
MAGNETISM AND FERROELECTRICITY

Electron Transition in Intercalated Disulfide CuCrS_2

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Abstract—Electrical, resonant, and magnetic properties of intercalated copper chromium disulfide CuCrS_2 are studied. It is established that CuCrS_2 is an antiferromagnetic semiconductor with Néel temperature $T_N = 40.7$ K and an effective magnetic moment of $4.3\mu_B$. Anomalies in the electrical, magnetic, and resonant properties of CuCrS_2 are found at $T_c = 110$ K, which suggest an electron transition accompanied by alteration of the valences of the 3d-metal ions. © 2004 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

The properties of the crystal structure and chemical bonds of dichalcogenides of transitional metals MeX_2 ($X = \text{S, Se, Te}$; $\text{Me} = \text{Ti, Cr, Ta}$) make them a likely base for the development of promising materials for the electronic industry of the future. The basic atomic structure of these materials consists of series of $X\text{--Me--}X$ trilayers within which atoms are coupled by ionic-covalent bonds and arranged with either trigonal prismatic or octahedral coordination [1, 2]. The trilayers are separated by tetrahedral hollows (a so-called van der Waals gap) and weakly coupled. Hollows of dichalcogenide lattices can be filled by auxiliary atoms (the process called intercalation) to create intercalated structures [1]. The physical properties of an intercalated structure can sometimes resemble those of multilayered thin-film materials. For example, structures consisting of a succession of magnetic and nonmagnetic, insulating and metallic, or magnetic and superconducting atomic layers can be created by intercalation [1, 3]. Due to a lack of experimental data, current notions of electron transport and magnetic ordering in intercalated structures (let alone the interrelation between the electrical and magnetic parameters) are semiempirical. Therefore, searching for intercalated compounds and complex study of their physical properties are highly topical.

According to the classification of layered disulfides of 3d metals by Wilson and Yoffe [1], copper chromium disulfide CuCrS_2 is an intercalated compound based on chromium disulfide CrS_2 . Trilayers in the lattices of intercalated disulfides MeCrS_2 ($\text{Me} = \text{Na, Cu, Ag}$) are formed by S--Cr--S layers, and univalent ions of Me are located in between in the van der Waals gap. The CuCrS_2 compound has a rhombohedral unit cell of the $\alpha\text{-NaFeO}_2$ type ($R3m$ Fedorov symmetry group) [1, 4]. In this compound, sulfur atoms form a distorted cubic

packing, which is often considered in hexagonal representation. Chromium atoms are located in the octahedral lattice sites, and copper atoms are in the tetrahedral sites. Half of the tetrahedral positions in the CuCrS_2 lattice are vacant; therefore, the structure of the disulfide is disordered and copper cations are mobile at high temperature. At the order-disorder structural phase transition temperature ($T \sim 670$ K), where the copper cation sublattice becomes disordered, copper chromium disulfide exhibits superionic properties [5]. We are unaware of any studies on the low-temperature electrical properties of this material. The magnetic properties of copper chromium disulfide were studied in [4, 5–7]. Intercalated disulfides MeCrS_2 are considered to be two-dimensional magnetic materials [4] whose magnetic properties are governed by ferromagnetic ordering of the magnetic moments of trivalent chromium ions in planes normal to the c axis and by antiferromagnetic ordering between the planes. Various authors report different values of the effective magnetic moment of CuCrS_2 in the paramagnetic state (for example, $5.5\mu_B$ [5], $3.985\mu_B$ [6], $3.8\mu_B$ [7]). The magnetic properties in the low-field region (below ~ 1 kOe) and the resonant properties of CuCrS_2 have not been studied previously. It is well known [8] that valuable information about free unpaired electrons, electron states, the interaction between them, and their interaction with the crystal lattice can be obtained by analyzing the temperature dependences of electron paramagnetic resonance (EPR). Further information about the electron states and charge transport mechanisms can be gained by simultaneously studying conductivity and magnetization in addition to EPR.

