

MAGNETISM
AND FERROELECTRICITY

Magnetic Properties, Magnetoresistance, and Raman Spectra of $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$

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Abstract—The results of investigations of the magnetic and Raman spectra, magnetic properties, and magnetoresistance of vanadium-substituted chromium copper disulfides $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ ($x = 0.1$) are presented.

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1. INTRODUCTION

The discovery of colossal magnetoresistance in non-magnetic superionic conductors (for instance, $\text{Ag}_{2+\delta}\text{Se}$ and $\text{Ag}_{2+\delta}\text{Te}$ [1], $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ [2]) has heralded new aspects in the problem of colossal magnetoresistance and spin-dependent electron transport. Among the specific features of the superionics are the fairly high defect density and lattice dynamics [3, 4], which dominates ionic transport and the possibility of formation of the so-called redox or mixed-valence pairs [5]. Of particular interest for development of spintronics are layered magnetic compounds [6] with mixed electronic–ionic conduction [5], in which charge transport can be mediated both by the electrons (holes) and by ions. The magnetic properties of such compounds and their relation with the electrical and structural characteristics are only poorly known.

The compound CuCrS_2 (rhombohedral structure, space group $R3m$) belongs to the class of mixed electronic–ionic conductors with fast ionic transport (superionics) and is an antiferromagnet with the critical temperatures of superionic and magnetic transitions $T_{\text{su}} = 675$ K and $T_N = 40$ K, respectively [7, 8]. We report here on the study of the Raman and magnetic spectra, the magnetic properties, and magnetoresistance of vanadium-substituted chromium copper disulfides $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ with $x = 0.1$ prepared by different technologies.

2. SAMPLES AND EXPERIMENTAL TECHNIQUES

The $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ polycrystalline sulfides with $x = 0.1$ were prepared by solid-phase synthesis from pure elements in evacuated quartz ampoules (samples **1**) and sulfiding of a mixture of oxides (samples **2**). Single crystal ingots (samples **3**) were prepared by crystallization from melted powdered sulfides **2**. The crystallization was conducted in sulfur vapor in RF-heated glass-ceramic containers, with the container drawn through a one-turn inductor with a velocity of 3–5 mm/h (vertical arrangement). The ingots thus prepared were 10 mm in diameter, up to 20 mm long, and 6 g in mass. The X-ray structural analysis was performed on a DRON diffractometer with CuK_α radiation. The X-ray diffraction analysis showed the $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ samples thus prepared to be solid solutions with a crystal structure typical of CuCrS_2 . The single crystal ingots contained inclusions of nano- or micro-sized copper droplets. Since the $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ disulfides undergo a superionic transition at a temperature of 670 K, [7], we can conclude that the high mobility of copper ions makes growth of crystals from the melt an inefficient technology.

Magnetic resonance spectra were measured on an X-band spectrometer. The magnetic properties were studied with a SQUID magnetometer in the temperature range 4.2–240.0 K and magnetic fields of up to 500 Oe, and with a vibrating-coil magnetometer in the temperature range 77–300 K and magnetic fields of up to 20 kOe. The electrical resistivity was investigated by

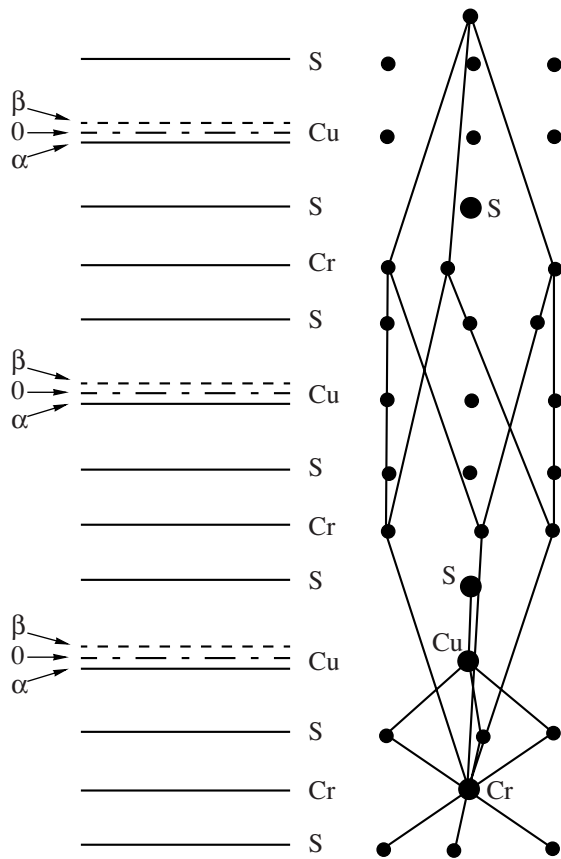


Fig. 1. Rhombohedral unit cell of CuCrS_2 . The atoms making up the primitive cell are identified.

