Metal-insulator transition, magnetoresistance, and magnetic properties of $3d$-sulfides (Review)

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Metal-insulator transition, magnetoresistance, and magnetic properties of 3*d*-sulfides (Review)

G. M. Abramova[a)] and G. A. Petrakovskii

L. V. Kirenskiĭ Institute of Physics, Siberian Division of the Russian Academy of Sciences, Krasnoyarsk, Akademgorodok 660036, Russia

The results of a study of the transport and magnetic properties of some sulfides of 3*d* elements are reported. The concentration transitions with a change of conductivity type and a change of magnetic order are considered, and the features of the colossal magnetoresistance in $Fe_xMn_{1-x}S$ and $CuV_xCr_{1-x}S_2$ solid solutions are discussed. © *2006 American Institute of Physics*.
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INTRODUCTION

The interdependence of the magnetic and electrical properties of materials is a topic of intensive research at the present time in connection with materials exhibiting colossal magnetoresistance (CMR).[1–7] In the applied sphere this topic is known in microelectronics as "spin electronics" or "spintronics."[3] One track in the search for new materials for spintronics is the synthesis of ferromagnetic semiconductors with improved CMR characteristics and which are compatible with standard semiconductor technology. The choice of the matrix materials for creating new compounds with CMR is being made predominantly on an intuitive basis, by trial and error, because at present there are no clear criteria for this effect to appear.

The relative magnetoresistance is calculated by the formula $\delta_H = 100\% [\rho(H) - \rho(0)] / \rho(H)$, where $\rho(0)$ is the resistivity of the material measured at zero magnetic field, and $\rho(H)$ is the resistivity measured at some given magnetic field.[5] The notation $\Delta\rho(H)/\rho(0)$ is often used. The term "negative" magnetoresistance corresponds to the situation when the value of the resistivity decreases with increasing magnetic field. Negative magnetoresistance is observed in thin-film metallic structures,[1–3] magnetic semiconductors,[4,5] and two-dimensional compounds and structures.[6–8] The phenomenon of negative magnetoresistance is called "giant magnetoresistance" in thin-film heterojunctions and "colossal magnetoresistance" in magnetic semiconductors.[4] In recent years this phenomenon has come to be described by the term "spin-polarized electron transport."[2]

The CMR materials now widely known are manganites based on $LaMnO_3$, europium chalcogenides, and the chromium selenides $CdCr_2Se_4$ and $HgCr_2Se_4$. In magnetic semiconductors the value of the magnetoresistance δ_H (expressed in percent) varies from tens of percent to several orders of magnitude ($10^{11}\%$ in europium chalcogenides). The question of the mechanism of colossal magnetoresistance in magnetic semiconductors remains a topic of discussion. In view of the fact that the application of magnetic field to magnetic semiconductors often results in a change of not only the value of the conductivity but also its type, the phenomenon of negative magnetoresistance can be classified with the metal-insulator transitions (MITs).[9–11] The term "MIT" describes not only transitions from the metallic to the insulator state (and vice versa) but also metal-semimetal and semiconductor-insulator transitions, i.e., it refers to transitions accompanied by a change of the structure of the electron energy spectrum of the material. A distinguishing feature of such transitions is a substantial change of the value of the resistivity and the conductivity type. The MIT phenomenon, as a rule, is accompanied by a critical change of a number of physical parameters of the material (thermal, structural, magnetic, optical, etc.) and can be caused by various external influences (temperature, pressure, electric or magnetic field, change of the chemical composition of the material). Metal-insulator transitions in magnetic field were considered in Ref. 7. The experimental data show[8] that CMR is accompanied by magnetothermal effects (giant magnetocaloric effect), possibly as a consequence of a phase transition occurring under the influence of the magnetic field. The colossal magnetoresistance in europium chalcogenides and in manganites is accompanied by a shift of the optical absorption edge (a change of the band gap in the electron spectrum) in the magnetic field, as is also typical for MITs.

The knowledge accumulated to date on CMR compounds indicates that the phenomenon of negative magnetoresistance is most often observed in solid solutions synthesized on the basis of magnetic substances exhibiting CMR which manifest a correlation in the behavior of the magnetic and electrical properties. Such substances include europium chalcogenides[12] (an inverse metal-insulator transition in the region of the magnetic transition) and the manganites[5] (whose physical properties largely resemble those of europium chalcogenides). Substances in which CMR is observed include the monosulfides of 3*d* elements and their solid solutions.[9] Colossal magnetoresistance has been observed in nickel monosulfide[13] in the region of the metal-insulator transition and in a number of solid solutions of manganese sulfides. In this review we discuss the features of the magnetic, electric, and magnetotransport properties of some solid solutions of 3*d*-sulfides.

I. GENERAL CHARACTERISTICS OF THE SOLID SOLUTIONS

The results of the experimental studies (see, e.g., Ref. 9) show that by using the method of directed cation-anion sub-

stitution one can control both the value and the type of conductivity of the compound, creating a continuous series of its solid solutions. The formation of the solid solution and the variation of its properties with respect to those of the prototype are determined by two factors—strain and chemical terms. The strain term comes from the difference of the geometric sizes of the host and substituent atoms. The chemical term derives from the difference of their electronic configurations. In the case of isoelectronic substitution of an atom of the host lattice by a guest atom, the physical properties of the substance will change only on account of the lattice strain (Vegard's law).[14–16] If the electronic configurations of the substituent and host atoms are different, then the character of the chemical bonds will change, and consequently so will the electron energy spectrum and the electrical and magnetic properties of the solid solution.[9,15–17] In the case when the initial matrix for the solid solution is characterized by a strong electron-phonon interaction, the two factors turn out to be interdependent. In real solid solutions it is necessary to take into account the imperfection of the lattice that forms and the increase of its degree of disorder (especially for polycrystalline materials). While in an ideal solid solution the cation of substitution occupies a lattice position corresponding to a host cation, in a real solid solution it can happen that the cation of substitution occupies an interstitial position or a site of the anion sublattice.

The mechanisms for the change of conductivity type in solid solutions of semiconductors has been studied in substances with various crystal lattices.[11,18,19] Progress in this area of physics has led to new ideas about the conductivity of substances, the introduction of new concepts such as, e.g., quantum dots and wires, weak localization, and the Coulomb blockade.[20–22] The experimental data on more than 50 semiconductor substances have permitted the conclusion[11,18,19] that the mechanism for the change of conductivity type of a solid solution as its chemical composition is varied (a concentration MIT) is determined less by the initial crystal structure of the host substance than by the distribution of impurities and defects in the semiconductor matrix and the formation of their microstructure. As an example, Figs. 1 and 2 show the curves of the temperature dependence of the resistivity and their evolution with changing degree of cation substitution for sulfides and disulfides of $3d$ elements. The behavior of the resistivity upon cation substitution in these substances is typical of systems in which concentration MITs are observed. Analogous concentration electronic transitions are also observed in solid solutions of CMR manganites.[5]

