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# Colossal magnetoresistance in the layered chromium sulfide $Cr_2S_{3-x}$ $(x=0.08)$

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We report structural, magnetic, and magnetotransport properties of the two-dimensional chromium sulfide $Cr_2S_{2.92}$, which contains both $Cr^{3+}$ and $Cr^{2+}$ ions. Below its magnetic-ordering temperature ($T_N=118$ K), $Cr_2S_{2.92}$ exhibits a weak spontaneous magnetization with a maximum around 90 K and a value of 0.013(4) $\mu_B$ per Cr ion at 5 K. The resistivity and magnetoresistance exhibit pronounced local maxima around $T_N$ (MR $=48\%$ in a field of 14 T). The magnetotransport properties are discussed in terms of magnetic-polaron formation.

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Since the discovery of colossal magnetoresistance (CMR) in the perovskite manganites $M_{1-x}A_x$MnO$_3$, there has been a renewed interest in the study of this type of material.[1] Although CMR in manganites has been rationalized in terms of a double-exchange mechanism, in which the magnetic alignment of neighboring $Mn^{3+}$ and $Mn^{4+}$ ions enhances the charge transport, some recent studies indicate that electron-phonon coupling plays an important role.[2] CMR has long been known in the rare-earth compounds Eu$X$ ($X=$O, S, Se or Te) and $Gd_{3-x}S_4$, in which localized $f$ electrons coexist with itinerant $s$-$d$ electrons.[1] In these materials, the large negative magnetoresistance is attributed to the existence of magnetic polarons. Recently, CMR has also been found in other systems, including the pyrochlore oxides, such as $Tl_2Mn_2O_7$,[3] the layered iodide $GdI_2$,[4] and chromium chalcogenide spinels $A$Cr$_2X_4$ ($A=$Cd, Fe; $X=$S, Se, Te).[5] The last-two systems differ from the manganites in that, although the resistivity shows an anomaly at the Curie temperature, the materials remain semiconducting below the magnetic-ordering temperature. However, most CMR materials share the common features of a localized magnetic band just below the Fermi energy and a broader conduction band that is polarized by the first. Large CMR effects also seem to require strongly spin-differentiated states at the Fermi level.[6] Moreover, for a large number of CMR materials, there is an universal linear dependence of the magnetoresistance (scaled to the square of the magnetization) on the density of the charge carriers (scaled to the unit cell volume).[7]

In this work, we report a series of structural, magnetic and magnetotransport measurements for sulfur-deficient rhombohedral $Cr_2S_{3-x}$ $(x=0.08)$. Earlier magnetotransport data indicate that $Cr_2S_{3-x}$ might exhibit a large magnetoresistance (a maximum value of $\sim 7\%$ was found in fields $\leqslant 1.5$ T).[8,9] The structure of $Cr_2S_{3-x}$ consists of hexagonally close-packed sulfide layers, with the octahedral sites between alternate pairs of anion layers fully and partially occupied by cations. In the ideal structure, cations reside at only one-third of the octahedral sites in the partially occupied layer and ordering of vacancies leads to a two-dimensional $\sqrt{3}a_p \times \sqrt{3}a_p$ superstructure. The $Cr_2S_{3-x}$ structure contains layers of edge-sharing octahedra parallel to the (110) plane and trimers of face-sharing octahedra that serve to link these layers.

A polycrystalline sample of $Cr_2S_{2.92}$ was prepared by heating an appropriate mixture of the elements in a sealed evacuated silica tube ($<10^{-4}$ torr) at 500 °C for 24 hrs. and then at 800 °C for four days. After regrinding, the powders were pressed into pellets and refired at 1000°C for four days before cooling to room temperature at 4 °C/min. Powder x-ray diffraction data confirmed that the material is a single phase with lattice parameters similar to those reported by Jellinek[10] for rhombohedral $Cr_2S_3$. Thermogravimetric analysis of the sulfur content, by oxidation in a flow of dry oxygen, produced a weight loss of 23.56(2)%, close to the calculated value of 23.08% for conversion to the binary oxide. Rietveld refinements using powder x-ray diffraction data collected at room temperature, suggest that sulfur deficiency corresponds to excess Cr ions and some disordering of vacancies in the partially occupied layers. While stoichimetric $Cr_2S_3$ contains only $Cr^{3+}$ ions, sulfur deficiency introduces an excess of electrons and creates formally a small amount of $Cr^{2+}$. Therefore, this material shares some features with the manganites. In particular, the presence of Jahn-Teller $[Cr^{2+}(d^4)]$ and non Jahn-Teller $[Cr^{3+}(d^3)]$ species.

