

From the Physics Department, Jadavpur University Calcutta-32, India

Investigation on self activated and copper activated zinc sulphide*

By

A. CHOUDHURY

With 9 Figures in the Text

(Received September 17, 1962)

The diamagnetic susceptibility of zinc sulphide decreases on heat treatment and becomes less temperature dependent. The susceptibilities or the differences in susceptibilities of the pure and activated samples do not obey Curie Law. The susceptibility follows a relation of the type $\chi_T = \chi_0 + \chi_1 e^{-E/KT}$ in which both χ_0 and χ_1 have the same sign. χ_0 is interpreted as true diamagnetic susceptibility of the sample and gradually increases in value with activation. χ_1 depends on the particle size and is found to decrease with the increase in particle size. This is interpreted as being due to surface electrons. “ E ” as measured in this way is found to be of the order of 0.01 ev. in all cases. Thus “ E ” seems to be the average surface trap depth of zinc sulphide.

It has also been found that in zinc sulphide with low copper concentration the luminescent centres are diamagnetic; copper ions are present presumably in substitutional positions. For zinc sulphide containing high concentration of copper, the presence of paramagnetic centres are detected. It is suggested that in this case copper is present not only at the regular lattice positions acting as luminescent centre but also settles at special lattice sites like dislocation jogs.

Introduction

Pure zinc sulphide is non-luminescent but can be made to luminesce either by impurity activation or by self activation due to heat treatment. The heat treatment, depending on the nature of the ambient gases, produces lattice vacancies, interstitials and stoichiometric excess of zinc. Such defects are supposed to be the cause of luminescence in zinc sulphide activated by heat treatment. It has been shown by BUBE¹ that the change from cubic to hexagonal structure, which may result from heat treatment, has little influence on the luminescent properties.

A large amount of work on the luminescence of sulphide phosphors has accumulated and various models for the luminescent and trapping centres have been suggested. The data on luminescence are felt to be not quite enough, and leave disputed alternatives regarding the nature of centres. So a combined work on the luminescent and magnetic

* The work was carried out in the Indian Institute of Technology, Kharagpur.

¹ BUBE, R.H.: Phys. Rev. **80**, 655 (1950).

properties of the phosphor may help in the better understanding of the defect centres. Quite a few semiconductors like germanium, indium antimonide show temperature dependent diamagnetism. The diamagnetic susceptibility of germanium, indium antimonide have been explained by STEVENS and CRAWFORD² as being due to free carriers. LARACH and TURKEVICH³ studied the magnetic changes in zinc sulphide phosphors and have concluded that the luminescent centres are diamagnetic. BOWERS and MELAMED⁴ also measured the magnetic properties of impurity activated sulphide phosphors. All such investigations show that in these phosphors the luminescent centres are diamagnetic.

The present investigation has been undertaken to study the magnetic and luminescent properties of these sulphides under different conditions of activation. The heat treatment of these materials can produce changes in the crystal structure, the particle size, the number and nature of the defects and also modify the surface condition. These changes will contribute to the magnetic and luminescent properties. Thus it is expected that a consolidated study of the magnetic and the luminescent properties of the material may lead to better understanding of the defect centres. It may also give some explanation of the temperature dependent diamagnetism exhibited by defective solids.

Experiments and Results

In the present work the magnetic susceptibilities of samples of pure and copper activated zinc sulphide have been measured and the temperature dependence of the magnetic susceptibility has been studied in most cases.

The absorption spectra have been studied by the method of diffuse reflectance. The fluorescence spectra as well as the temperature variation of the total intensity have been studied.

The average particle size of the fired or heat treated samples has been measured by a high power microscope; in case of samples having particle size smaller than 1×10^{-4} cm the same has been estimated from the width of the X-ray diffraction lines.

The X-ray diffraction pattern of the different samples has been taken to identify the phase changes that may occur with heat treatment; these patterns also indicate the degree of crystallinity of the powders.

² STEVENS, D. K., and J. H. CRAWFORD: *Phys. Rev.* **99**, 487 (1955); **100**, 1084 (1955).

³ LARACH, S., and J. TURKEVICH: *Phys. Rev.* **98**, 1015 (1955).

