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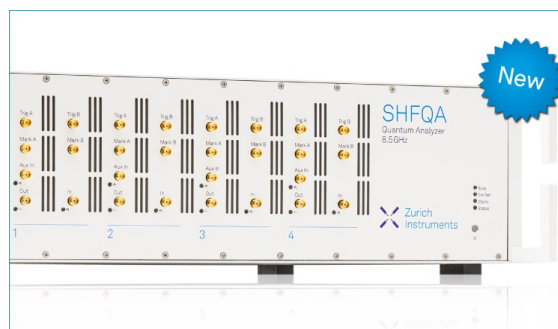
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Electron spin resonance in CuCrS_2 chrome-copper disulphides synthesized by different methods

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The electron spin resonance (ESR) in CuCrS_2 disulphides is found to be strongly dependent on a synthesis method used. At a temperature of 300 K, a polycrystalline CuCrS_2 sample is paramagnetic with a g -value of 1.95 at 40 K, it undergoes the magnetic transition. In the temperature range 4.2–290 K, a single-crystal sample prepared by a chemical vapor transport method exhibits the ESR features typical of a ferromagnet. It is shown that these features are related to the presence of a small amount of the single-crystal CuCr_2S_4 impurity in the CuCrS_2 single crystal. © 2010 American Institute of Physics. [doi:10.1063/1.3374679]

I. INTRODUCTION

The basic obstacle in the way of the development in thin-film multilayers for microelectronic applications is the necessity of using expensive technologies. The promising matrices for the creation of novel multilayers could be quasi-two-dimensional layered structures that represent three-dimensional (3D) crystals with the strong anisotropy of chemical bonds. The use of intercalation and cation substitution make it possible to obtain low-cost magnetic/nonmagnetic and dielectric/metal multilayers similar to heterostructures.

Layered transition-metal dichalcogenides and their intercalated complexes are of interest for practical applications, in particular, spintronic devices [see, for example (Ref. 1)] because of the features of their crystal structure^{2–4} and physical properties.^{4–6} These crystals are known to be highly anisotropic; most of them exhibit pronounced two-dimensionality resulting from the layered structure with weak bonds between the layers.⁴ More precisely, the crystals consist of stacks of TX_2 (T is the transition metal and X is the chalcogen) sandwiches separated by two layers of the empty tetrahedral positions called the van der Waals gaps, in which intercalant species (mostly, electron donors), such as alkali atoms, organic molecules, and 3D-transition-metal atoms can be inserted. A chrome-copper disulphide CuCrS_2 can be considered a Cu-intercalated dichalcogenide^{3,4} with Cu ions intercalated into the van der Waals gaps between the CrS_2 layers.

At room temperature, CuCrS_2 is a paramagnetic electron-ion semiconductor; at 670 K,⁷ it undergoes the superionic conductor-semiconductor transition; at 110 K,⁸ the electronic transition; and at 37 K,^{9,10} the paramagnet-antiferromagnet transition. Neutron diffraction studies^{9,10}

showed the incommensurate helimagnetic structure with the strong spin-phonon coupling below 37 K. The preliminary data we obtained previously⁵ revealed negative magnetoresistance in some CuCrS_2 solid solutions.

In this study, we present the results of the electron spin resonance (ESR) investigation of the CuCrS_2 samples synthesized using different methods.

II. EXPERIMENTAL

The experiments were carried out on polycrystalline and single-crystal CuCrS_2 samples. Polycrystalline samples were prepared from pure Cu, Cr, and S elements by heating in vacuum quartz ampoules; CuCrS_2 single crystals were grown by a chemical vapor transport (CVT) method in vacuum quartz ampoules.⁹ X-ray diffraction (XRD) spectra were recorded at room temperature with a DRON diffractometer with $\text{Cu } K\alpha$ radiation. ESR spectra were obtained with a SE/X 2544 spectrometer at a frequency of 9.4 GHz and a computer-controlled magnetic resonance spectrometer with the operating frequency range 25–80 GHz in pulse magnetic field.

