Low-temperature electronic and magnetic transitions in the antiferromagnetic semiconductor $Cr_{0.5}Mn_{0.5}S$

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Experimental-theoretical studies were carried out of the electrical and magnetic properties of the antiferromagnetic semiconductor $Cr_{0.5}Mn_{0.5}S$ in the temperature range 4.2–300 K. A magnetic antiferromagnetic-ferrimagnetic phase transition was observed along with a semimetal-semiconductor electronic transition. Monte Carlo calculations indicate that the changes in the type of magnetic ordering and conductivity are due to the cooperative Jahn–Teller effect caused by the Cr^{2+} ions. © *1999 American Institute of Physics.* [S1063-7834(99)02609-X]

At present, compounds with perovskite structure similar to $La_{1-x}Me_xMnO_3$ (where Me=Ca, Ba, Sr, etc.) are being studied intensely.[1] These compounds are interesting because they exhibit giant magnetoresistance and magnetically and electronically nonuniform states that preserve the compounds' crystallographically uniform structure. Since the mechanisms for magnetic biphase behavior and electronic stratification are not clear at this time, there is interest in studying compounds with a different crystal lattice but with similar physical properties.

The compound $Cr_{0.5}Mn_{0.5}S$ is a strongly doped antiferromagnetic semiconductor, belonging to the group of sulfides $Me_xMn_{1-x}S$ (where Me is a 3*d* metal), which crystallize in the cubic NaCl lattice.[2] Like the rare-earth manganite compounds, the $Me_xMn_{1-x}S$ sulfides exhibit changes in the type of conductivity and magnetic order as the concentration of 3*d* metal is varied. Thus, with Me=Fe, as x increases the magnetic order changes from antiferromagnetic to ferromagnetic, which precedes an electronic semiconductor-semimetal transition (at $x_c \sim 0.4$).[3] In the system $Cr_{0.5}Mn_{0.5}S$ ($0<x<0.67$), however, no noticeable change in the magnetic order is observed in the vicinity of the concentration-induced semiconductor—semimetal transition ($x_c \sim 0.67$). The semimetallic sulfides retain their antiferromagnetic order with increasing Néel temperature T_N up to ~ 175 K for $x \approx 0.5$ ($T_N \sim 148$ K for $x=0$).[4,5] Measurements of the magnetic susceptibility,[4] along with EPR data[6] and neutron-diffraction measurements,[7] indicate that increases in the Néel temperature with a simultaneous decrease (in absolute value) in the negative paramagnetic Curie temperature do not exclude the possible formation within the $Me_xMn_{1-x}S$ sulfides of a magnetically nonuniform state in the temperature range $T<T_N$ and a transition to a ferromagnetic state with changes in the temperature or magnetic field.

In this paper we investigate experimentally and theoretically the magnetic and electrical properties of the antiferromagnetic semiconductor $Cr_{0.5}Mn_{0.5}S$ in the temperature range 4.2–300 K in order to study the low-temperature ($T<77$ K) electronic and magnetic states of this compound.

1. EXPERIMENTAL RESULTS

Polycrystalline samples were synthesized from pure elements (electrolytic Mn, Cr and S with purity 99.999%) in vacuum quartz ampules over the course of a week. The temperature dependences of the electrical resistance of these samples were measured at constant current by a potentiometer method in the temperature range 4.2–300 K. The measurements of the magnetization in the range 4.2–100 K were made using a superconducting quantum interference (SQUID) magnetometer in fields up to 8 Oe.

According to *x*-ray structural data, our samples of $Cr_{0.5}Mn_{0.5}S$ were solid solutions with the fcc NaCl lattice characteristic of α MnS. Replacement of Mn ions with Cr ions is accompanied by compression of the cubic unit cell and decrease in the lattice parameter from $a=5.222$ (α MnS) to 5.165 Å while preserving the NaCl structure. Additional phases were not observed in the solid solution $Cr_{0.5}Mn_{0.5}S$.

