“Spin glass”-type magnetic order in a semiconducting thiospinellide $Ga_{0.67}Cr_2S_4$

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(Submitted 22 November 1979)
Pis'ma Zh. Eksp. Teor. Fiz. **31**, No. 2, 96–99 (20 January 1980)

A $Ga_{0.67}Cr_2S_4$ compound with spinel-like structure was obtained and investigated. At $T_f = 4.5$ K this semiconducting compound has a maximum on the susceptibility curves due to the temperature in the weak magnetic fields, whereas the neutron-diffraction patterns at 4.2 K indicate an absence of long-range magnetic order and a presence of short-range order. It is assumed that below 4.5 K “spin glass”-type magnetic order is established in this compound.

PACS numbers: 75.25. + z, 75.30.Cr, 75.50.Dd

It is well known that anomalies of electric, photoelectric, and thermoelectric properties in the region of the Curie point occur in a magnetic semiconductor $CdCr_2X_4(X = S, Se)$ as a result of doping it with Ga or In.[1-4] Therefore, the problem—to obtain and investigate the MCr_2X_4 compound, where M = Ga or In, certainly is of interest because it allows us to understand more clearly the processes occurring it $CdCr_2X_4$ as a result of doping it with Ga or In.

In present investigation we obtained a polycrystalline compound $Ga_{0.67}Cr_2S_4$, which has more than one phase when different quantities of Ga are added. This compound was found to have a semiconducting conductivity, and its magnetic properties are characteristic for “spin glass”-type ordering with the freezing point $T_f = 4.5$ K.

Since the cation-anion ratio in $Ga_{2/3}Cr_2S_4$ is lower than 3/4, this material must contain structural vacancies (□). The x-ray analyses showed that □ and Ga ions, which occupy the tetrahedral sites in the spinel lattice, are crystallographically ordered, i.e., the 4*a* positions are 95% occupied by Ga ions, whereas the 4*c* positions are only 37% occupied. Thus, the 1:1-type ordering in the tetrahedral sites reaches 95%, and the space group of the indicated compound is $F43m$ rather than the spinel type—$Fd3m$. We, therefore, call $Ga_{0.67}Cr_2S_4$ a spinellide. The ordering in tetrahedral sites was also confirmed by neutron-diffraction measurements. A significant shift (in fractions of the lattice constant) of the chromium atoms from the ideal positions $\delta = u - u_i = 0.633 - 0.625 = 0.008$ (0.0079 nm) in the [111] direction was determined from the x-ray photographs. The contributions to the nuclear reflections and the additional coherent magnetic maxima were missing in the neutron-diffraction patterns obtained at 4.2 K and 78 K. On the basis of the background at 4.2 K we can assume that the short-range magnetic order is very weak in the sample.

The temperature dependence of the electrical resistance ρ has a semiconductor behavior; moreover, at 4.2 K $\rho \cong 10^{12}$ Ω·cm, i.e., the material is almost compensated. The hole type conductivity was determined from the sign of the thermoelectromotive force.

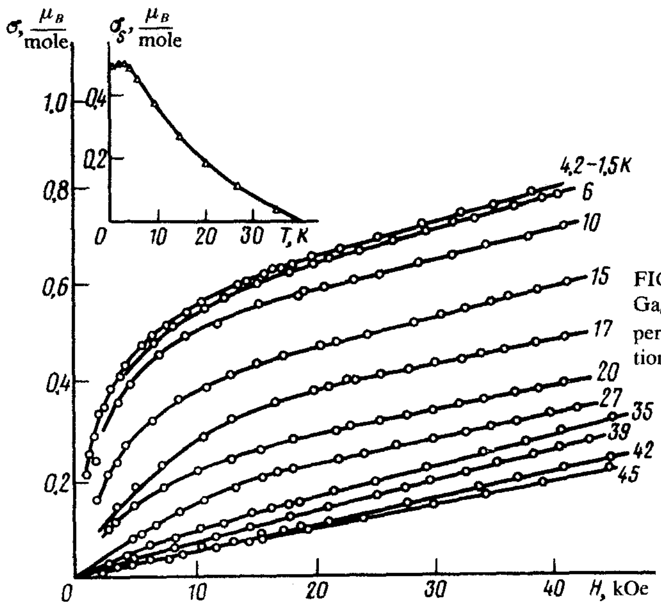

FIG. 1. Magnetization isotherms of $Ga_{0.67}Cr_2S_4$. The inset shows the temperature dependence of magnetization σ_s.

Figure 1 shows the magnetization isotherms σ of the given material and the inset shows the temperature dependence of magnetization σ_s, which was determined by extrapolating the linear part of the $\sigma(H)$ curves to zero field. As seen in Fig. 1, the $\sigma(H)$ curves are nonlinear in the temperature range 1.5–35 K, and there is no saturation in the 40 kOe fields. It is noteworthy that σ_s is small, $\sigma_s \sim 0.5\mu_B$/mole at 4.2–1.5 K. In the temperature interval 77–500 K the inverse susceptibility follows the Curie-Weiss law with the asymptotic Curie temperature $\Theta = 10$ K and the Curie constant $C_{//} = 1.025$ CGS M/mole. The effective moment of the Cr^{3+} ion calculated from $C_{//}$ is 2.86 μ_B, which is much smaller than the theoretical effective moment of 3.87 μ_B.

