Phase Transitions and Colossal Magnetoresistance in $CuV_xCr_{1-x}S_2$ Layered Disulfides

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New substances $CuV_xCr_{1-x}S_2$ are synthesized in which colossal magnetoresistance (T_C = 95 K, δ_H = –60%, H = 7 kOe), as well as the sequence of phase transitions with change in the conduction type and magnetic order, is observed as temperature is varied. The change found in the magnetic and electric properties of the $CuV_xCr_{1-x}S_2$ compounds may be a consequence of a specific disintegration into $Cu^+Cr^{3+}S_2$ and $Cu^{2+}Cr^{2+}S_2$ and a change in the concentration relation between these electronic phases in the substance bulk.

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1. INTRODUCTION

The search for and investigation of new materials with specific magnetic and electric properties are among the high-priority directions of the development of the physics of magnetism and solid state physics. Investigations of oxide [1] and sulfide [2, 3] solid solutions of 3*d* metals indicate that the method of directional cation–anion substitution is an efficient method for designing and synthesizing substances with qualitatively new physical–technical parameters. In this approach, the choice of the matrix material for synthesizing solid solutions is important. According to currently accumulated experimental data, the correlation between magnetic and electric properties is most pronounced in solid solutions synthesized on the basis of "layered" structures consisting of alternating cation and anion planes. Such a crystalline structure is characteristic of manganites [1]; europium and manganese chalcogenides EuX and MnX, respectively, where X = S, Se, Te [2, 4]; and monosulfides and disulfides of 3*d* metals [2, 5, 6]. The magnetic properties of these compounds corresponding to various crystallographic groups are determined by a specific type of the magnetic order: the atomic magnetic moments of cations are ordered ferromagnetically in separated layers and antiferromagnetically between layers. If the original antiferromagnetic matrix of such a type is a semiconductor or insulator, cation substitution can provide a number of solid solutions whose properties change from antiferromagnetic insulator to ferromagnetic semiconductor and metal as the substitution degree increases [2, 3]. The detailed

process of the effect of cation substitution on the electric properties of three-dimensional insulators is described in the percolation theory [7]. Mechanisms of spin-dependent electron transport and correlation between the magnetic and electric properties of solid solutions of magnetic semiconductors are already under discussion. For this reason, it seems reasonable to perform investigations for revealing the properties of the percolation and spin-dependent effects in "layered" magnetic materials whose crystalline structure and chemical bonds imply pronounced quasi-two-dimensional properties.

It is known [8, 9] that layered chromium–copper disulfide $CuCrS_2$ is an antiferromagnetic material with the Néel temperature T_N = 40 K that exhibits an order in the magnetic moments of atoms, which is similar to manganites, as well as to europium and manganese chalcogenides. The rhombohedral lattice of chromium–copper disulfide (structure type α-$NaFeO_2$) is a derivative of the NaCl structure and has the $R3m$ space group [5, 6, 8]. The rhombohedral distortion of the NaCl lattice in $CuCrS_2$ disulfide can be represented as a result of order in copper and chromium atoms in the alternating (111) planes. In this case, chromium ions have octahedral symmetry similar to manganese ions in manganese oxides and sulfides and copper ions occupy tetrahedral sites. The $CuCrS_2$ disulfide is of special interest, because this compound belongs to layered intercalated substances in which a weak (van der Waals) bond, along with ion-covalent bonds, plays an important role [5, 8]. The $CuCrS_2$ disulfide is treated [9] as a quasi-

two-dimensional antiferromagnetic material whose magnetic properties are determined by the ferromagnetic order of the magnetic moments of trivalent chromium ions in alternating triple CrS_2 layers and their antiferromagnetic order between the CrS_2–Cu–CrS_2 layers. In this paper, we present the results of investigation of the structure, electric, magnetoelectric, magnetic, and resonance properties of cation-substituted disulfides $CuV_xCr_{1-x}S_2$.