In the present paper, we report the results of studies on the structural, electrical, and magnetic properties and EPR spectra of layered intercalated copper chro-

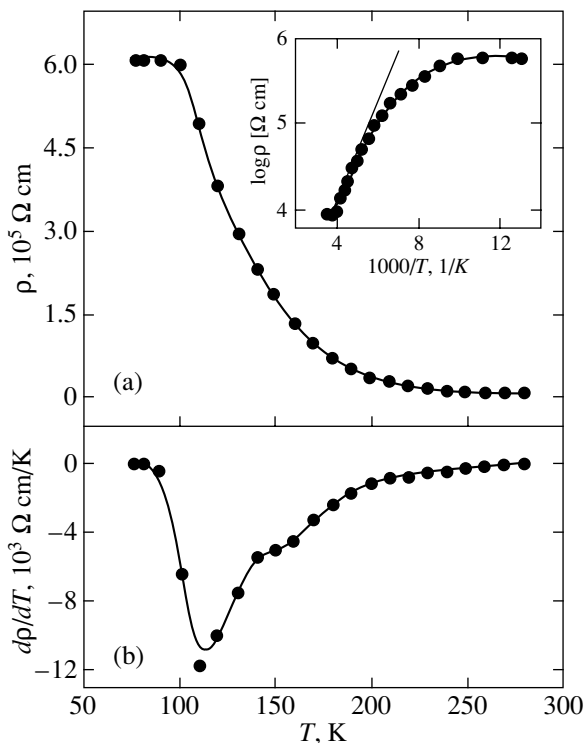


Fig. 1. Temperature dependences of (a) the resistivity ρ and (b) $d\rho/dT$ of CuCrS_2 . Insert shows the resistivity in logarithmic scale, $\log \rho$ ($1000/T$).

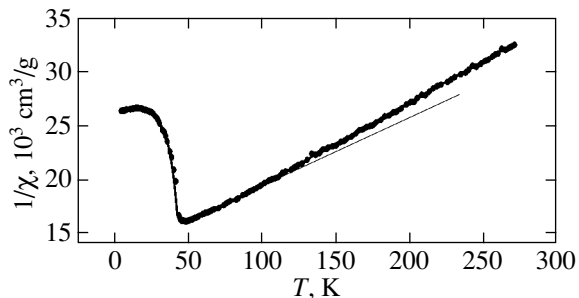


Fig. 2. Temperature dependence of the inverse magnetic susceptibility of CuCrS_2 in a magnetic field $H = 50$ Oe.

mium disulfide CuCrS_2 , which were conducted in order to establish interrelation between the magnetic and electrical parameters.

2. EXPERIMENT

We studied polycrystalline samples of CuCrS_2 . The sample preparation was described in detail in [5]. X-ray diffraction analysis was performed using a DRON-3M diffractometer ($\text{Cu-K}\alpha$ radiation) at temperatures of 113 and 300 K. Electrical resistivity was measured using the standard dc four-probe technique (current of 1 μA) in the temperature range 77–300 K. We used rectangular samples with dimensions $1 \times 0.3 \times 0.5 \text{ cm}^3$.

Samples were molded from powders and annealed at 1000°C in evacuated quartz ampoules. The accuracy of voltage measurements was 10^{-4} mV, and the accuracy of resistance measurements was 2%. EPR spectra were studied using an EPR spectrometer in the 3-cm range at temperatures of 77 to 300 K. The magnetic properties of the samples were studied using a SQUID magnetometer in magnetic fields of up to 1 kOe in the temperature range 4.2–300 K.

3. RESULTS AND DISCUSSION

According to x-ray analysis, the polycrystalline samples we synthesized are single-phased with an α - NaFeO_2 structure, typical of CuCrS_2 . At 300 K, the lattice parameters are $a = 3.48 \pm 0.01 \text{ \AA}$ and $c = 18.705 \pm 0.005 \text{ \AA}$, which are close to those of single-crystal copper chromium disulfide ($a = 3.482 \text{ \AA}$, $c = 18.686 \text{ \AA}$ [6]). As the temperature is lowered, the lattice is constricted mainly along the c axis without alteration of the crystal structure. At 113 K, the lattice parameters are $a = 3.47 \pm 0.01 \text{ \AA}$ and $c = 18.608 \pm 0.005 \text{ \AA}$.

Figure 1 presents the temperature dependences of sample resistance $\rho(T)$ (Fig. 1a), its first derivative $d\rho/dT$ (Fig. 1b), and resistance in the logarithmic scale (insert). The dc resistivity of CuCrS_2 (current of 1 μA) at 300 K is $8.4 \times 10^3 \text{ \Omega cm}$ and rises by two orders of magnitude as the temperature decreases, reaching $610 \times 10^3 \text{ \Omega cm}$ at 77 K. At room temperature, samples are semiconductors with an activation energy of 0.12 eV. As the temperature is lowered, the activation energy decreases and nonlinear variation of $\log \rho$ ($1/T$) is observed, which is typical of disordered Anderson semiconductors [9]. Below 110 K, almost no activation is observed in the conductivity of CuCrS_2 (insert to Fig. 1a). The activation energy for conductivity in the range 77–110 K is $\sim 3 \times 10^{-3}$ eV. The temperature dependence of the derivative $d\rho/dT$ exhibits an anomaly at $T_c = 110$ K, which suggests a phase transition in the electron subsystem of the material.

