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X-ray, electrical conductivity and magnetic hysteresis studies of the chalcogenide system $Zn_{1-x}Cu_xCr_2Se_4$

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X-ray diffraction studies performed here indicated solid-solution formation between $ZnCr_2Se_4$ and $CuCr_2Se_4$, and all the compounds could be indexed on the basis of cubic spinel lattice. The compositions between $0 \leqslant x \leqslant 0.8$ showed semi-conducting behaviour, while $CuCr_2Se_4$ ($x = 1.0$) exhibited metallic conductivity. Seebeck measurements showd P-type behaviour for $0 \leqslant x \leqslant 1$. Magnetic hysteresis indicated a ferromagnetic nature for all the compounds except $ZnCr_2Se_4$ ($x = 0$). The shapes of χ/χ_i plotted against T exhibited single domain behaviour, and Curie temperatures showed an increase with increasing copper concentration.

1. Introduction

Spinels possess interesting structural, electrical and magnetic properties which are suitable for a variety of applications. These properties depend on the nature of the valence states and the distribution of these metal ions over two sites in spinel, AB_2X_4 (X = oxygen, sulphur or selenium) lattice. From the literature, it is observed that comparatively little work has been reported on chalcogenide spinels due to difficult process of synthesis. Lotgering [1] investigated the system and reported limited solubility (up to $x = 0.5$) while recently Krok *et al.* [2] have shown complete miscibility between $ZnCr_2Se_4$ and $CuCr_2Se_4$. It was therefore thought interesting to study the system $Zn_{1-x}Cu_xCr_2Se_4$ with a view to investigating the extent of solid-solution formation, and also the electrical and magnetic hysteresis since they have not been examined so far.

2. Experimental procedure

All the compositions of the system were synthesized starting from high purity elements (99.9%, Fluka Grade): zinc, copper, chromium and selenium. They were mixed in stoichiometric proportions and ground in acetone medium for uniform mixing. The mixtures were then vacuum sealed (10^{-6} torr) in quartz ampoules (length 10 cm, and diameter 1.5 cm.) which were heated at 900° C for 40 h. The ampoules were then broken and samples were crushed for speedy homogenization, and again vacuum sealed and refired at 900° C for 40 h. The samples were then furnace cooled to room temperature, and X-ray analysis was carried out to check the spinel formation.

X-ray diffraction analysis was carried out using Philips X-ray diffractometer using CuK_α radiation with a nickel filter. Electrical conductivity measurements were carried out using an LCR bridge. The magnetic hysteresis loops at 300 and 80 K were taken on an alternating current electromagnet-type hysteresis loop tracer [3] using a 3-Koe field. Initial susceptibility studies were made for all the compounds, except $x = 0$, by a double-coil method. From the plots of χ/χ_i against T, the Curie temperatures (T_c) of the compounds were determined.

3. Results and discussion

X-ray diffractometer patterns of $CuCr_2Se_4$ (a) and $ZnCr_2Se_4$ (b) are given in Fig. 1. All the compounds of the series could be indexed on the basis of cubic spinel structure except $CuCr_2Se_4$, where two very weak reflections were observed which could not be indexed. Lotgering [1] also observed a similar X-ray diffractometer pattern. The plot of lattice constant against composition showed that Vegard's law is nearly obeyed (Fig. 2a). The lattice constant of $CuCr_2Se_4$ agrees fairly well with the value (1.032 nm) reported by Kanomata *et al.* [4] (Table I).

When electrical conductivity measurements were carried out up to 500 K, it was observed that all the compounds up to $x = 0.8$ exhibited semiconducting behaviour except $CuCr_2Se_4$ ($x = 1.0$) which showed metallic conductivity. Further, it was noted that ϱ decreases with an increase in copper concentration. $ZnCr_2Se_4$ showed $\varrho_{RT} = 533\,\Omega\,cm^{-1}$ while for $CuCr_2Se_4$ it was only $10\,\Omega\,cm^{-1}$, suggesting the presence of mixed valence in copper-containing chalcogenides. Ballal and Mande [5] investigated $CuCr_2Se_4$ using X-ray absorption spectroscopy and from the shift of the K-absorption edge suggested the monovalency of copper in $CuCr_2Se_4$. Similar results have also been observed by Robbins *et al.* [6] and Colominas [7] using the neutron diffraction technique.

