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INFLUENCE OF DOPING WITH COPPER ON THE MAGNETIC AND ELECTRICAL PROPERTIES OF THE CHALCOGENIDE SPINEL $CdCr_2S_4$

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Light doping with copper ($\lesssim$ 1 at.%) of the chalcogenide spinel $CdCr_2S_4$ resulted in a strong rise (by about 90 deg) of the paramagnetic Curie point Θ_p, compared with Θ_p of the pure material. The ferromagnetic Curie point Θ_f was not affected. This was attributed to the presence of giant magnetic quasimolecules formed around copper acceptor atoms. The electrical resistivity of the compound decreased strongly when the concentration of the dopant was increased: the addition of 1 at.% of copper reduced the resistivity by four orders of magnitude below the value for the pure material.

RECENTLY there has been an upsurge of interest in a new class of ferromagnets, which are chalcogenide compounds with the structure of the normal spinel and the formula $MeCr_2X_4$, where Me is Cu, Cd, Zn, Hg, and X is Se, S, Te. The compounds with the composition $CuCr_2X_4$ have metallic conduction, whereas other compounds are semiconductors.

Lotgering[1] established that the addition of about 0.2 at.% of copper to $CdCr_2Se_4$ reduced its electrical resistivity by about four orders of magnitude. Therefore, it would be interesting to study the solid solutions $xCuCr_2X_4 - (1 - x)CdCr_2X_4$. However, the compounds with the formula $CuCr_2X_4$ have a limited solubility and a single-phase spinel with X = Se exists in the range $0 \leq x \leq 0.05$.[1,2]

We synthesized the system $Cu_xCd_{1-x}Cr_2S_4$, where x = 0, 0.002, 0.005, and 0.01. We studied the temperature dependences of the paramagnetic susceptibility (Fig. 1) and of the electrical resistivity (Fig. 2). The ferromagnetic Curie point was deduced from the temperature dependence of the magnetization in weak magnetic fields. Our measurements indicated that all the samples had p-type conduction. The results obtained and the conditions during synthesis are given in Table I.

It is evident from Fig. 1 and Table I that the paramagnetic Curie point of the doped samples is on the average 90 deg higher than that of the pure material whereas the ferromagnetic Curie point is practically unaffected by the doping. The paramagnetic Curie point does not vary greatly with x when $x \rightarrow 0$; moreover, measurements carried out on different samples of the same composition show that the scatter of the paramagnetic Curie points lies approximately within the same limits as for samples with different x.

These results may be explained by the appearance of giant magnetic quasimolecules formed around copper atoms. Such giant quasimolecules have been predicted theoretically by Yanase and Kasuya[6] and by Nagaev.[7] According to Nagaev, an active electron (or a hole) of an un-ionized donor (or acceptor) gives rise to an indirect exchange between such a donor or an acceptor and magnetic atoms in its vicinity and the exchange effectively combines these atoms into a single quasimolecule. The indirect exchange tends to orient the spins of all the atoms in the quasimolecule parallel to some direction. The high value of the magnetic moment of such quasimolecules is responsible for the anomalously large contribution of these molecules to the para-

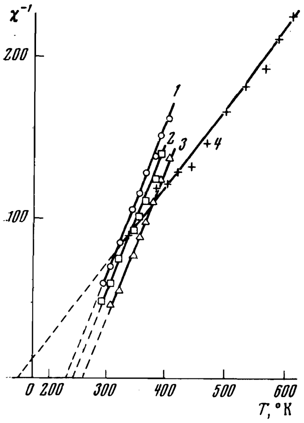

FIG. 1

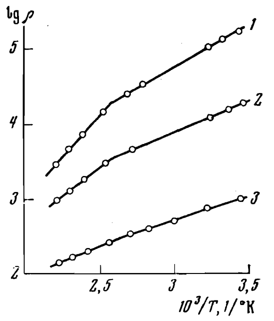

FIG. 2

FIG. 1. Temperature dependence of the reciprocal paramagnetic susceptibility, calculated per molecule of the $Cu_xCd_{1-x}Cr_2S_4$ system: 1–x = 0.005; 2–x = 0.002; 3–x = 0.01; 4–x = 0.

FIG. 2. Dependence of the logarithm of the resistivity ρ of the $Cu_xCd_{1-x}Cr_2S_4$ system on the reciprocal of temperature: 1–x = 0.002; 2–0.005; 3–x = 0.01.

