-phase. The crystals which did not pass through phase-IV gave the same B1-phase pattern as those which did.

The indexing of the B1-phase patterns was based on an orientation calculated from the $\{200\}_{B1}$ and $\{113\}_{B1}$ reflections. The diffraction patterns indicated only one B1-phase crystal and its orientation relation was the same as that found for the hexagonal platelets. The $(220)_{B1}$ and $(\bar{2}\bar{2}0)_{B1}$ reflections were present with equal intensity on the precession photographs, thereby indicating that $[110]_{B1}$ was perpendicular to the beam. Also on the precession photographs there were two $\{200\}_{B1}$ reflections but their $\text{MoK}\beta$ spots were absent and their centrally opposite reflections were either much fainter or also absent, thereby indicating that their plane normals were not perpendicular to the beam. Thus the precession results agreed with those from the Laue photographs.

The reflections which disappeared upon application of additional pressure were assigned to phase-IV. Both crystals gave the same Laue pattern and the reflections were indexed as $\{111\}_{IV}$, $(200)_{IV}$ and $\{211\}_{IV}$ from a single crystal. The $(020)_{IV}$ and $(0\bar{2}0)_{IV}$ reflections were present with equal intensity on the precession photographs, thereby indicating that $[010]_{IV}$ was perpendicular to the beam. This agreed with the orientation deduced from the Laue photographs. The orientation relation between the B4-phase and phase-IV was $(010)_{IV} \parallel (11\bar{2}0)_{B4}$, $(101)_{B1} \parallel (0001)_{B4}$. The orientation relation between phase-IV and the B1-phase is shown in Fig.4.3.c. and can be stated as $(110)_{B1} \parallel (100)_{IV}$, $(001)_{IV} \parallel (001)_{IV}$.

4.3.3 Pressure Reduction

4.3.3.1 Optical Microscopy

There were two types of effects. Some crystals transformed to phase-IV (the black phase) and did not become clear until pressure was further reduced, whereas other crystals immediately lost their striations to become clear and unmarked. All changes appeared to be instantaneous. Crystals which had passed through phase-IV

on increasing pressure, also passed through it on decreasing pressure. One crystal which had recrystallized whilst under pressure then transformed to phase-IV on partial release of pressure although it had not previously been in this phase.

4.3.3.2 Orientation Relations From X-ray Diffraction

The spread of reflections was $\pm 5^\circ$. Photography of the smaller crystals had required longer exposures during which time recrystallization occurred and produced many crystallites. Consequently, orientation data were only retrieveable from the two largest crystals, a platelet and a bipyramid.

4.3.3.2.a Platelet

After release of pressure the crystal was clear and the Laue and precession photographs showed 6-fold rotational symmetry. The interplanar spacings were 2.29 Å and 3.70 Å which could have been indexed on either the B4 or B3 lattices, (ie. $\{11\bar{2}0\}_{B4}$, $\{0002\}_{B4}$ or $\{220\}_{B3}$, $\{111\}_{B3}$). If the product was the B4-phase then there must have been six different crystallites with no other representative reflections on either the Laue or precession photographs. Also, as there were no $\{10\bar{1}0\}_{B4}$ reflections, none of the crystallites had the orientation of the original crystal. Alternatively the pattern could have been indexed on a single B3-phase crystal. Consequently the product was most likely the B3-phase. The B1-phase planes had retained their indices and the corresponding orientation relation is $[100]_{B3} || [100]_{B1}$, $[010]_{B3} || [010]_{B1}$. Some $\{111\}_{B3}$ reflections also appeared on the precession photograph, due to a slight misorientation of the original crystal.

4.3.3.2.b Bipyramid

After partial release of pressure the crystal became black and the diffraction pattern still showed B1-phase reflections in the same positions as under full pressure. There were also some additional reflections. Upon returning to atmospheric pressure only the B1-phase reflections disappeared.

The reflections which persisted from partial release to atmospheric pressure could have been indexed on either of the B4 or B3 lattices. If they were indexed on the B4-phase lattice then there must have been several crystallites with no other supporting reflections. Alternatively, if it was indexed on the B3-phase lattice then only one crystal need have been present. Consequently, the presence of the B3-phase was most likely. The orientation of the B3-phase, with respect to the B1-phase, was calculated from the $\{200\}_{B3}$ and $\{311\}_{B3}$ reflections and was found to be the same as that for the platelet crystal.

The presence of phase-IV, upon partial release of pressure, was indicated by the blackening of the crystals. However, because no reflections unique to phase-IV disappeared on full release of pressure, the reflections present at atmospheric pressure must have superimposed on those from phase-IV. This is possible for the $\{200\}_{IV}$ and $\{220\}_{IV}$ reflections as the *a*-axis of phase-IV is 4.58Å and the corresponding vector (according to MK) in the tetragonal subcell of the B3-phase is 4.59Å. The orientation of phase-IV was deduced from these two reflections and the orientation relation with the B1-phase was $(110)_{B1} \parallel (100)_{IV}$, $(001)_{B1} \parallel (001)_{IV}$ and is in agreement with the lattice correspondence proposed by MK.

4.3.3 Recrystallization in the Solid Phase

One or more days after transformation, recrystallization was noticeable, both whilst under pressure and after release of pressure. Many additional diffraction spots appeared and the ^{ia}str~~ai~~tions disappeared. The new diffraction spots were generally spherical and much sharper than the older spots. When the stabilized phase was the B1-phase under pressure, the existing diffraction spots became sharper and the new spots were also from B1-phase crystals. When the stabilized phase was the B3-phase, after full release of pressure, the existing spots became fainter and the new crystallites were confirmed to be from the B4-phase by the definitive $\{10\bar{1}0\}_{B4}$ reflection on precession photographs. Thus the wurtzite phase was growing at the expense of the zincblende phase. More crystallites formed when recrystallization occurred at

atmospheric pressure than when it occurred under higher pressure.

4.3.5 Martensitic Calculations and Comparisons

The principal distortion vectors for the A and B mechanisms are given in Table 4.1. The results of the theoretical martensitic calculations were fundamentally the same as those for MnS. The lattice invariant shear systems, which gave theoretically possible solutions for MnS, were also the only ones which gave solutions for AgI. As no B mechanism was experimentally observed in AgI, the theoretical martensitic predictions for this mechanism will not be shown.

From all the slip systems which were tested with the A mechanism for AgI, three gave martensitic solutions. Only variant number 1 of one of these three slip systems predicted an orientation relation which was in agreement with that observed experimentally. The agreement was well inside the region of experimental error. This slip system was $(10\bar{1}1)[01\bar{1}0]_{B4}$ which corresponds to the sodium chloride type slip system $(010)[\bar{1}01]_{B1}$. As the macroscopic shear was not experimentally measured it was not available for comparison with that predicted for the above L.I.S.. Some characteristics of this martensite variant are given in Table 4.2.

4.4 Discussion

4.4.1 The B4→B1 Transformation

The high degree of similarity between the theoretical calculations for AgI and for MnS is due to the corresponding similarity of their principal distortion vectors and the c/a ratios of the B4-phases. The calculations do not suggest that the A mechanism should be more dominant in AgI than in MnS. The fact that the B mechanism for the B4→B1 transformation was experimentally observed in MnS but not in AgI implies that the A mechanism must have a considerably lower activation energy than the B mechanism in AgI. This is most probably due to the high mobility of the silver ions,

a

	B4	B3	IV	B1
a	4.5922	6.495	4.58	6.08
c	7.510		6.00	

b

Mechanism A			Mechanism B	
	Direction	Magnitude	Direction	Magnitude
η_1	1 $\bar{1}$ 0 0.89216	0.78474	1 1 $\bar{2}$ 0	1.32398
η_2	1 1 $\bar{2}$ 0	0.93620	$\bar{1}$ 1 0 0	0.76440
η_3	$\bar{1}$ 1 0 1.25731	1.11526	0 0 0 1	0.80959
B	$\begin{bmatrix} .92906 & .00714 & -.15377 \\ .00714 & .92906 & .15377 \\ -.08624 & .08624 & .97807 \end{bmatrix}$		$\begin{bmatrix} 1.04419 & .27979 & 0 \\ .27979 & 1.04419 & 0 \\ 0 & 0 & .80959 \end{bmatrix}$	

Table 4.1 (a) Lattice parameters of AgI in Å (B4, ASTM powder file No. 9-374; B1 & IV, MK; B3, ASTM powder file No. 9-399) and (b) principle distortion vectors, η_1 , η_2 and η_3 , $\Delta V = -18.1\%$. The pure lattice strain matrices (B) are referred to the B4 phase.

$$P1 = \begin{bmatrix} .92786 & .02448 & -.24160 \\ .15279 & .94815 & .51174 \\ -.01692 & .00574 & .94333 \end{bmatrix} \quad P2 = \begin{bmatrix} 1 & 0 & 0 \\ -.18690 & 1 & -.18690 \\ 0 & 0 & 1 \end{bmatrix} \quad S = \begin{bmatrix} .92329 & .02448 & -.24617 \\ -.02441 & .94815 & .33453 \\ -.01799 & .00574 & .94226 \end{bmatrix}$$

Habit plane $(.28476 \quad .09663 \quad .18813 \quad .95372)$

Slip magnitude .244

Table 4.2 Theoretically predicted characteristics of the slip system $(10\bar{1}1)[01\bar{1}0]_{B4}$ for mechanism A. Variant No.1. Matrices are referred to the B4-phase unit cell.

because the A mechanism requires atoms to translate by relatively large distances (section 3.4.2). Thus the preference for the A mechanism in AgI is quite plausible. The higher speed of transformation (via the A mechanism) in AgI compared to MnS was also caused by the relative ease of atomic translations.

The ease of atomic movement in AgI implies that the B4→B1 transformation is not restricted by atomic shuffles. In the range of several unit cells, the large lattice deformation will become the dominant factor. This latter process, together with the rapid nature of the transformation and a possible operative slip system, suggest that the transformation is martensitic. However, the softness of the AgI crystals could allow substantial plastic distortion and thereby relax some of the geometrical features predicted by the phenomenological theory.

The striations seen in the B1-phase crystals may have been caused by the parallel slip planes of the martensitic mechanism. Mills, Perrott & Fletcher (1970) noted a crazed pattern after the B4→b.c.c. transformation and attributed this to a martensitic process.

4.4.2 The B4→IV Transformation

The fact the more bipyramidal crystals passed through phase-IV than did the platelet crystals, implies that the former crystals were subject to more non-hydrostatic pressure. One possibility is that some dimensional changes were needed on the $\{10\bar{1}1\}_{B4}$ face which was affixed to the anvil. Restriction of such changes would cause internal strains similar to the application of non-hydrostatic pressure.

The relative softness of the AgI crystals helps to explain why the presence of individual domains, with different lattice orientations of even different phases, were rare. The energy required to overcome a lattice defect opposing the mobile interface would be small and the defect would be readily accommodated in the new lattice.

The structure of phase-IV proposed by MK has an interesting aspect which these authors did not comment on. Some Ag-Ag and I-I interatomic distances are very short (namely 2.91Å). They are the same as the shortest Ag-I distance. The Ag-

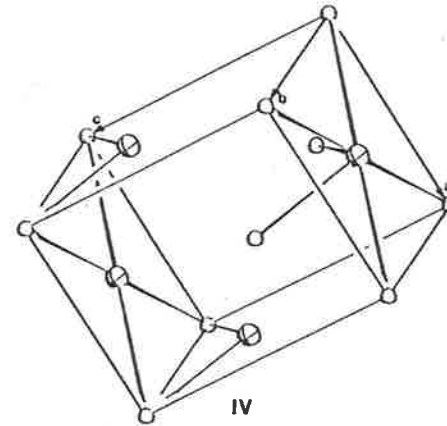
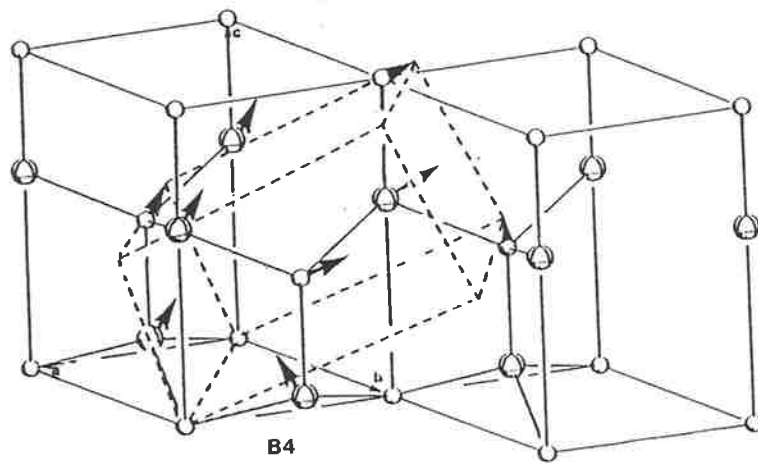


Figure 4.4 Atomic movements for the B4→IV transformation.

Ag and I-I linkages exist in continuous parallel chains along the a-axis. MK stated that the layering was similar to that in PbO. (They were most likely referring to the tetragonal phase of PbO as the orthorhombic phase consists of O-Pb-O chains). However, PbO does not have close cation-cation or anion-anion distances as does AgI and this represents a fundamental difference between the two structures. In the crystal structures of the individual Ag and I elements the shortest interatomic distances are 2.89 and 2.71 Å respectively (Kelly & Groves, 1970). These values are close to those in phase-IV of AgI, and especially so for the silver moieties. Duecker & Lippincott (1964) attributed the darkness of the intermediate phase to metallic silver or to free silver and iodine. This seems quite plausible, due to the elemental type component of phase-IV. The long chains in phase-IV should give it a high unidirectional conductivity, but this has not yet been tested.

The atomic movements for the B4→IV transformation are shown in Fig. 4.4. A large number of atoms must change their neighbours, which involves breaking some bonds and forming some new ones. The movements are not simple layer translations, like in the A mechanism in the B4→B1 transformation. The movements for the B4→IV transformation most resemble those proposed by MK for the B3→IV transformation in that some I-Ag-I linkages move as units. These linkages are in alternate $(1\bar{1}03)_{B4}$ planes and therefore represent a pseudo layer translation. Some additional cation translations along $[11\bar{2}0]_{B4}$ are required.

4.4.3 The IV↔B1 Transformations

The atomic movements for the IV→B1 transformation are much simpler than for the B4→IV transformation and are shown in Fig. 4.5. They basically consist of a coalescing of layers. The atoms on the surface of the layers translate with the opposing surfaces moving in the same directions. Moving in the opposite directions would still create the B1 structure, but would be a more disruptive and therefore higher energy process. The central plane of each layer remains unrotated. Thus the movements may be considered as another layer translation mechanism. The 90° unit cell angles do not

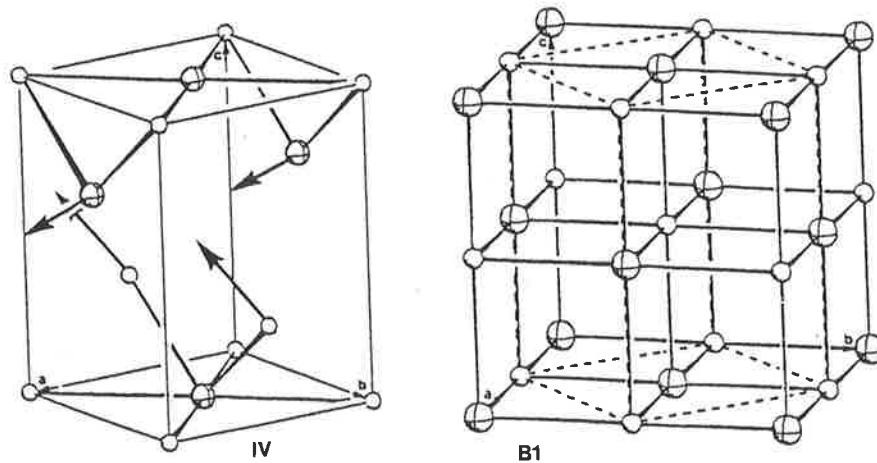


Figure 4.5 Atomic movements for the IV $\rightarrow$ B1 transformation.

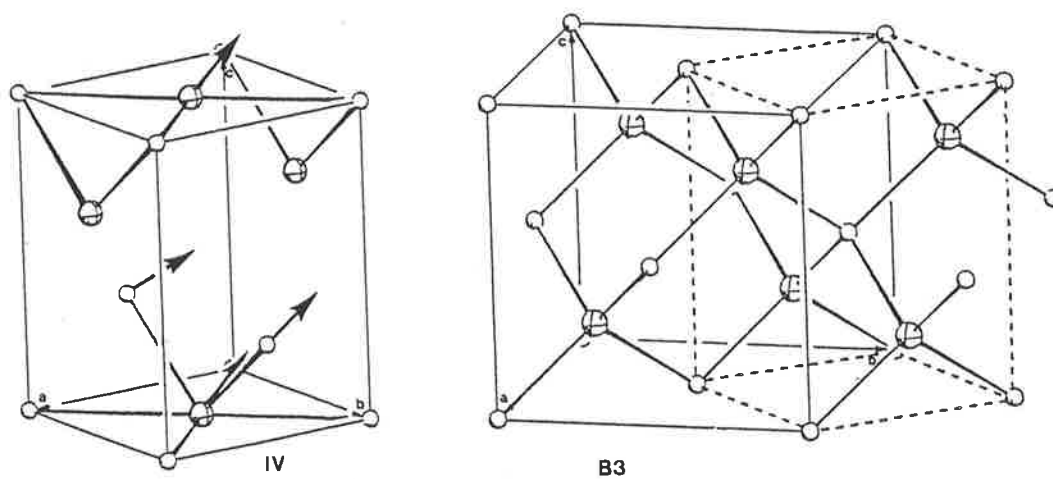


Figure 4.6 Atomic movements for the IV $\rightarrow$ B3 transformation.

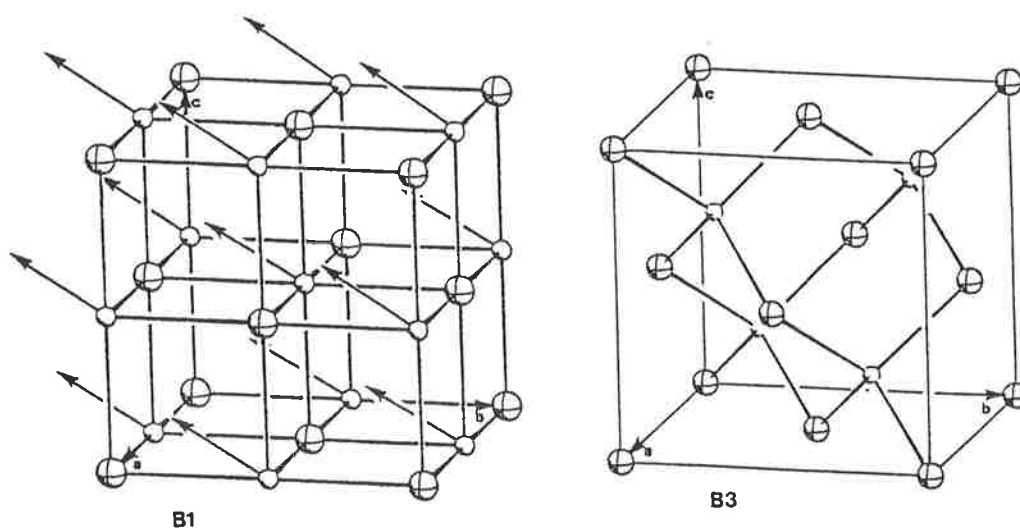


Figure 4.7 Atomic movements for the B1 $\rightarrow$ B3 transformation.

change and the principal distortion magnitudes along the unit cell axes are only 0.937 and 1.012. The atomic bonding rearrangements thus represent much larger movements than those due to the unit cell distortion. These movements occur in reverse for the B1→IV transformation.

4.4.4 The IV→B3 Transformation

The movements for the IV→B3 transformation are the reverse of those postulated by MK for the B3→IV transformation. The diagram of MK was a projection onto (001)_{IV} and so a more three-dimensional view is given in Fig. 4.6 for clarity. The movements basically consist of translations of some I-Ag-I linkages towards the upper layer. The linkages are in alternate (100)_{IV} planes and they represent a layer translation. Some bonds are broken and new ones are made. The lattice distortion is very small in comparison to the atomic translations and therefore the transformation is not martensitic.

4.4.5 The B1→B3 Transformation

The reason for the return to the B3-phase, rather than to the B4-phase, upon release of pressure from the B1-phase is that the anion array can be preserved in the former case (Rooymans, 1963). Only some small cation movements are needed. Basselt & Takahashi (1965) reported that, also, phase-IV always transforms to the B3-phase upon release of pressure. This is similarly most likely due to the less severe atomic movements needed as compared for a return to the B4-phase. The atomic movements for the B1→B3 transformation are the reverse of those described by Kennedy, Harris & Summerville (1980) and Kriven (1981) for the $\beta \rightarrow \alpha$ -MnS transformation. Their diagrams do not show all the atomic movements that occur in one unit cell and therefore they are shown in Fig. 4.7 for completeness. One may consider either the cations or the anions to be the atoms which move, but because of the higher Ag⁺ mobility in AgI, the cation displacements will be discussed. No bonds are broken. The cations form two extra bonds by passing from their octahedral to neighbouring tetrahedral sites.

The associated unit cell principal distortion magnitudes along each unit cell axis are all=1.064. The movements can be represented as layer translations on alternate {221} planes and consequently the mechanism is dominated by atomic translations rather than by a lattice distortion. The transformation is also not martensitic as there is a uniform expansion of the lattice and hence no possibility of an undistorted plane.

4.4.5 Possible Less Uniform Nature of the Atomic Movements During Transformation

In reality the atomic movements described above for the $IV \leftrightarrow B1$, $IV \rightarrow B3$ and $B1 \rightarrow B3$ transformations may proceed in different directions in separate parts of the crystal and still allow the product crystal to have the same orientation. This is in contrast to a lattice deformation dominant transformation which could generally result in different orientations for symmetry equivalent deformations (e.g. in $UO_2(OH)_2$).

The $B3 \rightarrow B4$ transformation observed in the present work occurred over many hours and therefore represented a diffusional mechanism. Consequently, although a description of coordinated atomic movements is possible, the true mechanism is most likely much more random. Bloch & Möller (1931) reported that the B3-phase was obtained by powdering any coarse crystalline material. This transformation may occur directly, but it is also possible that the material momentarily passed through the B4- or IV- phase whilst under pressure.

4.4.7 Recrystallization Effects

The recrystallization effects have not previously been noted and deserve some comment. The main features of recrystallization in solids have been discussed by Lücke (1976). The pronounced recrystallization in AgI is most probably due to the mobility of the Ag^+ ion.

The recrystallization of the B1-phase whilst under pressure was due to unresolved transformation strains or lattice defects such as those inherent in slip. A similar phenomenon has been observed after transformation at high temperature in $RbNO_3$

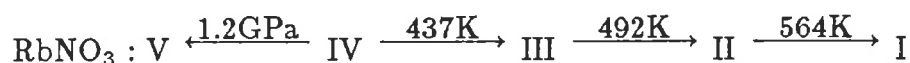
(Kennedy & Kriven, 1976), but in this case the recrystallization was induced by the large strain energy of fine twinning. The growth of the B4-phase from the B3-phase in AgI under STP conditions was a recrystallization effect but it also reflects the metastability of the B3-phase. The reason for the large number of B3-phase crystallites observed is most probably due to the B3→B4 type transformation which has four crystallographically equivalent options (Fleet, 1977).

CHAPTER 5

The Crystal Structures of Phase-IV Rubidium Nitrate and Phase-II Caesium Nitrate, and the Relationships with their Transformations

5.1 Introduction

Rubidium nitrate, caesium nitrate and thallium nitrate all have several polymorphs and there is isomorphism between them at different temperatures and pressures. The known polymorphic transformations (McLaren, 1962; Kalliomäki and Meisalo, 1979; Adams & Tan, 1981) are:



Walleront (1905) deduced from optical microscopy that TlNO_3 -II was isomorphous with RbNO_3 -IV and CsNO_3 -II. Patterson (1962) supported this from the similarity of their X-ray diffraction patterns. The isomorphism between RbNO_3 -IV and CsNO_3 -II was confirmed by Delacy & Kennard (1971) and by Brooker (1973).

Some of the above transformations have been reported as being martensitic: for example TlNO_3 -III $\leftrightarrow$ II (Kennedy & Patterson, 1965) and RbNO_3 -II $\rightarrow$ I (Kennedy & Kriven, 1981). Determination of the structures of these phases is therefore important in resolving which nitrate reorientations can occur in martensitic transformations. RbNO_3 is particularly topical as it has (via a rhombohedral phase) the $\text{CsCl}\leftrightarrow\text{NaCl}$ type structure change which is common to the alkali metal and ammonium halides. The metal (and ammonium) nitrates differ from the latter compounds by having more phase transformations, due to the diversity in nitrate ion orientations.

Various packing arrangements of the NO_3^- ions, including aragonite and calcite type orientations, have been proposed for some of the phases and consequently their transformations have geological significance. $\text{RbNO}_3\text{-IV}$ is distinctive as it has a rare structure type which has evaded determination for several decades, possibly due to growth twinning (Bury & McLaren, 1962). It is a room temperature phase, and therefore the thermal motion of the nitrate ion should not prohibit the structure determination by contemporary X-ray diffraction techniques.

Walleront (1905) and Zacharisen (1928) suggested a rhombohedral lattice for $\text{RbNO}_3\text{-IV}$. From X-ray Laue photography Pauling & Sherman (1933) declared that the lattice was orthorhombic but pseudo-hexagonal (p-h) with the space group $P31m$. The p-h unit cell had $a=10.45$ and $c=7.38\text{\AA}$ with $Z=9$. The Rb^+ ions were in a pseudo-(primitive) cubic (p-c) array with the cube body diagonal parallel to $[0001]_{\text{p-h}}$ and a cube edge parallel to $[11\bar{2}1]_{\text{p-h}}$. They also proposed that the NO_3^- ions were ordered in aragonite type orientations within the pseudo-cubes. In each unit cell the planes of three nitrate ions were parallel to $(0001)_{\text{p-h}}$ and two were parallel to each of the remaining $\langle 111 \rangle_{\text{p-c}}$. The majority of subsequent authors ratified this hexagonal unit cell and the arrangement of the Rb^+ ions. The space group and nitrate ion orientations within the pseudo-cubes were the goals of many ensuing investigations.

Brown & McLaren (1962a) from X-ray work suggested the trigonal space group $P3_112$ (or $P3_212$) which has a diad axis normal to $(10\bar{1}0)$. Newnes & Stavely (1966), on the basis of steric hinderance and entropy changes, stated that the nitrate ions had either aragonite type orientations or were parallel to the p-c faces, but decided that the latter orientation conflicted with the space group. Kennedy (1970) suggested that $\text{RbNO}_3\text{-IV}$ was similar to $\text{TlNO}_3\text{-III}$. The TlNO_3 structure to which he referred has nitrate ion planes parallel to the p-c faces and to face diagonals (Kennedy & Patterson, 1961) but has since been revised (Fraser, Kennedy & Snow, 1974 (abbreviated to FKS)). From X-ray powder diffraction Patterson (1962) endorsed the rhombohedral lattice of Walleront (1905). Bury & McLaren (1962), on the basis of microscopy and X-ray diffraction, deduced that the diad axis previously reported was only a pseudo-diad axis

and that the space group was $P3_1$ (or its enantiomorph $P3_2$). From neutron diffraction experiments Delacy & Kennard (1971) verified the same space group. Brooker (1973) from Raman spectroscopy added that there were three unique nitrate sites, each with C_1 symmetry but approximately C_2 or C_3 and that two of the three sites were similar. FKS found the $TlNO_3$ -III structure to have nitrate ion planes parallel to the Tl^+ p-c faces. From the characteristics of the transformation $TlNO_3$ -III $\rightarrow$ II, they predicted a small nitrate ion reorientation and that $TlNO_3$ -II (and consequently $RbNO_3$ -IV and $CsNO_3$ -II) would have a structure similar to $TlNO_3$ -III.

Thus the unit cell and space group of $RbNO_3$ -IV have previously been determined, but the orientation and packing of the nitrate ions have remained unknown. The crystal structures of $RbNO_3$ IV and $CsNO_3$ -II were determined independently from this investigation by Shamsuzzoha & Lucas (1982) (abbreviated to SL) and by Lucas (1983) (abbreviated to L) respectively and were published after the experiments were executed by the present author.

5.2 Experimental

5.2.1 Rubidium Nitrate Data Collection

Rubidium nitrate crystals were grown at room temperature by ethanol vapour diffusion into an aqueous solution of $RbNO_3$ (E. Merck). The transparent crystals were either c-axis columns with $\{11\bar{2}0\}$ faces or tabular. The crystal selected for data collection was a hexagonal prism 0.13mm long by 0.1mm wide cut from a column and mounted on a glass fibre. A Laue photograph indicated no significant asterism and no crystallites.

Lattice parameters (Table 5.1) were determined by least-squares refinement using the setting angles of twenty-five independent reflections with $24^\circ < \theta < 28^\circ$ on the CAD4 diffractometer (section 7.4). Theta profile analysis of reflection $(22\bar{4}2)$ indicated that intensity measurements using $\omega - (n/3)2\theta$ type scans would be optimized with $n=3$. The ω scan angle and horizontal aperture were $(1.00 + 0.35\tan\theta)^\circ$ and $(2.400 + \tan\theta)$ mm

respectively. For the intensity measurements the space group required the coverage of at least one sextant of reciprocal space. Data were collected in the θ range $(\sin\theta)/\lambda \leq .595 \text{ \AA}^{-1}$ and index ranges $(0 \leq h \leq 12, 0 \leq k \leq 12, -8 \leq l \leq 8)$ and $(-12 \leq h \leq 0, 0 \leq k \leq 12, 0 \leq l \leq 8)$. Of the 1259 unique reflections measured, 465 were inferior and omitted ($F < 5\sigma_F$) leaving 797 for refinement with $R_{\text{int}}^{\dagger} = 0.010$. The reflections $(\bar{3}300)$, $(\bar{2}111)$ and $(11\bar{2}1)$ which were measured after every 60 minutes of X-ray exposure time showed no significant variation.

Data reduction and Lp corrections were applied by program SUSCAD (Guss, 1979). Absorption corrections were applied by program ABSORB (Guss, 1980) giving the minimum and maximum transmission values of 0.15 and 0.23.

Table 5.1 RbNO₃ Crystal Data

Mr=147.47, $a=10.502(1)$, $c=7.473(1)\text{\AA}$, $V=713.8(1)\text{\AA}^3$, $T=27^\circ\text{C}$, $Z=9$,
 $D_x=3.106\text{gcm}^{-3}$, $\mu=152.5\text{cm}^{-1}$, $F(000)=612e^-$.

5.2.2 Caesium Nitrate Data Collection

Needle shaped crystals of CsNO₃ (E.Merck) were grown by evaporation of an aqueous solution and one approximately 0.1mm wide was chosen and cut to 0.19mm in length. The twenty-five independent reflections used for refinement of cell parameters (Table 5.2) had theta values in the range $15 < \theta < 21^\circ$. Theta profile analysis of reflections $(2\bar{4}22)$ and $(7\bar{2}5\bar{1})$ revealed that intensity measurements using $w-(n/3)2\theta$ type scans would be optimized with $n=1$. The ω scan angle and horizontal aperture were the same as for RbNO₃. Intensity data were collected within the theta range $(\sin\theta)/\lambda \leq 0.571\text{\AA}^{-1}$ and within the index ranges $(0 \leq h \leq 12, 0 \leq k \leq 12, -12 \leq l \leq 12)$. The reflections $(22\bar{4}\bar{2})$, $(2\bar{4}22)$ and $(1\bar{2}1\bar{1})$ which were measured after every 60 minutes of X-ray exposure time showed no significant variation. Of the 1065 measured reflections, 940 were unique and 180 were unobserved ($F < 5\sigma_F$) leaving 760 for refinement and giving $R_{\text{int}}=0.0245$. Data reduction and Lp corrections were applied

$^{\dagger} R_{\text{int}} = \sum (|I - \langle I \rangle|) / \sum I$

by program SUSCAD (Guss, 1979). Absorption corrections were applied by program ABSORB (Guss, 1980) giving the minimum and maximum transmission factors as 0.03 and 0.21 respectively.

Table 5.2 CsNO₃ crystal data.

Mr=194.91, $a=10.931(2)$, $c=7.763(3)\text{\AA}$, $V=803.1(4)\text{\AA}^3$, $T=27^\circ\text{C}$, $Z=9$,
 $D_x=3.626\text{gcm}^{-3}$, $\mu=100.96\text{cm}^{-1}$, $F(000)=774e^-$.

5.3 Structure Solution and Refinement

Scattering factors for the neutral metal atoms were copied from the International Tables for X-ray Crystallography (1974); those for N and O were contained in SHELX (Sheldrick, 1976). Until the test for absolute configuration, the structures were refined in space group P3₁. The structures of RbNO₃ and CsNO₃ were solved and refined by the same method. One metal atom position was calculated from the Patterson vectors and used to generate a difference map which displayed the other two metal atoms in the asymmetric unit. Refinement of the metals' coordinates and isotropic thermal parameters gave conventional $R^\dagger$ values of 19% and 15% respectively for RbNO₃ and CsNO₃. The nitrogen and oxygen atoms were located in subsequent difference maps and were refined using N-O bond length constraints. Due to the large correlation between x and y coordinates, the shifts in parameters had to be damped until the final stages of refinement. In the final cycles, atomic coordinates, anisotropic thermal parameters, a reflection weighting scheme and a correction for secondary extinction were refined.

The absolute configurations were affirmed to below the $\frac{1}{2}\%$ significance level (Hamilton, 1965) by changing the sign of the imaginary anomalous scattering factor f'' , of the metal atoms. For RbNO₃ R decreased from 3.9% to 3.5%, but for CsNO₃ R increased from 5.5% to 6.5%. Thus signifying that the space group for the RbNO₃ crystal was P3₂ and that for the CsNO₃ crystal was P3₁.

