SOME FACTORS AFFECTING THE TEMPERATURE COEFFICIENT OF ZINC SULPHIDE TYPE PHOSPHORS

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With reference to your PCAY:JM(D.716/62), you may make my thesis available for loan and photocopying.

Yours faithfully,

(D.H. Brown)

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SUMMARY

ACKNOWLEDGEMENTS

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SUMMARY

It is shown in a brief discussion that current theories do not explain the observed variation in the log of the intensity (B) with temperature for zinc sulphide type phosphors continuously excited with ultra-violet radiation.

The way in which the temperature coefficient of the phosphors depends on the silver and nickel concentrations is discussed. It is also shown that the temperature coefficient depends on the nature of the base matrix. This is changed by the addition of cadmium sulphide and by varying the conditions under which the phosphors are prepared.

It is found that the curves of log B v's 1/T can be normalized in a simple manner. In the process of the normalization a relationship is developed between the superlinearity of the phosphors to ultra-violet excitation and their temperature coefficient. An empirical equation, $B/I = 1/\left[C_1' \exp(-P_1'/T) + C_2' \exp(-P_2'/T) + C_3\right]$, is fitted to the log B v's 1/T curve.

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 and belief, this thesis contains no material previously written or published by another person, except where due reference is made in the text of the thesis.

1. INTRODUCTION

It has been known for many years that the luminescent efficiency of continuously excited zinc sulphide type phosphors has a strong temperature dependence[1]. However at the present time it is not possible to predict the shape of the curve of the log of the luminescent intensity[*] of the phosphor as a function of temperature. The purpose of this work is to study the effect of impurities and the method of preparation on the log B v's T curves of zinc sulphide type phosphors in order to be able to predict such quantities as temperature coefficient.

Results similar to some of those discussed here have been reported previously[2,3]. However these reports have been incomplete and it has been necessary to prepare phosphors in complete series so that all the preparation conditions might be known.

Two current theories of temperature quenching will be discussed and it will be shown that these theories appear to be inadequate.

The influence of temperature on luminescent efficiency is supposed

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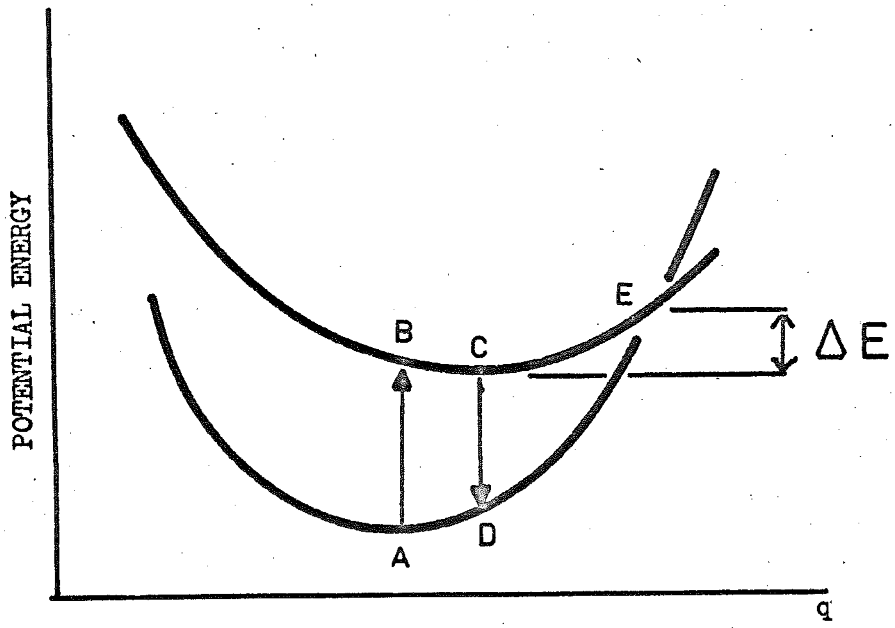
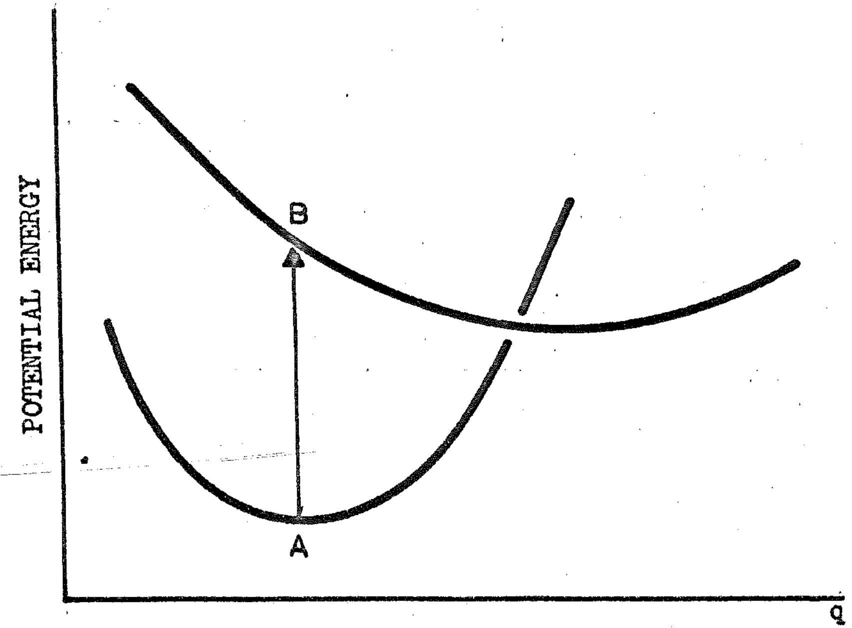
[*] In order to be consistent with the related literature the term "luminescent intensity" will be used throughout this thesis. However it is considered that the correct term should be "luminance".



CONFIGURATION CO-ORDINATE

FIGURE 1. CONFIGURATION CO-ORDINATE MODEL OF AN ACTIVATOR CENTRE



CONFIGURATION CO-ORDINATE

FIGURE 2. CONFIGURATION CO-ORDINATE MODEL OF A KILLER CENTRE

to arise from a competition between various energy release processes within the phosphor. A method by which these transfers can occur has been proposed by Mott[4] and Seitz[5]. A curve of the type proposed for an activator centre is illustrated in figure 1 page 2 by plotting the potential energy of the centre against a configuration co-ordinate. This configuration co-ordinate is a function of the positions of the constituent atoms. The absorption process is represented by the transition AB and the radiative process by the transition CD. However, a competing non-radiative process, CED, can be thermally activated. This occurs when sufficient energy, ΔE, is obtained by the activator centre for the excited state to overlap the ground state at the point E. The energy released in this process appears as thermal energy rather than luminescence.

With this mechanism the transitions will be predominantly radiative at low temperatures and non-radiative at high temperatures. This is qualitatively in accordance with the general behaviour of the phosphors when heated.

Figure 2 page 2 shows a situation where the return to the ground state is not accompanied by photon emission in the visible region and most of the energy is dissipated as heat. Centres which give rise to this type of non-radiative transition are usually called killer centres.

In the case shown in figure 1 page 2 if L centres are excited per cm^3 per sec then, when equilibrium has been reached,

$$L = p_L a + p_N a \qquad \text{---}(1)$$

where a = the number of excited centres/cm^3

P_L = the probability per cm^3 per sec for an excited centre to return to the ground state with a radiative transition.

P_N = the probability per cm^3 per second for an excited centre to return to the ground state with a non-radiative transition.

Hence, if the luminescent intensity is B photons per cm^3 per sec, the quantum efficiency of the radiative process is given by:

$$B/L = P_L/(P_L + P_N). \qquad \text{---}(2)$$

Since the probability of finding an excited centre in a vibrational state ΔE above the minimum is proportional to $\exp - \Delta E/kT$ then, assuming that P_L is not affected by the temperature,

$$B/L = 1/[1 + \text{const.} \exp(-\Delta E/kT)] \qquad \text{---}(3)$$

Since, in this model, the rates of both the radiative and non-radiative transitions are proportional to the rate of excitation it has no effect on the temperature dependence. Also the luminescent intensity of a phosphor which obeys this model is a linear function of the excitation intensity. However the luminescent intensity of zinc sulphide phosphors is, under certain conditions, a superlinear function of the excitation intensity[6,7,8]. Also, as has been shown by Klasens[9], equation 3 does not give a good fit for the curve of log B v's T for zinc sulphide type phosphors.

Klasens[9,10] has analysed a two level model with a filled activator level near the valence band and an empty killer level near the conduction band. A diagrammatic representation of this model is shown in Figure 3.

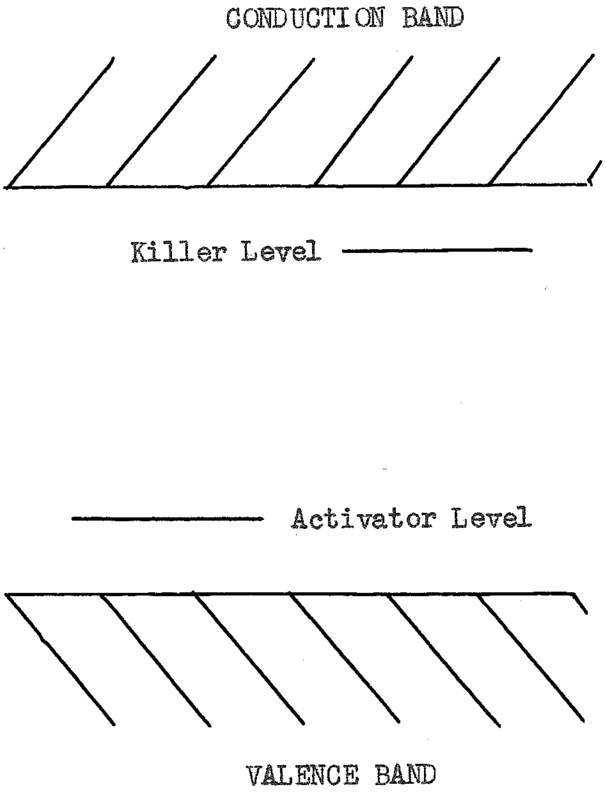


FIGURE 3. DIAGRAMATIC REPRESENTATION OF THE KLASENS TWO LEVEL MODEL

The conclusion reached by Klasen is that:

$$U = B + D^{r} \exp(-E'/kT)$$

where D = const.

U = ultra-violet excitation intensity

B = luminescent intensity of the phosphor

E' = an activation energy dependent on both the activator and the killer.

k = Boltzman's constant

T = temperature ($^{\circ}K$)

r = 1/superlinearity of the phosphor at high temperatures. The superlinearity at a given temperature is defined as the ratio $\frac{\log B}{\log U}$ at that temperature. This will be discussed in greater detail in section 4a pages 58 to 63.

Provided the efficiency of the phosphors at low temperatures is approximately equal to unity then, if B_o is the luminescent intensity at low temperature, $B_o = U$.

Hence:

$$B_o = B + DB^r \exp(-E'/kT). \qquad \text{---(5)}$$

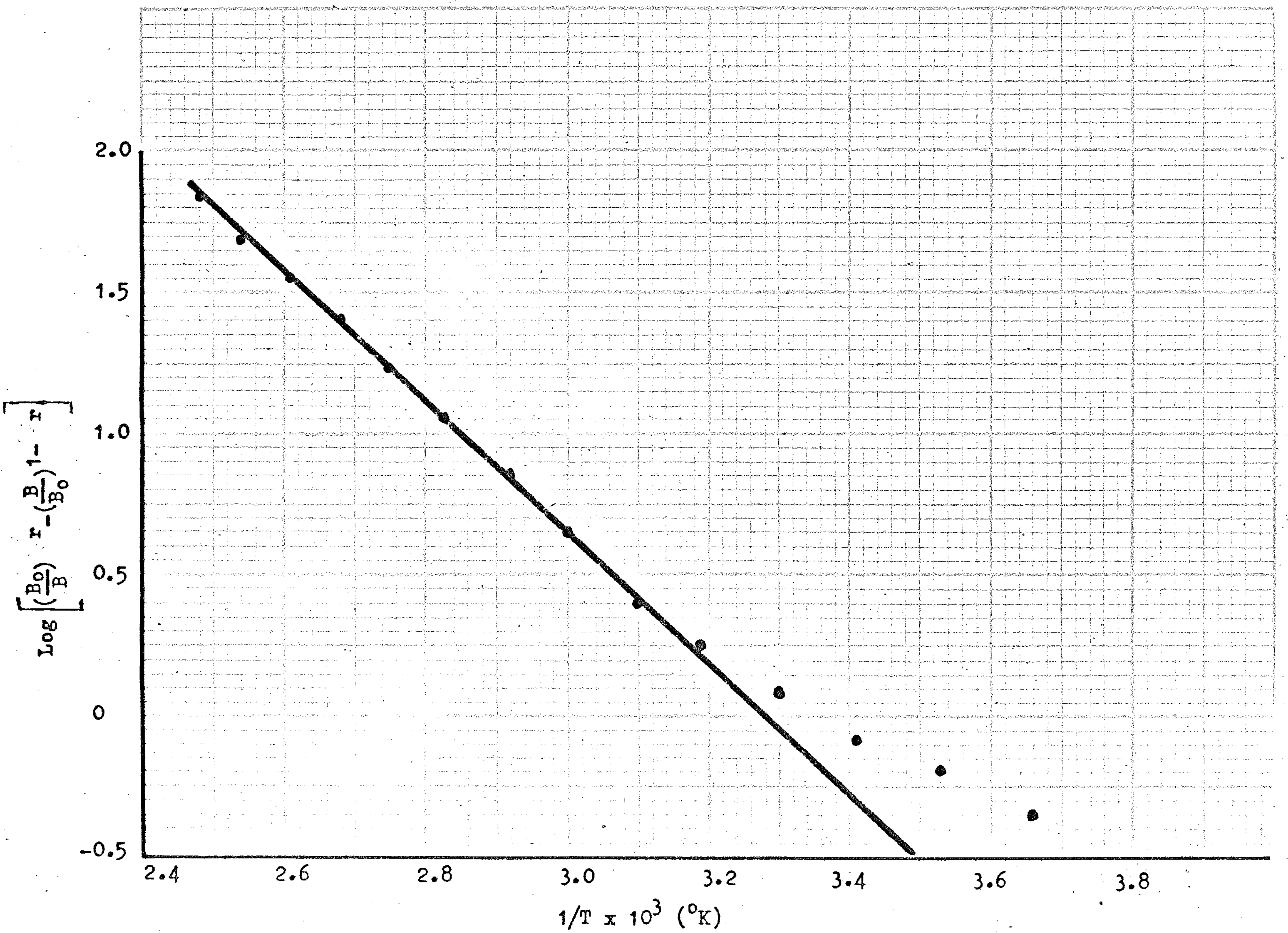
Thus a plot of

$$\log \left[(B_o/B)^r - (B/B_o)^{1-r}\right] \text{ v's } T^{-1} \qquad \text{---(6)}$$

should give a straight line with a slope $-E'/k$.

A graph of this function for a $[Zn(23\%)Cd]S$: $1{\cdot}8 \times 10^{-3}$ Ag: $6{\cdot}0 \times 10^{-6}$ Ni: 2·0% NaCl phosphor fired at 595°C for 45 min. in oxygen free nitrogen, which is typical of the phosphors prepared during this work, is shown in Figure 4 page 7.

FIGURE 4. Log $\left[\left(\frac{B_o}{B}\right)^{r} - \left(\frac{B}{B_o}\right)^{1-r} \right]$ v's 1/T for a $[Zn(23\%)Cd]S$: $1{\cdot}8 \times 10^{-3}$ Ag: $6{\cdot}0 \times 10^{-6}$ Ni: 2·0% NaCl phosphor fired at 595°C for 45 min. in oxygen free nitrogen.


2.0
1.5
1.0
0.5
0
-0.5
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
$\mathrm{Log}\left[\left(\frac{B_o}{B}\right)^r - \left(\frac{B}{B_o}\right)^{1-r}\right]$
1/T x 10^3 (°K)

The activation energy given by the straight line section of this curve is 0·46eV. In this case the superlinearity was measured at 140°C and was found to be equal to 2 (i.e. $r = \frac{1}{2}$). Curves were drawn using values of "r" other than $\frac{1}{2}$, but in all cases the deviations from linearity were in the same direction as is shown in Figure 4 page 7.

It can be seen therefore that the equation derived by Klasens is not applicable over the complete temperature range. It will be shown in Section 4a that the curve of log B v's T has the same basic shape for all the phosphors studied during this work. This means that, because the curve obtained in Figure 4 page 7 is not a straight line, Klasens' analysis does not describe any of the phosphors examined during this work.

2. INSTRUMENTATION

This can be divided into two parts:

(a) The furnace used to prepare the phosphors.

(b) The apparatus used to measure the temperature coefficient of the phosphors.*

2a The Furnace

The furnace consisted of a Kanthal wound silica tube placed in a metal box and insulated with diatomaceous earth. The temperature of the furnace was held just below the operating point by passing a continuous current through the windings. The small additional current required to bring the temperature up to the operating point was controlled by a temperature controller. This controller was operated by a chromel-alumel thermocouple placed in a thin walled silica tube in the centre of the hot zone directly above the position occupied by the centre of the boat in which the phosphor was fired.

With a constant heating current the variation in the furnace

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* This apparatus had been constructed in these laboratories some time before the commencement of this work. However, for completeness, a brief description of it is included.

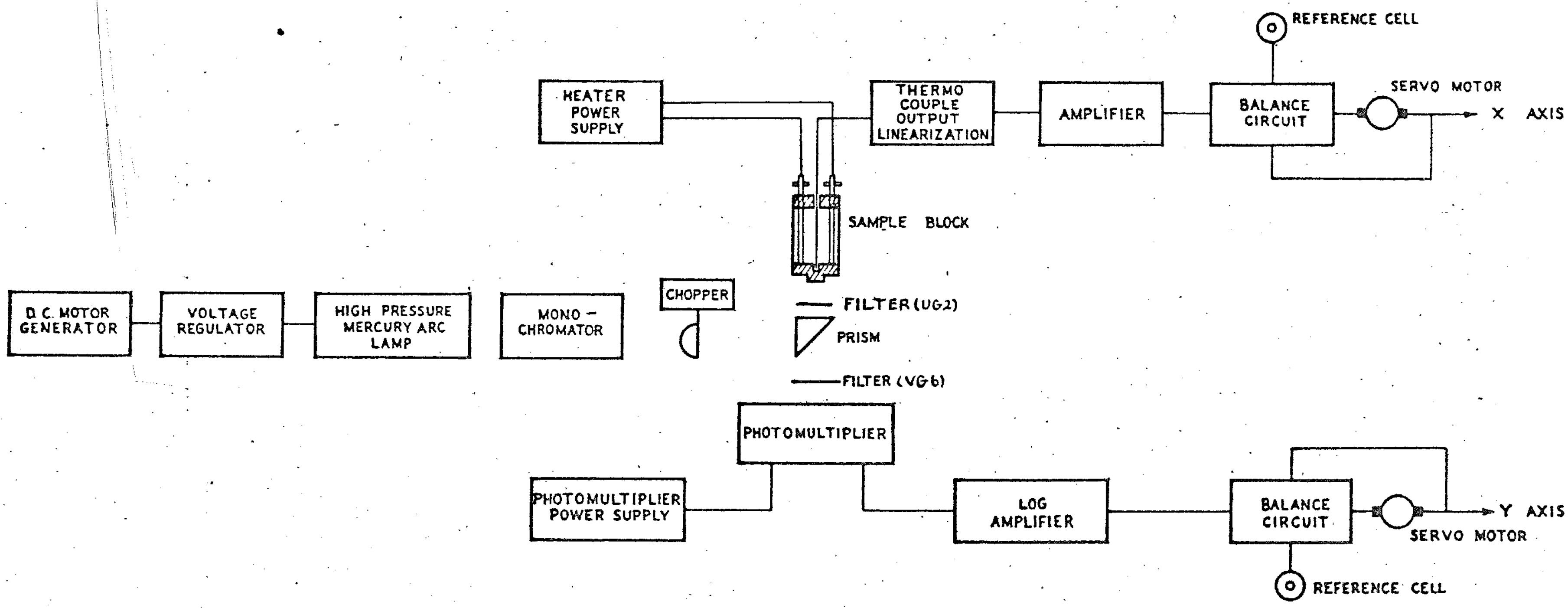


FIGURE 5. BLOCK DIAGRAM OF THE APPARATUS USED TO MEASURE THE TEMPERATURE COEFFICIENT OF THE PHOSPHORS.

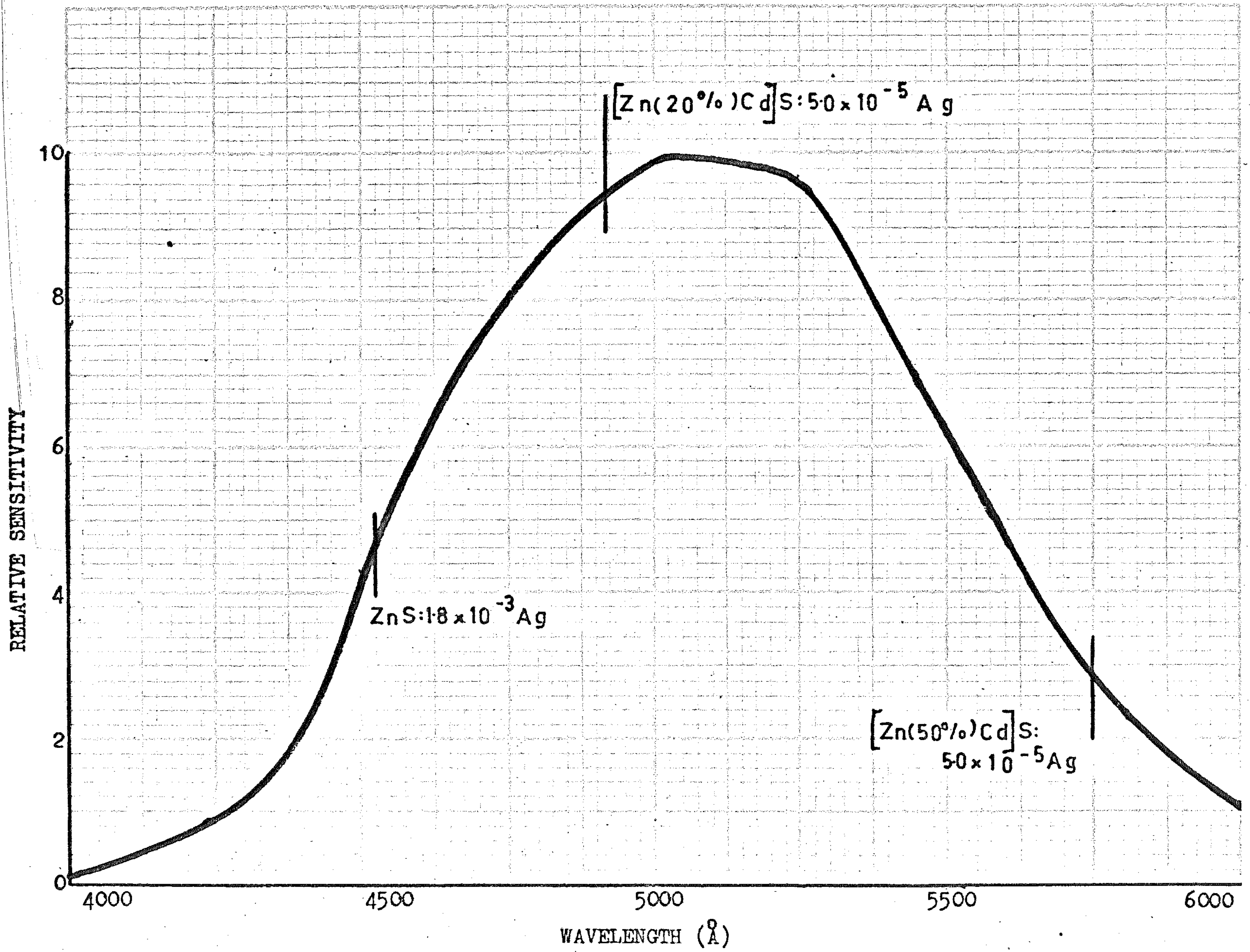
temperature over a distance of 4 inches (which was greater than the length of the boat used to hold the phosphor) was about ± 4°C at 600°C. This was measured using a chromel-alumel thermocouple and a potentiometer. In addition there was a ± 3°C swing between the "on" and "off" cycles of the controller. A further ± 4°C was allowed for possible misalignment of the boat and the thermocouple. It follows that the temperature of the phosphor was controlled, throughout its volume, to better than ± 11°C during the firing period. The nett effect on the properties of the phosphor introduced by this variation was small because the maximum temperature coefficient varied slowly when the firing temperature changed. This is shown in Figure 11 page 24.