⁴ BOWERS, R., and N. T. MELAMED: *Phys. Rev.* **99**, 1781 (1955); **100**, 1084 (1955).

The results of various measurements for the different samples are given below:

Pure zinc sulphide-ZnS: Pure zinc sulphide is heat treated in air in a platinum crucible for 15 minutes. To avoid any contamination, the lower part of the heat treated material is collected for measurement.

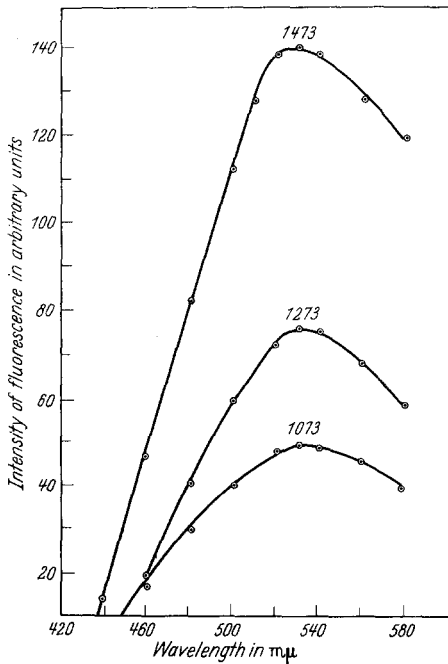


Fig. 1. The fluorescent spectra of ZnS fired at 1073°, 1273° and 1473° K measured at room temperature

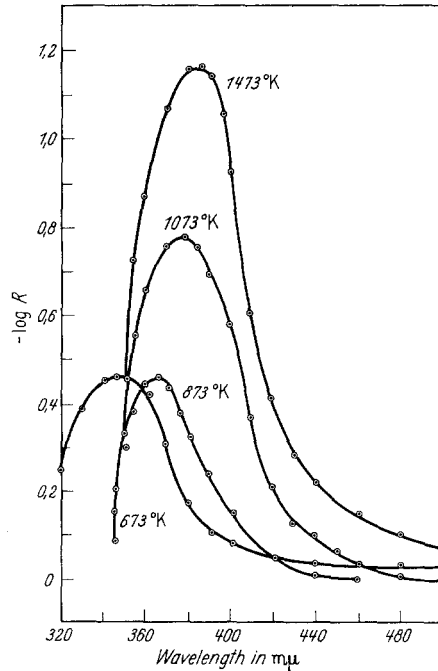


Fig. 2. $-\log R$ of fired samples of ZnS as a function of wavelength of light. (R is the relative reflectance of the specimen with respect to unfired ZnS)

Its fundamental absorption starts at about 330 $m\mu$ (not shown). When the sample is fired at different temperatures, it becomes fluorescent (Fig. 1) and a new absorption band on the long wave length side of the fundamental absorption edge is created (Fig. 2). For samples fired at about 1073° K or about the position of the band (380 $m\mu$) agrees closely with the absorption region of zinc oxide (in ZnO—ZnS mixed phosphor).

The fluorescent spectra (excited with 3130 AU) of a fired sample at liquid nitrogen and room temperature is shown in Fig. 3. The fluorescent spectrum at room temperature consists of a broad band with peak at 520 $m\mu$. At low temperature two distinct peaks at 480 and 514 $m\mu$ are obtained and the total intensity of fluorescence increases. On washing

Table 1. *The identification of the crystal structure of ZnS from X-ray diffraction photograph*

Specimen	Values of $h \cdot k \cdot l$	Measured value of $d \times 10^8$ cm	Remarks
Unfired	111	3.11	Cubic
	220	1.94	
	113	1.65	
	331	1.23	
	511	1.02	
	531	0.91	

Table 2. *Identification of the crystal structure of ZnS (fired at 1273° K) from X-ray diffraction photograph*