the four-point probe dc technique in the temperature range 77–300 K. The Raman spectra were measured at room temperature on an RFS 100/S Fourier-Raman spectrometer (Bruker, Germany). The monochromatic radiation was provided by a YAG : Nd laser operating at the wavelength $\lambda_0 = 1.064 \mu\text{m}$. The Raman and IR absorption spectra of CuCrS_2 were calculated within the valence force field model with the LADY program package [9].

3. RESULTS AND DISCUSSION

Figure 1 shows the rhombohedral unit cell (space group $R3m$) characteristic of the CuCrS_2 and AgCrS_2 isostructural sulfides [10]. Viewed along the trigonal crystallographic axis z , this structure can be treated as a sequence of sulfur-metal-sulfur trilayers (CrS_2 sandwiches) separated by two rows (α and β) of tetrahedral positions. The metal atoms inside the CrS_2 sandwich are octahedrally coordinated and linked with sulfur atoms by ionic-covalent bonding. The tetrahedral positions (α and β) are occupied by copper atoms. One can conceive of two ordered states, α and β (C_{3v}^5), and a disordered state γ . In the crystallographically ordered

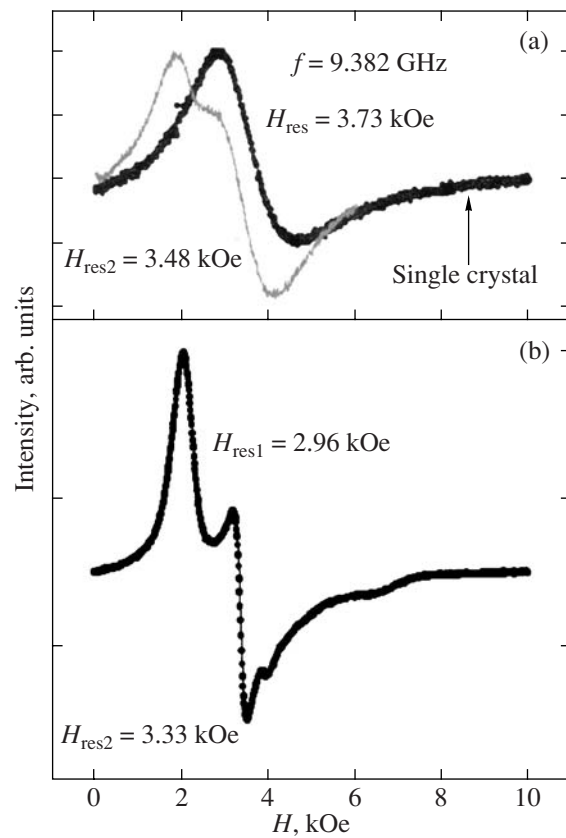


Fig. 2. Electron paramagnetic resonance spectra of $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ samples with $x = 0.1$ in the room-temperature range. Panels (a) and (b) relate to different synthesis technologies.

state of CuCrS_2 , either α or β positions are occupied, with half of the tetra-positions (either α or β) left vacant. The disorder on the copper sublattice (γ state, D_{3d}^5 symmetry) setting in at the transition of CuCrS_2 to the superionic state in the vicinity of the transition temperature $T = 670 \text{ K}$ originates [10, 11] from filling of both α and β tetrahedral positions, as well as of the previously vacant octahedral lattice positions (positions 0, Fig. 1).

The study of $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ samples with $x = 0.1$ revealed that their magnetic properties depend substantially on the technology of their preparation, which can tentatively be traced to vacancy redistribution. Figure 2 displays the magnetic resonance spectra (9.4 GHz) observed in the temperature range 150–300 K for samples in the $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ ($x = 0.1$) system prepared by different technologies. The EPR spectra can be interpreted as due to the presence in the material of paramagnetic ions of two types, with g factors of 1.9–1.96 and 2.18–2.5 (EPR lines 1 and 2, respectively). The second g factor is close in magnitude to the value characteristic of the Cu^{2+} ion. The charge neutrality condition allows two electronic configurations of the CuCrS_2 dis-

