

BRIEF COMMUNICATION

Large Intragrain Magnetoresistance above Room Temperature in the Double Perovskite Ba₂FeMoO₆

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Large intragrain magnetoresistance (MR) in the ordered double perovskite, Ba₂FeMoO₆, is shown for the first time. The latter appears near T_C (340 K), i.e., above room temperature. This effect originates from a double-exchange-like mechanism, based on antiferromagnetic coupling of localized high spin $3d^5\text{Fe}^{3+}$, and itinerant $4d^1\text{Mo}^{5+}$ species. Besides this bulk MR, low field tunneling MR at lower temperatures ($T < 250$ K), due to grain boundary effects, is also observed with large values of MR comparable to those previously observed for Sr₂FeMoO₆. Such a coexistence of both effects, intragrain and intergrain magnetoresistance, might extend to all members of this double perovskite family, suggesting the possibility of optimizing the MR for working at room temperature in a low magnetic field, by tuning the T_C of solid solutions of such perovskites. © 1999 Academic Press

The discovery of colossal magnetoresistance (CMR) in the manganites with the perovskite structure has stimulated the research on ferromagnetic metallic oxides. Such materials are indeed useful for the realization of magnetoelectronic devices and particularly, for magnetic storage applications. The spectacular decrease of resistance, by several orders of magnitude (1), by applying a magnetic field in these compounds, is an intragrain property which requires values of the magnetic field ($H > 2\text{T}$) that are too high for applications. In order to reach a sufficiently large magnetoresistance effect of low magnetic field, tunnel junctions and grain boundary properties were investigated, showing the existence of large low field magnetoresistance (2–6), but operating at rather low temperatures ($T < 150$ K). In a recent study of the double perovskite Sr₂FeMoO₆, Kobayashi *et al.* (7) have shown that this metallic ferromagnet (8–9) exhibits large low-field room temperature magnetoresistances due to grain boundary effects. Considering the localized high spin $3d^5$ configuration of Fe³⁺ and the itinerant $4d^1$ configuration of Mo⁵⁺, an antiferromagnetic coupling between these species can explain both metallicity

and ferromagnetism in this compound. Such a mechanism is similar to double exchange (DE) (10) so that bulk magnetoresistance should be expected, in addition to what has been observed by the authors. Bearing in mind that the maximum magnetoresistance effect in manganites often appears close to the Curie temperature (T_C), we believe that the authors have not seen the effect because they stopped their observations at 294 K, T_C being much higher for Sr₂FeMoO₆ (475 K). In order to check this point we have investigated the ferromagnetic metallic double perovskite Ba₂FeMoO₆ (8–9) whose T_C is much smaller (330 K) (8). In this communication, we show that this double perovskite exhibits large magnetoresistance in two temperature ranges, in the 10–250 K range, due to grain boundary tunneling, and close to $T_C \cong 330$ K, due to intragrain high-spin polarization of electrons.

Polycrystalline Ba₂FeMoO₆ ceramics were prepared according to the standard solid state reaction, starting from a stoichiometric mixture of BaO₂, Fe₂O₃, MoO₃, and Mo, pressed in the form of bars, heated in evacuated silica ampules progressively at 300°C per hour up to 1100°C, and sintered at this temperature for 10 h.

The X-ray powder diffraction (XRD) pattern registered with a Philips diffractometer using CuK α radiation and the electron diffraction (ED) study performed with a JEOL 200 CX electron microscope confirm that this phase is an ordered perovskite with a cubic symmetry ($a \sim 8$ Å). The reconstruction of the reciprocal space (ED) at room temperature evidences a cubic cell with $a \sim 2a_p$. The conditions limiting the reflection, $hkl: h + k, k + l, l + h = 2n$ are consistent with the space groups $F23$, $Fm3$, $F432$, $F\bar{4}3m$, and $Fm3m$. The energy dispersive analyses confirm that the actual cationic composition of the perovskite related crystallites is close to the nominal composition “Ba₂FeMo” and is homogeneous over all of the sample. The cell parameters were refined from XRD data, in the $Fm3m$ space group, leading to $a = 8.0579(2)$ Å. The ED investigation was

