

## Synthesis and properties of the $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4$ system

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**Abstract.** Monophasic compounds with composition  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4$  ( $0 \leq x \leq 0.2$ ) have been prepared. The compounds have defect nickel arsenide structure. The compositions are semiconductors with low energy of activation. Their Seebeck coefficients are temperature-independent. The compositions  $x = 0$  and  $0.1$  show temperature independent paramagnetism except for a small hump around 210 K. The peculiar behaviour of the susceptibility-temperature plot for the composition  $x = 0.2$  is not understood.

**Keywords.**  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4$  system ; defect NiAs structure ; electrical properties ; magnetic properties.

### 1. Introduction

Copper chromium selenide  $\text{CuCr}_2\text{Se}_4$  is a ferromagnetic metal with spinel structure with  $T_c = 460$  K (Lotgering 1964).  $\text{FeCr}_2\text{Se}_4$ , on the other hand, has defect NiAs structure and is reported to be antiferromagnetic at 4.2 K (Chevretton and Andron 1967). Electrical properties of the latter phase have been described as both metallic (Gibart *et al* 1973) and also as semiconducting (Morris *et al* 1970). A mixed selenide system  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4$  is expected to have interesting properties. The analogous sulphur system has been reported (Haacke and Beegle 1967). We report here the synthesis and properties of the  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4$  system ( $0 \leq x \leq 0.2$ ) that has not been reported so far.

### 2. Experimental

The required quantities of the finely-powdered elements of high purity were mixed, evacuated in quartz ampoules to  $10^{-6}$  torr and sealed. After one week

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firing at 800° C, the contents were again ground, pelletized and refired in evacuated, sealed quartz ampoules for two weeks. It was then quenched by dropping into liquid nitrogen.

X-ray diffraction (XRD) patterns were recorded using  $\text{CuK}_\alpha$  at a scanning rate 1°/minute. Electrical resistivity of the pellets were measured from 80–300 K using a four-probe method. The low temperature magnetic susceptibility of the powder was obtained using the Gouy method. The Seebeck voltage was measured in the same temperature range at a temperature gradient  $\sim 10$  K.

### 3. Results and discussion

All the lines in the XRD patterns could be indexed on the basis of the reported monoclinic structure of  $\text{FeCr}_2\text{Se}_4$ . The lattice parameters of  $\text{FeCr}_2\text{Se}_4$  obtained by us were a little different from those reported in the literature (Morris *et al* 1970), presumably because our samples were prepared by quenching and should have a higher defect concentration. The compounds were semiconductors with low energy of activation in the temperature range of study. The seebeck coefficient ( $\alpha$ ) is independent of temperature. The results are shown in table 1.

Figure 1 shows the plots of resistivity against reciprocal temperature. The magnetic susceptibility vs temperature plots are presented in figure 2.

It is known that stability of the spinel structure decreases when the anion polarisability increases. Generally spinels of composition  $\text{MCr}_2\text{Se}_4$  are formed when  $M$  is a bivalent ion with a strong tetrahedral site preference. In such compounds,  $\text{Cr}^{3+}$  ions always occupy the  $B$  sites (Von Philipsborn 1971) and  $M$  can be  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  or  $\text{Hg}^{2+}$  (Miller 1959) or  $\text{Cu}^{2+}$  (Lotgering 1964). Our attempts to obtain  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4$  generally gave a mixture of spinel and defect NiAs phases over the entire range of composition ( $0 \leq x \leq 1$ ) and even prolonged annealing did not give single phase spinel. Only in the iron-rich side it was possible to obtain monophasic compounds with defect NiAs structure, that too only by quenching to the temperature of liquid nitrogen.

Figure 1 shows that all the compositions are semiconductors. Resistivity was found to increase at the initial copper substitution ( $x = 0.1$ ) and then decreased

Table 1. Some properties of the compounds in the  $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4$  system.

Composition $x$	Lattice parameters				Activation energy (eV)	Seebeck coefficient ( $\mu\text{V/K}$ )
	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (°)		
0	6.14	3.60	11.73	88.61	0.026	+100
0.1	6.21	3.59	11.74	89.85	0.02	+145
0.2	6.21	3.60	11.73	89.77	0.01	+95