Figure 1a shows the temperature dependence of the electrical resistivity $\rho(T)$ for $Cr_{0.5}Mn_{0.5}S$. The behavior of $\rho(T)$ in the range 77–300 K agrees with the data of Ref. 5 and corresponds to the semimetallic type of conductivity, i.e., the compound is in the degenerate- semiconductor state. In the range below ~60 K a rapid increase (by an order of magnitude) in the electrical resistivity is observed, along with an anomalous change in the temperature coefficient of the resistivity $d\rho/dT$ (Fig. 1b). In this case the activation energy of the conductivity E_a changes discontinuously with decreasing temperature from 0.04 to 0.01 eV in the neighborhood of T_N, and then decreases continuously down to ~0.003 eV in the range below ~60 K (Fig. 1c).

Figure 2 shows temperature dependences of the magnetization of $Cr_{0.5}Mn_{0.5}S$ samples measured in the range 4.2–100 K, some cooled in zero magnetic field (ZFC samples, see curve *1*) and some in a field $H=8$ Oe (FC samples, see curve *2*). It is clear from the figure that the material enters a state with spontaneous magnetization at $T_c \approx 66$ K. The behavior of the ZFC magnetization is typical of the initial susceptibility of a ferromagnet (the Hopkinson effect).[8] In the

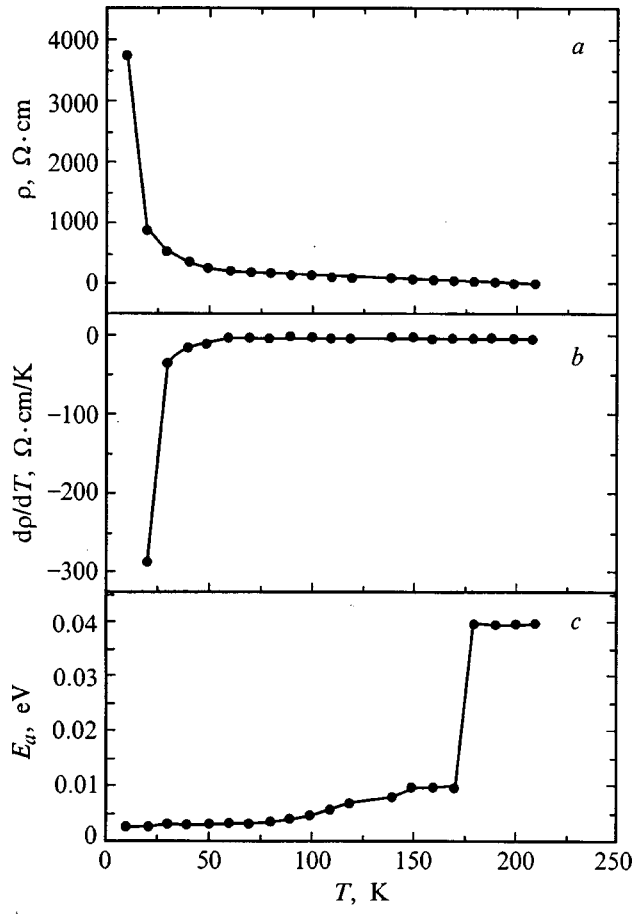

FIG. 1. Temperature dependences of the electrical resistivity ρ (a), the temperature coefficient of the resistivity $d\rho/dT$ (b), and the activation energy of the conductivity E_a (c) for $Cr_{0.5}Mn_{0.5}S$.

vicinity of ~35 K the ZFC magnetization curves exhibit an additional weakly expressed maximum. Below this temperature, the FC magnetization decreases with decreasing temperature.

2. DISCUSSION OF RESULTS

Analysis of the magnetic properties based on Monte Carlo calculations show that the behavior of the magnetization of $Cr_{0.5}Mn_{0.5}S$ in the 4.2–300 K range cannot be described in terms of magnetic ordering mechanisms that take into account two- and four-spin exchange interactions, which are normally used to describe the properties of the magnetically ordered state.[9,10] These calculations show that the behavior of the spontaneous moment in the fcc lattice of $Cr_{0.5}Mn_{0.5}S$ is due to the cooperative Jahn–Teller effect caused by the Cr^{2+} ions.