2. EXPERIMENTAL PROCEDURE

Experimental investigations were carried out with $CuV_xCr_{1-x}S_2$ polycrystalline samples with $0 \leq x \leq 0.25$. The samples were synthesized from pure elements by means of a solid state reaction in evacuated quartz ampules at 1000°C. X-ray diffraction analysis was performed using a DRON-3M diffractometer in CuK_α radiation at 120–300 K. Resistivity was measured for 77–300 K in transverse magnetic fields H up to 10 kOe. Magnetization was measured by means of a SKVID magnetometer for temperatures 4.2–270 K in magnetic fields up to 1 kOe. The electron-spin-resonance spectra were measured in the range 4.2–250 K at a frequency of 9.247 GHz.

3. EXPERIMENTAL RESULTS AND DISCUSSION

According to x-ray diffraction analysis, synthesized $CuV_xCr_{1-x}S_2$ compounds with $0 \leq x \leq 0.15$ are single-phase solid solutions, and their structure is typical for $CuCrS_2$ (space group $R3m$, rhombohedral lattice of the α-$NaFeO_2$ type). X-ray diffraction patterns for samples with $x = 0.2$ and 0.25 exhibit additional weak lines corresponding to the Cu_3VS_4 phase. This fact indicates that the region of existence of single-phase solid solutions in the system $CuV_xCr_{1-x}S_2$ is rather narrow and corresponds to $0 \leq x \leq 0.2$.

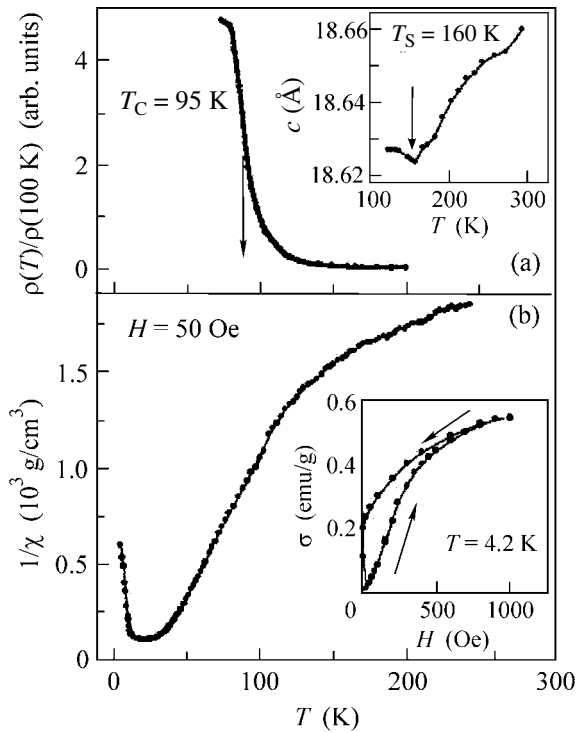Figure 1 shows the temperature dependences of the magnetic susceptibility of $CuV_xCr_{1-x}S_2$ samples. The measurements were carried out in a magnetic field of 50 Oe with samples cooled to 4.2 K in the absence of the magnetic field. The Néel temperature for $CuCrS_2$ chromium–copper disulfide is $T_N = 40$ K (Fig. 1, line 1). As x in $CuV_xCr_{1-x}S_2$ solid solutions increases, the magnetic transition temperature T_{max} at which the maximum magnetic susceptibility is observed in weak magnetic fields decreases to 11 K ($x = 0.25$, Fig. 1, line 4). The magnetic susceptibility χ_{max} increases in the range $0 \leq x \leq 0.1$ by two orders of magnitude from 6.2×10^{-5} cm³/g at $x = 0$ to 4.2×10^{-3} cm³/g at $x = 0.1$. The magnetic susceptibility χ_{max} decreases in the range $0.1 \leq x \leq 0.25$ and, at $x \sim 0.25$, is equal to 5.8×10^{-5} cm³/g, which is comparable to the value at $x = 0$. The behavior of the inverse magnetic susceptibility of the $CuV_xCr_{1-x}S_2$ samples at high temperatures can be
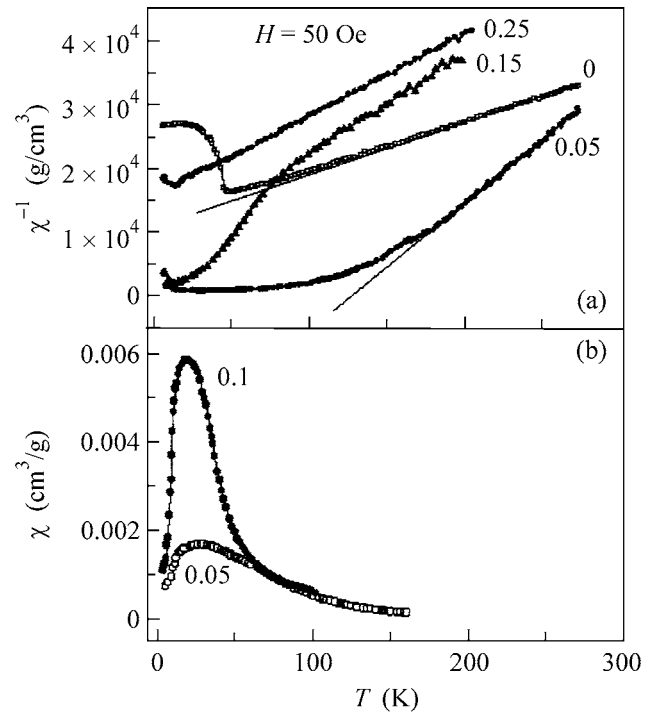
Fig. 1. Temperature dependences of (a) the inverse magnetic susceptibility and (b) magnetic susceptibility for $CuV_xCr_{1-x}S_2$ with x shown near the lines.

