Magnetoresistance in the Double Perovskite Sr₂CrMoO₆

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The double perovskite Sr_2CrMoO_6 with Cr^{3+}–O–Mo^{5+} pairs is ferrimagnetic ($T_N = 450$ K), but there is considerable site disorder. The disorder appears to be responsible for the low value of magnetization. At 5 or 6 T, the negative magnetoresistance (MR) is <5% at all temperatures, unlike Sr_2FeMoO_6 which shows MR upto 27%. Tunneling magnetoresistance behavior of Sr_2CrMoO_6 is comparable to that of Sr_2FeMoO_6, but the magnitude is considerably smaller in the former. © 2000 Academic Press

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INTRODUCTION

Following the surge of papers on the colossal magnetoresistance in rare earth manganates, substantial tunneling magnetoresistance (TMR) was reported at room temperature in the double perovskite Sr_2FeMoO_6 [1]. Sr_2FeMoO_6 is a ferrimagnet with a transition temperature (T_N) of 415 K. Electronic structure calculations support the presence of spin-polarized charge carriers in the ground state of this solid. The resistance and magnetoresistance behavior of Sr_2FeMoO_6 is attributed to the dominant role played by the spin-dependent scattering at the grain boundary or the magnetic domain boundary. Apart from the A_2FeMoO_6 (A = Ca, Sr, or Ba) systems [1–4], magnetoresistance studies have been reported on the A_2FeReO_6 with A = Ca, Sr, Ba [5, 6]. All of these compounds are ferrimagnetic with transition temperatures above room temperature.

In Sr_2FeMoO_6, the Fe^{3+} ions ($3d^5$; $t_{2g}^3 e_g^2$; $S = \frac{5}{2}$) contributes localized spin-up electrons while the itinerant spin-down electrons are contributed by the Mo^{5+} ($4d^1$; t_{2g}^1; $S = \frac{1}{2}$). Sr_2FeReO_6 has an electronic structure similar to that of Sr_2FeMoO_6, but with a higher charge carrier density due to the larger number of d electron in the Re^{5+} ion ($5d^2$). This would be expected to affect the magnetoresistance (MR) behavior of this compound, but the values of MR reported in A_2FeReO_6 are low compared to those in

A_2FeMoO_6 [5, 6]. Gracia-Landa *et al.* [7] have recently reported the results of neutron diffraction studies of Sr_2FeMoO_6 which indicate that the Fe atoms occupy the $4a$ position and the Mo atoms the $4b$ position in the ordered perovskite ($Fm3m$) structure. Surprisingly, there appears to be no magnetic contribution from $4b$ sites. Such an observation supports the presence of Fe^{2+}–O–Mo^{6+} pairs in Sr_2FeMoO_6. The mechanism for exchange interaction would, however, be different for the Fe^{3+}–O–Mo^{5+} pairs compared to the Fe^{2+}–O–Mo^{6+} pairs. We have investigated the magnetotransport properties of the double perovskite Sr_2CrMoO_6 in comparison with those of Sr_2FeMoO_6. The major difference between these two oxides is that in the Cr compound, there can be no valence compensation between the Cr and the Mo ions, since Cr can only be in the 3+ state (t_{2g}^3). This requires Mo to be in the 5+ state in Sr_2CrMoO_6, thereby limiting the system only to the Cr^{3+}–O–Mo^{5+} pairs. Sr_2CrMoO_6 is also reported to exhibit a magnetic transition around 473 K [8].

EXPERIMENTAL

Polycrystalline samples of Sr_2CrMoO_6 were prepared by two methods. Sr_2CrMoO_6 (I) was prepared by heating a thoroughly ground mixture of $SrCO_3$, MoO_3, and Cr_2O_3 at 1173 K in air for 3 h, following Kobayashi *et al.* [1] in the case of Sr_2FeMoO_6. The product so obtained was ground, pelletized, and heated at 1473 K for 2 h in a flowing H_2/Ar (14:86 cm³/mm) atmosphere. Preparations of both Sr_2CrMoO_6 and Sr_2FeMoO_6 could be obtained by this procedure. A sample of Sr_2CrMoO_6 was made under similar conditions by annealing at 1473 K for 6 h in a flowing H_2/Ar (14:86 cm³/mm) atmosphere. In many of the Sr_2CrMoO_6 (I) samples the particle size was relatively small. Some of the samples prepared by the procedure of Kobayashi *et al.* [1] had $SrMoO_4$ impurity. Sr_2CrMoO_6 (II) was prepared by a two-step procedure. A precursor oxide of the composition $Sr_2CrO_{3.5}$ was prepared by heating $SrCO_3$ and Cr_2O_3 at 1273 K in air. The resultant oxide was mixed with stoichiometric quantities of MoO_3 and MoO_2

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to obtain Sr_2CrMoO_6 (II). Pellets were heated at 1273 K in an evacuated sealed silica tube for 7 days with intermediate grinding to obtain a pure phase.