The ground state of Cr^{2+} ions in a lattice with cubic symmetry is characterized by twofold orbital degeneracy. In this case, two types of interactions are possible. The first is an interaction of the degenerate orbitals with the lattice. Here Pauli matrices for the effective spin τ are introduced in order to describe the orbital wave functions e_g.[11] The ordering of the pseudospins (orbitals) is accompanied by a structural phase transition. The second is an interaction between orbitals, which depends on the spins and is a function of the pseudospin exchange integral $J_s = J_s^0 + J_m\langle \tau_g \tau_{g+r}\rangle$.[11] Here J_s^0 is the exchange interaction integral between spins, and J_m is an interaction parameter between spins and orbitals. If $J_s^0 < 0$ and $J_m < 0$, it is possible for a critical temperature to exist at which the sign of the exchange interaction between the spins changes from negative to positive.

Let us assume that the variation of the pseudospin correlation function with temperature is analogous to that of spin-spin correlation function in the magnetically ordered phase, i.e., $|\langle \tau_g \tau_{g+r}\rangle| \sim (1 - T/T_N)^{2\beta}$, where β is a critical index for the magnetization; it is known that $\beta = 0.35$. As a result, the exchange interaction between nearest neighbor chromium ions depends on temperature like $J_{Cr-Cr} = J^0_{Cr-Cr} + J_m(1 - T/T_N)^{2\beta}$, where J_m is a fitting parameter determined from the condition that the exchange constant J_{Cr-Cr} should change sign at a certain critical temperature T_c. The temperature T_c corresponds to the appearance of ferromagnetic ordering. As a rule, the ordering temperature of the orbitals should coincide with the temperature of a structural transition and the Néel temperature T_N. In fact, *x*-ray analysis indicates that a lattice distortion analogous to the distortion at T_N observed in α MnS does indeed occur at $T_N \approx 175$ K in the solid solution $Cr_{0.5}Mn_{0.5}S$.[12] In this temperature range we observe[4] a 10% discontinuity in the susceptibility.

In our Monte Carlo calculations we used a lattice model of the solution $Cr_{0.5}Mn_{0.5}S$ with six exchange interaction parameters between the classical spins $S_{Mn} = 2.5\mu_B$ and $S_{Cr} = 2\mu_B$ (Mn–Mn, Cr–Cr, and Mn–Cr in the first and second coordination spheres). Some of these exchange interaction parameters were determined previously[4] from the concentration dependence of the Néel temperature for $Cr_xMn_{1-x}S$ ($0 < x < 0.67$): $J_{MnCr}/J_{MnMn} = -0.4$, $K_{Mn-Cr}/J_{MnMn} = -1.9$, and $K_{MnMn}/J_{MnMn} = -1.8$. The Cr–Cr exchange interaction parameters for the first and second coordination spheres are determined in the present paper. For an fcc lattice consisting of $N = 4 \times 12^3$ sites we calculated the magnetization, the susceptibility, the Edwards–Anderson parameter $q_\alpha = (1/N)\sqrt{\sum_{i=1}^{N}\langle S_i^\alpha\rangle^2}$ ($\alpha = x,y,z$), and the magnetic static structure factor along the cube edges and diagonals of the planes. Based on these characteristics, we determine the transition temperature from the antiferromagnetic state to a ferrimagnetic state with a spontaneous moment $m \approx (1/3)S_{Cr}\mu_B$ for $T \to 0$. The magnetic Hamiltonian for the solid solution $Cr_{0.5}Mn_{0.5}S$ can be written in the form

$$H = -\sum_{\alpha,\beta=Cr,Mn} I_{\alpha\beta} \sum_{i=1}^{N} \sum_{\Delta=1}^{Z_1} P_\alpha(i) P_\beta(i+\Delta) S_\alpha(i) S_\beta(i+\Delta) - \sum_{\alpha,\beta} K_{\alpha\beta} \sum_{i=1}^{N} \sum_{h=1}^{Z_2} P_\alpha(i) P_\beta(i+h) S_\alpha(i) S_\beta(i+h) - \sum_{\alpha} H \sum_{i} P_\alpha(i) S_\alpha^z(i),$$

where $I_{\alpha\beta}$ and $K_{\alpha\beta}$ are exchange interaction integrals between nearest neighbors ($Z_1 = 6$) and next-nearest neighbors ($Z_2 = 12$), H is the external magnetic field, and the projection operator $P_\alpha(i)$ equals unity at sites occupied by spin S_α.