Specimen	Values of $h \cdot k \cdot l$	Measured value of $d \times 10^8$ cm	Remarks
ZnS fired at 1273° K	100	3.29	ZnS (Hex)
	002	3.10	ZnS (Hex)
	101	2.89	ZnS (Hex)
	002	2.59	ZnO
	102	2.26	ZnS (Hex)
	110	1.88	ZnS (Hex)
	103	1.76	ZnS (Hex)
	200	1.65	ZnS (Hex)
	201	1.59	ZnS (Hex)
	112	1.37	ZnO
	210	1.29	ZnS (Hex)
	202	1.23	ZnO
	214	0.02	ZnS (Hex)
	220	0.95	ZnS (Hex)
	300	0.95	ZnO
	116	0.91	ZnS (Hex)
	215	0.88	ZnS (Hex)

Table 3. *Identification of the crystal structure of ZnS (fired at 1273° K from X-ray diffraction photograph, after washing the sample acetic acid*

Specimen	Values of $h \cdot k \cdot l$	Measured value of $d \times 10^8$ cm	Remarks
ZnS fired at (1273° K after washing with acetic acid	100	3.31	ZnS (Hex)
	002	3.13	ZnS (Hex)
	101	2.91	ZnS (Hex)
	110	1.91	ZnS (Hex)
	103	1.76	ZnS (Hex)
	200	1.62	ZnS (Hex)
	201	1.59	ZnS (Hex)
	210	1.29	ZnS (Hex)
	214	1.03	ZnS (Hex)
	220	0.95	ZnS (Hex)
	116	0.91	ZnS (Hex)

the sample with acetic acid so as to remove the oxide, the short wave length band at 480 μ becomes prominent while the band with peak at 510 μ diminishes in intensity. From this it is concluded that the band in the blue region (480 μ) is due to self activation of zinc sulphide while the green band is due to the presence of zinc oxide. The system is similar to the mixed phosphor⁵ of zinc oxide dissolved in zinc sulphide.

The X-ray diffraction patterns of the sample before and after firing at different temperatures have been given in Tables 1 to 3. Before firing, the sample is cubic in character and the X-ray diffraction lines are comparatively diffuse. The particle size estimated from the width of the diffraction line is about 1×10^{-6} cm. The measured values of the average particle size for different temperatures of firing are given in Table 4.

⁵ KROGER, F. A., and J. A. M. DIKHOFF: J. Electrochem. Soc. 99, 144 (1952).

The sample fired at about 1073° K is partially converted into hexagonal variety (Table not given) and complete conversion takes place after firing at 1273° K or above. The zinc oxide lines are also distinctly present on the X-ray diffraction patterns. These are removed on washing the samples with acetic acid (Table 3).

Table 4. The average particle size of ZnS for different temperatures of firing

Temperatur of firing T °K	Average particle size at 300° K
300	1.0×10^{-6} cm
1273	2.0×10^{-4} cm
1473	3.6×10^{-4} cm

The magnetic susceptibility and its variation with temperature between 87° to 300° K has been measured for various samples. The results are shown in Fig. 4. Before firing the diamagnetic susceptibility of this sample of zinc sulphide is -0.3805×10^{-6} e.m.u./gm. On firing the diamagnetic susceptibility decreases but its temperature dependence is reduced (Fig. 4).

The presence of zinc oxide has very little effect on the results; the diamagnetic susceptibility of zinc oxide is -0.36×10^{-6} e.m.u./gm and is practically independent of temperature. On removing zinc oxide by washing with acetic acid, the magnetic susceptibility remains practically unaltered.

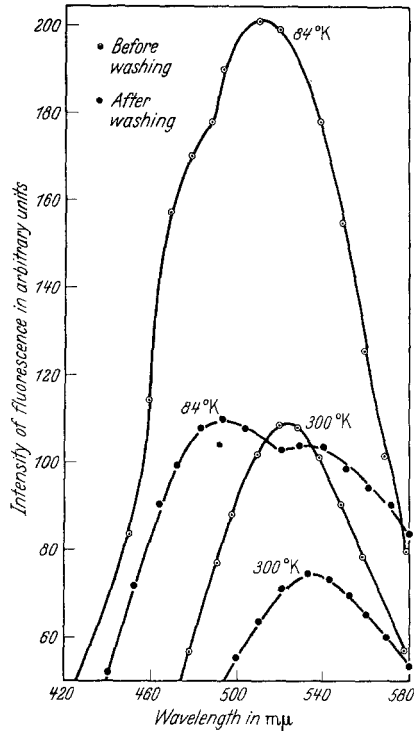


Fig. 3. The fluorescent spectra of ZnS fired at 1273° K, before and after washing with acetic acid. The measurements were made at 300 and 84° K

