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MAGNETISM

Magnetic Resonance in a Gallium-Doped Cu–Cr–S Structure

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Abstract—A layered Cu–Cr–S structure doped with Ga ions and consisting of single-crystal $CuCrS_2$ layers, embedded with thin plates of spinel phases $CuCr_2S_4$ and $CuGa_xCr_{2-x}S_4$, has been studied using the magnetic resonance and magnetic susceptibility methods. The Curie temperature and the saturation magnetization of the spinel phases of the samples have been determined. The spinel phase layer thickness has been estimated.

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1. INTRODUCTION

In our previous studies of the magnetic resonance in layered Cu–Cr–S structures, it was shown that thin plates of the $CuCrS_2$ single crystal grown by the chemical transport reaction method were single-crystal layers of disulfide $CuCrS_2$ with inclusions of islands of the $CuCr_2S_4$ spinel phase [1]. The geometric sizes of the $CuCr_2S_4$ phase inclusions and the wave vector of magnetostatic vibrations in them were estimated. It was assumed that the topology and the sizes of the spinel phase are strongly dependent on conditions of sample synthesis.

Since promising matrices for preparing new multilayer materials can be quasi-two-dimensional structures that are three-dimensional crystals with a strong anisotropy of chemical bonds, the use of various technologies of growing such crystals will make it possible to produce multilayer (magnetic/nonmagnetic, insulator/metal) structures. One of the methods of influencing the magnetic parameters of the structures is their doping with magnetic and diamagnetic ions.

In this work we continue the studies of thin $CuCrS_2$ plates doped with gallium ions.

2. PREPARATION AND CHARACTERIZATION OF THE SAMPLES

The crystals were grown by the chemical transport reaction method in a sealed quartz ampoule 22 mm in diameter and 15 mm long charged with 1 g of the 1 : 1 mixture of $CuGaS_2$ and $CuCrS_2$ prepared earlier; the concentration of the ion carrier was ~7 g/cm^3.

The ampoule with the charge was placed in a horizontal furnace with a "hot zone" temperature of 1050°C; another ampoule end was in a "cold zone" at 950°C. The synthesis time was 30 days. The samples prepared were black thin plates.

Figure 1 shows the X-ray diffraction pattern of the prepared $CuGaCrS_2$ plate. The intense peaks in the pattern correspond to the rhombohedral $CuCrS_2$ structure and made it possible to conclude that the crystal growth plane corresponds to plane (001). Low

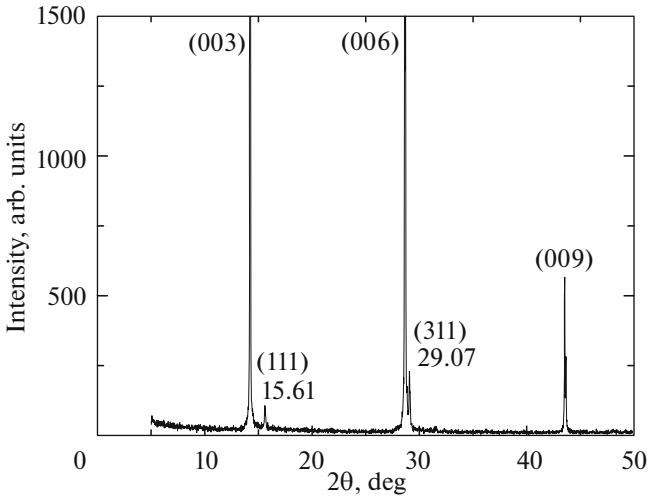

Fig. 1. X-ray diffraction pattern of the $CuGaCrS_2$ single crystal plate measured at 300 K.