$^\dagger R = \sum ||F_o| - |F_c|| / \sum |F_o|$

	x	y	z	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
a									
Rb(1)	2346(1)	7891(1)	3333	28(1)	31(1)	40(1)	2(1)	3(1)	13(1)
Rb(2)	8882(2)	4624(2)	9600(2)	26(1)	28(1)	27(1)	6(1)	1(1)	12(1)
Rb(3)	8872(2)	1089(2)	3183(5)	40(1)	39(1)	52(1)	6(1)	6(1)	23(1)
N(1)	2326(9)	-2318(9)	-1403(13)	32(2)	23(2)	33(2)	-5(2)	1(2)	16(2)
O(1)	2253(9)	-3288(10)	-392(11)	71(2)	74(2)	53(2)	21(2)	15(2)	44(2)
O(2)	1422(9)	-2685(10)	-2611(12)	47(2)	103(2)	42(2)	-7(2)	-13(2)	48(2)
O(3)	3180(8)	-1048(8)	-978(12)	33(2)	24(2)	87(2)	-23(2)	3(2)	6(2)
N(2)	5627(10)	1240(10)	1123(13)	52(2)	17(2)	21(2)	-6(2)	15(2)	10(2)
O(4)	5550(8)	2247(8)	87(10)	58(2)	24(2)	49(2)	1(2)	-11(2)	22(2)
O(5)	6441(10)	797(9)	696(13)	80(2)	51(2)	107(2)	-29(2)	-28(2)	59(2)
O(6)	4786(9)	884(10)	2395(10)	32(2)	64(2)	34(2)	18(2)	15(2)	-6(2)
N(3)	8769(9)	782(10)	-1482(11)	14(2)	31(2)	45(2)	22(2)	12(2)	19(2)
O(7)	7850(9)	204(10)	-2848(11)	50(2)	81(2)	52(2)	-19(2)	-20(2)	48(2)
O(8)	9466(10)	2046(10)	-1255(11)	61(2)	59(2)	79(2)	-13(2)	13(2)	34(2)
O(9)	8851(10)	-37(10)	-468(11)	79(2)	77(2)	52(2)	23(2)	22(2)	56(2)
b									
Cs(1)	7789(2)	8944(2)	3494(6)	47(1)	50(1)	21(1)	-1(1)	-2(1)	23(1)
Cs(2)	7837(2)	5583(2)	9822(6)	34(1)	34(1)	38(2)	6(1)	16(1)	16(1)
Cs(3)	4533(2)	5623(2)	6667	37(1)	31(1)	34(1)	-6(1)	0(1)	22(1)
N(1)	7829(16)	8861(15)	8773(22)	26(4)	17(4)	23(4)	0(3)	-3(3)	7(3)
O(1)	8791(20)	8917(17)	9578(21)	107(4)	55(4)	55(4)	-11(4)	17(4)	9(4)
O(2)	7589(17)	8327(18)	7418(19)	91(4)	72(4)	25(4)	-21(4)	1(4)	33(4)
O(3)	7630(16)	9908(17)	9272(20)	73(4)	97(4)	77(4)	30(4)	43(3)	80(3)
N(2)	7573(18)	2384(14)	1168(22)	45(4)	35(4)	24(4)	-15(4)	4(4)	21(3)
O(4)	6757(14)	2270(17)	292(17)	41(3)	88(4)	38(4)	-5(3)	-13(3)	48(3)
O(5)	8777(16)	3106(20)	608(22)	52(4)	114(4)	99(4)	-50(4)	4(4)	59(3)
O(6)	7363(25)	1539(21)	2438(20)	361(4)	164(4)	22(4)	12(4)	-7(4)	221(4)
N(3)	4554(17)	5702(14)	1856(23)	59(4)	20(4)	39(4)	0(4)	-27(4)	11(4)
O(7)	5528(15)	6520(20)	694(20)	54(4)	218(4)	40(4)	29(4)	23(3)	82(4)
O(8)	3740(19)	4643(17)	1768(27)	61(4)	50(4)	269(4)	-49(4)	-80(4)	6(4)
O(9)	4394(16)	6683(20)	2843(16)	76(4)	202(4)	14(3)	3(4)	2(3)	102(3)

Table 5.3 Positional ($\times 10^4$) and anisotropic thermal parameters ($\times 10^3$) for (a) RbNO_3 and (b) CsNO_3 .
Temperature factor = $\exp(-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots))$

a							
O(1)	---	N(1)	1.24(1)	O(2)	---	N(1)	1.22(1)
O(3)	---	N(1)	1.22(1)	O(4)	---	N(2)	1.34(1)
O(5)	---	N(2)	1.20(1)	O(6)	---	N(2)	1.22(1)
O(7)	---	N(3)	1.32(1)	O(8)	---	N(3)	1.16(1)
O(9)	---	N(3)	1.18(1)				
O(2)	-	N(1)	-	O(1)		118.1(9)	
O(3)	-	N(1)	-	O(2)		126(1)	
O(6)	-	N(2)	-	O(4)		111.7(9)	
O(8)	-	N(3)	-	O(7)		122.2(9)	
O(9)	-	N(3)	-	O(8)		120(1)	
				O(3)	-	N(1)	-
				O(5)	-	N(2)	-
				O(6)	-	N(2)	-
				O(9)	-	N(3)	-
				O(1)		117(1)	
				O(4)		119.0(9)	
				O(5)		129(1)	
				O(7)		118(1)	
b							
O(1)	---	N(1)	1.20(2)	O(2)	---	N(1)	1.17(2)
O(3)	---	N(1)	1.33(2)	O(4)	---	N(2)	1.08(2)
O(5)	---	N(2)	1.23(2)	O(6)	---	N(2)	1.29(2)
O(7)	---	N(3)	1.34(2)	O(8)	---	N(3)	1.05(2)
O(9)	---	N(3)	1.40(2)				
O(2)	-	N(1)	-	O(1)		118(2)	
O(3)	-	N(1)	-	O(2)		127(2)	
O(6)	-	N(2)	-	O(4)		124(2)	
O(8)	-	N(3)	-	O(7)		130(2)	
O(9)	-	N(3)	-	O(8)		121(2)	
				O(3)	-	N(1)	-
				O(5)	-	N(2)	-
				O(6)	-	N(2)	-
				O(9)	-	N(3)	-
				O(1)		109(2)	
				O(4)		114(2)	
				O(5)		119(2)	
				O(7)		103(1)	

Table 6.4 Nitrate ion interatomic distances ($\text{\AA}$) and angles ($^\circ$) for
(a) RbNO_3 and (b) CsNO_3 .

For RbNO_3 in the final cycle: $R=3.3\%$, $^{\dagger}R_w=3.5\%$; $w = k'(\sigma_F^2 + |g|F^2)$, $k=2.62$, $g=-0.00037$; $\max.(\frac{\Delta}{\sigma})=0.286$, max. and min. residual e^- density, 1.15 and $0.677e^- \text{\AA}^{-3}$; and the secondary extinction coefficient was 0.0016mm^{-1} .

For CsNO_3 in the final cycle: $R=4.7\%$, $R_w=5.5\%$, $w=k(\sigma_F^2 + |g|F^2)$, $k=19.8$, $g=0.00033$, max. and min. residual e^- density 1.64 and $-1.66e^- \text{\AA}^{-3}$; and the secondary extinction coefficient was $=0.0012\text{mm}^{-1}$.

Atomic coordinates and thermal parameters for RbNO_3 and CsNO_3 are shown in Table 5.3 and the bond lengths and angles in Table 5.4. The observed and calculated structure factors are in Appendix A.

5.4 Discussion

5.4.1 Comparison With Other Structural Solutions

When comparing ORTEP2 (Johnson, 1976) drawings of RbNO_3IV and CsNO_3II projected onto (0001) it was clear that the two structures were isomorphous. By this same process it was ascertained that the structures are in close agreement with those of SL and L, and the atoms are labelled accordingly in the tables. Rotation of the unit cell basis of RbNO_3 by 180° around the line $[\frac{1}{3}, y, \frac{1}{2}]$ will bring it into coincidence with the basis chosen by SL. The CsNO_3 cell basis coincides with that of L after rotation by 180° around the line $[x, x+\frac{1}{3}, \frac{1}{2}]$.

The atomic coordinates in Table 5.5 refer to the bases of SL and L. The standard deviations of the x coordinates for RbNO_3 are a complex function of the original x and y standard deviations and were not determined. Comparison of coordinates and bonding geometry with the neutron diffraction results of SL and L yielded some discrepancies above three standard deviations, the most significant of which are given in Table 5.6. The cell constants from this X-ray study have errors of about one tenth of those from the neutron work and have been used with the later fractional coordinates

$$^{\dagger} R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{\frac{1}{2}}$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
a				
Rb(1)	0.4557	0.5679 (1)	0.6267 (2)	2.9
Rb(2)	0.1190	0.2215 (2)	0.0000	2.4
Rb(3)	-0.2243	0.2206 (2)	0.6115 (5)	3.8
N(1)	0.4347	0.5659 (9)	0.1009 (13)	2.6
N(2)	0.1057	0.2097 (9)	-0.4850 (13)	3.1
N(3)	-0.2554	0.2101 (10)	0.1079 (11)	2.3
O(1)	0.3379	0.5586 (10)	-0.0011 (11)	5.8
O(2)	0.3980	0.4755 (10)	0.2205 (12)	5.1
O(3)	0.5618	0.6513 (8)	0.0573 (12)	4.3
O(4)	-0.0031	0.1086 (8)	-0.3822 (10)	4.2
O(5)	0.2309	0.2534 (9)	-0.4430 (13)	6.8
O(6)	0.0570	0.2450 (10)	-0.6132 (10)	4.1
O(7)	-0.3129	0.1184 (10)	0.2445 (11)	4.9
O(8)	-0.1288	0.2798 (10)	0.0851 (11)	5.8
O(9)	-0.3368	0.2186 (10)	0.0064 (11)	6.0
b				
Cs(1)	0.4488 (2)	0.5610 (2)	0.6328 (6)	3.6
Cs(2)	0.1079 (2)	0.2249 (2)	0.0000	3.1
Cs(3)	-0.2289 (1)	0.2133 (1)	0.6488 (6)	3.0
N(1)	0.4365 (15)	0.5528 (15)	0.1048 (22)	2.1
N(2)	0.0906 (14)	0.1856 (18)	-0.4679 (22)	3.2
N(3)	-0.2369 (14)	0.2112 (17)	0.1299 (23)	4.0
O(1)	0.3458 (17)	0.5583 (20)	0.0243 (21)	7.5
O(2)	0.4071 (18)	0.4993 (17)	0.2403 (19)	6.0
O(3)	0.5611 (17)	0.6575 (16)	0.0549 (19)	6.6
O(4)	0.0090 (17)	0.1153 (14)	-0.3803 (17)	4.4
O(5)	0.2110 (20)	0.2337 (16)	-0.4119 (22)	7.0
O(6)	0.0696 (21)	0.2490 (25)	-0.5950 (20)	17.0
O(7)	-0.3186 (20)	0.1138 (15)	0.2461 (20)	7.9
O(8)	-0.1310 (16)	0.2926 (19)	0.1387 (27)	11.0
O(9)	-0.3349 (20)	0.2272 (16)	0.0312 (16)	7.4

Table 5.5 Positional and equivalent isotropic thermal parameters for (a) RbNO_3 and CsNO_3 . (Referred to the bases of SL and L respectively).

$$B_{eq} = \frac{1}{3} \pi^2 \sum_i U_i a_i^* a_i^* a_i^* a_i^*$$

Discrepancies (in $\text{\AA}$) between coordinates

RbNO_3		CsNO_3	
Entity	Difference	Entity	Difference
Rb(3)x	0.20 (1)	Cs(1)x	0.046 (4)
N(2)y	0.06 (1)	Cs(1)y	0.04 (1)
N(2)z	0.13 (1)	Cs(2)x	0.11 (1)
N(3)y	0.05 (1)	Cs(2)y	0.22 (4)
N(3)z	0.07 (1)	Cs(3)x	0.075 (3)
O(1)z	0.08 (1)	Cs(3)y	0.070 (4)
O(3)z	0.07 (2)	N(1)y	0.23 (2)
O(4)z	0.05 (1)	N(2)x	0.16 (2)
O(6)z	0.06 (1)	N(2)y	0.20 (2)
O(9)z	0.06 (1)	N(3)x	0.23 (2)
		O(1)x	0.09 (2)
		O(2)z	0.13 (2)
		O(4)x	0.08 (2)
		O(5)x	0.15 (2)
		O(6)x	0.17 (3)
		O(7)z	0.07 (2)
		O(8)y	0.22 (2)
		O(8)z	0.13 (3)

Discrepancies in bonding geometry

RbNO_3		CsNO_3	
Entity	Difference	Entity	Difference
N(2)—O(4)($\text{\AA}$)	0.13 (2)	N(1)—O(1)($\text{\AA}$)	0.10 (3)
N(2)—O(5)($\text{\AA}$)	0.07 (2)	N(1)—O(3)($\text{\AA}$)	0.10 (3)
N(3)—O(9)($\text{\AA}$)	0.08 (1)	N(2)—O(4)($\text{\AA}$)	0.18 (3)
O(1)—N(1)—O(2)($^\circ$)	4 (1)	N(3)—O(8)($\text{\AA}$)	0.16 (3)
O(4)—N(2)—O(6)($^\circ$)	6 (1)	N(3)—O(9)($\text{\AA}$)	0.18 (3)
O(5)—N(2)—O(6)($^\circ$)	8 (1)	O(3)—N(1)—O(1)($^\circ$)	8 (2)
		O(9)—N(3)—O(7)($^\circ$)	14 (2)

Table 5.6 Discrepancies in structural results between this work and that of SL and L.

in the comparison. Discrepancies in the coordinates (with $\sum \sigma$ in brackets) for RbNO_3 are: $\text{Rb}(3)z$ 0.20 (1) and $\text{N}(2)z$ 0.13(1)Å. This leads to a difference of 0.13(2)Å in the $\text{N}(2)\text{--O}(4)$ bond length and of $8(1)^\circ$ in the $\text{O}(5)\text{--N}(2)\text{--O}(6)$ angle. Discrepancies in the coordinates for CsNO_3 are: $\text{N}(1)y$ 0.23(2), $\text{N}(2)y$ 0.20(2), $\text{N}(3)x$ 0.23(2) and $\text{O}(8)y$ 0.22(2)Å. The differences in bonding geometry are: $\text{N}(2)\text{--O}(4)$ 0.18(3), $\text{N}(3)\text{--O}(8)$ 0.16(3), $\text{N}(3)\text{--O}(9)$ 0.18(3)Å, $\text{O}(3)\text{--N}(1)\text{--O}(1)$ $8(2)$, $\text{O}(9)\text{--N}(3)\text{--O}(7)$ $14(2)^\circ$. The discrepancies in the N positions are associated with those in the O–N–O bond angles and N–O bond lengths. The N in the nitrate ions is strongly bonded to the O atoms and as there is inequality between O–N–O angles within any one nitrate ion the electron distribution (on which the present work depends) cannot wholly represent the position of the nucleus. The larger nitrate discrepancies of CsNO_3 (compared with RbNO_3) can be attributed to masking of the fine detail by the more highly scattering Cs atom. No explanation can be found for the difference between the two $\text{Rb}(3)z$ coordinates.

5.4.2 Description of the Structure

The nitrate ion planes (Fig. 5.1) are nearly parallel to the Rb^+ p–c faces with the nitrogen near the p–c body centre and one N–O bond nearly parallel to a p–c edge. Within each unit cell there are three nitrates in any one of the three perpendicular planes but in each plane there are only two nitrate orientations, these being 30° apart. It is shown in Fig 5.2 (a)–(c) that nitrate ions occupy sites of C_1 symmetry which is in agreement with Karpov & Shultin (1970). Their symmetry is set by the orientation of neighbouring nitrate ions. Nitrates 2 and 3 occupy more symmetrical sites than nitrate 1 and their symmetry is close to C_2 or C_s . This conforms with the conclusions of Brooker (1973). The structure is most similar to that of $\text{TiNO}_3\text{--III}$ (FKS) in which the nitrate ion planes are also parallel to the cation p–c faces.

5.4.3 The Transformation $\text{TiNO}_3\text{--III} \leftrightarrow \text{II}$

In $\text{TiNO}_3\text{--III}$, as shown in Fig. 2 of FKS, the nitrate ions are distributed amongst the three perpendicular planes in the ratio 2:1:1 compared with 1:1:1 for $\text{RbNO}_3\text{--IV}$

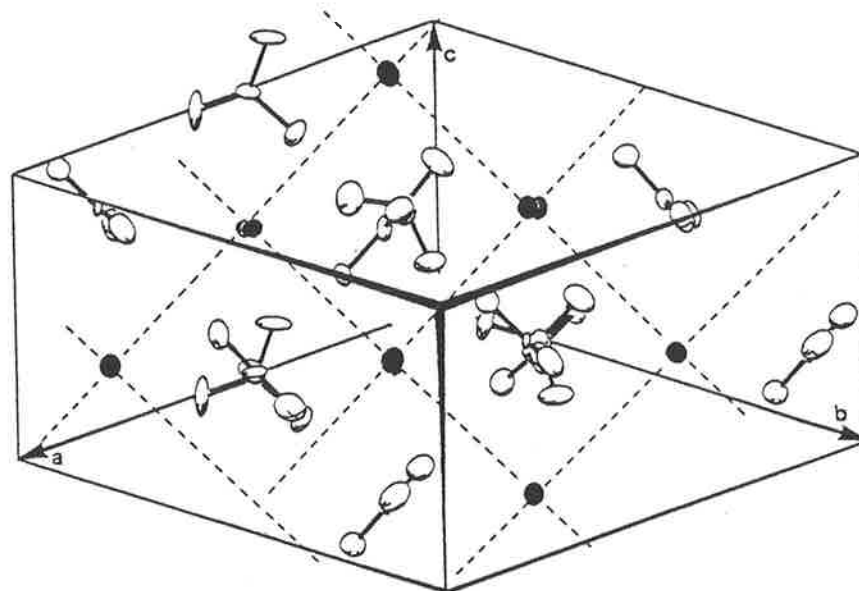


Figure 5.1 Unit cell projected down $[11\bar{2}]$. Drawn using program ORTEP-II (Johnson, 1976). Dashed lines show edges of Rb pseudo-cubes.

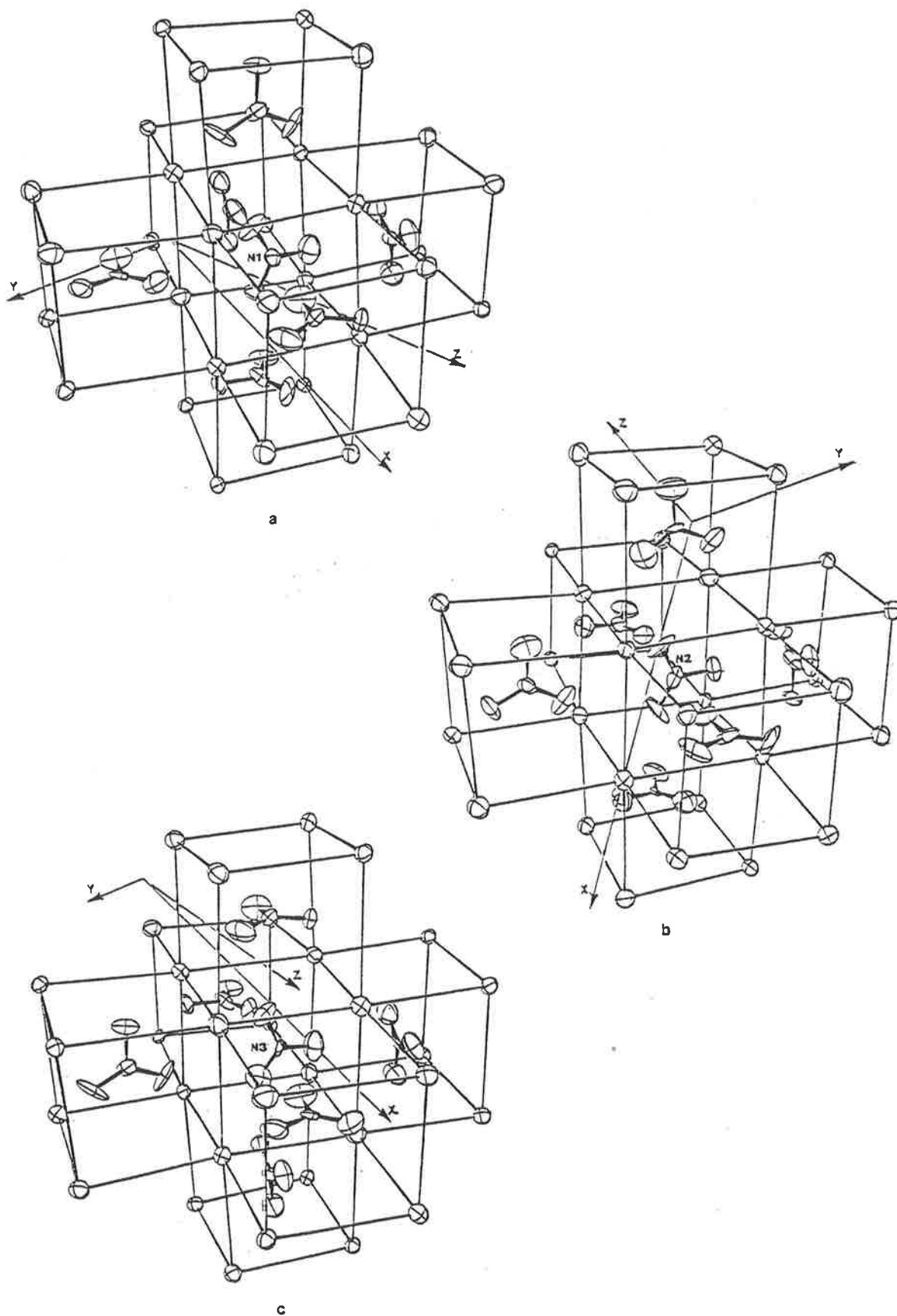


Figure 5.2 Nearest neighbour nitrate and Rb⁺ ions for (a) N1, (b) N2 and (c) N3. Axes directions are x||a, y||b and z||c. Drawn using program ORTEP-II (Johnson, 1976).

(and therefore $\text{TlNO}_3\text{-II}$). Another difference is that in any one plane the nitrate ions are at 60° to each other compared with 30° for $\text{TlNO}_3\text{-II}$. Consequently, during the transformation $\text{TlNO}_3\text{-III} \rightarrow \text{II}$, at least four nitrate ions in three unit cells (12.5% of the nitrates) must rotate by 90° about a line in their planes and some must rotate by 30° about their plane normals. The problem of assigning an atomic correspondence between $\text{TlNO}_3\text{-III}$ and $\text{TlNO}_3\text{-II}$ reduces to deciding the oxygen correspondence, as the other atoms only undergo very small movements. Kennedy & Patterson (1965) recorded orientation relations from X-ray diffraction for the $\text{TlNO}_3\text{-III} \leftrightarrow \text{II}$ transformations but phase-II was referred to a rhombohedral, p-c, lattice which was treated as cubic in their analysis. On the cooling transformation only, options complying with cubic symmetry were observed by optical microscopy. Thus, when considering the individual atomic correspondences between the two phases all the pseudo-cubes must be treated as cubic because more definitive orientation data are unavailable.

As a premise for finding the atomic correspondence during the transformation one can assume that one nitrate ion will remain unrotated because this would be more energetically favourable than if they all rotated. For any nitrate i in $\text{TlNO}_3\text{-III}$, becoming the nitrate j in $\text{TlNO}_3\text{-II}$, there are two possible correspondences of the remaining nitrates due to the approximate C_2 symmetry of i and j . Because there are two unique nitrate ions in $\text{TlNO}_3\text{-III}$ and three in $\text{TlNO}_3\text{-II}$, the number of different atomic correspondences is $2_{\text{III}} \times 3_{\text{II}} \times 2 = 12$. The symmetry operations of both phases do not create new lattice orientations which are discernable by diffraction photography, and so the number of possible lattice correspondences is also twelve. An analysis of minimum nitrate ion movement may reduce this number. One could either prepare a computer program to sum the atomic movements for each correspondence or do this manually by comparing structural drawings in different orientations. The number of possible correspondences could also be reduced by acquiring more definitive lattice orientation relation data by using a diffractometer to distinguish between $[0001]_{\text{II}}$ and $[11\bar{2}1]_{\text{II}}$. Knowledge of the precise atomic correspondence would permit one to approximate the theoretical enthalpy of transformation for comparison with the

observed value and so give further information on the bonding in the structure.

5.4.4 The Structure of RbNO_3 -III and the Transformation RbNO_3 -IV $\leftrightarrow$ III

Postulated structures for RbNO_3 -III have not yet converged towards a unique solution as they had for RbNO_3 -IV. This is probably due to the difficulties associated with the larger thermal motion at higher temperatures. From powder diffractometry Korhonen (1952) suggested a cubic cell with $Z=8$ and with the nitrate ions ordered in aragonite type orientations. Brown & McLaren (1962a) suggested that $Z=1$ from single crystal diffraction photography. From the Rb^+ component of the structure factors, Stromme (1971) decided on aragonite type plus 18% calcite type orientations and with $Z=1$. From powder neutron diffraction Ahtee & Hewat (1980) also decided on $Z=1$ but with the nitrate ions parallel to the p - c faces thereby giving a 12 fold static disorder model. From single crystal neutron diffraction using a similar method of analysis, Shamsuzzoha (1981) reported $Z=1$ and static disorder of aragonite type orientations. Kennedy & Kriven (1981) stated that the nitrate ions were parallel to p - c faces but also stated that $Z=8$, which is self conflicting for a cubic cell. They did not refer to any structural determination of this phase. In summary, the two most recent structural determinations of RbNO_3 -III (namely Ahtee & Hewat (1981) and Shamsuzzoha (1981)), although both working from neutron diffraction, gave conflicting results.

A more extensive structural analysis of RbNO_3 -III may be warranted as only about twenty reflections were measured in the investigations by the two latter authors. Barnes & Sesay (1979) stabilized CsNO_3 -I down to room temperature by crystallizing it from a heated aqueous solution containing only 0.05 mole% of CsNO_2 . Such a small amount of impurity would not noticeably alter the packing arrangement from that of pure CsNO_3 -I. A structural investigation of such a crystal by diffractometry at room temperature should readily give the correct structure. An analogous procedure with RbNO_3 (and RbNO_2) would yield clearer nitrate ion coordinates due to the less dominant scattering from Rb.

If the nitrate ions in $\text{RbNO}_3\text{-III}$ have the same type of orientations as in phase-IV then no nitrate planes need be tilted during the $\text{IV} \leftrightarrow \text{III}$ transformation, because the three allowed perpendicular planes are equally populated in both phases. However some nitrate ions must rotate by 30° about their plane normal. If $\text{RbNO}_3\text{-III}$ has aragonite type nitrate orientations then their planes must tilt by approximately 55° and adjust by a small rotation about their plane normal. Thus, whether the nitrate ions in $\text{RbNO}_3\text{-III}$ have aragonite or $\text{RbNO}_3\text{-IV}$ type orientations, the reorientations necessary during the $\text{IV} \leftrightarrow \text{III}$ transformation are small compared with those necessary for the $\text{V} \leftrightarrow \text{IV}$ transformation or for the $\text{TlNO}_3\text{-III} \leftrightarrow \text{II}$ transformation. This could explain why for the latter transformation Brown & McLaren (1962b) found crystal breakup and Kennedy & Patterson (1965) reported multiple domains, whilst many authors have reported that the $\text{RbNO}_3\text{-IV} \leftrightarrow \text{III}$ transformation preserves a single crystal.

5.5.5 Reorientations of Planar Ions in Other Structures

Tilting of planar anions by as much as 90° (as described above) has not previously been reported. Kennedy & Patterson (1965) in referring to the $\text{TlNO}_3\text{-III} \leftrightarrow \text{II}$ transformation suggested that nitrates are tilted but gave no details. Courtenay & Kennedy (1974) suggested that NO_3^- ions were "reoriented" in the martensitic transformation $\text{RbNO}_3\text{-II} \rightarrow \text{I}$. Merrill (1974) reported an 11° rotation of the CO_3^{2-} ion about its plane normal in the transformation $\text{CaCO}_3 \text{ I} \rightarrow \text{II}$ and reported a 13° rotation for NaNO_3 . Kriven & Kennedy (1981) mentioned a 30° nitrate ion rotation about its plane normal during the aragonite $\rightarrow$ calcite transformation in KNO_3 ($\text{II} \rightarrow \text{I}$). Shamsuzzoha (1981) stated that the nitrate ions undergo a "major rearrangement" during the $\text{RbNO}_3\text{-IV} \rightarrow \text{III}$ transformation.

The 90° tilt described above is also the largest known for a martensitic transformation (e.g. $\text{TlNO}_3\text{-III} \rightarrow \text{II}$) which implies that such a tilt does not prohibit a martensitic transformation although the effect of many nitrate ions undergoing this movement is unknown. This problem could be solved by ascertaining whether or not the transformations $\text{RbNO}_3\text{-IV} \rightarrow \text{V}$ and $\text{CsNO}_3\text{-III} \rightarrow \text{IV}$ have a martensitic character because in

these high pressure phases (Adams & Tan, 1981) all the nitrate ion planes are parallel.

The Crystal Structure of Anilinium-Vermiculite

6.1 Introduction

Due to the large amounts of static disorder in smectites and vermiculites, most structural work on these materials, after intercalation by organic species, has been one-dimensional. In the commonly chosen unit cell the plane of the silicate layers is parallel to (001) and the 1-D information is obtained from the {001} type reflections. The only reported three-dimensional structure of a non mica-type layered silicate intercalate was that of formamide-dickite (Adams & Jefferson, 1976). The team lead by P.G.Slade at C.S.I.R.O. has done 1- and 2-D work on a variety of organic-vermiculite intercalates (Slade, Telluria & Radoslovich, 1976; Slade & Stone, 1983). Their recent work (Slade & Stone, 1984 (abbreviated to SS)) on anilinium-vermiculite showed that 3-D order of the silicate layers was present. They refined the structure in the monoclinic space group C2 but stated that the true space group was P1 (triclinic). Recent NMR, ESR and IR experiments on anilinium-vermiculite by Pisaniello (1984) found that significant amounts of aluminium and magnesium ions, released from the crystal by acid attack, compete with the anilinium for interlayer adsorption sites. These metal cations and their hydration spheres would complicate the electron density distribution of the interlayer region but this was not taken into account by SS in their analysis.

Thus, due to the known extra complexity of the structure, it was considered necessary to investigate it further. The objective of this project was to determine the (3-D) crystal structure of anilinium-vermiculite. The molecular formula for anilinium is $C_6H_5NH_3^+$ and it can be derived from protonation of aniline ($C_6H_5NH_2$) by acid. The anilinium ion contains the ammonium group which is known to be an anchoring point for several other ions, e.g. benzidine (Slade & Raupach, 1982; McBride, 1985), diamino-stilbene (Tennakoon et al., 1974) and alkyl ammoniums (Walker, 1967). Because anilinium induces ordering of the silicate layers the 3-D reflection data should

also reveal accurate positions of the silicate layer atoms.

In the structure determined by SS the unit cell was situated in the typical setting with the $\{001\}$ type planes (basal planes) parallel to the planes of the silicate layers. The base of the unit cell was situated in the middle of one silicate layer and the top of the unit cell was in the middle of the neighbouring silicate layer. The interlayer region was centred half-way up the c -axis and occupied about half of the unit cell volume. SS reported that the anilinium ions were in eight possible orientations per unit cell. This implied only $1/8$ th of an anilinium ion (on average) in each of the possible orientations. Due to the small amount of anilinium present, it was decided to test three different vermiculites with different layer charges and water contents in the hope of finding an optimum sample for observation of the anilinium molecule. These vermiculites were from Llano, Texas; Phalaborwa, Transvaal; and Young River, Western Australia. They had charges per unit cell of approximately -1.9 , -1.6 and -1.5 respectively (Norrish, 1973).

SS reported the presence of some very weak reflections with $\{hk0\}$ type indices which corresponded to a loss of the C-centring of the typical vermiculite unit cell and to a lengthening of the a - and b -axes to $2a$ and $2b$ respectively. These weak reflections also overlapped each other along c^* . Due to the large amount of time required to measure these very weak reflections properly it was not considered practical to do so. Therefore the cell used in the present work was approximately the same size as that used by SS, namely; $a \approx 5.3$, $b \approx 9.9$, $c \approx 15 \text{ \AA}$, $\alpha \approx 90$, $\beta \approx 97$ and $\gamma \approx 90^\circ$.

6.2 Experimental

6.2.1 Crystal Preparation and Selection

The method of crystal preparation has been previously described by Slade & Stone (1983). The original Mg-vermiculite was soaked in aqueous NaCl to replace the Mg^{2+} by Na^+ . The Na-vermiculite was then refluxed in an aqueous solution of aniline hydrochloride with a pH of about 1.4 for a period of approximately one month. The

acidic conditions were necessary to form the anilinium cation rather than the neutral aniline molecule. All the reactions were carried out by P.Slade. The crystals were black platelets with {001} as the plate face. Those used for data collection were selected by P.Slade on the basis of sharpness of their diffraction spots.

6.2.2 X-ray Data Collections*

The data collections for the Phalaborwa and Young River crystals were carried out on the CAD4 diffractometer (section 7.4). In order to help detect the small amount of anilinium in any one of the possible orientations, it was considered desirable to reduce thermal motion of the molecules by cooling the crystal. Cooling was only undertaken on one crystal (Phalaborwa) in case of damage by water. The collection for the Llano crystal was done over several months by P.Slade and P.Stone at C.S.I.R.O. because such a long time span was not feasible on the CAD4 due to the needs of other users.

The space group which was assumed for the data collections was P1 with an additional condition of C face-centring. This non-standard space group will be called C1 (triclinic). The corresponding unit cell dimensions have been mentioned in the introduction (section 6.1). A cell of half this volume with space group P1 would have been the standard (correct) setting. However, it was decided to continue with the larger cell because it is the one usually chosen for vermiculite structures as it displays the monoclinic symmetry often encountered.

When obtaining initial cell dimensions and orientation on the CAD4 diffractometer there was a choice of cell orientations due to the high symmetry of the silicate layers. The individual silicate layers have approximately three-fold rotational symmetry but because successive layers do not superimpose exactly when viewed onto the {001} plane, the angles α and β are not equal to 90° and the unit cell does not have trigonal symmetry. However, there are still three similar unit cells and one of these shows pseudo-monoclinic symmetry, and it is this cell which is normally chosen for a structural investigation (Telluria, Slade and Radoslovich, 1977). It was in some cases necessary to refer data to this latter cell by applying an appropriate transformation matrix which corresponded

* P.K. Schultz collaborated in the data collection on the CAD4 and in the structure solution and refinement.

to a $\pm 120^\circ$ rotation around c^* .

The following sections (6.2.2.1 to 6.2.2.3) list the details of the data collections in the order in which they were performed.

6.2.2.1 Phalaborwa

A crystal measuring $690 \times 330 \times 8 \mu\text{m}^3$ was selected from a group of four supplied by P. Slade. Precession photographs of the other three crystals revealed the presence of crystallites. The chosen crystal was glued with silicone rubber sealant ("Silastic") to a thin glass rod. Initial tests had shown that silicone grease was an unsuitable adhesive as it did not prevent crystal movement even at -100°C . Common glues were too brittle at low temperatures.

The crystal was oriented on the CAD4 at room temperature (25°C). The orientation and lattice parameters were determined by least-squares refinement based on the setting angles of 25 unique reflections with 2θ between 18 and 42° . Using the Enraf-Nonius low temperature equipment (section 7.4.4) the crystal was slowly cooled to -97°C and the orientation and lattice parameters were remeasured at 30°C intervals. The crystal remained at $-97(\pm 5)^\circ\text{C}$ for the rest of the experiment.

As the reflections of anilinium-vermiculites have a large spread in one direction (along c^*) it was desirable to measure the reflection intensities by scanning along a path perpendicular to c^* . Although this method neglects some of the information (Mathieson, 1984) it ensured that neighbouring reflections did not interfere during measurement. Such a direction of scanning required the (001) plane to be perpendicular to the X-ray beam during reflection measurement. This configuration was made possible on the CAD4 by use of the feature designed to minimise intensity loss due to absorption (section 7.4.2). The 25 orientation determining reflections were re-centred using this type of orientation.

Theta-omega (θ - ω) profiles of three typical reflections indicated that the maximum balanced intensity could be measured with ω - 2θ scans. The ω scan angle and the horizontal aperture were $(1.2 + 2.3 \tan \theta)^\circ$ and $(3 + \tan \theta)\text{mm}$ respectively. The space

group C1 (triclinic) required intensity measurements over at least a hemisphere of reciprocal space. Data were collected in the θ range $1.3 \rightarrow 30^\circ$ and with the index ranges: $0 \leq h \leq 6$, $-10 \leq k \leq 10$, $-20 \leq l \leq 20$. The crystal orientation was checked after every 200 reflection measurements and the intensity of three standard reflections was checked after every 60 minutes of X-ray exposure time. These standard reflections had no significant variation. Reflections unique to the supercell ($2a \times 2b$) could not be detected. Of the 1,911 unique reflections measured, 62 were inferior ($F < 2\sigma_F$) and omitted leaving 1,849 for structure refinement with $R_{\text{int}}^\dagger = 0.028$. Data reduction and absorption corrections were applied by programs SUSCAD (Guss, 1979) and ABSORB (Guss, 1980) respectively.

Table 6.1 Cell parameters for anilinium-Phalaborwa vermiculite.