Figure 2 presents temperature dependences of the inverse magnetic susceptibility $\chi^{-1}(T)$ of CuCrS_2 samples measured with a SQUID magnetometer in a magnetic field of 50 Oe in the temperature range 4.2–270 K. The observed magnetic transition temperature $T_N = 40.7$ K, corresponding to a maximum in the temperature dependence of magnetic susceptibility, is close to the Néel temperature ($T_N = 39$ K) obtained for CuCrS_2 in [7]. The magnetic susceptibility $\chi(T_N)$ of the samples is $6.2 \times 10^{-5} \text{ cm}^3/\text{g}$. Between 110 and 270 K, the inverse susceptibility $\chi^{-1}(T)$ follows the Curie–Weiss law (Fig. 2) with a negative paramagnetic Curie temperature $\Theta = -148$ K and an effective magnetic moment $\mu_{\text{eff}} = 4.3\mu_B$. Around $T_c = 110$ K, where an anomaly in the resistivity of CuCrS_2 is observed, $\chi^{-1}(T)$ changes slightly in slope. Here, the paramagnetic Curie temperature changes to -176 K and the effective moment increases to $4.8\mu_B$.

In Fig. 3, the results of examining the resonant properties of CuCrS₂ at 9.4 GHz in the temperature range 77–300 K are presented. A single absorption line (1) is observed in the EPR spectrum at room temperature; its width is $\delta H = 953$ Oe, and the resonance field is $H_r = 3349 \pm 15$ Oe. The g factor at 280 K is estimated to be $g = 1.90 \pm 0.01$. In the region of electrical and magnetic anomalies ($T_c \sim 110$ K), the width and intensity of resonance line 1 increase sharply and the value of the resonance field sharply drops to $H_r \sim 3270 \pm 15$ Oe. The g factor at 100 K is equal to $g = 1.94 \pm 0.01$ and is close to the value typical of chromium atoms. The second line (2) arising in the EPR spectrum (Fig. 3) is experimental evidence for reconstruction of the electron system of copper chromium disulfide at around $T_c = 110$ K. The resonance field and width of the second line at 100 K are $H_r = 2911$ Oe ($g = 2.184 \pm 0.002$) and $\delta H = 178$ Oe. The g factor of line 2 is typical of the bivalent Cu²⁺ ion ($3d^9$, $S = 1/2$) [8]. Therefore, we can assume that below T_c the electron configuration of the disulfide matches Cu²⁺Cr²⁺S₂. In this case, line 1 in the EPR spectrum at $T < T_c$ pertains to chromium ions Cr²⁺. At room temperature, line 1 in the EPR spectrum has to correspond to trivalent chromium ions, since, according to [4, 5], copper ions at 300 K are in the nonmagnetic univalent state (electron configuration Cu⁺Cr³⁺S₂).

The anomalies and correlations found in the behavior of the magnetic, electrical, and resonant properties indicate that an electron phase transition takes place at $T_c = 110$ K in the paramagnetic state of CuCrS₂. The temperature dependence of resistivity typical of disordered semiconductors and the nonactivated type of conductivity despite the high values of resistivity ($610 \times 10^3 \Omega \text{ cm}$) in the low-temperature phase at $T < T_c$ suggest that the transition found at $T_c = 110$ K in CuCrS₂ may be related to localization of the charge carriers, for example, to the formation of a Fermi glass (Anderson insulator) [9].

According to [5], the conductivity of CuCrS₂ is of hybrid electronic–ionic type in the temperature range from 300 to 670 K. The charge transfer in the insulating phase of disordered electronic–ionic semiconductors [10, 11] can be considered to be associated with a recharging of univalent ions, for example, of copper ions: $2\text{Cu}^+ = \text{Cu}^{2+} + \text{Cu}^0$, where Cu⁰ denotes a complex consisting of a univalent ion and a charged vacancy. It is generally accepted [11, 12] that, in copper compounds, the ionic part of the conductivity σ_i is determined by the diffusion of univalent copper ions over lattice vacancies. The electronic part of the conductivity, σ_{el} , is p type and is determined by holes hopping over univalent copper ions with the formation of Cu²⁺ ions.