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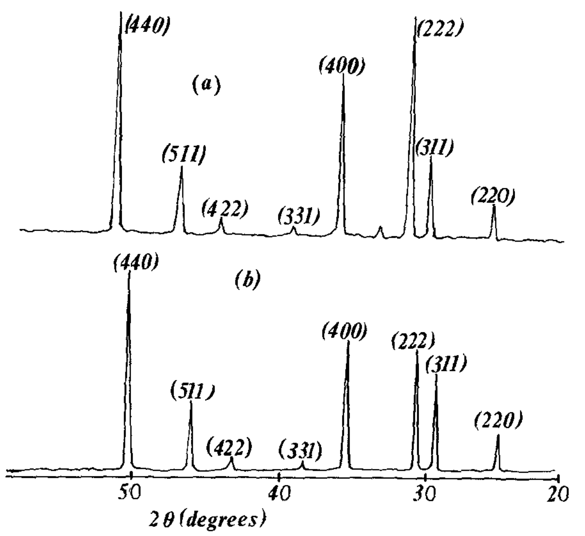

Figure 1 X-ray diffractometer patterns of (a) $CuCr_2Se_4$ and (b) $ZnCr_2Se_4$.

TABLE I Lattice constant, ϱ_{RT} and $\mu_{V/K}$ for the system $Zn_{1-x}Cu_xCr_2Se_4$

Compound	Lattice constant a (nm)	ϱ_{RT} (Ω cm^{-1})	($\mu_{V/K}$)
$ZnCr_2Se_4$	1.047	513	190
$Zn_{0.8}Cu_{0.2}Cr_2Se_4$	1.046	147	149
$Zn_{0.6}Cu_{0.4}Cr_2Se_4$	1.043	92	18
$Zn_{0.2}Cu_{0.8}Cr_2Se_4$	1.031	37	16
$CuCr_2Se_4$	1.029	10	11

Increased conductivity with increased x (copper concentration) in the series is due to the increase in Cr^{4+} concentration at site B, which is proportional to the increase in Cu^+ concentration at site A in the system. The oxidation state of copper (+ 1) suggested by the above authors [5–7] and by the high conductivity (Table II) observed for these compounds suggests the following cation distribution

$$Zn^{2+}_{1-x}Cu^{+}_{x}[Cr^{3+}_{2-x}Cr^{4+}_{x}]Se_4$$

In spinels electrical conduction generally takes place through the hopping of charge carriers at site B, and therefore in the compounds investigated electrical conduction must be taking place via the following process

$$Cr^{3+} + Cr^{4+} \rightleftarrows \overset{\frown}{Cr^{4+} + Cr^{3+}}$$

Since there is no possibility of Cr^{3+}-Cr^{4+} pair formation in $ZnCr_2Se_4$, conductivity should be taking place due to impurity conduction [8].

Thermoelectric measurements carried out between 300 and 500 K showed that all the compounds are P-type conductors. In all the compositions, the plots ΔV against ΔT were linear (see Fig. 2b). Thermoelectric measurements were calculated using the equation suggested by Honig [9]

$$\alpha \pm = \frac{K}{e}\ln\frac{1-S}{S} + \frac{\bar{S}_R}{K}$$

where K is the Boltz–Mann constant, e is electron charge, S is the probability of cationic site and S_R is the lattice relaxation entropy term. The α values varied between 190 and 11 μ_{VK} (Table I). Further, it is observed that zinc-rich compounds show more P-type behaviour than copper-rich compounds, and this can be attributed to the loss of some zinc in the firing process: as a result, cation vacancies are created at site A. Such a mechanism has been observed by Blasse [10] and Lotgering [11]. Another possible cause of the decreasing P-type behaviour in the series is the decreasing concentration of zinc. The P-type behaviour of $CuCr_2Se_4$ is attributed to the increase in acceptor concentration as opposed to the donor.

Initial susceptibility studies were carried out from 300 to 500 K for all the compounds except $x = 0$. From the plots of χ/χ_i, the Curie temperature (T_c) of the compounds was determined. The curves χ/χ_i against T are given in Figs 2c and d. In general χ/χ_i against T curves first increase (Fig. 2c) with temperature and then suddenly become zero just before Curie temperature. The shape of the curves (Figs 2c and d) suggests that the samples contain single domain (SD) grains [12, 13]. The Curie temperature (T_c) for all the compounds except $x = 0$ is calculated from these curves. T_c values are found to be increasing (Fig. 2e) with increase in the concentration of copper. The increase in Curie temperature with the increase in the value of x can be attributed to the increasing ferromagnetic character.