2b. The Apparatus used to Measure Temperature Coefficient

A block diagram of the apparatus used to measure the temperature coefficient of the phosphors is shown in Figure 5 page 10.

The phosphor was excited by a 250W high pressure mercury arc lamp operated from a stabilized D.C. motor generator. The current through the lamp was set for the optimum operating condition. However variations in the arc were not completely eliminated. The 3650Å line was isolated by a Hilger quartz monochromator and its intensity was adjusted by varying the slit width. The intensity was set with reference to a tungsten lamp which was run at a constant current. A green filter, type VG6, was placed in front of the photomultiplier to reject any scattered ultraviolet radiation (U.V.). Consequently in order to adjust the U.V. intensity its wavelength had to be changed for it to be transmitted by the

FIGURE 6. Relative spectral sensitivity of the detector system of the apparatus used to measure the temperature coefficient of the phosphors.


[Zn(20%)Cd]S:5·0×10^{-5} Ag
ZnS:1·8×10^{-3}Ag
[Zn(50%)Cd]S:
5·0×10^{-5}Ag
RELATIVE SENSITIVITY
0
2
4
6
8
10
4000
4500
5000
5500
6000
WAVELENGTH (Å)

filter. This was achieved by placing a thick wad of filter papers, which are effectively pure cellulose, over the photomultiplier housing. The intensity of the luminescence of these papers gave a measure of the U.V. intensity. The papers used were of the highest quality in order to ensure good batch to batch uniformity. Over the region of interest the brightness output of the filter papers was found to be a linear function of the U.V. input. In order to measure the superlinearity of the phosphor the radiation from the monochromator was attenuated, at a frequency of 1 cps, by a 0·24 absorptance neutral density filter, which eliminated the errors which would have arisen due to inaccuracies in setting the U.V. input and those due to variations in the intensity of the lamp during a measurement.

The output of the phosphor, after passing through the green filter, was detected by a photomultiplier.

The relative spectral sensitivity of the filter-photomultiplier combination is shown in Figure 6 page 12. The peak of the emission spectrum of several typical phosphors is also shown. When the phosphor is heated the peak of the emission spectrum shifts 0·4 to 1·0 $\mathring{A}/^{o}K$ towards longer wavelengths[11]. It can be seen from Figure 6 that, over a range of $100^{o}K$, this would have only a small effect on the shape of the log B v's T curve.

The output from the photomultiplier was fed through a logarithmic amplifier, having its output calibrated in db, to the pen (Y-axis) of an X-Y recorder. The current in the photomultiplier was proportional to the intensity of the light falling on it. Hence, because the output of the photomultiplier was recorded in db, the recorder read in units of $10 \log (B/B_o)^2$. This meant that a change of 1 decade in the luminescent intensity of the phosphor gave rise to a change of 20 db at the recorder.

The phosphor sample was slurried with a small amount of deionized water and then placed on a copper block and allowed to dry. The block was heated by passing a current through two spring loaded carbon contacts or cooled by a stream of cold, dry air, obtained by boiling liquid air. The temperature of the block was monitored by a copper-constantan thermocouple soldered into the block close to the phosphor. The thermocouple output, after linearization and amplification, was fed into the drum amplifier (X-axis) of the X-Y recorder. The apparatus, therefore, plotted the logarithm of the luminescent intensity of the phosphor (in db) against temperature (in °C).

Hence the curves had the form:

$$20\log(B/B_o) = f(T). \qquad \text{---(7)}$$

Changing to natural logs,

$$20\ln(B/B_o)/2\cdot3 = f(T). \qquad \text{---(8)}$$

Differentiating,

$$20\Delta B/2\cdot3\ B\Delta T = \Delta f(T)/\Delta T. \qquad \text{---(9)}$$

But, by definition,

$$\text{temperature coefficient} = \Delta B/B\Delta T \qquad \text{---(10)}$$

and hence $= 2{\cdot}3\Delta f(T)/20\Delta T$ ——(11)

$= 11{\cdot}5\Delta f(T)/\Delta T\%/^{\circ}C.$ ——(12)

Thus, by measuring the slope of the curves drawn by the apparatus, the temperature coefficient could be easily calculated.

The temperature coefficient of the phosphors is negative, but, for simplicity, the sign will, in general, be ignored.

The linearity of the temperature scale of the recorder was checked by placing the copper block in glycerol at 0°C and warming it slowly to 140°C. The greatest difference between the true temperature, as measured by a mercury thermometer immersed in the glycerol, and that indicated by the recorder was less than 1¼°C.

The calibration of the logarithmic converter was checked by using two 50 db decade attenuators, in series, as the input to the converter. This calibration was checked frequently and kept adjusted so that the deviation between the true value and the value as indicated by the recorder was less than 0•5 db. The useable range of the converter was about 55 db. However, it was possible to extend the range over which the luminscent intensity of the phosphor could be measured. This was done by adjusting the voltage across the photomultiplier, thus changing the output of the logarithmic converter at a given intensity of the standard lamp. This brought the converter back into its operating range. Using this method it was possible to measure the luminescent intensity of some of the phosphors over as much as 4 decades.

When working at very low intensities the dark level of the appara-

FIGURE 7. Log B v's T for Zn(23%)Cd S: 1·8 x 10^{-3}Ag: 2·0% NaCl fired at 595°C for zero min. in an atmosphere of oxygen free nitrogen. Curves are shown for various values of the exciting 3650Å radiation.

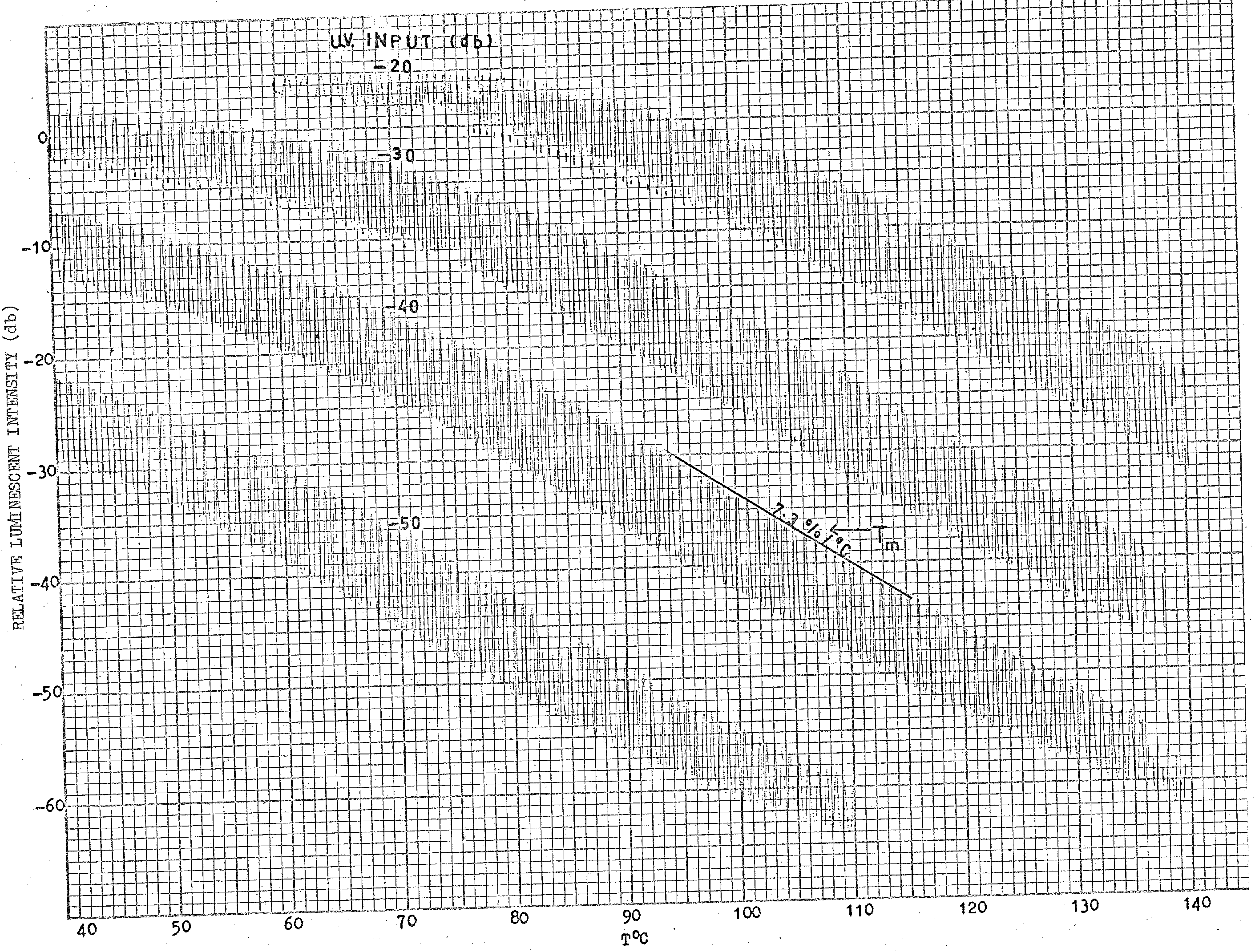
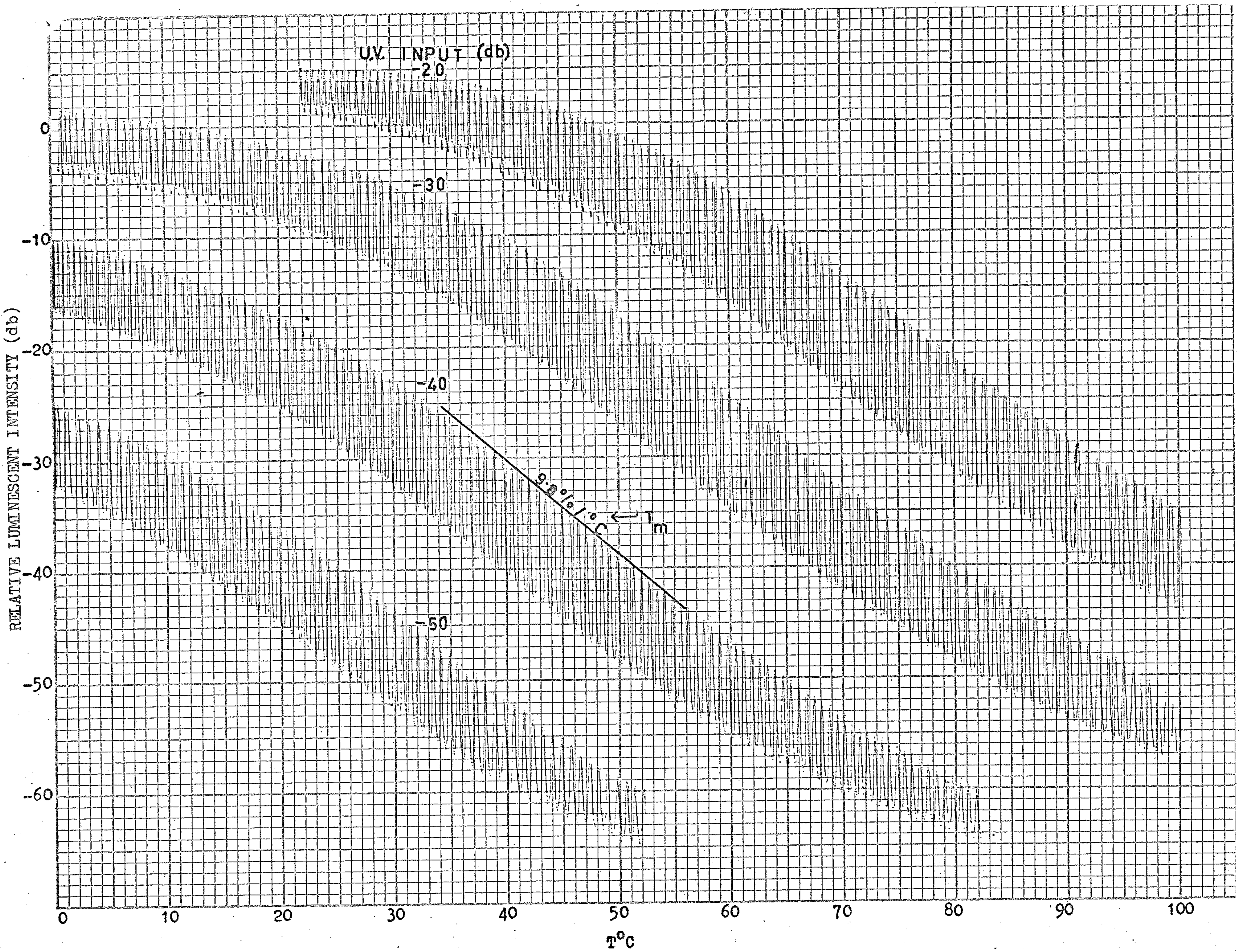

U.V. INPUT (db)
-20
-30
-40
-50
0
-10
-20
-30
-40
-50
-60
RELATIVE LUMINESCENT INTENSITY (db)
7.3 %/°C
T_m
40
50
60
70
80
90
100
110
120
130
140
T°C

FIGURE 8. Log B v's T for $[Zn(23\%)Cd]S$: $1{\cdot}8 \times 10^{-3}$ Ag: $6{\cdot}0 \times 10^{-6}$ Ni: $2{\cdot}0\%$ NaCl fired at 595°C for 45 min. in an atmosphere of oxygen free nitrogen. Curves are shown for various values of the exciting 3650Å radiation.


U.V. INPUT (db)
-20
-30
-40
-50
9.0 %/°C
Tm
RELATIVE LUMINESCENT INTENSITY (db)
0
-10
-20
-30
-40
-50
-60
T°C
0
10
20
30
40
50
60
70
80
90
100

tus had to be taken into account. The approximate dark level for various values of the U.V. input is shown in Table 1.

U.V. input (db)	Dark level (db)
-20	-68
-30	-78
-40	-84
-50	-88

TABLE 1 The value of the dark level of apparatus used to measure the temperature coefficient for various values of the U.V. input.

The dark level was partly due to small phosphor particles lodged in various parts of the photomultiplier housing. This would explain the variation in the dark level with the U.V. input. Some contribution to the dark level could come from the luminescence of various parts of the photomultiplier housing. Some of the luminescence of the housing was absorbed by a U.G.2 filter which was placed over the prism in the apparatus in the manner shown in Figure 5 page 10.

Typical curves drawn by the instrument are shown in Figures 7 and 8 on pages 16 and 17.

3. EXPERIMENTAL

3a Phosphor Preparation

The phosphors were prepared from luminescent grade zinc and cadmium sulphides. The silver, as silver nitrate, nickel, as nickel chloride, and sodium chloride flux, all of analytical reagent grade, were added as aqueous solutions. The water used in the preparation of these solutions was first distilled in glass and then deionized.

The flux and cadmium concentrations are expressed as mole % and the activator and killer concentrations as mole parts of the basic zinc-cadmium matrix. All the concentrations are those added before firing.

The zinc and cadmium sulphides were thoroughly ground and mixed. They were then slurried with the appropriate amounts of activator, killer and flux solutions. The slurries were dried in air at about 160°C. They were then ground and mixed, using an agate pestle and mortar, before being placed in an open silica boat. The phosphors were fired in lots of about 5 grams.

All glass and silica ware used in the preparations was first washed in hot aqua regia and then thoroughly rinsed in deionized water.

After firing, the phosphors had a thin rind which luminesced less brightly than the bulk of the sample. This rind was scraped off and discarded. Grinding, which decreases the maximum temperature coefficient of the phosphors, was avoided after the phosphors had been fired.

Zinc sulphide phosphors are very sensitive to impurities, so, to guard against accidental contamination and to check that the preparation technique was kept constant, several phosphors were duplicated at different times during this work. Although some small variations in the luminescent colour and intensity of the reproduced phosphors were observed, the maximum temperature coefficients usually fell within ± 10% of the previous value. This value was adopted as the criterion of a satisfactory preparation and so when a best fit curve was drawn through a set of points of the maximum temperature coefficient v's some variable, e.g. silver concentration, the maximum acceptable deviation of a point from the curve was ± 10% of the maximum temperature coefficient. The few phosphors that did not satisfy this criterion were discarded and the preparation was repeated. The ± 10% variation from the mean value probably arose from two main causes:

(1) Slight variations in the technique of preparing the phosphors.

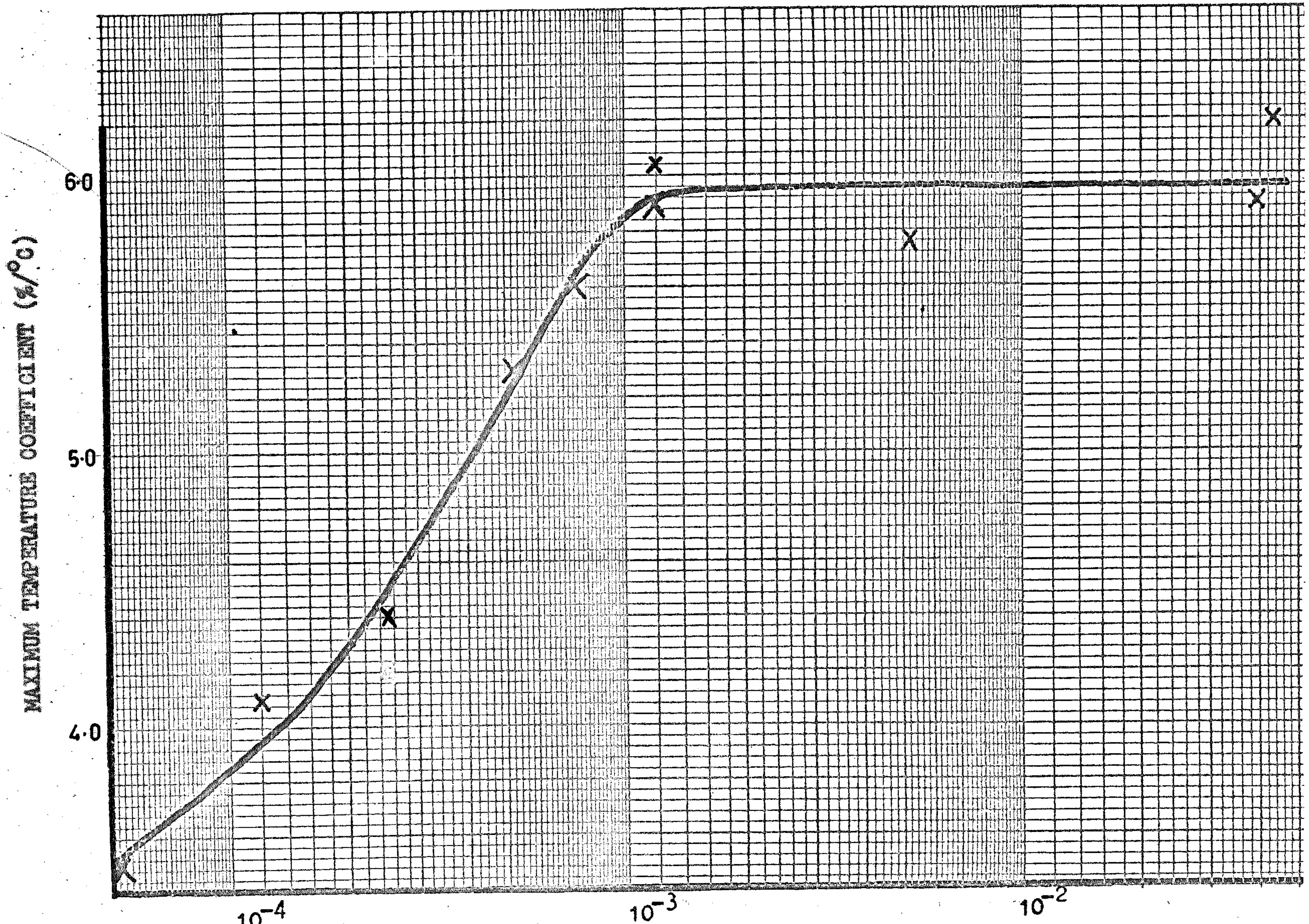
(2) Experimental error in measuring the maximum temperature coefficient of the samples, particularly in assessing the gradient of the curves.

The few phosphors whose maximum temperature coefficient fell outside this allowed variation were probably accidentally contaminated during their preparation.

3b The Effect of Silver Concentration

The effect on the temperature coefficient of varying the silver

FIGURE 9. Maximum temperature coefficient v's silver concentration of $[Zn(23\%)Cd]S$: x Ag: 2·0% NaCl fired at 595°C for 120 min. in oxygen free nitrogen.



← 30%/°C at zero
silver concentration

concentration was found by preparing several phosphors with the general formula [Zn(23%)Cd] S: xAg. The silver concentrations ranged from 0 to $4{\cdot}4 \times 10^{-2}$ mole parts. The phosphors were all prepared using a 2 mole % NaCl flux.

The furnace conditions were kept constant throughout this series at 590 ± 25°C. (At this time the furnace was wired so that the temperature controller switched the full furnace current. It was not until later it was rewired so that only a small proportion of the current was switched.). The phosphors were fired for 120 min. in a stream of dry oxygen free nitrogen. They were then allowed to cool in the furnace to a temperature of about 315°. This took approximately 1 hour.

Figure 9 page 21 shows a graph of the maximum temperature coefficient against the silver concentration. It can be seen that the maximum temperature coefficient rose steadily with increasing silver concentration until it reached a limiting value of 6·0%/°C at approximately 1×10^{-3} mole parts of silver.