Powder X-ray diffraction (XRD) data were collected with a Siemens 5005 X-ray powder diffractometer. Patterns of Sr_2CrMoO_6 with and without $SrMoO_4$ are given in Fig. 1. Rietveld refinement on the data set was carried out using the GSAS software suite (9). Four-probe dc electrical resistivity as well as magnetoresistance measurements were carried out using a cryo-cooled superconducting magnet. Magnetic susceptibility measurements were carried out with a Lewis Coil Force Magnetometer. Magnetization measurements were carried out using a vibrating sample magnetometer (Lakeshore VSM 7300).

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the polycrystalline samples of Sr_2CrMoO_6 and Sr_2FeMoO_6 are shown in Fig. 1. The diffraction patterns could be indexed on a cubic $Fm3m$ lattice of the double perovskite structure. We have carried out Rietveld refinement of the powder X-ray data of several of the Sr_2CrMoO_6 samples along with Sr_2FeMoO_6. The calculated profiles gave reasonably good fits as can be seen from Fig. 1. The atomic coordinates and R values for Sr_2CrMoO_6 are compared with those of Sr_2FeMoO_6 in Table 1. The R values as well as the goodness of fit ($\chi^2 \geq 0.95$) are quite satisfactory. From the Rietveld refinement of the X-ray data, the percent order in the Sr_2CrMoO_6 (I) and Sr_2FeMoO_6 was found to be 65 and 80, respectively. In an early report in the literature (8), 50% ordering was reported in Sr_2CrMoO_6.

In Fig. 2a, we show the electrical resistivity data of the Sr_2CrMoO_6 samples I and II, prepared by the two methods. The resistivity of Sr_2CrMoO_6 (I) decreased on annealing for a longer duration (6 h), possibly due to oxygen loss creating Cr^{3+}–O–Mo^{4+} units. We have therefore given the results of the sample of Sr_2CrMoO_6 (I) annealed for 2 h along with those of the Sr_2CrMoO_6 (II) prepared by the two-step procedure. The resistivity of sample I is an order of magnitude lower than that of sample II.

In Fig. 3, we show the dc magnetic susceptibility of a Sr_2CrMoO_6 (I) sample. In the inset we show the inverse susceptibility behavior. The compound is ferrimagnetic, with a transition temperature of ~450 K. The effective magnetic moment (μ_{eff}), calculated from the high-temperature data in the paramagnetic phase, is 2.94 BM. This value is low compared to the expected μ_{eff} of 4.24 BM for Cr^{3+} and Mo^{5+}. The low μ_{eff} value can be explained if we assume the presence of Cr^{3+}–O–Mo^{5+} pairs in the paramagnetic state with a ferrimagnetic type of interaction between the

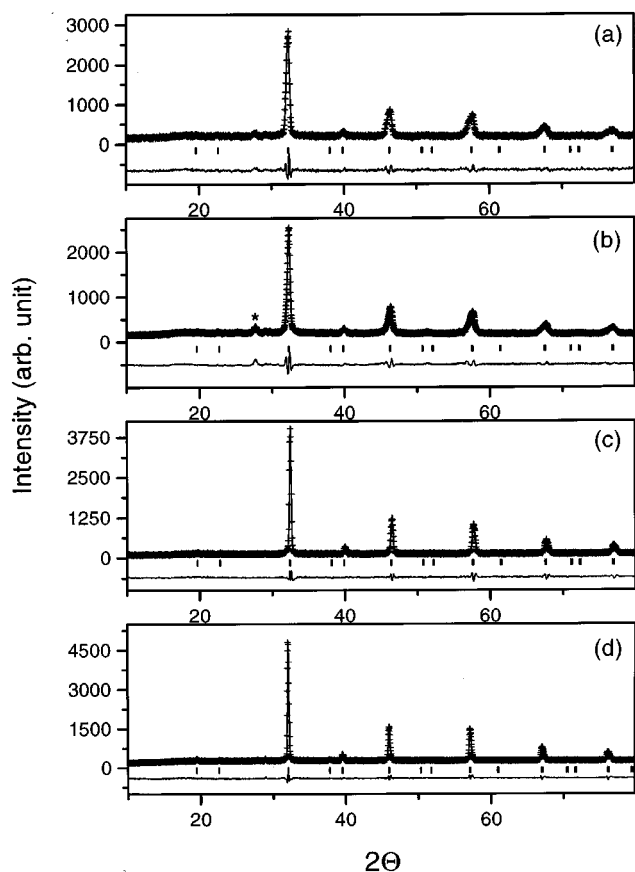FIG. 1. X-ray diffraction patterns of (a,b) two samples of Sr_2CrMoO_6 (I), (c) Sr_2CrMoO_6 (II), and (d) Sr_2FeMoO_6. The calculated profiles and the difference curves obtained from Rietveld analysis are shown. Asterisk indicates line due to $SrMnO_4$ impurity.