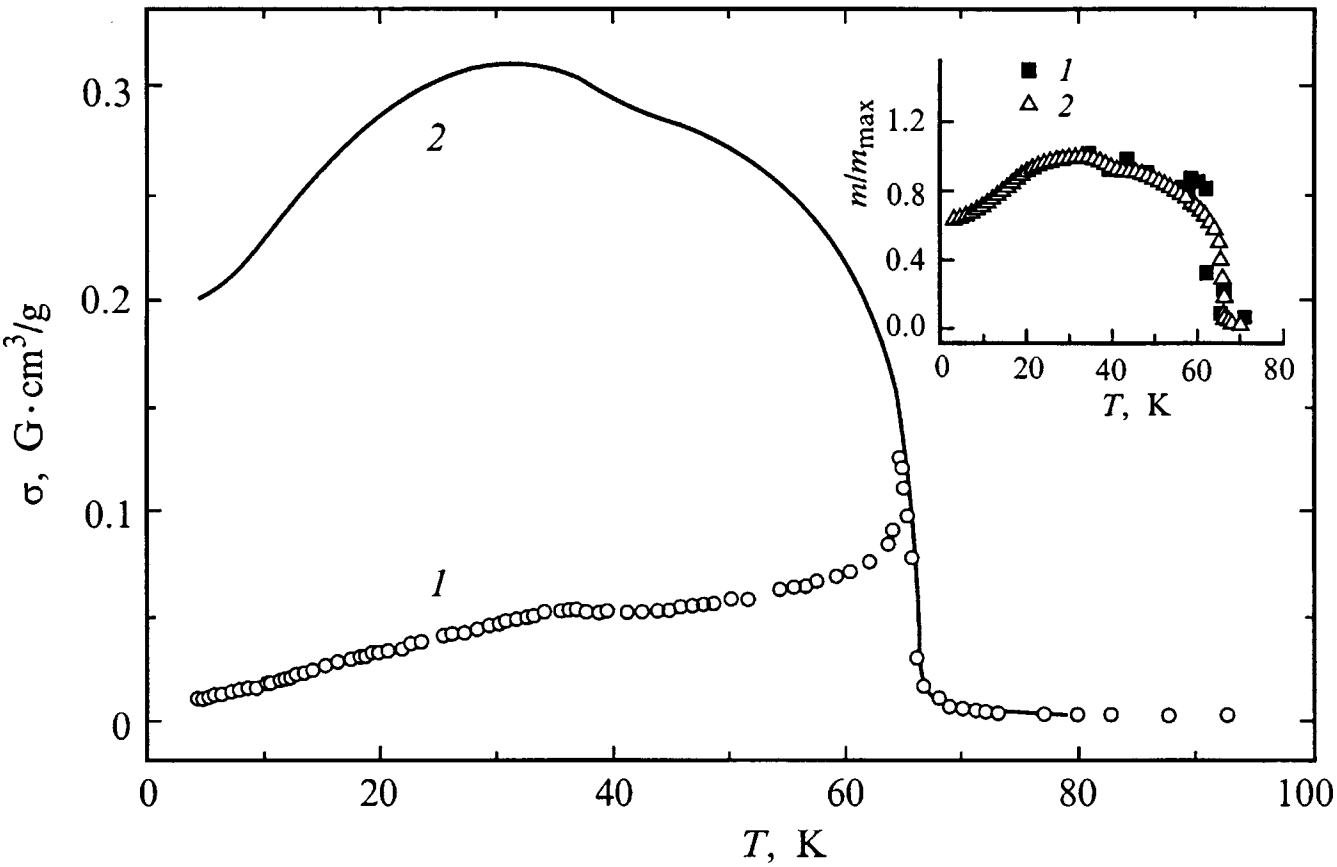

FIG. 2. Temperature dependences of the magnetization σ for samples cooled in zero magnetic field (ZFC—curve *1*) and in a field of 8 Oe (FC—curve *2*) for $Cr_{0.5}Mn_{0.5}S$. The inset shows the temperature dependence of the normalized value of the magnetic moment: *1*—calculated by the Monte Carlo method, *2*—experiment.

According to these calculations, the dependence of the Fourier spectrum of the pairwise spin correlation function on wave vector in the antiferromagnetic temperature range ($66 \pm 5 < T < 180 \pm 10$) K exhibits two maxima: at $q=0$ and π/a in the direction [101], as is shown in the inset to Fig. 3a. This indicates that spins in the four sublattices located at the vertices of a tetrahedron are pairwise antiparallel (Fig. 4a). The first effect of decreasing the temperature is propagation of the long-range ferromagnetic order along the spins of the chromium ions. Below $T \leqslant 130$ K, ordering of the moments of the manganese ions contributes to the magnetic structure factor, leading to a considerable increase in the magnitude $S(q)$ and the appearance of a modulation of the magnitude of the antiferromagnetism vector in the direction [101] with $q=\pi/12a$. The quantity $S(q)$ calculated by the Monte Carlo method exhibits a satellite peak at temperatures below ~140 K. For $T_c = 65 \pm 5$ K, the intensity of the magnetic structure factor at $q=\pi/a$ (curve *1* in Fig. 3a) reduces to zero, and a peak in $S(q)$ forms at $q = 0$ (curve *1* in Fig. 3b), i.e., ferromagnetic order is established along two directions of the planes (Fig. 4b), which leads to the formation of a spontaneous moment. The temperature dependence of the magnetic moment calculated by the Monte Carlo method (the inset to Fig. 2) is