The theory of electronic concentration transitions of the insulator-metal type (mainly for nonmagnetic substances) is what is known as percolation theory and is developed in the works by Mott and Davis,[11] Gantmakher,[18] and Shklovskiĭ and Efros.[19] This theory is also used for consideration of the electrical properties of superionic compounds[23] with a mixed electronic-ionic type of conductivity. According to percolation theory, impurities in a semiconductor matrix form a kind of superstructure, the parameter of which is determined by the localization radius a_B (the characteristic size of the localization region of a charge carrier around an impurity center). The largest value $a_B \approx 600$ Å has been observed for InSb. This value is much larger than the value of the unit cell

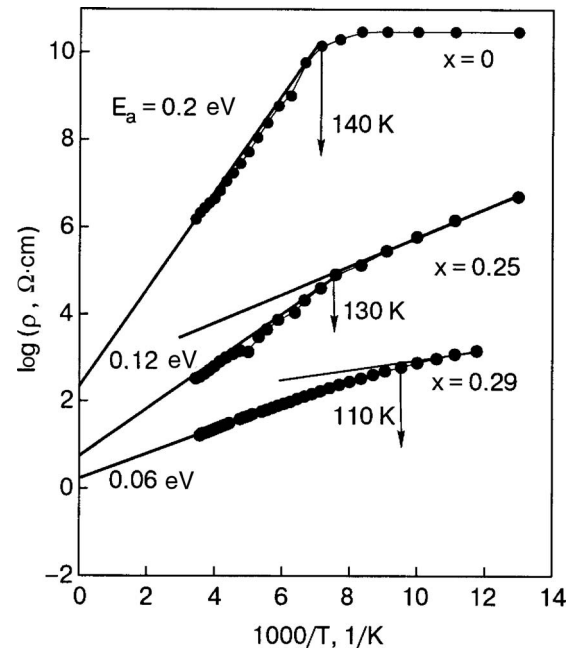FIG. 1. Temperature dependence of the resistivity of polycrystalline $Fe_{1-x}Mn_xS$ in zero magnetic field.

parameter of the substance. With increasing impurity concentration one observes a change of the localization radius and an electron percolation effect, which leads to a change of the conductivity type in the solid solution. The electron energy spectrum of such semiconductor materials differs from that of standard semiconductors by the presence of allowed states in the band gap ("tails" of the electron density).[11,18,19] The concentration MIT corresponds to the situation (the Anderson model) when for the electron density of states the condition $E_C = E_F$ holds, where E_F is the Fermi energy and E_C
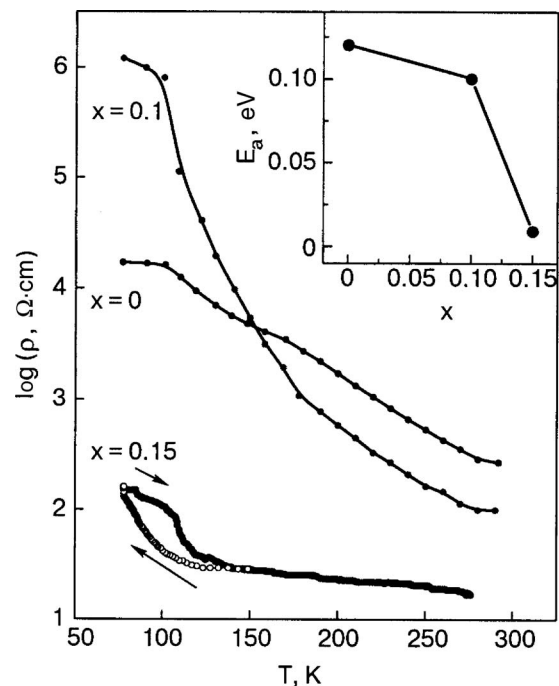

FIG. 2. Temperature dependence of the resistivity of polycrystalline $CuV_xCr_{1-x}S_2$. The inset shows the concentration dependence of the activation energy for conduction.

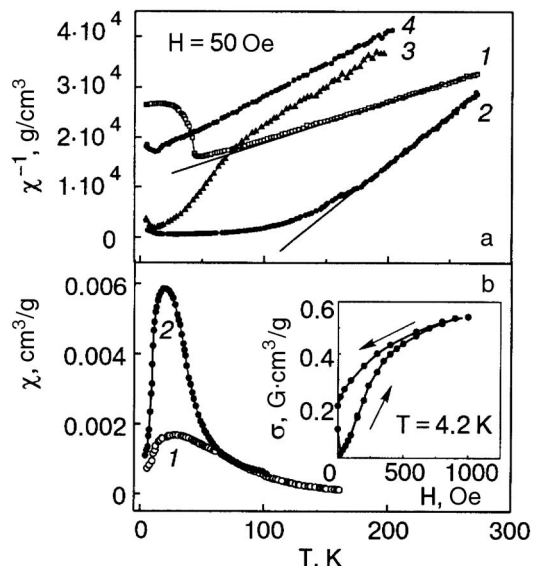FIG. 3. Temperature dependence of the magnetic susceptibility of $CuV_xCr_{1-x}S_2$ for different x: 0 (*1*), 0.05 (*2*), 0.15 (*3*), 0.25 (*4*) (a); 0.05 (*1*), 0.1 (*2*) (b).[63] Inset: magnetization for $x=0.1$.

(the mobility edge) is the energy that divides the regions of localized and delocalized states of the charge carriers.

In magnetic semiconductors and in nonmagnetic hosts that have been doped with magnetic ions, the electron percolation transition is often accompanied by a change of the type of magnetic order—a magnetic concentration transition. Such a situation is typical for manganites, manganese and europium chalcogenides, and gallium arsenide.[5,12,24] Concentration transitions of the antiferromagnet-ferromagnet type, accompanied by electronic concentration transitions, have also been found in a number of transition-metal sulfides, e.g., in the systems $Me_xMn_{1-x}S$ (Me=Fe,Cr; Refs. 25 and 26) and $CuV_xCr_{1-x}S_2$ (Ref. 27). Figure 3 shows the variation of the magnetic properties in the system $CuV_xCr_{1-x}S_2$ (Ref. 27). In the antiferromagnet $CuCrS_2$ a spontaneous moment arises with increasing degree of cation substitution.

The mechanisms of magnetic percolation transitions in solid solutions have been studied mainly for metal alloys.[28] For solid solutions of magnetic semiconductors a mechanism of simultaneous change of the type of conductivity and type of magnetic order has been proposed by Nagaev (the phase separation mechanism).[5]

Many years of research experience on manganites has shown that substantial dependence of the electrical properties on the external magnetic field is observed specifically in cation-substituted systems for compositions corresponding to the region of concentration magnetic and electronic transitions. Therefore, one expects that in the search for new CMR compounds the most promising host materials are those for which, by cation or anion substitution, one can synthesize a series of solid solutions whose physical properties vary continuously from antiferromagnetic semiconductor to ferromagnetic metal. The results of research based on this idea have stimulated the present interest in manganese sulfides.