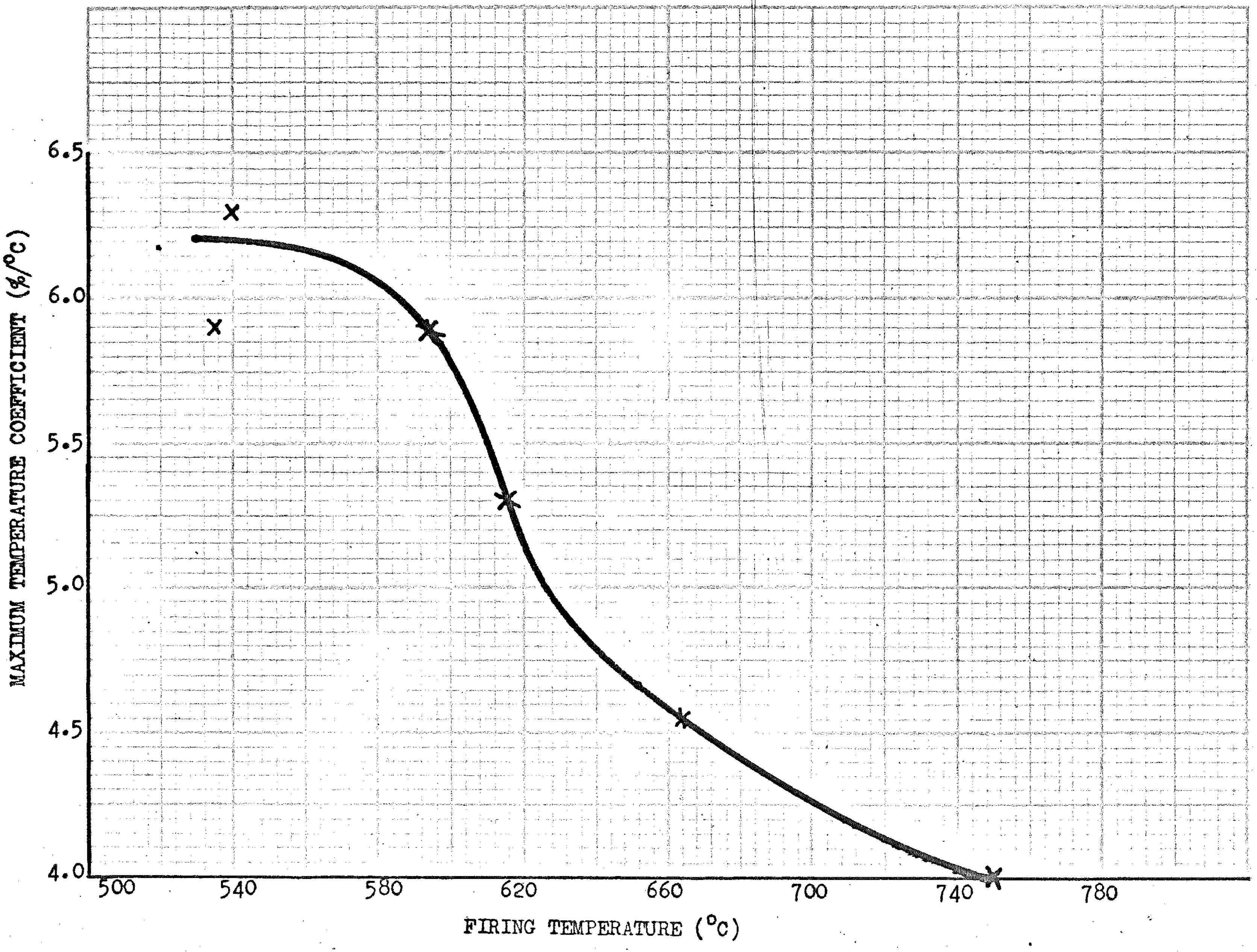
Another effect which occured when the silver concentration was increased was a shift towards shorter wavelengths in the peak of the emission spectrum of the phosphor. This shift appeared to occur until the silver concentration reached about 1×10^{-3} mole parts. This shift would not affect the shape of the log B v's T curves, but would cause a shift in the origin along the intensity axis. This observation is confirmed by the emission spectra given by Leverenz[12]. The increase in the maximum temperature is probably due to the corresponding decrease in the effective energy gap between the valence band and the activator level.

The spectral emission curves given by Leverenz show only a single peak. However, this could be because the shift in the emission peak of approximately 150Å when the silver concentration is increased from zero to $5{\cdot}1 \times 10^{-3}$ mole parts is smaller than the half width of the emission band, which is at approximately 800Å. This shift could therefore have arisen because of competition between self-activated and silver activated emission processes. This is shown diagramatically in Figure 10 page 26.

However, these levels would be sufficiently close together to be considered as a single level whose position, with respect to the valence band, depended on the silver concentration. Associated with the levelling off of Figure 9 was a decrease in the luminescent efficiency of the phosphors. There was also a change, from pale yellow to dark grey, in the colour of the phosphors under white light. This could be because the base matrix had become saturated with silver and any additional silver did not go into the solid solution[13]. Alternatively at high silver concentrations centres that absorb in the visible could be formed.

An interesting feature of the log B v's T curves is the temperature (T_m) at which the maximum temperature coefficient occurred at a given value of the U.V. input. Table 2 gives the value of T_m at -40 db U.V. input for various silver concentrations.

FIGURE 11. Maximum temperature coefficient v's firing temperature of $[\mathrm{Zn}(23\%)\mathrm{Cd}]\mathrm{S}$: $1{\cdot}8 \times 10^{-3}$ Ag: $2{\cdot}0$ NaCl fired at x°C for 120 min. in oxygen free nitrogen.


6.5
6.0
5.5
5.0
4.5
4.0
MAXIMUM TEMPERATURE COEFFICIENT (%/°C)
500
540
580
620
660
700
740
780
FIRING TEMPERATURE (°C)

Silver Concentration (mole parts)	T_m(°C) at -40 db U.V. input
0	96
$5{\cdot}2 \times 10^{-5}$	112
$1{\cdot}2 \times 10^{-4}$	94
$2{\cdot}5 \times 10^{-4}$	93
$2{\cdot}6 \times 10^{-4}$	91
$5{\cdot}2 \times 10^{-4}$	92
$7{\cdot}7 \times 10^{-4}$	84
$1{\cdot}2 \times 10^{-3}$	93
$1{\cdot}2 \times 10^{-3}$	97
$5{\cdot}2 \times 10^{-3}$	98
$1{\cdot}2 \times 10^{-2}$	95
$4{\cdot}0 \times 10^{-2}$	85
$4{\cdot}4 \times 10^{-2}$	83
AVE	93

TABLE 2 T_m at -40 db U.V. input for phosphors with the general formulae $[Zn(23\%)Cd]S$: x Ag: 2•0% NaCl fired at 595°C for 120 min. in oxygen free nitrogen.

It can be seen from the table that T_m is practically constant and so is independent of the silver concentration.

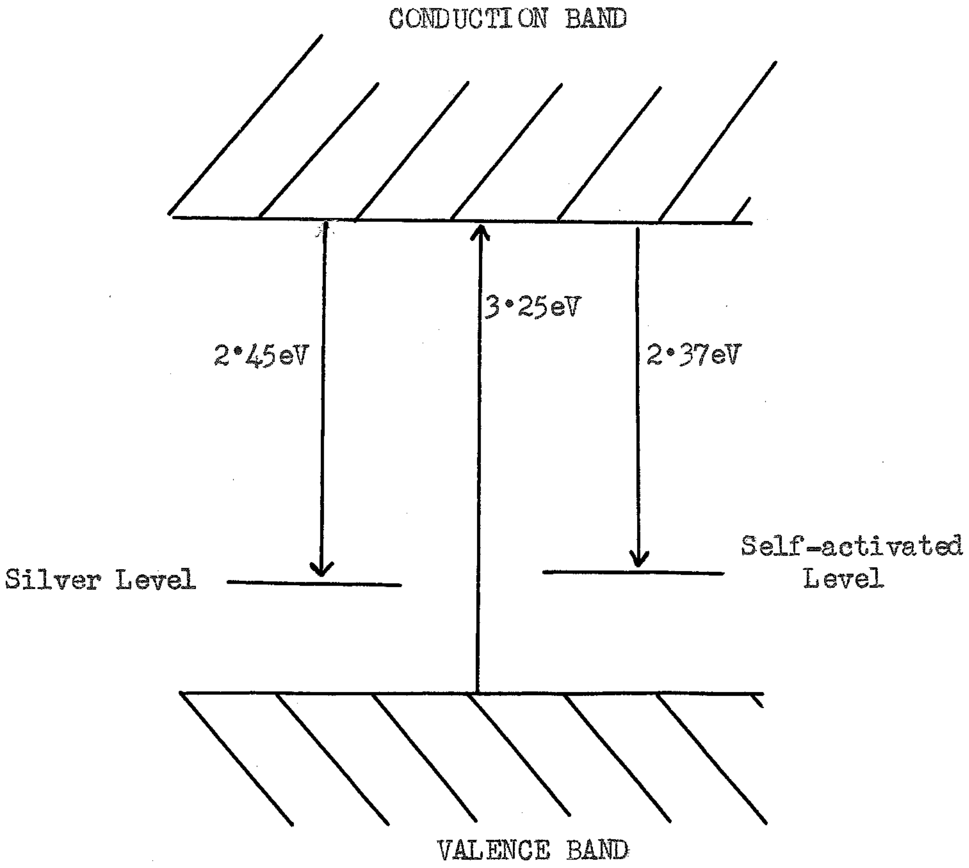


FIG. 10 Diagramatic representation of the silver and self-activated energy levels.

3c The Effect of the Firing Temperature

Figure 11 page 24 shows the variation of the maximum temperature coefficient with nominal firing temperature for [Zn(23%)Cd] S: $1 \cdot 8 \times 10^{-3}$Ag: 2•0% NaCl phosphors. These phosphors were fired for 120 min. in a stream of oxygen free nitrogen and allowed to cool in the furnace to approximately 315°C.

This was also done using a firing time of 45 min.

The results showed that as the firing temperature was increased the maximum temperature coefficient decreased. Also there was a reasonably sharp cut off at the low temperature end. This occurred at the point where the phosphor no longer activated, probably because the temperature was too low to allow the silver to diffuse into the lattice. The lack of activation was indicated by the failure of the phosphor to luminesce.

Associated with an increase in the firing temperature was a decrease in T_m. This is shown in Table 3, which includes phosphors prepared using two different firing times viz. 120 min. and 45 min. It also includes phosphors with different zinc-cadmium ratios. In all cases the silver concentration was about $1{\cdot}8 \times 10^{-3}$ mole parts. The values given are for -40 db U.V. input.

Zinc sulphide can exist in either of two crystalline modifications viz. cubic, which is the low temperature modification, and hexagonal, which occurs at higher temperatures. However cadmium sulphide exists only in the hexagonal form at all useful crystalization temperatures.

Ballentyne and Ray[14] have shown, using phosphors prepared at 1100°C and 700°C, that at low cadmium concentrations the phosphors are a mixture of cubic and hexagonal structures. They also showed that at the lower temperature there was a higher percentage of the cubic structure. Figure 11 can therefore be explained by assuming that as the firing temperature increased there was a gradual transition from the cubic to the hexagonal structure. It must also be assumed that the hexagonal silver activated zinc sulphide type phosphor has a lower temperature coefficient than the corresponding cubic form with the same cadmium content.

Composition (mole % Cd)	Firing time (min)	Furnace Temp. ($^\circ$C)	T_m($^\circ$C) at -40 db U.V. input
23	120	527	105
		536	86
		595 (ave)	93
		620	103
		670	87
		749	60
	45	595	100
		746	81
28	45	590	95
		675	83
		752	73
50	45	526	91
		599	90
		675	70
		735	46
0	45	675	100
		725	117

TABLE 3. T_m at -40 db U.V. input for phosphors with the general formulae $\left[Zn(x\%)Cd\right] S$: $1{\cdot}8 \times 10^{-3}$ Ag: 2·0% NaCl fired at y°C for z min.

Also, if it is assumed that T_m, for a given U.V. input, is lower for

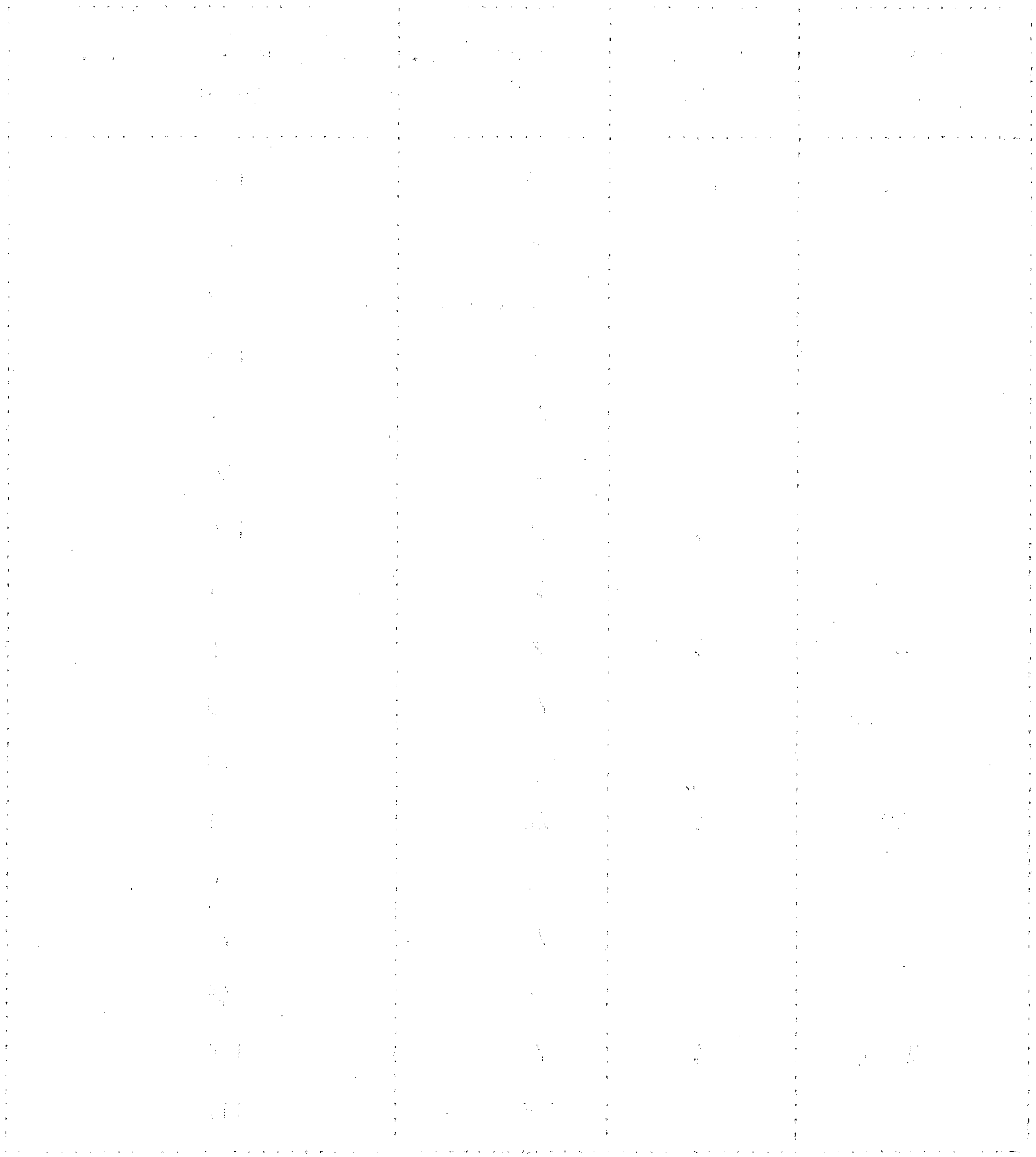
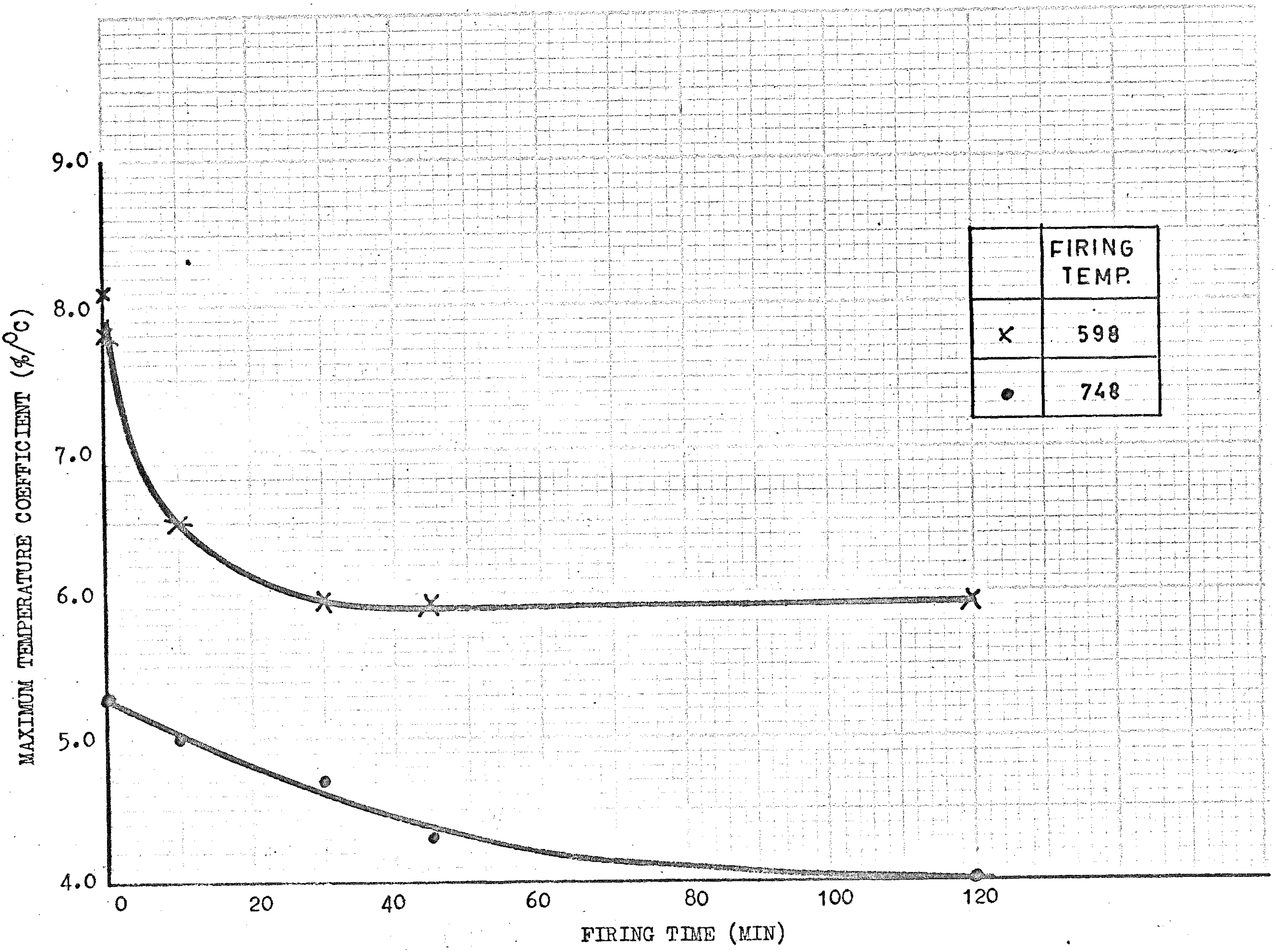


FIGURE 12. Maximum temperature coefficient v's firing time of [Zn(23%)Cd] S: $1{\cdot}8 \times 10^{-3}$ Ag: 2·0% NaCl fired for x min. in oxygen free nitrogen. Curves for firing temperatures of 598°C and 748°C are shown.


MAXIMUM TEMPERATURE COEFFICIENT (%/°C)
9.0
8.0
7.0
6.0
5.0
4.0
0
20
40
60
80
100
120
FIRING TIME (MIN)
FIRING TEMP.
× 598
● 748

the hexagonal structure, the figures given in Table 3 can be explained in a similar manner. It is obvious that further experimental evidence is required to confirm this theory.

An attempt was made to measure the cubic to hexagonal ratio of these phosphors by using a polarizing microscope to measure the number of anisotropic particles. However no effect was observed, possibly because any effect could have been obscured by light scattered by the particles.

It may be possible to eliminate the scattering by embedding the particles in a medium of suitable refractive index.

Other possible ways of measuring the cubic-hexagonal ratio are X-ray diffraction and the electronic paramagnetic resonance technique that has been described by Aven and Parodi[15].

3d The Effect of the Firing Time

(1) Preparation of the phosphors

To find the effect of varying the firing time, at a given furnace temperature, a series of phosphors with the general formula $[Zn(23\%)Cd]S$: $1{\cdot}8 \times 10^{-3}$Ag: 2·0% NaCl was prepared. Firing temperatures of 598°C and 748°C were used.

The furnace was preheated to the required firing temperature and then the boat, containing the phosphor, was pushed into the furnace and located centrally in the hot zone. When the boat was inserted the indicated furnace temperature decreased by about 30°C. To compensate for this the heating current was increased. The firing time was taken from the time when the furnace temperature was about 2°C below the required firing temperature. The heating current was then reduced to its operating value. The time required for the furnace temperature to reach its operating value was approximately 5 min.

When the phosphor had been fired for the required time it was allowed to cool in the furnace to a temperature of approximately 315°C.

The uniformity of these phosphors, even with zero minutes firing time, was equivalent to that of the phosphors prepared with longer firing times.

(2) Results

It can be seen from Figure 12 page 29 that the maximum temperature coefficient of the phosphors decreased when the firing time was increased. Also the ratio maximum temperature coefficient at zero minutes firing time/maximum temperature coefficient at 120 min. firing time was, within the limits of the experimental error, independent of the firing temperature for the two temperatures considered here.

It can be seen from Table 4 that T_m is, more or less, independent of firing time.

The variation in the maximum temperature coefficient with firing time was found to be independent of the silver concentration. This was found by preparing two self-activated phosphors with the composition $[Zn(23\%)Cd]S$: 2·0% NaCl by firing them at 598°C for 120 min. and 0 min. respectively. The ratio maximum temperature coefficient at 0 min. firing time/maximum temperature coefficient at 120 min. firing time was the same for both the self-activated and silver activated phosphors.