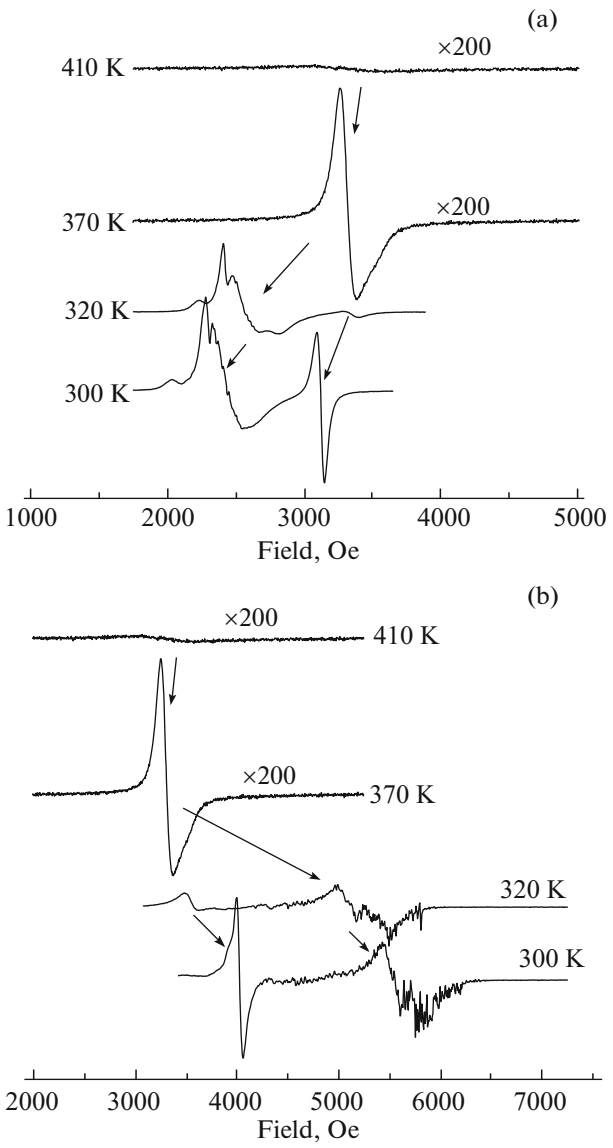

Fig. 2. Temperature evolution of the magnetic resonance spectra in $CuGaCrS_2$ at the external magnetic fields directed (a) in parallel and (b) perpendicularly to the plate plane, respectively.

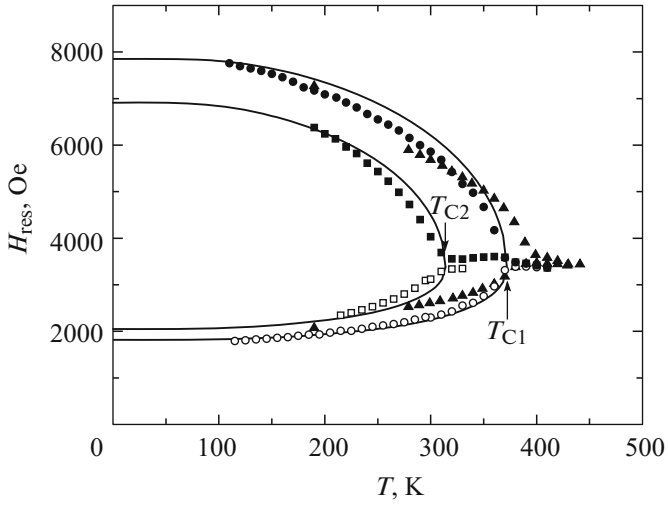

Fig. 3. Temperature dependence of resonance fields for two lines of ferromagnetic resonance in $CuGaCrS_2$. The dark and bright symbols correspond to the perpendicular and parallel direction of the external magnetic field with respect to the sample plane. Circles and squares correspond to the signals from two magnetic phases in the sample (the text). The solid lines is the fitting of the resonance fields to $T = 0$ K using the Brillouin function. Triangles are the data of [1].

peaks at angles of 15.61° and 29.07° corresponded to $CuCr_2S_4$ spinel phase.

We observed similar X-ray diffraction patterns when grew nonsubstituted $CuCrS_2$ plates by the chemical transport reaction method [2].