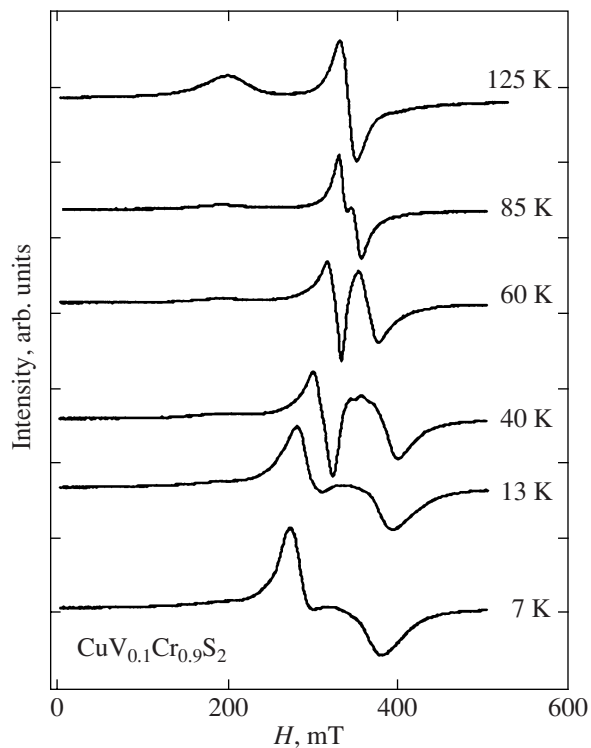


Fig. 3. Electron magnetic resonance spectra of $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ polycrystals with $x = 0.1$ at low temperatures.

ulfide with different paramagnetic moments: $\text{Cu}^{2+}\text{Cr}^{2+}\text{S}_2^{4-}$ ($S_{\text{Cu}^{2+}} = 1/2$ and $S_{\text{Cr}^{2+}} = 2$) and the universally accepted one $\text{Cu}^+\text{Cr}^{3+}\text{S}_2^{4-}$ ($S_{\text{Cr}^{3+}} = 3/2$). This suggests that the two lines in the magnetic resonance spectrum should be attributed to coexistence of two electronic phases.

In order to establish the valence state of ions of the 3d elements, the $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ crystals were studied by X-ray electron spectroscopy [12, 13]. The $\text{Cu}2p_{3/2, 1/2}$ spectra were found to contain a characteristic spin doublet whose principal components can be decomposed into two constituents with energies corresponding to copper ions in two charge states, Cu^+ and Cu^{2+} . Cation substitution occurs primarily in the chromium layers.

Figure 3 shows the variation in the magnetic resonance spectrum of a polycrystalline sample **1** in the temperature range 7–125 K. Lowering of the temperature brings about disappearance of the “copper” line and splitting of line 1, whose parameters allow its assignment to chromium ions. A similar splitting of the trivalent chromium line was observed in the weakly polar $\text{Li}_2\text{Ge}_7\text{O}_{15}$ in the region of the ferroelectric transition [14]. In polycrystalline samples **2**, no splitting of the magnetic resonance line 1 was observed. In sample **3**, one observed one resonance line which broadened with decreasing temperature, to disappear finally at the magnetic transition temperature $T = 37$ K.

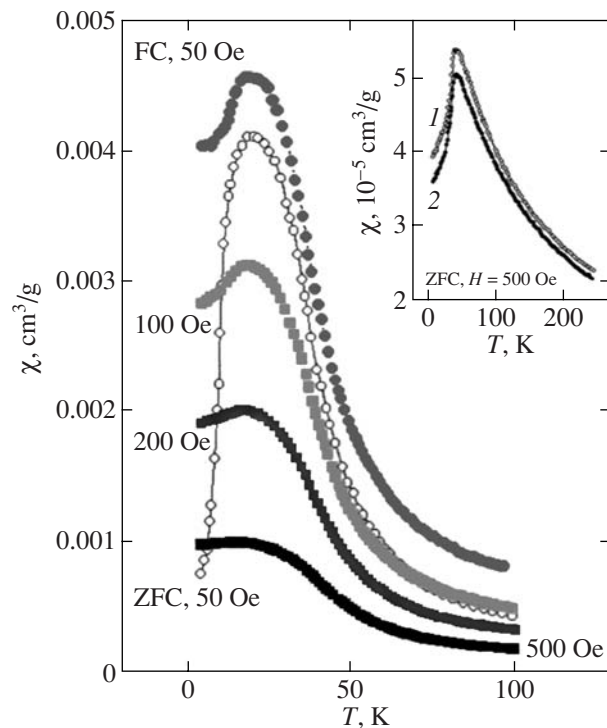


Fig. 4. Temperature dependences of the magnetic susceptibility of polycrystalline $\text{CuV}_{0.1}\text{Cr}_{0.9}\text{S}_2$ and single-crystal ingots of the compound (inset) in different magnetic fields.