approximated by the Curie–Weiss law. The paramagnetic Curie temperature changes sign twice as the sample composition varies. It is negative for $x \sim 0$ ($\theta = -148$ K), positive for $x \sim 0.05$ ($\theta = 120$ K), and again negative for $0.1 \leq x \leq 0.25$. The field hysteresis of magnetization, which is characteristic of ferromagnetic and ferrimagnetic compounds, is observed (inset in Fig. 2b, $x = 0.1$) in the low-temperature phase at 4.2 K in substances ($0.05 \leq x \leq 0.1$) with large magnetic susceptibilities. The results of investigation of the magnetic properties indicate that cation substitution in the $CuV_xCr_{1-x}S_2$ system leads to a change in the magnetic ordering type such as in cation-substituted manganese oxides and chalcogenides.
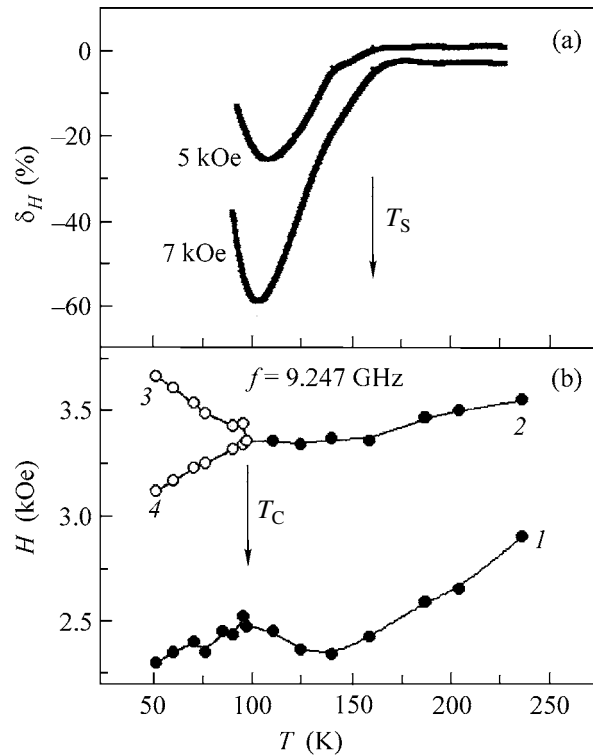
Experimental investigations of the electric properties indicate that chromium–copper disulfide ($x = 0$) undergoes an electronic transition at $T_C = 110$ K, which is accompanied by a change in the valence of chromium and copper ions [10]. Such an electronic transition is also found in $CuV_xCr_{1-x}S_2$ cation-substituted samples. In order to illustrate this fact, the temperature dependences of the resistivity and inverse magnetic susceptibility are shown in Fig. 2 for $x = 0.1$. The inset in Fig. 2a shows the temperature dependence of the lattice constant $C(T)$, which is evidence of the presence of changes in the crystalline structure that precede ($T_S = 160$ K) the electronic transition ($T_C = 95$ K). It is found that the magnetic properties of the samples for temperatures below 100 K depend on the thermomagnetic pre-

Fig. 2. Temperature dependences of (a) the electric resistivity, (a, inset) lattice constant, and (b) inverse magnetic susceptibility for $CuV_xCr_{1-x}S_2$ with $x = 0.1$. The inset in panel (b) shows the field dependence of magnetization at 4.2 K.