in good agreement with the experimental results. At T_c, the lifting of orbital degeneracy causes the sign of the exchange interaction between chromium ions J_{Cr-Cr} to change from negative to positive. By comparing the experimental and theoretical values of T_c and T_N, we can determine the value of the exchange constants between Cr–Cr ions: $J_{Cr-Cr}/J_{MnMn} = -2.7$, $K_{Cr-Cr}/J_{MnMn} = 6$, and $J_m/J_{MnMn} = -2.5$, where $J_{MnMn} = (7.8 \pm 0.3)$ K.

From our calculations of the magnetic structure factor it follows that the ions of chromium and manganese are located randomly in the lattice and form two infinite clusters containing chromium and manganese respectively. The Edwards–Anderson parameter (Fig. 5) exceeds the value of the magnetic structure factor by a few times. This indicates that independent finite clusters are also contained in the material and randomly distributed. The temperatures of the paramagnetic-antiferromagnetic (T_N) and antiferromagnetic-ferrimagnetic (T_c) phase transitions determined from the temperature dependences of the Edwards–Anderson parameter (Fig. 5) are in good agreement with the data obtained from the magnetic structure factor: $T_N \approx 180 \pm 10$ K, $T_c \approx 70 \pm 6$ K.

The decrease in magnetic moment at low ($T < 30$ K) temperatures and the temperature hysteresis of the magnetic moments of ZFC and FC samples are probably due to the formation of domain structures in weak magnetic fields. It is also known that the original α MnS exhibits a structural transition at $T \approx 25$ K.[13] This transition is probably preserved in the solid solution $Cr_{0.5}Mn_{0.5}S$ as well, leading to a change in the exchange constants between Mn ions due to lattice distortion and the appearance of non-Heisenberg types of