II. MAGNETORESISTANCE OF $Fe_xMn_{1-x}S$ SOLID SOLUTIONS

Among the widely known compounds with high CMR parameters are the europium chalcogenides, which crystal-

lize in a cubic structure of the NaCl type.[12] However, the practical use of these substances is limited by the low temperatures of the magnetic transition. Isostructural substances include the monoxides of a number of $3d$ elements and manganese monosulfide. The Néel temperature of manganese monosulfide MnS is 147 K,[9] much higher than the temperature of the magnetic transition in the europium chalcogenides. The basic structural element of the NaCl lattice in manganese monosulfide is an octahedron—the manganese atom is found in an octahedral environment of anions, similarly to the case of the widely studied manganites.[5,15] Like the compound $LaMnO_3$, which is a representative host material for creating CMR materials, manganese monosulfide is an antiferromagnetic insulator. In the region of the magnetic transition in MnS one observes a sharp change of the activation energy for conduction, E_a (Ref. 9). E_a equals 0.3 eV in the paramagnetic state and decreases by an order of magnitude upon the establishment of magnetic order.

Studies over many years[9,25,29] have shown that the value and type of conductivity in manganese monosulfide can be controlled by the method of cation substitution. With increasing degree of cation substitution in the systems of solid solutions $Me_xMn_{1-x}S$ (Me=V,Fe,Cr,Co)[25,26,29,30] the substances formed have values of the resistivity at 77 K that vary over 6 orders of magnitude. Concentration transitions from the antiferromagnetic insulator to the ferromagnetic semimetal in the low-temperature region have been established in the systems $Me_xMn_{1-x}S$ (Me=Fe,Cr).[26,31] Among the known cation-substituted systems[25,26,29,30] synthesized on the basis of manganese monosulfide ($Me_xMn_{1-x}S$, Me =V,Fe,Cr,Co), ferromagnetism has been observed only in the system $Fe_xMn_{1-x}S$ at 300 K.[31]

The difference of the ionic radii (the ionic radius is equal to 0.91 Å for Mn^{2+} and to 0.80 Å for Fe^{2+}; Ref. 15) leads to compression of the unit cell of the NaCl structure when the solid solution $Fe_xMn_{1-x}S$ is formed. Such compression in a number of europium oxides and chalcogenides is accompanied by a change of the type of magnetic order. For ferromagnetic europium oxide ($T_C=76$ K) the unit cell parameter of the NaCl structure has a value $a=5.14$ Å, whereas for the antiferromagnetic europium telluride $a=6.60$ Å and T_N =10 K.[12] It was established in Refs. 25 and 31–33 that ferromagnetic properties arise in the $Fe_xMn_{1-x}S$ system in the concentration region $x=0.25$, and the critical concentration for the concentration electronic transition is $x=0.4$.

The simple crystal structure, high saturation magnetization, and the band character of the conduction for some compositions of the $Fe_xMn_{1-x}S$ system have attracted the interest of researchers. The first results on the magnetoresistance of iron-manganese sulfides[26,32] have shown the promise of research on these materials. In polycrystalline $Fe_{1-x}Mn_xS$ the maximum value of the negative magnetoresistance is found at a manganese concentration (in the stock) of $x=0.29$.[26,32,33] At a temperature of 50 K the magnetoresistance reaches a value of -450% at a magnetic field of 30 kOe. In a field of 50 kOe the value of the magnetoresistance has decreased, and at 40 K it is not larger than -100% (Fig. 4).[26,33,35] Figure 5 shows the field dependence of the magnetization, resistance, and charge carrier density at 77 K for polycrystals with $x=0.29$; it is seen that the decrease of the resistance in
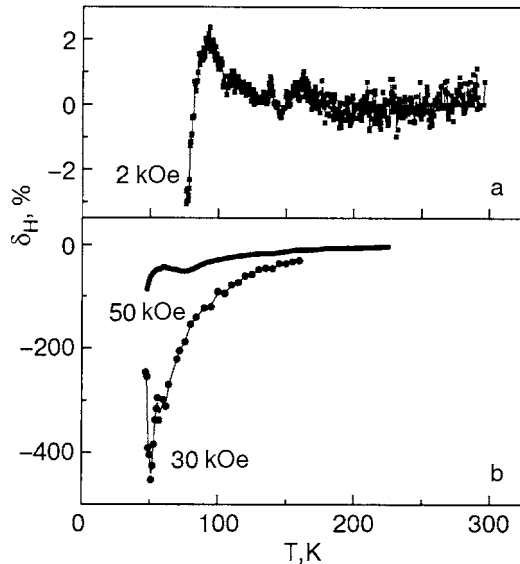
FIG. 4. Temperature dependence of the magnetoresistance of polycrystalline $Fe_{1-x}Mn_xS$ (x=0.29).[35]

a magnetic field is accompanied by growth of the magnetization and charge carrier density, similar to what is observed in manganites and europium chalcogenides. At 77 K the magnetoresistance reaches −20% in a field of 7 kOe for the sample with concentration x=0.29 (Fig. 5b). The change of the charge carrier density in the magnetic field suggests a change of the electron energy spectrum of these substances.

The synthesis of single crystals of iron-manganese sulfides has revealed that the physical properties of the single-crystal and polycrystalline samples of $Fe_{1-x}Mn_xS$ are substantially different. In the cubic single crystals of $Fe_{1-x}Mn_xS$ with x=0.29 (Ref. 39), for which the lattice parameter has the value a=5.179 Å, the behavior of the resistivity is much like that of the europium chalcogenides. At zero magnetic
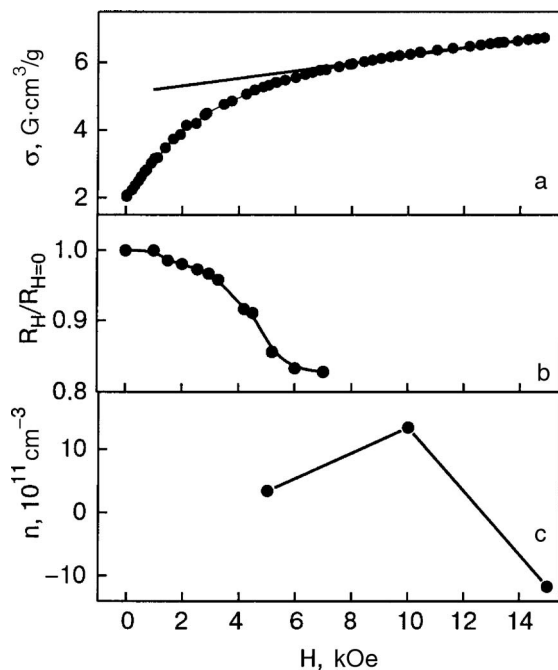

FIG. 5. Field dependence of the magnetization (a), relative resistance (b), and charge carrier density (c) for polycrystalline $Fe_{1-x}Mn_xS$ (x=0.29) at 77 K.

field the resistivity of the single crystal with x=0.29 at 300 K is two orders of magnitude lower than for the polycrystalline samples, and the temperature dependence of the resistivity has a maximum at around 75 K (an inverse metal-insulator transition). Colossal magnetoresistance is not observed in the cubic single crystals of $Fe_{1-x}Mn_xS$. The magnetic properties of polycrystalline and single-crystal samples are also found to have substantially different behavior. In the single crystal a smeared maximum of the susceptibility is observed near 200 K,[37] while no such maximum has been found in polycrystalline samples.[26]