Figure 4 plots temperature dependences of the magnetic susceptibility of polycrystalline $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ samples **1**. For the chromium copper disulfide CuCrS_2 , the Néel temperature is 36–40 K [8]. Substitution of vanadium ions for chromium in $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ polycrystals **1** and **2** is accompanied by a lowering of temperature of the maximum in magnetic susceptibility to 20 K and manifestation of spin glass properties below 100–140 K (the difference in behavior between the ZFC (zero-field cooling) and FC (field cooling) susceptibilities). The inset to Fig. 4 shows the temperature dependences of the magnetic susceptibility plotted in the same coordinates as used in the main panel for the plate cut from the single-crystal ingot, sample **3**; the measurements were performed for two magnetic field directions, along the plate (curve 2) and perpendicular to its plane (curve 1). In this case, the Néel temperature was 37 K, and no difference was observed between the ZFC and FC susceptibilities measured in zero and preset magnetic field. Figure 5 displays the field dependences of the magnetization for polycrystalline $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ samples with $x = 0$ and 0.1. The dependences $\sigma(H)$ measured on $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ samples are not typical of the paramagnetic state. We observed also the variation in the magnetization with time at a constant magnetic field. The inset in Fig. 5 shows the variation in the relative resistance ($R(0)$ and $R(H)$ are electrical resistances in zero and preset magnetic fields) with increasing magnetic field. At 77 K and in a magnetic field of 10 kOe, the negative magnetoresis-

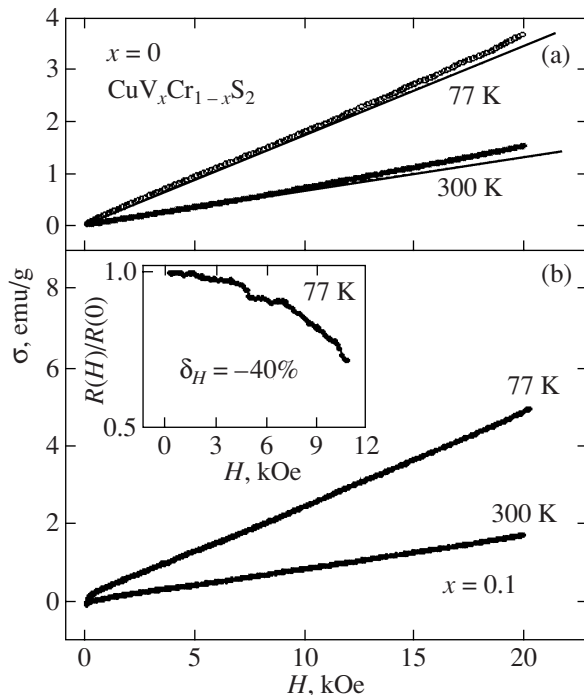


Fig. 5. Field dependences of the magnetization and the relative electrical resistance (inset) of $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ polycrystals with $x =$ (a) 0 and (b) 0.1.

tance (NMR) is -40% . The NMR effect is observed in polycrystalline samples and not seen in single-crystal copper-deficient alloys.

Unlike classical magnets, the chromium copper disulfide CuCrS_2 belongs to mixed electronic–ionic systems [11] whose conductivity is mediated both by the ionic, σ_i , and electronic, σ_e , components. Copper ions are responsible for the ionic component. In the isostructural CuCrS_2 and AgCrS_2 compounds, it is the dynamic state of the lattice that contributes to the ionic conductivity [10]. In order to establish the dynamic structural properties, we performed Raman studies of polycrystalline $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ samples ($x = 0.1$) at 300 K. Figure 6 shows a calculated Raman spectrum for CuCrS_2 (line spectrum) and a spectrum measured for polycrystalline $\text{CuV}_{0.1}\text{Cr}_{0.9}\text{S}_2$. Our calculations suggest that cation substitution of vanadium for chromium ions should not change noticeably the Raman spectrum of CuCrS_2 . The lattice of CuCrS_2 is similar in dynamic properties to that of AgCrS_2 [10]. The phonon spectrum of $\text{CuV}_{0.1}\text{Cr}_{0.9}\text{S}_2$ contains low-frequency vibrations (more detailed data of the study will be presented elsewhere), which allow copper ions to displace from the center of their tetrahedral positions. It is pointed out [10] that displacement of a univalent ion from the tetrahedron center makes possible formation of a pyroelectric state with a static dipole moment along the z axis. Formation of the dipole state can give rise, in its turn, for instance, to magnetic resonance line splitting (see, for instance, [14]).