TABLE 1
Atomic Coordinates of Sr_2CrMoO_6 and Sr_2FeMoO_6 Samples

	Atom	Site	x	y	z	Frac
$Sr_2CrMoO_6{}^a$	Sr	8c	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	1.00
	Cr	4a	0	0	0	0.65(3)
	Mo	4a	0	0	0	0.35(3)
	Cr	4b	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.35(3)
	Mo	4b	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.65(3)
	O	24e	0.253(4)	0	0	1.00
$Sr_2FeMoO_6{}^b$	Sr	8c	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	1.00
	Fe	4a	0	0	0	0.80(4)
	Mo	4a	0	0	0	0.20(4)
	Fe	4b	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.20(4)
	Mo	4b	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.80(4)
	O	24e	0.251(4)	0	0	1.00

$^a a = 7.840(3)$; $wR_p = 6\%$; $R_p = 4\%$. The fit was good for Sr_2CrMoO_6 (I) with or without $SrMoO_4$, and also for Sr_2CrMoO_6 (II). One could refine the structure on the basis of a monoclinic cell with additional data, but the R values were roughly the same.
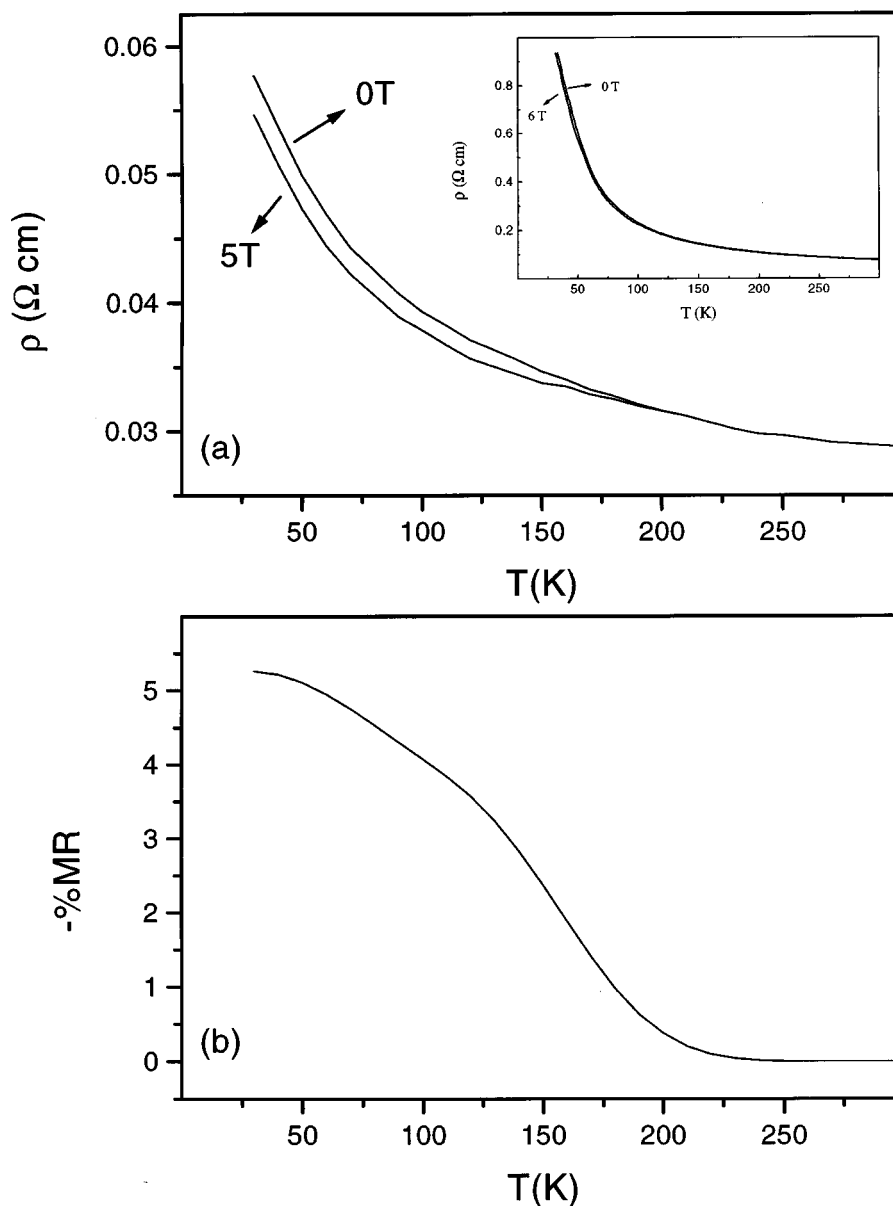$^b a = 7.899(1)$; $wR_p = 4\%$; $R_p = 3\%$.