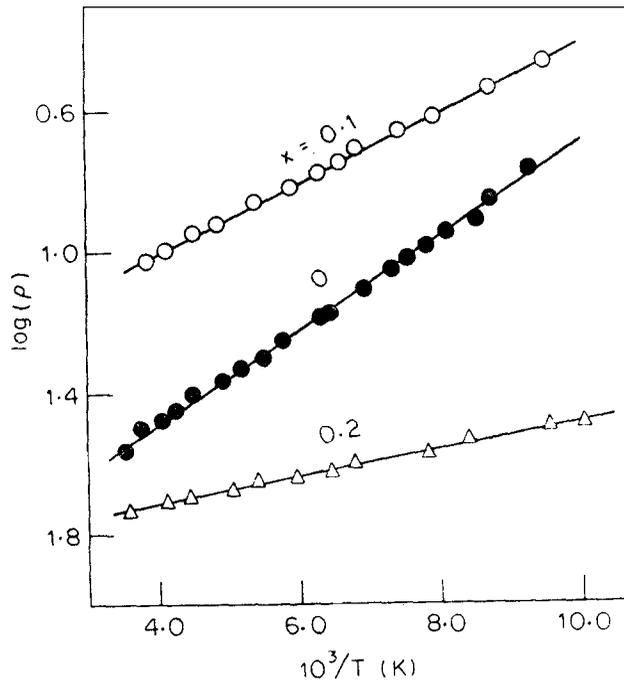


Figure 1. Resistivity vs temperature plots for the  $Fe_{1-x}Cu_xCr_2Se_4$  system.

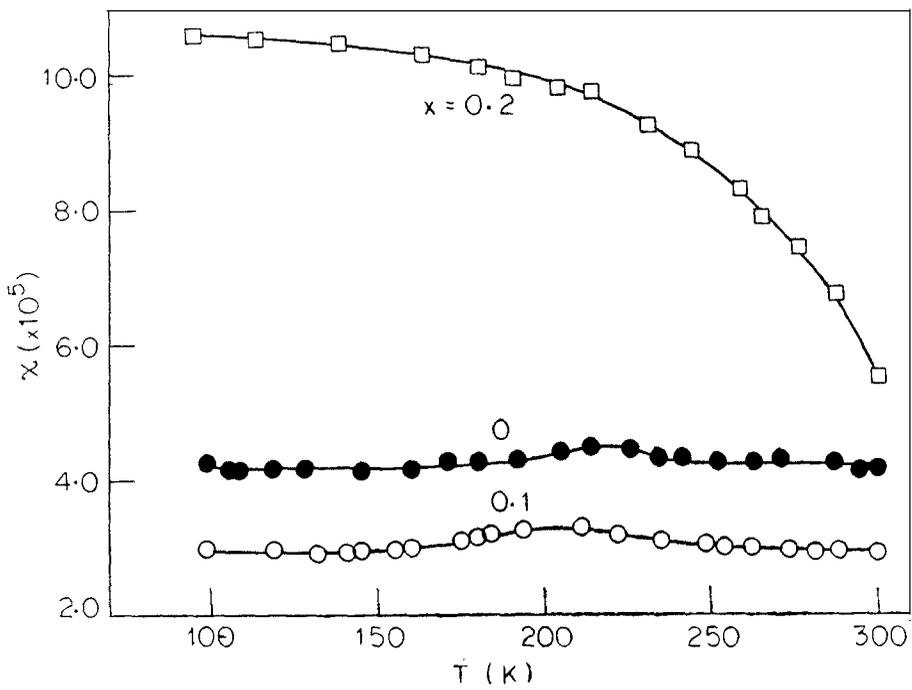


Figure 2. Magnetic susceptibility vs temperature plots for iron copper chromium selenides.

at  $x = 0.2$ . In fact, this peculiar behaviour at  $x = 0.2$  is also reflected in the structure, the Seebeck coefficient and the magnetic susceptibility.

The magnetic susceptibility vs temperature plots (figure 2) show that for  $x = 0$  and  $0.1$ , susceptibility is temperature-independent except for the presence of a small hump around 210 K. The temperature independent susceptibility is sufficiently high and hence does not seem to be Pauli paramagnetism. A proper explanation of this behaviour is not available. Mössbauer studies by Hong and Ok (1975) suggested that  $\text{FeCr}_2\text{Se}_4$  has Neel temperature around 218 K. Although magnetic susceptibility of  $\text{FeCr}_2\text{Se}_4$  reported by Morris *et al* (1970) showed a hump around this temperature, this cannot be considered as Neel temperature. Thermomagnetic curves reported by Morris *et al* (1970) show somewhat lower values of susceptibility. The same is true for their Seebeck coefficient data. The difference may be due to the difference in the methods of preparation. While Morris *et al* (1970) cooled their samples in the furnace, we quenched them from 800 to 80 K. The neutron diffraction studies, on the other hand, (Chevreton and Andron 1967) have shown that this compound is antiferromagnetic at 4.2K.

We are not able to explain the peculiar behaviour of  $\text{Fe}_{0.4}\text{Cu}_{0.2}\text{Cr}_2\text{Se}_4$ . It was shown by Andron and Bertaut (1966) that there are several super-exchange interactions in  $\text{NiCr}_2\text{S}_4$  some of which are ferromagnetic and others are antiferromagnetic. The same must be true for the compounds reported here. An understanding of these competing interactions is essential to explain the peculiarities of the thermomagnetic plots reported here.

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