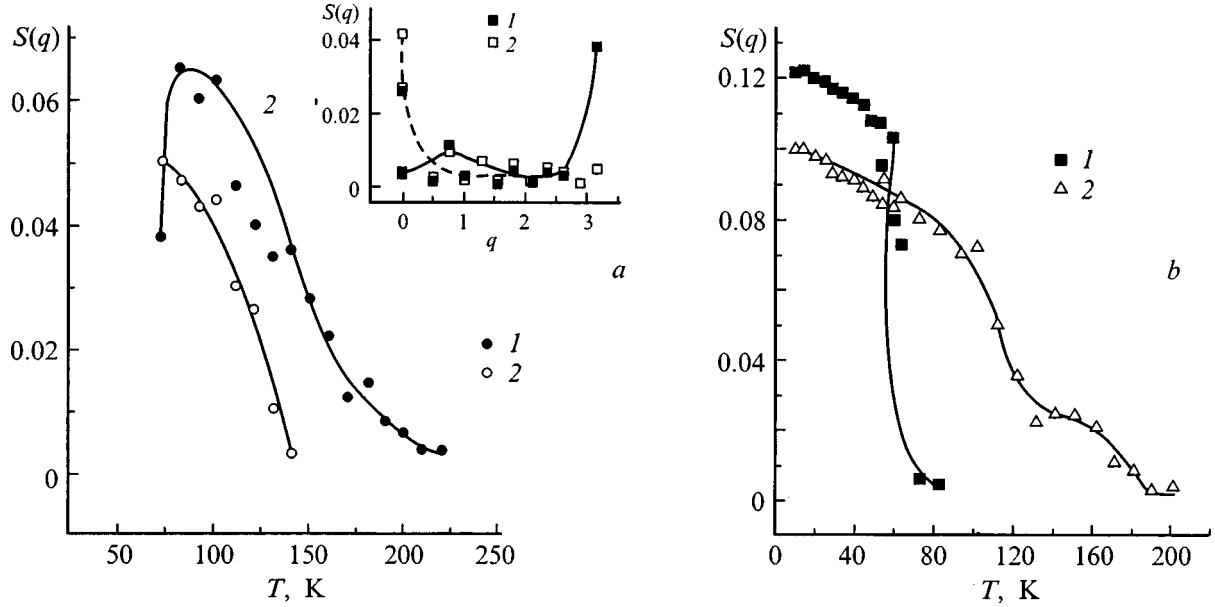

FIG. 3. Temperature dependence of the magnetic structure factor $S(q)$. a: Curve *1*—$q=\pi/a$ in the direction [101]; curve *2*—$q=\pi/12a$ in the direction [011]; b: curve *1*—$q=0$ in the direction [101]; curve *2*—$q=0$ in the direction [110]. The inset shows the Fourier spectrum of the pairwise spin correlation function for the direction [101] (*1*) and [110] (*2*) at a temperature 115 K.

interactions, for example biquadratic and four-spin. This causes the modulus of the spin on a site to contract, thereby decreasing the noncollinearity of the spins. Our Monte Carlo calculations show that this structural transition can decreasse the exchange parameter J_{MnMn} by a factor of 2, which in turn decreases the magnetization by about 15% at 4 K.

Based on this model we can predict two effects. In a magnetic field, the sign of the spin-spin correlation function $\langle S_g S_{g+r}\rangle$ changes from negative to positive at a distance $r/a=1$ in the vicinity of the Néel temperature, increasing the exchange interaction between orbitals $J_\tau=J_\tau^0+J_m\langle S_g S_{g+r}\rangle$, which in turn increases the temperature for orbital ordering. This will enhance the orbital correlations $\langle \tau_g \tau_{g+r}\rangle$ and decrease the exchange interaction between chromium atoms, leading to a decrease in the Néel temperature and an increase in the Curie temperature for ferrimagnetism with increasing field. As a result, in strong magnetic fields there should exist a tetracritical point where the phase transition lines T_c and T_N are in contact. Uniaxial pressure along a principle diagonal of the cube should lead to an analogous effect.