As seen in the inset of Fig. 1, the temperature of magnetic ordering is difficult to determine even approximately from the temperature dependence $\sigma_s(T)$, since it differs significantly from the Brillouin function. To determine this temperature, we measured the magnetic susceptibility χ in weak fields by using the induction method; its temperature dependence is shown in Fig. 2, in which it can be seen that the $\chi(T)$ function has a maximum at $T_f = 4.5$ K, which is very sensitive to the magnetic field: its largest value was observed in the 500 Oe field and it disappeared completely at $H \geqslant 2$ kOe.

Thus, we can assume that "spin glass"-type magnetic ordering occurs in the semiconducting compound $Ga_{0.67}Cr_2S_4$ below $T_f = 4.5$ K, since a susceptibility maximum was observed in T_f in weak magnetic fields, and below T_f, as the neutron-diffraction data show, the long-range magnetic order is missing. This assumption also confirms that cooling in the magnetic field has an influence on the curve for $\sigma(H)$ in weak magnetic fields. Figure 3 shows the curves for $\sigma(H)$ in fields up to 2 kOe at 1.5 K, which were obtained under different cooling conditions: (1) the sample was cooled without the field and (2) the sample was cooled below T_f from $T > T_f$ in a 2-kOe field.

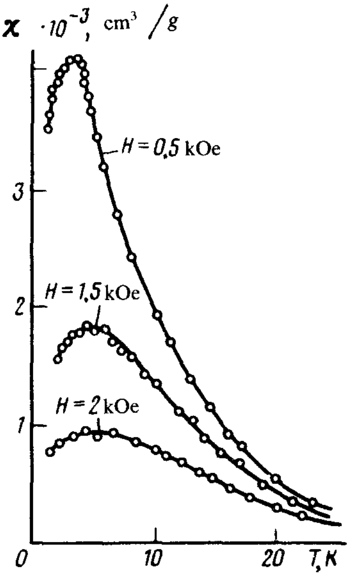

FIG. 2. Temperature dependence of the magnetic susceptibility in weak magnetic fields of $Ga_{0.67}Cr_2S_4$ spinellide.

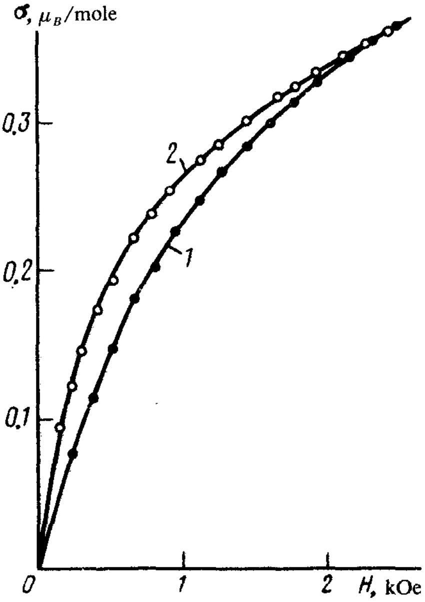

FIG. 3. Magnetization curves plotted as a function of the field at 1.5 K. Curve 1 represents a cooled sample without the field; curve 2 represents a cooled sample in a 2-kOe field from $T < T_f$. The sample is $Ga_{0.67}Cr_2S_4$.

It can be seen that curve 2 is above curve 1. Such hysteresis is typical for spin glass. The absence of long-range magnetic order below T_f is also confirmed by quadratic dependence on H of the magnetostriction of this material, which was obtained in pulsed fields up to 210 kOe at $T = 4.2$ K. Such dependence is usually characteristic for a paramagnetic material.

The magnetostriction turned out to be rather large $\sim 6 \times 10^{-5}$ at 4.2 K and

$H = 210$ kOe; this may be due to a shift of the Cr^{3+} ions indicated above, which causes elastic strains in the lattice. Because of this, the magnetoelastic anisotropy in this material may be rather large, which accounts for the nonsaturability of the magnetization curves due to the field.

The "spin-glass"-type ordering usually occurs in metallic alloys with a low concentration of magnetic impurity, in which the long-range RKKI interaction is responsible for the cooperative quenching of spins. However, the ordering mechanism in $Ga_{0.67}Cr_2S_4$ is different since its conductivity is of semiconducting type.

Let us assume that the magnetic clusters produced near the lattice defects are responsible for σ_s being below T_f. The most probable reason for the existence of these clusters is the localization of electrons in the neighborhood of the defects, in which they maintain magnetic order among the moments of the Cr^{3+} ions due to the advantage in the energy of the *s-d* exchange. Such states of the current carriers are called ferronic states.[5]

In conclusion, we thank É. L. Nagaev for a discussion of the results.

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