3. EXPERIMENTAL RESULTS AND DISCUSSION

The magnetic resonance spectra were measured using a Bruker Elexsys E580 spectrometer operating in the X diapason at temperatures 100 K $\leqslant T \leqslant$ 440 K. We studied the temperature and angular dependences of the line width and the resonance field.

The temperature evolution of the magnetic resonance spectra is shown in Fig. 2. At temperatures higher than 372 K, the paramagnetic phase has a single Lorentz-shaped line with parameters $H_{res} = 3363$ Oe, $g = 2.017$, and $\Delta H = 490$ Oe; this line corresponds to the paramagnetic resonance in the sample. At $T_{C1} =$ 372 K, a more intense ($\Delta H \sim 100$ Oe) line appears (Fig. 2), corresponding to the ferromagnetic resonance of phase $CuCr_2S_4$ [1, 3]. The temperature dependence of the resonance field of this signal is shown in Fig. 3 by circles. Dark and bright circles correspond to the directions of the external magnetic field along a normal and in parallel to the sample plate plane, respectively. At $T <$ 370 K, we observed the appearance of additional magnetostatic vibrations (Fig. 2) similar to those that were observed earlier in undoped $CuCrS_2$ compound [1]. A similar spectrum of magnetostatic vibrations was also observed in ferromagnetic $HgCr_2S_4$ compound [4], where the sample was a thin disc. The further decrease in temperature led to the appearance of additional resonance signal at $T_{C2} =$ 314 K in a field of 3365 Oe (Fig. 2) that we ascribed to the $CuCr_2S_4$ spinel phase that has a lower Curie temperature. The temperature dependence of the resonance field of this signal is shown in Fig. 3 by squares. The dark and bright squares correspond to the directions of the external magnetic field along a normal and in parallel to the sample plate plane, respectively. It should be noted that magnetostatic modes were not observed in the signal that appeared at $T_{C2} =$ 314 K over the entire temperature range under study.

It was shown in [1] that thin (thickness $d \sim 1 \times 10^{-4}$ cm) plates of the $CuCr_2S_4$ spinel phase also form during synthesizing $CuCrS_2$ plates. It was shown that the thickness of those spinel interlayers was dependent on the sample synthesis conditions. It is reasonable to suggest that similar $CuCr_2S_4$ spinel phase exists in a doped $CuGaCrS_2$ sample.

In this case, the changes in the resonance field of the intense signals of the spinel phase were caused by an increase in the demagnetizing fields as temperature decreases and are well described by expressions for the consideration of the demagnetizing fields in a thin ferromagnetic plate [5]

$$\omega_0/\gamma = (H_{res\parallel}(H_{res\parallel} + 4\pi M_0))^{1/2}, \quad \omega_0/\gamma = H_{res\perp} - 4\pi M_0, \tag{1}$$

where ω_0 is the microwave radiation frequency, γ is the giromagnetic ratio, H_{res} are resonance fields for corresponding orientations, and M_0 is the saturation magnetization extrapolated to $T = 0$ K. According to the data of magnetization measurement [6], $M_0 = 365$ G. Taking into account the data of this work (Fig. 3), M_0 is 355.8 G for phase 1 (with $T_{C1} = 372$ K) and 309 G for phase 2 ($T_{C2} = 314$ K). We calculated theoretically the saturation magnetization of the $CuCr_2S_4$ spinel phase that was 391 G, assuming that its ferromagnetic structure is

$$\uparrow Cr^{3+} (S = 3/2) \uparrow Cr^{3+} (S = 3/2) \downarrow Cu^{2+} (S = 1/2).$$

It is known as well that the Curie temperature of the $CuCr_2S_4$ spinel phase is dependent on geometric sizes of the plates prepared (due to the influence of surface effects) and on the existence of additional impurities or defects in it. It is of 340 K for the nanosized particles, while it is 420 K for the bulk sample [7, 8]. Thus, it can be suggested that the $CuGaCrS_2$ sample contained thin interlayers of the $CuCr_2S_4$ spinel phase (like [1]) with various Curie temperatures $T_{C1} = 372$ K and $T_{C2} = 314$ K.