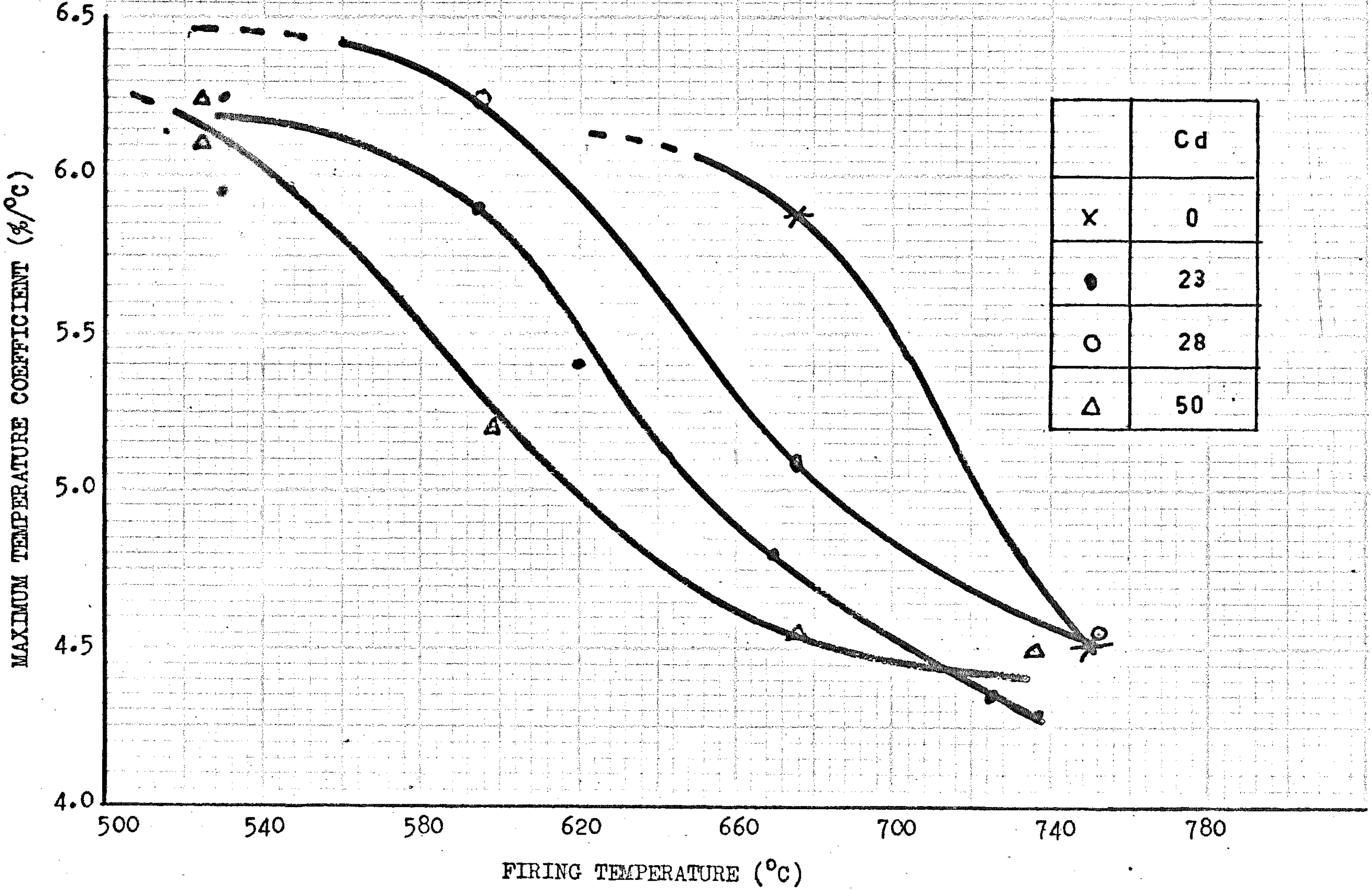
Firing Time (min)	Furnace Temp. (^{o}C)	T_m(^{o}C) at -40 db U.V. input
120 (ave)	598	93
45	595	101
30	598	101
10	598	83
0	598	88
0	598	93
120	749	60
45	749	81
30	742	65
10	742	69
0	745	87

TABLE 4. T_m at -40 db U.V. input for $[Zn(23\%)Cd]S: 1{\cdot}8 \times 10^{-3}Ag:$ 2·0% NaCl phosphors fired at x^{o}C for y min.

(3) Discussion

During this series it was observed that the average particle size of the phosphors decreased when the firing time was decreased. A series of commercial zinc sulphide type phosphors (obtained from Derby Luminescents Ltd) had been separated in these laboratories, by sedimentation, into particle size ranges and the maximum temperature coefficient of each range was measured. The ranges used were less than 1μ, 1-2μ, 5-10μ and greater than 10μ. It was found that the maximum temperature

FIGURE 13. Maximum temperature coefficient v's firing temperature of $[Zn(x\%)Cd]S$: $1{\cdot}8 \times 10^{-3}$ Ag: 2·0% NaCl fired at y°C for 45 min. in oxygen free nitrogen. Curves are shown for cadmium concentrations of 0, 23, 28 and 50 mole %.

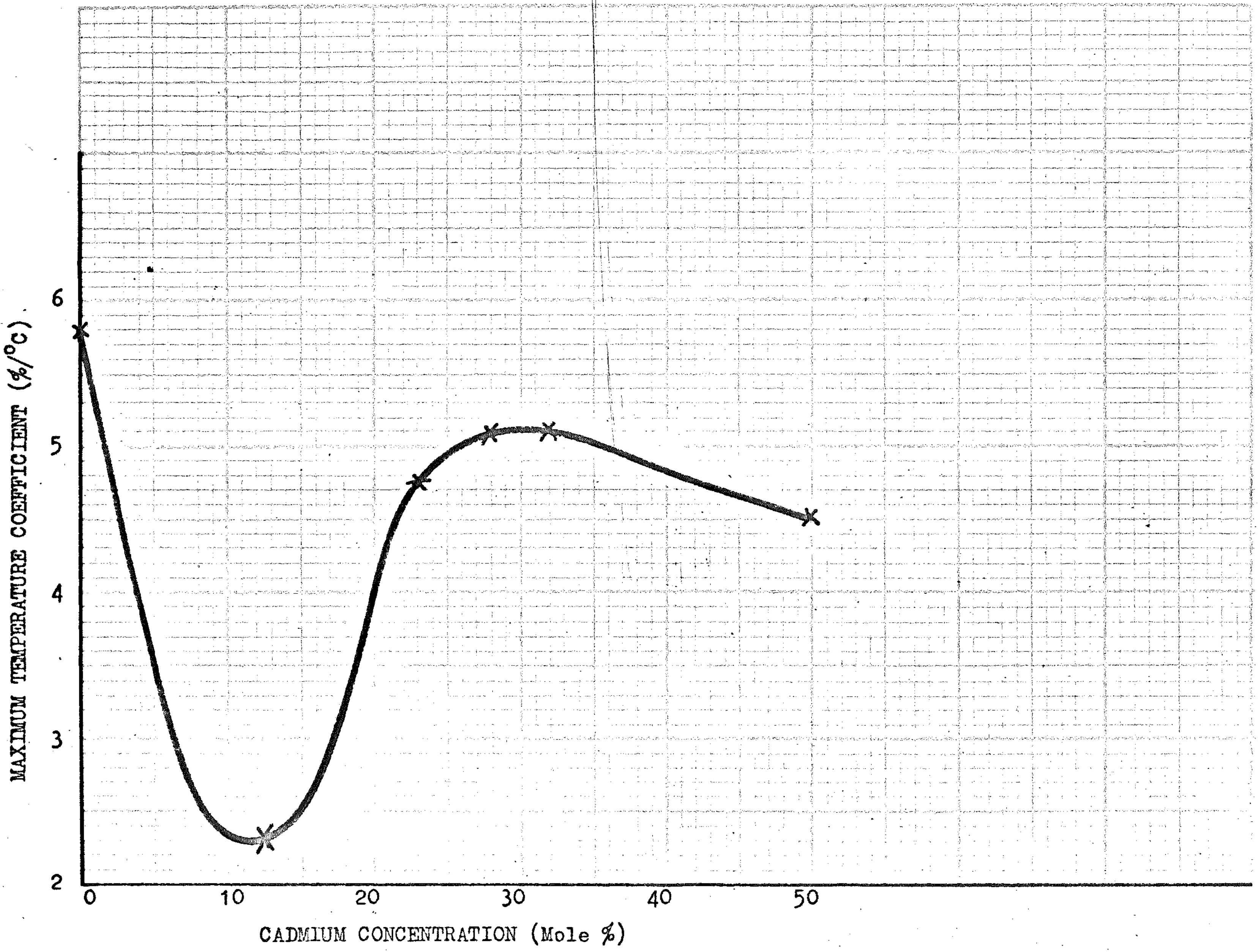

6.5
6.0
5.5
5.0
4.5
4.0
MAXIMUM TEMPERATURE COEFFICIENT (%/°C)
500
540
580
620
660
700
740
780
FIRING TEMPERATURE (°C)
Cd
X 0
● 23
O 28
Δ 50

coefficient was independent of particle size except for the smallest particles. These were discarded because many of them had failed to activate.

It would be expected that there would be some evaporation of the phosphor components during the firing and that the amount evaporated would depend on the firing time. Therefore two phosphors were prepared in capsules that were evacuated, filled with dry oxygen free nitrogen and then sealed off. These capsules were fired at 595°C for 45 min. and 0 min. respectively. It was found that, although there could not have been any evaporation of the phosphor components, the ratio maximum temperature coefficient at zero minutes firing time/maximum temperature coefficient at 45 min. firing time was very nearly the same as that obtained for phosphors fired in an open boat. There was, however, a small difference in the absolute values of the maximum temperature coefficients between the encapsulated and unencapsulated cases. This will be discussed further in Section 3g page 45, where it will be suggested that this difference was probably due to a small percentage of oxygen being incorporated in the phosphors prepared in the open boats.

Because the ratio maximum temperature coefficient at zero minutes firing time/maximum temperature coefficient at 120 min. firing time is independent of the silver concentration it appears that the variation in the maximum temperature coefficient with firing time was dependent on a lattice effect rather than an impurity effect. A lattice variation could cause a change in the recombination mechanism. This appeared to be supported in the case of the self-activated phosphors by the phosphores-

FIGURE 14. Maximum temperature coefficient v's cadmium concentration of $[\mathrm{Zn}(x\%)\mathrm{Cd}]\mathrm{S}$: $1\cdot8 \times 10^{-3}$ Ag: 2·0% NaCl fired at 675°C for 45 min. in oxygen free nitrogen.


MAXIMUM TEMPERATURE COEFFICIENT (%/°C)
6
5
4
3
2
0
10
20
30
40
50
CADMIUM CONCENTRATION (Mole %)

cent decay. The self-activated phosphor fired for zero minutes had no observable phosphorescence but that fired for 120 min. had a fairly long decay time (i.e. of the order of seconds). This effect indicated the presence of electron traps in the phosphor that was fired for 120 min.

Because the maximum temperature coefficient was measured under equilibrium conditions, the thermal release of electrons from these traps would not have any significant effect on it. However, the appearance of these traps could be associated with some change in the mechanism causing the log B v's T curves. It may be possible to obtain further information on this point by measuring the rise and decay times of these phosphors. This effect was not apparent with the silver activated phosphors. However, the addition of the silver may merely shorten the time constants involved in such a way as to make the effect unobservable to the unaided eye.

A further interesting effect was that the colour of the phosphors under visible light depended on the firing time. The self-activated phosphor fired for zero min. was white while that fired for 120 min. was pale yellow. For the unencapsulated, silver activated phosphors the colour changed from grey to yellow-grey. In the case of the encapsulated phosphors the colour changed from white to grey. It appeared therefore, as if some type of centre which absorbs in the visible was formed.

3e. The Effect of the Zinc-Cadmium Ratio

Several phosphors, with the general formula

$\left[Zn(x\%)Cd\right]S\colon 1{\cdot}8 \times 10^{-3} Ag\colon 2{\cdot}0\%\ NaCl$, were prepared at firing temperatures between 525°C and 750°C. Firing times of 45 min. and 120 min. were used.

Four compositions (0, 23, 28 and 50 mole % cadmium) were studied over a range of furnace temperatures and two compositions (12 and 32 mole % cadmium) were studied using a firing temperature of 675°C.

Figure 13 page 33 shows the variation in the maximum temperature coefficient with firing temperature for four zinc-cadmium ratios. The firing time used was 45 min. in an atmosphere of oxygen free nitrogen. It can be seen that each of these curves has the characteristics that were discussed in relation to Figure 11 page 24. The low temperature cut off shifts to lower temperatures when the Cd concentration increases. The approximate cut off is indicated in Figure 13 page 33 by the low temperature end of the curves. In all cases a phosphor was fired at a temperature that was too low to allow it to activate. This is probably because the addition of cadmium sulphide to the base matrix allows the silver to diffuse into the lattice at lower temperature. This idea is supported by the "Tammann principle", which relates the temperature at which diffusion starts to take place to the melting point of the solid[16]. Because cadmium sulphide has a lower vaporization temperature than zinc sulphide it would be expected that phosphors with a high cadmium content would activate at a lower temperature than those with a lower cadmium content.

Figure 14 page 35 shows the maximum temperature coefficient against the cadmium concentration for a series of phosphors fired at 675°C. This curve has two turning points, a minimum at about 12 mole %

FIGURE 15. Maximum temperature coefficient v's nickel concentration of $[\mathrm{Zn}(23\%)\mathrm{Cd}]\,\mathrm{S}$: $1{\cdot}8 \times 10^{-3}$ Ag: x Ni: 2·0% NaCl fired at 595°C for 45 min. in oxygen free nitrogen.

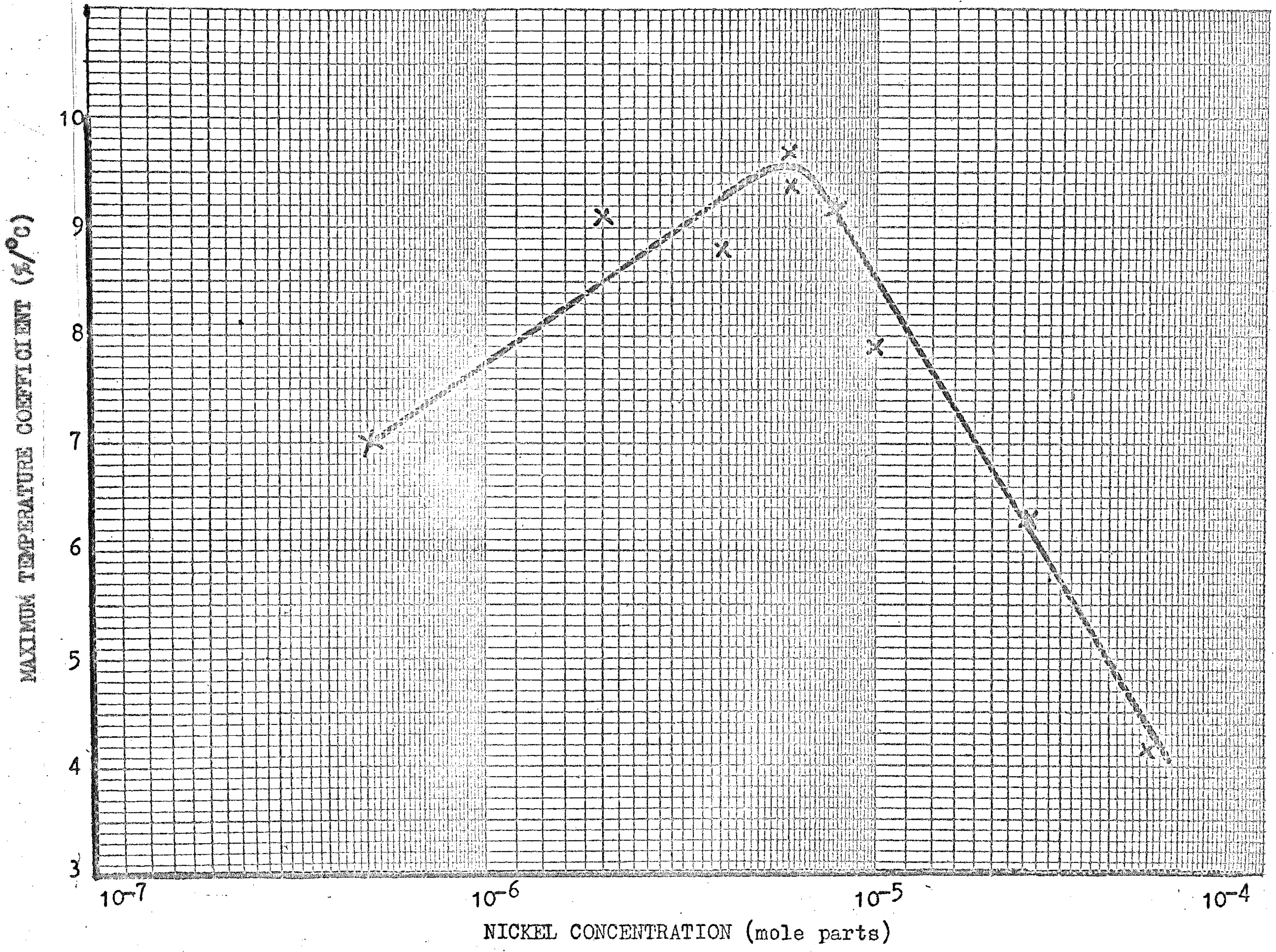
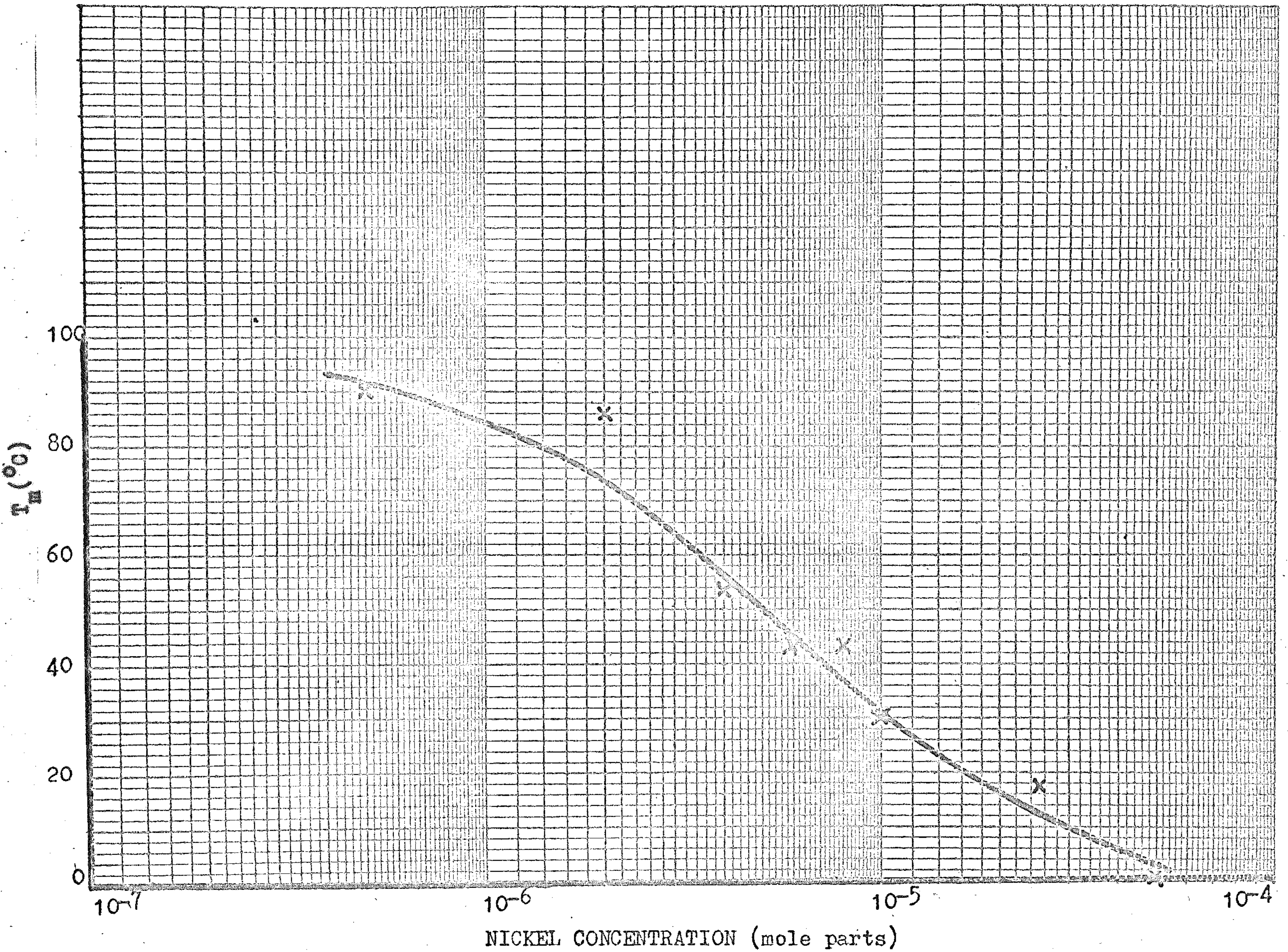

MAXIMUM TEMPERATURE COEFFICIENT (%/°C)
10
9
8
7
6
5
4
3
10^{-7}
10^{-6}
10^{-5}
10^{-4}
NICKEL CONCENTRATION (mole parts)

FIGURE 16. T_m v's nickel concentration for $[Zn(23\%)Cd]S$: $1{\cdot}8 \times 10^{-3}$Ag: xNi: 2·0% NaCl fired at 595°C for 45 min. in oxygen free nitrogen.


100
80
60
40
20
0
T_H (°C)
10^{-7}
10^{-6}
10^{-5}
10^{-4}
NICKEL CONCENTRATION (mole parts)

cadmium and a maximum at about 30 mole % cadmium.

When considering the effect of varying the cadmium concentration several factors must be taken into account.

Any change that may occur in the energy gap between the activator band and the valence band (ΔE) would be expected to affect the temperature coefficient. It was found in Section 3b pages 20 to 25 that when the silver concentration increases the corresponding decrease in ΔE is accompanied by an increase in the maximum temperature coefficient while T_m remains constant.

L. Drodz and V. Levshin[17], using emission and absorption spectra, have found that, over the range of cadmium concentrations considered here, ΔE decreases when the cadmium concentration increases. These measurements were carried out on self-activated phosphors. It is probable that a similar effect occurs for silver activated phosphors. It would be expected therefore that the decrease in ΔE would affect the maximum temperature coefficient and T_m in the manner discussed above.

It has been suggested in Section 3c pages 26 to 30, that when the hexagonal content of the phosphors increases, both the maximum temperature coefficient and T_m decrease. A. Dreeben[18] has shown that increasing the cadmium concentration, at a given firing temperature, increases the hexagonal content of the phosphor. This would be expected to cause a corresponding decrease in both T_m and the maximum temperature coefficient.

Table 3 page 28 shows that T_m does decrease when the cadmium concentration is increased at a given firing temperature.

However, it is difficult to explain the double peaked nature of

Figure 14 page 35 as a combination of these two effects. This could be associated with an observable phosphorescence that occurred with the 10 mole % cadmium phosphors, but which did not occur to any significant extent with any of the other cadmium concentrations considered here. Associated with the phosphorescence was an increase in the rise time of the 10 mole % cadmium phosphors. As has been previously discussed in Section 3d pages 34 and 36, this effect could be associated with a change in the mechanism of the log B v's T effect.