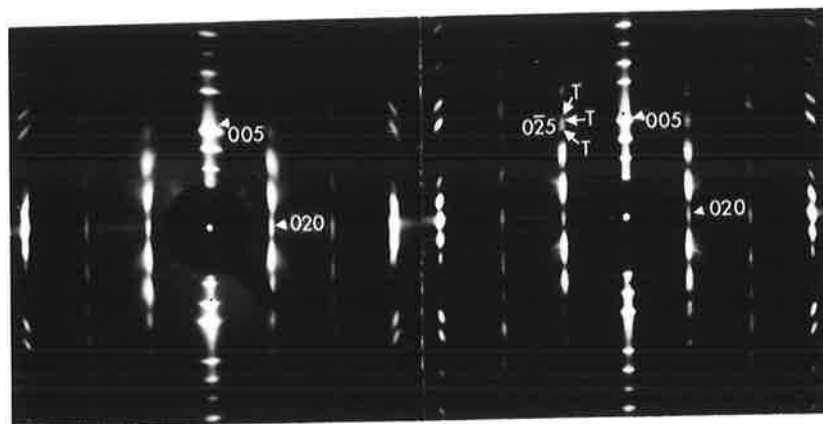
Triclinic C1, $T = 25^\circ\text{C}$: $a = 5.360(1)$ $b = 9.292(2)$ $c = 14.832(6)\text{\AA}$, $\alpha = 89.81(4)$ $\beta = 96.71(4)$ $\gamma = 90.03(2)^\circ$, $V = 734.2\text{\AA}^3$, $D_x = 2.247\text{g.cm}^{-3}$
 $T = -97^\circ\text{C}$: $a = 5.363(2)$ $b = 9.291(3)$ $c = 14.808(5)\text{\AA}$, $\alpha = 89.87(5)$ $\beta = 96.66(5)$ $\gamma = 89.95(3)^\circ$, $V = 732.9\text{\AA}^3$
 (Standard cell at 25°C : Triclinic P1, $a = 5.3564$ $b = 14.888$ $c = 5.351\text{\AA}$, $\alpha = 96.93$ $\beta = 119.89$ $\gamma = 87.33^\circ$, $V = 363.8\text{\AA}^3$)

6.2.2.2 Young River

The crystal was supplied by P. Slade and measured $600 \times 400 \times 50\text{\AA}$. Lattice parameters (Table 6.2) were determined by least-squares refinement based on the setting angles of twenty-five independent reflections with $24 < 2\theta < 43^\circ$ on the CAD4 diffractometer. Reflections were measured in the minimum absorption arrangement as described in section 6.2.1. Theta-omega distribution analyses of three typical reflections indicated that intensity measurements would be optimised with ω - 2θ type scans. The ω scan angle and the horizontal aperture were $(1.2 + 2.3\tan\theta)^\circ$ and $(3 + \tan\theta)\text{mm}$ respectively. Data were collected in the θ range $1.3 \rightarrow 30^\circ$ and the index ranges were

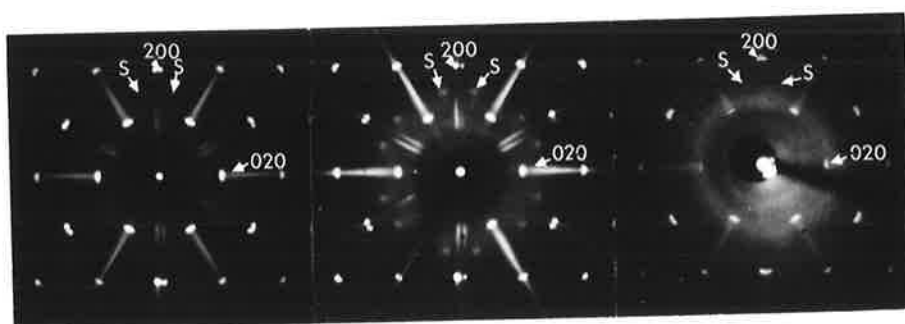
$$^\dagger R_{\text{int}} = \sum |I - \langle I \rangle| / \sum I$$

Figure 6.1 Zero-level precession photographs of anilinium-
(a), (c) Phalaborwa, (b), (d) Young-river and (e) Llano
vermiculites. (a) and (b) are viewed onto (100)
and show the $0kl$, $k \neq 3n$ spots (section 6.2.2.2).
(c), (d) and (e) are viewed onto (001) and show the
supperlattice spots (section 6.4.3)



a

b



c

d

e

Figure 6.1

$0 \leq h \leq 6$, $-10 \leq k \leq 10$, $-20 \leq l \leq 20$. The maximum counting time per reflection was 10 minutes. The crystal orientation was checked after measuring every 200 reflections and the intensity standards were measured after every 60 minutes of X-ray exposure time. These standard reflections had no significant variation. Reflections unique to the supercell ($2a \times 2b$) were detected but could not be measured with adequate accuracy. Of the 2,315 unique reflections which were measured, 232 were omitted ($F < 2.5\sigma_F$), leaving 2,083 for structure refinement with $R_{\text{int}} = 0.0071$.

Precession photographs showed that some of the $\{0kl\}$ ($k \neq 3n$) reflections had a tendency to split into three reflections along the c^* direction. The $\{0kl\}$ reflections are usually spread along this direction without being split (Fig.6.1 and Brindley, 1980). The tripling of the reflections indicated that the true c -axis was $\approx 45\text{\AA}$ rather than $\approx 15\text{\AA}$. Each of the split reflections had intensity which spanned the distance between its three components and therefore the splitting was incomplete. The reflection data corresponding to only the larger unit cell were not collected as neighbouring diffraction spots were too close. Such a collection would have required X-rays with a longer wavelength (e.g. from a Cu source) and it was not permissible to change the source on the CAD4.

Precession photography also revealed that the c -axis of the smaller unit cell was not $15.06\text{\AA}$ but was $14.85\text{\AA}$ and the corresponding standard unit cell parameters are given in Table 6.2. The erroneous determination by the CAD4 was most probably an effect of the tripling. However, the error was not fatal because reflections would still have fallen well within the scan range for intensity measurements with θ up to 24° . Consequently all reflections with $\theta > 24^\circ$ were discarded leaving 969 for structure solution and refinement.

Table 6.2 Cell parameters for anilinium-Young River vermiculite at 25°C .

Triclinic C1, $a=5.343(1)$ $b=9.255(5)$ $c=14.85\text{\AA}$, $\alpha=89.91(5)$ $\beta=95.30(5)$ $\gamma=90.00(4)^\circ$,
 $V=728.7\text{\AA}^3$, $D_x=2.209\text{g.cm}^{-3}$

(Standard cell: Triclinic P1, $a=5.343$ $b=14.85$ $c=5.343\text{\AA}$, $\alpha=95.30$ $\beta=120.00$

$$\gamma=87.28^\circ V=365.6\text{\AA}^3)$$

6.2.2.3 Llano

As mentioned above, the data for anilinium-Llano vermiculite was collected by P.Slade and P.Stone at C.S.I.R.O. The technique will be described in detail elsewhere (Slade et al., 1986). The reflections were measured with ω - 2θ scans with a maximum θ of 30° and had indices in the range $0 \leq h \leq 4$, $-10 \leq k \leq 01$, $-20 \leq l \leq 20$. The maximum counting time per 0.05° increment of the 2θ scan was 90 seconds which resulted in a precise data set. Of the 1,928 unique reflections which were measured, 577 had unclear profiles and were omitted ($F < 0.7$), leaving 1,351 for structure refinement with $R_{\text{int}} = 0.67$. Unfortunately no σ_F were supplied with the reflection data and so reflections could not be rejected on the basis of high experimental uncertainty.

Table 6.3 Cell parameters ^{of} anilinium-Llano vermiculite at 25°C .

Triclinic C1, $a=5.326$ $b=9.264$ $c=14.82\text{\AA}$, $\alpha=90.31$ $\beta=96.72$ $\gamma=89.54^\circ$, $V=726.0\text{\AA}^3$,
 $D_x=2.207\text{g.cm}^{-3}$

(Standard cell: Triclinic P1, $a=5.326$ $b=14.819$ $c=5.324\text{\AA}$, $\alpha=93.09$ $\beta=119.55$
 $\gamma=83.28^\circ$, $V=363.0\text{\AA}^3$)

6.2.3 Chemical Composition

Due to the variety of elements present in the starting materials and the detrimental effects of an acidic environment, it was necessary to know the amount of each element present in the unit cell before undertaking the structure solution. The inorganic cation content was determined by electron microprobe analysis by P.K.Schultz using the microprobe described in section 7.3. The technique used will be reported elsewhere (Slade et al., 1986). The C, H and N content was determined by the Canadian Microanalytical Service (Vancouver, Canada). The amount of oxygen present was not measured.

		Tetrahedral			Octahedral					Interlayer					Layer charge	$\mu(\text{cm}^{-1})$	F(000)(e ⁻)
		Si	Al	Fe ³⁺	Mg	Ti	Mn	Fe ²⁺	Fe ³⁺	Al	K	Na	Ca	Anil	H ₂ O		
P	Ca	5.83	.93	1.24	5.36	.14	.01	.08	.39	.00	.02	.00	.78	.00	—	-1.58	—
	Anil	6.14	.96	1.24	5.23	.15	.00	.00	.39	.00	.07	.00	.00	1.49	1.25	—	484.8
YR	Ca	5.57	2.43	.00	4.94	.01	.02	.06	.78	.18	.05	.01	.70	.00	—	-1.47	—
	Anil	5.66	2.35	.00	5.02	.00	.00	.00	.64	.18	.00	.05	.00	1.66	0.74	—	477.8
L	Ca	5.79	2.21	.00	5.62	.04	.01	.00	.13	.16	.03	.00	.93	.00	—	-1.90	—
	Anil	6.04	2.21	.00	5.65	.04	.00	.00	.05	.16	.00	.00	.00	1.22	3.00	—	480.4

Table 6.4

Unit cell contents for Ca- and anilinium- Phalaborwa (P), Young River (YR) and Llano (L) vermiculites. The number of oxygen and hydrogen atoms in the silicate layer are assumed to be 24 and 4 respectively. "—" means unknown.

The applicable units of analysis were atoms/unit cell, but the analytical results were supplied in units of weight%. Two independent methods of transforming these wt% were used. The first method was the standard crystallographic approach which uses the volume of the unit cell and the measured density of the crystals to determine the mass of the unit cell. The densities of the crystals were determined by immersion in organic liquids. From the unit cell mass the absolute weights of each element in the cell were calculated and these were converted to the absolute number of atoms of each element. The second method was a standard geological derivation (Deer, Howie & Zussman, 1966) based on assigning to each cation (including anilinium) an appropriate number of oxygen atoms and scaling the analyses so that the total number of oxygens in the silicate layer was the ideal number according to the molecular formula for vermiculite. The second method gave the same results as the first method to well within experimental error and the results from the first method are given in Table 6.4. The composition of the three corresponding Ca-vermiculites (Norrish, 1973) were inspected (Table 6.4) so that any changes which had occurred in the silicate layer, during the course of the chemical reaction, could be recognized.

The number of water molecules in the interlayer region was calculated on the basis of the H content (per unit cell). The amounts of H due to silicate hydroxyl groups and due to the anilinium were subtracted from the total H content and the remainder was assigned to H₂O. Due to accumulative errors the resulting error in the water contents may be as large as 15%. The distribution of the metallic elements between the tetrahedral, octahedral and interlayer sites in the anilinium intercalates was indefinite and will be discussed in section 6.4.

6.3 Structure Solution and Refinement

6.3.1 General Technique

The correctness of the model for the atoms in the silicate layers was crucial because these atoms are known to represent at least 70% of the total scattering power. Thus it

was akin to obtaining the position of a heavy metal atom in a metal-complex structure. The starting model was that found for Llano vermiculite by SS and the residual, $R^\dagger$, converged to a satisfactory value after several cycles of refinement for each of the three materials. The direct methods program MITHRIL (Gilmore, 1984) also predicted the same model. Due to the pseudo monoclinic symmetry, there were large correlations between some of the variables and in order to reduce this it was necessary to apply damping to the calculated shifts of variables during least-squares refinement. A damping factor of 500 was applied which made the reduction in the residual (R) after about 4 cycles of refinement comparable with that after 1 cycle of undamped refinement.

The scattering factors assigned to the metallic elements were those of the most commonly found ionization states (International Tables for X-ray Crystallography, 1974). Although the metallic sites in the silicate layer are known to contain small, non-stoichiometric amounts of alternative elements, it was not considered worthwhile to incorporate them into the standard scattering curves. The scattering factor for the oxygen atoms of the silicate layers was that for O^{2-} (Tokonami, 1965). The scattering factors used for the water and anilinium molecules were those for the neutral atoms (program SHELX, Sheldrick, 1976).

Atoms of the same element were mostly given a common isotropic temperature factor. The exception to this procedure was if the atoms were in different coordination environments. For example the temperature factor for the tetrahedral (surface) oxygens was not tied to that for the octahedral oxygens. All temperature factors were isotropic. Group rather than individual temperature factors were usually assigned because the broad anisotropic diffuseness of the electron density peaks indicated that the structures had a low degree of crystallinity and did not warrant individual thermal parameters. Also, the number of reflections (observations) did not permit the use of more variables. For some atoms in disordered sites it was necessary to refine both site occupancy factors and thermal parameters. Feedback between these variables was minimised by

$$^\dagger R = \sum (|F_o - F_c|) / \sum (|F_o|)$$

damping and by the use of common thermal parameters for groups of atoms with different site occupancy factors.

Program SHELX was the main algorithm used for structure refinement. Due to the large number of electron density peaks (apart from those for the standard set of silicate atoms) it was necessary to use contoured difference Fourier maps (section 7.7) to interpret the peaks. The interpretation of these maps was done in conjunction with P.Slade.

6.3.2 Phalaborwa

After 25 cycles of damped least-squares refinement of the positional coordinates and thermal parameters of the typical silicate layers (section 6.3.1) and refinement of an overall scale factor, the residual R was 24.7%. The largest remaining peaks in the difference list calculated by SHELX were in the silicate layer and corresponded to shifts of the whole layer by approximately $\pm b/3$ (Fig. 6.2). There were also smaller amounts of the layer shifted by $\pm na/5$ where $n=1 \rightarrow 4$ (Fig. 6.2). The displacement of alternate silicate layers by $\pm b/3$ has been noted in Mg-Llano vermiculite (Shirozu & Bailey, 1966 (abbreviated to SB)). Because the original Mg^{2+} ions were separated by $b/3$ there were no extra peaks due to their $\pm b/3$ shifts. The strongest peak due to the $\pm b/3$ displacement of the silicate layer was at the silicon level because the original Si^{4+} ions were separated by approximately $2b/3$ and so the $\pm b/3$ displacements overlapped. The actual displacements (in any one direction) were not exactly the same for all atoms and therefore it was not possible to model the displacements by a rigid group translation. Consequently the coordinates of each of the constituent atoms were refined. The shifts were closer to $\pm .31b$ rather than the ideal " $\pm b/3$ ". Refinement of the site occupancy of the atoms in the $\pm b/3$ shifts revealed that the proportion of the silicate layer which had translated along b was .22. The occupancy for atoms at $+a/5$ or $-a/5$ was .03. After refinement of all the above mentioned atoms in the silicate layer region the residual R was 22.8%. Due to the small site occupancy and large number of atoms associated with the $\pm a/5$ shifts, these atoms were not further refined.

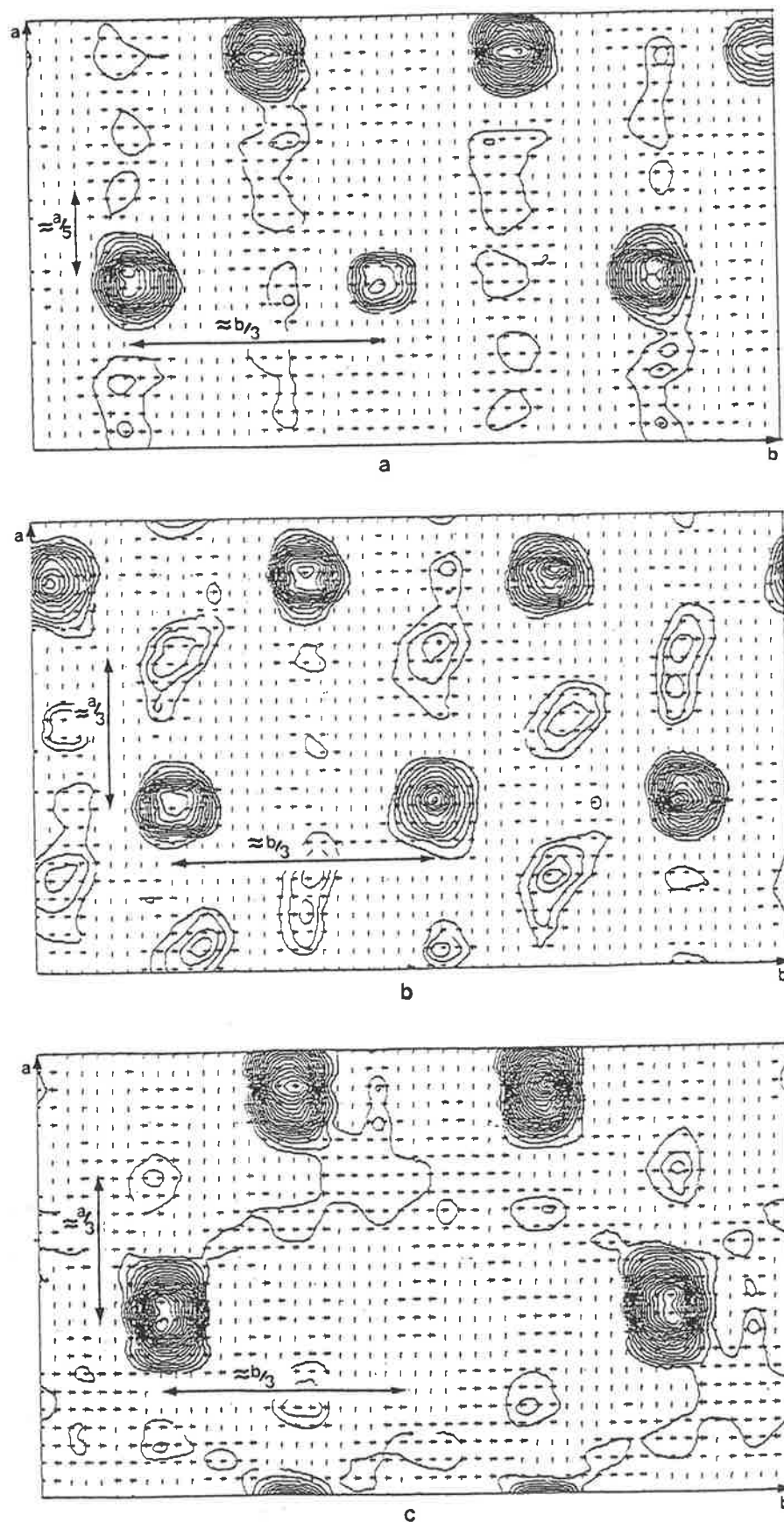


Figure 6.2 Contoured difference Fourier sections parallel to (001) at the level of the Si (tetrahedral) atoms ($z \approx .18$), in anilinium- (a) Phalaborwa, (b) Young River and (c) Llano vermiculites. The maps show the amounts of translational disorder of the silicate layer parallel to the a- and b- axes. The contour intervals are (a) $50 \text{ e}^{-\text{\AA}^{-3}}$, (b) $22 \text{ e}^{-\text{\AA}^{-3}}$ and (c) $96 \text{ e}^{-\text{\AA}^{-3}}$. The most intense peaks (4 on each map) correspond to the original, untranslated atoms.

There were many remaining peaks in the interlayer region and their arrangement was investigated using contoured difference maps. The interlayer electron density could be divided into peaks due to the intercalated anilinium ions and peaks due to hydrated metallic cations.

The interlayer metal cation and water packing arrangement was very similar to that for Mg-Llano vermiculite (SB) but there were also substantial positional deviations from this arrangement. In Mg-vermiculite the Mg^{2+} ions are in the middle level ($z=0.5$) of the interlayer region and the water molecules lie in two sheets one on either side of the plane at $z=0.5$. The metallic cations in the present material were split into two adjacent sites, one either side of the mid-plane and there was associated spreading of the water sites. The water sites were also spread into the middle level of the interlayer region such that their positions were primarily a projection of their positions from either side of this plane. There was also a small electron density peak in the middle of the interlayer region and centred half-way between the two ditrigonal cavities. This was assumed to be iron, as large metallic cations are known to occupy this site (Brindley, 1980).

Due to the large amount of disorder, the inorganic cation-water system could not be properly modelled and refined. However, some atoms were placed at the positions of sharp, maximum electron density. Interlayer metallic cations were assigned the scattering curve of Mg^{2+} and their thermal parameters were fixed at $U=0.02$. Interlayer water sites were assigned the scattering curve of neutral oxygen and their thermal parameters were fixed at $U=0.05$. The interlayer Mg^{2+} ions were given a common site occupancy factor to be refined and similarly for the water molecules. A weighting scheme was incorporated in which reflections were given weights $=k/(\sigma^2 + |g|F^2)$ where k and g were given random values and then refined. The residuals reduced to $R=20.3\%$ and $R_w^\dagger = 21.4\%$. The total site occupancy of the interlayer Mg^{2+} and water were 0.4 and 1.9 respectively per unit cell.

The ammonium groups of alkyl ammoniums and anilinium are known to lodge deeply into the ditrigonal hole of vermiculite (Walker, 1961 and SS respectively). This

$$^\dagger R_w = \sum (|F_o - F_c| \sqrt{w}) / \sum (|F_o| \sqrt{w})$$

fact aided in the location of the nitrogen atom in the present work. Since there are four ditrigonal cavities in the unit cell, there are four sites to which the ammonium groups can be attached. Two are over the ditrigonal cavities near the base of the cell and two are below the cavities near the top of the cell. The ditrigonal cavities are almost vertically centred over one another and consequently so are the ammonium groups. Due to the C-centring of the cell, these four positions reduce to two unique ones; one near the base of the cell and one near the top. The largest remaining peaks in the difference Fourier list calculated by SHELX were possible positions of the nitrogen atoms from two anilinium ions. These nitrogen atoms were assigned an isotropic thermal parameter of $U=0.05$, which is a typical value for such atoms. Their positions and site occupancies were refined. The resulting site occupancies for the individual lower and upper nitrogen atoms (N(1) and N(2) respectively) were both 0.27 which implied a total of 1.1 anilinium ions per unit cell. The position of the ipso-carbon(s) (named C(1)) of anilinium ions were in such positions with respect to the nitrogen as to imply that the plane of the aromatic ring was approximately perpendicular to the plane of the silicate layer and consequently the para-carbon atoms (named C(4)) would have to be near the N and C(1) atoms of the opposing ring. These C(4) atoms were located on contoured difference maps. Refinement of the anilinium ion as a rigid group required that the N-C(1) bond length be fixed. Refinement of the N, C(1) and C4 atoms gave a N-C(1) distance of 1.29 Å. However, literature values (Handbook of Chemistry & Physics, 1983b) gave this bond distance as 1.43 Å and so a compromise of 1.32 Å was chosen. The ortho- and meta-carbon atoms (wing atoms) of anilinium ions could not be clearly located in the difference maps and so they were placed in geometrically correct positions with a C-C distance of 1.395 Å using SHELX. The aromatic hydrogens were included, these being placed in ideal positions with C-H=1.08 Å. Due to the likelihood of planar tilts of the anilinium about the N-C(1) bond, the wing C and H atoms were assigned site occupancies of half the occupancy of the nitrogen atoms. The thermal parameters of the atoms in the anilinium ions were set at $U=0.05$. The two geometrically ideal aniliniums were refined as rigid groups.

	x	y	z	U
Mg(1)	.000	.5000	.0000	.004(1)
Mg(2)	.001(1)	.8334(6)	.0005(4)	.004(1)
Mg(3)	.001(1)	-.8332(6)	.0003(4)	.004(1)
O(1)	.867(2)	-.014(1)	.072(1)	.003(1)
O(2)	-.842(2)	-.011(1)	-.073(1)	.003(1)
O(3)	.374(2)	.153(1)	.075(1)	.003(1)
O(4)	.377(2)	-.180(1)	.075(1)	.003(1)
O(5)	-.339(2)	.156(1)	-.077(1)	.003(1)
O(6)	-.346(2)	-.178(1)	-.076(1)	.003(1)
Si(1)	.416(1)	.1475(7)	.1874(5)	.009(1)
Si(2)	.409(1)	.8343(7)	.1879(5)	.009(1)
Si(3)	.616(1)	.1725(7)	.8143(5)	.009(1)
Si(4)	.622(1)	.822(7)	.8140(5)	.009(1)
O(7)	.147(3)	.222(2)	.226(1)	.012(1)
O(8)	.173(3)	-.242(2)	.228(1)	.012(1)
O(9)	-.120(3)	.227(2)	-.227(1)	.012(1)
O(10)	-.139(3)	-.241(2)	-.227(1)	.012(1)
O(11)	.454(3)	-.008(2)	.226(1)	.012(1)
O(12)	-.427(3)	-.009(2)	-.225(1)	.012(1)
N(1)	.478(4)	.483(4)	.330(3)	.050
C(1)	.520(4)	.492(4)	.419(3)	.050
C(4)	.598(4)	.510(4)	.607(3)	.050
N(2)	.571(4)	.485(4)	.672(3)	.050
C(12)	.568(4)	.483(4)	.584(3)	.050
C(42)	.561(4)	.473(4)	.396(3)	.050
IM(1)	.506(4)	.165(4)	.495(4)	.050
IM(2)	.521(4)	.134(4)	.524(4)	.050
IM(3)	.453(4)	.491(4)	.501(4)	.050
IM(4)	.514(4)	.830(4)	.474(4)	.050
WA(1)	.850(4)	.470(4)	.438(3)	.050
WA(2)	.189(4)	.471(4)	.568(3)	.050
WA(3)	.864(4)	.486(4)	.522(3)	.050
WA(4)	.270(4)	.182(4)	.408(3)	.050
WA(5)	.355(4)	.291(4)	.491(3)	.050
WA(6)	.862(4)	.420(4)	.518(3)	.050
WA(7)	.318(4)	.638(4)	.508(3)	.050
WA(8)	.846(4)	.715(4)	.476(3)	.050

Mg1 -- 03	2.10(2)	Si1 -- 011	1.55(3)	N1 -- 08	2.87(5)
-- 02	2.02(2)	-- 03	1.66(3)	-- 07	2.89(5)
-- 05	2.08(2)	-- 07	1.77(3)	-- 011	3.03(5)
-- 01	2.13(2)	-- 08	1.77(3)	-- 011	3.13(5)
-- 04	2.14(2)		<u>1.59</u>	-- 08	3.28(5)
-- 06	2.23(2)			-- 07	3.29(5)
	<u>2.14</u>	Si2 -- 011	1.59(3)		
		-- 08	1.62(3)	N2 -- 010	2.87(5)
Mg2 -- 01	1.97(2)	-- 04	1.67(3)	-- 012	2.93(5)
-- 02	2.04(2)	-- 07	1.68(3)	-- 09	2.97(5)
-- 06	2.06(2)		<u>1.64</u>	-- 09	3.17(5)
-- 03	2.15(2)			-- 012	3.23(5)
-- 04	2.18(2)	Si3 -- 05	1.61(3)	-- 010	3.27(5)
-- 05	2.26(2)	-- 010	1.63(3)		
	<u>2.11</u>	-- 09	1.68(3)		
		-- 012	1.80(3)		
Mg3 -- 04	1.99(2)		<u>1.58</u>		
-- 05	2.03(2)	Si4 -- 010	1.60(3)		
-- 06	2.05(2)	-- 06	1.63(3)		
-- 01	2.15(2)	-- 09	1.63(3)		
-- 03	2.17(2)	-- 012	1.67(3)		
-- 02	2.22(2)		<u>1.63</u>		
	<u>2.10</u>				

Table 6.5 Anilinium-Phalaborwa vermiculite (a) Atomic positional coordinates and thermal parameters. (b) Silicate bonds and N-O distances in Å.

The final positions of the wing atoms were coincident with those of the perturbed interlayer water sites and consequently no definitive set of coordinates could be obtained for these wing atoms. At this stage it was decided to analyse the anilinium-Young River vermiculite for which the chemical analyses indicated less interlayer water and more anilinium. The data collection for anilinium-Llano vermiculite was simultaneously undertaken at C.S.I.R.O.. The final residuals for anilinium-Phalaborwa vermiculite were $R=19.0\%$ and $R_w=20.2\%$. For the weighting scheme, k and g refined to 5.53 and .0085 respectively. Selected atomic coordinates and bond lengths are given in Table 6.5.

6.3.3 Young River

After refinement of the positional coordinates and group temperature factors of the typical silicate layer atoms (section 6.3.1) the residual, R , was 35%. A large number of intense peaks remained in the difference map of the silicate layer region. Contoured difference maps revealed that these peaks corresponded to the $\pm b/3$ type of disorder but the sites were more highly occupied than in the Phalaborwa structure. The disorder parallel to the a -axis was $\pm a/3$ and not $\pm na/5$ as in Phalaborwa. The atoms corresponding to the most highly occupied of the shifted sites were included in the model. Their positional coordinates and site occupancies were refined and R reduced to 27%.

The largest remaining peaks in the difference Fourier maps were in the interlayer region and their z coordinates implied that they corresponded to the N and C(1) of the anilinium ions. These atoms were disordered in a pattern which was reminiscent of the disorder pattern of the silicate layer. The organic atoms were assigned the same thermal parameters as those in the Phalaborwa material. After refinement of their positional coordinates and site occupancies and a weighting scheme, the residuals were $R=23.1\%$ and $R_w=21.8\%$. The site occupancies for the N and C(1) atoms were as high as 0.6 in some sites and 0.2 in others. Due to the large amount of disorder both in the silicate layer and in the interlayer region, it was considered impractical to pursue

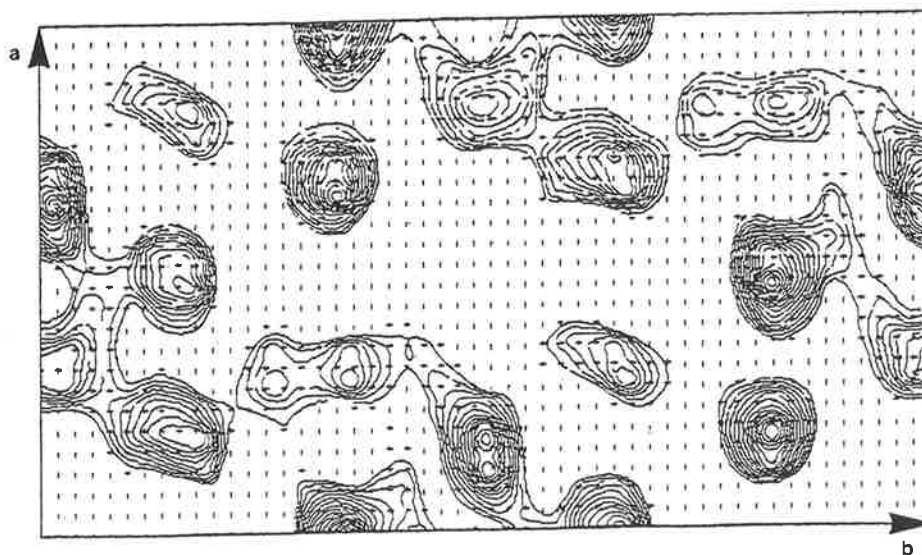
investigation of the Young River material. Instead the data set from anilinium-Llano vermiculite was analyzed.

6.3.4 Llano

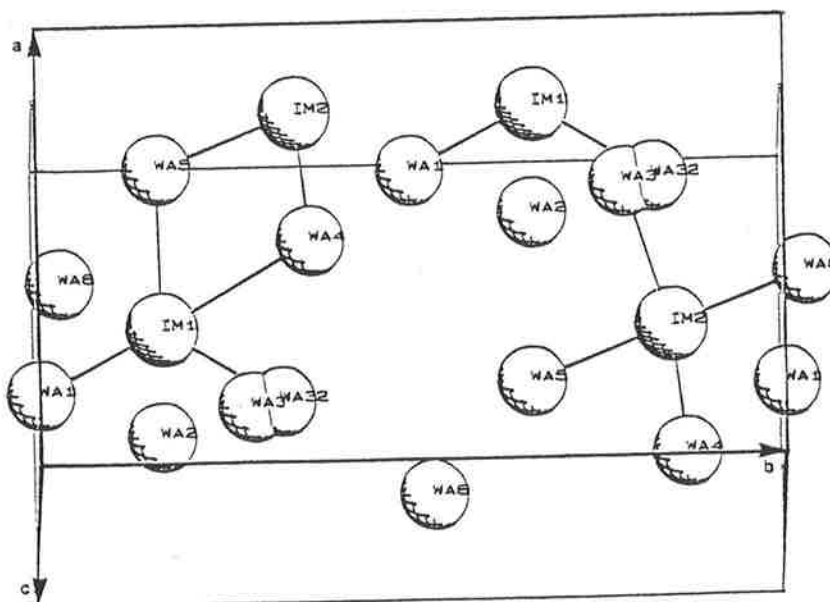
The initial model consisted of the atoms in the silicate layers as discussed in section 6.3.1. After 50 cycles of damped least-squares refinement of the positional coordinates, thermal parameters and interlayer scale factors, the residual R , was 17.8%.

Contoured difference maps of the interlayer region revealed the presence of hydrated metallic cations. The corresponding individual atoms were in similar positions to those suggested by SB for Mg-Llano vermiculite. The arrangement was therefore similar to that in Phalaborwa but the perturbation of water sites was much less. The plane containing the water molecules was a little below the plane at $z=0.5$ and the plane containing the metals was a little above it (Fig. 6.3). The oxygen atoms of the water molecules were assigned a common isotropic thermal parameter and site occupancy. The interlayer metallic cations were assigned the scattering curve of Mg^{2+} and a common isotropic thermal parameter and site occupancy. After refinement of the positional coordinates, site occupancies and thermal parameters, the residual reduced to 16.0%. A reflection weighting scheme based on experimental error could not be applied as errors in the F_o were not supplied with the data from C.S.I.R.O.. Instead a weighting scheme was applied which gave reflections weights $=k/(1+|g|F^2)$, where k and g were refined.

Possible positions of two nitrogen atoms from anilinium ions were the largest remaining peaks in the difference list calculated by SHELX. Their positions were the same as those in the Phalaborwa material. The nitrogens were assigned a common isotropic thermal parameter of 0.07. Their positions and site occupancy factors were refined. The resulting site occupancy factors for the lower and upper nitrogen atoms were 0.26 and 0.39 respectively, thus giving a total anilinium content per unit cell of 1.3. The carbon atoms of four anilinium ions were found on contoured difference maps of the interlayer region. The four molecules could be considered as two pairs such that



a



b

Figure 6.3 Hydrated metal cation system in anilinium-Llano vermiculite in projection onto the (001) plane. (a) Contoured difference Fourier section condensed from $z = .49 \rightarrow .51$: contour interval = $.09 \text{ e}^{-\text{\AA}^{-3}}$. (b) Plot of atoms after least-squares refinement and showing a possible bonding scheme. All the atoms are drawn although in any one particular unit cell only a few may be present. Plotted using a modified ORTEP-II (section 7.8).

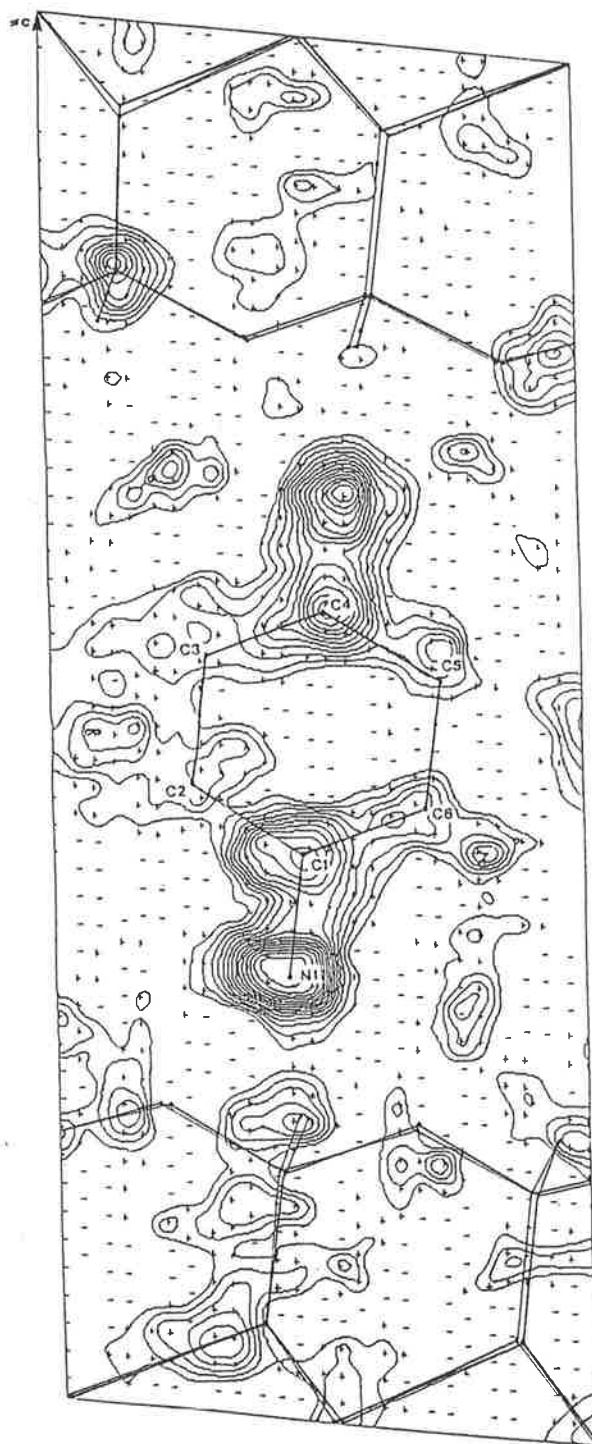


Figure 6.4 Contoured difference Fourier section parallel to the plane of anilinium ion number 1 (ring1) in Llano vermiculite. The silicate layer bonds are approximately projected onto this plane for reference. The contour interval is $.14\text{e}^{-3}$.