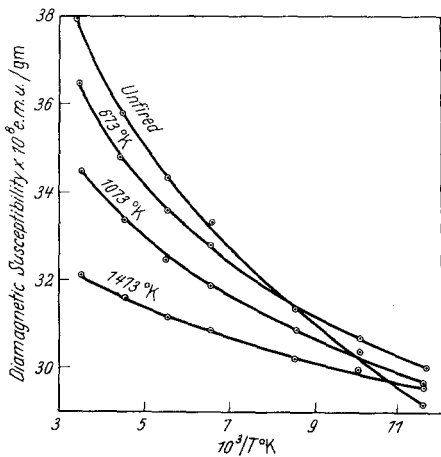


Fig. 4. The diamagnetic susceptibility of unfired and fired samples of ZnS as a function reciprocal of temperature

Copper activated zinc sulphide — ZnS—Cu (0.01%). This sample emits green fluorescence under ultraviolet excitation (3130 AU). The absorption edge as measured by reflectance is shifted towards longer wavelength (390 m μ). The average particle size measured under microscope is about 7.8×10^{-4} cm.

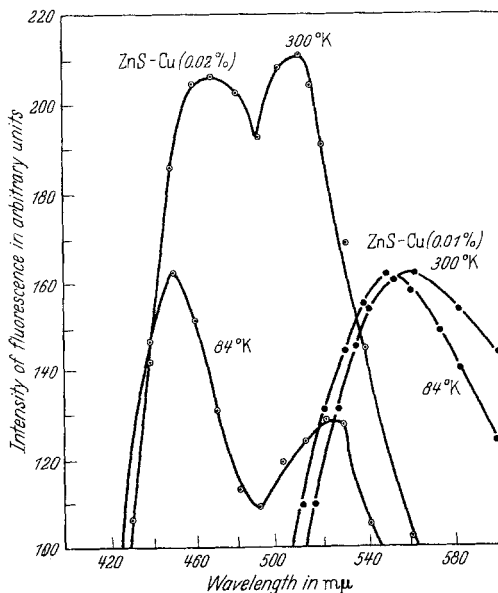


Fig. 5. The fluorescent spectra of ZnS activated with copper. The measurements were made at 300° and 84° K

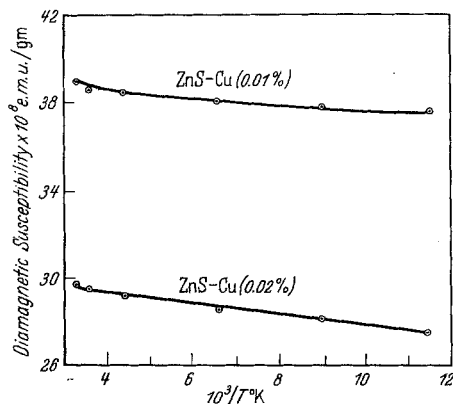


Fig. 6. The magnetic susceptibility of ZnS—Cu (0.01%) and ZnS—Cu (0.02%) as a function of the reciprocal of temperature

The fluorescence spectrum under ultraviolet excitation at 84° and 300° K is shown in Fig. 5, it consists of a green band with a peak at about 550 m μ when measured at 300° K.

The X-ray diffraction pattern of this sample consists of sharp lines and indicates the presence of cubic variety alone (Table not given).

The magnetic susceptibility of the sample measured at different temperatures in the range of 87° to 300° K is shown in Fig. 6. The diamagnetic susceptibility of the sample at room temperature (300° K) is -0.3895×10^{-6} e.m.u./gm.

The magnetic susceptibility of the sample measured at different temperatures in the range of 87° to 300° K is shown in Fig. 6. The diamagnetic susceptibility of the sample at room temperature (300° K) is -0.3895×10^{-6} e.m.u./gm.