Previously it had been assumed that when there was a mixture of cubic and hexagonal structures the phosphor consisted of some microcrystals that were cubic in structure and some that were hexagonal. However, if it is assumed that at low cadmium concentrations a single microcrystal is part cubic and part hexagonal, then the strains introduced into the lattice due to this may give rise to the trapping levels associated with the phosphorescence. Evidence of this type of structure has been found by T. Koda and S. Shionoya[19].

It is interesting to note that L. Drodz and V.L. Levshin[17] found that a plot of the luminescent intensity of the room temperature self-activated emission band against Cd concentration has two turning points. These points are in approximately the same position as those described above. They also found that these turning points were absent when the phosphors were prepared by firing them at 1200°C where the phosphors would have been completely hexagonal in structure.

3f The Effect of Nickel

The effect of nickel, which gives rise to killer type centres, on the maximum temperature coefficient was found by preparing a series of phosphors with the general formula $[Zn(23\%)Cd]S$: $1{\cdot}8 \times 10^{-3}$Ag: $xNiCl_3$: 2·0% NaCl. These phosphors were fired for 45 min., at 595°C, in a stream of dry oxygen free nitrogen and then allowed to cool in the furnace to approximately 315°C.

The maximum temperature coefficient increased from 6·0%/°C, which was the value without any killer, to a maximum of 9·5%/°C, which occurred at approximately $6{\cdot}0 \times 10^{-6}$ mole parts of nickel. When the nickel concentration was increased beyond this value the maximum temperature coefficient decreased. This is shown in Figure 15 page 38.

Associated with the increase in nickel concentration was a monotonic decrease in T_m, as is shown in Figure 16 page 39.

The luminescent intensity of the phosphors at T_m, for -40 db U.V. input, showed a slight decrease with increasing nickel concentration up to $6{\cdot}0 \times 10^{-6}$ mole parts of nickel. Beyond this concentration the luminescent intensity decreased more rapidly.

Although the transitions associated with killer centres are usually described as non-radiative it may be possible to find an infrared transition associated with the nickel centre. Also it has been found by Hoogenstraaten[20] that nickel produces traps in zinc sulphide type phosphors. Information on these two effects could help clarify the mechanism of killer centres.

3g. The Effect of Oxygen

The phosphors discussed previously were fired in a stream of oxygen free nitrogen. Nitrogen was chosen because it provided a convenient inert atmosphere, thus eliminating oxidation. However, many of the phosphors described in the literature were prepared by firing in air using a covered crucible. Using this method it would be difficult to either estimate or control the oxygen content of the phosphors.

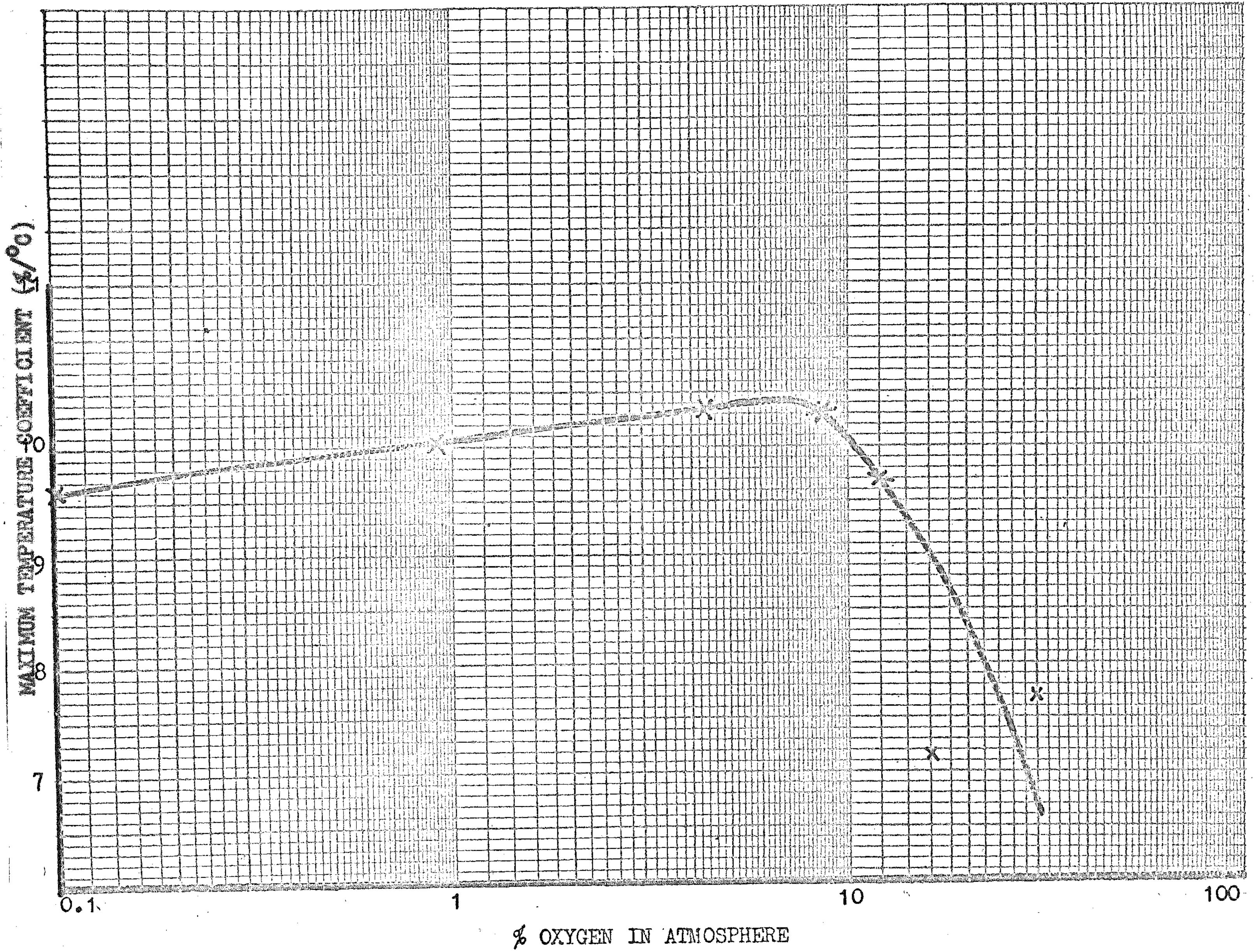
The effect of oxygen was investigated by firing a phosphor, with the general formula $[Zn(23\%)Cd]S\colon 1{\cdot}8 \times 10^{-3} Ag\colon 5{\cdot}5 \times 10^{-6} Ni\colon 2{\cdot}0\% \ NaCl$, in an atmosphere containing a known percentage of oxygen.

A length of thermometer capillary was placed in the nitrogen line and the flow rate was calibrated in cc/min. for various pressures, as indicated on the outlet gauge of the nitrogen cylinder. The flow rate was calibrated by passing the gas into a burette, which contained a small amount of detergent solution, and measuring the time required for the thin detergent films formed to pass through a known volume. Because a larger range of flow rates was required for the oxygen a number of capillaries were calibrated. In this way the pressure on the oxygen outlet could be kept sufficiently high (about 30 p.s.i.) for stability to be obtained. The flow rate of the gas, or mixture of gases, was kept constant at 60cc/min. The oxygen content of the gas is expressed as a percentage, by volume, of the gas mixture.

It can be seen from Figure 17 page 44 that as the oxygen content of the gas increased there was a gradual rise in the maximum temperature coefficient until a maximum of 10·4%/°C was attained. This occurred when the oxygen content of the gas was about 8%.

During this series it was found, using an oxygen analyzer, that there was a small oxygen content in the atmosphere which had been

FIGURE 17. Maximum temperature coefficient v's % of oxygen in the atmosphere for $[\mathrm{Zn}(23\%)\mathrm{Cd}]\,\mathrm{S}$: $1{\cdot}8 \times 10^{-3}$ Ag: $6{\cdot}0 \times 10^{-6}$ Ni: $2{\cdot}0\%$ NaCl fired at 595°C for 45 min. in an atmosphere which was a mixture of oxygen and nitrogen. The oxygen content is expressed as a % by volume of the atmosphere.


MAXIMUM TEMPERATURE COEFFICIENT (%/°C)
11
10
9
8
7
0.1
1
10
100
% OXYGEN IN ATMOSPHERE

previously described as oxygen free nitrogen. This amounted to less than 0·15%. It can be seen from Figure 17 page 44 that any small variations that might have occurred in this oxygen concentration would have only an insignificant effect on the maximum temperature coefficient. Because there was no oxygen in the nitrogen at the furnace inlet, the oxygen content was assumed to be due to:

(a) Possible leaks around the bungs at the ends of the furnace.

(b) Diffusion of oxygen through the walls of the furnace.

Also some oxygen could be introduced into the phosphor by the air which must have been trapped between the finely ground phosphor particles when they were being placed in the silica boat prior to being placed in the furnace for firing.

This small oxygen content could explain the difference in the maximum temperature coefficients between the phosphors that were fired in an open boat and those which were placed in silica capsules, evacuated and filled with oxygen free nitrogen before being inserted into the furnace.

The increase in the maximum temperature coefficient with increasing oxygen content could be because the oxygen increases the solubility of silver in zinc sulphide[20], with a corresponding decrease in Δ E. The decrease in Δ E cannot be easily related to a change in the emission spectrum because when the oxygen concentration in the zinc sulphide increases there is a decrease in the band gap. This decrease has been measured by Kroeger and Dikhoff[21]. This results in a shift in the emission spectrum towards longer wavelengths. To measure any change that occurs in Δ E it would be necessary to measure both the emission and absorption spectra. It would be expected that this change would be small and so it would be difficult to detect.

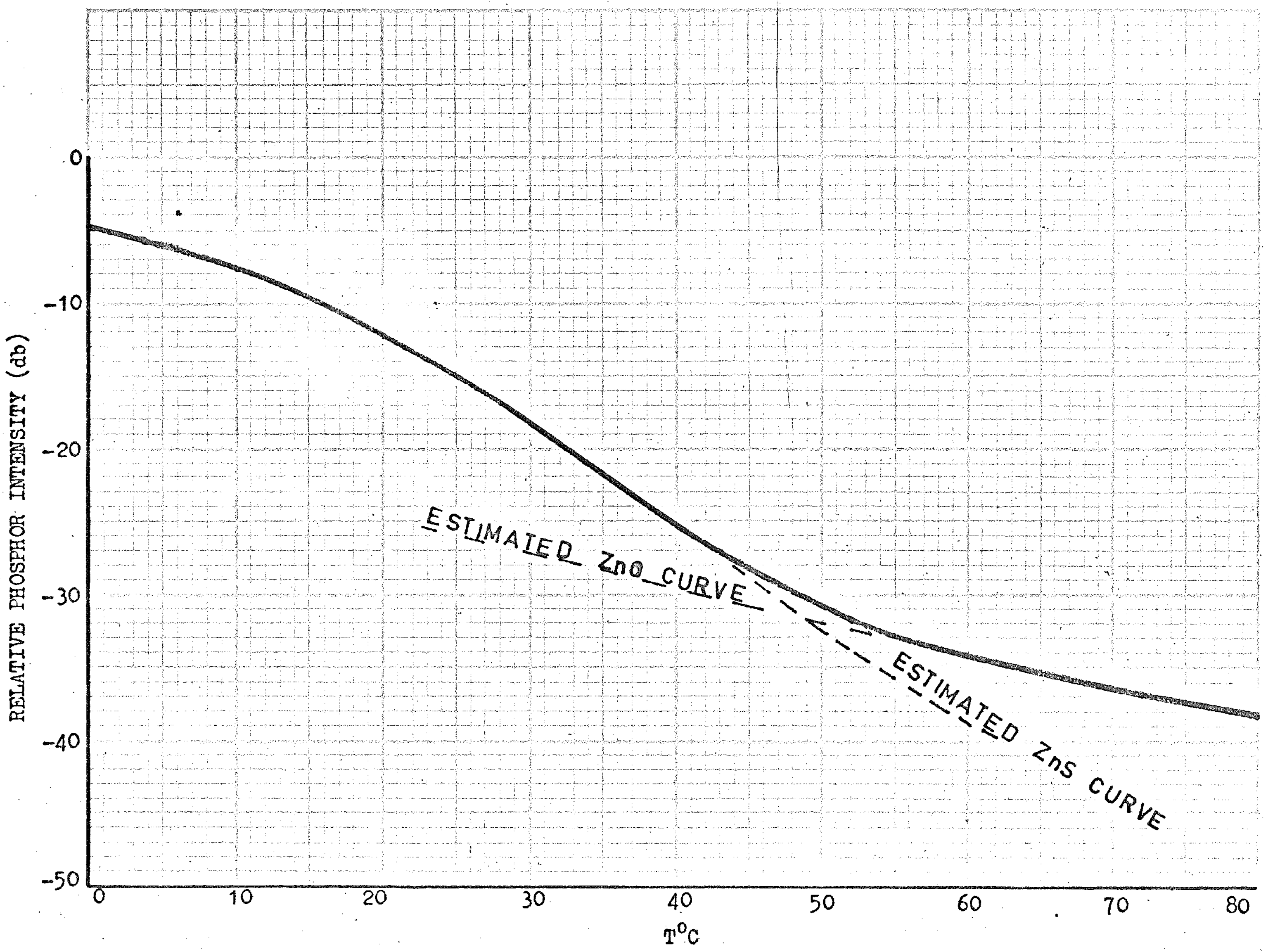
The sharp decrease in the maximum temperature coefficient when the oxygen content of the atmosphere exceeds 8% is probably due to the presence of zinc oxide in the final phosphor as opposed to small numbers of oxygen atoms substitutionally replacing the sulphur in the lattice. This would give a log B v's T curve in which the luminescent intensity of the phosphor is due to the sum of the intensities of the original zinc-cadmium sulphide phosphor, now containing some substitutional oxygen and a small percentage of zinc oxide. The nett effect of this on the log B v's T curve is shown in Figure 18 page 47 which is for a phosphor fired in an atmosphere containing 34·8% oxygen. It can be seen that, because the zinc oxide has a much lower maximum temperature coefficient (about 2·6%/$^{\circ}$C) than the zinc-cadmium sulphide phosphor, beyond 50°C the luminescence of the phosphor, at -30 db U.V. input, is due mainly to zinc oxide.

When the luminescent intensity of the zinc oxide is greater than that of the zinc-cadmium sulphide phosphor at a temperature less than T_m, then there is a decrease in the maximum temperature coefficient.

The scatter in the points for oxygen concentrations greater than 8% was greater than usual. This was because the effect of zinc oxide on the curve made the maximum temperature coefficient more difficult to estimate.

The uniformity of the samples prepared using an atmosphere containing a percentage of oxygen was equivalent to that of the phosphors which have been discussed previously.

FIGURE 18. Log B v's T for [Zn(23%)Cd] S: $1{\cdot}8 \times 10^{-3}$ Ag: $6{\cdot}0 \times 10^{-6}$ Ni: 2·0% NaCl fired at 595°C for 45 min. in an atmosphere of nitrogen and 34·8% oxygen. The U.V. input is −30 db.


RELATIVE PHOSPHOR INTENSITY (db)
0
-10
-20
-30
-40
-50
0
10
20
30
40
50
60
70
80
T°C
ESTIMATED ZnO CURVE
ESTIMATED ZnS CURVE

4. ANALYSIS OF RESULTS

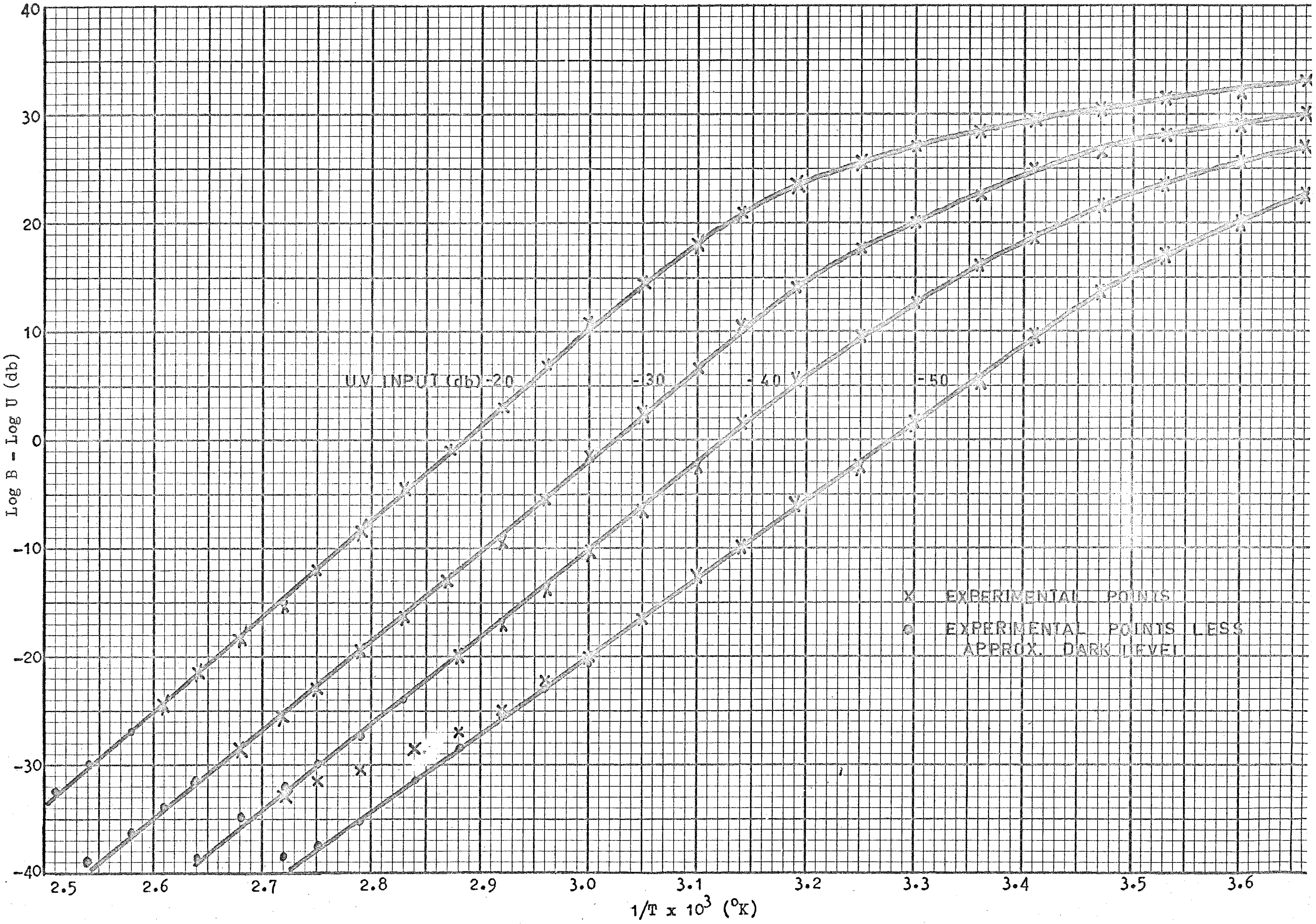
4a. Curve Normalization

It can be seen from Figures 7 and 8 pages 16 and 17 that the shapes of the log B v's T curves appear to be similar. If this is the case then it should be possible to normalize the curves in such a way that they all become coincident. It would then be possible to fit a general equation to the curves.

The curves used in the normalization were all measured over the maximum possible brightness range by adjusting the photo-multiplier potential, as was discussed in Section 2b page 15.

Because it would be expected that any equation that could be found to fit the curves would contain an expression of the form $1/\exp(-\Delta E/kT)$, the curves were replotted with log B - log U v's 1/T. Figure 19 page 49 shows a curve of log B - log U v's 1/T for a [Zn(23%)Cd]S: $1{\cdot}8 \times 10^{-3}$ Ag: $6{\cdot}0 \times 10^{-6}$ Ni: 2·0% NaCl phosphor. In one of the curves two sets of points are shown, one set is a replot of the recorded curve and the other set takes into account the approximate dark level. It can be seen that the curves become linear for low values of 1/T and that, within the limits of the experimental error, the slope of the lines is independent of the U.V. input over a range of 30 db in the U.V. input.

FIGURE 19. Log B - log U v's 1/T for [Zn(23%)Cd] S: $1 \cdot 8 \times 10^{-3}$ Ag: $6 \cdot 0 \times 10^{-6}$ Ni: 2·0% NaCl fired at 595°C for 45 min. in oxygen free nitrogen. Curves for various values of the 3650Å exciting radiation are shown. Both the experimental points and the points obtained after allowing for the estimated dark level are shown on the -50 db curve.


40
30
20
10
0
-10
-20
-30
-40
Log B - Log U (db)
2.5
2.6
2.7
2.8
2.9
3.0
3.1
3.2
3.3
3.4
3.5
3.6
1/T x 10^3 (^{o}K)
U.V. INPUT (db) -20
-30
-40
-50
X EXPERIMENTAL POINTS
● EXPERIMENTAL POINTS LESS APPROX. DARK LEVEL

To normalize the curves several steps had to be taken:

(1) The curves were made linear with respect to the U.V. input. That is the curves were shifted along the 1/T axis until the curves of log B - log U v's 1/T became coincident.

(2) The slopes of the linear section of the curves were normalized to a constant value.

(3) Because the curves shift bodily up and down the 1/T scale due to variations in the composition, the origin of the 1/T scale was adjusted to make the curves co-incident. This shift is the one which has been discussed previously as the variation in T_m with composition.

(1) <u>Linearization of the log B v's 1/T curves with respect to the U.V. input</u>

It can be seen from Figure 19 page 49 that a shift in 1/T will make the log B - log U v's 1/T curves coincident for a particular phosphor. The amount by which the curves had to be shifted was found by plotting log U v's $1/T_m$ for all compositions. This was plotted by taking a horizontal line, through the curves of log B - log U v's 1/T, which passed through the points $T = T_m$ at all values of the U.V. input. This point has no particular physical significance; it was selected because it was relatively easy to locate all the curves. The plot of log U v's $1/T_m$ is shown in Figures 20 to 24 pages 51 to 55. It can be seen that the points lie on a series of straight lines. The slopes of these lines are shown in Table 5 page 56. It can be seen from this table that the average slope, A', is $-1{\cdot}45 \times 10^{-5}$ $1/^{\circ}K$ db and that this is relatively independent of the phosphor composition. However, the intercept of these

FIGURE 20. $1/T_m$ v's log U for [Zn(23%)Cd]S: x Ag: 2·0% NaCl fired at 595°C for 120 min. in oxygen free nitrogen. Curves are shown for silver concentration of 0, $5\cdot2 \times 10^{-4}$, $1\cdot2 \times 10^{-3}$ and $5\cdot2 \times 10^{-2}$ mole parts.

