Experimental evidence for the existence of afmons in the antiferromagnetic semiconductor $Cu_{0.75}Co_{0.25}Cr_{1.625}Sb_{0.375}S_4$

L. I. Koroleva, A. G. Odintsov, M. Kh. Mashaev, and D. A. Saĭfullaeva
M. V. Lomonosov Moscow State University, 119899 Moscow, Russia

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A giant negative magnetoresistance, ~16% in a field of 27 kOe, has been observed along with a positive value $\Theta = 45$ K in the antiferromagnetic semiconductor $Cu_{0.75}Co_{0.25}Cr_{1.625}Sb_{0.375}S_4$. This is a solid solution of $CuCr_{1.5}Sb_{0.5}S_4$, with a checkerboard antiferromagnetic structure (with a paramagnetic Curie temperature $\Theta = -156$ K), and the ferrimagnet $CoCr_2S_4$. These experimental facts are evidence for the existence of afmons in this compound.

In Ref. 1 we described a new antiferromagnetic (AFM) semiconductor, $CuCr_{1.5}Sb_{0.5}S_4$, and its solid solution with the ferrimagnet $CoCr_2S_4$. Each compound has the spinel structure. They have the following valence distributions according to x-ray data:

$$Cu^{1+}[Cu^{3+}_{1.5}Sb^{5+}_{0.5}]S^{2-}_4, \quad (1)$$

$$Cu^{1+}_{0.75}Co^{2+}_{0.25}[Cr^{3+}_{1.625}Sb^{5+}_{0.375}]S^{2-}_4. \quad (2)$$

The magnetic properties of these compounds are characteristic of antiferromagnets: The magnetization is a linear function of the magnetic field H, and the susceptibility goes through a maximum at the Néel temperature T_N [23.7 K for composition (1) and 32 K for (2)]. The paramagnetic susceptibility of each composition obeys a Curie–Weiss law with a paramagnetic Curie temperature $\Theta = -156$ K for composition (1) and $\Theta = 45$ K for composition (2).

A giant negative magnetoresistance $\Delta\rho/\rho$ has been observed in the AFM semiconductor $Cu_{0.75}Co_{0.25}Cr_{1.625}Sb_{0.375}S_4$. Figure 1a shows the temperature dependence of the magnetoresistance of this sample. We see a giant magnetoresistance, ~ 16%, in a field $H = 27$ kOe. The maximum modulus of the magnetoresistance is observed near 25 K, which falls between the Néel temperatures of compositions (1) and (2) (23.7 and 32 K, respectively). In a field of 27 kOe, which is the maximum field at which the measurements were carried out, the magnetoresistance isotherms are still far from saturation (Fig. 1b). In AFM semiconductor (1), on the other hand, there is essentially no magnetoresistance at the error of these measurements, ~ 0.01%. These two compositions differ radically in the value of Θ: $\Theta = -156$ K for composition (1) and $\Theta = 45$ K for (2). The giant negative magnetoresistance in composition (2) can be explained on the basis that this compound contains afmons—quasiparticles predicted theoretically by Nagaev.[2]

An "afmon" is a new type of self-trapped state of a charge carrier in an AFM semiconductor with a sufficiently high T_N, in which the energy conditions are unfa-

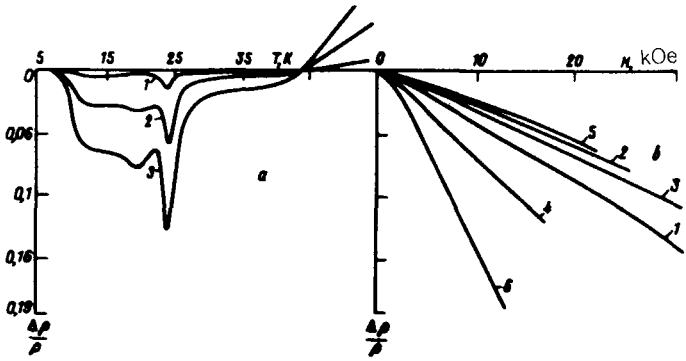

FIG. 1. Results on the composition $Cu_{0.75}Co_{0.25}Cr_{1.625}Sb_{0.375}S_4$. a: Temperature dependence of the magnetoresistance $\Delta\rho/\rho$ for external magnetic fields $H=1$(1), 15 (2), and 27 kOe (3). b: $\Delta\rho/\rho$ versus H at $T=12.4$ (1), 15 (2), 19.2 (3), 20.4 (4), 22.8 (5) and 24.1 K (6).

