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## Effect of Pressure on Curie Temperatures of Calcogenide Spinel $\text{CuCr}_2\text{X}_4$ (X=S, Se and Te)

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The pressure coefficient of the Curie temperature of  $\text{CuCr}_2\text{X}_4$  was obtained from the result of measurement of the variation with pressure in the self inductance of search coil wound on the specimen vessel. The coefficients,  $dT_c/dp$ , were founded to be  $-11.3 \times 10^{-4} \text{ }^\circ\text{K kg}^{-1}\text{cm}^2$  for  $\text{CuCr}_2\text{S}_4$ ,  $-4.1 \times 10^{-4} \text{ }^\circ\text{K kg}^{-1}\text{cm}^2$  for  $\text{CuCr}_2\text{Se}_4$  and nearly zero for  $\text{CuCr}_2\text{Te}_4$ , respectively. If the main exchange interaction in a pair of Cr ions is thought to be the ferromagnetic superexchange of the Cr-X-Cr type and the antiferromagnetic direct interaction of the Cr-Cr type, it can be seen from the results of the present experiment that the direct Cr-Cr interaction is more sensitive to lattice compression than the superexchange Cr-X-Cr. The magnetic properties of those compounds are also reported.

### § 1. Introduction

Lotgering<sup>1)</sup> first studied magnetic and electrical properties of the compound  $\text{CuCr}_2\text{X}_4$  (X=S, Se and Te) with the normal spinel structure. It was found that these compounds exhibited metallic conduction and were ferromagnetic with a moment of about  $5 \mu_B$  per molecule. On the other hand, in the anion solid solution  $\text{CuCr}_2\text{Se}_x\text{S}_{4-x}$ <sup>2)</sup> the lattice parameter increased linearly with X,

but the Curie temperature decreased first with increasing X, took a minimum value at about X=1, and then increased until X=4. This fact shows the absence of the linear dependence of the Curie temperature on the lattice parameter in the anion-substituted solid solutions. In these solutions, the anion substitution may have an influence on the interaction between the cations. In the present research, the effect of pressure on

Curie temperatures of these component spinels were measured. Experimental results of magnetic properties of the compounds are also reported.

## § 2. Preparation of Specimens and X-Ray Analysis

For the preparation of specimens, powdered copper (99.999%), selenium (99.999%), chromium (99.9%) and tellurium (99.9999%) were mixed in desired proportions, sealed in evacuated silica tubes and heated at about 600°C.

For the preparation of  $\text{CuCr}_2\text{Se}_4$ , the mixture was first heated at 750°C for 100 hr. The reaction product was pulverized, mixed, heated again in vacuum at 750°C for 100 hr and then cooled slowly. Similarly, for  $\text{CuCr}_2\text{Te}_4$ , the mixture was heated at 500°C for 160 hr. The reaction product was then pulverized, heated at 500°C for 100 hr and cooled slowly. For  $\text{CuCr}_2\text{S}_4$ , the mixture was heated at 600°C for 200 hr and cooled slowly.

The X-ray analysis data on the  $\text{CuCr}_2\text{Se}_4$  specimen, are illustrated in Table I. As shown in the table, each diffraction line can be indexed as the one with cubic structure. The lattice constants of  $\text{CuCr}_2\text{S}_4$ ,  $\text{CuCr}_2\text{Se}_4$  and  $\text{CuCr}_2\text{Te}_4$  were found to be  $9.833 \pm 0.019 \text{ \AA}$ ,  $10.321 \pm 0.014 \text{ \AA}$  and  $11.127 \pm 0.005 \text{ \AA}$  respectively. The intensities of the reflection lines agreed with the calculated results for the normal spinel structure. For the diffraction patterns of the  $\text{CuCr}_2\text{Se}_4$  specimen, no extra lines were observed, but for the  $\text{CuCr}_2\text{S}_4$  speci-