Fig. 3. Temperature dependences of (a) the magnetoresistance and (b) resonance field for $CuV_xCr_{1-x}S_2$ disulfide with $x \sim 0.1$.

history. The magnetic-transition temperature for $x = 0.1$ is $T_{max} = 20$ K. Figure 3a shows the temperature dependences of magnetoresistance for $CuV_xCr_{1-x}S_2$ disulfide ($x \sim 0.1$). It is seen that negative magnetoresistance is observed for temperatures $T \sim T_C$, and its maximum absolute value $\delta_H = (\rho_H - \rho_0)/\rho_H$ in a field of 7 kOe is equal to about 60%. Figure 3b shows temperature dependences of the resonance field of absorption lines observed in the spectrum of the electronic spin resonance of $CuV_xCr_{1-x}S_2$ samples with $x \sim 0.1$. It is found that the magnetic-resonance spectrum for these compounds is similar to the spectrum of $CuCrS_2$ stoichiometric disulfide, which is observed for $T \le T_C = 110$ K [10] and contains two absorption lines with g factors characteristic of bivalent copper ($g_1 = 2.4$) and chromium ($g_2 = 1.9$) ions. Near the electronic transition $T_C \sim 95$ K, lines 3 and 4 appear in the magnetic-resonance spectrum, which is evidence of magnetic and electron states of the substance.

It has been previously assumed [9] that the electronic configuration of chromium–copper disulfide corresponds to $Cu^+Cr^{3+}S_2^{4-}$. Our investigations [10] show that the electronic transition at $T_C = 110$ K in $CuCrS_2$ is accompanied by anomalies in the electric, magnetic, and resonance properties, which are evidence of change in the valence of $3d$ ions and coexistence of two mag-

netically different phases $Cu^+Cr^{3+}S_2^{4-}$ ($S_{tot} = 3/2$) and $Cu^{2+}Cr^{2+}S_2^{4-}$ ($S_{tot} = 5/2$). The presence of uni- and bivalent copper in oxide and chalcogenide compounds of copper is not a unique situation; however, the mechanism of this coexistence has not yet been studied in detail. The closeness of the electron affinities of sulfur (2.15 eV) and copper (2.4 eV) ions is a possible cause of the coexistence of magnetically different phases in copper sulfides. The results of resonance investigations of $CuV_xCr_{1-x}S_2$ for $x = 0.1$ can be explained under the assumption that cation substitution stabilizes the $Cu^{2+}Cr^{2+}S_2^{4-}$ ($S_{tot} = 5/2$) phase and leads to an increase in the concentration of bivalent copper and chromium ions. Change in the magnetic and electric properties of $CuV_xCr_{1-x}S_2$ compounds that is observed when varying temperature, composition, and magnetic field can be a consequence of both a specific phase separation into $Cu^+Cr^{3+}S_2^{4-}$ and $Cu^{2+}Cr^{2+}S_2^{4-}$ and a change in the concentration relation between these electronic phases in the substance bulk.

Thus, the experimental investigations show that, in the system of $CuV_xCr_{1-x}S_2$ sulfides synthesized on the basis of the $CuCrS_2$ layered intercalated antiferromagnetic compound, the magnetic order type changes when changing the cation substitution degree. As the temperature decreases, compounds with $x \sim 0.1$ undergo a

sequence of phase transitions: structural transition at $T_S = 160$ K, electronic transition at $T_C \sim 95$ K, and magnetic transition at $T_{max} = 20$ K. Colossal magnetoresistance is observed for temperatures below 160 K and reaches a value of about –60% in a magnetic field of 7 kOe near the electronic transition at $T_C \sim 95$ K.

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