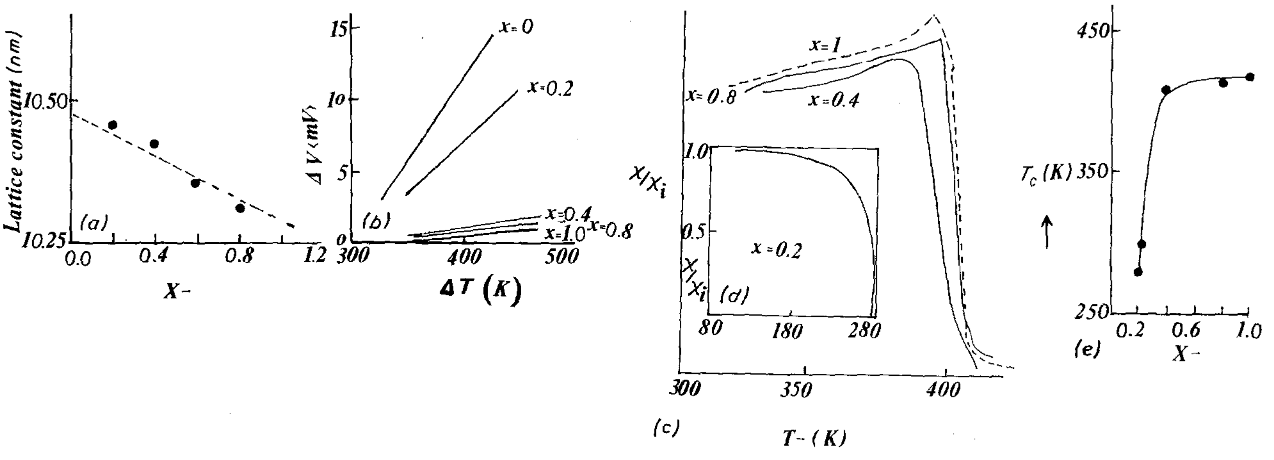

Figure 2 (a) Plot of lattice constant against compositions for the system $Zn_{1-x}Cu_xCr_2Se_4$. (b) Plot of ΔV against ΔT. (c, d) Plot of χ/χ_i against T for the system $Zn_{1-x}Cu_xCr_2Se_4$. (e) Plot of T_c versus X (composition) for the system $Zn_{1-x}Cu_xCr_2Se_4$.

TABLE II Coercivity (H_c), remanance ratio J_r/J_s, saturation magnetization σ_S, magnetic moment (n_B) and Curie temperature (T_c) for the system $Zn_{1-x}Cu_xCr_2Se_4$

Compound	Coercivity (H_c) (Oe)		Remanance ratio J_r/J_s		σ_S (μ g^{-1})		n_B (μB) (80 K)		T_c (K)
	300 K	80 K	300 K	80 K	300 K	80 K	Obs.	Calc	
$ZnCr_2Se_4$	–	–	–	–	–	–	–	–	–
$Zn_{0.8}Cu_{0.2}Cr_2Se_4$	150	325	0.227	0.357	10.30	12.21	1.06	5.8	281
$Zn_{0.6}Cu_{0.4}Cr_2Se_4$	150	250	0.285	0.333	17.69	20.15	1.75	5.6	408
$Zn_{0.2}Cu_{0.8}Cr_2Se_4$	75	100	0.166	0.111	37.20	45.22	3.92	5.2	415
$CuCr_2Se_4$	50	100	0.062	0.111	40.60	44.21	3.83	5.0	420

All the compounds of the system except for $x = 0$ show magnetic hysteresis loops at 300 and 80 K (Fig. 3). The coercive force H_c, the remanance ratio J_r/J_s, saturation magnetisation σ_s, magnetic moment n_B and ferromagnetic Curie temperature (T_c) are listed in Table II. The magnetic moment is calculated from the σ_s values at 80 K using the relation

$$n_B = \frac{\sigma_s \times \text{mol wt}}{5585}$$

Further it has been observed that the coercivity and remanance ratios were found to decrease with increase in copper concentration; this can be attributed to the changes in the magnetic anisotropy.

From the literature, it is observed that so far no work has been reported on the magnetic hysteresis of the systems, $Zn_{1-x}Cu_xCr_2Se_4$. All the compounds of the system except $x = 0$ show magnetic hysteresis loops at 300 and 80 K, suggesting the ferromagnetic nature of the compounds (Fig. 3). The first compound, $ZnCr_2Se_4$, has been reported to be antiferromagnetic from neutron-diffraction studies [14] which have predicted a helical structure for $ZnCr_2Se_4$.

For spinels in general, if both sites A and B are occupied by magnetic ions, then a stronger A–B interaction controls the magnetic behaviour of the materials. We cannot get much information regarding the B–B interaction. However, if site A is occupied by a diamagnetic ion, then B–B interaction becomes quite predominant [10, 15]. Jain and Darshane [16] investigated the system $ZnFe_{1-x}Mn_xCrO_4$ and from low-temperature magnetic-susceptiblity studies, they observed all the compounds to be antiferromagnetic, due to the presence of diamagnetic Zn^{2+} at site A.