Magnetic measurements were performed using a Quantum Design MPMS2 SQUID susceptometer in the temperature range $5 \leqslant T \leqslant 300$ K and a measuring field of 0.01 T, while isotherms were measured up to a field of 5 T. Data were collected upon warming after cooling the sample in zero applied magnetic field and after cooling the sample in a field of 0.01 T [Fig. 1(a)]. The magnetization increases abruptly below 125 K, reaches a maximum at 94 K and then decreases at low temperature. This behavior is characteristic of a ferrimagnetic material. The Néel temperature, defined as the temperature corresponding to the maximum of $|dM/dT|$, is $T_N=118.1(6)$ K. The inverse susceptibility $1/\chi$ exhibits

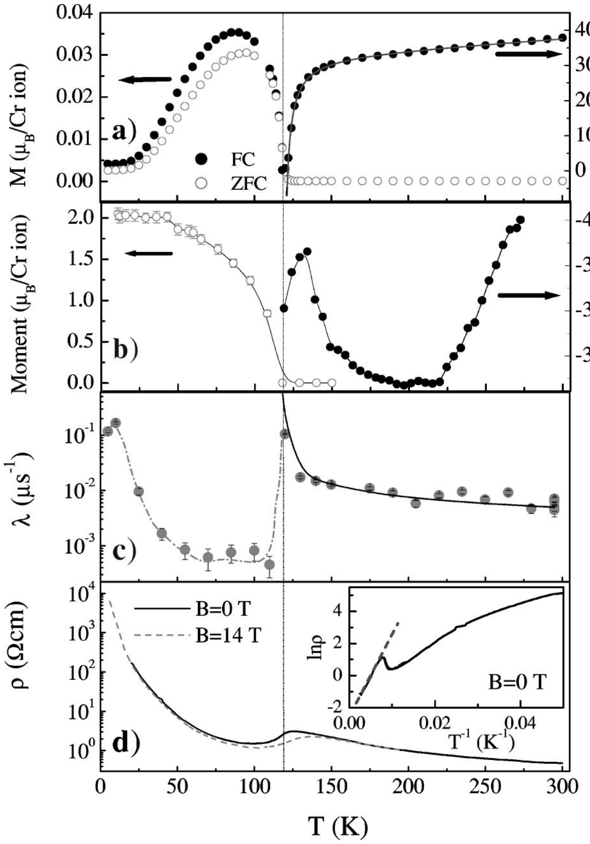

FIG. 1. Temperature dependence of (a) magnetization (left) and the inverse of susceptibility (right), with the fit to Eq. (1) shown by the solid line, (b) the ordered magnetic moment per Cr atom (left) and Seebeck coefficient (right) (c) muon relaxation rate with the fit to a simple exponential function shown by the solid line and d) resistivity (in $B=0$ T and $B=14$ T) for $Cr_2S_{2.92}$. The inset shows the logarithm of resistivity as a function of the inverse temperature. The continuous vertical line is drawn at $T_N=118$ K.

the temperature dependence, predicted from a molecular-field theory treatment for a ferrimagnetic material:[11]

$$\frac{1}{\chi}=\frac{T}{C}+\frac{1}{\chi_0}-\frac{\sigma}{T-\theta}. \quad (1)$$

The best fit to the data [Fig. 1(a)] resulted in parameters of: $C=2.4(1)$ emu K mole$^{-1}$, $1/\chi_0=264.8(5)$mole emu$^{-1}$, $\theta=118(1)$ K, and $\sigma=1120.7(6)$ K mole emu$^{-1}$. The effective moment of 4.33 $\mu_B$ per Cr ion is larger than the spin-only value of 3.97 $\mu_B$. This discrepancy is likely to be due to the development of short-range correlations in the paramagnetic region at temperatures close to $T_N$.