FIG. 2. (a) Temperature variation of resistivity of the Sr_2CrMoO_6 (I) sample annealed for 2 h. Effect of a magnetic field of 5 T is shown. Resistivity data of Sr_2CrMoO_6 (II) prepared by the two-step procedure are shown in the inset. (b) Plot of $-\%MR$ against temperature for Sr_2CrMoO_6 (I) annealed for 2 h.

two ions. A μ_{eff} of 2.94 BM would result if 94% of the ions form Cr^{3+}–O–Mo^{5+} pairs. Annealing for a longer period (6 h) reduced the μ_{eff} possibly due to the presence of Cr^{3+}–O–Mo^{4+} pairs along with Cr^{3+}–O–Mo^{5+} pairs. From the magnetization measurements carried out with a vibrating sample magnetometer at a field of 1 T, we could obtain the magnetic moments in the ferrimagnetic phase of Sr_2CrMoO_6. The magnetic moment for the sample was 0.2 BM/(formula unit) at 45 K. This value is much lower than the expected value of 2.0 BM for the fully ordered phase of Sr_2CrMoO_6. On the other hand, the magnetic moment for Sr_2FeMoO_6 is ~ 1.9 BM at a field of 1 T at

300 K and reaches a value of ~ 2.9 BM at 4.2 K (1). Magnetization data of Sr_2CrMoO_6 (II) was no better than that of I. The low value of the magnetic moment in the case of Sr_2CrMoO_6 can arise from the absence of long-range magnetic ordering due to site disorder in the double perovskite.

The effect of magnetic fields on the electrical resistivity of the Sr_2CrMoO_6 samples prepared by the two methods is shown in Fig. 2a. We see that a magnetic field of 5 or 6 T causes only a small decrease in resistivity in the both of the samples. The magnetoresistance of Sr_2CrMoO_6 (I) at 5 T is plotted against temperature in Fig. 2b. The magnitude of MR at the lowest temperature is considerably smaller
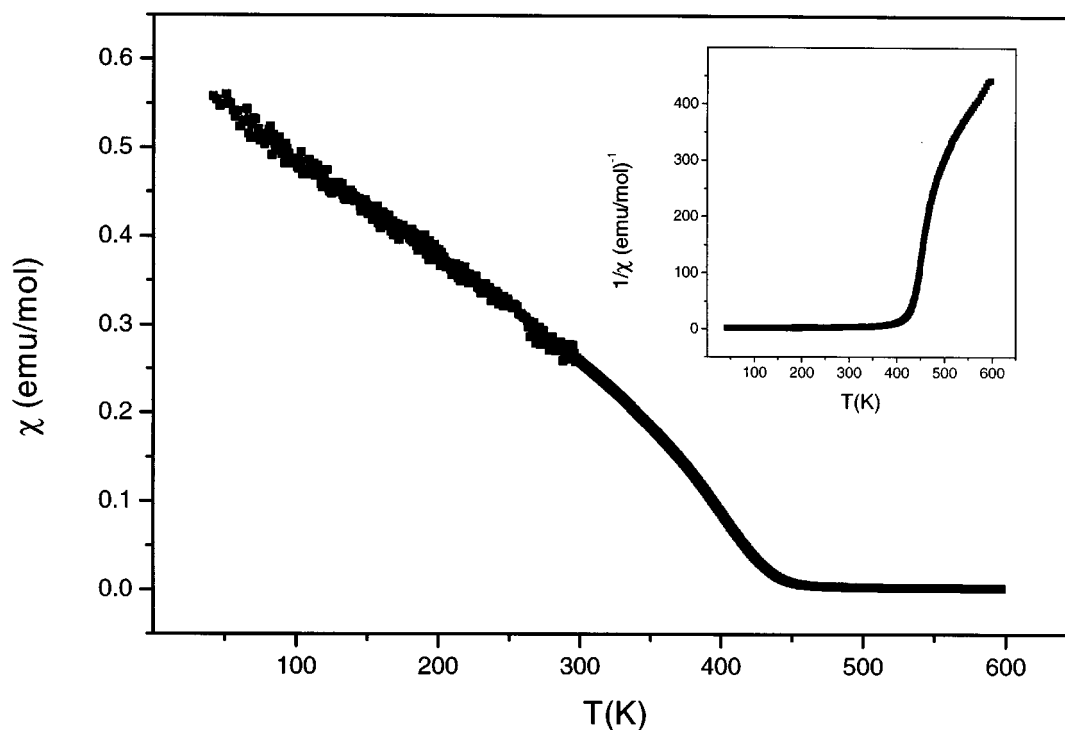
FIG. 3. Temperature variation of the magnetic susceptibility of the Sr_2CrMoO_6 (I) sample.