III. FEATURES OF THE SOLID SOLUTIONS $Fe_{1-x}Mn_xS$

The complexity of research on cation-substituted monosulfides is possibly due to a number of features of the initial host substance. Three structural modifications of this substance are known,[38–44] one of which, α-MnS (the fcc NaCl structure, space group $O_h^5 - Fm3m$) is characteristic for monoxides of the $3d$ series and europium chalcogenides, while the other two modifications are isostructural with the zinc compounds having a crystal structure derived from the NaCl structure (cubic—sphalerite; hexagonal—wurtzite). In α-MnS, as in manganese monoxide, a rhombohedrally distorted NaCl lattice with symmetry $R3m$ is formed with decreasing temperature.[44] The decrease of the symmetry $Fm3m \rightarrow R3m$ and the lattice strain in MnS come about as a result of a sequence of transformations (T_1=160 K, T_2=147 K, T_3=125 K, T_4=60 K).[41,44] The results of studies done by different authors attest that the temperature at which the rhombohedral strain of the fcc lattice of α-MnS appears can vary in the range 160–200 K. The lattice distortion arises continuously and is manifested in a deviation of the edge angle of the cube from 90°. With decreasing temperature the fcc lattice parameter decreases down to 4.2 K, with a kink in the T_1 region.[44] The mechanism of the structural transition in manganese monosulfide has not been studied in detail. In Ref. 45 the distortion of the NaCl structure was considered for several sulfide materials and it was shown that the resulting deformation of the fcc lattice, depending on the state of the electronic system and the electron-phonon interaction, can be either tetragonal or rhombohedral (as is typical for α-MnS). The importance of taking the electron-phonon interaction into account in the analysis of the physical properties of manganese monosulfide is indicated by the results of a study of the parameters of this substance under pressure. With increase of pressure and compression of the fcc phase of α-MnS at 300 K the symmetry of the lattice is lowered from cubic to hexagonal and lower.[46,47] At the same time, one observes a decrease of the band gap and a transition from the semiconductor to the metallic state.[46]

There have been no studies of the magnetic properties of α-MnS under pressure. It is known, however, that the three crystal phases of manganese monosulfide[41,48] formed at the same composition of the substance Mn:S=1:1 are antiferromagnetic. For β-MnS (the cubic structure of the ZnS sphalerite type, space group $T_d^2 - F\bar{4}3m$) the Néel temperature equals 160 K (magnetic moment $6.0\mu_B$). For the γ phase of MnS, with a hexagonal structure of the ZnS wurtzite type (space group $C_6^4 - P6_3mc$) the Néel temperature is decreased to 100 K (magnetic moment $6.1\mu_B$). Information about the
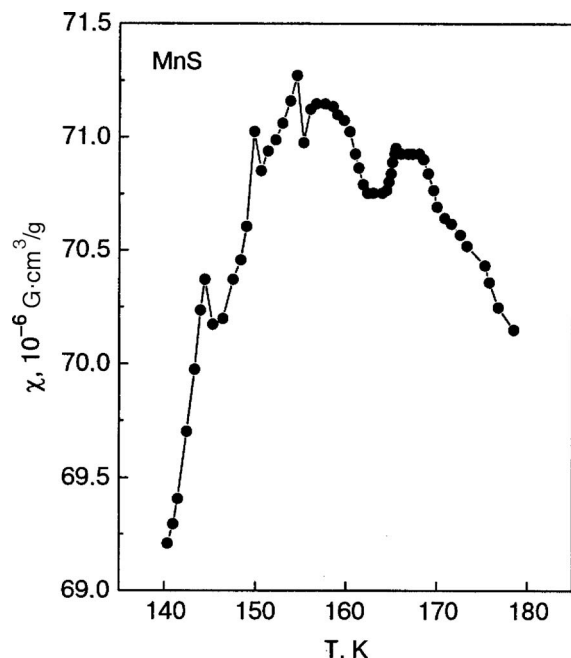
FIG. 6. Temperature dependence of the magnetic susceptibility of manganese monosulfide.[50]

magnetic properties of the cubic phase of α-MnS is contradictory. It is traditionally assumed that α-MnS, which has a cubic structure with the NaCl lattice, has a magnetic structure analogous to the antiferromagnet MnO ($T_N \sim 122$ K). The chemical bonds and magnetic structure in MnO and MnS with the cubic NaCl lattice are similar to manganites.[49] The magnetic order is determined by the ferromagnetic ordering of the magnetic moments of the Mn^{2+} atoms in planes perpendicular to the cube diagonals and their antiferromagnetic ordering between planes. The compounds MnO and MnS are considered as classical antiferromagnets (AFs) with a 180° superexchange interaction of the manganese ions via the anion (in the direction of the cube edge).[9] At the same time, the experimental results[36] attest that antiferromagnetic order is established in α-MnS in the strained fcc lattice. The lowering of the lattice symmetry $Fm3m \rightarrow R3m$ and the deformation of the MnS_6 octahedron should cause a change of the angle of the chemical bond Mn–S–Mn, and the degree of hybridization of the cation and anion wave functions and also the parameters of the 180° superexchange interaction should change as a result. Theoretical calculations[52] show a substantial dependence of the magnetic moment on the unit cell volume in manganese monosulfide: the effective magnetic moment decreases on compression of the cell.

According to the results of a study of the electron paramagnetic resonance (EPR) spectra, the Néel temperature of α-MnS is ~ 147 K (the magnetic moment is $5.8\mu_B$), whereas the maximum of the magnetic susceptibility is observed in the region of the structural transition (160 K). The susceptibility maximum is smeared over a wide temperature interval. In Ref. 50 a reversible sequence of susceptibility maxima was observed in manganese monosulfide at magnetic fields of 1–1.9 kOe (Fig. 6). Steps in the susceptibility were observed in Ref. 44. In Ref. 51 a weak spontaneous moment was observed in a MnS single crystal in the range 4.2–300 K.

Studies of the electrical and magnetic properties of manganese monosulfide show that they depend on the synthesis technology. For example, the resistivity and magnetization (at $H=8.6$ kOe) for polycrystalline α-MnS have the values $\rho(300$ K$)=8.50\times10^2$ $\Omega\cdot$cm   (Ref. 9)   and $\sigma(300$ K$)$ $=0.6$ G$\cdot$cm^3/g,[31] whereas for the single crystal of similar composition, $\rho(300$ K$)=3.17\times10^5$ $\Omega\cdot$ cm   and $\sigma(300$ K$)$ $=0.4$ G$\cdot$cm^3/g,[31,36] For the α-MnS single crystal the resistivity has been found to be anisotropic. In the magnetically ordered state ($T<T_N=147$ K) the resistivity $\rho_{[100]}$ in the [100] direction, corresponding to the 180° exchange interaction, is two orders of magnitude lower than the value $\rho_{[111]}$ measured in the plane perpendicular to the [111] direction (in which ferromagnetic ordering of the magnetic moments of the manganese ions is realized). Negative magnetoresistance is observed for $\rho_{[111]}$ in the paramagnetic phase of the single crystal at temperatures above the structural transition; it amounts to -12% in a field of 10 kOe.[36,51]

For FeS, which differs from MnS by an additional $3d$ electron, the characteristic structure is of the hexagonal NiAs type.[9] At 300 K the stoichiometric manganese monosulfide crystal (the γ phase) can also have a hexagonal (wurtzite) structure.[42] FeS is a antiferromagnetic low-resistivity semiconductor ($T_N=590$ K; effective moment $1.8\mu_B$) that undergoes a MIT around 420 K. The antiferromagnetic order of FeS is determined by the ferromagnetic ordering of the cation magnetic moments in the distinguished planes of metal ions and their antiferromagnetic ordering between planes.[9,53] The magnetic properties of FeS are explained by the coexistence of localized and delocalized $3d$ electrons.[9] This compound is more covalent than MnS, and the correlation effects in it are less pronounced.[52] For α-MnS the resistivity at 300 K is $\sim 10^5$ $\Omega\cdot$ cm, while for FeS it is 6 orders of magnitude lower. For the FeS single crystal the resistivity equals 0.6 $\Omega\cdot$ cm at 300 K and increases to 2 $\Omega\cdot$ cm at 77 K. Our experimental studies have shown that in the temperature range 77–300 K the magnetoresistance at a field of 10 kOe in this substance is not more than -2%.