III. RESULTS AND DISCUSSION

The x-ray diffraction spectrum of the synthesized polycrystalline CuCrS_2 sample presented in (Fig. 1, curve 1) corresponds to the crystal structure with an R3m rhombohedral space group (the card 74–0196). Polycrystalline CuCrS_2 was found to be single-phase with the lattice parameters $a = 3.480 \text{ \AA}$ and c ranged from 18.70 to 18.72 Å for different samples. The XRD spectrum (Fig. 1, curve 2) makes one conclude that the CVT crystal plate corresponds to the (001) plane of the CuCrS_2 R3m lattice with the c -axis perpendicular to the plate. In addition, the spectrum of the CVT CuCrS_2 single crystals contains an additional line corresponding to the CuCr_2S_4 phase with a spinel lattice (Fd3m space group) and the lattice parameter $a = 9.79 \text{ \AA}$.

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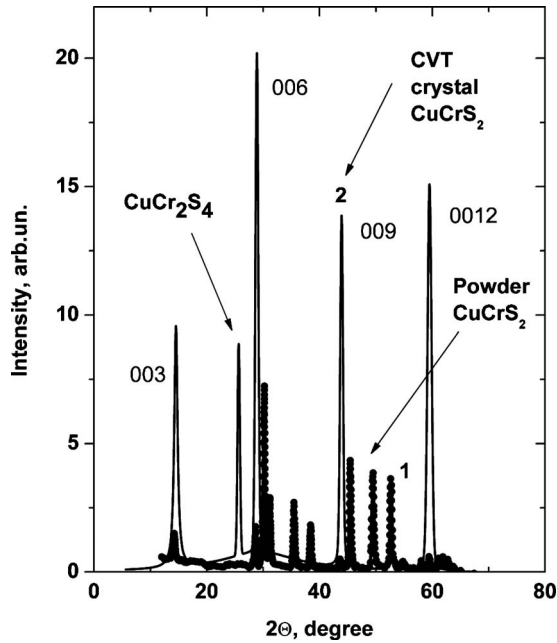


FIG. 1. XRD spectra of the CVT single-crystal and polycrystalline CuCrS_2 samples at 300 K.

The frequency-field dependences (FFDs) of magnetic resonance of the polycrystalline and single-crystal CVT CuCrS_2 samples taken at 90 K are presented in Fig. 2. The linear gapless FFD with a g -value of 1.95 (Fig. 2, curve 1) observable for the polycrystalline CuCrS_2 indicates the paramagnetic state of the sample at $T > T_N$. Similar paramagnetic-type magnetic resonance was found for blocking single crystals synthesized by crystallization from powder CuCrS_2 sulfide melt. However, the CVT CuCrS_2 single crystal was found to possess the strong anisotropy of the resonance properties. At a temperature of 90 K, different FFDs for parallel and perpendicular orientations of magnetic field relative to the CVT single crystal plate were obtained (see also Fig. 2). Angular dependences of the resonance field and linewidth measured at 300 K for the CVT CuCrS_2 single crystal are shown in Fig. 3. They indicate the anisotropy of the resonance properties of the sample at room temperature. The resonance fields at 300 K vary from 1.9 to 4.8 kOe upon

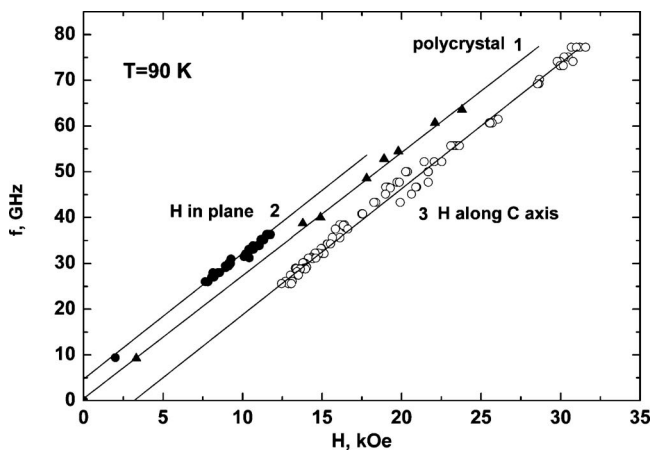


FIG. 2. FFDs of the magnetic resonance at 90 K for the polycrystalline and CVT single-crystal CuCrS_2 samples.