In the temperature range $T \geq 300$ K, the activation energy of mobile copper ions, for instance, in Cu_{2-x}Se [12], is 0.14 eV and their mobility at 673 K is 0.003 cm²/V s. We measured the full dc conductivity σ_{tot} , which is equal to the sum of the ionic σ_i and elec-

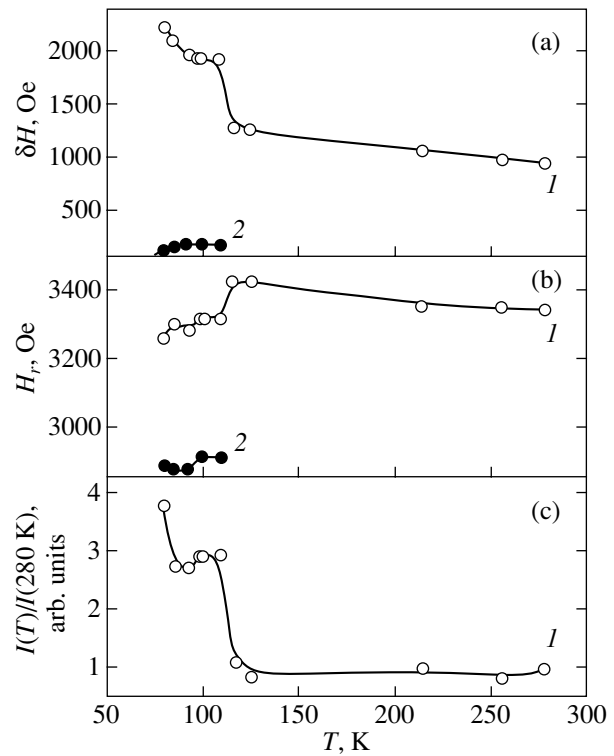


Fig. 3. Temperature dependences of (a) the EPR line width, (b) the resonance field, and (c) the normalized line intensity of CuCrS₂.

tron σ_{el} conductivities. The activation energy for CuCrS₂ in the range 250–300 K is found to be 0.12 eV, which is close to the activation energy of mobile copper ions. No details are known of the charge transfer in CuCrS₂. At reduced temperatures, diffusion freezes out, because an activation energy is required for hopping of either electrons or ions in such materials [11]. The ensuing localization of the charge carriers, namely, the hole localization on the copper ions with the formation of bivalent ions Cu²⁺, could well be the reason for the observed change in behavior of the conductivity of copper chromium disulfide at $T_c = 110$ K.

At least two different electron configurations of copper chromium disulfide (differing in magnetic moment) should be considered for recharging processes: Cu²⁺Cr²⁺S₂ ($S = 5/2$, $\mu_{eff} = 5.91\mu_B$) and Cu⁺Cr³⁺S₂ ($S = 3/2$, $\mu_{eff} = 3.87\mu_B$). In this case, the magnetic ground state of the compound would be determined by the recharging rate of copper ions and by the state of these ions in the “frozen” phase. The observed behavior and magnitude of the effective magnetic moment in the paramagnetic region, as well as the resonant properties of our samples, can be described well if one assumes that CuCrS₂ is a mixture of both electronic phases, Cu²⁺Cr²⁺S₂ and Cu⁺Cr³⁺S₂, with the proportion between them changing sharply at T_c . The behavior of the magnetic and resonant properties of the samples is correlated with the behavior of their electric properties

and shows evidence that the localization of charge carriers about T_c is related to the formation of bivalent copper ions. The anomalies observed in the parameters of absorption line I in the EPR spectrum of CuCrS_2 at 110 K suggest that the change in the valence of the copper ions is accompanied by a modification of the electronic state of the chromium ions. Therefore, the magnetic properties and the conductivity mechanism of the compound are interrelated. The dispersion of data on the effective moment of the paramagnetic state of CuCrS_2 presented by different authors could be explained by assuming there are fluctuations in the valences of the copper and chromium ions in the compound; the mechanism of these fluctuations is likely related to specific features of the transport properties.

4. CONCLUSIONS

To summarize, our study has shown that, at low temperatures, intercalated disulfide CuCrS_2 is an antiferromagnetic semiconductor with Néel temperature $T_N = 40.7$ K. In the paramagnetic semiconductor phase, the electrical and magnetic properties of CuCrS_2 are interrelated and the compound undergoes an electronic transition at $T_c = 110$ K, whose nature is likely associated with charge carrier localization and a change in the valences of the copper and chromium ions. The correlation of changes in spin and electronic states, as well as the observed magnetic state of the copper cations (Cu^{2+}), suggests that further study is needed into the mechanisms of electronic and ionic transport around $T_c = 110$ K and the nature of magnetic ordering at $T_N = 40.7$ K.

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