Copper activated zinc sulphide (Blue) — ZnS—Cu (0.02%). This sample containing higher concentration of copper has a blue fluorescence under ultraviolet excitation (3130 AU). The fluorescence spectra measured at 300° and 84° K are shown in Fig. 5. The absorption edge is shifted towards longer wavelength (400 m μ) compared to the previous samples.

The X-ray diffraction pattern of the sample shows lines of the hexagonal variety (Table not given). The average particle size measured under the microscope is about 5.4×10^{-4} cm.

The X-ray diffraction pattern of the sample shows lines of the hexagonal variety (Table not given). The average particle size measured under the microscope is about 5.4×10^{-4} cm.

The magnetic susceptibility of the sample, measured at different temperatures between 87° to 300° K is shown in Fig. 6. The diamagnetic susceptibility at room temperature is -0.2987×10^{-6} e.m.u./gm and it falls to a value of -0.2757×10^{-6} e.m.u./gm at 87° K.

Discussion

The blue luminescence of self activated zinc sulphide according to KROGER and VINK⁶, is due to cation vacancies that have lost one electron (V_c^+), while the green fluorescence is due to anion vacancies that have captured one electron (V_A^-); interstitial zinc, which is likely to be in the ionic state is also believed to produce green luminescence. Such centres should be paramagnetic, but LARACH and TURKEVICH³ conclude from their magnetic measurements of zinc sulphide that the fluorescent centres are diamagnetic in character. The luminescence of self activated zinc sulphide is thus supposed to be due to simple ionic vacancies⁷.

It is found from the present measurements that pure zinc sulphide, prior to any heat treatment is cubic in structure, is of poor crystallinity and have very small average particle size (1×10^{-6} cm). Heat treatment in air, at temperatures of about 1073° K or above, increases the average particle size and improves crystallinity, as well as starts oxidation; heat treatment at temperature about 1273° K converts the cubic variety into hexagonal modification. The samples heat treated even at as low a temperature as 673° K show bluish fluorescence and the new absorption band with maximum at 340 m μ is detectable.

The luminescent spectra of zinc sulphide heat treated at 1273° K show two peaks at 480 and 510 m μ (Fig. 3). As a matter of fact as the temperature of heat treatment is raised from 673° to 1273° K, the position of the absorption band peak shifts from 340 to 380 m μ . Thus in zinc sulphide heat treated in air at temperatures at about 1273° K or above, two types of luminescent centres are created. On washing the phosphor with acetic acid, zinc oxide present as separate phase is removed and the corresponding diffraction lines of the oxide disappears in X-ray pattern. The blue band in emission increases in intensity but the green band, although comparatively weak, is still present. It may, therefore, be concluded that the surfaces of the crystallinities of the heat treated specimens, consist mainly of a solid solution of zinc oxide in zinc sulphide and in addition to this, they also contain the luminescent centres characteristic of self activation.

Zinc sulphide containing 0.01% of copper, shows a peak at about 550 m μ (Fig. 5); zinc sulphide containing 0.02% of copper shows two peaks at 470 and 510 m μ (Fig. 5).

⁶ KROGER, F.A., and H. J. VINK: J. Chem. Phys. **22**, 250 (1954).

⁷ BROWNE, F.F.: J. Electronics **2**, 154 (1956).

The luminescence yield of heat treated zinc sulphide increases rapidly on lowering the temperature (Fig. 7). For zinc sulphide (0.01% Cu) the luminescence yield is also temperature dependent and for zinc sulphide (0.02% Cu) the luminescence yield slightly decreases at liquid nitrogen temperature. Thus, the luminescent centres responsible for the different emission bands^{8,9} discussed above are distinctly different.