Table I. Results of X-ray diffraction of  $\text{CuCr}_2\text{Se}_4$  at 293°K by Cu K radiation.  $\theta$  is the Bragg angle,  $I(\text{obs.})$  and  $I(\text{cal.})$  are intensities of diffraction lines observed and calculated respectively.  $I(\text{cal.})$  was calculated for the normal spinel with a  $u$  parameter of 0.384.<sup>20</sup>

(hkl)	$2\theta^\circ$	$I(\text{obs.})$	$I(\text{cal.})$
220	24.43	16.3	15.27
311	28.73	36.2	35.74
222	30.05	68.8	66.31
400	34.80	87.1	83.53
331	38.00	3.1	2.60
422	42.75	6.3	5.72
511	45.70	24.6	27.39
333			
440	50.00	100.0	100.00

men, one extra line with the relative intensity of 5 was observed. For the  $\text{CuCr}_2\text{Te}_4$  specimen, 3 extra lines with the relative intensities of 10, 6 and 3 were detected, indicating the existence of small amounts of other phases. Further annealing of the specimens at 600°C for 200 hr resulted in no variation in the intensity of the diffraction lines.

## § 3. Experimental Procedure and Results

The magnetizations of powdered  $\text{CuCr}_2\text{X}_4$  were measured in magnetic fields up to 16 kOe at liquid helium, liquid air, dry ice and room tempera-

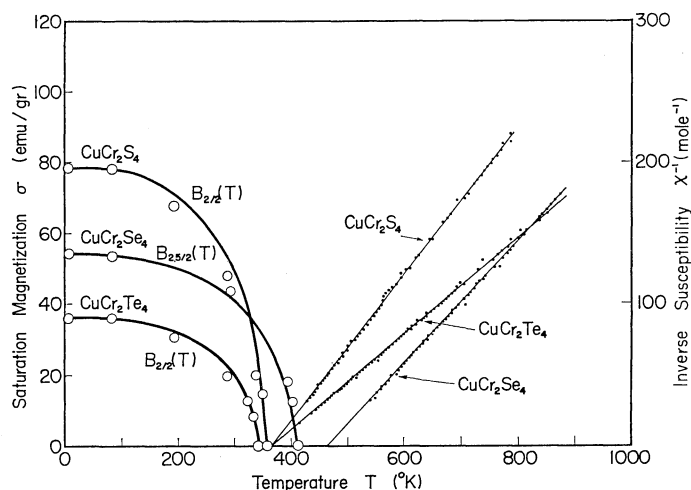


Fig. 1. Temperature dependence of saturation magnetizations and inverse susceptibilities of  $\text{CuCr}_2\text{X}_4$  ( $\text{X}=\text{S}, \text{Se}$  and  $\text{Te}$ ). The circles indicate the experimental values and  $B_{2S/2}(T)$  is the Brillouin function with spin value  $S$ .

tures. The saturation magnetization  $\sigma_0$  at each temperature was determined by applying the law of approach,

$$\sigma = \sigma_0 \left( 1 - \frac{b}{H^2} \right) + \chi_0 H,$$

where  $\sigma$  is the magnetization,  $H$  the effective external field,  $b$  a constant due to anisotropy and  $\chi_0$  the susceptibility due to parasitic magnetization. The temperature vs. saturation magnetization curves thus obtained are shown in Fig. 1. The absolute saturation magnetizations given in Table II were obtained by extrapolating the saturation magnetization to 0°K. The Curie temperatures in the same table were determined from the linear relation between  $\sigma_0^2$  and  $T$  just below the Curie temperatures. These values obtained are somewhat smaller than those reported by Lotgering.<sup>1)</sup>

On the other hand, the temperature dependence of the inverse of susceptibility  $1/\chi_m$  above the Curie temperature was studied in the temperature range from 410 to 850°K, as shown in Fig. 1. The observed  $1/\chi_m$  versus  $T$  curves can be well expressed by the Curie-Weiss law. From these results, the paramagnetic Curie temperature  $\theta_p$  and the effective Bohr magneton  $\mu_{eff}$  were determined, the results of which are tabulated in Table II. The values of  $\mu_{eff}$  for each specimen determined in the present experiment agreed fairly well with those reported by Lotgering.<sup>1)</sup>

Table II. Magnetic data for  $\text{CuCr}_2\text{X}_4$ . The values in brackets were obtained by Lotgering.<sup>1)</sup>  $S$  is the spin value calculated from  $\mu_{eff}$  in the 5th column, assuming orbital moment quenched.