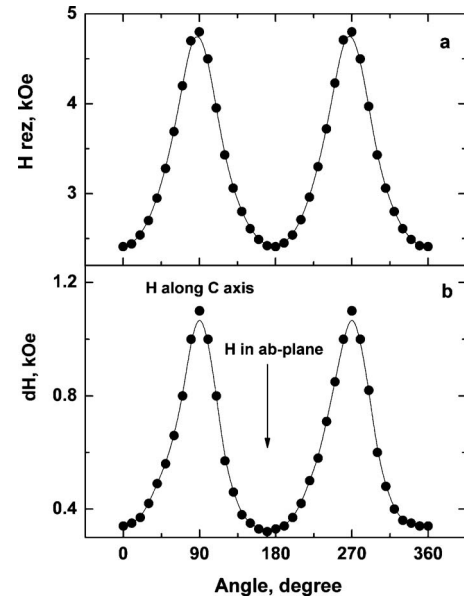


FIG. 3. Angular dependences of the resonance field (a) and linewidth (b) at 300 K for the CVT CuCrS_2 single crystal.

turning the magnetic field from the ab -plane to c -axis. The observed behavior of the resonance properties of the CVT CuCrS_2 single crystal is typical of an easy-axis ferromagnet. The difference between the FFDs of the polycrystalline and CVT single crystal samples can be explained by the presence of the ferromagnetic ordered state with easy and hard magnetization directions parallel and perpendicular to the CVT single crystal plate, respectively. Obviously, the ferromagnetic properties of the CVT CuCrS_2 crystal are connected with an additional CuCr_2S_4 impurity phase (5%–20% for different samples) discovered by an XRD analysis and confirmed by the temperature dependences of the magnetization and resonance fields of the CVT CuCrS_2 single crystal (Fig. 4).

Figure 4(a) depicts temperature dependences of the magnetization for the polycrystalline and CVT CuCrS_2 single crystal. The temperature of the magnetic transition in CuCrS_2 depends on a synthesis method used and varies within 37–40 K. A value of CuCrS_2 magnetic susceptibility also changes for different samples but the linear field dependence of the magnetization measured at 300 K for the polycrystalline sample in applied magnetic fields up to 50 kOe [inset in Fig. 4(a)] indicates the paramagnetic state of the CuCrS_2 sample at room temperature. One can see in Fig. 4(a) that the magnetization of the CVT single-crystal CuCrS_2 (curve 2) contains an additional magnetic contribution (curve 3), which can be related to the presence of ferromagnetic CuCr_2S_4 with the Curie temperature close to 400 K. Temperature dependences of the resonance field taken at 35 GHz for parallel and perpendicular orientations of magnetic field relative to the CVT single-crystal CuCrS_2 plate are given in Fig. 4(b). The difference between the resonance fields for the two orientations of the external magnetic field proportional to the magnetic anisotropy of the impurity phase decreases with the increasing temperature and vanishes at approaching a temperature of about 400 K, which is consistent with the Curie temperature of CuCr_2S_4 (Ref. 11).

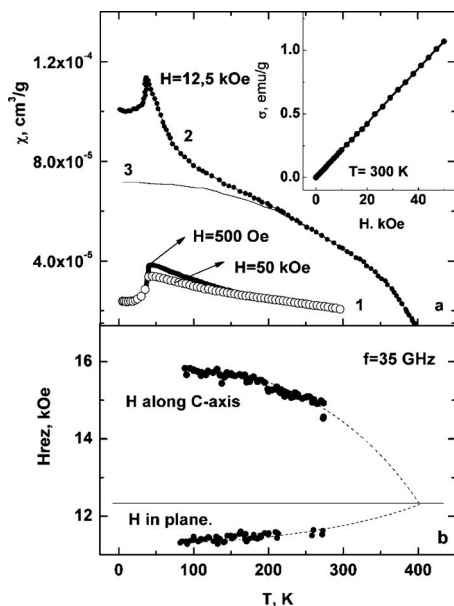


FIG. 4. Temperature dependence of magnetic susceptibility for the polycrystalline (1) and CVT single-crystal (2) CuCrS₂ samples (a) measured at the different magnetic fields. Inset: field dependence of magnetization for the polycrystalline sample at 300 K. Temperature dependences of the magnetic resonance field for the external magnetic field directed along *c*-axis and in *ab*-plane of the CVT single crystal (b).