In view of the substantial difference in Néel temperatures (150 and 450 K) and resistivities, one expects that $Fe_xMn_{1-x}S$ solid solutions will have a concentration electronic transition, with a simultaneous increase of the magnetic transition temperature.

In addition to the studies mentioned above, $Fe_xMn_{1-x}S$ solid solutions have been investigated in Refs. 54–58. The results obtained by different authors have shown that the structural properties of the solid solution $Fe_xMn_{1-x}S$ depend on the preparation technology, since there are differences in the data. The authors of Ref. 58 report that the $Fe_{1-x}Mn_xS$ crystal with 5% iron content has the antiwurtzite structure at 300 K. According to Ref. 57, $Fe_xMn_{1-x}S$ solid solutions have the NaCl structure, with the fcc cell parameter decreasing monotonically from a value of 5.22 Å at $x=0$ to 5.14 Å at $x=0.5$. In Ref. 25 it is reported that with increasing iron content the fcc lattice parameter decreases from 5.222 Å ($x=0$) to 5.165 Å ($x=0.5$).

The results of a study of the cubic and hexagonal solid solutions $Fe_{1-x}Mn_xS$ by XANES spectroscopy are reported in Ref. 57. The data show that the compression of the fcc lattice parameter of manganese monosulfide with increasing

degree of substitution in $Fe_xMn_{1-x}S$ is accompanied by a shift of the sulfur absorption edge to the lower energies characteristic of the more covalent iron monosulfide.

Figure 1 shows the temperature dependence of the resistivity $\rho(T)$ for the manganese monosulfide single crystal[36] and polycrystalline samples of $Fe_{1-x}Mn_xS$ with concentrations $x=0.25$ and $x=0.29$, measured at zero magnetic field. While in the cation-substituted systems $Co_{1-x}Mn_xS$ and $Cr_{1-x}Mn_xS$ the behavior of the resistivity with temperature in the range 77–300 K is analogous to that of manganese monosulfide[30,25] (substitution causes only an overall lowering of the resistivity), in $Fe_{1-x}Mn_xS$ solid solutions the behavior of the resistivity as a function of temperature is of a different character.[33,34] The kink in $\rho(T)$ and the susceptibility maximum at 150 K (Ref. 26), which are characteristic for stoichiometric manganese monosulfide with the fcc structure, vanish in $Fe_{1-x}Mn_xS$ solid solutions with $x=0.29$ (Fig. 1).

According to Ref. 44, at 300 K MnS is a semiconductor with a predominantly p-type hole conductivity. The mobility of p-type charge carriers in MnS is 0.065 cm^2 V^{-1} s^{-1}. Polycrystalline $Fe_xMn_{1-x}S$ solid solutions have a semiconductor-metal transition in the high-temperature region ($\sim$800 K).[33,34] At temperatures of 77–300 K the predominant conduction in these substances is of the impurity type (Anderson semiconductor). The decrease of the low-temperature resistivity of $Fe_xMn_{1-x}S$ solid solutions (by 6 orders of magnitude at 77 K) with increasing degree of cation substitution was explained by the formation of an impurity band near the top of the valence band of MnS. The Fe^{2+} atom has an "extra" $3d$ electron in comparison with the Mn^{2+} atom. Increasing the iron concentration in $Fe_xMn_{1-x}S$ leads to growth of the conduction electron density in the impurity electron band and an Anderson concentration transition. This model can explain the change of sign of the charge carrier on increasing degree of cation substitution in $Fe_xMn_{1-x}S$ at 300 K for $x=0.3$.[34] The metallization and the change of sign of the charge carriers in $Fe_xMn_{1-x}S$ solid solutions are correlated with growth of the magnitude of the spontaneous magnetization. For the compound with $x=0.29$ the magnetization is independent of temperature above the Curie point (800 K).[31] This gives us grounds to assume that the mechanism of spontaneous magnetization at 300 K in $Fe_xMn_{1-x}S$ solid solutions may be due to itinerant electrons, as in pure iron.

According to x-ray and neutron-diffraction data in the temperature interval 4.2–300 K, the crystal structure of the polycrystalline compound $Fe_{1-x}Mn_xS$ ($x=0.29$) with CMR differs from the typical fcc structure of manganese monosulfide. Besides the structural reflection characteristic of the cubic lattice, the x-ray diffractograms for the compound with $x=0.29$ exhibit weak structure reflections similar to those observed in thin-film structures of MnS with the hexagonal structure.[43] The fcc structure parameter at 300 K is $a=5.19$ Å. In the vicinity of 150 K one observes a change in the temperature dependence of the lattice parameter, which attest to the presence of a structural transition. However, the temperature dependence of the lattice parameter of the solid solution with $x=0.29$ (Fig. 7a) differs substantially from the known dependence for fcc manganese monosulfide[44]—the lattice parameter increases with decreasing temperature. Ac-
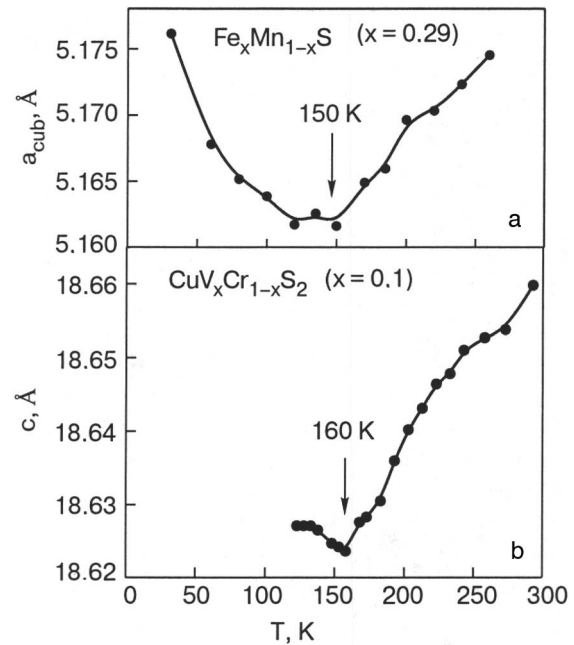

FIG. 7. Temperature dependence of the lattice parameters.