The present investigation shows that the diamagnetic susceptibility of pure zinc sulphide decreases on lowering the temperature. The nature

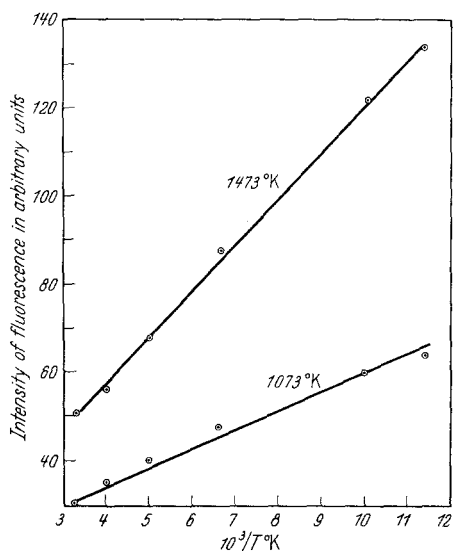


Fig. 7. The intensity of fluorescence of ZnS fired at 1073° and 1473° K as a function of $1/T$ °K

of temperature variation however, does not follow Curie Law or modified Curie Law. This appears to be a case of real decrease in diamagnetism of the material.

The temperature dependent diamagnetism has been observed and reported for a number of semiconductors like germanium, indium antimonide etc.; the decrease of diamagnetic susceptibility on lowering of temperature, observed in indium antimonide has been successfully explained as being due to corresponding changes in carrier concentration². For a material like zinc sulphide the carrier concentration in the

normal temperature range will remain very low due to large band gap. Besides STEVENS and CRAWFORD² show that $\log(\Delta\chi/T^{3/2})$ plotted against $1/T$ is a straight line if the effect be due to the carriers; such an analysis of the results of the present measurement has been carried out, but the plot does not approximate to a straight line.

After various trials of curve fitting it has been found that the diamagnetic susceptibilities of pure and heat treated zinc sulphide can best be described in the form $\chi_T = \chi_0 + \chi_1 e^{-E/KT}$. Following standard method of curve fitting¹⁰, the parameters, χ_0 , χ_1 and E have been determined in each case from the measured values of the susceptibilities, χ_T ; these are given in Table 5. The straight line plots of $\log(\chi_T - \chi_0)$ against $(1/T)$

⁸ TOMLINSON, T.B.: J. Electronics 2, 166 (1956).

⁹ SCHRADER, R.E., and S. LARACH: Phys. Rev. 193, 1899 (1956).

¹⁰ LIPKA, J.: Graphical and Mechanical Computation. New York: John Wiley & Sons. Inc. 1918.

are shown in Fig. 8 and the variation from straight line fit of the results with small changes in the values of the parameter χ_0 are also indicated in Fig. 9.

The temperature independent part of the diamagnetic susceptibility of pure zinc sulphide, ZnS is -0.236×10^{-6} e.m.u./gm; for heat treated samples its value increases (Table 5). LARACH and TURKEVICH³ obtained a value of diamagnetic susceptibility, -0.26×10^{-6} e.m.u./gm for a cubic sample of pure zinc sulphide which was temperature independent; it has satisfactory agreement with the value of χ_0 obtained in the present measurement for pure ZnS. For samples heat treated at temperatures between 1073° to 1473° K, the value of χ_0 increases from -0.287×10^{-6} to -0.294×10^{-6} e.m.u./gm the complete conversion to hexagonal modification has taken place and the corresponding value of $\chi_0 = -0.294 \times 10^{-6}$ e.m.u./gm agrees very closely with the temperature independent diamagnetic susceptibility of the hexagonal modification of zinc sulphide reported by LARACH and TURKEVICH³ (-0.29×10^{-6} e.m.u./gm).

Table 5. The value of the parameters χ_0 , χ_1 and E as determined from the measured values of susceptibilities

Specimen	$-\chi_0 \times 10^6$	$-\chi_1 \times 10^6$	E in e.v.
ZnS (unfired)	0.236	0.212	0.010
ZnS (673)	0.277	0.144	0.013
ZnS (1073)	0.287	0.108	0.016
ZnS (1473)	0.294	0.060	0.016

The temperature dependent part of the diamagnetic susceptibility is determined by the value of χ_1 and E ; the value of χ_1 is largest for unfired pure zinc sulphide and decreases gradually as the firing temperature is raised (Table 5) while the value of E is about 0.01 e.v. and changes only slightly for different samples. It may also be seen that the value of χ_1 decreases with increase in average particle size. It can then be tentatively suggested that the electrons are trapped presumably in the surface trapping states, which have a depth of the order of 0.01 e.v., these are immobilised with corresponding decrease in diamagnetism.