Compound	Moment at 4.2°K ( $\mu_B$ )	$T_c$ (°K)	$\theta_p$ (°K)	$\mu_{eff}(\mu_B)$	$S$
$\text{CuCr}_2\text{S}_4$	3.9(4.58)	364.0(420)	365.0(390)	4.0(4.4)	1.6
$\text{CuCr}_2\text{Se}_4$	4.5(4.94)	414.5(460)	460.0(465)	4.3(4.5)	1.7
$\text{CuCr}_2\text{Te}_4$	4.2(4.93)	344.6(365)	367.0(400)	4.9(4.8)	2.0

The constant,  $b$ , in the expression of the law of approach can be expressed as  $b=0.76(K_1/I_s)^2$  in the case of a cubic crystal. The anisotropy constant  $K_1$  at each temperature in Fig. 2 was calculated from the values of  $b$ .

The Curie temperatures of the specimens were determined under hydrostatic pressures up to 4000 kg/cm<sup>2</sup>. For this purpose, the powdered specimens were put in a cylindrical pressure vessel 3 mm in the inner diameter and 14 mm in the outer diameter. The search coil was wound on the vessel and the self inductance of the search

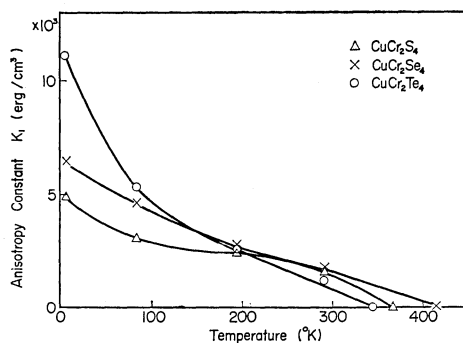


Fig. 2. Temperature dependence of anisotropy constant  $K_1$  calculated from the magnetization curves.

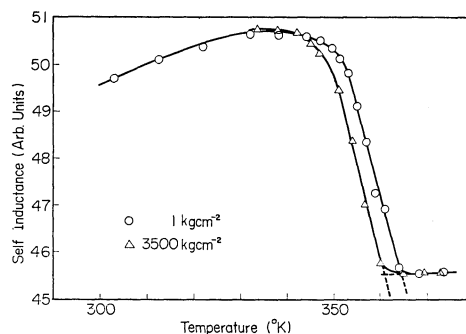


Fig. 3. Temperature dependence of the self inductance of the search coil under normal and high pressures.

coil were measured at various temperatures under normal and high pressures. For example, the measured values of  $\text{CuCr}_2\text{S}_4$  are shown in Fig. 3. The self-inductance decreases linearly at about 350°K with increasing temperature, and then takes a nearly constant value with further rise in temperature. The cross point of the linear extrapolation lines from both the higher and lower temperature ranges may reasonably be assumed to give the Curie temperature as shown by the broken lines in the figure. The Curie temperature was found to shift from 364°K at normal pressure to 360°K under a pressure of 3500 kg/cm<sup>2</sup>.

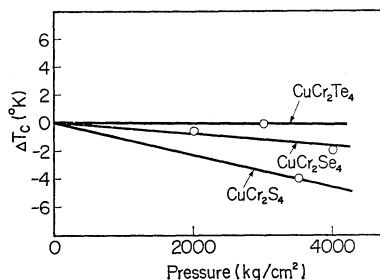


Fig. 4. The shift of the Curie temperature with pressure.

$\text{cm}^2$ . By a similar method, the pressure dependence of the Curie temperatures for  $\text{CuCr}_2\text{Se}_4$  and  $\text{CuCr}_2\text{Te}_4$  are shown in Fig. 4. For  $\text{CuCr}_2\text{Te}_4$ , the pressure coefficient of the Curie temperature was negative but the absolute value could not be determined. The results are given in Table III. These pressure coefficients are all negative and decrease in the order of sulphide, selenide and telluride.