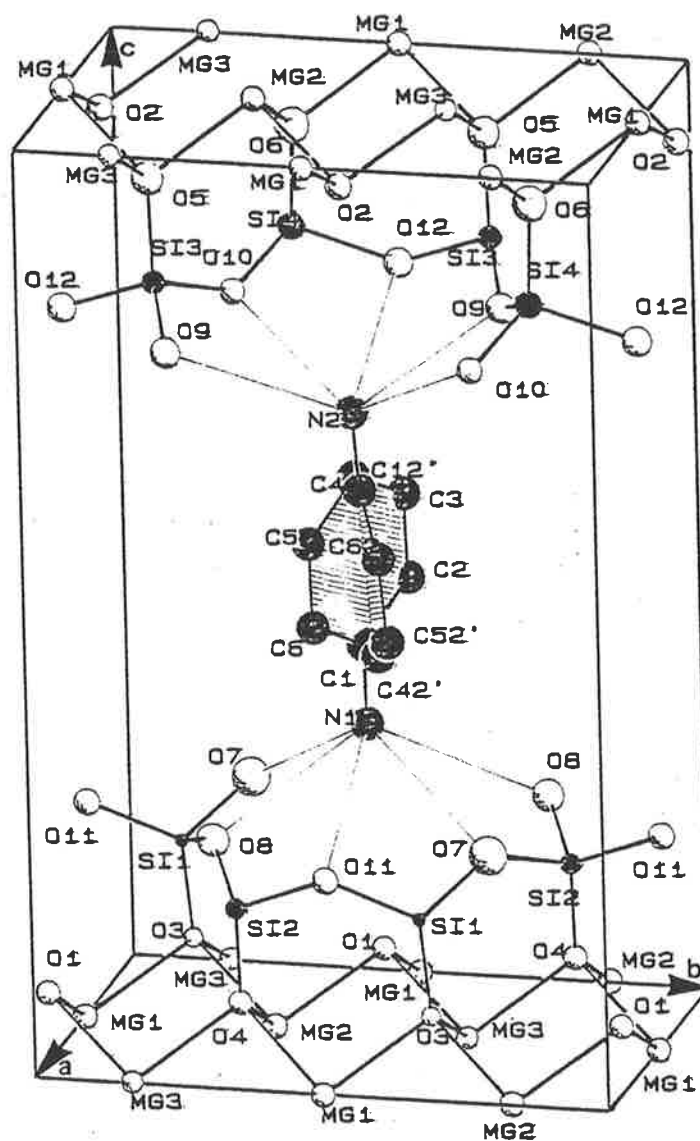


Figure 6.5 Skew view of the unit cell of anilinium-Llano vermiculite showing anilinium rings 1 and 4 and silicate layer atoms after least-squares refinement. Drawn using a modified ORTEP-II (section 7.8).

within each pair, the two nitrogen atoms were coincident. The N, C(1) and C(4) atoms of the two lower molecules approximately coincided, and similarly for the two upper molecules. The four anilinium molecules will be referred to as rings 1,2,3 and 4, where rings 1 and 3 are attached to the lower layer of surface oxygens and rings 2 and 4 are attached to the upper layer. The contoured difference map in Fig. 6.4 shows the location of ring1 and approximate location of ring2. The aniliniums were idealized to the same geometric shape as those in the Phalaborwa structure (section 6.3.2). The four idealized, planar ions were treated as rigid groups in all further refinements. The site occupancy factors for the two lower anilinium ions were set to a common value ($.26/2$); and similarly for the two upper rings ($.39/2$). The thermal parameters of all the atoms in the anilinium ions were refined as a single value. In the final cycles of refinement, the atoms in the silicate layer were given individual isotropic thermal parameters. After refinement of the silicate layer atoms, the hydrated-metal cation system and the anilinium ions, the residuals were $R=14.4\%$ and $R_w=15.8\%$. The total interlayer Mg^{2+} and water site occupancies per unit cell refined to 0.7 and 2.9 respectively. Two of the anilinium molecules (numbers 2 and 3) were affected by diffuse water sites during refinement and they drifted into areas of high water occupancy. However the anilinium molecules numbered 1 and 4 remained in uniquely anilinium sites and they are shown in Fig. 6.5. the largest shift/e.s.d. in the final cycle was -0.12 and was associated with the positional variation of a water molecule. The largest remaining peak in the difference map was $2.9e^{-\text{\AA}^{-3}}$ and represented small positional displacements of the magnesium ions in the silicate layer. The atomic coordinates and bonding lengths are given in Table 6.6.

6.4 Discussion

6.4.1 Chemical Composition

From Table 6.4 it is evident that some alteration has occurred to the silicate layer of the three intercalates during the reaction with anilinium. The main effect

appears to be an increase in silicon. Reference to some previous chemical studies on the behaviour of vermiculites in acidic solutions will help to explain the anomaly. MacEwan & Wilson (1980) stated that in dilute acid, octahedral magnesium and aluminium are displaced from the silicate layer, and that in a strongly acidic environment a residue of amorphous silica remains. The pH of the solutions during formation of anilinium-vermiculite indicated a strongly acidic environment. The wt% of Si in the siliceous regions would have been higher than in the undamaged areas due to the octahedral cation losses and partial collapse of the structure (Norrish, 1954). This would cause an increase in Si content of an average unit of volume on a macroscopic scale which leads to an apparent increase in an average anilinium-vermiculite unit cell.

There appears to be no significant decrease in the Mg and Al contents. This is probably due to adsorption of these elements into the interlayer region. MacEwan & Wilson (1980) stated that the octahedral Mg and Al, displaced by acid, move into the interlayer region. They also reported that hydroxy-hydrates of Mg and Al are present in the interlayer under acidic conditions. From the results of the present work it is not possible to say whether or not Mg is more strongly adsorbed than Al. Pisaniello (1984) noted that both Mg^{2+} and Al^{3+} were released into acidic solution and found a 5→10% increase in octahedrally coordinated Al after reaction with anilinium. This increase could represent Al in the interlayer region or it may indicate that more aluminium is leached from the tetrahedral sites than from the octahedral sites.

According to the refined site occupancy of interlayer metallic cations in the Llano intercalate, 0.7 of the Mg and/or Al which was assigned to tetrahedral or octahedral sites in Table 6.4 must be reassigned to the interlayer region. The refined total site occupancy of anilinium ions (namely 1.3) agrees with that found by atomic analysis, i.e. 1.2. The refined total water site occupancy of 2.9 was also close to that deduced from chemical analysis, namely 3.0. However more water and anilinium is implied by the contoured difference maps as they showed a substantial number of very diffuse sites which were not included in the least-squares refinement. If the interlayer metallic cations were Mg^{2+} , then according to the refined site occupancies of the interlayer

atoms, the charge of the silicate layer was -2.7 which is greater than that of the original Na-vermiculite, namely -1.9 . An increase in charge is unlikely and instead an argument can be put forward for a lower interlayer metal site occupancy than that found by least-squares refinement. The metallic atoms in the silicate layer were each assigned a site occupancy of 1.0 but this should have been less due to some cation vacancies caused by acid attack and due to some translational disorder of the silicate layer. Introduction of such a decrease into the least-squares refinement would have lowered the overall scale factor and in turn lowered the number of interlayer cations observed. If one assumes that the charge of the silicate layer is the same as before the reaction with anilinium and that the amount of anilinium found by chemical analysis is correct, then the total charge of the interlayer metallic cations per unit cell is $+7$ which corresponds to ≈ 4 Mg^{2+} ions.

From Table 6.4 it is evident that more anilinium and less water occupies the interlayer of the lower charged vermiculites. This must be due to the higher size:charge ratio for anilinium than for the hydrated metallic cations. Pisaniello (1984) found that neutral anilinium can be formed by electron transfer facilitated by Fe^{2+} . As iron is present in all of the three vermiculites studied in the present work it is likely that neutral anilinium exists in all three anilinium-vermiculites. For example the number of anilinium molecules per unit cell of the Young River material, namely 1.66, is greater than the silicate layer charge of -1.47 which suggests that about 0.19 neutral anilinium molecules are in the average unit cell.

6.4.2 Description of the Structure

Although the silicate layer and interlayer affect each other, they can be initially treated separately for the purposes of discussion. The remainder of the discussion will refer to the Llano material only except when explicit reference is made to the Phalaborwa or Young River intercalates. This is because the reduced disorder in Llano vermiculite led to a much more definitive result.

6.4.2.1 Silicate Atoms

No major structural discrepancies of the silicate atoms were noted compared to the structure seen in other investigations (e.g. SB or SS). This is indicated by the relative positions of atoms and by the bond lengths. SB from their analysis of Mg-Llano vermiculite, posulated long range ordering of the Al substituted in the Si (tetrahedral) sites. Recent NMR work (Barron, Slade & Frost, 1985) supports at least short range Al ordering in such minerals due to minimization of Al-O-Al and Al-O-Si-O-Al contacts. No ordering of either kind was indicated by the bond lengths in the present work even though four individual sites were refined compared with the two of SB. Our average values for each of the four tetrahedra are within the range given by SB. They reported very small standard deviations on their bond lengths but if the magnitude of error from the present work is taken as an approximately correct value and applied to their bond lengths then it is evident that their two tetrahedral sites are equivalent and thereby do not imply ordering. The apparent absence of ordering may be due to interruption of the ordered sequence by crystal faults or by the non-integral amount of Al substituted for Si.

Silicate layers are known to exist in a more ordered arrangement in the higher charged vermiculites due to the greater attractive forces between the interlayer cations and the silicate layers. The contoured difference maps in Fig. 6.2 show the increase in silicate disorder from Llano to Phalaborwa to Young River vermiculites in accordance with a reduction in the negative charge of the silicate layers. As mentioned in section 6.2.2.2 the Young River material probably has a three layer cell and it is quite likely that the large disorder apparent in the one layer cell analysed in this work, is actually a three layer structure condensed into one layer. This means that consecutive silicate layers in the Young River material are not stacked the same as the typical layers in Phalaborwa and Llano. Consequently the anilinium ions would have different orientations with respect to the layer surface in Young River compared with those in Llano because the ditrigonal cavities would not be vertically coincident. A tripled c-axis has also been noted (Slade, 1985) in rubeanic acid-Young River vermiculite.

6.4.2.2 The Hydrated Metallic Cation System

The positions of the interlayer metallic cations and their waters of hydration were very similar to those for Mg-Llano vermiculite (SB) except that in the present case the water molecules were approximately in one plane near $z=0.5$, rather than above and below the plane at $z=0.5$. As mentioned earlier the electron density associated with these water sites in anilinium-vermiculite at $z=0.5$ was diffused towards the positions of the two sheets of water in Mg-vermiculite. Possible causes for the extensive elongation of the water sites are firstly, the combination of heat and plentiful water during the intercalation reaction and secondly, the presence of anilinium molecules may have influence on neighbouring water molecules.

When a vermiculite with two sheets of interlayer water (such as Mg-vermiculite (SB)) is heated, some water evaporates and the remaining water forms one sheet. Recent work on such vermiculites (de la Calle, Suquet & Pezerat, 1985) has revealed that more than two modes of packing in the interlayer region can occur. This adds further complexity to the system and prevents the suggestion of a unique bonding scheme for the metal-water contacts.

6.4.2.3 The Anilinium Ions

The positions of the N, C(1) and C(4) atoms of the anilinium ions approximately agree with those of SS but the positions of the wing atoms (C(2), C(3), C(5) and C(6)) disagree. No electron density of the wing atoms was found (in the present work) at the positions suggested by SS. They postulated two orientations 90° apart for both the two lower and two upper rings. In the present work the rings were found to be approximately 40° apart such that a molecule half way between them would point with its plane normal parallel to either the a- or b-axis. Substantial tilting of the anilinium ions about the N-C(1) bond was noted during refinement, which could be interpreted as a $\pm 5^\circ$ error in the direction of the rings' plane normals. This error was due to the influence of the diffuse water sites and the low site occupancy of the wing carbon atoms. Pisaniello (1984) stated that some rotation occurs around the N-C(1) bond. Such rotation would

make a large contribution to the low site occupancy of the wing carbon atoms. The wing atoms refined by SS had been located by analyzing difference Fourier electron density projections onto (100) based on (hk0) reflection data only. Such projections would contain significant contributions from the hydrated metal system which would mask the effect of the wing atoms.

The N atom is keyed into the ditrigonal cavity on the surface of the silicate layer and the N-O distances indicate that strong hydrogen bonding occurs. (The sum of $N+2H+O$ van der Waal's radii approximately equals the shorter N-O distances). The C(4)-O distances are shorter than the corresponding van der Waal's radii although the H(-C(4)) atom is nestled into the ditrigonal cavity on the opposing surface.

Mingelgrin & Tsvetkov (1985) suggested that the amine group of substituted anilines may have hydrogen bonds to the hydration spheres of interlayer metal cations. This is less likely to occur in anilinium-Llano vermiculite due to close proximity of the ammonium group to the silicate layer resulting in steric hinderance for any other bonding. However in the anilinium-Phalaborwa and Young River vermiculites the formation of uncharged anilinium would substantially reduce the strength of the bond to the silicate layer and permit some hydrogen bonding to water molecules.

6.4.3 The Superlattice

The superlattice in organic intercalated vermiculites has been discussed at length by Slade, Raupach & Emerson (1978), Slade & Raupach (1982) and Slade & Stone (1983). This latter paper was concerned with anilinium-Llano vermiculite. The superlattice in anilinium-vermiculite has a unit cell of dimensions $2a \times 2b$ and is C-face centred. The strength of the superlattice spots increases from Llano to Phalaborwa to Young River which is also the sequence for increasing anilinium content. Therefore the superlattice is most probably due to the packing of the organic molecules rather than to ordering of organic molecules amongst hydrated metal cations. The four possible orientations of an anilinium ion over a ditrigonal cavity allow many possible packing arrangements inside the $2a \times 2b$ cell and some of these have been discussed by Slade &

Stone (1983).

Using contour maps of the interlayer electron density projected onto (001), it was possible to study various packing arrangements of anilinium ions and hydrated metals. The approximate numbers of anilinium ions, interlayer metals and waters in one superlattice cell are 4.8, 2.8 and 12 respectively. Van der Waal's radii circles were used to simulate the interlayer species and it was found impossible to pack a mixture of organic and hydrated metal cations in the interlayer region. However, they could all be accommodated if they were segregated into domains of concentrated organic or concentrated hydrated metal atoms. The size of these domains in the crystal is unknown but is expected to be at least $15a \times 15b$ to ensure a uniform interior of each domain. Where an organic domain meets an inorganic domain there would be packing difficulties resulting in substantial perturbation of the preferred atom locations and high potential energy. This disturbance could be a contributing factor towards the diffuse electron density seen in the interlayer.

6.4.4 Possible Improvements to Crystal Quality

The main problems which hampered the structure solution of anilinium-vermiculite were silicate layer disorder and the presence of interlayer hydrated metal cations. Both of these factors increased the complexity of the electron density distribution and increased the number of variables to be refined.

The silicate layer disorder was greater in the lower charged vermiculites which suggests that only highly charged vermiculites should be used in future investigations unless the layers can be fixed into a single relative position before intercalation with the organic molecule of interest. Such fixing may be possible by bonding the layers together by a "cross-linking" process like that studied in montmorillonite (Tokarz & Shabtai, 1985).

The adsorption into the interlayer of metal cations released by acid attack suggests that intercalation reactions should only be undertaken in an environment of low acidity. If the reaction must proceed in a solution of low pH then vermiculites containing a

greater variety of metallic elements should be avoided as these create further complexity of the interlayer electron density distribution. If the molecule to be intercalated was adsor^bbed much more strongly than the hydrated metal cations then the reaction could still be carried out in acidic conditions.

Another reason for the diffuseness of the interlayer region was the large number of possible positions of the anilinium molecule. This aspect was due to the symmetry of the silicate layers and of the anilinium ion and there^efore cannot be altered.

Chapter 7

Apparatus**7.1 Introduction**

Reports on experimental work always contain some information on the apparatus used so as to give the reader an indication of the nature and quality of the data. Consequently the apparatus used in the present work is described. Ideally, the type of apparatus used should be determined by the required data, but in reality the equipment available dictates the course of experimentation. This latter effect can be partially counteracted by constructing one's own apparatus, but this is restricted by resources and practical time limitations. The apparatus constructed for the present work is described in the following sections of this chapter.

The first step in most of the experiments was to grow the desired crystals. Apparatus for most methods of growth from solution were available but a high temperature furnace was constructed for growth from the melt. Adequate optical microscopes were available for studying the transformation effects of the crystals. A microscope hot stage was available but a cold stage had to be constructed. Orientation relations for transformations were determined on an X-ray camera called a Stoe Reciprocal Lattice Explorer. To perform transformations on this device, a heater and cooler were built. A pressure cell was also constructed to allow both X-ray and optical analysis of transformations induced by hydrostatic pressure. For crystal structure determination and lattice parameter measurement a CAD4 (computer assisted) diffractometer was available. Computer software for the subsequent intensity data interpretation existed on a separate computer. For the analysis of the transformation data and for the more complex crystal structures, it was necessary to build a significant proportion of the computer software. The computers available for programing and data processing were a CDC-Cyber 173 and a DEC-Vax 785. The Cyber was a much faster computer but it had less memory storage space. For plotting drawings, there was a Calcomp

and a Nicolet-Zeta 1453 hardcopy plotter and in the later stages a Visual-550 graphics terminal and a DEC-LVP16 hardcopy plotter were used.

7.2 Mechanical and Electrical Devices

7.2.1 High Temperature Furnace for Crystal Growth

Study of the transformations of lead monoxide (PbO) and manganese fluoride (MnF₂) required that the crystals be grown from the melt. Their respective melting points are 883 and 856°C.

The main supporting components consisted of a silica tube and an asbestos casing. The tube was .4 metres long with internal and external diameters of 41 and 47mm. The chosen heating element wire, (wrapped around the silica tube) was "Kanthal-A1" (Shah, 1975) with a 1mm diameter.

The required power was 1800W. The maximum current and voltage available were about 9A and 240V, therefore the minimum and maximum lengths of the wire were 11m and 16m respectively. After winding on the wire, it was coated with firing clay and baked. The resistance of the furnace was 25Ω. Two ceramic plugs were fitted in the ends of the tube and one of the plugs had a hole through which a heavy-gauge chromel-alumel thermocouple passed.

The departmental electronics workshop constructed the electronic controls so that a maximum temperature and a cooling rate could be selected. Tests of the furnace showed that it could heat up to 1200°C.

7.2.2 Reichert Zetopan Optical Microscope

A Reichert microscope was used for studying optically observable details such as interfaces and other transformation characteristics. Both reflected and transmitted light were used and a Nomarski interference-contrast attachment was available. The latter device was particularly useful for examining surface relief. Dark field illumination

in reflected light was useful for examining the internal detail of crystals. The objective lenses ranged in magnification from $4\times$ to $45\times$. There was a Reichert automatic camera attached which could hold 35mm film for photomicrography. The film employed was black and white Ilford HP5 with 400ASA/27DIN. Although colour photographs contain more information they are difficult to publish in journals and consequently the extra information available could not have been conveyed to the readers. The microscope had a translating and rotating stage with a slide holder to which heaters or coolers could be attached.

7.2.2.1 Cooling Stages

The first cold stage was constructed to transform crystals of uranyl hydroxide from the β - to the α -phase (chapter 2). A minimum temperature of -10°C was adequate and due to the infinite hysteresis of the transformation the low temperature did not have to be maintained for more than a few seconds. These requirements permitted a simple design. The device basically consisted of a ducted aluminium block, 4mm thick, through which cold dry nitrogen was passed. The crystals were laid on a glass slide on top of the aluminium block. The cold dry nitrogen was fed from a coiled copper tube immersed in a 5 litre Dewar containing liquid nitrogen. The dry nitrogen gas was supplied from a pressurised cylinder. This cooler could cool crystals to $-20 \pm 5^{\circ}\text{C}$.

A second cold stage was constructed (Fig. 7.1) to transform crystals of ammonium iodide (NH_4I) which has a transformation temperature of -17°C (Hovi, Paavola & Nurmi, 1969). These crystals supercooled and it was necessary to construct a cooler which could stay at about -50°C for half an hour without ice damage to the crystals. The principle of the cooling method was to blow cold dry nitrogen directly at the crystals. The main body of the cooler was machined from copper sections and soldered together. The cold gas was passed into a circular channel between two concentric copper rings. The inner-most ring was perforated with small holes through which the cold gas escaped in the direction of the specimen. The substage condensor, mechanical stage, cooler and objective lens were surrounded by a thin, clear plastic envelope which

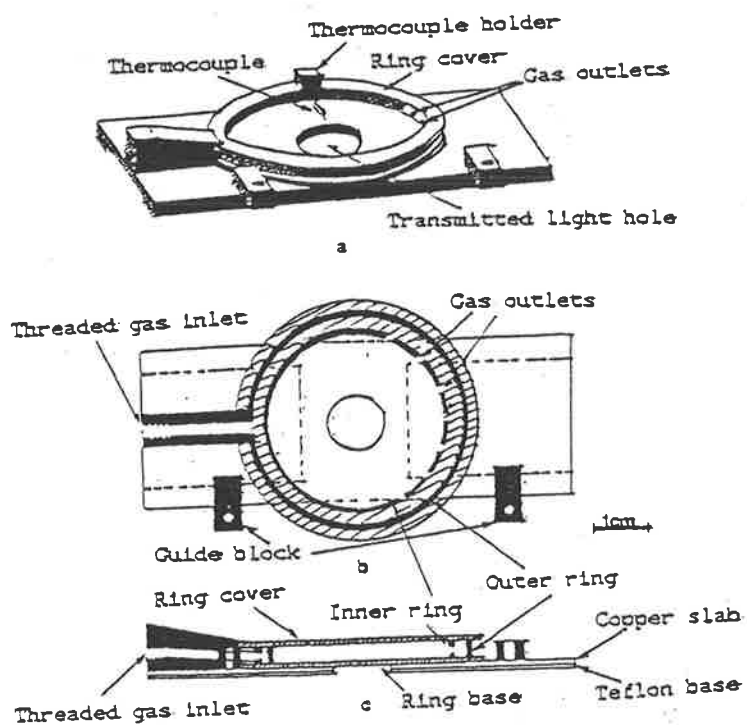


Figure 7.1 Microscope cooling stage. Views: (a) skew (b) top and (c) side.

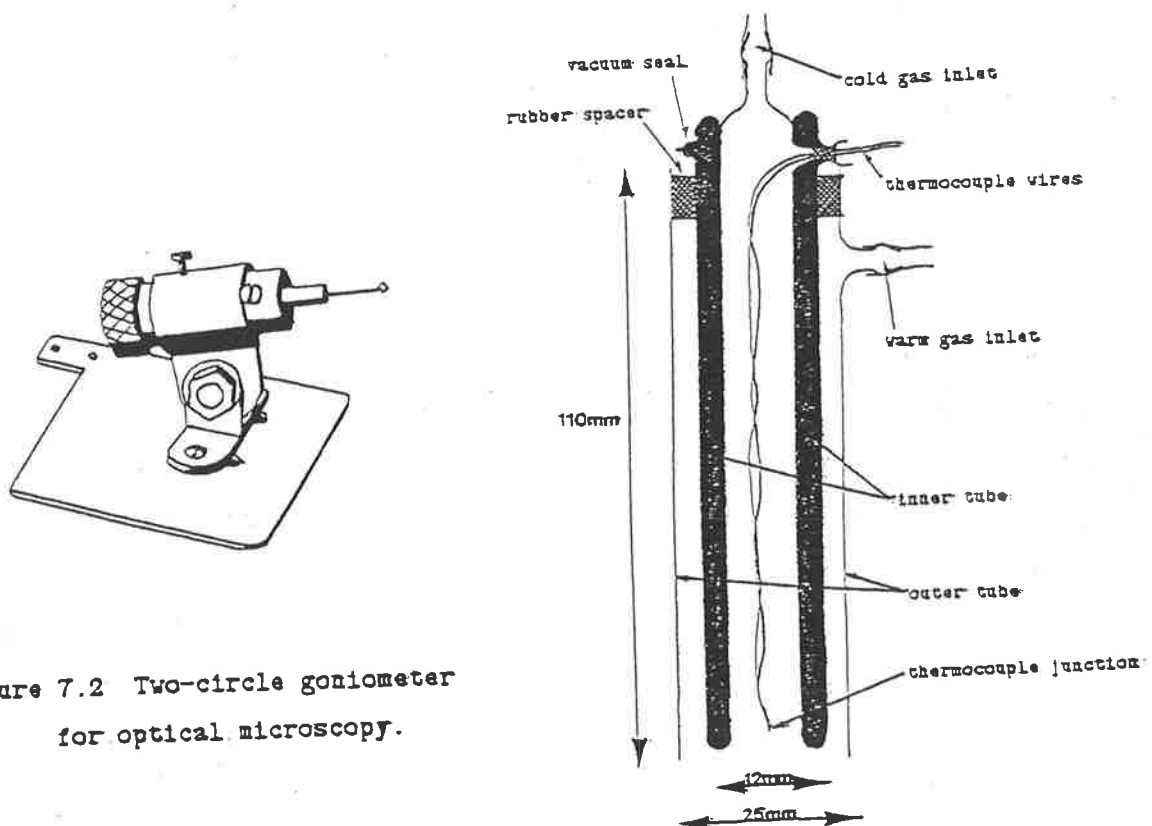


Figure 7.2 Two-circle goniometer for optical microscopy.

Figure 7.3 Sample cooler for the X-ray camera.

prevented ice from collecting on the specimen. Dry nitrogen gas at room temperature was fed into the envelope to maintain a positive pressure of a dry atmosphere. The method of cooling the dry nitrogen was the same as that for the other cold stage described above. The temperature of the cold stage could be adjusted with regulating taps and read via a chromel-alumel thermocouple connected to a "Trendicator" (Doric temperature indicator). The specimen could be maintained at -70°C for periods of up to half an hour.

7.2.2.2 Heating Stage

The heater was the same one as used for the experiments on MnS by Kennedy, Harris & Summerville (1979) and by Kennedy & Summerville (1981). The heating element was a microscope slide coated with a thin film of SnO_2 doped with In_2O_3 . The slide was recessed into an asbestos base which could be fitted in the slide holder of the mechanical stage. The temperature was controlled by adjusting a Variac (coil potentiometer). The heater was calibrated (by the author) to $\pm 10^{\circ}\text{C}$ between 200°C and 430°C from known melting points. This was achieved by recording the current flowing when the solid-liquid interface could be moved to and fro across the sample. The temperature of the specimen was higher when using the $45\times$ objective lens than with the lower power (longer working distance lenses) because the $45\times$ lens was under 1mm away from the sample and thereby acted as a thermal insulator. The same size circular coverslips (20mm diameter) were used as crystal bearers throughout all the heating experiments.

7.2.2.3 Two-circle Goniometer

In order to obtain three-dimensional data on the shape changes or interface planes of crystals it was necessary to rotate them. Due to the small size of many of the crystals and the close proximity of the objective lens, turning the crystals over onto an alternative face was precarious and very often unsuccessful with a hand-held needle. Also, the crystals often did not have the necessary faces on which to rest them. For these

reasons a two-circle goniometer was constructed from brass and it could be attached to the mechanical stage of the microscope (Fig 7.2). It could hold the types of stubs commonly used for X-ray diffraction work.

7.2.3 Binocular Microscope

Another microscope which was found to be particularly useful was a binocular microscope with a long working distance of about 5cm. This microscope was used primarily for mounting crystals intended for X-ray diffraction analysis. Transmitted or reflected light illumination was available and the magnification was 15 $\times$. An Enraf-Nonius goniometer head holder could be fitted to the stage and allowed a 360° rotation of the goniometer head about a horizontal axis. The holder and microscope ensemble was very useful for mounting crystals in the pressure cell (section 7.2.4.3).

7.2.4 The Reciprocal-Lattice Explorer (X-ray Camera)

The Stoe "Reciprocal-Lattice Explorer" was an X-ray camera capable of recording Laue, rotation, oscillation, de Jong-Bouman and Buerger precession photographs on flat film. The theory, mechanics and operation of the X-ray camera have been discussed by Wölfel (1971). The camera was used for almost all of the X-ray diffraction work except for structure factor intensity measurements and precision lattice parameter determinations; these were done on the CAD4 diffractometer (section 7.4). Transformations induced by cooling, heating and pressure were studied on the X-ray camera and the associated apparatuses are described in the following three sections.

The X-ray source for the Reciprocal-Lattice Explorer was a Mo tube operating at 45kV and 20mA. A Zr filter could be used to absorb the Mo-K β peak. Diffraction photographs were recorded on Polaroid film. Initial orienting of crystals on the camera was greatly facilitated by using the complementary microscope-telescope with reflected light illumination. Each crystal was tilted until one of its faces was in a strong reflecting position and then the spindle axis was turned by 90° to make the crystal

face perpendicular to the X-ray beam to within about 1° . The crystal was then further adjusted by standard diffraction methods.

7.2.4.1 Low Temperature Device for the X-ray Camera

Various cooling apparatuses for X-ray cameras have been comprehensively reviewed by Rudman (1976) and an example of an efficient, easy to use system is the Enraf-Nonius CAD4 cooler mentioned in section 7.4.1. Unfortunately this latter apparatus was not available for use other than on the diffractometer. The Stoe company manufactured a cooler designed for the Reciprocal Lattice Explorer but this device was apparently not on the market (Kennedy, 1982); consequently a low temperature device had to be constructed. The main requisites of the device were that it could cool a crystal down to about -20°C and maintain it at this temperature for about 15 minutes to allow the recording of a clear diffraction pattern and without the complications of ice. Such a device was reported by Rudman (1967) and it was decided to copy his design as closely as possible.

The main body of the cooler was a double-walled, silvered and evacuated glass tube surrounded by a concentric glass tube (Fig. 7.3). Cold dry nitrogen gas was forced along the central tube and room-temperature dry nitrogen along the outer cylinder. The warmer stream prevented ice forming near the crystal. The device was clamped to the Reciprocal Lattice Explorer and the end of the inner tube was positioned about 4mm from the specimen crystal. The inner and outer gas streams were provided by the same arrangement used for the second microscope cold stage (section 7.2.2.1). A chromel-alumel thermocouple was situated near the cold gas outlet and was connected to the Trendicator. The apparatus could maintain crystals at $-30^\circ(\pm 10)^\circ\text{C}$ for periods of up to 20 minutes.

7.2.4.2 Heater for the X-ray Camera

A heater was constructed for transforming crystals, such as MnS (chapter 3), on the Reciprocal Lattice Explorer. Its design was based on a heater already in existence

for the Charles Supper precession camera in the same laboratory. The heater basically consisted of a nichrome wire coiled inside a vertical silica tube which ended a few millimeters below the crystal. The diameter of the wire was 11mm and it had a total resistance of 25Ω . The surrounding air in the vertical tube also became hot and so the crystal was heated by both convection and radiation. The temperature was controlled by adjusting a Variac in the circuit.

The upper limit of temperature was set by the fusing of the wire and partially by the thermal stability of the "Bakelite" (thermoset plastic) base. The heater was calibrated between 200 and 500°C to within $\pm 50^{\circ}\text{C}$ by substituting a chromel-alumel thermocouple in place of the crystal.

7.2.4.3 Design and Use of the Diamond-Anvil Pressure Cell

7.2.4.3.a Requirements

Some of the transformations which were of interest are known to occur under increasing hydrostatic pressure. For example; CdS 25 kbar (Yu & Gielisse, 1971), AgI 4 kbar (Bassett & Takahashi, 1965), NH_4F 4 kbar (Pistorius, 1976), MnF_2 17 kbar (Hazen & Finger, 1981a) and NH_4I 0.55 kbar (Heyns, Hirsch & Holzapfel, 1980). A pressure cell was needed in order to record Laue and precession photographs which were necessary to determine the orientation relations of the transformations.

Optical observation of the transformation was necessary for two reasons. Firstly because it could provide information on the possible shape change. Secondly, it was an instantaneous test of sufficient pressure for transformation, compared with taking diffraction photographs after each incremental increase in pressure. In order to position the crystal such that low index reciprocal lattice levels appeared on the photograph before transformation, goniometer arcs and the associated translational movements for centring were also needed.

The type of apparatus which meets these requirements is commonly referred to as a diamond-anvil pressure cell. The typical central region of one of these devices

is shown diagrammatically in Fig. 7.4.a. The two opposing diamonds have the brilliant cut, but with the culet levelled off to form an "anvil" face. The table face is seated over a viewing tunnel drilled in a beryllium disc which has low X-ray absorptivity. The diamonds are separated by a thin metal gasket, with a small central hole, which is the sample chamber containing the crystal of interest and a liquid for hydrostatic pressure.

7.2.4.3.b History of Design

The first pressure cell for single crystal work on a precession camera was reported by Fourme (1968). The pressure was generated by a pneumatic device and required construction of a double based goniometer head with appropriate modification of a standard precession camera. In the design of Weir, Piermarini & Block (1969) the pressure was transmitted to the anvils from a screw plate via a long lever. The size of the apparatus necessitated construction of a large camera. Merrill & Bassett (1974) reported a much smaller cell which could be attached to a standard goniometer head and used on a standard precession camera. The pressure was applied more directly to the anvils by tightening three symmetrically situated screws which pulled the two halves together. Beyond 25 kbar the gaskets were known to fail due to misalignment of the diamonds. The convenience and simplicity of this cell has resulted in its wide use and it is referred to as the "Merrill-Bassett" cell. Keller & Holzapfel (1977) introduced a more precise instrument which could produce pressures up to 100 kbar using two coupled levers. Their cell could be fitted to a standard short goniometer head and used on a standard precession camera. The beryllium components were hemispherical to permit angle independent absorption corrections for the beryllium. Hazen & Finger (1977) reported an improved Merrill-Bassett cell which could reach 96 kbar. The beryllium discs were strengthened by having a thinner viewing tunnel and by the absence of recesses for the diamonds. The anvil faces were wider for easier alignment and thereby decreased the likelihood of gasket failure. The goniometer head included vertical translation for crystal centring on a diffractometer. The modification, reported by Okai (1980), of the Merrill-Bassett cell included replacement of the beryllium by steel, whilst

maintaining sufficient unhindered diffracted rays for precession photography. The large diamonds cut their own recesses by using them as the drill bit on an ultrasonic drill. Hazen & Finger (1981a) gave explicit plans for a high-temperature version of their 1977 cell. The new cell could operate at 30 kbar and 450°C.

Many advances are still being made in the design and consequent performance of diamond-anvil pressure cells (e.g. Malinowski, 1984; Dieterich et al., 1984). Commercially made suitable pressure cells were available from between US\$1,500 (High Pressure Diamond Optics Inc.) and US\$9,000 (Stoe).

7.2.4.3.c Choice and Construction

For the present work the Merrill-Bassett type cell was chosen in preference to the design of Keller & Holzapfel (1977) because the latter required much more machining and the purchase of a short goniometer head. The crystals to be examined under pressure were chosen on the basis of their known structure types and therefore it was not necessary to incorporate features necessary for structure analysis on a diffractometer (such as a vertical translation and hemispherical beryllium parts). Using a pressure cell on the CAD4 diffractometer would have also required modifying the CAD4 program to make it aware of the loss of diffracted rays due to the steel components of the pressure cell.

The usual method for measuring pressure in the Merrill-Bassett type of pressure cell is based on measuring the pressure shift in the sharp R-line fluorescence spectrum of a ruby crystal (Barnett, Block & Piermarini, 1973) using a spectrometer system. Such a system was not available for the present work. However, as the transformation pressures were already known, it was not crucial to measure the pressures in the sample chamber.