To verify this statement, we measured the temperature and field dependences of the magnetization of $CuGaCrS_2$. The results are shown in Fig. 4.

As expected, the temperature dependence of the magnetization of $CuGaCrS_2$ has three anomalies at temperatures $T_{C1} = 372$ K, $T_{C2} = 314$ K, and $T_N = 37$ K for two phases of spinel $CuCr_2S_4$ and antiferromagnetic phase $CuGaCrS_2$, respectively. Neglecting the contribution of antiferromagnetic phase $CuGaCrS_2$ and assuming that all the magnetization is due to $CuCr_2S_4$ spinel phases, we can estimate the percentage spinel in the sample to be ~1.5%.

Based on the obtained experimental results, we can perform a more detailed analysis of the properties of phases of spinel $CuCr_2S_4$ observed in the $CuGaCrS_2$ sample.

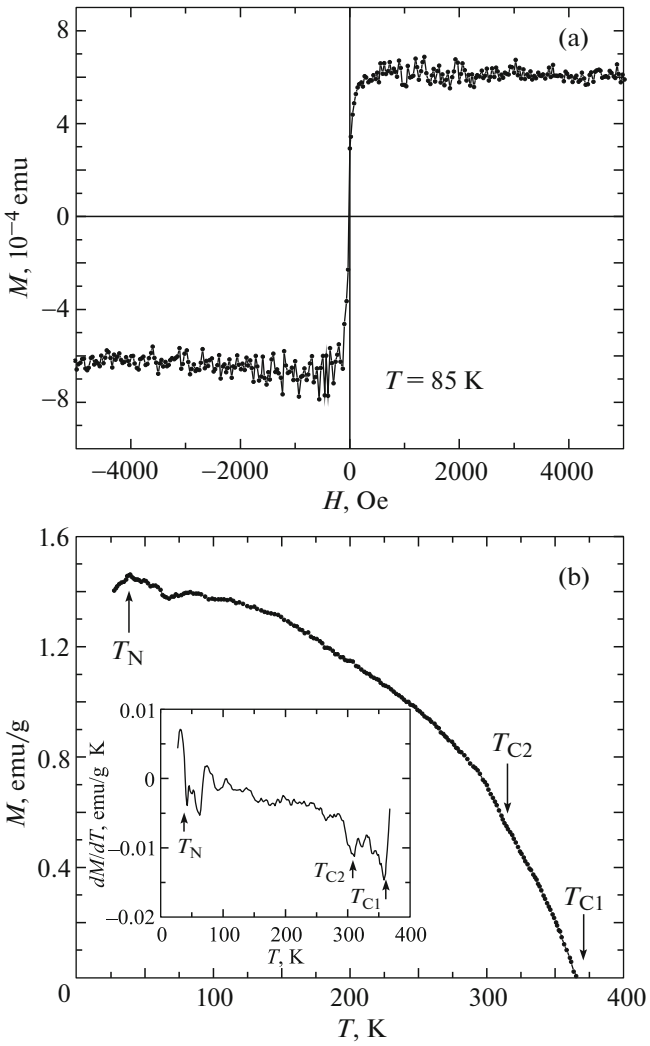

Fig. 4. (a) Field and (b) temperature dependences of the magnetization of $CuGaCrS_2$. The external magnetic field is directed along the plate plane. Temperature dependence $M(T)$ was measured in the saturation field 250 Oe. The insert shows derivative dM/dT.

First, it relates to the estimation of the thickness of spinel phase interlayers. It was shown in [1] that the magnetostatic vibrations due to thin interlayers of the $CuCr_2S_4$ spinel phase were observed in pure $CuCrS_2$ over the entire range of resonance fields of magnetostatic vibrations predicted theoretically for thin plates [5]

$$\sqrt{(\omega_0/\gamma)^2 + (2\pi M_0)^2} - 2\pi M_0 \le H \le \omega_0/\gamma, \quad \omega_0/\gamma \le H \le \omega_0/\gamma + 4\pi M_0 \tag{2}$$

for the parallel and perpendicular orientations, respectively. In our case, the magnetostatic vibrations were observed only near the main signal of phase $CuCr_2S_4$ with $T_{C1} = 372$ K (Fig. 2).