Table III. Pressure coefficients of  $\text{CuCr}_2\text{X}_4$ .

Compound	$1/T_c(dT_c/dp) \text{ kg}^{-1} \text{ cm}^2$
$\text{CuCr}_2\text{S}_4$	$-3.1 \times 10^{-6}$
$\text{CuCr}_2\text{Se}_4$	$-1.0 \times 10^{-6}$
$\text{CuCr}_2\text{Te}_4$	$0 \gtrsim$

#### § 4. Discussion

Assuming that the orbital moment is in a quenched state, spin values  $S$  were calculated from the  $\mu_{\text{eff}}$  in Table II. They are smaller than those from  $\sigma_0$  in all specimens. Goodenough<sup>3)</sup> explained this fact by an assumption that the molecular field coefficient  $W$  has a temperature dependence; decreases with the expansion of the lattice constant. However, this assumption is inconsistent with the present result of pressure effect of Curie temperatures, which shows that  $W$  increases with the increase of the lattice constant.

It is shown that in the anion solid solution  $\text{CuCr}_2\text{Se}_x\text{S}_{4-x}$  the dependence of Curie temperature on the lattice parameter  $a$ ,  $dT_c/da$ , is negative on the S-rich side, and positive on the Se rich-side. From the pressure dependence of the Curie temperature for pure  $\text{CuCr}_2\text{S}_4$  and  $\text{CuCr}_2\text{Se}_4$ ,  $dT_c/da$  is positive at both spinels. In those solid solutions, the anion substitution may have an influence on the nature of interaction between the cations.

According to the molecular field theory, the Curie temperature  $T_c$  is given by the relation  $T_c = \frac{2JzS(S+1)}{3K}$ , where  $J$  is the coupling coefficient and  $z$  the number of the nearest neighbour magnetic atoms. Accordingly, the variation in Curie temperature with pressure,  $dT_c/dp$ , is caused by variation in  $J$  or  $S$  with pressure. In the following discussion, only the variation in the exchange integral  $J$  with pressure is taken into account.

According to Baltzer *et al.*<sup>4)</sup> the nearest neighbour Cr-Cr interaction in the lattice of  $\text{CdCr}_2\text{X}_4$  ( $\text{X}=\text{S}, \text{Se}$ ) was found to be large and positive

(ferromagnetic), while the interaction in a pair of more distant Cr-Cr atoms was found to be much smaller; the latter is 1 to 3% of the former. Therefore, the pressure dependence of the Curie temperature is probably caused by the variation in the nearest-neighbour Cr-Cr interaction. The nearest-neighbour interaction contains the  $90^\circ$  Cr-X-Cr superexchange interaction and the Cr-Cr direct exchange interaction.

From the data on neutron diffractions<sup>5,6)</sup> and Goodenough's consideration,<sup>3)</sup> Cr is assumed to be in a state of trivalent ion,  $\text{Cr}^{3+}$ . According to Anderson,<sup>7)</sup> Kanamori<sup>8)</sup> and Anderson,<sup>9)</sup> the Cr-X-Cr superexchange interaction is ferromagnetic and the Cr-Cr direct exchange interaction is antiferromagnetic. The decrease in the lattice parameter with pressure is considered to result in increasing the charge cloud overlapping of adjacent ions. Therefore, both the super- and direct-exchange interactions are increased by pressure. On the basis of this model, the decrease in the Curie temperature with pressure as shown in Fig. 4 indicates that the direct exchange is more sensitive than the superexchange to the decrease in the lattice parameter. As a result, the ferromagnetic interaction between Cr ions is considered to be weakened by pressure.

As mentioned above, the pressure dependence of the Curie temperature was mainly attributed to the variation in  $J$ , but the variation in  $S$  with pressure may also affect the pressure dependence of the Curie temperature. The variation in  $S$  with pressure is being investigated by the present authors.

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