The cell was constructed from the explicit details given by Hazen & Finger (1981a) but with some simplifications. Beryllium discs with viewing tunnels were used in place of the boron carbide discs and no heating mantle was incorporated. Thus, although the dimensions were taken from Hazen & Finger (1981), the nature of the cell more closely

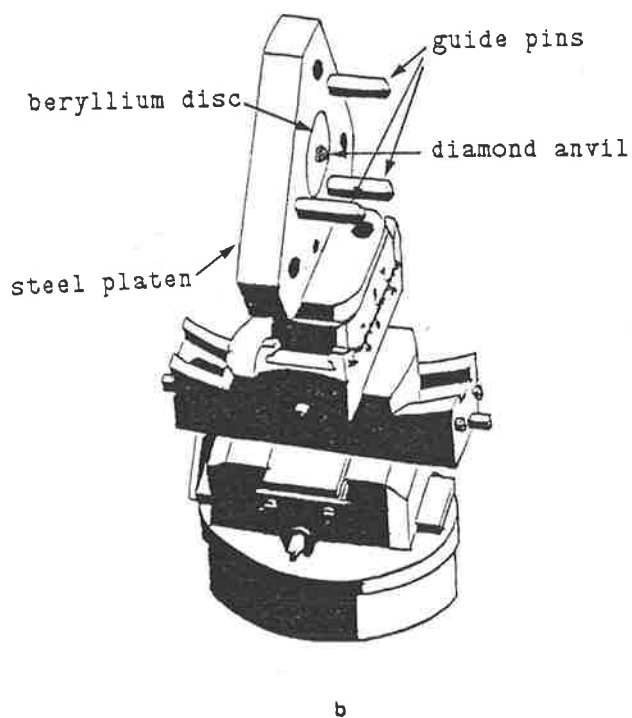
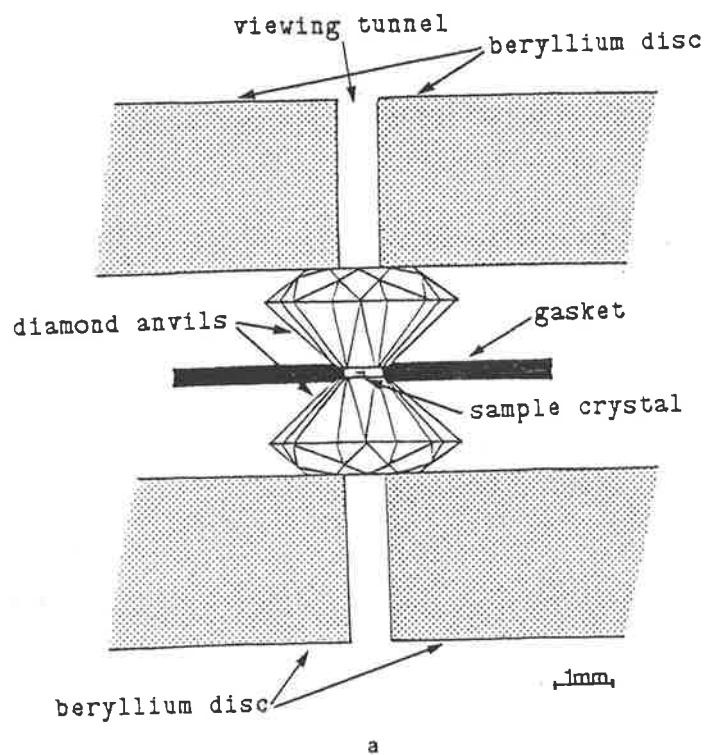


Figure 7.4 Diamond anvil pressure cell showing (a) scaled cross-section of sample chamber and (b) skew view of assembled cell without opposing half.

resembled the original Merrill & Bassett (1974) cell. The cell was fitted onto a Charles Supper goniometer head (Fig. 7.4.b)

The anvils were polished industrial diamonds, each 0.185 carats, with an anvil face diameter of $0.95(\pm 0.05)$ mm. They had to be accurately centred with respect to each other to prevent gasket rupture and with respect to the viewing holes in the beryllium discs to prevent beryllium failure. A small amount of water-soluble wood glue ("Aquadhere") was used to stick the two diamond-anvil faces together. The ensemble was viewed under a binocular microscope and the diamonds were moved to make their faces concentric before the glue dried. One beryllium disc was then glued in place in a steel platen. The diamond ensemble was then centred over the viewing hole in the beryllium disc and glued in place with epoxy resin adhesive ("Araldite"). The whole cell was then assembled, but without tightening the pressure producing screws. Next, the second disc was centred in its recess with respect to the diamonds and then it was glued to its adjacent diamond and metal platen. After the Araldite had set the anvil junction was softened with water and split apart with a thin blade and the cell was ready for use.

The gasket material was Inconel 750X, 0.2mm thick with 0.5mm diameter holes. Phosphor-bronze gaskets, 0.3mm thick with 0.7mm holes were used for the experiments below 7 kbar. Either a 1:4 methanol:ethanol mixture (Piermarini, Forman & Block, 1978) or n-heptane was used as the hydrostatic pressure medium (depending on the solubility of the sample).

7.2.4.3.d Crystal Mounting

The crystals had to be large so that their reflections were distinguishable from the background scatter. The maximum crystal size was limited to .3mm across and .1mm in thickness so that it would not be crushed inside the sample chamber. If the crystal was stuck to the anvil face with silicone grease then it moved when fluid was added. Movement was prevented by gluing one corner of the crystal to the anvil face with a small amount of Araldite. The crystal was oriented by precession photography

and then the goniometer was laid horizontally on the binocular microscope ready for addition of the gasket, fluid, and opposing anvil.

To allow centring of the gasket on the anvil face a supporting turret of silicone grease (High Vacuum, Dow Corning Ltd.) was deposited around the diamond. In order to prevent air bubbles entering the sample chamber the liquid level had to be higher than the top side of the gasket. This was achieved by building a turret of silicone grease on the top side of the gasket. The greased gasket was rested on top of the lower grease turret and prodded down into contact with the lower anvil face and centred. After addition of the liquid from a Pasteur-pipette, the opposing half of the pressure cell was quickly added and secured with a light tightening of the pressure transmitting screws. The diffraction pattern was checked for indications of crystal movement before inducing the transformation.

The pressure was increased by tightening the three pressure transmitting screws by equal, small amounts whilst viewing the crystal for signs of transformation under the binocular microscope. In some cases the gasket split and quickly crept towards the crystal and so the procedure had to be repeated with a new gasket and crystal. After transformation, X-ray diffraction photographs were taken in order to determine the orientation of the product. The cell was too thick to allow optical photography of the crystal on the Reichert microscope and a camera could not be attached to the binocular microscope.

7.3 Scanning Electron Microscope and Electron Microprobe

Before the crystals could be used in either of these two instruments the samples had to be coated with a conductive film to prevent charge accumulation. Samples for the S.E.M. were coated with gold and those for the E.M.P. analyses were coated with carbon. The coating unit used was an Edwards "Speedi-Vac" and the coating was deposited under a 2×10^{-5} mmHg vacuum.

The S.E.M. was on Etec "Autoscan" with a translating, rotating and tilting stage. The electron accelerating voltage was set at 20kV. A camera attachment allowed either

Polaroid or 120mm roll film. A heating stage was constructed by P.K. Schultz from nichrome wire and machineable ceramic. The heater incorporated a chromel-alumel thermocouple and could reach up to 650°C. From calibration it was evident that the precision of the temperature reading was about $\pm 40^\circ\text{C}$.

The E.M.P. was a Jeol "733 Super Probe" and was primarily used for determining chemical analyses but it could also be used as an S.E.M. and a Polaroid camera was attached. The stage could only be translated in two dimensions and could not be tilted. A small vertical adjustment was possible in conjunction with a 400 $\times$ optical microscope for focusing on the specimen surface. The accelerating voltage could be set at 15, 20 or 25kV and the beam current could be set up to 30nA. Both energy dispersive (EDS) and wavelength dispersive (WDS) spectrometers were available. Absorption corrections etc. were applied by software on an attached PDP-11/73 computer. Standard samples were available for most of the commonly encountered elements.

7.4 The CAD4 Diffractometer

The Enraf Nonius "CAD4" was a computer assisted four-circle diffractometer. Movement within the four circles was processed in terms of four angular settings which were linked to the computer. The three angles corresponding to crystal movement were labelled ϕ , κ and ω , where ϕ corresponded to rotation of the goniometer head about its longitudinal axis. The detector's movement in a horizontal plane was described by the fourth angle, θ , and the detected X-ray intensities were transferred to the executing program. The four angles could be set by manual or computer assisted control. The manual control of the first three angles was necessary for centring the crystal with respect to these angular movements. The X-ray source was a Mo fine-focus tube running at 50kV and 20mA and the beam was monochromated by a curved graphite crystal to give Mo-K α radiation ($\lambda = .71073$).

The computer hardware consisted of a PDP-8/a (DEC) central processor with a hard disk, a Kennedy 9-track, 800bpi magnetic tape drive and a Decwriter-II (DEC) hardcopy terminal which acted as the main user interface. The software operating

system was OS8 and the program called CAD4 and its subsidiaries were coded in FORTRAN-IV. The programs allowed for nearly all the necessary manipulations. For example, the systematic searching of reciprocal space for reflections, indexing these reflections and calculating a unit cell, obtaining an ω - θ intensity distribution of a reflection, various vector and matrix calculations and the collection of reflection intensities. The intensities of up to 9000 reflections could be temporarily stored on disk before being transferred to another computer via magnetic tape.

7.4.1 Unit Cell Parameters and Orientation Determination

The procedure for determining a crystal's unit cell parameters and orientation with respect to the diffractometer was often an arduous task depending on the mosaic spread and singularity of the sample. As a preliminary precaution the crystals always had to be examined by microscopy to check for twinning, and by precession photography to check for crystallites and the amount of mosaicity.

The first command to the diffractometer was to search systematically through four separate areas of reciprocal space for 25 reflections and record their setting angles and intensities in a table called "Refdump". The reflections' indices, and the unit cell parameters and orientation could then be obtained by using the command INDEX. Some reflections which did not correspond to integral reciprocal lattice points were automatically suppressed.

If the computed unit cell appeared dubious then one could examine and choose from a list of 10 alternative cells. If the cell dimensions still appeared unsatisfactory then Refdump had to be amended by deleting reflections with exceptionally large scan angles or low intensities, and collecting more reflections from another region of reciprocal space. The command INDEX was then reissued and so on. This improvement process was repeated up to about five times after which an alternative crystal was chosen.

If one was familiar with the unit cell parameters from previous work then there were two more avenues available. Firstly one could use a different mode of the INDEX command for which the cell parameters were a prerequisite. The second approach

was to use the command RAMCEL, which required the input of cell parameters and the indices and setting angles of two reflections. The necessary reflection data were acquired by assigning trial indices to a pair of reflections in Refdump according to their interplanar spacings.

Reflection intensity measurements and thermal expansion studies required precise determination of the crystal orientation and unit cell parameters. A measure of how accurately the cell dimensions and orientation were calculated was given by the standard deviations of the cell parameters and by the angular deviation' between the calculated and measured positions of the reflections in Refdump.

The reflections which yielded more precise cell parameters and orientation were those with large θ values because their relative angular error and background intensity were less. However, the reflections also had to be intense and sharp enough for detection of the correct peak centre. Another upper limit on θ was due to peak broadening resulting from separation of the Mo-K_{α_1} and Mo-K_{α_2} peaks. High angle reflections ($\theta \approx 25^\circ$) with intensities approximately 50 times that of the background were found to be most suitable.

7.4.2 Reflection Intensity Data Collection

One of the most influential parameters for data collection was the period of individual reflection measurement. From a recorded prescan of a reflection the CAD4 calculated the period necessary for the second (and final) scan. The maximum possible measuring time on a second scan was 10 minutes, but was also limited by the needs of other users. Another important parameter was the rotation speed around the ω -axis relative to the speed around the θ -axis. This determined the path through the two-dimensional distribution of the reflection. This ratio was chosen by selecting the longest path through a few representative reflections. The horizontal aperture on the detector and the total omega scan angle were set according to the angular spread of several representative reflections.

The range of reflections to be measured could be selected according to θ limits,

Miller indice limits and systematic absences. For columnar or platelet crystals the data collection could be set to proceed in such a way as to scan with a different unit cell orientation for each reflection measurement, so that absorption effects were minimised. Intensity and orientation checks could be performed at regular intervals during the data collection to correct for crystal decomposition and movement respectively. The information recorded on disk for a data collection was transferred via magnetic tape to the Cyber computer for processing.

7.4.3 The CAD4 Low Temperature Device

Crystals on the CAD4 could be cooled to approximately -140°C by a stream of cold dry nitrogen gas from cooling equipment (Enraf-Nonius) designed specifically for the CAD4. The cold stream was surrounded by a stream of warm dry nitrogen to prevent ice collecting on the crystals. The velocity and temperature of both streams could be adjusted by an electronic control box. Both the cold and warm streams were supplied by heating liquid nitrogen in the same 5 litre Dewar which was automatically refilled from a 75 litre Dewar acting as a reservoir. When the reservoir became empty (after 12 to 36 hours use), it had to be refilled, during which time another Dewar temporarily took its place.

The temperature of the crystal, which was 5mm from the tip of the nozzle, could be altered by varying the production rate, or the temperature, of the cold gas stream. The temperature of the crystal could be measured by a copper-constantan thermocouple situated 2mm inside the cold nozzle and connected to a cold junction and then to a mV meter. The temperature was then calculated from thermocouple tables. For the work on $\text{UO}_2(\text{OH})_2$ (section 2.2.3.2) the reading from the copper-constantan thermocouple was calibrated over the range $-40 \rightarrow 40^{\circ}\text{C}$ by placing a chromel-alumel thermocouple connected to the Trendicator, in place of the crystal. For the work on Phalaborwa vermiculite the cold junction and mV reader were replaced by an Anritsu temperature reader (Anritsu Meter Co. Ltd.).

To overcome some ice formation it was necessary to seal the box containing the

X-ray tube, diffractometer arcs and motors, and to keep this box under a positive pressure of dry nitrogen. Some ice was introduced into the system when refilling the liquid nitrogen reservoir and it subsequently reached the crystal via the warm stream.

7.5 An Interactive Program for Crystal Orientation and Martensitic Transformation Investigations: COATI

7.5.1 Introduction

The function of program COATI was to assist in the experimental study of martensitic transformation characteristics and to facilitate the intelligible comparison between experimental and theoretical data. The orientations of the parent and product lattices could be determined by computer assisted interpretation of the relative spot positions or by transcribing the diffraction patterns into lattice projections. The theoretical data from MRTNST (section 7.6) are expressed as matrices and Miller indices of lattice vectors but these had to be represented in stereographic, morphological and numeric formats for assimilation with the experimental data. The multitude of requisites necessitated considerable latitude, resulting in a general program for orientation and martensitic transformation analysis.

A procedure for orientation evaluation from the locations of two or more diffraction spots on Laue or zero layer reciprocal lattice patterns was formulated. The method most resembled that of Laugier and Filhol (1983). A more integral analysis for transmission electron microscopy was not incorporated as the complexities are still being elucidated (e.g. Sodré Borges (1983)) and a library-comparison approach (Tokiwai et al.(1983)) is plausibly paramount. As a universal reinforcement for orientation determination, the program could generate orthographic, stereographic, gnomonic, Laue and zero layer reciprocal lattice projections of lattice vectors, small circles and latitude-longitude nets with separate lattice and net rotations.

A facility was provided for calculation of habit plane indices from surface trace data and for delineating the plane on a crystal morphology drawing. Theoretical

transformation data could be administered to both the projections and morphology drawings for comparison with the experimental results. Inter-vector angle calculations for more precise correlations could be effected. The method derived by Christian (1965d) for calculating the magnitudes and directions of the principal distortions for the pure lattice distortion was incorporated in COATI.

To facilitate the graphical method of the theoretical (martensitic) calculations (Lieberman, 1958), strain ellipsoids, great circles and vectors with irrational Miller indices could also be projected. Any region of the projection could be enlarged to enhance the veracity of the graphical method and any point on the projection could be indexed. COATI was coded in (ANSI) FORTRAN-77 (Control Data Corporation, 1982 and Digital Equipment Corporation, 1982) on the Cyber and was also successfully run on the Vax. The stipulation records had to begin with a key word ensued by numeric and/or literal data.

Output from program MRTNST (section 7.6) could be read directly by COATI for storage of the transformation matrices. Command sequences could be stored and invoked when for example one required a series of composite plots. In the interactive mode control could be readily alternated between the stored and direct commands.

7.5.2 Bases Used

Bases in the following text will be denoted by a bold-face capital letter; vectors (in lower case) and matrices referred to a particular basis will be appropriately subscripted (e.g. the vector $y_{e\mathbf{x}}$). Three concentric bases were utilized to derive the plotter coordinates of a pretransformation lattice vector. An input vector referred to any of these bases was acceptable thus allowing (for example) more flexible rotations. The foremost basis is that of the unit cell $\mathbf{U}$ (defined by a, b, c, α, β and γ) and the sequel is an orthonormal basis $\mathbf{O}$, as described by Rollett (1965). Directions in $\mathbf{U}$ are referred by pre-multiplication to $\mathbf{O}$ by the matrix $\mathbf{H}$. The fundamental metric tensor is then: $= \mathbf{H}^t \mathbf{H}$, and the unit cell volume is the determinant of $\mathbf{H}$. The matrix for referring a

plane $\underline{f}_U$ by pre-multiplication to $\mathbf{O}$ is $(H^{-1})^t$ and the interplanar spacing is s :

$$s = 1/|(H^{-1})^t \underline{f}_U|.$$

The third basis is the orthonormal plotter basis $\mathbf{P}$. The plotter's software was assumed to have an (x,y) addressable area with basis vectors $\underline{x}||[100]_{\mathbf{P}}$ and $\underline{y}||[010]_{\mathbf{P}}$. Vectors in $\mathbf{O}$ are referred by pre-multiplication to $\mathbf{P}$ by the matrix VI:

$$VI = (\underline{r}_1 \mathbf{O}, \underline{r}_2 \mathbf{O}, \underline{r}_3 \mathbf{O})^{-1},$$

where unit column vectors $\underline{r}_j \mathbf{O}$, ($j = 1 \rightarrow 3$) are parallel to the basis vectors of $\mathbf{P}$. If the elements of VI were not supplied by the user, the view vector, $\underline{r}_3$ was required and $\underline{r}_1$ (unless provided) was reckoned from $\underline{r}_1 = \underline{r}_4 \times \underline{r}_3$ where $\underline{r}_4$ is an axis of $\mathbf{O}$ remote from $\underline{r}_3$. Then $\underline{r}_2$ was calculated by: $\underline{r}_2 = \underline{r}_3 \times \underline{r}_1$ thereby retaining a right-handed system. In case the $\underline{r}_1$ furnished by the user was not perpendicular to $\underline{r}_3$ it was recalculated by: $\underline{r}_1 = \underline{r}_2 \times \underline{r}_3$.

Accumulative rotations could be administered to the unit cell orientation and the renovated orientation matrix is VN: $VN = R_P VI$ where R_P is the rotation matrix. R_P also applied to the morphology drawings but rotations of the net were separate. The turning angles about any pair of axes of $\mathbf{P}$ necessary to align a particular vector with $[001]_{\mathbf{P}}$ could be enumerated.

Up to five transformation matrices could be stored and applied to a projection or morphology drawing. The net and ellipsoid vectors are unaffected. Besides entering the transformation data in matrix form, they could be presented as rotation components or general invariant plane strain factors (Wayman, 1964) in which case the transformation matrix T was assembled in $\mathbf{O}$ and referred to $\mathbf{U}$ by the similarity transformation:

$$T_U = H^{-1} T_O H.$$

In the course of transferring matrices from MRTNST output, either all variants in the file or a particular solution and variant could be selected, but in both instances the stored commands were automatically executed after the processing of a variant. A

lattice correspondence matrix C could be specified for correct indexing of projected lattice vectors after transformation. Directions in the two unit cells are related by:

$$\underline{y}_N = C\underline{y}_U$$

where N is the new basis and the elements of C are disclosed by

$$C(i,j) = \underline{y}_j \cdot \underline{u}(i)$$

in which the column vectors $\underline{y}_j$ ($j = 1 \rightarrow 3$) are axes vectors of U referred to N . Post transformation vectors indexed using C were assigned different symbols on the projection.

7.5.3 Types of Vector Projection

Employment of the linear features of similar triangles for multiple projection types conceded an algorithm requiring less central memory than existing ones (e.g. Preuss (1979)a). Lattice vectors with rational Miller indices in all the seven projection classes listed below could be screened for systematic absences (planes only) and/or for prime triplets.

7.5.3.1 Orthographic, Stereographic and Gnomonic

The plotter plane coordinates (x,y) of the orthographic projection of a unit vector $\underline{y}_P$ which is extended to intersect a sphere concentric with P and of radius r are:

$$x = r\underline{y}_P(1), y = r\underline{y}_P(2).$$

From Fig. 7.5a and the length ratio properties of similar triangles the plotter plane coordinates for stereographic and gnomonic projection types are:

$$x = r\underline{y}_P(1)d'/d, y = r\underline{y}_P(2)d'/d,$$

in which, $d = \sin \phi$ where ϕ is the angle between $\underline{y}_P$ and $[001]_P$. For the stereographic projection: $d' = \tan(\phi/2)$ so that (proof in appendix C):

$$d'/d = 1/(1 + \cos \phi),$$

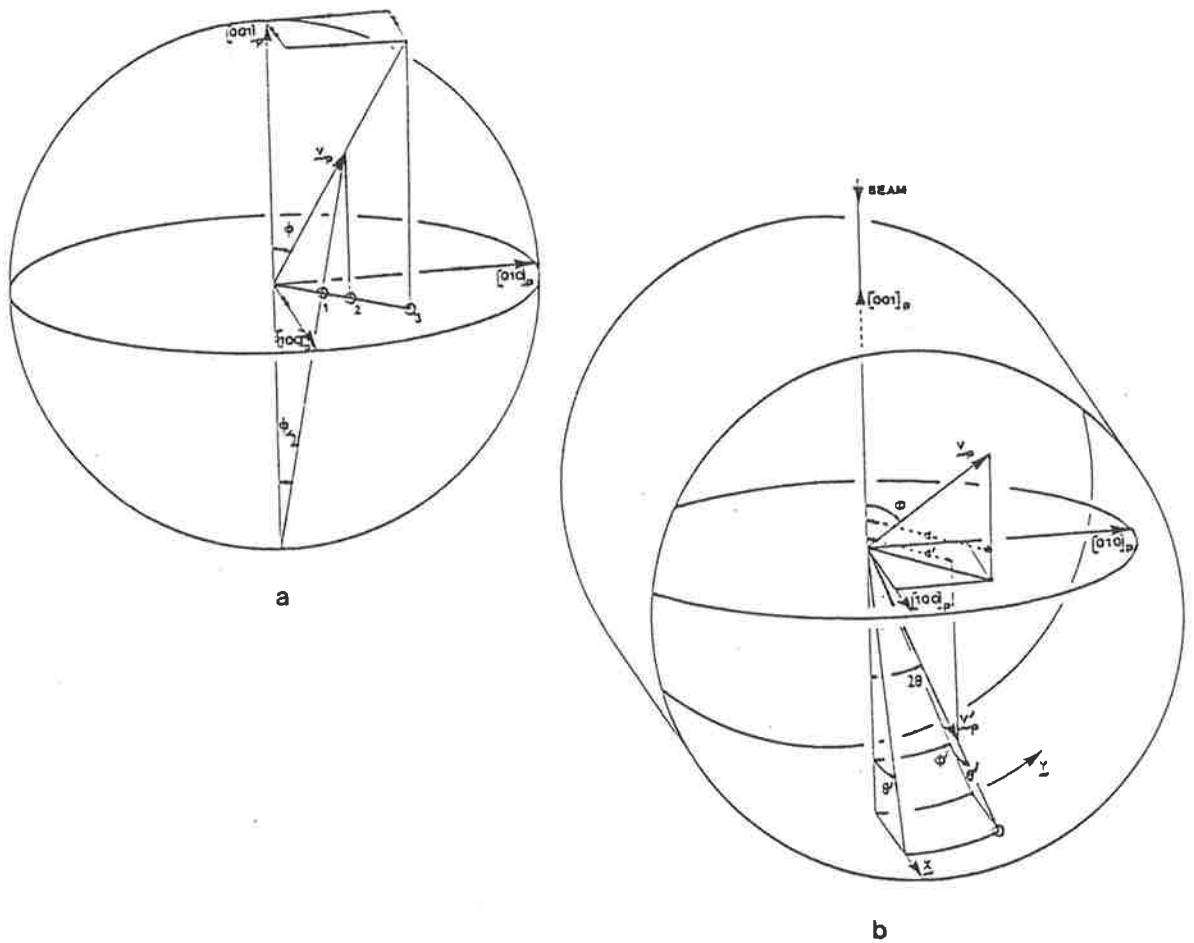


Figure 7.5 (a) Points in the plotter plane of 1. stereographic 2. orthographic and 3. gnomonic projections of y_p . (b) For a cylindrical film Laue photograph the plotter plane may be visualised as curled. The small circle pin-points the diffraction spot.

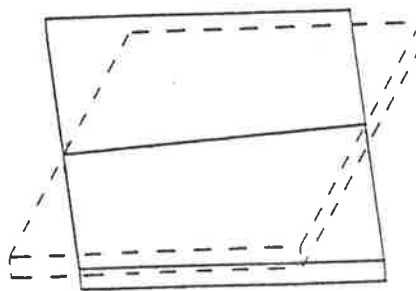


Figure 7.6 Morphology of a β -uranyl hydroxide crystal (full lines) and the product α -uranyl hydroxide crystal (dashed lines) as drawn by COATI. The transformation matrix was obtained from program MRTNST for $(112)[021]$ slip.

but for the gnomonic case: $d' = \tan \phi$, hence:

$$d'/d = 1/\cos \phi.$$

7.5.3.2 Flat Film Laue

Lattice planes registered on all classes of simulated diffraction photographs had to have $\lambda_1 < 2s_{hkl} \sin \theta < \lambda_2$ where $\theta = 90^\circ - \phi$, s_{hkl} is the interplanar spacing and $\lambda_{1,2}$ are the permitted wavelength limits. Also in this context the annotated sphere is tangible because r is the crystal to film distance. The coordinates of the diffracted ray $\underline{y}'_P$ are:

$$\underline{y}'_P(1) = \underline{y}_P(1)d'/d$$

$$\underline{y}'_P(2) = \underline{y}_P(2)d'/d$$

$$\underline{y}'_P(3) = \cos(2\theta),$$

where d is as above and $d' = \sin(2\theta)$. The gnomonic projection of $\underline{y}'_P$ gives its plotter plane coordinates.

7.5.3.3 Cylindrical Film Laue

$\underline{y}'_P$ is invariable with the flat film category. Fig. 7.5.b shows that x is the distance of the spot from a plane containing the x-ray beam and perpendicular to the cylinder axis. y is the shortest arclength to the spot from a line in the film furthestmost from the beam source.

$$x = r \tan(\theta') = r(\tan(\arcsin(\underline{y}'_P(1))))$$

$$y = r\theta^c = r(\arctan(\underline{y}'_P(2)/\underline{y}'_P(3))).$$

For back reflection y must be modified:

$$y = |\pi^c - |y|| (y/|y|)$$

7.5.3.4 Zero Layer Reciprocal Lattice

The approximation that a reciprocal lattice layer, lying perpendicular to the beam, will produce a spot pattern, was adopted from transmission electron microscopy theory (Andrews, Dyson and Keown, 1971) but could also be availed for simulating X-ray zero level precession photographs. The plotter plane coordinates of the diffraction spot are:

$$x = ry_P(1) \tan(2\theta), y = ry_P(2) \tan(2\theta),$$

where θ is procured from Bragg's law for the first order maximum. For the electron microscope case r corresponds to L where $L\lambda$ is the "camera constant".

7.5.4 Laue and Zero Level Reciprocal Lattice Photo Solution

A procedure independent of comparison with nearby orientations (unlike those of Preuss, 1979b and Cornelius, 1981) is that of Ploc (1978) which searches for a set of test-vectors, whose inter-vector angles match those of the n experimental vectors: $ye_{1 \rightarrow nP}$. A swifter approach developed by Riquet and Bonnett (1979) and refined by Laugier and Filhol (1983) includes calculating an orientation matrix from the first two satisfactory test vectors, and this method was incorporated in COATI. Using the inverse of VI the $(n-2)$ test vectors are generated from the $ye_{3 \rightarrow nP}$, approximated to reciprocal lattice vectors, and screened for their angular proximity to the $ye_{3 \rightarrow nP}$. Spot location data from front Laue, back Laue, cylindrical Laue and zero layer reciprocal lattice photographs were admissible.

For each spot, ye_P can be calculated using the simulation equations in reverse, except for the cylindrical film case where:

$$ye'_P(1) = \sin(\arctan(x/r))$$

$$ye'_P(2) = ye'_P(1) \sin(y^c)/x$$

$$ye'_P(3) = ye'_P(1) \cos(y^c)/x.$$

For the test vector yt_1 of the first spot, a range of indices; $h_1 \rightarrow h_2$, $k_1 \rightarrow k_2$, $l_1 \rightarrow l_2$, which represents an asymmetric region in reciprocal space, was required from the user.

The range; $-h_2 \rightarrow h_2$, $-k_2 \rightarrow k_2$, $-l_2 \rightarrow l_2$ is deployed to generate y_{t_2} and as a boundary for the $y_{t_3 \rightarrow n}$. All y_t are screened for systematic absences and for the restriction $s_{i\min} < s_i < s_{i\max}$, where the interplanar spacing confines for the i^{th} spot are evaluated from $\lambda_1, \lambda_2, \theta_i$, Bragg's law and a reserved uncertainty in s . y_{t_2} is selected by its angular proximity to y_{t_1} . VI is derived from y_{t_1O} , y_{t_2O} , y_{e_1P} and y_{e_2P} (International Tables for X-Ray Crystallography, 1974) and employed to refer each $y_{e_3 \rightarrow nP}$ to **O**:

$$y_{e_iO} = VI^{-1}y_{e_iP},$$

and then:

$$y_{e_iU} = H^t y_{e_iO}.$$

y_{e_iU} is divided by its elements j of largest magnitude. A series of test vectors (y_{e_iU}), is generated from y_{e_iU} by successive multiplication by the integers from 1 to the limit for $y_{t_iU}(j)$. The number of test vectors for the i^{th} spot ($i = 3 \rightarrow n$) therefore equals the upper index limit for the j^{th} element. The elements of each y_{t_iU} are rounded off to integers and y_{t_iU} is screened for its angular proximity to y_{e_iP} .

Whenever a suitable set of $y_{t_1 \rightarrow n}$ is acquired, the stored command sequence is executed. Input diffraction spots could be plotted on the simulated photos. The execution durations for some examples are given in Table 7.1

Table 7.1 Comparison of execution times for four crystals each having seven diffraction spots from front-reflection Laue photos. $\Delta\Lambda$ is the angular tolerance in degrees, t the execution time in seconds and N_s the number of solutions found.

Compound	Space group	$(h_1 k_1 l_1 \rightarrow h_2 k_2 l_2)$	$\Delta\Lambda$	N_s	t
TlNO ₃	Pnma	(000) $\rightarrow$ (444)	4	1	90
CsNO ₃	P3 ₁	(00 $\bar{3}$) $\rightarrow$ (333)	4	8	110
β -NiS	R3m	(0 $\bar{3}\bar{2}$) $\rightarrow$ (332)	3	1	11
β -NiS	R3m	(0 $\bar{3}\bar{3}$) $\rightarrow$ (333)	3	1	24
α -UO ₂ (OH) ₂	Cmca	(000) $\rightarrow$ (334)	3	0	18
α -UO ₂ (OH) ₂	Cmca	(000) $\rightarrow$ (446)	3	6	108

For orientation determination the first two diffraction spots selected had to be far apart to enhance the accuracy of VI (Riquet and Bonnet (1979)). Lower indices limits decreased the computation time and consequently the spots should be from the intersection of zone curves (Amorós, Beurger and Canut de Amorós (1975)). To lessen the number of solutions a large number of spots with small angular errors were chosen from sparse areas. Reflections from transformed crystals were more diffuse (e.g. Kennedy and Patterson (1965)) and therefore required greater tolerance in the calculations. This tolerance could be reduced by employing smaller crystals and minimising non-hydrostatic stresses on the crystal during transformation. A problem which required a more discerning choice of spots after transformation was that additional lattice orientations may have arisen due to symmetry equivalent transformations at separate nucleation sites or even due to the mechanisms of other martensite variants.

7.5.5 Circle Drawing

The intersection of a sphere with a cone of half-angle ω and axis $\underline{n}$ is a circle centred around $\underline{n}$. Vectors $\underline{y}_Q$ in the cone are synthesized in an orthonormal basis Q which has $[001]_Q$ parallel to $\underline{n}$. If ρ is the angle between $[100]_Q$ and $\underline{y}_Q$ projected onto $(001)_Q$, then:

$$\underline{y}_Q = (\cos(\rho) \sin(\omega), \sin(\rho) \sin(\omega), \cos(\omega)).$$

The vectors are referred to P by:

$$\underline{y}_P = W \underline{y}_Q$$

where W is a matrix embodying the rotation around $[001]_P \times \underline{n}_P$ necessary to move $[001]_P$ into colinearity with $\underline{n}_P$.

7.5.6 Ellipsoid Drawing

The essential data were the three principal distortions $\eta_{1 \rightarrow 3}$ and the directions $\underline{d}_1, \underline{d}_2$ of η_1 and η_2 , ($\underline{d}_3 = \underline{d}_1 \times \underline{d}_2$). The method of constructing vectors $\underline{y}_i$ in the initial

ellipsoid reflected that of Lieberman, Read and Wechsler (1957) except that the polar coordinates were referred to an orthonormal basis $\mathbf{E}$. Vectors $\mathbf{y}_{f\mathbf{E}}$ in the final ellipsoid are obtained from the initial ones by:

$$\mathbf{y}_{f\mathbf{E}}(j) = \eta_j \mathbf{y}_{i\mathbf{E}}(j), (j = 1 \rightarrow 3).$$

The vectors $\mathbf{y}_{i\mathbf{E}}$ and $\mathbf{y}_{f\mathbf{E}}$ are referred to $\mathbf{O}$ by:

$$\mathbf{y}_{\mathbf{O}} = \mathbf{M} \mathbf{y}_{\mathbf{E}}$$

where: $M(i,j) = d_{j\mathbf{O}}(i)$. The vectors are then referred to $\mathbf{P}$ by VI.

7.5.7 Experimental Interface Plane Calculation

The indices of a fourth vector $\mathbf{y}_4$ situated at established angles to three other vectors ($\mathbf{y}_1, \mathbf{y}_2$ and $\mathbf{y}_3$) can be enumerated from the simultaneous equation:

$$\begin{bmatrix} \mathbf{y}_4(1) \\ \mathbf{y}_4(2) \\ \mathbf{y}_4(3) \end{bmatrix} = \begin{bmatrix} \mathbf{y}_1 \\ \mathbf{y}_2 \\ \mathbf{y}_3 \end{bmatrix}^{-1} \begin{bmatrix} \cos(\mathbf{y}_1 \wedge \mathbf{y}_4) \\ \cos(\mathbf{y}_2 \wedge \mathbf{y}_4) \\ \cos(\mathbf{y}_3 \wedge \mathbf{y}_4) \end{bmatrix}$$

The direction of the surface trace of an interface plane could therefore be derived if the angles it made with two crystal edges were known (the third angle was 90° and was between the face normal and the interface trace). Once two non-parallel directions of traces had been determined, their cross product gave the habit plane.

7.5.8 Morphology Drawings

The Miller indices of each crystal face and their distances from the origin had to be provided. The corresponding distance after transformation is:

$$= \text{previous distance} / |((\mathbf{T}^{-1})^t) \mathbf{O} \cdot \mathbf{f}_{\mathbf{O}}|,$$

where $\mathbf{T}$ is the transformation matrix and $\mathbf{f}_{\mathbf{O}}$ is the plane's unit normal. (Proof given in appendix C). The crystal was delineated by the orthographic projection of edges which were each ascertained by detecting two intersecting planes and checking for two

more planes producing the vertices. The minimum volume crystal was appropriated by verifying that both vertices were on the origin side of all faces in the same hemisphere. If an opaque crystal was stipulated then edges with both adjoining faces pointing below the plotter plane were not drawn. Planes specified as containing the origin were not recognized as faces and only their traces appeared on the drawing. For easy identification of faces after transformation they could be numbered and the edges dashed.