In light of these magnetic calculations, we can explain the behavior of the electrical resistance of $Cr_{0.5}Mn_{0.5}S$ in the following way. According to Ref. 5, the temperature behavior of the electrical resistivity of the sulfides $Cr_xMn_{1-x}S$ arises from changes in the activation energy of the conductivity E_a due to a red shift in the mobility edge E_c caused by the contribution of the ferromagnetic component of the exchange interaction in the second coordination sphere of the NaCl lattice. In this picture, the Fermi level E_F is located in the vicinity of the *d* atom-like states of the chromium atoms

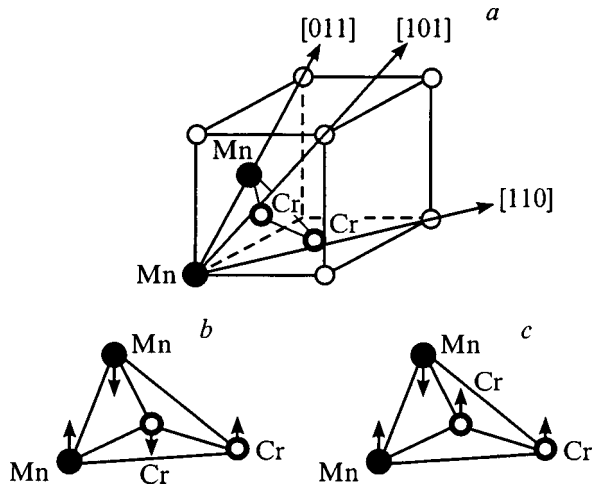

FIG. 4. Sketch of magnetic order in the solid solution $Cr_{0.5}Mn_{0.5}S$: a—unit cell of the fcc lattice; b—antiferromagnet ($T>T_c$); c—ferrimagnet ($T<T_c$).

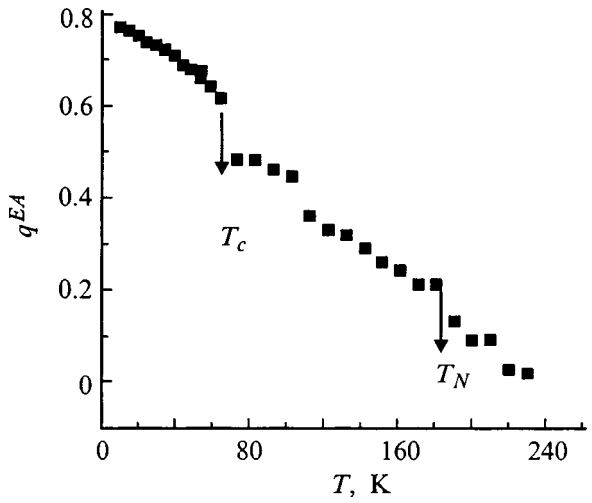

FIG. 5. Temperature dependence of the Edwards–Anderson parameter q^{EA} for the longitudinal components of the spin.

and the top of the valence $p-d$ hybridized band. The shift δE_c in $Cr_{0.5}Mn_{0.5}S$ as it enters the antiferromagnetic phase $E_{a\mathrm{PM}}-E_{a\mathrm{AFM}}\approx 0.05$ eV, and the activation energy of the conductivity below the Néel temperature reaches values of ~ 0.01 eV. As the temperature decreases, the shift δE_c is probably increased by the appearance of a contribution from the ferromagnetic exchange interaction in the first coordination sphere. This leads to a still larger decrease in the conductivity activation energy. However, the Jahn–Teller transition lifts the orbital degeneracy of the *d* levels of chromium ions located near the valence band, and the splitting between e_g sublevels increases as the magnitude of the exchange field in the ferromagnetic phase increases. As a result of this splitting, the Fermi level can end up in an energy range with lower density of states, increasing the magnitude of the electrical resistance despite the fact that $E_c \sim E_F$.

Thus, at low temperatures the antiferromagnetic semiconductor $Cr_{0.5}Mn_{0.5}S$ exhibits a magnetic transition from antiferromagnet to ferrimagnet, and an electronic transition from a semimetallic to a semiconducting phase. The mechanisms for these transitions can be explained by the cooperative Jahn–Teller effect caused by Cr^{2+} ions.

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