A neutron-diffraction study of the magnetic structure of stoichiometric $Cr_2S_3$,[12] determined that there are three magnetic sublattices, $m_a$, $m_b$, and $m_c$, of which $m_a$ and $m_b$ are parallel with each other and antiparallel with $m_c$. As there are twice as many ions on the $m_c$ sublattice than on $m_a$ or $m_b$, complete cancellation of the moments is expected. It was suggested that the weak ferrimagnetism arises from the temperature dependence of the spin canting of the moments out of the *a*-*b* plane. A second neutron diffraction study, together with magnetization measurements on a single crystal of $Cr_2S_3$, concluded that the spins are oriented perpendicular to the *c*-axis.[13] In this second study, the small spontaneous magnetization was explained by differences in occupancy of the three crystallographic sites of chromium. In order to investigate the magnetic structure of $Cr_2S_{2.92}$, and its evolution with temperature, powder-neutron-diffraction data were collected on the D1B diffractometer ($\lambda=2.54$ Å) at ILL, Grenoble, over the temperature range $11\leqslant T\leqslant 150$ K in increments of $\sim 10$ K. The thermal evolution of the neutron diffraction pattern of $Cr_2S_{2.92}$ is shown in Fig. 2(a). Below the magnetic-ordering temperature, no new reflections appear, but the relative intensity of some lines changes on cooling below 118(5) K. This indicates that the magnetic and crystallographic unit cells are of the same size. In the refinements, the magnitude of the moments on the three sublattices was constrained to the same value. The validity of this approximation is supported by the very low spontaneous magnetization, $M_s$ of 0.013(4) $\mu_B$ per Cr ion at 4.2 K (Fig. 3), obtained by extrapolation of the linear portion of $M(B)$ to zero field. The limited Q range of the data produces an unreliable overall thermal parameter. Attempts to introduce an excess of Cr atoms at the empty sites in the vacancy layer [6(c) $(0,0,\sim 1/6)$], as required for nonstoichiometry, did not result in a significant improvement in the

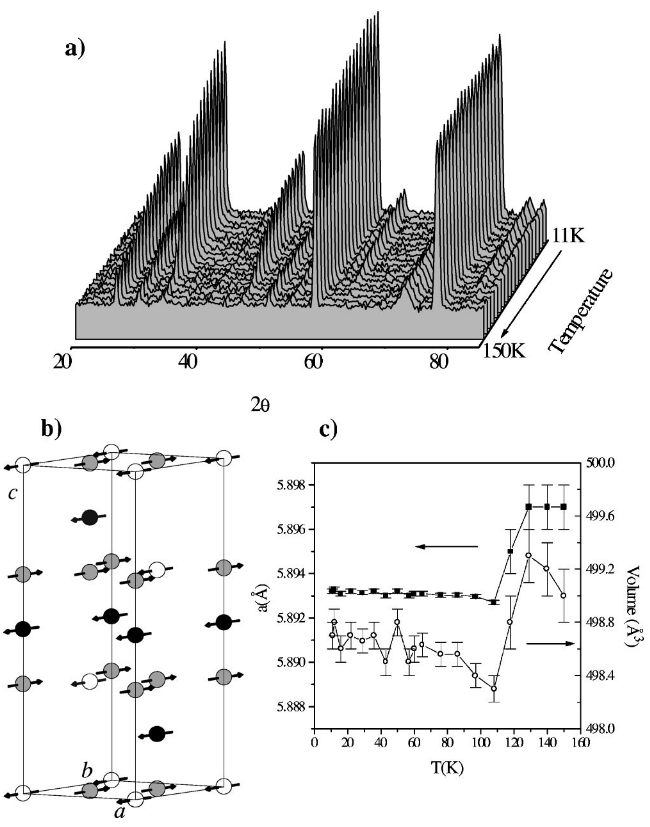

FIG. 2. (a) Powder-neutron-diffraction data over the temperature range $11\leqslant T\leqslant 150$ K for $Cr_2S_{2.92}$. (b) The magnetic structure of $Cr_2S_{2.92}$. Anions are omitted for clarity. White, black, and gray circles represent Cr atoms in the *a*, *b*, and *c* sublattices, respectively. (c) Temperature dependence of the lattice parameter *a* and the unit-cell volume of $Cr_2S_{2.92}$.