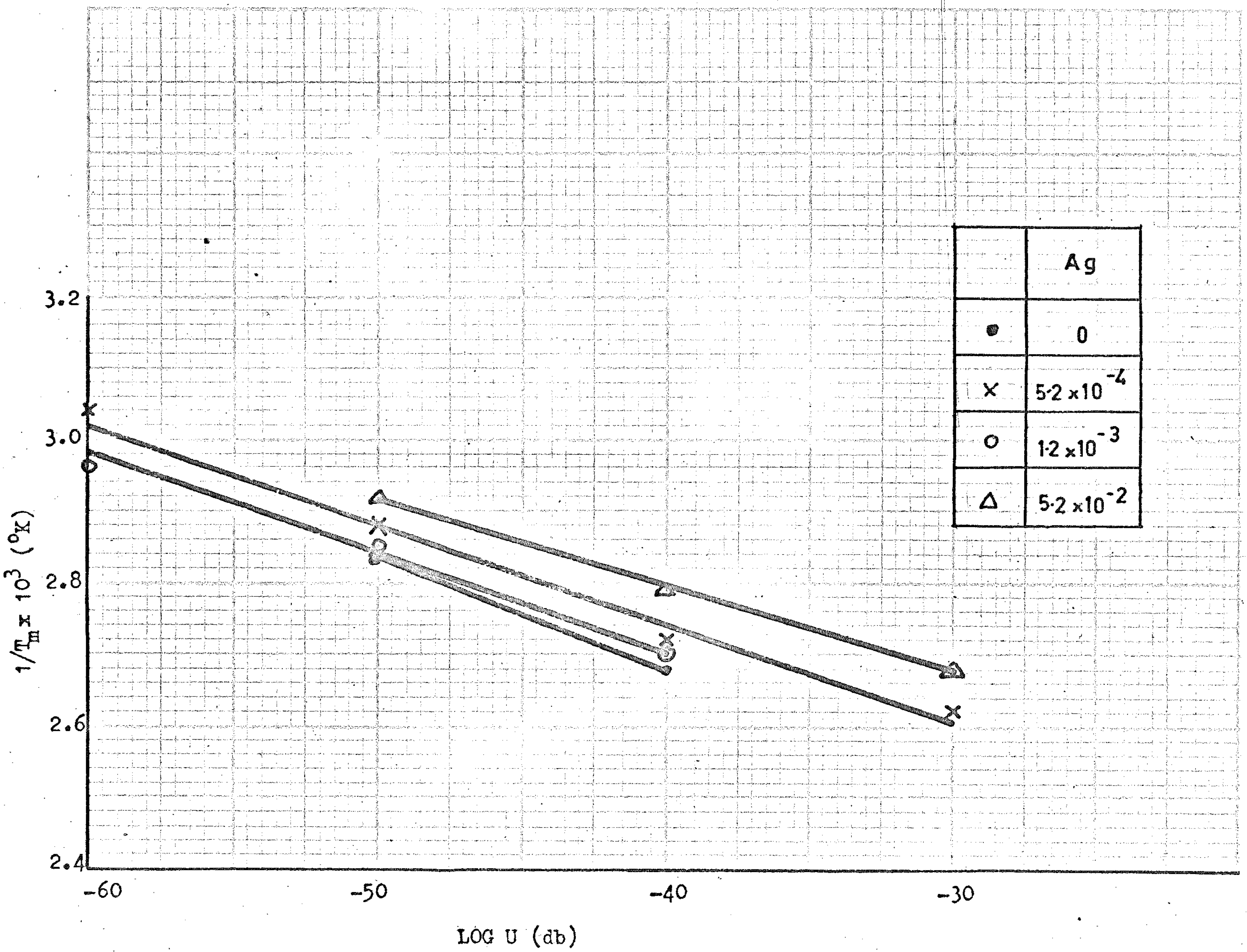

3.2
3.0
2.8
2.6
2.4
1/T_m x 10^3 (°K)
-60
-50
-40
-30
LOG U (db)
Ag
● 0
× 5·2 x 10^-4
o 1·2 x 10^-3
Δ 5·2 x 10^-2

FIGURE 21. $1/T_m$ v's log U for [Zn(23%)Cd] S: $1\cdot8 \times 10^{-3}$ Ag: $2\cdot0$% NaCl fired at x°C for 120 min. in oxygen free nitrogen. Curves are shown for firing temperatures of 527, 600, 670 and 749°C.

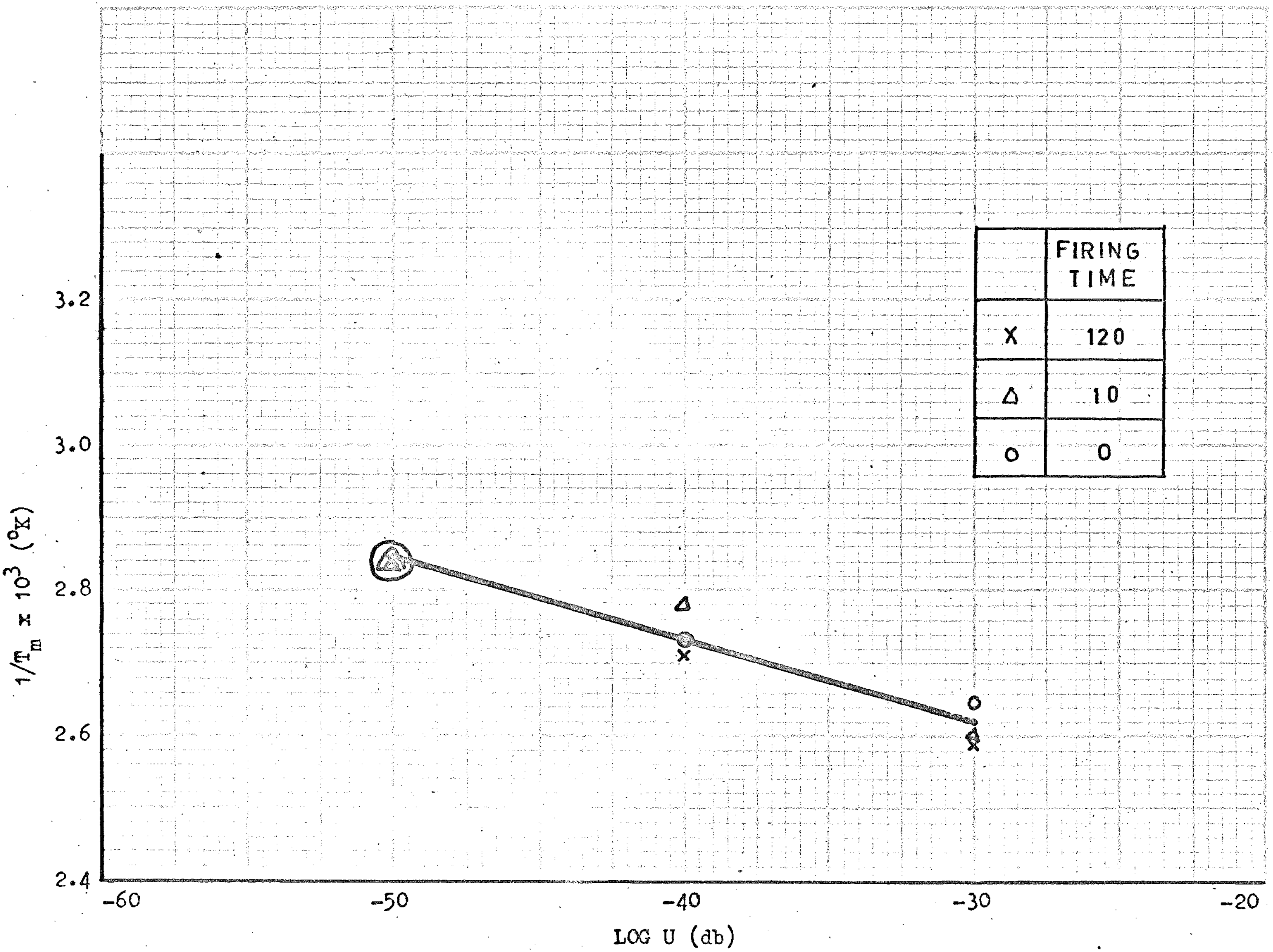

FIRING TIME
X 120
Δ 10
O 0
3.2
3.0
2.8
2.6
2.4
$1/T_m \times 10^3$ (°K)
-60
-50
-40
-30
-20
LOG U (db)

FIGURE 23. $1/T_m$ v's log U for $[Zn(x\%)Cd]S$: $1{\cdot}8 \times 10^{-3}$ Ag: $2{\cdot}0\%$ NaCl fired at 595°C for 45 min. in oxygen free nitrogen. Curves are shown for cadmium concentrations of 0, 28 and 50 mole %.

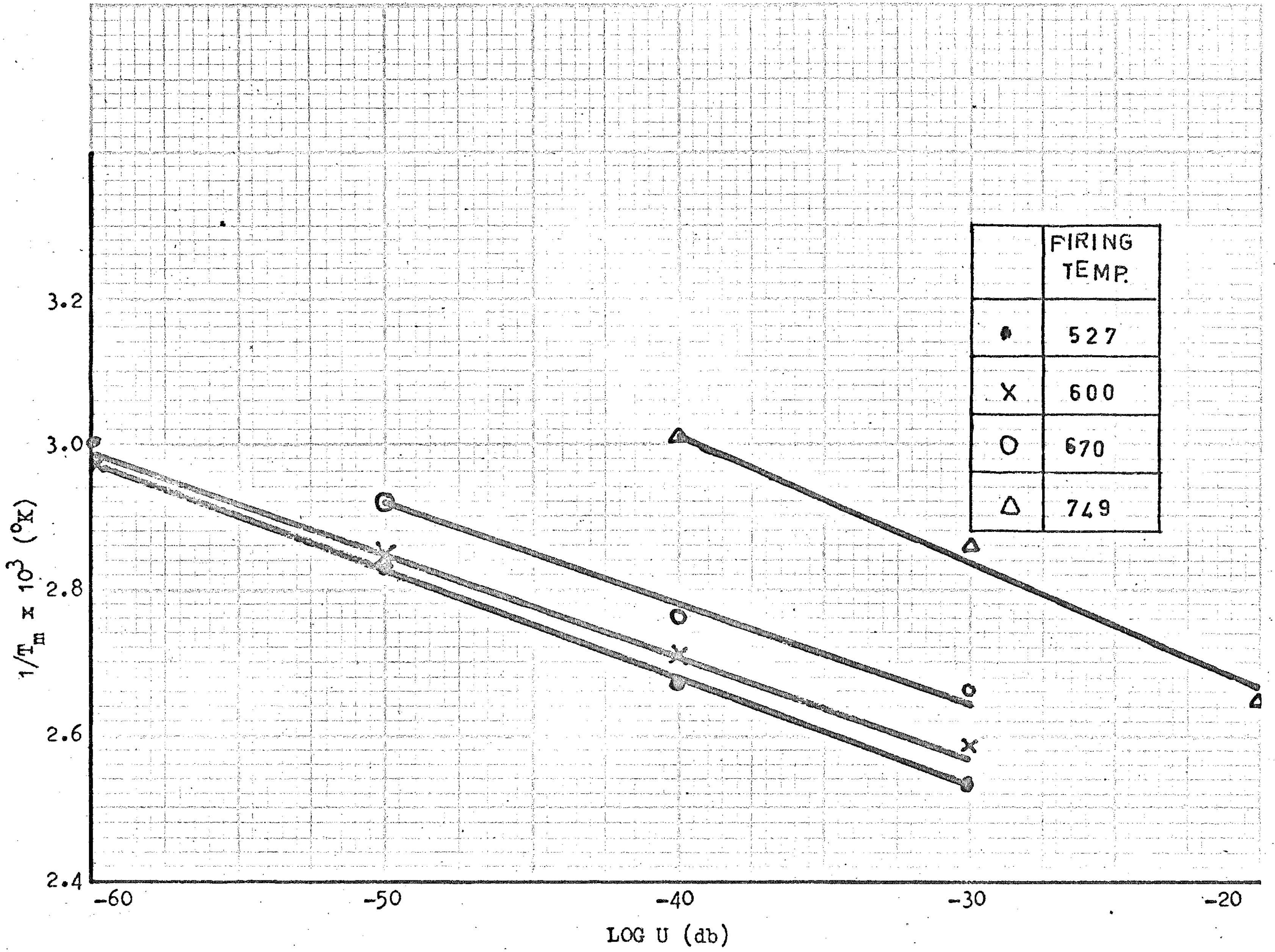

3.2
3.0
2.8
2.6
2.4
-60
-50
-40
-30
-20
LOG U (db)
$1/T_m \times 10^3$ (°K)
FIRING TEMP.
● 527
X 600
O 670
Δ 749

FIGURE 22. $1/T_m$ v's log U for $[Zn(23\%)Cd]\,S$: $1{\cdot}8 \times 10^{-3}$ Ag: $2{\cdot}0\%$ NaCl fired at 595°C for x min. in oxygen free nitrogen. Points are shown for firing times of 0, 10, and 120 min.

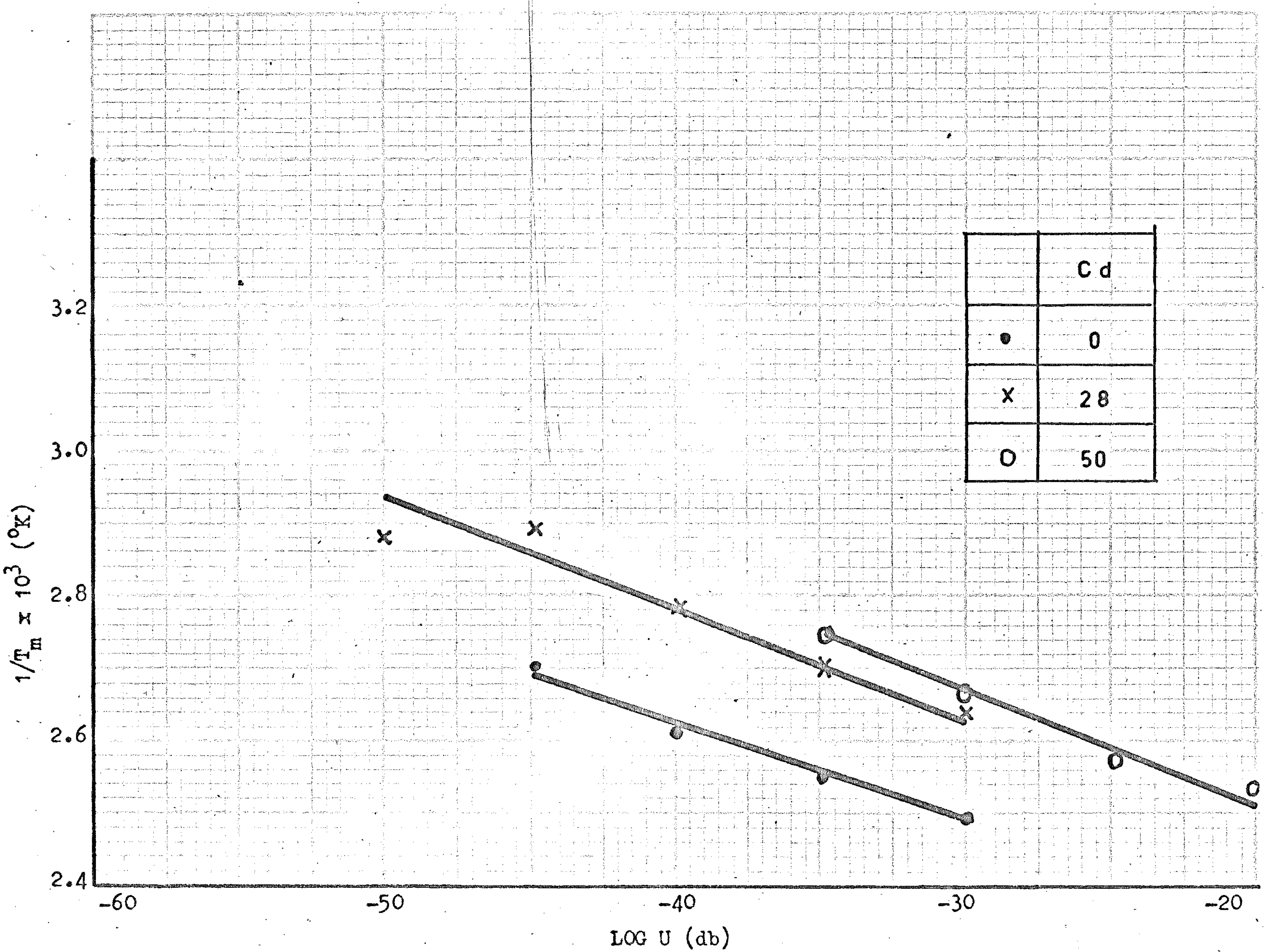
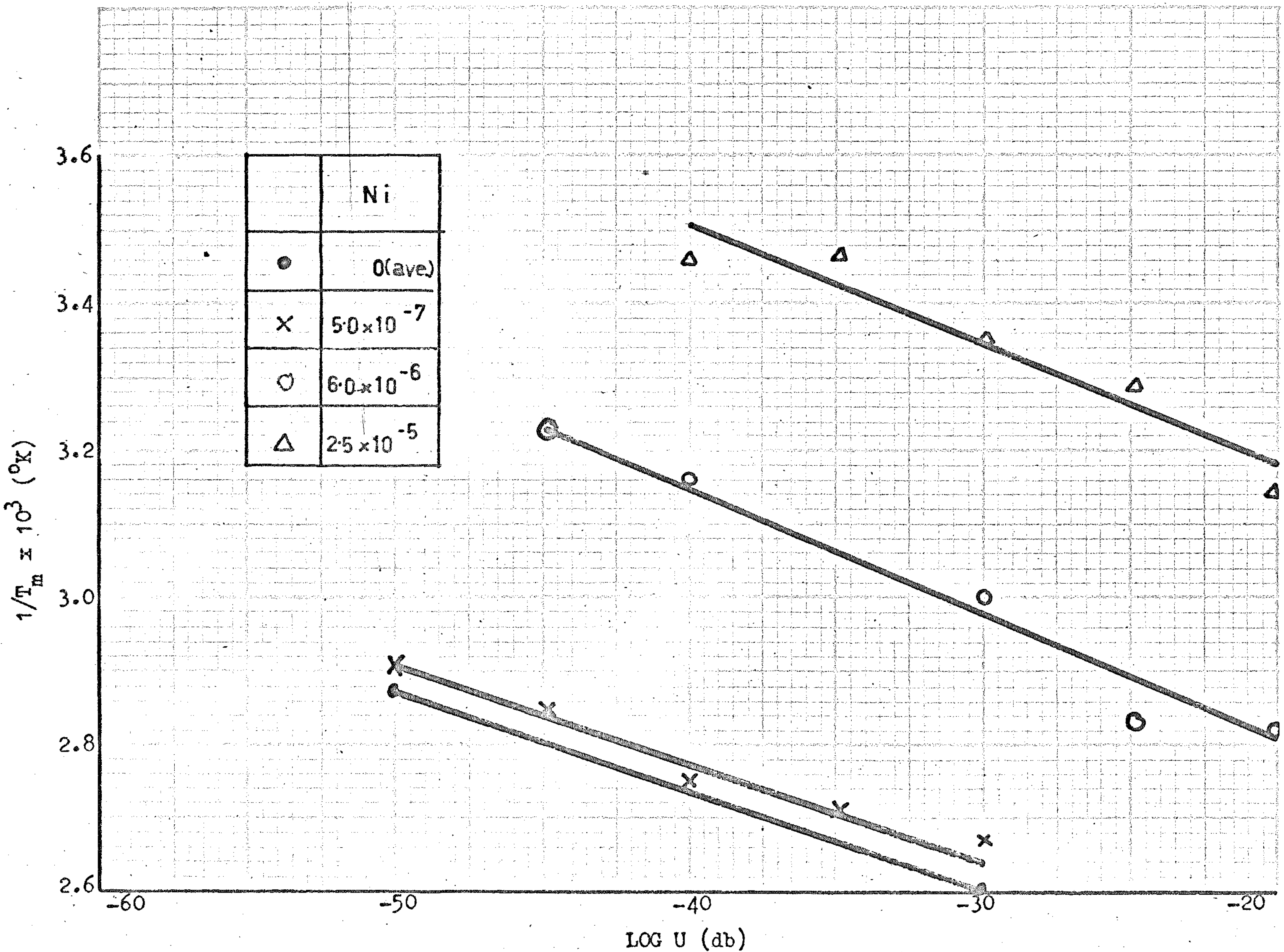

3.2
3.0
2.8
2.6
2.4
-60
-50
-40
-30
-20
LOG U (db)
1/T_m x 10^3 (°K)
Cd
● 0
x 28
O 50

FIGURE 24. $1/T_m$ v's log for [Zn(23%)Cd] S: $1{\cdot}8 \times 10^{-3}$ Ag: x Ni; 2·0% NaCl fired at 595°C for 45 min. in oxygen free nitrogen. Curves are shown for nickel concentrations of 0, $5{\cdot}0 \times 10^{-7}$, $6{\cdot}0 \times 10^{-6}$ and $2{\cdot}5 \times 10^{-5}$ mole parts.


Ni
● 0(ave)
× $5{\cdot}0\times10^{-7}$
○ $6{\cdot}0\times10^{-6}$
△ $2{\cdot}5\times10^{-5}$
3.6
3.4
3.2
3.0
2.8
2.6
$1/T_m \times 10^3$ (°K)
-60
-50
-40
-30
-20
LOG U (db)

Phosphor Series		Slope of the lines log U v's $1/T_m \times 10^5$
Silver concentration	0	-1·75
(mole parts)	5·2 x 10^{-4}	-1·35
	1·2 x 10^{-3}	-1·35
	5·2 x 10^{-2}	-1·20
Firing time (min)	120	-1·30
	10	-1·30
	0	-1·15
Firing temp. (°C)	527	-1·70
	600	-1·40
	670	-1·40
	749	-1·40
Cadmium composition	0	-1·60
(mole parts)	28	-1·55
	50	-1·40
Nickel concentration	0	-1·40
(mole parts)	5·0 x 10^{-7}	-1·30
	6·0 x 10^{-6}	-1·70
	2·5 x 10^{-5}	-1·65
	AVERAGE	-1·45

TABLE 5. T_m at -40 db U.V. input for [Zn(x%)Cd]S: y Ag: z Ni: 2·0%NaCl fired at a°C for b min. in oxygen free nitrogen.

lines with the line 20 log U = -40 db depends on the composition and preparation conditions of the phosphor, as has been previously discussed.

This, therefore, gives the following equation:-

$$1/T = 20A' \log U + B \qquad \text{---(13)}$$

$$\therefore \; U = \exp(A/T - BA) \qquad \text{---(14)}$$

where B depends on the composition and preparation conditions of the phosphor and

$$A = \frac{2\cdot3}{20A'}$$

$$= -7\cdot9 \times 10^3.$$

If this equation is expressed in the form

$$U = \exp(-\Delta E'/kT - BA) \qquad \text{---(15)}$$

where $\Delta E'$ = constant

and k = Boltzman's constant

then $\Delta E' = -kA$ ---(16)

$= 0\cdot68$eV.