7.5.9 Calculation of Principal Distortion Vectors

In martensitic transformations, where at least one of the unit cell angles of the parent or product lattices is not equal to 90° , the principal distortion vectors in the parent cell are not necessarily parallel to the unit cell axes and maybe along irrational directions. In such cases the distortion vectors are usually not evident from inspection and must be calculated arithmetically.

When the parent cell has orthogonal axes and the product cell has only one angle $\neq 90^\circ$ (or vice-versa) then only one of the principal distortions is parallel to a unit cell axis. Kriven, Fraser & Kennedy (1981) reported a method for calculating the principal distortions in such an instance and applied it to the monoclinic to tetragonal transformation in zirconia (ZrO_2). Their method was derived from the formulation given by Jaeger (1964) for a general linear transformation in two dimensions. However, Jaeger's formulation incorporated a rotation of the principal distortions. Christian (1965c) stated that the lattice deformation in martensitic transformations is a pure strain and gave the following definition of a pure strain:

"...a deformation such that the three orthogonal directions which remain orthogonal retain their directions and senses."

Also the rotation of the distortion vectors is not accounted for in the IPS martensite theory. Hence an alternative to the method of Kriven, Fraser & Kennedy (1981) had to be found. The principal distortion vectors calculated by the latter authors (for ZrO_2) rotated by approximately 0.2° . For larger lattice distortions the rotations would be

more significant.

Hazen & Finger (1982) reported a method for calculating the orthogonal principal distortion vectors for thermal expansion of a general crystal lattice. After testing their method it was found that the calculated distortion vectors rotated during the transformation. Also, if the parent and product lattice parameters were cyclically permuted then different distortion vectors resulted. Using the test example given by Hazen & Finger(1982), after applying a cyclic permutation, the magnitudes of the principal strains differed by 0.3% and their directions differed by 0.4° . These differences were not due to loss of precision in the computer as the calculations were done by the Cyber which stored approximately fourteen decimal digits.

The phenomenological theory of martensitic transformations according to Acton et al (1970) (the CRAB theory) includes an equation relating the pure strain to the lattice parameters of the two cells. However their notation was too difficult to decipher. Crocker (1982) interpreted the CRAB theory in terms of vectors and matrices, but did not translate the equation for the pure strain. Flewitt, Ash & Crocker (1976) referenced the CRAB theory coded in a FORTRAN program. This was obtained by the present author and implemented on the Vax. Unfortunately documentation and code in the program indicated that the parent cell had to be cubic.

Mackenzie & Bowles (1954) gave an equation relating the pure strain (for a martensitic transformation) to the lattice parameters of the parent and product cells. Christian (1965d) expanded their formula to yield a solution for the principal distortion vectors. This method was used by Kelly & Ball (1985) for their work on ZrO_2 and was encoded in program COATI. Initial tests showed that the calculated distortion vectors did not rotate during the distortion. However, in some instances it was noted that an incorrect unit cell for the product lattice was predicted by the principal distortion vectors. Some of these cases could be solved by using the input data for the reverse transformation. Correct results were only obtainable for the more symmetric cases (e.g. hexagonal to cubic) and also depended on the lattice correspondence. Consequently only a partially satisfactory solution was found to the problem of calculating principal

distortion vectors.

7.6 Program MRTNST

Program MRTNST, as mentioned in Chapter 1, was used for performing the phenomenological calculations of martensite crystallography according to the theory of Bowles & MacKenzie (1954). The program was originally written by Ledbetter & Wayman (1971) and was intended to be applicable to all lattice types. For work with non cubic lattices there was the option of supplying a matrix to refer input (and output) vectors and matrices to (and from) an internally used cubic lattice. However the columns of this matrix were individually normalised and so the matrix was essentially redundant except in some cases for cubic lattices. The fact that a correspondence matrix had to be supplied by the user was itself a cumbersome feature. Hence the program was converted by the present author to handle triclinic lattices in a similar way to that done by program COATI. The multiplications applied were as follows:

$$\begin{aligned} \text{On input: directions} & - \underline{d}_O = H \underline{d}_U \\ \text{planes} & - \underline{f}_O = (H^{-1})^t \underline{f}_U \\ \text{On output: directions} & - \underline{d}_U = H^{-1} \underline{d}_O \\ \text{planes} & - \underline{f}_U = H^t \underline{f}_O \\ \text{matrices} & - T_U = H^{-1} T_O H. \end{aligned}$$

The style of the command language for MRTNST was also made the same as that for COATI. No changes were made to the format of the printout.

7.7 Programs for Determination of Crystal Structures

Reflection intensity data from the CAD4 diffractometer had to be corrected for Lorentz and polarization (Lp) effects and for crystal decomposition. These corrections were done by program SUSCAD (Guss, 1979). Absorption corrections were applied by program ABSORB (Guss, 1980). For the more complex crystal shapes, ABSORB was inoperative, although the morphologies were checked by independent means. As

there was no source code available the error could not be corrected. Both SUSCAD and ABSORB were only available on the Cyber.

Program MITHRIL (Gilmore, 1984) was used for structure solution by direct methods. It was only implemented on the Vax as its large storage requirements would have necessitated overlaying on the Cyber.

Program SHELX (Sheldrick, 1976) was used for structure solution by the heavy atom method and for structure refinement. The program is very widely used and consequently its functions will not be further discussed. SHELX was available on both the Cyber and Vax.

During structure solution, when difference electron density peaks were too small or diffuse to be detected by the peak searching routine in SHELX, it was necessary to examine contoured difference maps. Various suitable contouring methods have been reviewed by Diamond(1982). The structure solution package XTAL (Spadaccin, Spackman & Imerito, 1984) can produce the desired type of contour maps. However, at that time, the rigid group refinement part of XTAL was inoperative (Skelton, 1985) and so one would have had to reformat and interchange data frequently between SHELX and XTAL. SHELX84 (Sheldrick, 1984) can also produce the desired maps but the program has not yet been distributed. Consequently it was necessary to construct a contouring procedure.

SHELX could be instructed to print out maps in numerical format at specified intervals along any of the three axes of the unit cell. It was decided to intercept these maps before they were printed and to transcribe their information for input to a contouring algorithm. The contouring program CONTOR (Lilly, 1975) was converted to FORTRAN-77 and applied. It was necessary to write an interface program (SHECON) between SHELX and CONTOR. A feature which allowed one to specify any desired plane in the unit cell was incorporated into SHECON. Data points up to any desired distance from the plane could be projected onto it. The command language for SHECON was designed for easy use and to permit full control over the nature of the maps when necessary. The contouring package was used on both the Cyber and

Vax computers and on the Calcomp and Nicolet-Zeta plotters.

Two computer programs were available for drawing crystal structures. Program PLUTO78 (Motherwell, 1978) was designed for drawing molecular structures, whereas program ORTEP-II (Johnson, 1976) had a wider command language which allowed the drawing of any type of structure. Program ORTEP-II was modified by the author to allow the drawing of planes, such as the faces of silicate tetrahedra, and to allow various types of shading of the atoms. Both programs were implemented by the author on the Cyber and Vax computers and the plots were drawn on the Calcomp, Zeta 1453 and DEC-LVP16 plotters and on a Visual-550 graphics terminal.

CHAPTER 8

Suggestions for Subsequent Experimental Research on Martensitic Transformations

8.1 Introduction

Results from the present work have shown that the nature of transformations which appear potentially martensitic, varies greatly between different compounds. Consequently, if one is to observe trends which can lead to definitive classification and prediction of detailed transformation characteristics, then many more potentially martensitic transformations will have to be examined. Accordingly, preliminary investigations were undertaken on a few other substances and they are briefly discussed in this chapter.

8.2 Ammonium Fluoride (NH_4F) and Cadmium Sulphide (CdS)

The wurtzite→sodium chloride type transformation was studied in MnS and AgI (Chapters 3 and 4) and therefore studying the same structure change in a few more compounds would greatly help to complete the understanding of this seemingly complex transformation. For example, the choice between the A and B mechanisms and the possible lattice orientation relations.

The transformation pressure of NH_4F is 4 kbar (Pistorius, 1976). Wurtzite phase crystals of NH_4F with irregular morphology were obtained from B.D.H. (A.R. grade). They had strong cleavage on $\{1\bar{1}00\}$ and were mounted on this face in the diamond anvil pressure cell. The pressure transmitting fluid was n-heptane and Inconel gaskets were used. The transformation was almost instantaneous and was accompanied by a slight darkening of the previously clear crystals. Unfortunately no diffracted rays from the crystals could be detected. This was most probably due to the low X-ray scattering power of the constituent elements and indicates that analysis by neutron diffraction (e.g. Shil'stein et al., 1983) would be more fruitful.

Wurtzite phase CdS crystals were obtained from Metron Inc. (Allamuchy, N.J., USA) and they were mounted in the diamond anvil pressure cell on their $\{10\bar{1}0\}$ faces. A 1:4 methonal:ethanol mixture was used as the pressure transmitting medium inside Inconel gaskets. The minimum and maximum reported transformation pressures of CdS are 21 and 28 kbar respectively (Kabalkina, Serebrjanaja & Malyushitskaja, 1980). Single crystal experiments have tended to yield the higher pressures which are near the limit of the Merrill-Bassett type cell. Unfortunately the pressure necessary to induce the transformation could not be obtained with the cell used in the present work. The beryllium discs cracked whilst increasing the pressure. High strength "silvered steel" discs were constructed to replace the beryllium discs. The viewing tunnel in the new discs was turned into a cone shaped depression in order to allow a sufficient number of diffracted rays. Further experiments on CdS would most probably be successful. The background intensity on the diffraction pattern was much less with the steel discs than with the beryllium discs and the opportunity for reinvestigation of NH_4F appears promising.

8.3 Ammonium Iodide (NH_4I)

Both a martensitic mode and a mode with a curved interface have been observed in the sodium chloride→caesium chloride type ($\text{B1} \rightarrow \text{B2}$) transformation in NH_4Br (Kennedy et al., 1974). Predictions from the phenomenological theory of martensitic transformations using several different lattice shears were found to agree with the experimental observations (Fraser & Kennedy, 1974). Data on a martensitic mechanism in NH_4I would provide a vital comparison with NH_4Br and metal halides. Very little work has been done on the optical observation of the transformation in NH_4I and so there is much scope for further work. The approximate transformation temperature for NH_4I is -17°C and is complicated by a transformation to a tetragonal phase at -45°C (Hovi, Paavola & Nurmi, 1969).

B1 -phase NH_4I crystals were grown by slow evaporation of an aqueous solution (B.D.H., A.R. grade). The crystals were cooled on the optical microscope using the

second cooler described in section 7.2.2.1. Two transformation modes were observed, both of which involved slow progression of an interface across the crystal without any noticeable shape change. One mode was accompanied by a darkening of the crystal under crossed polars, and by a straighter interface. This most probably indicated the presence of the tetragonal phase. Both slow and fast cooling rates were used without any change in the nature of the transformation. Many crystals supercooled to at least -70°C . The absence of anything resembling a martensitic transformation in NH_4I was probably due to its high plastic deformability.

8.4 Manganese Difluoride (MnF_2)

Numerous transformations of MX_2 type compounds under pressure have been documented by Mingh et al. (1980). The sequence of structure types with increasing pressure is:

rutile $\rightarrow$ "distorted fluorite" $\rightarrow$ post-"distorted fluorite".

However, MnF_2 at STP has the rutile type structure and at 17 kbar transforms to the $\alpha\text{-PbO}_2$ type structure, before changing to the "distorted fluorite" structure (Hazen & Finger, 1981b). The $\alpha\text{-PbO}_2$ structure is maintained upon release to STP.

Hazen & Finger (1981b), upon increasing pressure from STP, reported:

"The single crystal of MnF_2 was observed in the diamond cell to transform from a square (011) plate to a diamond-shaped plate ..."

This indicates that the transformation is most likely martensitic as it is dominated by a lattice distortion. Dacheville & Roy (1960) reported that the transformation could be induced by deformation. Comparison of this transformation with the predictions of phenomenological theory of martensitic transformations would provide an interesting test of its applicability. The orientation relation would show the atomic movements during transformation and thereby serve as a guide to the likely movements in other transformations of the MX_2 compounds. Possible mechanisms have been discussed by Hyde et al. (1972). The rutile structure consists of edge and corner linked MX_6 octahedra and therefore the transformation could also be compared with that in uranyl

hydroxide.

Hazen & Finger (1981b) stated that MnF_2 crystals could be grown by slow evaporation of a solution of manganese dissolved in hydrofluoric acid. This method and several similar ones were tried but without success. Only clear rhombic crystals of MnCO_3 resulted. Through personal communication with R.M.Hazen it was found that his crystal had been grown from the melt. T.Yagi, who supplied that crystal, suggested that I should purchase one, but none were available. Guggenheim (1960) reported a suitable method which required an evacuated platinum capsule. For this method of growth a high temperature furnace (section 7.2.1) was constructed. However, no workshop capable of evacuating and fuse sealing a platinum capsule could be found in Adelaide. Consequently a graphite crucible was constructed following the design of Weinberg & Srinivasan (1974) who used their crucible for growing a single of MnF_2 in an atmosphere of argon. Subsequent experimentation on MnF_2 appears promising.

8.5 Lead Monoxide (PbO)

Lead monoxide undergoes a deformation induced transformation from the massicot (yellow) phase to the litharge (red) phase (Dachille & Roy, 1960). The reverse transformation can be induced by heating to 540°C or by a hydrostatic pressure of 6 kbar (White, Dachille & Roy, 1961). A mechanism of atomic movements was deduced by Söderquist & Dickens (1961) from an orientation relation for the reverse transformation (litharge $\rightarrow$ massicot) at room temperature in metastably grown crystals. This transformation was slow enough to enable separate X-ray diffraction photographs to reveal its progress; whereas the massicot $\rightarrow$ litharge transformation is virtually instantaneous. The possibility of a different mechanism for the forward transformation exists and so an investigation into the massicot $\rightarrow$ litharge transformation was started.

Crystals of massicot were grown from molten PbO by slow cooling ($15^\circ\text{C}/\text{min}$) in a platinum crucible inside a furnace (section 7.2.1). The crystals were $\approx 4\text{mm}$ across and were readily cleaved on $\{001\}$. Transformation to litharge could only be induced by bending the flakes or by denting them with a sharp needle. Crystals used for the

determination of an orientation relation would have to have been reverted to their original shape after bending, which could result in large analysis errors. Completion of the experiment appears infeasible although still desirable.

8.6 Other Compounds of Interest

Some other compounds which warrant further analysis of their possibly martensitic transformations are NaClO_3 , $(\text{CaO})_2\text{SiO}_2$ and KAlF_4 . All these compounds have been subjected to some experimental analysis (Meyer & Rimsky, 1979; Groves, 1983; Launay et al., 1985; respectively^{el}) but the predictions of phenomenological martensite theory have not yet been compared with the experimental observations.

Appendix A

Observed (F_o) and Calculated (F_c) Structure Factors for $RbNO_3$ -IV and $CsNO_3$ -II

A.1 $RbNO_3$ -IV

H	K	L	LOFD	LOFC	H	K	L	LOFD	LOFC	H	K	L	LOFD	LOFC	H	K	L	LOFD	LOFC	H	K	L	LOFD	LOFC
-1	1	-3	297	299	1	2	-6	337	326	-4	4	-5	152	162	-7	5	-4	1007	1024	2	4	-1	629	617
0	1	-3	227	227	-5	3	-6	258	279	0	4	-5	147	140	-5	5	-4	203	209	-9	5	-3	271	264
1	1	-3	412	385	-4	3	-6	213	206	1	4	-5	317	333	0	5	-4	255	240	-7	5	-3	191	205
-3	2	-8	278	282	-3	3	-6	754	792	2	4	-5	162	159	2	5	-4	978	1009	-6	5	-3	299	312
-2	2	-8	266	269	0	3	-6	761	771	4	4	-5	610	569	3	5	-4	662	681	-5	5	-3	207	221
0	2	-8	126	126	1	3	-6	250	242	-3	5	-5	193	207	-10	5	-4	298	291	0	5	-3	241	236
1	2	-3	231	223	2	3	-6	233	232	-5	5	-5	194	205	-3	6	-4	103	112	1	5	-3	282	268
-5	3	-9	270	276	3	3	-6	761	740	0	5	-4	226	216	-4	6	-4	196	203	2	5	-3	190	194
-4	3	-9	187	191	-7	4	-6	260	258	3	5	-5	241	241	-7	6	-4	134	139	4	5	-3	225	234
1	3	-8	218	225	-6	4	-6	347	356	-10	6	-5	145	154	1	6	-4	154	146	5	5	-3	115	106
2	3	-3	244	220	-4	4	-6	135	135	-4	6	-5	252	256	2	6	-4	206	206	-3	6	-3	801	782
-5	4	-4	114	114	0	4	-6	117	114	-4	6	-5	201	203	4	6	-4	123	114	-6	6	-3	1054	1048
-4	4	-4	193	190	2	4	-6	433	415	2	6	-5	255	242	-10	7	-4	100	105	0	6	-3	1095	1080
1	4	-3	127	105	3	4	-6	243	227	3	6	-5	152	154	-7	7	-4	362	330	3	6	-3	420	400
-1	1	-7	202	207	-4	5	-6	275	287	-8	7	-5	570	554	0	7	-4	323	315	-4	7	-3	232	238
0	1	-7	195	207	-6	5	-6	335	351	1	7	-5	626	605	3	7	-4	247	257	0	7	-3	34	46
-2	2	-7	207	208	0	5	-6	250	239	0	8	-5	234	236	-10	8	-4	521	553	2	7	-3	260	266
0	2	-7	223	210	1	5	-6	278	281	-1	1	-6	405	405	2	8	-4	339	323	-10	8	-3	144	137
2	2	-7	577	565	3	5	-6	133	131	0	1	-6	357	336	1	9	-4	227	227	-9	8	-3	210	224
-4	3	-7	169	172	4	5	-6	242	243	1	1	-6	108	119	0	0	-3	2063	2105	1	8	-3	172	181
1	3	-7	207	190	-6	6	-6	622	623	-3	2	-6	231	233	-1	1	-3	127	117	-9	4	-3	560	594
-3	4	-7	135	112	0	6	-6	613	589	-2	2	-6	326	318	0	1	-3	144	148	0	9	-3	733	599
-4	4	-7	225	233	-7	7	-6	229	231	0	2	-6	169	154	-3	2	-3	305	306	-1	1	-2	131	128
0	4	-7	226	215	0	7	-6	225	210	1	2	-6	192	192	-2	2	-3	125	127	0	1	-2	108	103
-7	5	-7	410	376	-1	1	-5	244	248	2	2	-6	1418	1435	0	2	-3	143	124	1	1	-2	2511	2520
-5	5	-7	189	137	0	1	-5	254	254	-5	3	-6	243	227	1	2	-3	134	144	-3	2	-2	323	326
0	5	-7	210	204	1	1	-5	1310	1343	-4	3	-6	340	326	-3	3	-3	256	287	-2	2	-2	522	511
2	5	-7	414	386	-3	2	-5	297	297	-3	1	-6	203	203	-3	1	-3	1496	1586	0	2	-2	398	335
0	6	-7	138	113	-2	2	-5	358	376	0	3	-6	225	220	0	1	-3	1535	1560	1	2	-2	332	310
1	6	-7	177	182	0	2	-5	162	163	1	3	-6	415	424	2	3	-3	242	243	2	2	-2	322	343
0	0	-6	782	798	1	2	-5	263	251	2	3	-6	230	232	3	3	-3	1167	1180	-5	3	-2	251	277
-1	1	-6	291	316	-5	3	-5	276	254	3	3	-6	254	263	-6	4	-3	410	418	-3	3	-2	516	515
0	1	-6	263	263	1	3	-5	181	172	-7	4	-6	374	375	-3	4	-3	133	123	0	3	-2	554	594
-3	2	-6	181	408	2	3	-5	275	284	-4	4	-6	495	491	-4	4	-3	223	216	1	3	-2	129	144
-2	2	-6	128	313	-6	4	-5	128	129	0	4	-6	409	424	0	4	-3	225	226	2	3	-2	291	280
0	2	-6	396	389	-5	4	-5	809	813	3	4	-6	334	330	1	4	-3	164	166	3	3	-2	144	147
-6	4	-2	177	164	-7	4	-1	352	328	-2	3	0	181	173	6	6	0	623	622	0	2	1	110	117
-5	4	-2	1535	1598	-6	4	-1	161	149	-1	3	0	186	188	-12	7	0	173	177	2	2	1	424	423
1	4	-2	1604	1635	-5	4	-1	342	333	0	3	0	2728	2709	-9	7	0	191	201	-5	3	1	176	171
2	4	-2	172	170	-4	4	-1	468	456	1	3	0	227	210	-5	7	0	225	215	-4	3	1	411	417
4	4	-2	1056	1065	0	4	-1	474	460	2	3	0	164	156	-2	7	0	191	182	-3	3	1	184	174
-8	5	-2	241	238	1	4	-1	315	297	3	3	0	1613	1641	2	7	0	200	215	-2	3	1	161	175
-5	5	-2	270	281	2	4	-1	138	144	-6	4	0	287	303	5	7	0	179	185	-1	3	1	177	170
-5	5	-2	270	281	2	4	-1	132	313	-5	4	0	170	170	-12	8	0	172	191	0	3	1	223	232
0	5	-2	267	279	-3	4	-1	1332	1543	-3	4	0	237	220	-10	8	0	120	105	1	3	1	399	380
3	5	-2	287	293	-7	5	-1	213	226	-2	4	0	327	340	-9	8	0	188	204	2	3	1	205	205
-11	6	-2	370	344	1	5	-1	254	250	-1	4	0	203	184	-6	8	0	171	167	-7	4	1	247	250
-6	6	-2	185	196	2	5	-1	1565	1514	1	4	0	171	178	-5	8	0	95	108	-6	4	1	263	263
0	6	-2	180	160	5	5	-1	819	807	2	4	0	302	284	1	8	0	200	217	-5	4	1	1994	1651
2	6	-2	393	360	-10	6	-1	252	235	-9	5	0	206	202	4	8	0	186	177	-4	4	1	466	467
5	6	-2	278	262	-7	6	-1	284	286	-8	5	0	100	106	-10	9	0	175	182	-3	4	1	242	242
-11	7	-2	737	773	1	6	-1	277	279	-7	5	0	184	170	-9	9	0	988	1005	-2	4	1	2259	2096
-8	7	-2	1007	1052	4	6	-1	247	247	-4	5	0	181	176	-8	9	0	186	194	-1	4	1	247	238
1	7	-2	1056	1059	-10	7	-1	212	218	-3	5	0	164	162	-7	9	0	211	204	0	4	1	489	458
6	7	-2	779	752	-7	7	-1	251	256	-2	5	0	160	155	-6	9	0	1125	1110	1	4	1	1643	1616
-11	8	-2	224	249	0	7	-1	237	226	-1	5	0	174	175	-5	9	0	202	197	2	4	1	248	240
-8	8	-2	283	277	3	7	-1	199	189	2	5	0	212	221	-4	9	0	204	205	3	4	1	281	283
0	8	-2	314	295	-10	8	-1	668	671	4	5	0	215	222	-3	9	0	1183	1113	4	4	1	1095	1117
1	8	-2	127	116	-9	8	-1	143	144	5	5	0	156	163	-2	9	0	209	199	-8	5	1	194	190
3	8	-2	273	252	-8	8	-1	161	192	-11	6	0	152	145	-1	9	0	231	210	-6	5	1	161	150
-11	9	-2	230	256	0	8	-1	165	154	-10	6	0	118	146	0	9	0	1037	1013	-5	5	1	110	113
2	9	-2	252	237	1	8	-1	166	165	-9	6	0	1105	1104	2	9	0	164	172	-4	5	1	314	295
1	1	-1	155	160	2	8	-1	669	673	-7	6	0	146	149	-8	10	0	132	120	-1	5	1	340	332
-3	2	-1	170	166	-9	9	-1	111	90	-6	6	0	1496	1544	-6	</								

M	K	L	10FO	10FC	M	K	L	10FO	10FC	M	K	L	10FO	10FC	M	K	L	10FO	10FC	M	K	L	10FO	10FC	M	K	L	10FO	10FC
2	6	1	260	259	0	1	2	331	320	4	5	2	201	207	-7	11	2	750	760	-3	5	3	245	242	-6	9	3	787	791
-11	7	1	694	709	-3	2	2	173	181	5	5	2	634	635	-6	11	2	265	257	-2	5	3	279	285	-5	9	3	246	250
-9	7	1	137	152	-2	2	2	540	537	-11	6	2	182	195	-5	11	2	280	284	-1	5	3	151	142	-4	9	3	282	267
-8	7	1	963	978	-1	2	2	2787	2603	-8	5	2	235	236	-4	11	2	771	755	0	5	3	206	203	-3	9	3	923	798
-7	7	1	246	256	0	2	2	531	511	-6	6	2	176	179	-3	11	2	291	238	1	5	3	172	163	-2	9	3	259	252
-6	7	1	289	287	2	2	2	2445	2485	-4	6	2	176	170	-2	11	2	243	252	2	5	3	168	173	-1	9	3	220	211
-5	7	1	1545	1543	-5	3	2	245	255	-3	6	2	137	150	0	0	3	2102	2128	3	5	3	154	168	0	9	3	714	701
-4	7	1	322	333	-4	3	2	176	180	-2	6	2	181	170	-1	1	3	128	132	3	5	3	114	129	-1	1	4	163	164
-3	7	1	357	319	-3	3	2	519	556	0	6	2	182	187	0	1	3	137	132	5	5	3	144	149	0	1	4	331	356
-2	7	1	1594	1524	-2	3	2	328	311	1	6	2	105	110	1	1	3	500	501	-11	6	3	165	176	-3	2	4	294	307
-1	7	1	292	293	-1	3	2	342	325	2	6	2	233	225	-2	2	3	337	341	-9	6	3	748	773	-2	2	4	323	316
0	7	1	249	234	0	3	2	540	511	3	6	2	138	52	-1	2	3	103	107	-8	6	3	222	225	1	3	4	218	200
1	7	1	952	936	1	3	2	159	161	4	6	2	120	133	0	2	3	333	314	-7	6	3	203	211	0	3	4	214	200
2	7	1	142	151	2	3	2	252	254	5	6	2	186	190	1	2	3	100	106	-6	6	3	1066	1092	1	3	4	397	386
3	7	1	697	692	3	3	2	286	288	-9	7	2	159	191	-5	3	3	240	240	-5	6	3	293	299	-4	3	4	146	148
-11	8	1	157	118	-6	4	2	156	157	-1	7	2	166	166	-4	3	3	275	285	-4	6	3	434	432	-3	3	4	1398	1392
-8	8	1	160	167	-5	4	2	168	178	2	7	2	171	161	-3	3	3	1535	1593	-3	6	3	422	412	-2	3	4	160	157
-5	8	1	160	157	-3	4	2	125	116	-11	8	2	215	226	-2	3	3	341	323	-2	6	3	314	292	-1	3	4	167	167
-3	8	1	167	167	-2	4	2	349	338	-10	8	2	756	747	-1	3	3	350	335	-1	6	3	1095	1102	0	3	4	206	204
0	8	1	162	175	-1	4	2	126	123	-9	8	2	262	264	0	3	3	1565	1600	0	6	3	243	237	1	3	4	172	150
-11	9	1	172	150	0	4	2	92	100	-8	8	2	288	305	1	3	3	274	282	1	6	3	206	204	2	3	4	146	82
-9	9	1	146	82	1	4	2	148	149	-7	8	2	1027	1050	2	3	3	258	251	2	6	3	243	237	3	3	4	1510	516
-11	10	1	510	516	4	4	2	164	162	-6	8	2	341	337	3	3	3	875	926	3	6	3	767	768	-5	4	4	171	148
-10	10	1	171	148	-9	5	2	172	171	-5	8	2	277	269	-6	4	3	120	154	5	6	3	176	181	-4	4	4	160	165
-9	10	1	160	165	-8	5	2	316	319	-4	8	2	1056	1061	-5	4	3	185	179	-8	7	3	179	177	-5	4	4	160	165
-8	10	1	657	671	-7	5	2	1516	1552	-3	8	2	248	239	-4	4	3	218	228	-7	7	3	92	80	-4	4	4	160	165
-7	10	1	201	216	-6	5	2	257	254	-2	8	2	396	367	0	4	3	223	217	-5	7	3	202	196	-3	7	3	143	128
-6	10	1	256	264	-5	5	2	275	279	-1	8	2	1076	1056	1	4	3	210	207	-3	7	3	202	207	-2	7	3	172	177
-5	10	1	823	815	-4	5	2	1662	1611	0	8	2	280	267	3	4	3	90	55	-2	7	3	122	98	-1	7	3	168	142
-4	10	1	236	239	-3	5	2	277	265	1	8	2	297	300	4	4	3	133	112	1	7	3	172	177	-9	5	3	149	104
-3	10	1	220	209	-2	5	2	303	295	2	8	2	782	771	-9	5	3	134	208	-8	5	3	187	180	-7	5	3	152	111
-2	10	1	705	681	-1	5	2	1643	1613	3	8	2	205	201	-8	5	3	152	111	-10	6	3	710	695	-6	5	3	140	130
-1	10	1	172	160	0	5	2	262	264	-5	9	2	108	116	-7	5	3	152	111	-10	6	3	188	196	-5	5	3	259	254
0	10	1	167	164	1	5	2	250	256	-2	10	2	109	84	-6	5	3	140	130	-8	9	3	266	262	-4	5	3	161	157
1	10	1	529	512	2	5	2	1565	1563	-9	11	2	209	231	-5	5	3	259	254	-7	9	3	266	262	-4	5	3	161	157
-1	1	2	307	311	3	5	2	295	304	-8	11	2	743	252	-4	5	3	161	157										
-6	9	3	787	791	4	4	4	975	963	-6	8	4	216	207	-4	4	5	146	136	-6	8	5	235	239	-4	4	5	146	136
-5	9	3	246	250	-9	5	4	318	322	-3	8	4	126	137	-3	4	5	179	179	-4	8	5	573	580	-3	4	5	179	179
-4	9	3	282	267	-8	5	4	140	148	-2	8	4	209	200	-1	4	5	168	176	-3	8	5	232	224	-1	4	5	168	176
-3	9	3	923	798	-6	5	4	332	328	0	8	4	142	80	0	4	5	142	170	-2	8	5	261	264	0	4	5	142	170
-2	9	3	259	252	-5	5	4	235	233	1	8	4	189	180	2	4	5	175	188	-1	8	5	595	605	2	4	5	175	188
-1	9	3	220	211	-3	5	4	219	221	-7	9	4	134	124	3	4	5	154	129	0	8	5	185	191	3	4	5	154	129
0	9	3	714	701	-2	5	4	247	236	-6	9	4	117	97	4	4	5	238	228	1	8	5	231	228	4	4	5	238	228
1	9	3	163	164	0	5	4	216	214	0	9	4	144	82	-9	5	5	165	181	-8	9	5	88	53	-8	5	5	165	181
-1	1	4	331	356	1	5	4	360	353	-9	10	4	220	238	-8	5	5	140	141	-3	9	5	154	154	-8	5	5	140	141
0	1	4	397	386	3	5	4	140	85	-8	10	4	518	540	-7	5	5	735	721	0	0	6	780	796	-7	5	5	735	721
1	1	4	1330	1393	4	5	4	340	321	-7	10	4	250	259	-6	5	5	205	206	-1	1	6	767	270	-6	5	5	205	206
-3	2	4	274	283	-10	6	4	155	149	-6	10	4	329	319	-5	5	5	210	231	0	1	6	298	307	-5	5	5	210	231
-2	2	4	364	360	-7	6	4	172	169	-5	10	4	648	677	-4	5	5	786	839	-3	2	6	254	256	-4	5	5	786	839
-1	2	4	318	319	-6	6	4	137	145	-4	10	4	281	278	-3	5	5	255	263	-2	2	6	369	383	-3	5	5	255	263
0	2	4	323	316	-3	6	4	256	263	-3	10	4	296	299	-2	5	5	277	289	0	2	6	335	319	-2	5	5	277	289
1	2	4	318	307	-2	6	4	137	141	-2	10	4	542	534	-1	5	5	817	837	1	2	6	301	294	-1	5	5	817	837
2	2	4	294	307	0	6	4	153	148	-1	10	4	209	218	0	5	5	194	203	0	5	6	297	291	0	5	5	194	203
-5	3	4	201	201	1	6	4	157	166	-1	1	5	240	247															

A.2 CsNO₃-II

H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC
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0	1	-8	500	484	0	5	-7	235	225	-8	6	-6	264	260	0	5	-5	300	318	-7	4	-4	318	116
-3	2	-8	287	297	1	5	-7	243	242	-7	6	-6	483	479	1	5	-5	379	372	-6	4	-4	610	610
-2	2	-8	549	537	2	5	-7	124	116	-6	6	-6	1192	1143	2	5	-5	1314	1330	-5	4	-4	2259	2215
0	2	-8	332	342	-7	6	-7	334	297	0	6	-6	1140	1138	3	5	-5	193	180	-4	4	-4	455	436
1	2	-8	491	485	-6	6	-7	75	35	1	6	-6	357	363	4	5	-5	383	348	0	4	-4	661	663
2	2	-8	826	929	1	6	-7	191	199	2	6	-6	424	421	5	5	-5	861	811	1	4	-4	2193	2216
-3	3	-8	279	282	0	0	-6	1609	1568	1	6	-6	870	835	-10	6	-5	157	138	2	4	-4	501	478
-4	3	-8	104	208	-1	1	-6	311	306	-6	7	-6	123	140	-8	5	-5	153	140	3	4	-4	493	474
1	3	-8	191	179	0	1	-6	482	463	-7	7	-6	220	200	-7	6	-5	136	155	-9	5	-6	363	333
2	3	-8	191	390	-3	2	-6	291	271	0	7	-6	287	287	-6	6	-5	199	201	-8	5	-6	216	200
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2	3	-3	455	454	-9	8	-3	105	93	0	5	-2	309	317	1	2	-1	95	99	-7	7	-1	287	240
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0	5	-3</																						

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2	2	0	216	231	2	7	0	249	231	-7	5	1	2224	2261	-1	1	2	453	454	-11	7	2	1168	1132
-2	3	0	164	162	5	7	0	218	210	-6	5	1	254	261	0	1	2	337	347	-9	7	2	177	134
-4	3	0	171	164	-17	8	0	234	252	-5	5	1	141	143	1	1	2	4245	3537	-8	7	2	1655	1655
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0	3	0	3557	3593	-9	8	0	242	275	1	5	1	303	271	-2	2	2	604	596	2	7	2	162	168
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1	4	3	163	175	0	2	4	562	545	-9	7	4	140	113	-7	5	5	95	58	2	3	6	241	234
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-6	5	3	438	427	2	3	4	316	319	-8	8	4	134	124	-9	6	5	158	139					

Appendix B

Observed (F_o) and Calculated (F_c) Structure Factors for anilinium-vermiculite

B.1 Phalaborwa

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
2	-2	20	9	16	3	-3	-17	84	61	1	5	-18	12	13	0	8	-15	10	13	1	-9	-13	47	41
2	0	-20	28	47	2	-2	-17	18	21	3	5	-18	7	8	2	8	-16	13	11	3	-9	-13	64	44
1	1	-20	14	7	4	-2	-17	17	15	0	8	-16	69	66	1	-9	-14	30	25	0	8	-13	25	22
2	2	-20	11	16	3	-1	-17	6	9	2	6	-18	14	17	0	8	-14	18	17	2	-8	-13	16	14
1	-5	-19	13	10	2	0	-17	21	26	0	8	-16	19	17	2	-8	-14	11	14	4	-8	-13	20	20
0	-4	-19	7	10	3	1	-17	9	10	2	-8	-16	10	12	3	-7	-14	13	12	1	-7	-13	9	10
2	-4	-19	12	7	2	2	-17	20	24	2	-8	-16	10	12	4	-8	-14	48	39	2	-8	-13	12	12
0	-2	-19	12	13	4	2	-17	11	13	3	-7	-16	10	12	1	-5	-14	12	14	4	-6	-13	29	24
0	0	-19	18	30	3	3	-17	86	64	2	-6	-16	41	34	5	-6	-14	14	14	1	-5	-13	11	16
3	1	-19	9	9	0	4	-17	7	7	4	-6	-16	28	25	5	-6	-14	14	14	3	-5	-13	15	18
2	2	-19	9	14	2	4	-17	9	10	1	-5	-16	9	13	2	-4	-14	10	8	5	-5	-13	19	16
0	4	-19	8	10	4	4	-17	16	16	3	-5	-16	6	7	4	-4	-14	24	28	0	-4	-13	35	31
2	4	-19	9	5	1	5	-17	9	7	2	-4	-16	12	15	2	-2	-14	19	20	2	-4	-13	12	14
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1	-5	-18	8	14	2	6	-17	10	10	6	-3	-16	27	24	4	-2	-14	10	14	1	-3	-13	73	87
0	-4	-18	18	22	1	7	-17	10	9	2	-2	-16	28	26	5	-1	-14	14	10	3	-3	-13	57	57
2	-4	-18	8	15	0	8	-16	12	15	4	-2	-16	8	11	2	0	-14	41	51	6	-3	-13	7	14
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4	-2	-18	24	9	2	-6	-16	22	30	5	-1	-16	13	7	5	-1	-14	12	12	4	-2	-13	9	12
3	-1	-18	7	4	1	-5	-16	8	12	2	0	-16	59	62	0	2	-14	17	17	6	-2	-13	23	18
2	0	-18	8	15	0	-4	-16	15	21	4	0	-16	22	33	4	2	-14	10	15	1	-1	-13	8	12
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2	2	-18	17	13	5	-3	-16	41	43	3	3	-16	28	27	2	4	-14	24	25	4	0	-13	23	19
4	2	-18	11	5	0	-2	-16	7	10	5	3	-16	35	24	1	4	-14	24	25	6	0	-13	78	64
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[illegible]

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B.2 Young River

b	k	l	Fo	Fc	b	k	l	Fo	Fc	b	k	l	Fo	Fc	b	k	l	Fo	Fc	b	k	l	Fo	Fc	b	k	l	Fo	Fc
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B.3 Llano

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Appendix C

Mathematical derivations for program COATI**C.1 Trigonometry for Stereographic Projection**

Have to prove that:

$$\tan(\phi/2)/\sin(\phi) = 1/(1 + \cos \phi).$$

Expanding $\tan(\phi/2)$ the L.H.S. becomes:

$$= \sin(\phi/2)/(\cos(\phi/2) \sin(\phi))$$

expand $(\phi/2)$ terms to $\cos \phi$:

$$= \left(\frac{1}{2}(1 - \cos \phi)\right)^{\frac{1}{2}} / \left(\left(\frac{1}{2}(1 + \cos \phi)\right)^{\frac{1}{2}} \sin \phi\right)$$

multiply by $(1 + \cos \phi)^{\frac{1}{2}}(1 + \cos \phi)^{-\frac{1}{2}}$:

$$= (((1 - \cos \phi)(1 + \cos \phi))/((1 + \cos \phi)(1 + \cos \phi)))^{\frac{1}{2}} (1/\sin \phi)$$

$$= (1 - \cos^2 \phi)^{\frac{1}{2}} / ((1 + \cos \phi) \sin \phi)$$

$$= \sin \phi / ((1 + \cos \phi) \sin \phi)$$

$$= 1/(1 + \cos \phi),$$

which equals the R.H.S.