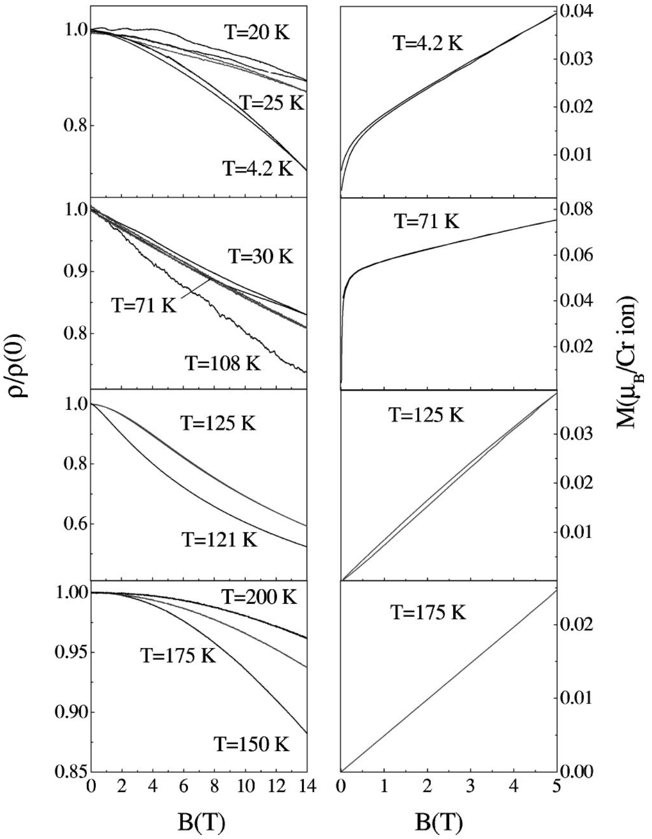

FIG. 3. Field dependence of (left) resistivity normalized to the zero-field value $[\rho/\rho(0)]$ and, (right) the magnetization for $Cr_2S_{2.92}$ at temperatures above and below $T_N$.

refinement. The refined magnetic structure of $Cr_2S_{2.92}$ [Fig. 2(b)] is similar to that of stoichiometric $Cr_2S_3$, although it was not possible to determine the angle of the moments with the $c$ axis. Figure 1(b) shows the temperature dependence of the ordered magnetic moment, which at low temperature is reduced by ~30% from the spin-only value. This is due to the covalency of the Cr-S interaction, which results in a transfer of spin from the cation. Similar reductions have been observed in structurally related chalcogenides.[14,15] Table I lists the final refined parameters for data collected at 11 and 150 K. Sequential Rietveld refinements using data collected in the temperature range $11 \leqslant T \leqslant 150$ K reveal that the lattice parameter $a$ and the unit-cell volume exhibit a discontinuity at the magnetic-ordering temperature [Fig. 2(c)].

The temperature dependence of the muon relaxation rate [Fig. 1(c)] was determined using the $\mu$SR instrument at ISIS. Two different regimes can be distinguished. Above $T_N$, where the muon experiences fast fluctuations of the local fields, the muon depolarization is described by a simple exponential function. The relaxation rate λ increases slowly with decreasing temperature suggesting a slowing down of the local-field fluctuations as the system approaches the magnetic transition. Below $T_N$ the drop of the initial asymmetry to one-third of its value at room temperature, indicates the transition to a magnetically ordered phase. Data in this region were fitted by a stretched exponential, $A(t)=A_0\exp(-\lambda t)^{\beta}$, with $\beta=0.5$. The relaxation rate is an order of magnitude smaller than in the paramagnetic region, but increases markedly below 50 K and shows a second maximum at ~10 K. This behavior is unusual in a magnetically ordered system where the relaxation rate usually decreases with cooling.[16]

Magnetotransport measurements were carried out on a sintered bar using a four-terminal method with a direct current of $<10\mu$A. The sample was mounted in a variable temperature insert that was loaded into a 17 T superconducting magnet. The field was applied perpendicular to the current direction. Figure 1(d) shows the temperature dependence of the resistivity $\rho(T)$ in zero and 14 T applied field. Above $T_p=125$ K, $\rho$ increases with decreasing temperature, consistent with semiconducting behavior, but drops abruptly on cooling below $T_p$, reaching a minimum at ~100 K, before increasing again on further cooling. This behavior is similar to that reported for the CMR thiospinels[5,17] and for $GdI_2$.[4] The behavior of $\rho(T)$ is strongly dependent on the sulfur content. The resistivity of the stoichiometric material is 89 kΩ cm at room temperature, and rises to 9 MΩ cm at 200 K. Furthermore, stoichiometric samples and those prepared with an excess of sulfur, do not exhibit an anomaly at 125 K. Even apparently stoichiometric single crystals that exhibit an anomaly in $\rho(T)$, actually have a ratio Cr:S $>2:3$.[9] Over the temperature range $140 \leqslant T \leqslant 340$ K, the resistivity of $Cr_2S_{2.92}$ follows an Arrhenius law [inset of Fig. 1(d)], with an activation energy of 0.044(1) eV, while below 80 K the behavior is better described by a variable range hopping expression $\rho=\rho_0\exp[(T/T_0)^p]$, with $0.25 \leqslant p \leqslant 0.5$.

Measurement of the Seebeck coefficient $S$ in the temperature range $110 \leqslant T \leqslant 273$ K, using a temperature gradient of 3–4 K, indicates that the dominant carriers are electrons [Figure 1(b)]. The large value of $S$ $(-391\ \mu$V/K at 273 K) is consistent with semiconducting behavior. The temperature dependence of $S$ is complex and does not vary as $1/T$ in the measured temperature range, but exhibits an anomaly at $T_p$.