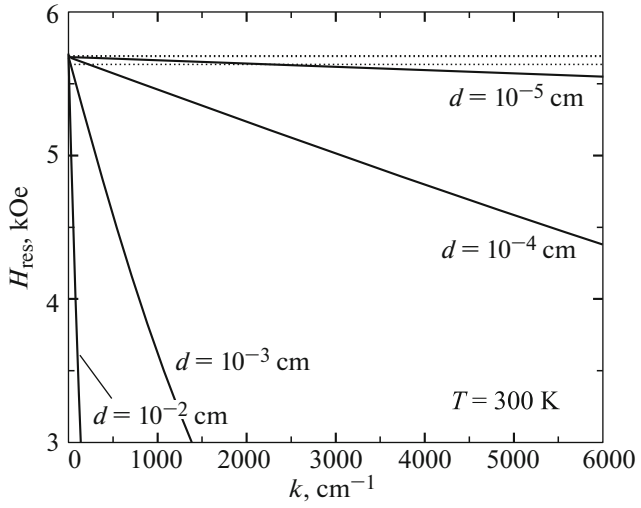

Fig. 5. Dispersion dependences $H(k)$ of the thin $CuCr_2S_4$ plate measured at various plate thicknesses d [1]. The dotted line shows the region corresponding to the line width of the uniform resonance.

Figure 5 shows the dispersion dependence of the spectrum of magnetostatic vibrations at various thicknesses d of spinel phase interlayers taken from [1].

It is seen from Fig. 5 that as the plate thickness decreases, almost all spectrum of magnetostatic vibrations is observed near uniform vibrations. Thus, we can conclude that the plate thickness of the attendant spinel phase in the $CuGaCrS_2$ compound is at least an order smaller than that in pure (undoped) $CuCrS_2$ compound.

Second, the fitting of the experimental resonance fields of both spinel phases (Fig. 3), assuming that the temperature dependence of the magnetization follows the Brillouin function, gives M_0 equal to 355.8 and 309 G for phases with $T_{C1} = 372$ K and $T_{C2} = 314$ K, respectively. If the value $M_0 = 355.8$ G of the phase with $T_{C1} = 372$ K is 91% of theoretical value for this spinel phase and the decrease can be ascribed to a small thickness of this phase (size effect), this difference for the phase with $T_{C2} = 314$ K is already 20%. In addition, the quite low Curie temperature of this phase ($T_{C2} = 314$ K) cannot be explained by size effects, since it is known that $T_C = 340$ K already in nanosized $CuCr_2S_4$ samples [7]. In this case, it can be assumed that the attendant phase of $CuCr_2S_4$ spinel in the gallium-doped $CuGaCrS_2$ compound also can contain gallium ions. Assuming that gallium ions substitute for chromium ions in this phase (phase $CuGa_xCr_{2-x}S_4$), the gallium ion concentration in this phase can be estimated taking $M_0 = 309$ G. It is $x \sim 0.35$.

4. CONCLUSIONS

Plates of the $CuGaCrS_2$ compound were grown by the chemical transport reaction method. It was shown that the plates contained thin inclusions of spinel $CuCr_2S_4$ and $CuGa_xCr_{2-x}S_4$, as was the case with undoped $CuCrS_2$ films [1]. Unlike pure $CuCrS_2$ compound, spinel phase inclusions in the gallium-doped sample had thicknesses one order smaller. We found that the Curie temperatures of spinel phases $CuCr_2S_4$ and $CuGa_xCr_{2-x}S_4$ were $T_{C1} = 372$ K and $T_{C2} = 314$ K, respectively, the saturation magnetizations of these phases were $M_0 = 355.8$ and 309 G, respectively; the gallium ion concentration in one of attendant spinel phases of the sample under study was $x \sim 0.35$.

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