Table I

Synthesis conditions*	Composition of spinel	Θ_p, °K		Θ_Φ, °K		ρ, 10^3 Ω·cm T = 300° K
		Our results	Published results	Our results	Published results	
Synthesis from a stoichiometric mixture at 750°C applied for 48 h	$CdCr_2S_4$	145	135 [3] 156 [4] 152 [5]	85	97 [3] 86 [4] 84 [5]	10^1 **
Synthesis from a stoichiometric mixture at 650°C applied for several weeks, followed by quenching	$Cu_{0,002}Cd_{0,998}Cr_2S_4$	240	—	85	—	160
	$Cu_{0.005}Cd_{0,995}Cr_2S_4$	240	—	86	—	19
	$Cu_{0.01}Cd_{0,99}Cr_2S_4$	240	—	86	—	0,8 **

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*First annealing during synthesis carried out at 550°C for 72 h.

**Electrical resistivity of p-type semiconductor.

tion may be $z(z+1)$ times greater than the relative concentration of the impurity in a crystal (z is the coordination number). Therefore, at temperatures below that at which the quasimolecules are destroyed the susceptibility of the doped crystal is considerably higher than that of the pure material. According to Nagaev, the presence of even 1% of the impurity can double the paramagnetic susceptibility. A similar phenomenon has been observed experimentally in EuO with small admixtures (about 1 at.%) of Gd and La.[8] It has been found that in practice the presence of giant quasimolecules is manifested by an increase in the paramagnetic Curie point without a change in the ferromagnetic point.

Obviously, a similar explanation can be provided in our case. We can see from Fig. 1 that in the range of temperatures below the point of intersection of the dependences $\chi^{-1}(T)$ the susceptibility of the doped samples is considerably higher than that of the pure material. The point of intersection of the dependences $\chi^{-1}_{\text{doped}}(T)$ and $\chi^{-1}_{\text{pure}}(T)$ is obviously the temperature at which the giant magnetic quasimolecules are destroyed. It is interesting to note that this temperature is approximately equal to the paramagnetic Curie point of the compound $CuCr_2S_4$.

It is evident from Fig. 2 that electrical conduction in our $Cu_xCd_{1-x}Cr_2S_4$ system is of semiconducting nature and the electrical resistivity ρ decreases continuously with increasing x. For example, when $x = 0.01$, the value of ρ is almost four orders of magnitude less than the value corresponding to $x = 0$. It is interesting to note the fact that the kink in the rectilinear dependences $\lg \rho(T)$ is observed at a temperature ~ 377°K, which is equal to the ferromagnetic Curie point of the compound $CuCr_2S_4$.[1)]

The increase in the paramagnetic susceptibility of the doped samples below 335°K could be explained by the presence of ferromagnetic inclusions of $CuCr_2S_4$ if this compound were not fully soluble. However, elementary calculations show that the very small amounts of copper present in the samples would make a negligibly small contribution to χ.

[1)] According to our measurements, the ferromagnetic Curie points of $CuCr_2S_4$ and $CuCr_2Se_4$ are 40-50 deg higher than the paramagnetic Curie points.

[1] F. K. Lotgering, J. Phys. Chem. Solids **29**, 699 (1968).

[2] F. K. Lotgering and P. R. van Stapele, Solid State Commun. **5**, 143 (1967).

[3] P. K. Baltzer, H. W. Lehmann, and M. Robbins, Phys. Rev. Lett. **15**, 493 (1965).

[4] N. Menyuk, K. Dwight, R. J. Arnott, and A. Wold, J. Appl. Phys. **37**, 1387 (1966).

[5] P. K. Baltzer, P. J. Wojtowicz, M. Robbins, and E. Lopatin, Phys. Rev. **151**, 367 (1966).

[6] A. Yanase and T. Kasuya, J. Phys. Soc. Jap. **25**, 1025 (1968).

[7] É. L. Nagaev, Zh. Eksp. Teor. Fiz. **56**, 1013 (1969) [Sov. Phys.-JETP **29**, 545 (1969)]; Fiz. Tverd. Tela **11**, 3438 (1969) [Sov. Phys.-Solid State **11**, 2886 (1970)].

[8] F. Holtzberg, T. R. McGuire, S. Methfessel, and J. C. Suits, Phys. Rev. Lett. **13**, 18 (1964).

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