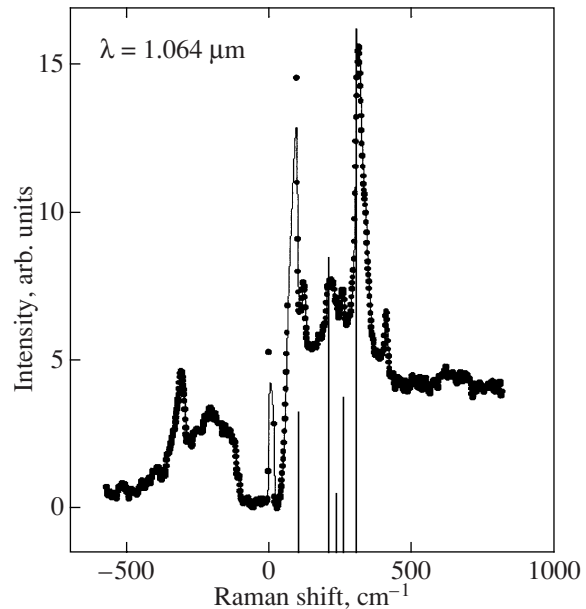


Fig. 6. Raman spectra of $\text{CuV}_x\text{Cr}_{1-x}\text{S}_2$ disulfides at 300 K according to the results of the calculation for CuCrS_2 and the experimental data for the $\text{CuV}_{0.1}\text{Cr}_{0.9}\text{S}_2$ polycrystal.

The vibrations seen in the IR and Raman spectra of CuCrS_2 have the same frequencies, a feature characteristic of crystals without inversion symmetry. Decomposition of a vibrational representation into irreducible representations at the Brillouin zone center for the rhombohedral phase can be written as

$$\Gamma = 4A_1 + 4E.$$

The calculated vibration frequencies are A_1 —0, 198, 240, and 307 cm^{-1} and E —0, 99, 211, and 257 cm^{-1} . The strongest line of the spectrum at 307 cm^{-1} corresponds to the irreducible representation A_1 ; it is associated primarily with displacement of Cu and Cr atoms along the threefold axis, and of S atoms, in the opposite direction. The 240-cm^{-1} line (A_1) derives from Cu vibrations and antisymmetric vibrations of S atoms along the same axis. The doubly degenerate vibrations of type E occur in the plane perpendicular to the threefold axis.

It is known that magnets without inversion symmetry can support formation of long-period modulated spiral-shaped structures. Preliminary studies [15] have demonstrated that polycrystalline disulfide does indeed have a spiral incommensurate structure. The presence of lattice defects in such structures can bring about pinning of the period of the magnetic structure.

The above discussion, as well as the layered character of the lattice of the compounds of interest and the presence of vacancies, give one grounds to expect that the distribution of copper ions in different copper sheets

and the displacements from the centers of tetrahedra should depend on the technology chosen for synthesis. This suggestion can shed light on the difference in resonance and magnetic properties between $\text{CuV}_{0.1}\text{Cr}_{0.9}\text{S}_2$ samples prepared by different technologies.

4. CONCLUSIONS

Thus, our studies have established that the magnetic and transport characteristics of $\text{CuV}_{0.1}\text{Cr}_{0.9}\text{S}_2$ depend on the technology used for the preparation of samples. This property stems from the inherent disorder of the crystal structure of the starting chromium copper disulfide. The presence of vacancies, diffusion of copper ions, the possibility of their displacement from the centers of the tetrahedra, as well as random distribution of ions in different copper layers permit one to assign CuCrS_2 to the class of materials with positional lattice disorder. Such materials have typically a rigid framework (the CrS_2 sandwich in our case) and a labile, restructurable copper sublattice (the copper sublattice in our case). In order to gain insight into the fundamental properties of the solid solutions of such compounds, high quality single crystals are needed. On the other hand, the specific features of the magnetic and transport properties of $\text{CuV}_{0.1}\text{Cr}_{0.9}\text{S}_2$ and their dependence on technology suggest strongly the need for exploring nanocrystalline compounds of the chromium copper disulfide.

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