The temperature dependence of the diamagnetic susceptibility of copper activated zinc sulphide is very small. It is minimum for ZnS—Cu (0.01%) which is cubic in structure and has the largest particle size 7.8×10^{-4} cm, the temperature dependent part of the diamagnetic susceptibility is so small in this case that the determination of χ_1 and E by curve fitting becomes very unreliable. The value of χ_0 is roughly about -0.33×10^{-6} which is higher than that of pure ZnS this is in agreement with the conclusion of BOWERS and MELAMED⁴.

Zinc sulphide containing 0.02% of copper is of hexagonal structure and of average particle size 5.4×10^{-4} cm. The variation in magnetic susceptibility within this temperature range is also small and χ plotted

against $1/T$ shows a straight line fit (not shown) within experimental error. It is also known that copper present as Cu^+ is responsible for luminescence of copper activated zinc sulphide. But the result of the present investigation imply that at higher concentration of copper, paramagnetic centres as well are created. TOMLINSON⁸, MCKEAG and

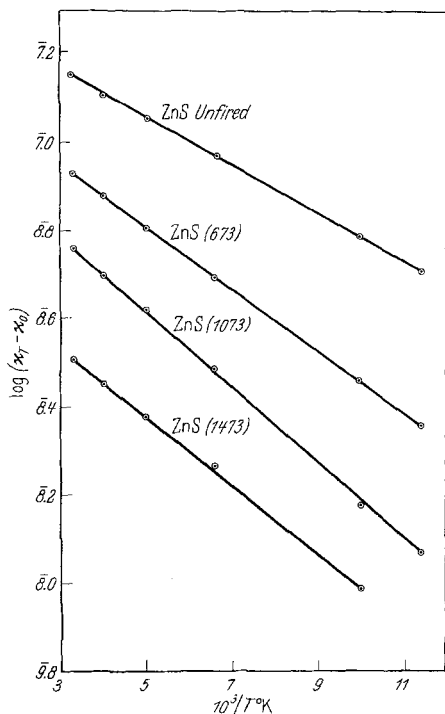


Fig. 8. $\log(\chi_T - \chi_0)$ as a function of the reciprocal of temperature. (χ_T is the susceptibility at any temperature T and χ_0 is the temperature independent diamagnetic susceptibility)

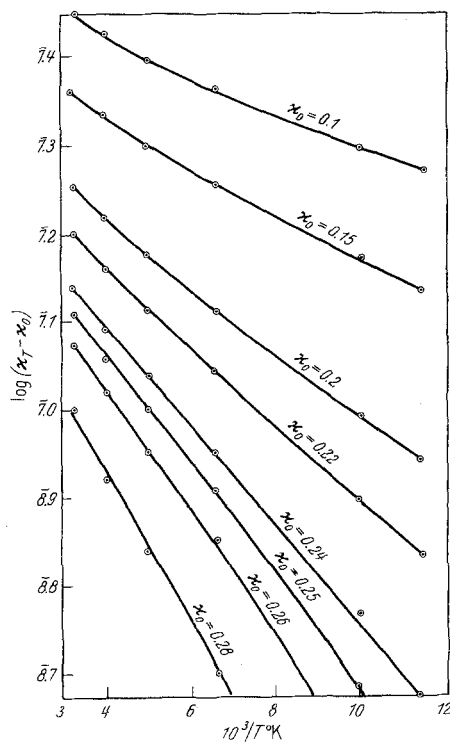


Fig. 9. $\log(\chi_T - \chi_0)$ as a function of the reciprocal of temperature. The plot has been shown with different values of χ_0

STUARD¹¹ have clearly shown that at higher copper concentration, copper is also present in some other association in addition to that in solid solution. The copper in solid solution produces normal ultraviolet luminescence while the excess copper possibly goes to dislocations or special points on the surfaces.

The author is indebted to Prof. G. F. J. GARLICK, F. R. S., for providing the specimens of zinc sulphide and to Prof. H. N. BOSE for his valuable guidance. The author is also indebted to Prof. S. D. CHATTERJEE for his kind interest in the work.

¹¹ MCKEAG and STUARD: J. Electrochem. Soc. **104**, 41 (1957).