(2–5%) than that of Sr_2FeMoO_6 (~27%). The presence of $SrMoO_4$ impurity in sample I does not appear to affect the magnitude of MR significantly just as in Sr_2FeMoO_6 (1, 7, 10). Garcia-Landa et al. (7) do not find the effect of $SrMoO_4$ impurity on MR in their sample of Sr_2FeMoO_6, even though the impurity was as much as 10%. We found little effect of the magnitude of $SrMoO_4$ impurity on the properties of Sr_2CrMoO_6 (I). The magnitude of magnetoresistance of Sr_2CrMoO_6 (II) without any $SrMoO_4$ is even smaller

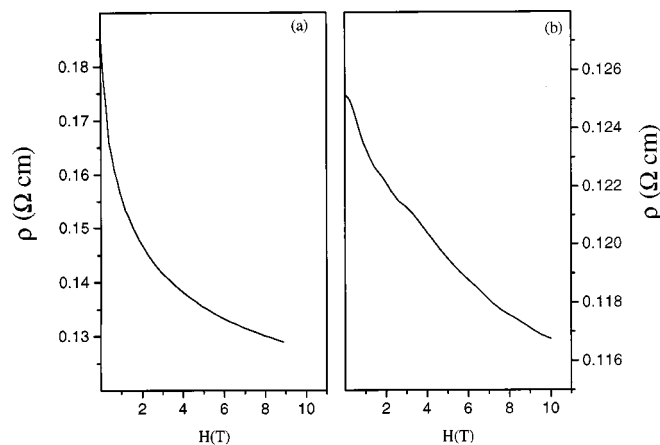than in I, being less than 2%. Part of the reason for the low MR values in the Cr compound may be site disorder. Disorder is known to lower the MR in Sr_2FeMoO_6 as well (11).

In Fig. 4, we show the resistivity–magnetic field plots at 40 K for Sr_2FeMoO_6 and Sr_2CrMoO_6 (I) annealed for 2 h and exhibiting maximum MR. The $\rho(H)$ curves are similar, showing that tunneling magnetoresistance (TMR) occurs in both of these materials. The resistivity of Sr_2FeMoO_6 changes from $0.185\,\Omega$ cm to $0.129\,\Omega$ cm in a magnetic field of 9 T ($-\%MR \approx 30$). The resistivity of Sr_2CrMoO_6, on the other hand, changes from $0.125\,\Omega$ cm to $0.117\,\Omega$ cm ($-\%MR \approx 6$). The difference in the magnitude of MR may also be related to the greater site disorder in Sr_2CrMoO_6.

In conclusion, the double perovskite Sr_2CrMoO_6, where there can be no valence compensation between Cr and Mo ions, shows the effect of disorder on the magnetization and magnetoresistance, in that the values of both are rather small. The low value of the TMR in this compound is also likely to be related to disorder effects.

FIG. 4. Variation of the resistivity with magnetic field in (a) Sr_2FeMoO_6 and (b) Sr_2CrMoO_6 (annealed for 2 h).

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