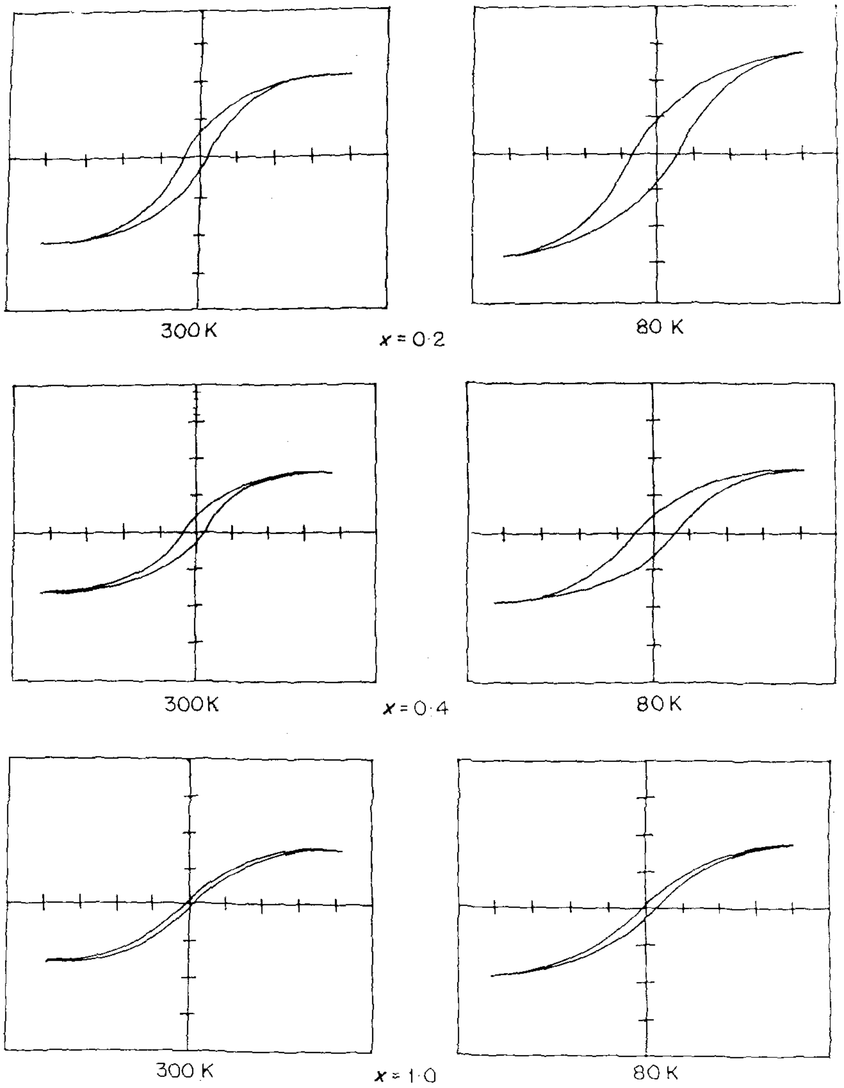

Figure 3 Hysteresis loops at 300 and 80 K for the compounds of the system $Zn_{1-x}Cu_xCr_2Se_4$.

Since, in the compounds investigated, site A is occupied by diamagnetic ions (Zn^{2+}, Cu^{+}) the question of an A–B interaction does not arise, and only B–B interactions are predominant. However, in the case of chalcogenides, the B–B interactions do not take place through direct overlap, but through a super-exchange mechanism due to larger interatomic distance (the Cr^{3+}–Cr^{3+} distance in oxides is 0.294 nm compared to a Cr^{3+}–Cr^{3+} distance in selenides of 0.371 nm).

From Table II, it is seen that the observed magnetic moment values for the composition $x = 0.2$ to 0.4 show wide variation from the theoretical mode (ferromagnetic) and for the compositions $x = 0.8$ to 1.0, nearly identical values have been observed. The discrepancy in the earlier compositions can be attributed to the mixed-exchange interactions (antiferromagnetic) occurring at site B.

It is generally accepted by various authors [1, 2] that there are two sets of superexchange interactions in spinels: (i) Cr–Se–Se–Cr (antiferromagnetic); and (ii) Cr–Se–Cr (ferromagnetic). It has been observed from hysteresis studies that the compositions $x = 0.2$ to 1.0 are all ferromagnetic. However, in zinc-rich compounds the deviation in observed and calculated magnetic moment is due to the coexistence of antiferromagnetic interactions with ferromagnetic ones. The ferromagnetic interaction becomes much stronger in the case of copper-rich compounds. Therefore, there is reasonable agreement of the observed and calculated magnetic moments.

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