It is interesting to note that Drodz and Levshin[17] have found, from absorption edge and emission spectra measurements, that the energy gap, ΔE, between the valence band and the self-activated level is approximately 0·88eV for a [Zn(23%)Cd]S phosphor. As has been previously discussed in Section 3b page 23 there is a decrease in ΔE of approximately 0·08eV when the silver concentration is increased from zero to

$1{\cdot}8 \times 10^{-3}$ mole parts. Hence at this concentration ΔE would be approximately 0·80 eV. This is in fairly good agreement with the value of $\Delta E'$ found above. It was, therefore, assumed that:

$$\Delta E' = \Delta E.$$

If this is the case it would be expected that A' would be independent of the killer concentration, because the emission spectrum and hence ΔE are independent of the killer concentration. However, because E depends on the activator concentration and the zinc-cadmium ratio, if the relationship deduced above is correct A' should depend on these factors. Therefore, it would be expected that reducing the silver concentration from $1{\cdot}8 \times 10^{-3}$ mole parts to zero would change A' from $-1{\cdot}45 \times 10^{-5}$ to $-1{\cdot}30 \times 10^{-5}/^{\circ}K$ db. Drodz and Levshin[17] give the increase in ΔE on going from 23 mole % cadmium to zero cadmium as 0·10eV. Hence zero cadmium should correspond to a slope of about $-1{\cdot}25 \times 10^{-5}$ $/^{\circ}K$ db. An increase in the cadmium content from 23 mole % to 50 mole % would correspond to a decrease in ΔE of about 0·15eV and so A' would decrease to about $-1{\cdot}75 \times 10^{-5}/^{\circ}K$ db.

It can be seen from Table 5 page 56 that these changes are within the scatter of the experimental points.

(1) <u>Superlinearity</u>

The relationship between the log U v's $1/T_m$ curve, the temperature coefficient and the superlinearity is illustrated in Figure 25 page 60 in which it is shown that there is a simple geometric relationship between these factors. In other words the superlinearity and the temperature coefficient are the result of the same mechanism. In Figure 25, "E" and "F" are two sections of the curve log B v's 1/T. Also AB is a section of the line log U v's $1/T_m$. Hence the slope of the line AB is the reciprocal of the slopes obtained in Table 5 page 56 which are the slopes of the lines $1/T_m$ v's log U.

The U.V. input of curve "E" is "d" db lower than that of curve "F". Corresponding to the change in the U.V. input is a change of (d + b)db in the luminescent intensity of the phosphor. It should be noted that for the previous statement to be valid the U.V. input and the luminescent intensity must be recorded on the same logarithmic scale.* The way in which this was done is described in Section 2b page 13

It can be seen, therefore, that

$$b = -g \tan \theta. \qquad (17)$$

Hence the superlinearity of the phosphor, which is defined as the ratio:-

---

* It follows that the intensity is independent of the luminescent efficiency of the filter papers used to set the U.V. input. It does, however, require the luminescent output of the papers to be a linear function of the U.V. input. The linearity has been verified over the range of the values of the U.V. input. However, because the filter papers do not have an efficiency of unity, a given value, say - 30 db, for the luminescent intensity and the U.V. input does not imply the same flux density in each case.

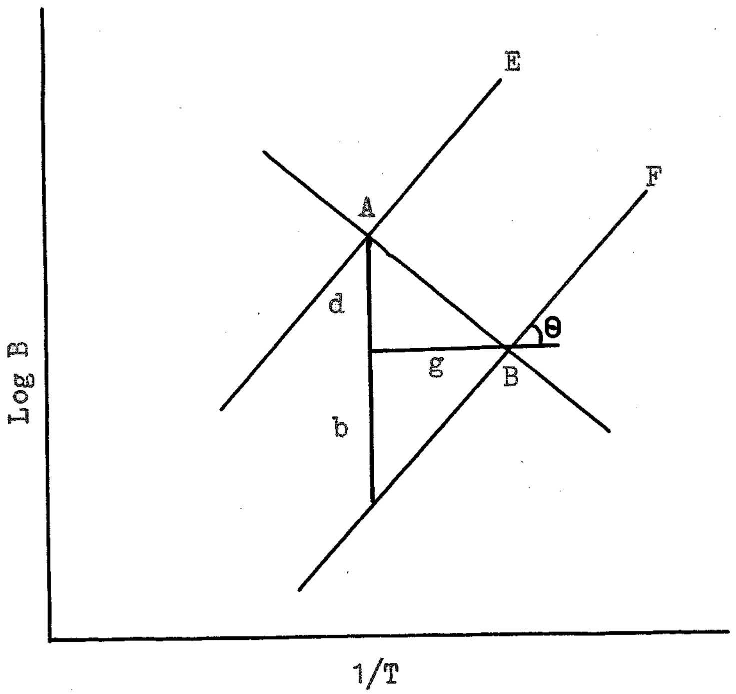


FIGURE 25. Diagram used to illustrate the relationship between the slope of the log B v's 1/T curve and the superlinearity of the phosphors.

$$\Delta \text{ log luminescent intensity}/\Delta \text{ log U.V. input} \qquad \text{——(18)}$$

$$= \frac{-g \tan \theta + d}{d} \qquad \text{——(19)}$$

$$= \frac{-g}{d} \tan \theta + 1 \qquad \text{——(20)}$$

$$= \frac{-g}{d} \frac{d(20 \log B) + 1}{d(1/T)} \qquad \text{——(21)}$$

where d/g is the slope of the line log U v's 1/T. Changing the variable to T gives

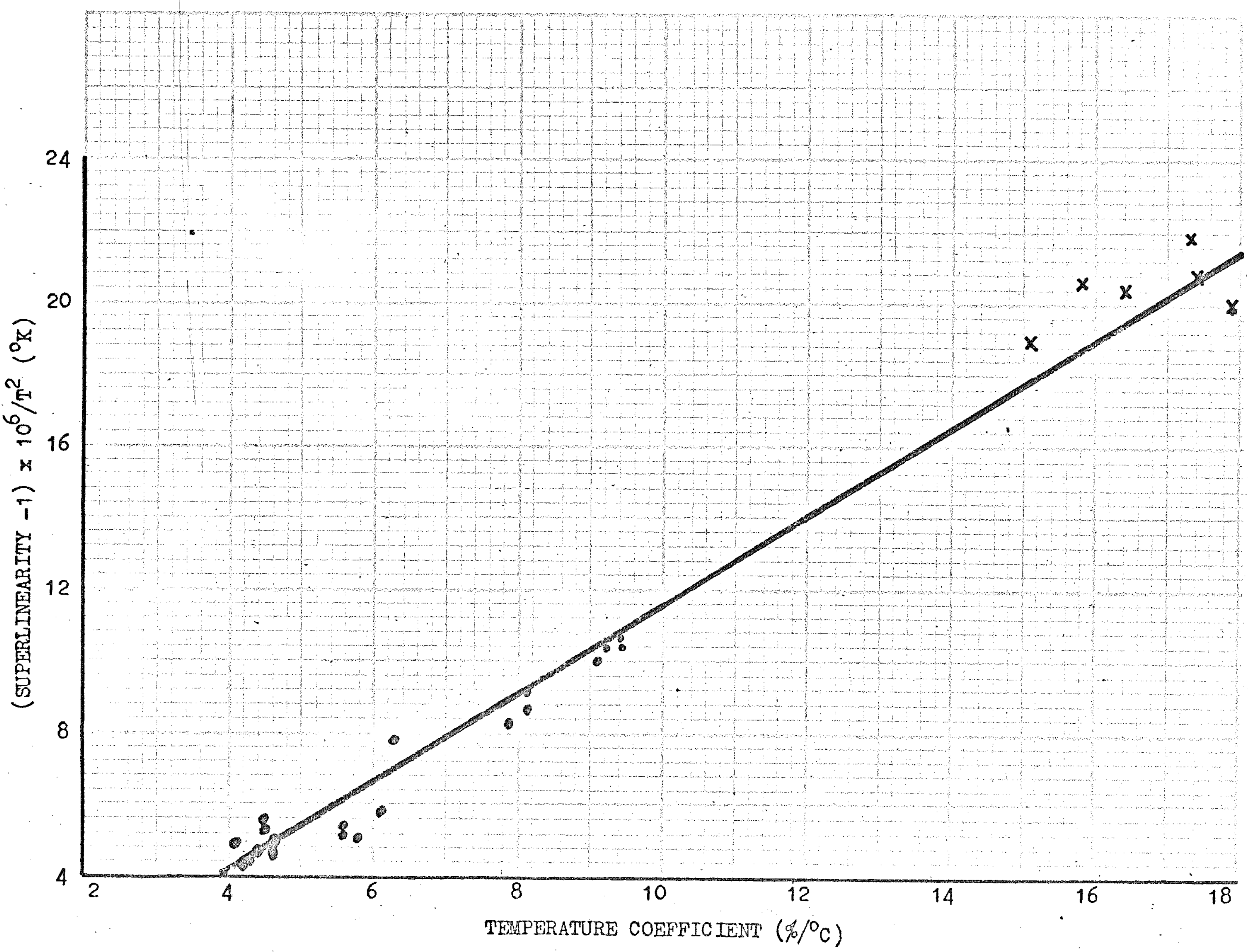
$$\text{Superlinearity} = \frac{g}{d} T^2 \frac{d(20 \log B)+1}{d(T)}. \qquad \text{——(22)}$$

Hence a plot of (superlinearity − 1)/T^2 v's − temperature coefficient should give a straight line with a slope = $-g/11{\cdot}5d = 1{\cdot}25 \times 10^{-6}$. Also this line should pass through the point (0,0). For this to be true the curves of log B v's T must be very nearly parallel. Hence the U.V. attenuation must be small. This was achieved, as has been previously discussed, by using a 4·8 db attenuator to chop the U.V. input at a frequency of 1 c.p.s. Also the temperature at which the measurements are taken should be approximately equal to, or greater than, T_m for the curves to be approximately parallel. A plot of (superlinearity − 1)/T^2 v's − T.C. is shown in Figure 26 page 62. In this figure two sets of points are shown. The dots are points obtained from the phosphors that were prepared in these laboratories and the crosses are points obtained from a number of commercial phosphors. The commercial phosphors were all silver activated, nickel killed zinc-cadmium sulphide phosphors. The source of supply was Derby Luminescents Ltd (England). The slope of the line drawn through the points is $1{\cdot}2 \times 10^{-6}/^{\circ}K$.

It can be seen from the foregoing that the log B − log U v's 1/T curves, for a particular zinc sulphide type phosphor, can be made coincident by subtracting approximately $1{\cdot}45 \times 10^{-5} \times 20 \log U$ from 1/T for each value of the U.V. input. It has been shown that this factor may depend on ΔE and hence on the composition of the phosphor, but, for the range of phosphors considered here, this dependence can be neglected.

A set of log B v's 1/T curves which have been normalized in this

FIGURE 26. (Superlinearity - 1) x $10^6/T^2$ v's temperature coefficient. This is shown for phosphors with various compositions and for some zinc sulphide type phosphors obtained from Derby Luminescents Ltd.


(SUPERLINEARITY -1) x 10^6/T^2 (°K)
24
20
16
12
8
4
2
4
6
8
10
12
14
16
18
TEMPERATURE COEFFICIENT (%/°C)

way is shown in Figure 27 page 64. These curves are for a $[Zn(23\%)Cd]S$: $1{\cdot}8 \times 10^{-3}$Ag: $6{\cdot}0 \times 10^{-6}$Ni: 2·0% NaCl phosphor which was fired for 45 min. at 598°C. It can be seen that, within the limits of experimental error, the curves are co-incident. The experimental error arose mainly from fluctuations in the output of the mercury arc lamp, the error in setting the U.V. input and also from the difficulty experienced in estimating the dark level.

The fact that these curves can be made coincident by this process shows that equation 22 page 61 holds throughout the temperature range that has been considered here. Previously this had only been shown for relatively high temperatures.

(2) Normalization of the slopes

As was indicated previously, the next step in normalizing the log B v's 1/T curves is to normalize the slope of the straight line section of these curves to a constant value. This was done by multiplying the 1/T scale by a factor which normalized the slopes to 10^5 db °K. This factor varied with the composition of the phosphor.

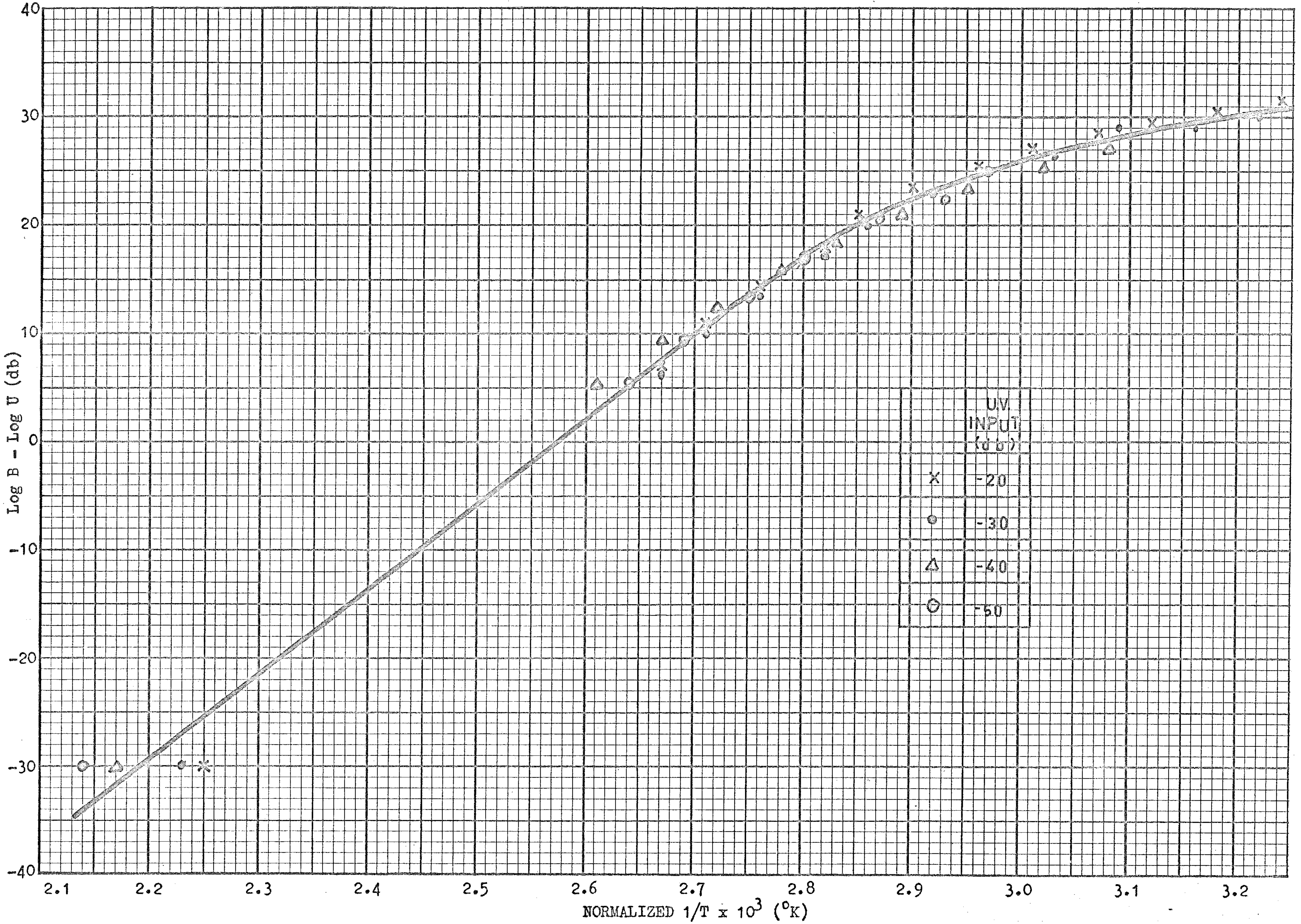
(3) Normalization of T_m

The third normalization process consisted of a shift in the origin of the 1/T scale, which allowed for the fact that, at a given value of the U.V. input, the value of $1/T_m$ depends on the composition of the phosphor. As was mentioned previously $1/T_m$ should not be considered as having any special physical significance. It is merely a method of locating a point which occupies a similar position on all the curves.

FIGURE 27. Log B - log U v's $1/T_n$ where T has been normalized by the equation

$$1/T_n = 1/T - 2{\cdot}90 \times 10^{-4} \log U.$$

Points are shown for various values of the 3650Å exciting radiation. The phosphor shown has the composition $[\mathrm{Zn}(23\%)\mathrm{Cd}]\,\mathrm{S}$: $1{\cdot}8 \times 10^{-3}$ Ag: $6{\cdot}0 \times 10^{-6}$ Ni: 2·0% NaCl and was fired at 595°C for 45 min. in oxygen free nitrogen.


Log B - Log U (db)
40
30
20
10
0
-10
-20
-30
-40
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3.0
3.1
3.2
NORMALIZED 1/T x 10^3 (°K)
UV INPUT (db)
× -20
● -30
△ -40
○ -50

When these two additional processes were carried out on a group of curves from different phosphors, the results shown in Figure 28 page 66 were obtained. It can be seen that these curves do not lie on top of each other. This is probably due to several factors:-

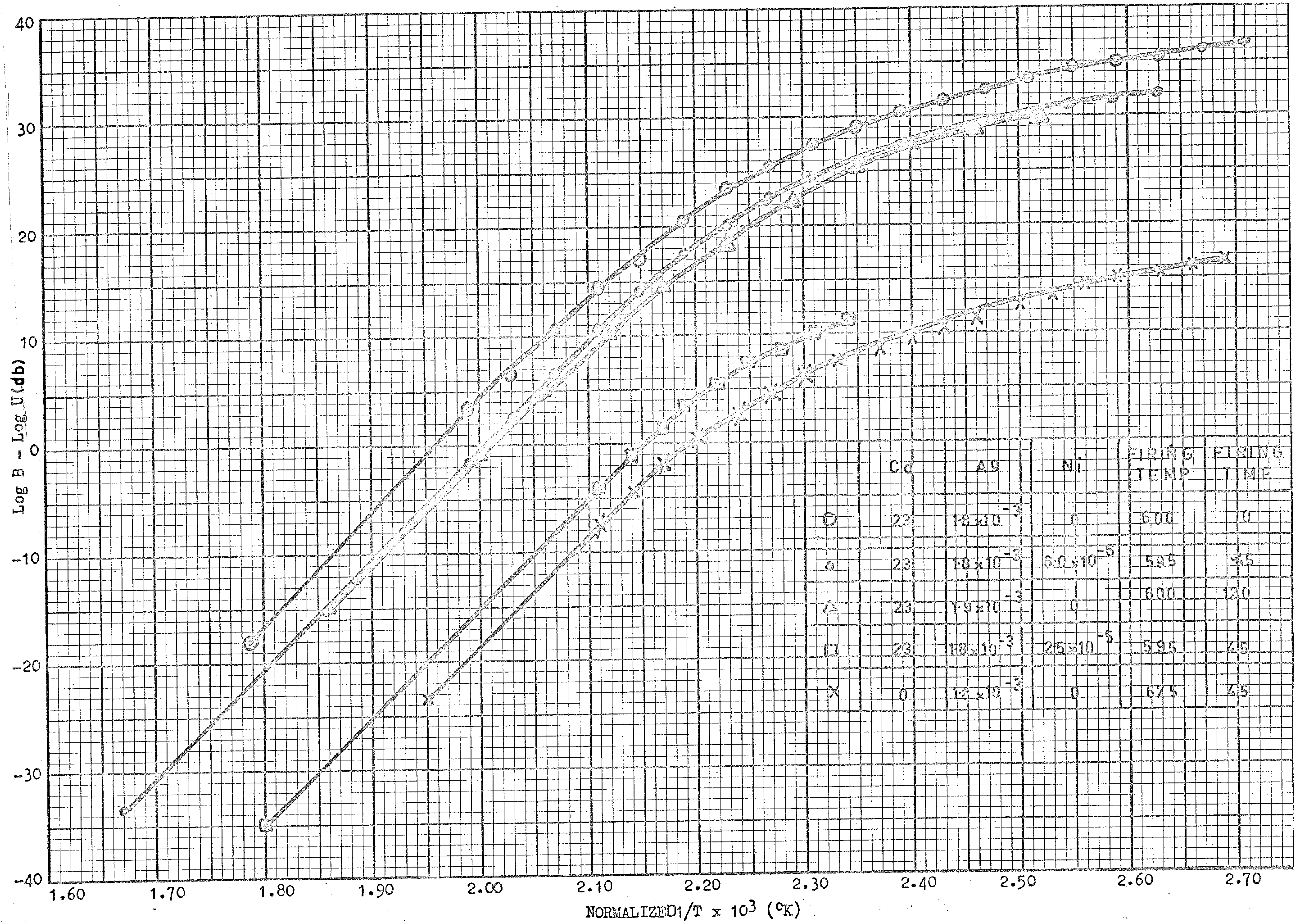
(i) The phosphors used for the normalization have different emission spectra and, as can be seen from Figure 6 page 12, the sensitivity of the detector system has a strong wavelength dependence. This factor would affect the recorded intensity of a series of phosphors with different spectral characteristics but it would not affect the shape of the log B v's T curves.

(ii) As has been previously discussed, the colour of the phosphor under visible light depends on both the composition and the preparation conditions. The darker coloured phosphors would absorb more of their own luminescent output than the lighter ones, thus reducing the efficiency of the phosphor. To obtain an estimate of the magnitude of this effect it would be necessary to measure the reflection spectra of the phosphors at wavelengths in the region of their respective emission peaks.

(iii) It is probable that the low temperature efficiency of a phosphor depends on its composition and method of preparation.

The nett effect of these factors would be to modify the luminescent intensity of the phosphors. However none of these effects would be temperature dependent and so it should be possible to compensate for them by shifting the curves up the brightness scale. The curves, after being adjusted in this way, are shown in Figure 29 page 68.

FIGURE 28. Curves obtained for a series of phosphors after the first three normalization processes. The phosphors were all fired in oxygen free and their compositions are listed on the graph.



	Cd	Ag	Ni	FIRING TEMP	FIRING TIME
○	23	$1{\cdot}8\times10^{-3}$	0	600	0
●	23	$1{\cdot}8\times10^{-3}$	$6{\cdot}0\times10^{-6}$	595	45
△	23	$1{\cdot}9\times10^{-3}$	0	600	120
□	23	$1{\cdot}8\times10^{-3}$	$2{\cdot}5\times10^{-5}$	595	45
×	0	$1{\cdot}8\times10^{-3}$	0	675	45

It can be seen that these curves are very nearly coincident.

This result seems to indicate that the processes causing the temperature dependence of the luminescent intensity of continuously excited zinc sulphide type phosphors are similar for all the phosphors studied during this work.

4b. Curve Fitting

It has been shown previously that the curves derived from current theories do not fit the experimental curves. It was therefore decided to fit an empirical curve to the results.

The most satisfactory equation appears to be

$$B_n = \frac{1}{C_1 \exp -P_1/T_n + C_2 \exp - P_2/T_n} \qquad \text{—(23)}$$

where B_n and T_n are the normalized intensity and temperature respectively. C_1, P_1, C_2 and P_2 are constants.