vorable for ferrons. Nagaev showed that an AFM phase different from that which exists in a crystal may serve as a potential well for a charge carrier in an antiferromagnet of this sort. The energy of a charge carrier in a layered AFM is lower than that in a checkerboard AFM phase; the difference can reach several tenths of 1 eV. In a semiconductor with a checkerboard AFM order, a carrier may thus become self-trapped in a microscopic region with a layered AFM order. The energy of such a quasiparticle (an afmon) can be lowered even further if the moments of the sublattices are skewed in this region, so that an afmon acquires a magnetic moment. However, the requirement that the energy conditions be unfavorable for ferrons from the energy standpoint rules out greatly skewed sublattice moments.

Since the paramagnetic Curie temperature in $CuCr_{1.5}Sb_{0.5}S_4$ is negative and large in magnitude, this antiferromagnet apparently has a checkerboard AFM structure. The addition of $CoCr_2S_4$ to this compound apparently gives rise to microscopic regions with a layered AFM structure of the afmon type, whose existence causes a substantial rise in the Curie temperature. This conclusion is drawn from the following considerations: In the ferrimagnet $CoCr_2S_4$, the moments of the Cr^{3+} ions occupying octahedral positions have a ferromagnetic order. They form a sublattice whose moment is ordered antiferromagnetically with respect to the moment of the sublattice of Co^{2+} ions, which occupy tetrahedral positions in the spinel structure. The addition of $CoCr_2S_4$ to the checkerboard AFM $CuCr_{1.5}Sb_{0.5}S_4$ creates favorable conditions for the formation, near Co^{2+} ions, of microscopic regions with a layered AFM structure. A localization of carriers in these microscopic regions promotes their stabilization if their energy is lower in this layered structure than in the main checkerboard structure.

We have previously determined the band gap in $CoCr_2S_4^3$ from measurements of the spectra of the diffuse-reflection coefficient. The width of the band gap turned out to be ~ 0.9 eV. In the present study we carried out similar measurements for compound (1). Figure 2 shows spectra of the absorption coefficient α and of the refractive index n for composition (2), as calculated from the spectra of the diffuse-reflection

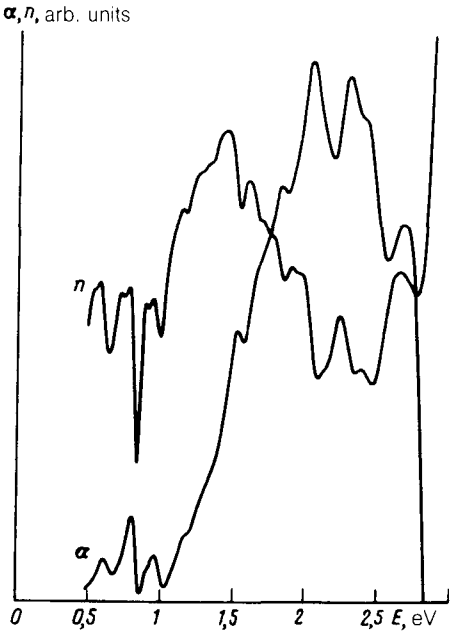

FIG. 2. Spectra of the absorption coefficient α and the refractive index n of $CuCr_{1.5}Sb_{0.5}S_4$ at room temperature.

coefficient by means of the Kramers–Kronig relations. We see from Fig. 2 that the α spectrum rises sharply in the energy interval $1 \leqslant E \leqslant 2$ eV; this rise is characteristic of an intrinsic absorption and is accompanied by a maximum in n at $E = 1.45$ eV. According to Velisky,[4] this value of E should be regarded as the width of the band gap. The carrier energy in $CoCr_2S_4$ is thus lower than that in $CuCr_{1.5}Sb_{0.5}S_4$. The trapping of carriers near Co^{2+} ions thus stabilizes microscopic regions with a layered AFM structure, forming afmon states. The imposition of an external magnetic field destroys the afmons and delocalizes the current carriers in them; i.e., it leads to a giant negative magnetoresistance, as observed in $Cu_{0.75}Co_{0.25}Cr_{1.625}Sb_{0.375}S_4$. The fact that Θ for composition (2) is sharply higher than that for composition (1) indicates that positive exchange interactions make a substantial contribution to the overall exchange in the crystal which comes from microscopic regions with a layered AFM structure. This contribution cannot be attributed to ferrons, since they cannot form in this AFM semiconductor because of the high Néel temperature—which is more than twice the highest T_N at which ferrons can exist in an AFM.[5]

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