cording to the neutron-diffraction data,[35] at temperatures below 250 K for the polycrystal with $x=0.29$ one observes the coexistence of two magnetic phases—antiferromagnetic and ferromagnetic. The antiferromagnetic structure of the solid solution with $x=0.29$ is similar to the magnetic structure of manganese monosulfide (the magnetic cell parameter corresponds to twice the parameter of the crystallographic structure; Fig. 8a). Figure 8b shows the temperature dependence of the intensity of the magnetic reflection observed on neutron-diffraction patterns of the samples and corresponding to the AF phase. The increase of the lattice parameter below 150 K is accompanied by a decrease of the intensity of the magnetic reflection, which indicates an interdependence of the structural and magnetic properties of this sub-
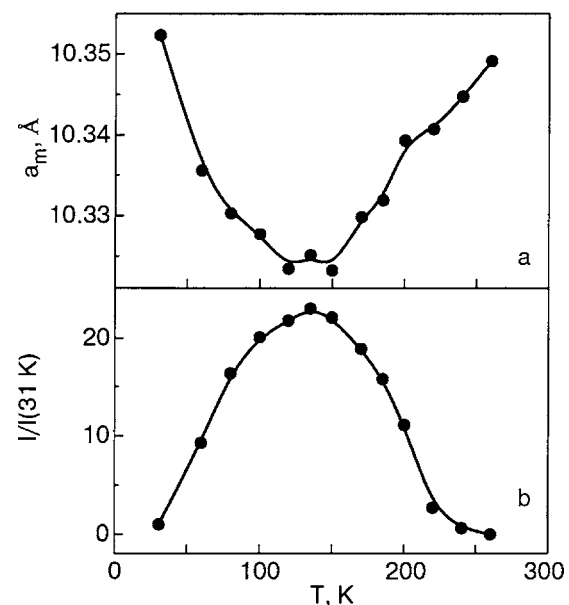

FIG. 8. Temperature dependence of the magnetic cell parameter (a) and of the relative intensity of the magnetic reflection on the neutron-diffraction pattern (b) for polycrystalline $Fe_{1-x}Mn_xS$ ($x=0.29$).

Low Temp. Phys. **32** (8-9), August-September 2006
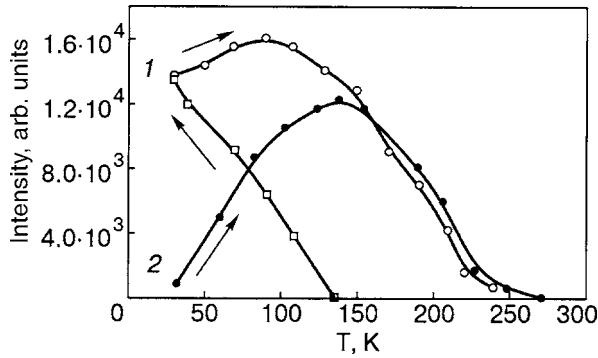
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FIG. 9. Temperature dependence of the intensity of the magnetic reflection on the neutron-diffraction patterns of polycrystalline $Fe_{1-x}Mn_xS$ ($x=0.29$) for slow (*1*) and fast (*2*) cooling of the samples.

stance. It was found in the neutron-diffraction experiment that the behavior of the magnetic properties of polycrystals ($x \sim 0.29$) at a temperature below 250 K depends substantially on the rate of cooling (Fig. 9). Analogous dependence is observed for the lattice parameter: on slow cooling the temperature at which the change in $a(T)$ is observed is shifted to lower temperatures (~ 100 K). The observed coexistence of the antiferromagnetic and ferromagnetic phases in the CMR compound with $x=0.29$ is similar to that observed in manganites and is evidence of magnetic inhomogeneity of the material.

Figure 10 shows the temperature dependence of the charge carrier density for polycrystalline samples with $x=0.25$ and $x=0.29$.[34] For compositions $x<0.3$ the the majority charge carriers at low temperatures are p-type (conduction in the valence band).[34] It is seen in Fig. 10 that for $x=0.25$ the density n_p of the p-type charge carriers decreases sharply below the temperature 130 K at which the bend in $\lg \rho(1/T)$ is observed. Here the mobility of the charge carriers increases, equalling 1.2×10^4 cm²/(V·s) at 100 K. It is possible that the rather sharp decrease of the density of p-type carriers in this substance accompanies the establish-
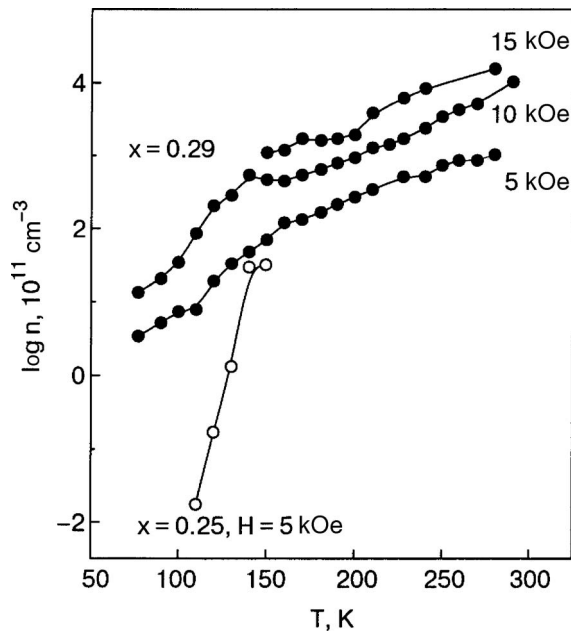

FIG. 10. Temperature dependence of the density of p-type charge carriers for polycrystalline $Fe_{1-x}Mn_xS$ (Ref. 34).
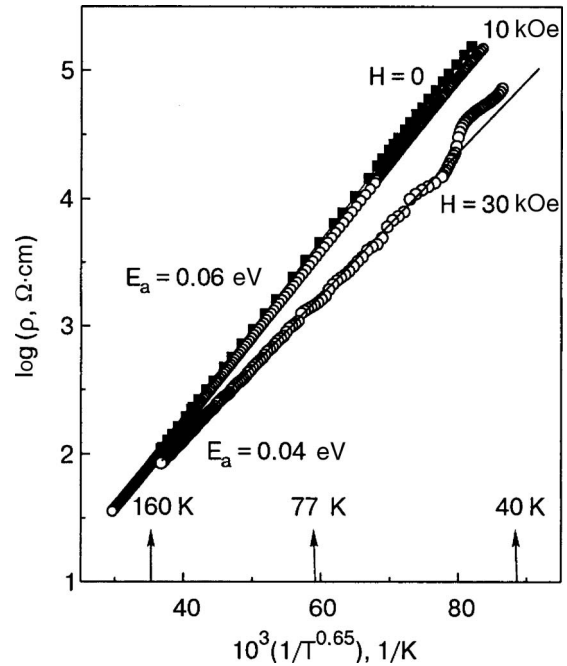

FIG. 11. Temperature dependence of the resistivity of polycrystalline $Fe_{1-x}Mn_xS$ ($x=0.29$) at different magnetic fields.

ment of antiferromagnetic order. For the compound with $x=0.29$ the density n_p at the same field (5 kOe) increases (Fig. 10), and the jump in the region below 150 K becomes less pronounced. At 100 K the value of n_p for the sample with $x=0.29$ is three orders of magnitude larger than for the compound with $x=0.25$. The rather sharp decrease of the resistivity in magnetic field at 77 K for $x=0.29$ (Fig. 5), accompanied by growth of the magnetization, is observed in the existence region of the p-type conductivity. On the basis of these data it can be supposed that the p-type charge carriers play an important role in the mechanism of magnetoresistance in $Fe_xMn_{1-x}S$.