C.2 Crystal Size after Transformation

The following derivation of the distance from the origin to a crystal face after transformation is done in an orthonormal basis for clarity. A point $\underline{d}$ in a plane with normal $\underline{f}$ is chosen such that $\underline{d}$ is colinear with $\underline{f}$. If the equation of the plane is: $\underline{f}^t \cdot \underline{d} = s^2$ then the unit normal of the plane is $\underline{f}_n$, where $\underline{f} = s \underline{f}_n$. After transformation the distance to the origin is s' , $\underline{f}$ becomes $\underline{f}'$ and $\underline{d}$ is transformed to $\underline{d}'$ by the transformation matrix T .

From Fig. 4 the face to origin distance after transformation is:

$$s' = |\underline{d}'| \cos \psi$$

expanding the dot product:

$$= |\underline{d}'| (\underline{f}'^t \cdot \underline{d}') / (|\underline{f}'| |\underline{d}'|)$$

in terms of the pre-transformation vectors:

$$\begin{aligned} &= (((T^{-1})^t \underline{f})^t \cdot (T \underline{d})) / |(T^{-1})^t \underline{f}| \\ &= (\underline{f}^t T^{-1} T \underline{d}) / |(T^{-1})^t \underline{f}| \\ &= (\underline{f}^t \cdot \underline{d}) / (s |(T^{-1})^t \underline{f}_n|) \end{aligned}$$

using equation of the plane:

$$\begin{aligned} &= s^2 / (s |(T^{-1})^t \underline{f}_n|) \\ &= s / (|(T^{-1})^t \underline{f}_n|) \end{aligned}$$

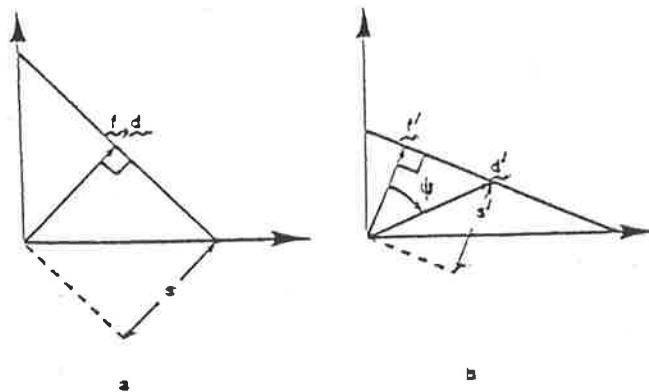


Figure. (a) The crystal surface with normal $\underline{f}$ and containing the point $\underline{d}$ becomes (b) $\underline{f}'$ after transformation.

Appendix D

Scientific Papers

Listed below, in chronological order, are the scientific papers corresponding to work done during the course of my candidature for the degree of Doctor of Philosophy. My contribution to the work on metal complexes (Bruce et al., 1985, 1986; Sargeson, 1986) involved solving and refining the crystal structures of $[\text{Ru}\{\text{C}=\text{CPh}(\text{C}_7\text{H}_7)\}(\text{DPPE})(\eta\text{-C}_5\text{H}_5)][\text{PF}_6].0.63\text{CH}_2\text{Cl}_2$ and $[\text{Mn}\{\text{sar}\}][\text{SO}_3\text{CF}_3]_3$. Photocopies of those papers which have been printed are also provided.

Dean, C., Hambley, T.W. & Snow, M.R. (1984). *Acta Cryst.* **C40**, 1512–1515.

“Structure of Phase-IV Rubidium Nitrate, RbNO_3 , and Phase-II Caesium Nitrate, CsNO_3 ”.

Dean, C. (1985). *J. Appl. Cryst.* **18**, 159–164.

“An Interactive Program for Crystal Orientation and Martensitic Transformation Investigations: COATI”.

Kennedy, S.W. & Dean, C. (1985). Soc. Cryst. Aust. Crystal XV Conf., Adelaide, South Aust.

“Transformation Mechanisms in $\text{UO}_2(\text{OH})_2$, MnS and AgI ”.

Bruce, M.I., Dean, C., Duffy, D.N., Humphrey, M.G. & Koutsantonis, G.A. (1985). *J. Organomet. Chem.*, **295**, C40–c44.

“Reactions of Transition Metal σ -Acetylide Complexes III. Synthesis of Some Aryl-diazovinylidene and Cycloheptatrienylvinylidene Complexes. X-ray Structures of $[\text{Ru}(\text{C}=\text{CPhN}=\text{NC}_6\text{H}_3\text{Me}_2\text{-3,4})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4].0.67\text{CH}_2\text{Cl}_2$ and $[\text{Ru}\{\text{C}=\text{CPh}(\text{C}_7\text{H}_7)\}(\text{DPPE})(\eta\text{-C}_5\text{H}_5)][\text{PF}_6].0.63\text{CH}_2\text{Cl}_2$ ”.

Bruce, M.I., Dean, C., Duffy, D.N., Humphrey, M.G., Koutsantonis, G.A. & Nicholson, B.K. (1985). Inorg. Chem. Aust. Conf., Melbourne Univ., Aust.

"Electrophilic Addition to σ -Acetylide Complexes: Synthesis and Structure of Some Aryldiazo-cycloheptatrienyl-, and Halo-vinylidene Complexes".

Dean, C. & Kennedy, S.W. (1986). In Preparation.

"Martensitic Analysis of the $\beta \rightarrow \alpha$ Transformation in Uranyl Hydroxide ($\text{UO}_2(\text{OH})_2$)".

Slade, P.G., Dean, C., Schultz, P.K. & Self, P.G. (1986). In Preparation.

"The Crystal Structure of an Anilinium-Vermiculite Intercalate".

Dean, C. & Kennedy, S.W. (1986). In Preparation.

"Structural Phase Transformations in AgI Under Hydrostatic Pressure".

Kennedy, S.W. & Dean, C. (1986). In Preparation.

"The B4 $\rightarrow$ B1 Transformation in Manganese Sulphide (MnS)".

Sargeson, A.M., Snow, M.R., Dean, C. & Horn, E. (1986). In Preparation.

"Crystal Structure of $[\text{Mn}\{\text{sar}\}][\text{SO}_3\text{CF}_3]_3$ ".

Acta Cryst. (1984). **C40**, 1512–1515

Structures of Phase IV Rubidium Nitrate, RbNO_3 , and Phase II Caesium Nitrate, CsNO_3

BY CHRISTOPHER DEAN, TREVOR W. HAMBLEY* AND MICHAEL R. SNOW

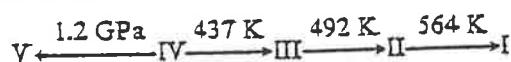
Department of Physical and Inorganic Chemistry, University of Adelaide, GPO Box 498, Adelaide, South Australia 5001, Australia

(Received 23 December 1983; accepted 7 June 1984)

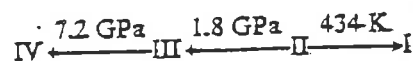
Abstract. RbNO_3 : $M_r = 147.47$, trigonal, $P3_1$, $a = 10.502$ (1), $c = 7.473$ (1) Å, $V = 713.8$ (1) Å³, $Z = 9$, $D_x = 3.106$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 152.5$ cm⁻¹, $F(000) = 612$, $T = 299.5$ K, final $R = 3.3\%$ for 797 unique observed reflections. CsNO_3 : $M_r = 194.91$, trigonal, $P3_1$, $a = 10.931$ (2), $c = 7.763$ (3) Å, $V = 803.1$ (4) Å³, $Z = 9$, $D_x = 3.626$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 100.96$ cm⁻¹, $F(000) = 774$, $T = 299.5$ K, final $R = 4.7\%$ for 760 unique observed reflections. The structures were found to be isomorphous and similar to that of $\text{TlNO}_3(\text{III})$. The three unique nitrates have site symmetries of C_1 but the symmetry of two of them is close to C_2 or C_2' . Large nitrate-ion reorientations are

proposed for transformation to the high-pressure phases.

Introduction. The known polymorphs of RbNO_3 are related as follows:



and CsNO_3 undergoes the polymorphic transformations:



(Kalliomäki & Meisalo, 1979; Adams & Tan, 1981). A comprehensive review of the above thermal-phase transformations is given by Pistorius (1976). It has been suggested (Brooker, 1973; DeLacy & Kennard, 1971) that the room-temperature phases $\text{RbNO}_3(\text{IV})$

* Present address: CSIRO Division of Energy Chemistry, Lucas Heights Research Laboratories, Private Mail Bag 7, Sutherland, New South Wales 2232, Australia.

and $\text{CsNO}_3(\text{II})$ are isomorphous and it was the object of this series of experiments to determine these two structures in order to allow correlation with the transformation properties. The structures of $\text{RbNO}_3(\text{IV})$ and $\text{CsNO}_3(\text{II})$ have recently been solved by neutron diffraction [Shamsuzzoha & Lucas (1982) and Lucas (1983) respectively].

Experimental. Source, E. Merck. Enraf–Nonius CAD-4 diffractometer. Crystals cut from *c*-axis needles with $\{2\bar{1}0\}$ and $\{001\}$ form faces.

RbNO₃: Recrystallized from aqueous solution by ethanol vapour diffusion, crystal 0.1 mm across $\times$ 0.13 mm long. Cell parameters from setting angles of 25 reflections, $24 < \theta < 28^\circ$, transmission values from absorption corrections: min. = 0.15, max. = 0.23. For intensity measurements max. $\sin(\theta)/\lambda = 0.595 \text{ \AA}^{-1}$, index ranges ($0 \leq h \leq 12$, $0 \leq k \leq 12$, $-8 \leq l \leq 8$) and ($-12 \leq h \leq 0$, $0 \leq k \leq 12$, $0 \leq l \leq 8$), standard reflections $\bar{3}00$, $\bar{2}11$ and 111 with no variation, 1259 reflections measured, all unique and 465 unobserved ($F < 5\sigma_F$), $R_{\text{int}} = 0.0104$. Structure solved by Patterson and successive Fourier synthesis, $\sum w(\Delta F)^2$ minimized. Atomic coordinates, anisotropic thermal parameters, scale factor, weighting scheme and secondary extinction refined. Final $R = 3.3\%$, $R_w = 3.5\%$, $w = k(\sigma_F^2 + |g|F^2)$, $k = 2.62$, $g = -0.00037$, max. $(\Delta/\sigma) = 0.286$, max. and min. heights 1.15 and $0.677 \text{ e \AA}^{-3}$, secondary extinction coefficient = 0.0016 mm^{-1} .

CsNO₃: Recrystallized from aqueous solution by evaporation, crystal 0.1 mm across $\times$ 0.19 mm long. Cell parameters from setting angles of 25 reflections, $5 < \theta < 21^\circ$, transmission values from absorption corrections: min. = 0.03, max. = 0.21. For intensity measurements max. $\sin(\theta)/\lambda = 0.571 \text{ \AA}^{-1}$, index ranges ($0 \leq h \leq 12$, $0 \leq k \leq 12$, $-12 \leq l \leq 12$), standard reflections $22\bar{2}$, 242 and $1\bar{2}1$ with no variation, 1055 reflections measured, 940 unique and 180 unobserved ($F < 5\sigma_F$), $R_{\text{int}} = 0.0245$. Structure solved by Patterson and successive Fourier synthesis, $\sum w(\Delta F)^2$ minimized. Atomic coordinates, anisotropic thermal parameters, scale factor, weighting scheme and secondary extinction correction refined. Final $R = 4.7\%$, $R_w = 5.5\%$, $w = k(\sigma_F^2 + |g|F^2)$, $k = 19.8$, $g = 0.00033$, max. $(\Delta/\sigma) = 0.381$, max. and min. heights 1.64 and $-1.66 \text{ e \AA}^{-3}$, secondary extinction coefficient = 0.0012 mm^{-1} .

The absolute configurations were affirmed (Hamilton, 1965) to below the $\frac{1}{2}\%$ significance level by changing the sign of the imaginary anomalous-scattering factor f'' for the metal atoms.

Scattering factors for Rb and Cs from *International Tables for X-ray Crystallography* (1974), for N and O from *SHELX76* (Sheldrick, 1976). Computer programs: *SUSCAD* (Guss, 1979) for data reduction and *Lp* corrections, *ABSORB* (Guss, 1980) for absorption corrections, *SHELX76* for structure solution and

refinement, and *ORTEP* (Johnson, 1976) for structure drawings.

Discussion. The structures of RbNO_3 and CsNO_3 are the same and in general agreement with those determined by Shamsuzzoha & Lucas (1982) and Lucas (1983) respectively. Atoms are numbered accordingly in the tables. Rotation of the unit-cell basis of RbNO_3 by 180° around the line $[\frac{1}{2}, y, \frac{1}{2}]$ will bring it into coincidence with the basis chosen by Shamsuzzoha & Lucas (1982). The CsNO_3 cell basis coincides with that of Lucas (1983) after rotation by 180° around the line $[\frac{1}{2}, \frac{1}{2}, z]$ with a further 180° around the line $[x, x + \frac{1}{2}, \frac{1}{2}]$.

The coordinates in Table 1 refer to the basis of Shamsuzzoha & Lucas (1982) and Lucas (1983). The standard deviations of the *x* coordinates for RbNO_3 are a complex function of the original *x* and *y* standard deviations and were not determined. Coordinates and anisotropic thermal parameters referred to the original unit-cell bases of RbNO_3 and CsNO_3 are deposited.* Distances and angles are in Table 2.

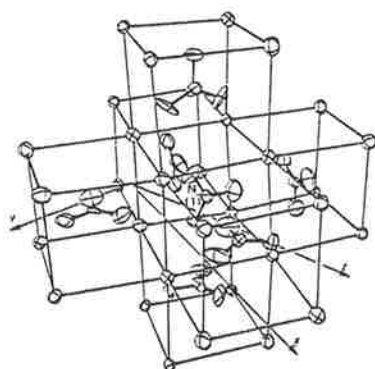
Comparison of coordinates and bonding geometry with the neutron-data results of Shamsuzzoha & Lucas (1982) and Lucas (1983) yielded some discrepancies above three standard deviations, the most significant of which are given in Table 3. The cell constants from this X-ray study have errors about one tenth of those of the previous work and have been used with the latter fractional coordinates in the comparison. Discrepancies in the coordinates (with $\Sigma\sigma$ in brackets) for RbNO_3 are: $\text{Rb}(3)z$ 0.20 (1) and $\text{N}(2)z$ 0.13 (1) $\text{\AA}$. This leads to a difference of 0.13 (2) $\text{\AA}$ in the $\text{N}(2)\text{--O}(4)$ bond length and of $8 (1)^\circ$ in the $\text{O}(5)\text{--N}(2)\text{--O}(6)$ angle. Discrepancies in the coordinates for CsNO_3 are: $\text{N}(1)y$ 0.23 (2), $\text{N}(2)y$ 0.20 (2), $\text{N}(3)x$ 0.23 (2) and $\text{O}(8)y$ 0.22 (2) $\text{\AA}$. The differences in bonding geometry are: $\text{N}(2)\text{--O}(4)$ 0.18 (3), $\text{N}(3)\text{--O}(8)$ 0.16 (3), $\text{N}(3)\text{--O}(9)$ 0.18 (3) $\text{\AA}$, $\text{O}(3)\text{--N}(1)\text{--O}(1)$ $8 (2)^\circ$, $\text{O}(9)\text{--N}(3)\text{--O}(7)$ $14 (2)^\circ$. The discrepancies in the N positions are associated with those in the O--N--O bond angles and N--O bond lengths. The N in the nitrates is strongly bonded to the O atoms and as there is inequality between O--N--O angles within any one nitrate ion the electron distribution (on which the present work depends) cannot wholly represent the position of the nucleus. The larger nitrate discrepancies for CsNO_3 (compared with RbNO_3) can be attributed to masking of the fine detail by the more highly scattering Cs atom. No explanation can be found for the difference between the two $\text{Rb}(3)z$ coordinates.

* Lists of structure factors and anisotropic thermal parameters and Figs. 1(b) and (c) showing nearest-neighbour nitrate and Rb^+ ions for $\text{N}(2)$ and $\text{N}(3)$ respectively have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39513 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional and equivalent isotropic thermal parameters

$$B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
(a) $\text{RbNO}_3(\text{IV})$				
Rb(1)	0.4557	0.5679 (1)	0.6267 (2)	2.9
Rb(2)	0.1190	0.2215 (2)	0.0000	2.4
Rb(3)	-0.2243	0.2206 (2)	0.6115 (5)	3.8
N(1)	0.4347	0.5659 (9)	0.1009 (13)	2.6
N(2)	0.1057	0.2097 (9)	-0.4850 (13)	3.1
N(3)	-0.2554	0.2101 (10)	0.1079 (11)	2.3
O(1)	0.3379	0.5586 (10)	-0.0011 (11)	5.8
O(2)	0.3980	0.4755 (10)	0.2205 (12)	5.1
O(3)	0.5618	0.6513 (8)	0.0573 (12)	4.3
O(4)	-0.0031	0.1086 (8)	-0.3822 (10)	4.2
O(5)	0.2309	0.2534 (9)	-0.4430 (13)	6.8
O(6)	0.0570	0.2450 (10)	-0.6132 (10)	4.1
O(7)	-0.3129	0.1184 (10)	0.2445 (11)	4.9
O(8)	-0.1288	0.2798 (10)	0.0851 (11)	5.8
O(9)	-0.3368	0.2186 (10)	0.0064 (11)	6.0
(b) $\text{CsNO}_3(\text{II})$				
Cs(1)	0.4488 (2)	0.5610 (2)	0.6328 (6)	3.6
Cs(2)	0.1079 (2)	0.2249 (2)	0.0000	3.1
Cs(3)	-0.2289 (1)	0.2133 (1)	0.6488 (6)	3.0
N(1)	0.4365 (15)	0.5528 (15)	0.1048 (22)	2.1
N(2)	0.0906 (14)	0.1856 (18)	-0.4679 (22)	3.2
N(3)	-0.2369 (14)	0.2112 (17)	0.1299 (23)	4.0
O(1)	0.3458 (17)	0.5583 (20)	0.0243 (21)	7.5
O(2)	0.4071 (18)	0.4993 (17)	0.2403 (19)	6.0
O(3)	0.5611 (17)	0.6575 (16)	0.0549 (19)	6.6
O(4)	0.0090 (17)	0.1153 (14)	-0.3803 (17)	4.4
O(5)	0.2110 (20)	0.2337 (16)	-0.4119 (22)	7.0
O(6)	0.0696 (21)	0.2490 (25)	-0.5950 (20)	17.0
O(7)	-0.3186 (20)	0.1138 (15)	0.2461 (20)	7.9
O(8)	-0.1310 (16)	0.2926 (19)	0.1387 (27)	11.0
O(9)	-0.3349 (20)	0.2272 (16)	0.0312 (16)	7.4

Fig. 1. (a) Nearest-neighbour nitrate and Rb^+ ions for N(1). Axes directions are $x//a$, $y//b$, $z//c$.

As shown in Figs. 1 (a)–(c) (b and c are deposited) the nitrate planes are nearly parallel to the pseudocube faces with the N near the cube centre and one N–O bond nearly parallel to a cube edge. It can be seen that nitrates occupy sites of C_1 symmetry which is in agreement with Karpov & Shultin (1970). The figures also show that nitrates 2 and 3 occupy more symmetrical sites than nitrate 1. Their symmetry is close to C_2 or C_2 which conforms with the conclusions of Brooker (1973).

Table 2. Nitrate-ion interatomic distances ($\text{\AA}$) and angles ($^\circ$)

(a) $\text{RbNO}_3(\text{IV})$			
O(1)–N(1)	1.237 (11)	O(2)–N(1)	1.221 (11)
O(3)–N(1)	1.217 (10)	O(4)–N(2)	1.343 (12)
O(5)–N(2)	1.200 (11)	O(6)–N(2)	1.220 (11)
O(7)–N(3)	1.322 (11)	O(8)–N(3)	1.162 (12)
O(9)–N(3)	1.179 (11)		
O(2)–N(1)–O(1)	118.1 (9)	O(3)–N(1)–O(1)	116.7 (10)
O(3)–N(1)–O(2)	124.6 (10)	O(5)–N(2)–O(4)	119.0 (9)
O(6)–N(2)–O(4)	111.7 (9)	O(6)–N(2)–O(5)	129.3 (10)
O(8)–N(3)–O(7)	122.2 (9)	O(9)–N(3)–O(7)	117.5 (10)
O(9)–N(3)–O(8)	120.2 (10)		
(b) $\text{CsNO}_3(\text{II})$			
O(1)–N(1)	1.198 (23)	O(2)–N(1)	1.168 (20)
O(3)–N(1)	1.325 (18)	O(4)–N(2)	1.079 (20)
O(5)–N(2)	1.226 (20)	O(6)–N(2)	1.291 (20)
O(7)–N(3)	1.340 (20)	O(8)–N(3)	1.052 (17)
O(9)–N(3)	1.398 (22)		
O(2)–N(1)–O(1)	117.9 (17)	O(3)–N(1)–O(1)	108.8 (16)
O(3)–N(1)–O(2)	127.0 (17)	O(5)–N(2)–O(4)	114.2 (18)
O(6)–N(2)–O(4)	123.9 (18)	O(6)–N(2)–O(5)	118.8 (19)
O(8)–N(3)–O(7)	130.0 (21)	O(9)–N(3)–O(7)	102.7 (14)
O(9)–N(3)–O(8)	121.2 (21)		

Table 3. Discrepancies in structural results between this work and that of Shamsuzzoha & Lucas (1982) and Lucas (1983)

Discrepancies (in $\text{\AA}$) between coordinates

RbNO_3		CsNO_3	
Entity	Difference	Entity	Difference
Rb(3) $_y$	0.20 (1)	Cs(1) $_x$	0.046 (4)
N(2) $_y$	0.06 (1)	Cs(1) $_y$	0.04 (1)
N(2) $_z$	0.13 (1)	Cs(2) $_x$	0.11 (1)
N(3) $_y$	0.05 (1)	Cs(2) $_y$	0.22 (4)
N(3) $_z$	0.07 (1)	Cs(3) $_x$	0.075 (3)
O(1) $_z$	0.08 (1)	Cs(3) $_y$	0.070 (4)
O(3) $_z$	0.07 (2)	N(1) $_y$	0.23 (2)
O(4) $_z$	0.05 (1)	N(2) $_x$	0.16 (2)
O(6) $_z$	0.06 (1)	N(2) $_y$	0.20 (2)
O(9) $_z$	0.06 (1)	N(3) $_x$	0.23 (2)
		O(1) $_x$	0.09 (2)
		O(2) $_z$	0.13 (2)
		O(4) $_x$	0.08 (2)
		O(5) $_x$	0.15 (2)
		O(6) $_x$	0.17 (3)
		O(7) $_z$	0.07 (2)
		O(8) $_y$	0.22 (2)
		O(8) $_z$	0.13 (3)

Discrepancies in bonding geometry

RbNO_3		CsNO_3	
Entity	Difference	Entity	Difference
N(2)–O(4)($\text{\AA}$)	0.13 (2)	N(1)–O(1)($\text{\AA}$)	0.10 (3)
N(2)–O(5)($\text{\AA}$)	0.07 (2)	N(1)–O(3)($\text{\AA}$)	0.10 (3)
N(3)–O(9)($\text{\AA}$)	0.08 (1)	N(2)–O(4)($\text{\AA}$)	0.18 (3)
O(1)–N(1)–O(2)($^\circ$)	4 (1)	N(3)–O(8)($\text{\AA}$)	0.16 (3)
O(4)–N(2)–O(6)($^\circ$)	6 (1)	N(3)–O(9)($\text{\AA}$)	0.18 (3)
O(5)–N(2)–O(6)($^\circ$)	8 (1)	O(3)–N(1)–O(1)($^\circ$)	8 (2)
		O(9)–N(3)–O(7)($^\circ$)	14 (2)

The structure is most similar to that of phase III of TiNO_3 (Fraser, Kennedy & Snow, 1975) which has a pseudo primitive tetragonal array of cations. Phase III of TiNO_3 transforms on heating to phase II which is isomorphous with $\text{RbNO}_3(\text{IV})$ (Kennedy & Patterson, 1961). From Fig. 2 in the TiNO_3 structure report it is

evident that the ratio of nitrate groups in each of the three perpendicular planes is 2:1:1 and some nitrates within each plane are oriented at 60° to each other. However, in RbNO₃ the corresponding ratio is 1:1:1 and there are two orientations at 30° to each other for nitrates in any one plane. Consequently during the transformation TlNO₃(III) → TlNO₃(II) at least four nitrate groups in three unit cells must rotate by 90° about a line in their plane and some nitrates must rotate by 30° about their plane normals. In RbNO₃ and CsNO₃ similar nitrate rotations must occur when the crystals transform to and from the high-pressure structures.

The authors would like to thank Drs E. Horn and J. Rodgers for helpful comments. Dr S. W. Kennedy proposed the undertaking of the RbNO₃ structure solution.

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An Interactive Program for Crystal Orientation and Martensitic Transformation Investigations: *COATI*

BY CHRISTOPHER DEAN

Department of Physical and Inorganic Chemistry, University of Adelaide, GPO Box 498, Adelaide, South Australia 5001

(Received 4 May 1984; accepted 3 January 1985)

Abstract

An interactive program for comparison of experimental with theoretical martensitic transformation data and for orientation determination from Laue and zero-layer reciprocal-lattice photographs is described. The program can generate orthographic, gnomonic, Laue and zero-layer reciprocal-lattice projections of lattice vectors, circles and latitude–longitude nets. A utility for habit-plane calculation from surface trace data and its diagrammatical representation is provided. Drawings before and after transformation can be superimposed. Output from program *MRTNST* [Ledbetter & Wayman (1971). *Mater. Sci. Eng.* **7**, 151–157] (altered to handle triclinic lattices) can be read directly by *COATI*, which also facilitates the graphical method of martensitic calculations. A lucid command language allows easy manipulation of previously complex procedures.

Introduction

Martensitic transformations entail a sudden alteration in crystal structure concurrent with a specific lattice orientation and distinctive shearing of both the crystal morphology and lattice segments. Inherent in the macroscopic shear are the tilting of crystal faces and an associated kinking of the edges. If the transformation front is immobilized all the junctions of inclined edges are observed to lie on an interface plane (Bilby & Christian, 1961). The principal axes of the pure lattice deformation may distort by 40% (Fraser & Kennedy, 1974) and rotate by as much as 15° (Kennedy & Dean, 1985). Theories manifesting these phenomena have been presented from 1948 (Jaswon & Wheeler, 1948) up to the present day (Crocker, 1982). The function of the program described here is to assist in the experimental study of the above mentioned transformation characteristics and to facilitate the intelligible comparison between experimental and theoretical data. The experimental macroscopic shear is typically investigated by micrography and various characteristic angles are recorded. Deriving the empirical orientation relationship involves orienting the parent crystal

and finding the alignment of the product lattice from diffraction patterns. These orientations can be determined by computer-assisted interpretation of the relative spot positions or by transcribing the diffraction patterns into lattice projections. The theoretical data are expressed as matrices and Miller indices of lattice vectors but these have to be represented in stereographic, morphological and numeric angular format for assimilation with the experimental data. The multitude of requisites necessitates considerable latitude resulting in a general program for orientation and martensitic transformation analysis.

A procedure for orientation evaluation from the locations of two or more diffraction spots on Laue or zero-layer reciprocal-lattice patterns is formulated. The method most resembles that of Laugier & Filhol (1983). A more integral analysis for transmission electron microscopy was not incorporated as the complexities are still being elucidated (*e.g.* Borges, 1983) and a library-comparison approach (Tokiwai, Moriguchi, Shinkawa & Watanabe, 1983) is plausibly paramount. As a universal reinforcement for orientation determination the program will generate orthographic, stereographic, gnomonic, Laue and zero-layer reciprocal-lattice projections of lattice vectors, small circles and latitude–longitude nets with separate lattice and net rotations.

A facility is provided for calculation of habit-plane indices from surface-trace data and for delineating the plane on a crystal morphology drawing. Theoretical transformation data can be administered to both the projections and morphology drawings for comparison with the experimental results. Inter-vector angle calculations for more precise correlations can be effected. The method derived by Jaeger (1964) for calculating the magnitudes and directions of the principal distortions for a 2D general linear transformation as exemplified by Kriven, Fraser & Kennedy (1981) is also coded.

To facilitate the graphical method of the theoretical (martensitic) calculations (Lieberman, 1958), strain ellipsoids, great circles and vectors with irrational Miller indices can also be projected. Any region of the projection can be enlarged to enhance the veracity of

the graphical method and any point on the projection can be indexed.

COATI was coded in (ANSI) Fortran-77 (Control Data Corporation, 1982; Digital Equipment Corporation, 1982) on a CDC Cyber 173. The diagrams are currently materialized by Calcomp and Nicolet Zeta1435 plotters although the program was also designed with VDT graphics use envisaged. Operation can be in either interactive or batch mode. The stipulation records begin with a key word ensued by numeric and/or literal data, thereby resembling those for *PLUTO78* (Motherwell, 1978) but transliterated more quickly in Fortran-77. Output from program *MRTNST** (Ledbetter & Wayman, 1971) is admissible for storage of the transformation matrices. Command sequences can be stored and invoked when, for example, one requires a series of compound plots. In the interactive mode control can be readily alternated between the stored and direct commands.

Methods of calculations

1. Bases used

Bases in the following text will be denoted by a bold-type capital letter and vectors (in lower case) and matrices referred to a particular basis will be appropriately subscripted (e.g. the vector $\mathbf{v}_x$). Three concentric bases are utilized to derive the plotter coordinates of a pretransformation lattice vector. An input vector referred to any of these bases is acceptable, thus allowing, for example, more flexible rotations. The foremost basis is that of the unit cell $\mathbf{U}$ (defined by a, b, c, α, β and γ) and the sequel is on orthonormal basis $\mathbf{O}$, as described by Rollett (1965). Directions in $\mathbf{U}$ are referred by pre-multiplication to $\mathbf{O}$ by the matrix H . The fundamental metric tensor is then $H^t H$, and the unit-cell volume is the determinant of H . The matrix for referring a plane $\mathbf{f}_U$ by pre-multiplication to $\mathbf{O}$ is $(H^{-1})^t$ and the interplanar spacing is s :

$$s = 1/|(H^{-1})^t \mathbf{f}_U|.$$

The third basis is the orthonormal plotter basis $\mathbf{P}$. The plotter's software is assumed to have an (x, y) addressable area with basis vectors $\mathbf{x} \parallel [100]_{\mathbf{P}}$ and $\mathbf{y} \parallel [010]_{\mathbf{P}}$. Vectors in $\mathbf{O}$ are referred by pre-multiplication to $\mathbf{P}$ by the matrix VI :

$$VI = (\mathbf{r}_{10}, \mathbf{r}_{20}, \mathbf{r}_{30})^{-1},$$

where unit column vectors $\mathbf{r}_{j0} (j = 1 \rightarrow 3)$ are parallel to the basis vectors of $\mathbf{P}$. If the elements of VI are not

supplied by the user, the view vector, $\mathbf{r}_3$, is required and $\mathbf{r}_1$ (unless provided) is reckoned from $\mathbf{r}_1 = \mathbf{r}_4 \times \mathbf{r}_3$, where $\mathbf{r}_4$ is an axis of $\mathbf{O}$ remote from $\mathbf{r}_3$. Then $\mathbf{r}_2$ is calculated by: $\mathbf{r}_2 = \mathbf{r}_3 \times \mathbf{r}_1$, thereby retaining a right-handed system. In case the $\mathbf{r}_1$ furnished by the user was not perpendicular to $\mathbf{r}_3$ it is recalculated by $\mathbf{r}_1 = \mathbf{r}_2 \times \mathbf{r}_3$.

Accumulative rotations can be administered to the unit-cell orientation and the renovated orientation matrix is VN : $VN = R_P VI$, where R_P is the rotation matrix. R_P also applies to the morphology drawings but rotations of the net are separate. The turning angles about any pair of axes of $\mathbf{P}$ necessary to align a particular vector with $[001]_{\mathbf{P}}$ can be enumerated.

Up to five transformation matrices can be stored and adhibited to a projection or morphology drawing. The net and ellipsoid vectors are unaffected. Besides entering the transformation data in matrix form they may be presented as rotation components or general invariant plane strain factors (Wayman, 1964), in which case the transformation matrix T is assembled in $\mathbf{O}$ and referred to $\mathbf{U}$ by the similarity transformation:

$$T_U = H^{-1} T_O H.$$

In the course of transferring matrices from *MRTNST* output, either all variants in the file or a particular solution and variant may be selected, but in both instances the stored commands are automatically executed after the processing of a variant.

A lattice correspondence matrix C can be specified for correct indexing of projected lattice vectors after transformation. Directions in the two unit cells are related by

$$\mathbf{v}_N = C \mathbf{v}_U,$$

where $\mathbf{N}$ is the new basis and the elements of C are disclosed by

$$C(i, j) = \mathbf{u}_{jU}(i),$$

in which the column vectors $\mathbf{u}_{jU} (j = 1 \rightarrow 3)$ are the axes vectors of $\mathbf{U}$ referred to $\mathbf{N}$. Post transformation vectors indexed using C are assigned different symbols on the projection.