At high temperatures

$$\ln B_n = \frac{P_1}{T_n} - \ln C_1. \qquad \text{—(24)}$$

This was fitted at the point

$$1/T = 1{\cdot}942 \times 10^{-3}, \; 20 \log B = 0,$$

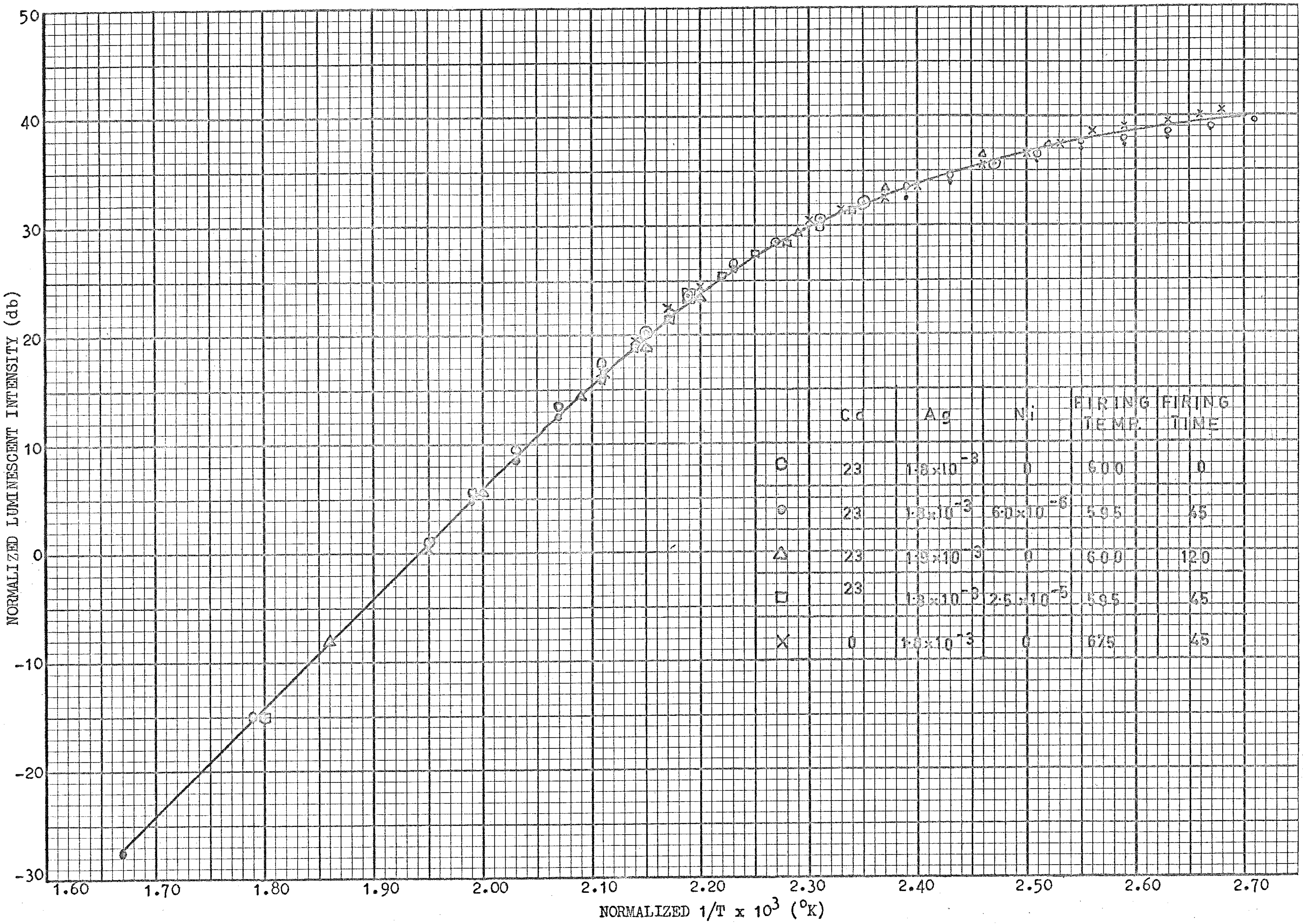
where the slope is 10^5 db °K.

At low temperatures

$$\ln B_n = \frac{P_2}{T_n} - \ln C_2. \qquad \text{—(25)}$$

This was fitted at the point

FIGURE 29. Curves shown in Figure 28 after complete normalization. The compositions of the phosphors are listed on the graph.



	Cd	Ag	Ni	FIRING TEMP.	FIRING TIME
○	23	$1{\cdot}8\times10^{-3}$	0	600	0
●	23	$1{\cdot}8\times10^{-3}$	$6{\cdot}0\times10^{-6}$	595	45
△	23	$1{\cdot}8\times10^{-3}$	0	600	120
□	23	$1{\cdot}8\times10^{-3}$	$2{\cdot}5\times10^{-5}$	595	45
×	0	$1{\cdot}8\times10^{-3}$	0	675	45

$$1/T = 2{\cdot}900, \; 20 \log B = 41{\cdot}5 \quad ,$$

where the slope is $1{\cdot}21 \times 10^3$ db $^\circ$K.

Hence $P_1 = 1{\cdot}00 \times 10^5$ db $^\circ$K

$C_1 = 5{\cdot}00 \times 10^9$

$P_2 = 1{\cdot}21 \times 10^3$ db $^\circ$K

$C_2 = 0{\cdot}284$.

Figure 30 page 70 shows the experimental curve (as a continuous line) together with the points derived from equation 23 (shown as circles). For comparison a series of crosses, which have been derived from the one level model, is shown. It can be seen that the points derived from equation 23 are a good fit for the experimental curve.

This equation predicts that as $T \rightarrow 0$, $B \rightarrow \infty$. In order to make B tend to a saturation value a further constant must be added to the bottom line (C_3). Provided the saturation value is sufficiently above the -42 db level, this constant will not have any significant effect on the points shown. If the saturation value does have a significant effect on the points shown, then it should be possible to compensate for this by a slight adjustment of the constants C_2 and P_2. Hence the complete equation for the normalized curve is:

$$B_n = \frac{1}{C_1 \exp(-P_1/T_n) + C_2 \exp(-P_2/T_n) + C_3}. \qquad \text{---}(26)$$

Referring this back to the original log B v's 1/T curves gives

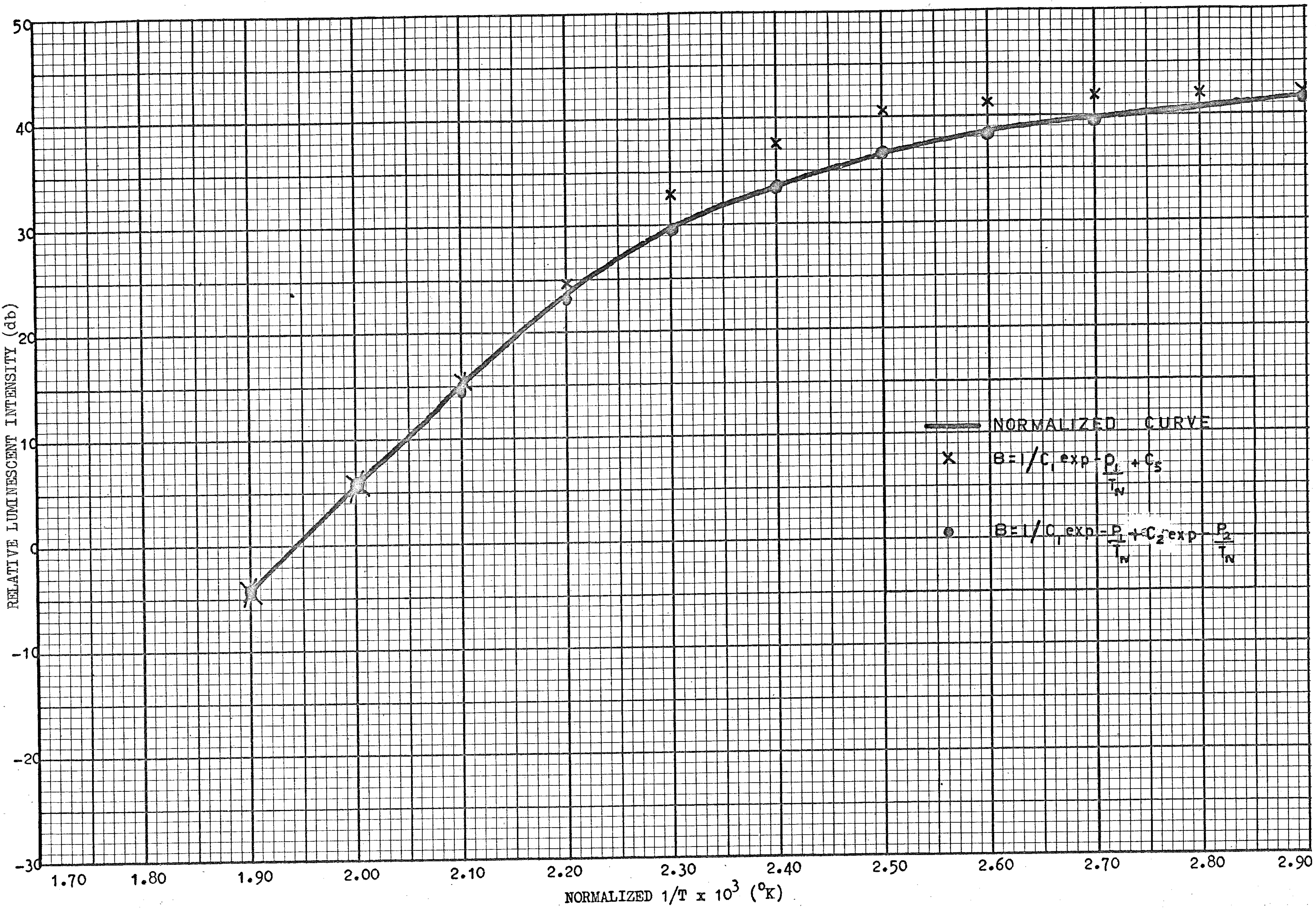
FIGURE 30. Two equations are shown fitted to the normalized curve in Figure 29. The equations fitted to the curve are

$$B = \frac{1}{C_1 \exp - \frac{P_1}{T_n} + C_5},$$

which is the equation derived from the one level model, and

$$B = C_1 \exp - \frac{P_1}{T_n} + C_2 \exp - \frac{P_2}{T_n},$$

which is the empirical equation developed in this thesis.


50
40
30
20
10
0
-10
-20
-30
RELATIVE LUMINESCENT INTENSITY (db)
1.70
1.80
1.90
2.00
2.10
2.20
2.30
2.40
2.50
2.60
2.70
2.80
2.90
NORMALIZED 1/T x 10^3 (°K)
NORMALIZED CURVE
× $B=1/C_1 \exp -\frac{P_1}{T_N} + C_5$
● $B=1/C_1 \exp -\frac{P_1}{T_N} + C_2 \exp -\frac{P_2}{T_N}$

$$\frac{B}{U} = \frac{1}{C_1 \exp - P_1'(1/T + \frac{2 \cdot 90 \times 10^{-4}}{2 \cdot 3} \ln U + C_4) + C_2 \exp - P_2'(1/T + \frac{2 \cdot 90 \times 10^{-4}}{2 \cdot 3} \ln U + C_4) + C_3}. \qquad \text{——(27)}$$

In the above expression

$\frac{2 \cdot 90}{2 \cdot 3} \times 10^{-4} \ln U$ allows for the superlinearity of the phosphor,

P_1' depends on the slope of the high temperature section of the curves,

P_2' depends on the slope of the low temperature section of the curves,

and C_4 depends on the amount by which T_m had to be changed to make the curves coincident.

Equation 27 can be expressed more simply as

$$\frac{B}{U} = \frac{1}{C_1' \exp - P_1'/T + C_2' \exp - P_2'/T + C_3} \qquad \text{——(28)}$$

where C_1' and C_2' depend upon the superlinearity and T_m for each individual phosphor.

At this stage it is not possible to relate the individual energy levels in the phosphor to P_1' and P_2'. These two factors are each a function of all the energy levels that take part in the process. However, because the curves can be normalized in the manner described previously, the ratio P_1'/P_2' is a constant.

It is interesting to compare the curves of $\Delta E' = kP_1'$ v's silver concentration and the other variables with those of the maximum temperature coefficient against these variables. Also because $\Delta E'$ is independent of the U.V. input it probably has a more fundamental physical significance than the maximum temperature coefficient.

Figure 31 page 73 shows $\Delta E'$ v's silver concentration. The curve has the same shape as the curve of the maximum temperature coefficient against the silver concentration. This is because T_m is practically independent of the silver concentration.

When the nickel concentration is increased the curves of log B v's 1/T shift to lower temperatures. It can be seen by comparing Figure 32 page 74 with Figure 15 page 38 that this shift causes a considerable difference to occur between the shape of the maximum temperature coefficient against the nickel concentration and that of $\Delta E'$ against the nickel concentration.

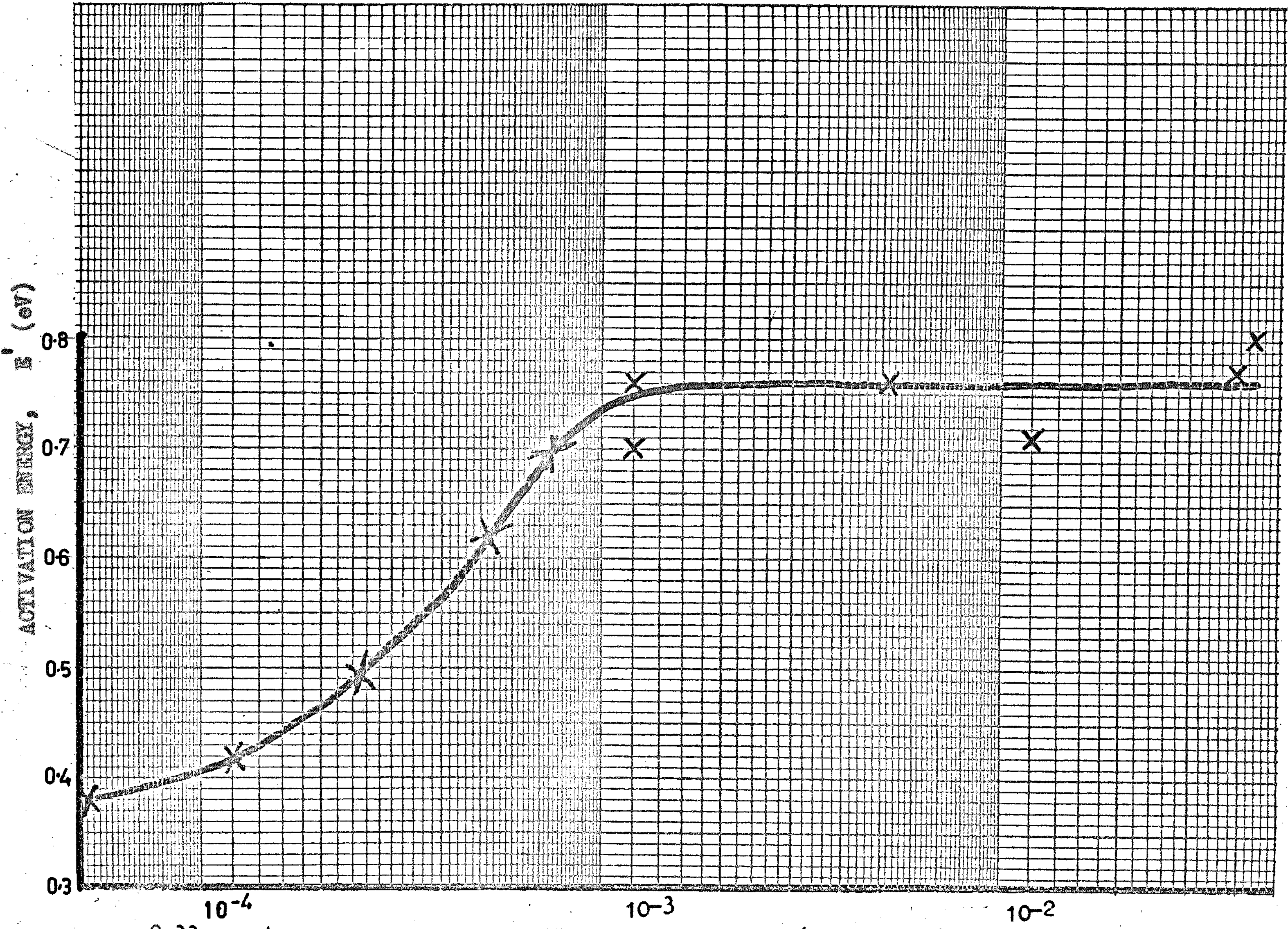
The general features of the other variables against the maximum temperature coefficient are similar to those of $\Delta E'$ against these variables.

4c. Possible Second Order Effects in the Log B v's 1/T Curves

Two effects which could produce second order effects in the log B v's 1/T curves are:

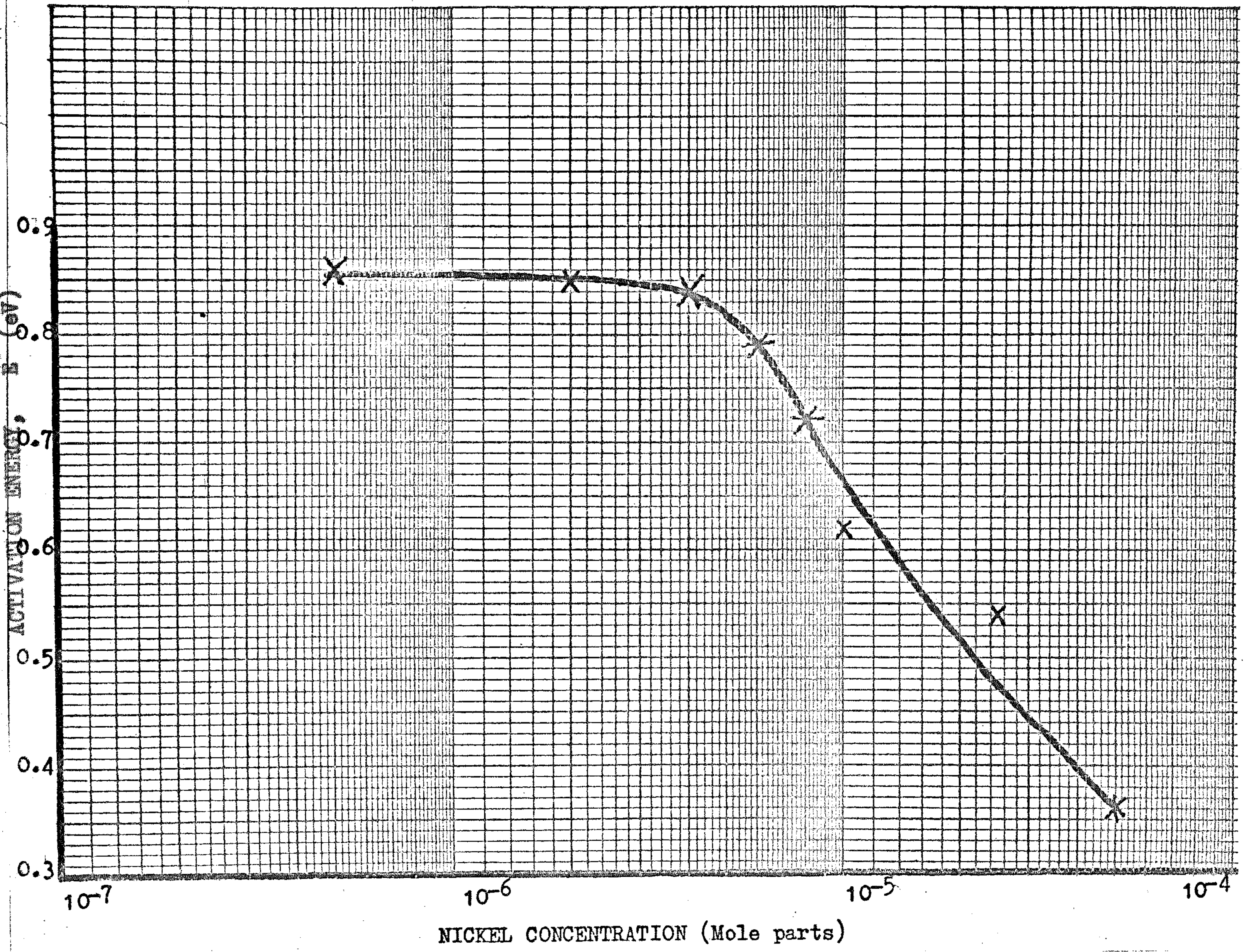
(1) Variations with temperature in the absorption edge and emission spectra of the phosphors. Leverenz[11] has found that heating silver activated zinc sulphide phosphors causes both the absorption edge and emission spectra to shift towards longer wavelengths. These shifts occur at approximately the same rate and so ΔE remains unchanged. However, the shift in the peak of the emission spectrum of between 0·4 and 1Å/°K would cause a small deviation from the actual curve because of the spectral

FIGURE 31. Activation energy v's silver concentration of $[Zn(23\%)Cd]S$: x Ag: 2·0% NaCl fired at 595°C for 120 min. in oxygen free nitrogen. The activation energy was obtained from the straight line section of the curves of log B v's 1/T.



0.33 ev at zero
silver concentration

FIGURE 32. Activation energy v's nickel concentration of [Zn(23%)Cd] S: $1\cdot8 \times 10^{-3}$ Ag: xNi: 2·0% NaCl fired at 595°C for 45 min. in oxygen free nitrogen. The activation energy was obtained from the straight line section of the curves of log B v's 1/T.


ACTIVATION ENERGY, E' (eV)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
10^{-7}
10^{-6}
10^{-5}
10^{-4}
NICKEL CONCENTRATION (Mole parts)

characteristics of the filter-photomultiplier combination.

(2) Levshin and Tunitskaya[22] have found that the absorption coefficient of ZnS:Mn is temperature dependent. It is probable that a similar effect occurs in silver activated zinc-cadmium sulphide phosphors. This effect is greatest when the exciting radiation is near the absorption edge of the phosphor, as is the case when a ZnS:Ag phosphor is excited by 3650Å radiation. Over the temperature range considered, the deviation of the temperature quenching curves due to this effect may amount to about 2db for the ZnS:Ag phosphors and to less than this for the phosphors containing cadmium sulphide.

5. CONCLUSIONS AND FUTURE WORK

The effects on the maximum temperature coefficient of the addition of silver and nickel to zinc sulphide type phosphors have been investigated. Also the effects of the preparation conditions and the zinc-cadmium ratio have been examined. These results have been analyzed and an empirical equation has been fitted to them.

Because of the complexity of the system being studied it was not possible to find a model which fully explained the results. Further information is required about the types of levels taking part in the processes before a final solution to the problem can be obtained.

During the course of this work several experiments which could help to find the processes involved were suggested. These experiments include a search for an infra-red emission which could be associated with killer centres. It was found that an increase in the number of electron traps can be associated with a decrease in the maximum temperature coefficient. This effect could be investigated by comparing the rise and decay times of the phosphors with their maximum temperature coefficient. Using crystallographic studies it should be possible to find a relationship between the cubic to hexagonal ratio and the maximum temperature coefficient. Accurate measurements of the emission and reflection spectra would determine the relationships between the activaton energy and the maximum temperature coefficient. These results could also be used to check the relationship that was found in equation 22 page 61 between the superlinearity and the activaton energy.

ACKNOWLEDGEMENTS

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