Anomalous paramagnetic susceptibility in sulfate chrome-chalcogenite spinels

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(Submitted June 2, 1977)
Pis'ma Zh. Eksp. Teor. Fiz. **26**, No. 2, 68–71 (20 July 1977)

The temperature dependence of the paramagnetic susceptibility of the compounds $Cd_{1-x}Ga_xCr_2S_4$, $CdCr_2S_{4-\gamma}$, and $CuCr_2S_{4-\gamma}$ were investigated. It was observed that the paramagnetic Curie point is lowered with increasing doping level. It is suggested that this phenomenon is due to the presence of antiferron states of the donor electrons.

PACS numbers: 75.20.Ck, 75.30.Cr

We have studied the temperature dependence of the paramagnetic susceptibility of polycrystalline samples with composition $Cd_{1-x}Ga_xCr_2S_4$ ($x=0.01$; 0.03; 0.05; 0.15), $CdCr_2S_{4-\gamma}$ ($\gamma=0$; 0.05; 0.07; 0.19) and $CuCr_2S_{4-\gamma}$ ($\gamma=0$; 0.06; 0.09; 0.13). The samples were synthesized by the solid-phase method, and their production is described in[1]. An x-ray phase analysis has shown the compositions to be single-phase.

For all the investigated samples, the temperature dependence of the paramagnetic susceptibility χ satisfies the Curie-Weiss law. By way of example, Fig. 1 shows plots of $\chi^{-1}(T)$ for the system $CdCr_2S_{4-\gamma}$. Table I lists, for all the investigated systems, the paramagnetic Curie point Θ. It is seen from Table I and from Fig. 1 that Θ decreases with increasing impurity or with increasing number of sulfur defects in the sample (n describes the type of doping). From an extrapolation of the steepest part of the magnetization curve $\sigma(T)$ to the temperature axis we determined the ferromagnetic Curie point for all the investigated samples. It turned out that T_c is practically independent of the doping and is equal to T_c of the undoped material. (The scatter in T_c for each system was less than three degrees). It must be noted that a "blue" shift of the edge of absorption band was observed earlier[2] in the compound $CdCr_2S_4$ with decreasing temperature.

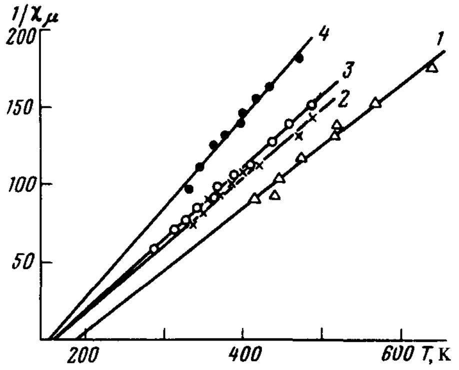

FIG. 1. Temperature dependence of the reciprocal paramagnetic susceptibility of the compound $CdCr_2S_{4-\gamma}$, with γ having the following values for the respective curves: 1—0; 2—0.05; 3—0.07; 4—0.19.

It is known that in magnetic semiconductors with a red shift of the absorption edge, such as EuSe doped with Cd and La[3] or $CdCr_2Se_4$ doped with Cu and Ag,[4,5] the paramagnetic Curie point rises with increasing level of the additive. This phenomenon was attributed to the presence of the so-called "ferron" states of the carriers. It was shown in a number of theoretical papers[6–8]

TABLE I.

Composition	Paramagnetic Curie point, Θ, K
$Cd_{1-x}Ga_xCr_2S_4$	
$x = 0$	190
0.01	186
0.03	180
0.05	172
0.15	168
$CdCr_2S_{4-\gamma}$	
$\gamma = 0$	190
0.05	160
0.07	160
0.19	152
$CuCr_2S_{4-\gamma}$	
$\gamma = 0$	390[1)]
0.06	360
0.09	350
0.23	340

1) Taken from[14].

that intraband s-d exchange makes energywise more convenient for carriers in magnetic semiconductors to surround themselves by a ferromagnetic cluster of magneto-active ions drawn from the environment. This ferromagnetic cluster has been dubbed ferron. In particular, ferrons can be produced around a donor or an acceptor impurity. In this case, as shown in[9-11] they introduce an anomalously large contribution to the magnetic susceptibility, thus raising the parmagnetic Curie temperature.

In some cases, however, an interband rather than intraband s-d exchange is produced in magnetic semiconductors. As shown by Nagaev, when ferromagnetic order is established the gap between the valence and conduction bands is increased by the enhanced interband s-d exchange and the ensuing repulsion of these bands.[12] This is precisely the explanation offered in[12] for the anomalous gigantic blue shift of the absorption edge in $CdCr_2S_4$.[2] Since the bottom of the conduction band drops in this case when the ferromagnetic order is destroyed, "antiferron" states of the carrier are possible in a material with a blue shift, and constitute regions where the ferromagnetic order is destroyed in the ferromagnet. The superexchange energy loss to the production of these regions is offset by the decrease of the electron energy, since these regions are potential wells for the carriers. These non-ferromagnetic regions can be produced around donor defects and decrease Θ in comparison with undoped material.

The cited experimental facts, namely the lowering of the paramagnetic Curie temperature Θ with increasing doping with Ga in $CdCr_2S_4$ can be attributed to the presence of "antiferron" states of the carriers, which were theoretically predicted by Nagaev.[12] In two other investigated systems, namely in $CdCr_2S_{4-\gamma}$ and $CuCr_2S_{4-\gamma}$, the donors are not singly charged, as in $Cd_{1-x}Ga_xCr_2S_4$, but doubly charged and the situation here is more complicated. As shown in[13] for magnetic semiconductors with red shift, in the ferromagnetic region, an energywise more profitable state may be the $(1s)(2s)$ state of the doubly charged donor (helium-like model), where the spins of both electrons are parallel and surround themselves by a ferron. With rising temperature, however, term inversion is possible and the donors turn out at high temperatures to be in the state $(1s)^2$ with antiparallel spin orientation. Superposition of an external magnetic field can transfer the donors again from the state $(1s)^2$ to $(1s)(2s)$.

Unfortunately, theoretical investigations of the states of doubly charged donors have not been made for magnetic semiconductors with blue shift. None the less, if we assume the existence of "antiferron" states of doubly charged donors in the systems $CdCr_2\ddot{S}_{4-\gamma}$ and $CuCr_2S_{4-\gamma}$ investigated by us, then it follows that the $(1s)^2$ state is stable in the region of the investigated temperatures (from 300 to 600 K) and magnetic fields (the paramagnetic susceptibility was investigated in fields up to 10 kOe).

In conclusion, we thank E. L. Nagaev for a discussion of the results and I. V. Gordeev for preparing the samples.

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