Figure 11 shows the change of the temperature dependence of the resistivity with increasing magnetic field for a polycrystal with $x=0.29$, according to the data of Refs. 26 and 33. The change of the curve is similar to that of the curves $\lg \rho(1/T)$ for $Fe_xMn_{1-x}S$ at zero magnetic field upon a change of the degree of cation substitution (Fig. 1). Both upon an increase of the degree of substitution (local deformation of the lattice) in $Fe_{1-x}Mn_xS$ and upon an increase of the external magnetic field for samples with $x=0.29$ the slope of the $\lg \rho(1/T)$ curves, which characterizes the activation energy for conduction, decreases. The temperature trend of the logarithm of the resistivity for samples with $x=0.29$ in magnetic fields can be described by a linear dependence on $1/T^\alpha$ ($\alpha=0.65$) (Fig. 11), which is close to the typical dependence for disordered systems with electron-electron interaction (the Shklovskii-Efros mechanism). Similar temperature dependence of the resistivity in magnetic field is observed for a number of disordered magnetic semiconductors, e.g., manganese-doped gallium arsenide.[24] The dependence of the resistivity on external magnetic field in $Fe_{1-x}Mn_xS$ is most clearly manifested at temperatures below 200 K, which is also typical for disordered systems (polycrystals, defect lattices, granular materials).

The set of experimental data obtained to date permits the conclusion that polycrystalline $Fe_{1-x}Mn_xS$ solid solutions must be classified as substantially disordered materials. Besides the electronic-magnetic inhomogeneity (of the phase-separation type), these materials can have crystallographic inhomogeneity by virtue of the presence of structural transformations. Clarification of the situation is possible only through a comprehensive study of single crystals obtained by a single technology.

IV. MAGNETORESISTANCE OF SOLIDS SOLUTIONS OF 3d-DISULFIDES

The accumulated research experience on cation-substituted oxide and sulfide systems suggests that an interrelationship between magnetic and electric properties is most often exhibited by solid solutions synthesized on the basis of "layered" structures comprising alternating planes of cations and anions. Such a crystal structure is typical for manganites (fcc structure of the perovskite type), for europium and manganese chalcogenides EuX and MnX with the fcc NaCl structure, where $X = S, Se, Te$, and for mono- and disulfides of $3d$ metals with the hexagonal lattice.[15,16] The magnetic properties of compounds of these different crystallographic groups are determined by a special type of magnetic ordering: the atomic magnetic moments of the cations are ordered ferromagnetically in distinguished layers and antiferromagnetically between layers. Such a magnetic structure is also typical for thin-film heterostructures with CMR. In this connection it is useful to conduct research designed to clarify the interrelationships of percolation and spin-dependent effects in "layered" magnets.

Because of the features of the crystal structure and of the formation of solid solutions,[60] intercalated layered substances are of great interest for spintronics. Examples of intercalated layered substances are compounds of the type $CuCrS_2$, $CuFeS_2$, and $MeTiS_2$ synthesized on the basis of disulfides of $3d$ elements from the start of the series. In contrast to solid solutions of $3d$-monosulfides, in which the atoms of substitution are randomly distributed over the volume of the substance, double sulfides of $3d$ elements from the start of the series can be used to create three-dimensional structures in which the intercalated atoms form distinguished layers in the lattice. This gives us a way of creating a new type of multilayer structures for electronics.

The crystal structure of double sulfides of $3d$ elements from the start of the series can be represented as a sequence of sulfur-metal-sulfur trilayers.[60] Within the trilayer the chemical bond of the cation and two anions has an ionic-covalent character, as is typical for $3d$-sulfides. The coordination of the metal atoms in the trilayers can be trigonal-prismatic or octahedral. The binding energy between trilayers is comparable to a van der Waals energy and is tens of times lower than the binding energy within the layer. Therefore, the tetrahedral positions of this lattice are often called the van der Waals gap.[60] Because of this gap, double sulfides of the $3d$ series can be used to create intercalated structures with unique qualities. Studies of the distribution of electron density in chromium disulfide, intercalated by silver atoms, for example, have shown that the intercalant forms electronic layers between the trilayers of the initial

disulfide.[61] An extreme case of intercalation corresponds to the situation in which layers of a completely different compound form between the trilayers of the initial substance. A single crystal of such a material is a sequence of layers of different crystal lattices with different physical properties.[62]

In this class of compounds, colossal magnetoresistance has been observed[63] in the sulfides $CuV_xCr_{1-x}S_2$. The prototype of the crystal structure of the initial compound, chromium-copper disulfide $CuCrS_2$ (structure type α-NaFeO$_2$, space group $R3m$) is taken to be the fcc NaCl structure,[60,64] which is the structure of manganese monosulfide. As we have said, a rhombohedral deformation of the fcc lattice is observed in manganese sulfides on decreasing temperature, and a structural phase with space group $R3m$ is formed. At room temperature chromium-copper disulfide has a rhombohedral lattice. In $CuCrS_2$ the chromium ions retain an octahedral anion environment, while the copper ions are located in tetrahedra (in the van der Waals gap). One notices that the lattice parameters of $CuV_xC_{1-x}S_2$ and $Fe_{1-x}Mn_xS$ have similar temperature dependence (Fig. 7).

$CuCrS_2$ is an antiferromagnet,[65] with a magnetic structure determined by the ferromagnetic ordering of the magnetic moments in the planes of the chromium atoms and their antiferromagnetic ordering between planes. Besides the overall structural and magnetic properties inherent to monosulfides, chromium-copper disulfide has a number of specific features. It is an intercalated material[60] with mixed electronic-ionic conductivity, and in the 670 K region it undergoes a transition to a superionic state.[66] The term electronic-ionic conductivity reflects the fact that this compound manifests a combination of properties of two states with different types of conductivity.[67] Conductors of the first type (ordinary semiconductors) the conduction is due to charge carriers of the electron or hole type. Conductors of the second type (superionics) are substances whose conduction is governed by the mobility of ions (cationic conduction). In mixed electronic-ionic substances these two types of conduction coexist.[67] As a rule, such compounds have anisotropic conductivity: the electronic conduction occurs primarily in the trilayers, and the ionic conduction in the intercalant layers. It is assumed[23,67] that in compounds of the mixed electronic-ionic type the conduction occurs as a result of the formation of so-called redox pairs, i.e., pairs with a variable valence, and the mechanism of conduction is comparable to that in heterostructures and nanostructures. Quantum size effects might also be present.