The field dependence of the resistivity (Fig. 3) is parabolic above $T_N$. At temperatures just below $T_N$, $\rho(B)$ is linear, but the degree of linearity decreases with decreasing temperature and hysteresis is observed below 50 K. In the vicinity of the magnetic ordering temperature, there is a

TABLE I. Final refined parameters for $Cr_2S_{2.92}$ at 11 K and 150 K. Cr(1) in $3(b)$ (0,0,1/2), Cr(2) in $3(a)$ (0,0,0), Cr(3) in $6(c)$ (0,0,z) and S in $18(f)$ $(x,y,z)$ (Space group $R\overline{3}$).

| Temperature(K) | | 11 | 150 |
|---|---|---|---|
| $a$(Å) | | 5.8932(1) | 5.897(1) |
| $c$(Å) | | 16.581(2) | 16.575(2) |
| B(Å$^2$) | | -1.1(4) | -0.5(3) |
| Moment($\mu_B$) | | 2.05(7) | - |
| Cr(3) | z | 0.329(3) | 0.331(1) |
| S | x | 0.352(5) | 0.339(3)) |
| | y | -0.015(3) | -0.003(3) |
| | z | 0.2495(9) | 0.2538(6) |
| $R_{wp}$(%) | | 2.5 | 1.45 |
| $\chi^2$ | | 2.25 | 1.99 |

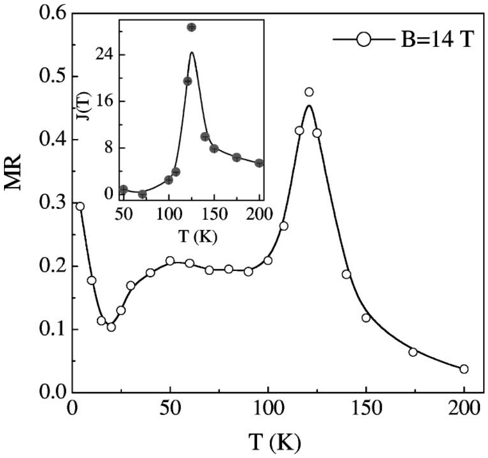

FIG. 4. Temperature dependence of magnetoresistance in a field of 14 T. The inset shows the temperature dependence of the total spin moment of a magnetic cluster $J(T)$, obtained by using the model developed by Wagner *et al.*[18]

large negative magnetoresistance $(MR=-[\{\rho(B)-\rho(0)\}/\rho(0)])$, which has a maximum value of 48% in 14 T at 121 K (Fig. 4), but does not saturate even at the highest field. On cooling further, the MR attains a constant value of $\sim$ 20% before increasing below 20 K. This feature may be associated with the anomalous behavior of the muon relaxation rate and the hysteresis in $\rho(B)$, both of which appear below 50 K. There is no discernible low-field MR indicating that the MR effect is intrinsic. Apparent differences in the field dependence of the MR above and below $T_N$ may be reconciled by considering the effect of magnetic polarons. The model developed by Wagner *et al.*[18] allows an estimate to be made of the number of spins contained in these polarons in the paramagnetic $[\mathrm{MR}\sim B_J^2(x)\sim M^2]$ and ferrimagnetic regions $[MR\sim B_J(x)]$. Calculations using the magnetoresistance data reported here, lead to a temperature dependence of the spin moment, $J(T)$, (inset of Fig. 4) which shows the behavior expected for magnetic polarons, formed by self-trapping a ferromagnetically aligned cluster in the paramagnetic region.[19]

As the temperature is lowered towards $T_N$, the polaron becomes more stable, grows in size and an increase in the spin moment from $J=5$ at 200 K to $J=28$ at 121 K is observed. This value is considerably larger than that for a bare $\mathrm{Cr}^{3+}$ ion $(J=3/2)$. At the onset of magnetic order the spin moment decreases significantly, and below 100 K suggests the delocalization of magnetic polarons. This leads to the dominance of the naked carrier conduction and a decrease in resistivity below $T_p$. Increasing the magnetic field inhibits polaron formation, reducing the resistivity and therefore increasing the magnetoresistance.

In conclusion, the maximum magnetoresistance in $\mathrm{Cr_2S_{3-x}}$ $(x=0.08)$ is related to an anomaly in $\rho(T)$ and the onset of long-range magnetic order. The resistivity anomaly is associated with sulfur deficiency and the formation of a mixed-valence phase. The magnetotransport properties may be understood by considering a two-fluid model involving both magnetic polarons and naked carriers.

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