It should be emphasized that both the host CuCrS₂ and the impurity phases in the CVT CuCrS₂ samples are single-crystal. The presence of the single-crystal CuCr₂S₄ impurity in the rhombohedral CuCrS₂ single crystal may be attributed to the similarity of their crystal structures. The structural spinel-rhombohedral transition is characteristic of some Cu-containing compounds, such as CuTi₂S₄ (Ref. 12) and CuFeO₂.¹³ The description of this transition and the comparison of the spinel and rhombohedral lattices for CuFeO₂ were presented in Ref. 13.

The Cu²⁺ and Cr³⁺ ions in the spinel CuCr₂S₄ lattice occupy tetra-sites and octa-sites, respectively, similar to the R3m lattice of CuCrS₂. Both the spinel and rhombohedral lattices can be presented as a layer sequences of the tetrahedral and octahedral sites along the [001] and [111] directions for the R3m and Fd3m structures, respectively (Fig. 5). Both the CuCrS₂ and CuCr₂S₄ lattices contain similar layers of the octahedral sites occupied by Cr³⁺-ions. The length of chemical bonds between Cr and S ions in CuCr₂S₄ is close to 2.34 Å. The Cr–S chemical bond length in CuCrS₂ lies within 2.42–2.38 Å and strongly depends on a synthesis method used. We suggest the Cr³⁺ layers in the CVT crystal marked by arrow in the picture to be common for two adjacent layer stacks with the different crystal structures. Thus, the CuCrS₂ solid solutions can be perspective matrices for synthesis of single-crystal heterostructures.

IV. CONCLUSIONS

The CuCrS₂ single crystals prepared by the CVT possess the intriguing resonance properties, which may be attributed

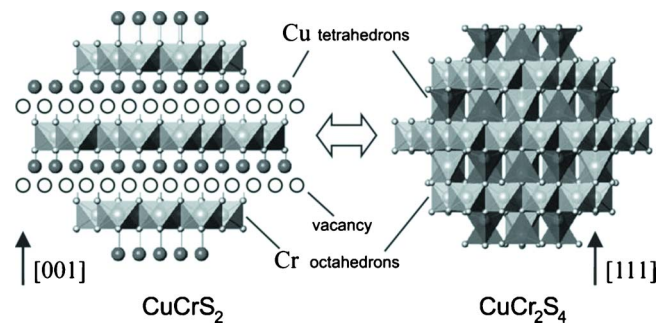


FIG. 5. (Color online) Comparison of the CuCrS₂ (s.g. R3m) and CuCr₂S₄ (s.g. Fd3m) crystal lattices.

to a small amount of the CuCr₂S₄ impurity phase. In the temperature range 90–300 K, the ESR spectra of the samples are typical of ferromagnets and the FFDs vary with the external magnetic field orientation. The obtained temperature and FFDs of the ESR suggest that the features of the resonant properties of the crystal are related to the CuCr₂S₄ impurity layers with the single-crystal structure. As the XRD data show, the CuCr₂S₄ [111] crystal planes are parallel to the CuCrS₂ [001] planes. In the temperature range 90–300 K, the resonance and magnetic properties of pure CuCrS₂ are typical of paramagnets.

The presence of the CuCr₂S₄ impurity in the chrome-copper disulphide is caused by the intercalation ability of the CuCrS₂ crystal structure. This property can be used to prepare heterostructures with single-crystal layers of CuCr₂S₄ or another magnetic impurity between the single-crystal CuCrS₂ layers.

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