Experiments have shown[68] that polycrystalline samples of chromium-copper disulfide undergo two transitions: an AF-FM magnetic transition in the 40 K region (Fig. 3), and an electronic transition, similar to that observed in MnS, in the vicinity of $T_C = 110$ K (Fig. 2). It has been conjectured on the basis of EPR and magnetic susceptibility data that the mechanism of the electronic transition involves a change of the valence of the $3d$ ions and the coexistence of two electronic phases, $Cu^+Cr^{3+}S_2$ ($S = 3/2$) and $Cu^{2+}Cr^{2+}S_2$ ($S = 5/2$) with different magnetic moments. The possibility of coexistence of the two electronic phases from an energy standpoint can be explained by a feature of copper, whose electron affinity is close to that of sulfur.
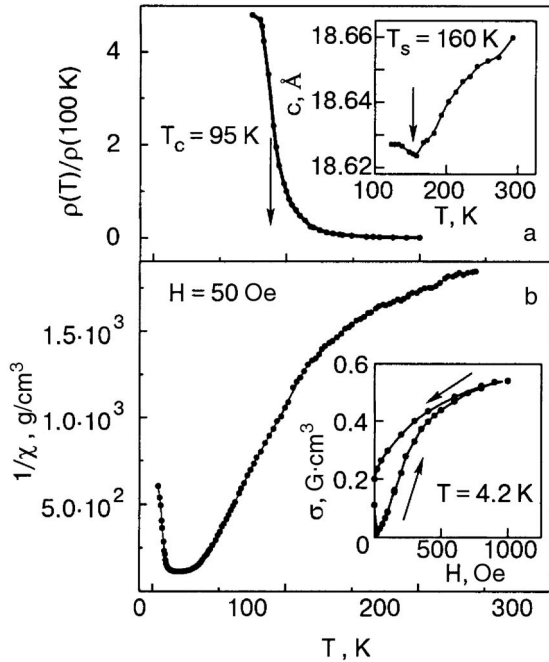
FIG. 12. Temperature dependence of the resistivity (a), lattice parameter a (inset), and inverse magnetic susceptibility (b) for $CuV_xCr_{1-x}S_2$ ($x=0.1$).[63] Inset b: field dependence of the magnetization at 4.2 K.

FIG. 13. Temperature dependence of the magnetoresistance (a) and resonance field (b) for the disulfide $CuV_xCr_{1-x}S_2$ with a composition $x \sim 0.1$.[63]

The results of a study of the influence of cation substitution in the sulfides $CuV_xCr_{1-x}S_2$ have shown that the electronic and magnetic properties of chromium-copper disulfide can be controlled by cation substitution. With increasing degree of substitution in $CuV_xCr_{1-x}S_2$ concentration transitions of the electronic (Fig. 2) and magnetic (Fig. 3; Ref. 26) types occur, without affecting the crystal structure (up to $x=0.25$).

Samples of $CuV_xCr_{1-x}S_2$ with $x=0.1$ have been investigated in more detail.[63] Samples with this composition have the maximum value of the magnetic susceptibility and resistivity in the low-temperature region and undergo a sequence of phase transitions. In the 670 K region a semiconductor-superionic transition is observed,[66] at $T_S=160$ K a structural transition, at $T_C=95$ K an electronic transition, and at $T_m=20$ K a magnetic transition (Figs. 12 and 13). At 4.2 K one observes hysteresis of the magnetization, typical of ferromagnets and ferrimagnets (inset in Fig. 12b). The presence of an electronic transition in the 100 K region is confirmed by the results of an ESR study at a frequency of 9.247 GHz in the temperature range 4.2–240 K (Fig. 13b). The value and temperature trend of the magnetization of the substance at low temperatures depends on the magnetic prehistory.[27] Below 100 K a ferromagnetic contribution to the magnetization is observed (Fig. 14a). Colossal magnetoresistance is observed below the temperature of the structural transition, and in the 100 K region it has a value of -60% in a magnetic field of 7 kOe (Fig. 14b). The drop in resistivity is correlated with growth of the magnetization of the material, as is observed in manganites and iron-manganese sulfides. The similarity of the physical properties of these different compounds suggests a similarity of the mechanisms for the magnetotransport properties.

V. CONCLUSION

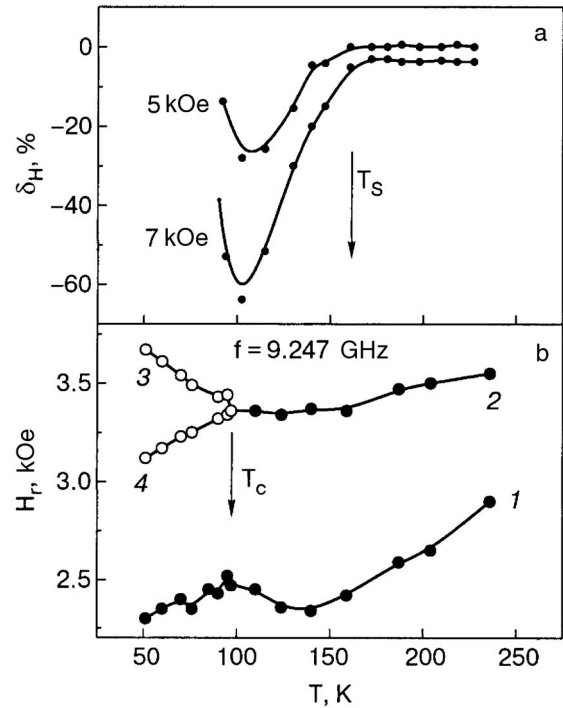The pace of development of electronics relies on the search for new materials. In this review article we have dis-

cussed only a few of the wide class of $3d$-sulfides. Many questions that arise in the study of these materials remain unanswered. The accumulated experimental data on sulfide and oxide compounds of $3d$ elements suggest that the most promising substances in which to search for CMR are magnetic materials with a metal-insulator transition. The study of such materials can not only promote an understanding of the mechanisms of MIT and CMR phenomena but can also further the development of methods for prognostication of substances with specified physical properties.
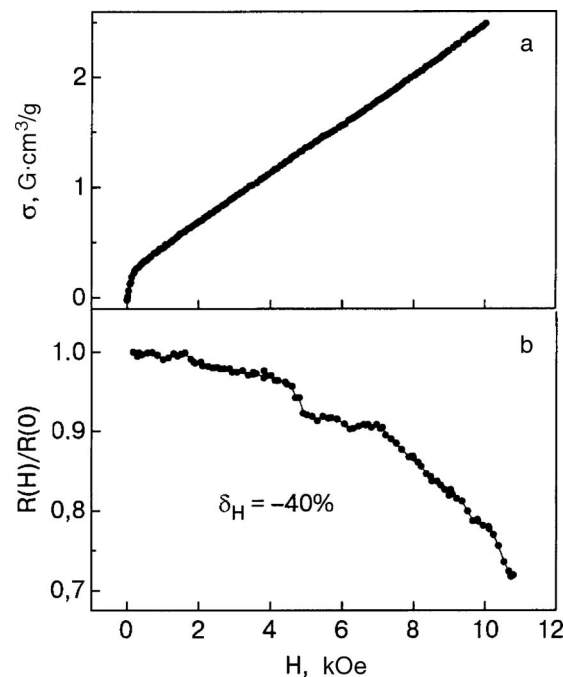

FIG. 14. Field dependence of the magnetization (a) and relative resistance (b) for $CuV_xCu_{1-x}S_2$ with $x=0.1$.

a)E-mail: agm@iph.krasn.ru

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