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Magnetic and electric properties of Sr_2FeMoO_6

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Abstract

We present electrical resistivity (ρ) and magnetic susceptibility (χ) data of the Sr_2FeMoO_6 double perovskite. We found that the as prepared sample shows semiconducting $\rho(T)$ in the whole temperature range and a magnetoresistance behavior typical of electron tunneling at the grain boundaries (gb). When the oxygen of the gb is removed ρ drops one order of magnitude. Below the magnetic ordering temperature $T_C \approx 405$ K and above 590 K this sample is metallic ($d\rho/dT > 0$), while for $T_C < T < 590$ K we observe a weak localization. The $\chi(T)$ data follow the Curie–Weiss law only in a short temperature range above T_C. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Grain boundaries; Electrical resistivity; Magnetoresistance

Recently, polycrystalline samples of an ordered double perovskite Sr_2FeMoO_6 were reported as a promising material for practical devices due to the presence of magnetoresistance (MR) at room temperature (RT) [1]. Early magnetic [2], Mössbauer and neutron diffraction [3] experiments showed that Sr_2FeMoO_6 is ferrimagnetic with Fe^{3+} and Mo^{5+} electronic configuration. A band calculation [1] predicts half-metallic band structure, where the charge carriers are highly spin polarized even at RT ($T \leqslant T_C$). In this case the MR is related to electron tunneling [4] through the energy barrier generated by the grain boundaries.

We present magnetic and electric properties of Sr_2FeMoO_6. A powdered sample was prepared by the solid state reaction route. The raw materials were mixed and heated at 950°C in a 10% H_2/Ar atmosphere. A final heat treatment at 1150°C under vacuum was done for 12 h.

X-ray diffraction data at RT were refined by the Rietveld method [5] assuming the I4/m space group. The obtained lattice parameters were $a = b = 5.5770(2)$ Å and $c = 7.9053(3)$ Å.

Electrical resistivity (ρ) was obtained by the standard four probe method. Magnetization (M) data were measured in a home-made Faraday balance with a magnetic field $H = 5$ kOe.

In Fig. 1a, we show the $\rho(T)$ curve of the as prepared sample. The insulating character of the electrical properties in the whole T range is obvious. At $T_C \approx 405$ K, no features are visible in ρ. The MR in the magnetic ordered phase (Fig. 1b) shows the typical behavior of electron tunneling through the barriers formed by the grain boundaries (gb) [4]. The half-metallic character of this compound [1] favors this transport mechanism. According to this picture, it is reasonable to think that the $\rho(T)$ curve of Fig. 1a is determined by the scattering at the gb [6].

Therefore, the bulk electrical resistivity (ρ_b) data were obtained after heating the sample up to 900 K under a vacuum of 10^{-6} Torr. During this process the oxygen at the gb is removed. The resulting $\rho_b(T)$ curve on cooling can be seen in Fig. 2a. It can be noted that at RT, ρ_b is

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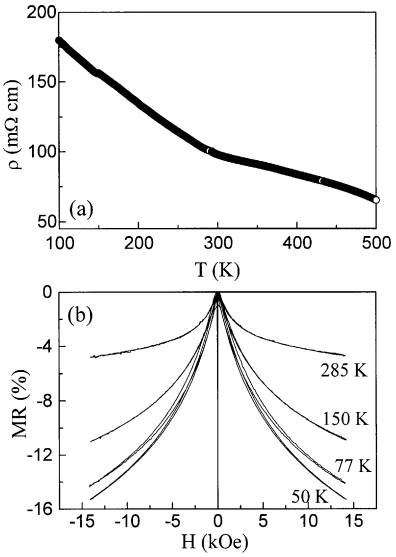

Fig. 1. (a) $\rho(T)$ curve for the as prepared sample. (b) Magnetoresistance at several $T < T_C$.

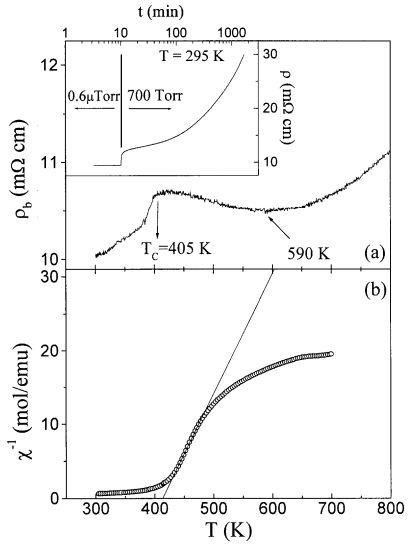

Fig. 2. (a) Bulk resistivity vs. T, obtained under vacuum. Inset: Time evolution of ρ at RT when the vacuum is broken. (b) $\chi^{-1}(T)$ curve. The straight line represents a Curie–Weiss law.

10 times lower than the ρ measured before the heat treatment (Fig. 1a). Below $T_C \approx 405(10)$ K, $\rho_b(T)$ presents a metallic behavior. Above this temperature can be seen a localization of the electrical carriers ($d\rho/dT < 0$) up to $T \approx 590$ K, where the material becomes metallic again.

A proof of the influence of the oxygen content at the gb is the curve shown in the inset of Fig. 2a. There we show the time evolution of ρ at RT, having initially the sample under vacuum ($\rho \approx \rho_b$). When we broke the vacuum to atmospheric pressure, ρ began to increase notably with time. This behavior is due to the incorporation of oxygen at the gb, increasing the gb resistivity ρ_{gb} and affecting the total electrical resistivity $\rho = \rho_{gb} + \rho_b$.

The M vs. T data were used to determine the Curie temperature as the inflection point in the $M(T)$ curve. The obtained critical temperature was $T_C \approx 405(4)$ K. In Fig. 2b, we plot the inverse of the magnetic susceptibility $\chi^{-1} = H/M$ as a function of T, and it is observed that it does not follow a Curie–Weiss (C–W) law at all. The linear $\chi^{-1}(T)$ behavior only applies in a small temperature range, showing a deviation at higher T. This deviation probably indicates the coexistence of localized spins with itinerant electrons adding a constant value to χ. A band calculation [1] shows that the 4d electrons of the Mo^{5+} ions should be partially filling the conduction band. These observations could indicate that these electrons are itinerant.

The semiconducting region in Fig. 2a could be related to a weak Anderson localization [7,8] with an associated gap of ~ 3 meV. This localization should be induced by some disorder in the Fe and Mo sites [9], or by the presence of oxygen vacancies. At $T \approx 590$ K the Fermi level equals the energy of the mobility edge and the compound becomes metallic again. In a completely ordered perovskite without gb effect, it should be metallic in the whole T range.

According to this picture, the paramagnetic susceptibility should be $\chi = \chi_{loc} + \chi_{it}$, where the first term is the contribution of the localized moments (they should present a C–W dependence) and the second term is the metallic contribution, for which we expect a constant value. A more deep insight must be gained in order to understand this behavior at high T.

In summary, we have presented electrical resistivity and magnetic susceptibility data for the Sr_2FeMoO_6 double perovskite. We found that this compound is very sensitive to oxidation and ρ is strongly dominated by the carrier scattering at the gb. When the oxygen atoms placed at the gb are removed, we observe two metal–insulator transitions, being metallic below $T_C \approx 405$ K and above 590 K. For intermediate T, the system presents a possible Anderson localization of the carriers with semiconducting behavior. Above T_C, a deviation of $\chi(T)$ from the Curie–Weiss law could be showing the coexistence of localized and itinerant electrons.

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