2. Types of vector projection

Employment of the linear features of similar triangles for multiple projection types concedes an algorithm requiring less central memory than existing ones (e.g. Preuss, 1979a). Lattice vectors with rational Miller indices in all the seven projection classes listed below may be screened for systematic absences (planes only) and/or for prime triplets.

2.1. *Orthographic, stereographic and gnomonic.* The plotter-plane coordinates (x, y) of the orthographic projection of a unit vector $\mathbf{v}_P$ that is extended to

* Alterations are given in the Appendix, which has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39934 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

intersect a sphere concentric with $\mathbf{P}$ and of radius r are

$$x = r\mathbf{v}_P(1), y = r\mathbf{v}_P(2).$$

From Fig. 1 and the length ratio properties of similar triangles the plotter-plane coordinates for stereographic and gnomonic projection types are

$$x = r\mathbf{v}_P(1)d'/d, y = r\mathbf{v}_P(2)d'/d,$$

in which $d = \sin \varphi$ where φ is the angle between $\mathbf{v}_P$ and $[001]_P$. For the stereographic projection: $d' = \tan(\varphi/2)$ so that*

$$d'/d = 1/(1 + \cos \varphi),$$

but for the gnomonic case: $d' = \tan \varphi$, hence

$$d'/d = 1/\cos \varphi.$$

2.2. Flat film Laue. Lattice planes registered on all classes of simulated diffraction photographs must have $\lambda_1 < 2s_{hkl} \sin \theta < \lambda_2$, where $\theta = 90^\circ - \varphi$, s_{hkl} is the interplanar spacing and $\lambda_{1,2}$ are the permitted wavelength limits. Also in this context the annotated sphere is tangible because r is the crystal-to-film distance. The coordinates of the diffracted ray $\mathbf{v}_P$ are

$$\mathbf{v}_P(1) = \mathbf{v}_P(1)d'/d$$

$$\mathbf{v}_P(2) = \mathbf{v}_P(2)d'/d$$

$$\mathbf{v}_P(3) = \cos 2\theta,$$

where d is as above and $d' = \sin(2\theta)$. The gnomonic projection of $\mathbf{v}_P$ gives its plotter-plane coordinates.

2.3. Cylindrical film Laue. $\mathbf{v}_P$ is invariable with the flat-film category. Fig. 2 shows that x is the distance of the spot from a plane containing the X-ray beam and perpendicular to the cylinder axis. y is the shortest

arclength to the spot from a line in the film furthest from the beam source.

$$x = r \tan \theta' = r(\tan \{\arcsin [\mathbf{v}_P(1)]\})$$

$$y = r\theta'^c = r\{\arctan [\mathbf{v}_P(2)/\mathbf{v}_P(3)]\}.$$

For back reflection y must be modified:

$$y = |\pi^c - |y||(|y|/|y|).$$

2.4. Zero-layer reciprocal lattice. The approximation that a reciprocal-lattice layer perpendicular to the beam will produce a spot pattern is adopted from transmission electron microscopy theory (Andrews, Dyson & Keown, 1971) but can also be used for simulating X-ray zero-level precession photographs. The plotter-plane coordinates of the diffraction spot are

$$x = r\mathbf{v}_P(1) \tan 2\theta, y = r\mathbf{v}_P(2) \tan 2\theta,$$

where θ is procured from Bragg's law for the first-order maximum. For the electron-microscope case r corresponds to L , where $L\lambda$ is the camera constant.

3. Laue and zero-level reciprocal-lattice photo solution

A procedure independent of comparison with nearby orientations [unlike those of Preuss (1979b) and Cornelius (1981)] is that of Ploc (1978), which searches for a set of test vectors whose inter-vector angles match those of the n experimental vectors $\mathbf{v}_{e1 \rightarrow nP}$. A swifter approach developed by Riquet & Bonnett (1979) and refined by Laugier & Filhol (1983) includes calculating an orientation matrix from the

*Proof is given in the Appendix. See deposition footnote.

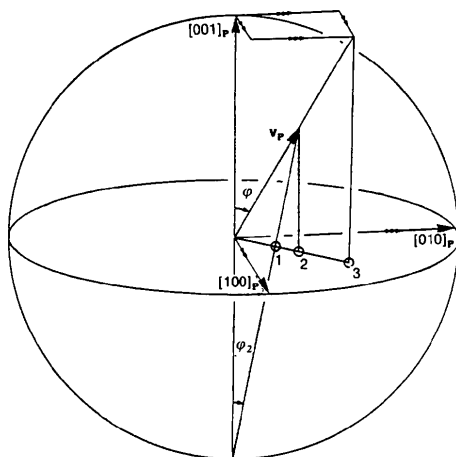


Fig. 1. Points in the plotter plane of 1 stereographic, 2 orthographic and 3 gnomonic projections of $\mathbf{v}_P$.

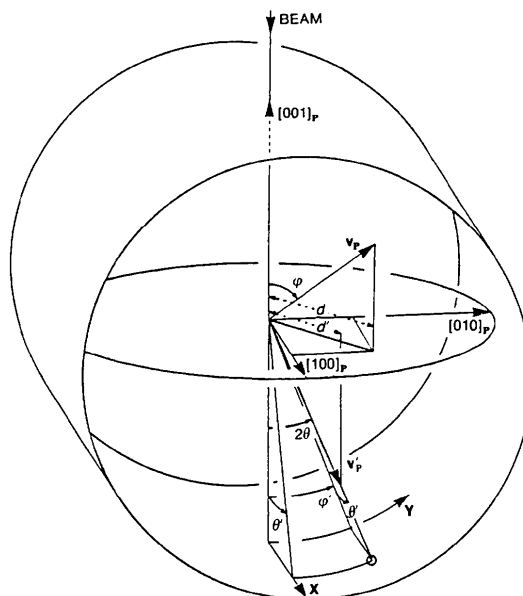


Fig. 2. For a cylindrical-film Laue photograph the plotter plane may be visualized as curled. The small circle pin-points the diffraction spot.

Table 1. Comparison of execution times for four crystals each having seven diffraction spots from front-reflection Laue photos

ΔA is the angular tolerance in degrees, t the execution time in seconds and N_s the number of solutions found.

Compound	Space group	$(h_1 k_1 l_1 \rightarrow h_2 k_2 l_2)$	ΔA	N_s	t
TiNO ₃	<i>Pnma</i>	(000) $\rightarrow$ (444)	4	1	90
CsNO ₃	<i>P3₁</i>	(003) $\rightarrow$ (333)	4	8	110
β -NiS	<i>R3m</i>	(032) $\rightarrow$ (332)	3	1	11
β -NiS	<i>R3m</i>	(033) $\rightarrow$ (333)	3	1	24
α -UO ₂ (OH) ₂	<i>Cmca</i>	(000) $\rightarrow$ (334)	3	0	18
α -UO ₂ (OH) ₂	<i>Cmca</i>	(000) $\rightarrow$ (446)	3	6	108

first two satisfactory test vectors. Using the inverse of VI the $(n-2)$ test vectors are generated from the $ve_{3 \rightarrow nP}$, approximated to reciprocal-lattice vectors and screened for their angular proximity to the $ve_{3 \rightarrow nP}$. Spot location data from front Laue, back Laue, cylindrical Laue and zero-layer reciprocal-lattice photographs are admissible.

For each spot, ve_P can be calculated using the simulation equations in reverse, except for the cylindrical film case, where

$$ve'_P(1) = \sin[\arctan(x/r)]$$

$$ve'_P(2) = ve'_P(1) \sin(y^c)/x$$

$$ve'_P(3) = ve'_P(1) \cos(y^c)/x.$$

For the test vector vt_1 of the first spot a range of indices $h_1 \rightarrow h_2$, $k_1 \rightarrow k_2$, $l_1 \rightarrow l_2$, which represents an asymmetric region in reciprocal space, is required from the user. The range $-h_2 \rightarrow h_2$, $-k_2 \rightarrow k_2$, $-l_2 \rightarrow l_2$ is employed to generate vt_2 and as a boundary for the $vt_{3 \rightarrow n}$. All vt are screened for systematic absences and the restriction $s \min_i < s_i < s \max_i$, where the interplanar-spacing confines for the i th spot are evaluated from λ_1 , λ_2 , θ_i , Bragg's law and a reserved uncertainty in s . vt_2 is selected by its angular proximity to vt_1 . VI is derived from vt_{10} , vt_{20} , ve_{1P} and ve_{2P} (*International Tables for X-ray Crystallography*, 1974) and employed to refer each $ve_{3 \rightarrow nP}$ to O :

$$ve_{iO} = VI^{-1} ve_{iP},$$

and then

$$ve_{iU} = H^i ve_{iO}.$$

ve_{iU} is divided by its element j of largest magnitude. A series of test vectors (vt_{iU}) is generated from ve_{iU} by successive multiplication by the integers from 1 to the limit for $vt_{iU}(j)$. The number of test vectors for the i th spot ($i = 3 \rightarrow n$) therefore equals the upper-index limit for the j th element. The elements of each vt_{iU} are rounded off to integers and vt_{iU} is screened for its angular proximity to ve_{iP} .

Whenever a suitable set of $vt_{1 \rightarrow n}$ is acquired the stored command sequence is executed. Input diffrac-

tion spots are plotted on the simulated photos. The execution durations for some examples are given in Table 1.

4. Circles

The intersection of a sphere with a cone of half-angle ω and axis $\mathbf{n}$ is a circle centred around $\mathbf{n}$. Vectors $\mathbf{v}_Q$ in the cone are synthesized in an orthonormal basis $\mathbf{Q}$, which has $[001]_Q$ parallel to $\mathbf{n}$. If ρ is the angle between $[100]_Q$ and $\mathbf{v}_Q$ projected onto the $(001)_Q$ plane then

$$\mathbf{v}_Q = (\cos \rho \sin \omega, \sin \rho \sin \omega, \cos \omega).$$

The vectors are referred to $\mathbf{P}$ by

$$\mathbf{v}_P = W \mathbf{v}_Q,$$

where W is a matrix embodying the rotation around $[001]_P \times \mathbf{n}_P$ necessary to move $[001]_P$ into collinearity with $\mathbf{n}_P$.

5. Ellipsoids

The essential data are the three principal distortions $\eta_{1 \rightarrow 3}$ and the directions $\mathbf{d}_1$, $\mathbf{d}_2$ of η_1 and η_2 ($\mathbf{d}_3 = \mathbf{d}_1 \times \mathbf{d}_2$). The method of constructing vectors $\mathbf{v}_i$ in the initial ellipsoid reflects that of Lieberman, Read & Wechsler (1957) except that the polar coordinates are referred to an orthonormal basis $\mathbf{E}$. Vectors $\mathbf{v}_E$ in the final ellipsoid are obtained from the initial ones by

$$\mathbf{v}_E(j) = \eta_j \mathbf{v}_E(j), j = 1 \rightarrow 3.$$

The vectors $\mathbf{v}_E$ and $\mathbf{v}_F$ are referred to $\mathbf{O}$ by

$$\mathbf{v}_O = M \mathbf{v}_E,$$

where

$$M(i, j) = \mathbf{d}_{jO}(i).$$

The vectors are then referred to $\mathbf{P}$ by VI .

6. Interface planes

The indices of a fourth vector $\mathbf{v}_4$ situated at established angles to three other vectors ($\mathbf{v}_1$, $\mathbf{v}_2$ and $\mathbf{v}_3$) can be enumerated from the simultaneous equation

$$\begin{bmatrix} \mathbf{v}_4(1) \\ \mathbf{v}_4(2) \\ \mathbf{v}_4(3) \end{bmatrix} = \begin{bmatrix} \mathbf{v}_1 \\ \mathbf{v}_2 \\ \mathbf{v}_3 \end{bmatrix}^{-1} \begin{bmatrix} \cos(\mathbf{v}_1 \wedge \mathbf{v}_4) \\ \cos(\mathbf{v}_2 \wedge \mathbf{v}_4) \\ \cos(\mathbf{v}_3 \wedge \mathbf{v}_4) \end{bmatrix}.$$

The direction of the surface trace of an interface plane can therefore be derived if the angles it makes with two crystal edges are known (the third angle is 90° to the face containing the trace). Once two non-parallel directions of traces have been determined their cross product gives the habit plane.

7. Morphology drawings

The Miller indices of each crystal face and their distances from the origin must be provided. The

corresponding distance after transformation is

$$\text{previous distance}/|[(T^{-1})']_0 \cdot \mathbf{f}_0|,$$

where T is the transformation matrix and $\mathbf{f}_0$ is the plane's unit normal. (The proof is given in the Appendix; see deposition footnote.) The crystal is delineated by the orthographic projection of edges, which are ascertained by detecting two intersecting planes and checking for two more planes producing the vertices. The minimum-volume crystal is appropriated by verifying that both vertices are on the origin side of all faces in the same hemisphere. If an opaque crystal is stipulated then edges with both adjoining faces pointing below the plotter plane are not drawn. Planes specified as containing the origin are not recognized as faces and only their traces appear on the drawing. For easy identification of faces after transformation they can be numbered and the edges dashed.

Discussion

After compilation with minimum optimization on the Cyber the program requires 53 000 octal words of central memory to load with the FTN5 and Calcomp libraries or 62 000 octal words with additional access to the Zeta1453 library. The program was also successfully tested on a DEC Vax-11 following minor changes to some of the calls to the Zeta's subroutine *SYMBOL*.

For orientation determination the first two diffraction spots selected should be far apart to enhance the accuracy of VI (Riquet & Bonnet, 1979). Lower index limits decrease the computation time and consequently the spots should be from the intersection of zone curves (Amorós, Beurger & Canut de Amorós, 1975). To lessen the number of solutions a large number of spots with small angular errors should be chosen from sparse areas. Reflections from transformed crystals are more diffuse (e.g. Kennedy & Patterson, 1965) and therefore require greater tolerance in the calculations. This can be reduced by employing smaller crystals and minimizing non-hydrostatic stresses on the crystal during transformation. A problem that requires a more discerning choice of spots after transformation is that additional lattice orientations may arise due to symmetry-equivalent trans-

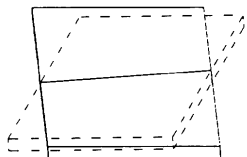


Fig. 3. Morphology of a β -uranyl hydroxide crystal (full lines) and the product α -uranyl hydroxide crystal (dashed lines) after transformation as drawn by *COATI*. The transformation matrix was obtained from *MRTNST* for $(112)[02\bar{1}]$ slip.

formations at separate nucleation sites or even the mechanisms of other martensite variants. Determining the orientation of transformed crystals on an automatic diffractometer (an Enraf-Nonius CAD4; Kennedy & Dean, 1985) invariably protracted to two hours using the reflection locating and orientation confirmation routines provided. The duration could be substantially shortened if hand-picked spots from Laue photos could be interpreted by the diffractometer and the simulated photos viewed on an online VDT. This procedure would also facilitate determination of the product's orientation in partly transformed crystals. Experiments with crystals in strongly diffracting pressure cells on automated diffractometers where discrimination is a major problem (Merrill & Bassett, 1974) could be similarly expedited.

A large number of theoretically possible slip mechanisms were computed by program *MRTNST* for the $\beta \rightarrow \alpha$ martensitic transformation of uranyl hydroxide (Kennedy & Dean, 1985). Using the stored command utility stereograms showing the orientation relationship, intervector angle calculations and morphology drawings were produced for each variant. The few variants that agreed with the experimental results were qualified by elimination. A morphology drawing of one such variant is shown in Fig. 3. For the transformation in NaClO_3 (Meyer & Rimskey, 1979), the principal distortion directions and magnitudes were calculated using *COATI* (Dean & Kennedy, 1985). Alterations to *MRTNST* were checked by the graphical method for NaClO_3 and uranyl hydroxide. Calculation of the lattice-invariant shear magnitude by the graphical method is simpler than the technique described by Lieberman (1958) if the projection is on the shear plane as the invariant normals can be directly spotted if a very fine net is used.

The program with instructions is available from the author upon written request with a magnetic tape.

I am grateful to my colleagues for suggesting their requirements and providing test data.

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Preliminary communication

REACTIONS OF TRANSITION METAL σ -ACETYLIDE COMPLEXES

III*. SYNTHESIS OF SOME ARYLDIAZOVINYLDENE AND CYCLO-HEPTATRIENYLVINYLDENE COMPLEXES. X-RAY STRUCTURES OF $[\text{Ru}(\text{C}=\text{CPhN}=\text{NC}_6\text{H}_3\text{Me}_2-3,4)(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)] [\text{BF}_4] \cdot 0.67\text{CH}_2\text{Cl}_2$ AND $[\text{Ru}(\text{C}=\text{CPh}(\text{C}_7\text{H}_7))(\text{DPPE})(\eta\text{-C}_5\text{H}_5)] [\text{PF}_6] \cdot 0.63\text{CH}_2\text{Cl}_2$

MICHAEL I. BRUCE*, CHRISTOPHER DEAN, D. NEIL DUFFY, MARK G. HUMPHREY
 and GEORGE A. KOUTSANTONIS

*Jordan Laboratories, Department of Physical and Inorganic Chemistry, The University of
 Adelaide, Adelaide, South Australia 5001 (Australia)*

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Summary

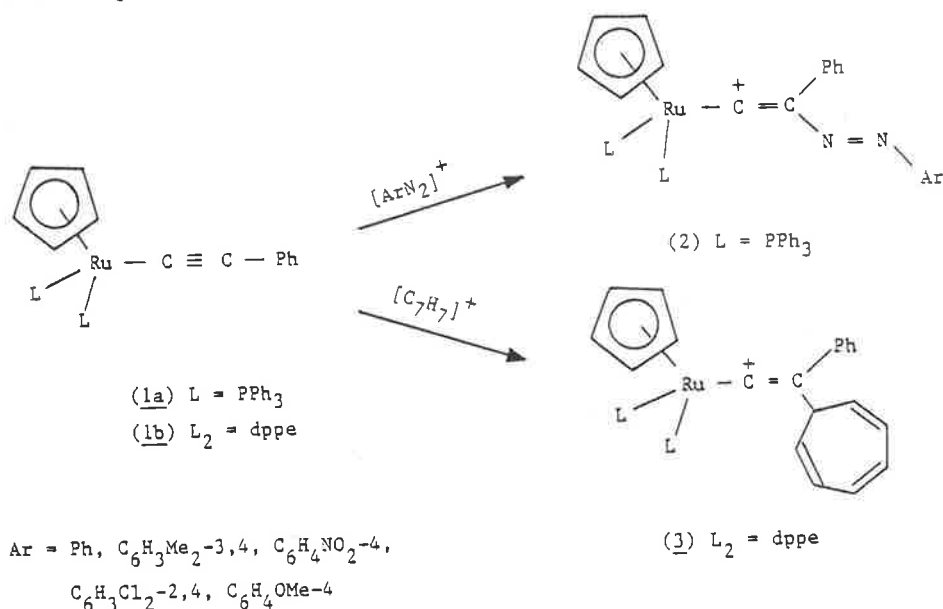
Addition of arenediazonium or tropylium salts to $\text{Ru}(\text{C}_2\text{Ph})(\text{L})_2(\eta\text{-C}_5\text{H}_5)$ ($\text{L}_2 = (\text{PPh}_3)_2$ or DPPE) gives the corresponding cationic aryldiazovinyldene and cycloheptatrienylynylvinylidene complexes, respectively; the X-ray structures of the title complexes confirm the presence of the new ligands. The Ru—C and C=C distances are 1.823(9) and 1.34(1) Å for the aryldiazo complex, and 1.848(9) and 1.32(1) Å for the cycloheptatrienyl derivative.

The most commonly used methods for the synthesis of transition metal complexes containing vinylidene ligands are by direct reaction of 1-alkynes with a suitable metal substrate, or by protonation or alkylation of a metal acetylide complex [1]. Electrophilic addition to the β -carbon of the acetylide ligand has been extensively studied with reagents such as HBF_4 or HPF_6 [2], $[\text{R}_3\text{O}][\text{BF}_4]$ ($\text{R} = \text{Me}$ or Et) or FSO_3Me [2, 3] and with alkyl halides [4]. Double addition of an electrophile has been reported in the successive reactions of $[\text{W}(\text{C}_2\text{Bu}^t)(\text{CO})_5]^-$ with FSO_3Me or $[\text{Et}_3\text{O}]^+$ followed by $\text{CF}_3\text{SO}_3\text{H}$ [5], and the addition of reactive metal hydrides to metal acetylides has given binuclear complexes with μ -vinylidene ligands [6].

Seeking to extend the range of known vinylidene ligands, we have studied the reactions of two classes of cationic organic reagents, arenediazonium and

*For Part II, see ref. 12.

tropylium salts. Addition of $[\text{ArN}_2][\text{BF}_4]$ to solutions of $\text{Ru}(\text{C}_2\text{Ph})(\text{PPh}_3)_2$ - $(\eta\text{-C}_5\text{H}_5)$ (1a) in THF readily affords the corresponding aryldiazovinylidene complexes $[\text{Ru}(\text{C}=\text{CPhN}=\text{NAr})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (2), which are isolated as bright red, air stable crystalline solids. The IR spectra contain bands at ca. 1550 cm^{-1} which can be assigned to $\nu(\text{C}=\text{C}) + \nu(\text{N}=\text{N})$. In the NMR spectra, the expected resonances are found, with the characteristic low-field triplet ($J(\text{CP})$ 15.8 Hz) of the metal-bonded vinylidene α -carbon occurring at δ 362 ppm in the PhN_2 derivative. Similarly, the reaction between $\text{Ru}(\text{C}_2\text{Ph})(\text{DPPE})$ - $(\eta\text{-C}_5\text{H}_5)$ (1b) and $[\text{C}_7\text{H}_7][\text{PF}_6]$ gave $[\text{Ru}\{\text{C}=\text{CPh}(\text{C}_7\text{H}_7)\}(\text{DPPE})(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$ (3) as a rose-pink powder. The ^1H NMR spectrum contains multiplets at δ 2.85, 5.34, 6.28 and 6.53 ppm (relative intensities 1/2/2/2), which are assigned to the protons attached to the C_7 ring, indicating the presence of a cycloheptatrienyl group; a triplet at δ 347 ppm in the ^{13}C NMR spectrum in the analogous PPh_3 complex confirmed their formulation as substituted vinylidene complexes.



We have fully characterised these novel ligands by single-crystal X-ray studies of the title complexes. Suitable crystals were grown from dichloromethane/methanol (2) and dichloromethane/ethanol mixtures (3). Diffraction data for both complexes were collected on an Enraf-Nonius CAD 4 four-circle diffractometer using graphite-monochromated $\text{Mo-K}\alpha$ radiation, $\lambda(\text{Mo-K}\alpha)$ 0.7107 Å.

Crystal data: $\text{C}_{57}\text{H}_{49}\text{BF}_4\text{N}_2\text{P}_2\text{Ru} \cdot 0.67\text{CH}_2\text{Cl}_2$ (2), $M = 1069.33$, monoclinic, space group $P2_1/n$; a 22.424(6), b 10.215(5), c 23.292(7) Å, β 104.64(2)°, U 5160 Å³; D_m 1.37, $D_c = 1.37\text{ g cm}^{-3}$ for $Z = 4$; $F(000)$ 2196 electrons, $\mu(\text{Mo-K}\alpha)$ 4.44 cm⁻¹. $T = 293\text{ K}$.

$\text{C}_{46}\text{H}_{41}\text{F}_6\text{P}_3\text{Ru} \cdot 0.63\text{CH}_2\text{Cl}_2$ (3), $M = 955.4$, triclinic, space group $P\bar{1}$; a 11.67(3), b 12.10(3), c 15.98(4) Å, α 76.6(2), β 88.3(1), γ 86.8(1)°, U 2191(8) Å³; D_c 1.45 g cm⁻³ for $Z = 2$; $F(000)$ 972.9 electrons, $\mu(\text{Mo-K}\alpha) = 5.56\text{ cm}^{-1}$. $T = 293\text{ K}$.

For 2, 4451 unique data (for 3, 3809) were collected in the range $1.2 < \theta < 21^\circ$ ($1.3 < \theta < 21^\circ$), of which 2847 (3432) with $I > 2.5\sigma(I)$ were refined to $R = 0.046$, $R_w = 0.049$ ($R = 0.059$, $R_w = 0.069$). Both structures were solved by obtaining the coordinates of the Ru atom from a Patterson map; all other non-hydrogen atoms were revealed in subsequent refinement and Fourier difference maps [7]. Neutral atom scattering factors were obtained from reference [8]. Both structures contain dichloromethane of crystallisation, the site occupancies of which were refined to 0.67 and 0.63 of a molecule for 2 and 3, respectively. The BF_4 anion in 2 was disordered, satisfactory refinement being obtained using a model with three orientations with site occupancies of 0.65, 0.25 and 0.10. For 2, all non-hydrogen atoms except phenyl group carbons and fluorines had anisotropic thermal parameters; for 3, only the phenyl carbons of the non-hydrogen atoms had isotropic thermal parameters. In the final cycles of the blocked-matrix least squares refinement, the phenyl and

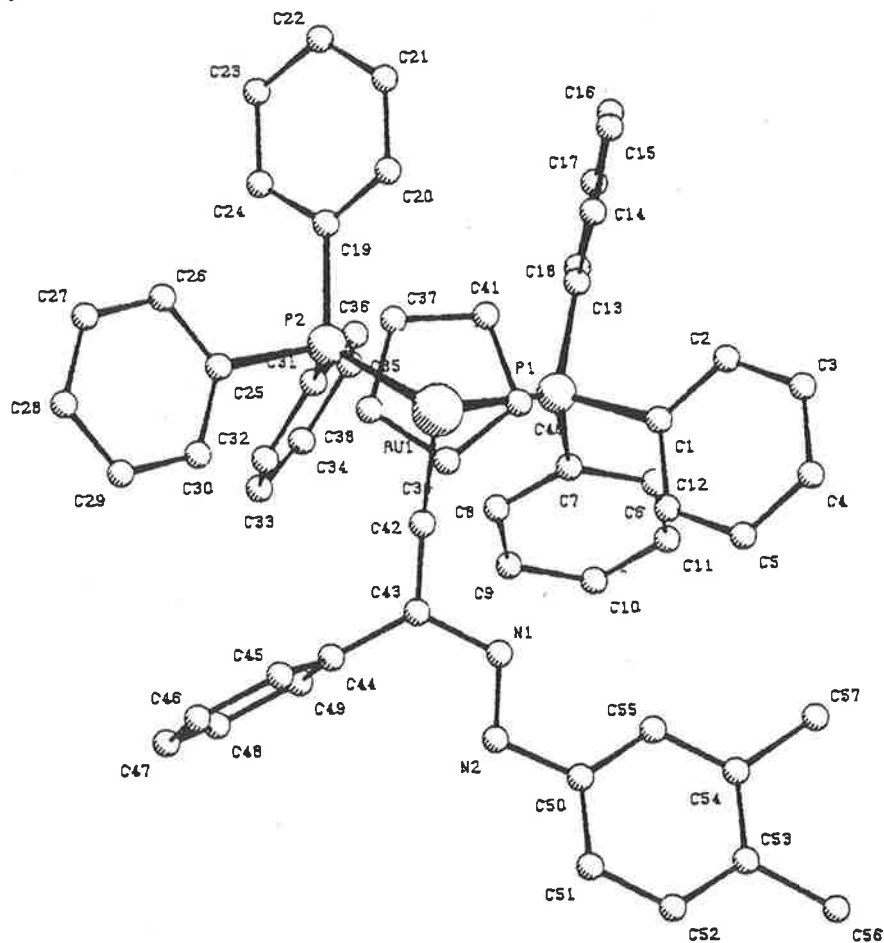


Fig. 1. PLUTO plot of cation in $[\text{Ru}(\text{C}=\text{CPhN}=\text{NC}_6\text{H}_4\text{Me}_2\text{-3,4})(\text{PPh}_3)_2(\eta\text{-C}_6\text{H}_5)][\text{BF}_4]$ (2), showing atom numbering scheme. Bond distances: $\text{Ru}(1)\text{—C}(\text{cp})$ (av.) 2.28, $\text{Ru}(1)\text{—P}(1)$ 2.362(3), $\text{Ru}(1)\text{—P}(2)$ 2.360(3), $\text{Ru}(1)\text{—C}(42)$ 1.823(9), $\text{C}(42)\text{—C}(43)$ 1.34(1), $\text{C}(43)\text{—C}(44)$ 1.48(1), $\text{C}(43)\text{—N}(1)$ 1.42(1), $\text{N}(1)\text{—N}(2)$ 1.27(1), $\text{N}(2)\text{—C}(50)$ 1.42(1) Å; bond angles: $\text{P}(1)\text{—Ru}(1)\text{—P}(2)$ 98.8(1), $\text{P}(1)\text{—Ru}(1)\text{—C}(42)$ 96.1(3), $\text{P}(2)\text{—Ru}(1)\text{—C}(42)$ 89.7(3), $\text{Ru}(1)\text{—C}(42)\text{—C}(43)$ 169.9(7), $\text{C}(42)\text{—C}(43)\text{—C}(44)$ 121.4(8), $\text{C}(42)\text{—C}(43)\text{—N}(1)$ 114.4(8), $\text{C}(43)\text{—N}(1)\text{—N}(2)$ 114.9(7), $\text{N}(1)\text{—N}(2)\text{—C}(50)$ 113.0(7)°.

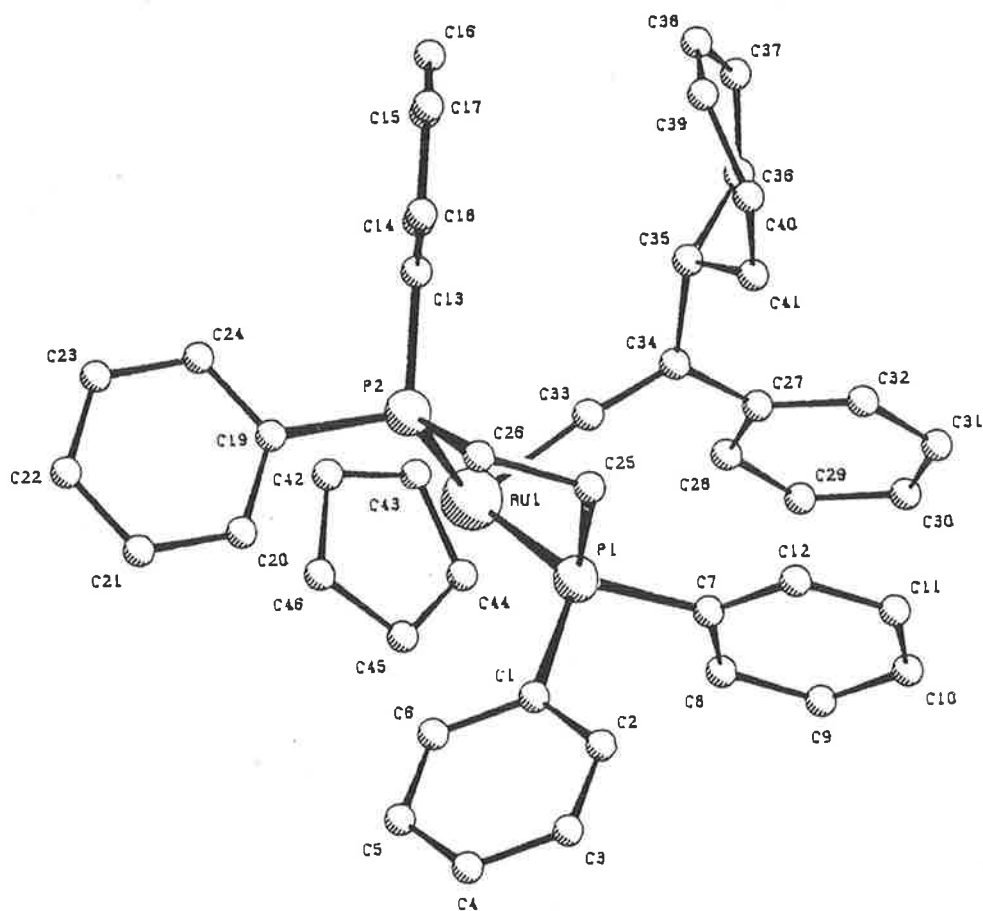


Fig. 2. PLUTO plot of cation in $[\text{Ru}\{\text{C}=\text{CPh}(\text{C}_6\text{H}_5)\}(\text{DPPE})(\eta\text{-C}_5\text{H}_5)] [\text{PF}_6]$ (3), showing atom numbering scheme. Bond distances: $\text{Ru}(1)\text{—C}(\text{cp})$ (av.) 2.26, $\text{Ru}(1)\text{—P}(1)$ 2.298(2), $\text{Ru}(1)\text{—P}(2)$ 2.305(2), $\text{Ru}(1)\text{—C}(33)$ 1.848(9), $\text{C}(33)\text{—C}(34)$ 1.32(1), $\text{C}(34)\text{—C}(27)$ 1.483(9), $\text{C}(34)\text{—C}(35)$ 1.55(1) Å; bond angles: $\text{P}(1)\text{—Ru}(1)\text{—P}(2)$ 83.9(1), $\text{P}(1)\text{—Ru}(1)\text{—C}(33)$ 81.6(2), $\text{P}(2)\text{—Ru}(1)\text{—C}(33)$ 95.8(2), $\text{Ru}(1)\text{—C}(33)\text{—C}(34)$ 174.9(6), $\text{C}(33)\text{—C}(34)\text{—C}(27)$ 121.1(6), $\text{C}(33)\text{—C}(34)\text{—C}(35)$ 118.1(7)°.

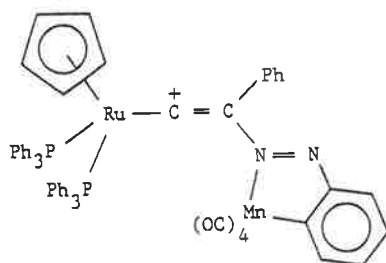
cyclopentadienyl rings were included as rigid groups (C—C 1.395 and 1.42 Å respectively) and the hydrogen atoms were placed in calculated positions (C—H 1.08 Å) with a common thermal parameter. The structures of the cations of 2 and 3 are illustrated in Figs. 1 and 2, respectively, which also give some selected bond distances and angles*.

Both cations are of the now familiar, nearly octahedral $\text{RuLP}_2(\eta\text{-C}_5\text{H}_5)$ structural type, and contain disubstituted vinylidene ligands. The Ru—C distances (1.823(9) Å in 2, 1.848(9) Å in 3) are considerably shorter than that expected for an $\text{Ru—C}(\text{sp})$ single bond; indeed, comparison with the Ru—CO distance recently determined [9] in $[\text{Ru}(\text{CO})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)] [\text{BPh}_4]$ indicates an even greater degree of backbonding from the metal into the vinylidene π^* orbitals. Both the Ru—C and the C=C distances of the vinylidene ligand

*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (England). Any request should be accompanied by the full literature citation for this Communication.

(1.34(1) Å in 2, 1.32(1) Å in 3) are comparable with those found previously in $[\text{Ru}(\text{C}=\text{CHMe})(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)] [\text{PF}_6]$ (1.845(7) and 1.313(10) Å, respectively) [10]. The Ru—C—C system is nearly linear (RuC(42)C(43) 169.9(7)° in 2, RuC(33)C(34) 174.9(6)° in 3).

In 2, the phenyldiazo group adopts the usual *trans* configuration, the N—N and N—C parameters not differing significantly from those found for *trans*-azobenzene [11]. In 3, the C₇ ring has the tub conformation; of interest is the calculated location of the hydrogen atom attached to C(35), the C—H bond being directed towards the centre of a Ph group of the DPPE ligand.



(4)

The reactivity of these new complexes has been investigated briefly. Reaction with anionic nucleophiles (H^- , Me^- , OMe^-) results in displacement of the addend and regeneration of the neutral phenylacetylide complexes. The diazo function in 2 exhibits a remarkable tendency to bind to electrophiles such as H^+ or Me^+ ; the dicationic $[\text{Ru}(\text{C}=\text{CPhNMe}=\text{NPh})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]^{2+}$ and tricationic $[\text{Ru}(\text{C}=\text{CPhNH}=\text{NHPH})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]^{3+}$ complexes resulting from such reactions have been identified so far. Not surprisingly, reaction with $\text{MnMe}(\text{CO})_5$ affords the cyclometallated derivative 4. Full details of these and related complexes will be given elsewhere.

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