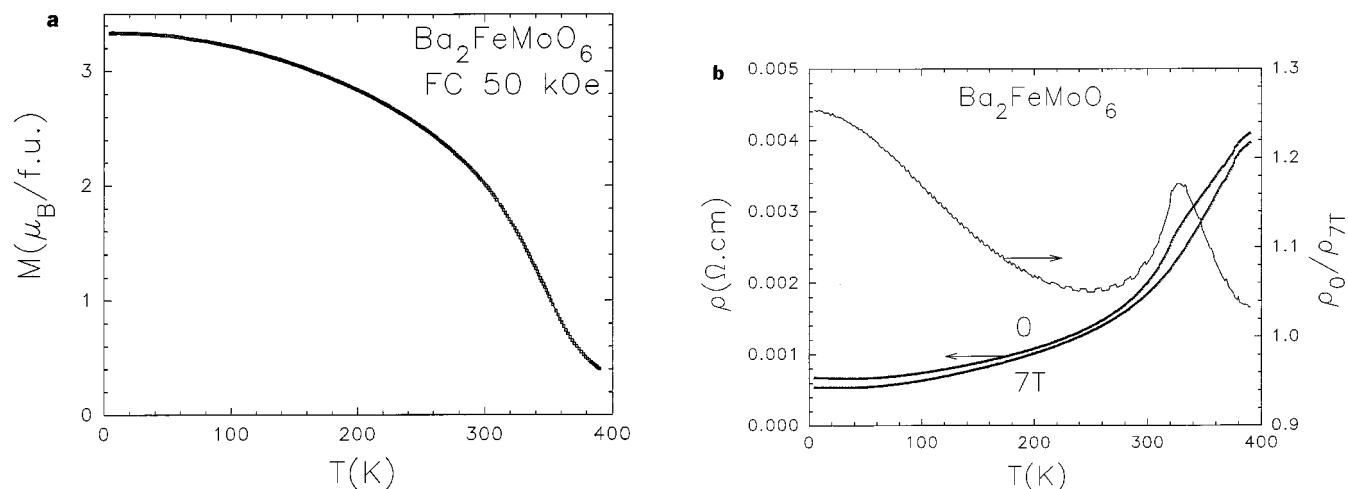


FIG. 1. (a) Temperature (T) dependent magnetization (M) of the as-prepared $\text{Ba}_2\text{FeMoO}_6$ double perovskite registered on cooling in 5 T. (b) Temperature dependent resistivity (ρ) registered upon cooling in the absence of magnetic field and in 7 T. The T dependent ρ_0/ρ_{7T} ratio is also shown (right y axis).

also carried out by warming the sample up to 350 K and cooling down 250 K; no significant structural transformation was detected at T_C .

The resistance and magnetic measurements as a function of temperature, performed with the four probe technique and a SQUID magnetometer Quantum Design respectively, are shown in Fig. 1. The $M(T)$ curve of this phase (Fig. 1a) confirms its ferrimagnetic behavior, with a magnetic moment at 5 K of $3.32 \mu_B$ per ($\text{Fe}^{3+}-\text{Mo}^{5+}$), i.e., slightly smaller than the theoretical value ($4 \mu_B$) and a T_C close to 330 K. The $\rho(T)$ curves at 0 and 7 T (Fig. 1b) confirm metallicity over the whole temperature range, from 5 to 390 K, and show a significant magnetoresistance effect at 7 T. More importantly, starting from 5 K the magnetoresistance, ρ_0/ρ_{7T} (Fig. 1b, y axis), tends to decrease as T

increases, being at a minimum around 250 K, and then increases again reaching a maximum around $T_C \cong 330$ K.

The results of the resistance measurements versus magnetic field at different temperatures are shown in Fig. 2. Two temperature ranges can be distinguished. In the 10–250 K domain (Fig. 2a), a large negative magnetoresistance characterized by an abrupt drop at low fields is observed, followed by a slower decrease in higher field. Moreover, the slope of the drop in low fields increases significantly as T decreases. These results are very similar to those observed by Kobayashi *et al.* (7) for $\text{Sr}_2\text{FeMoO}_6$ and can be attributed to the result of grain boundary effects, as stated by these authors. In the second temperature range (Fig. 2b), from 280 to 350 K, a large negative MR is also encountered. More importantly, the slope of the $\rho(H)$ curves increases as

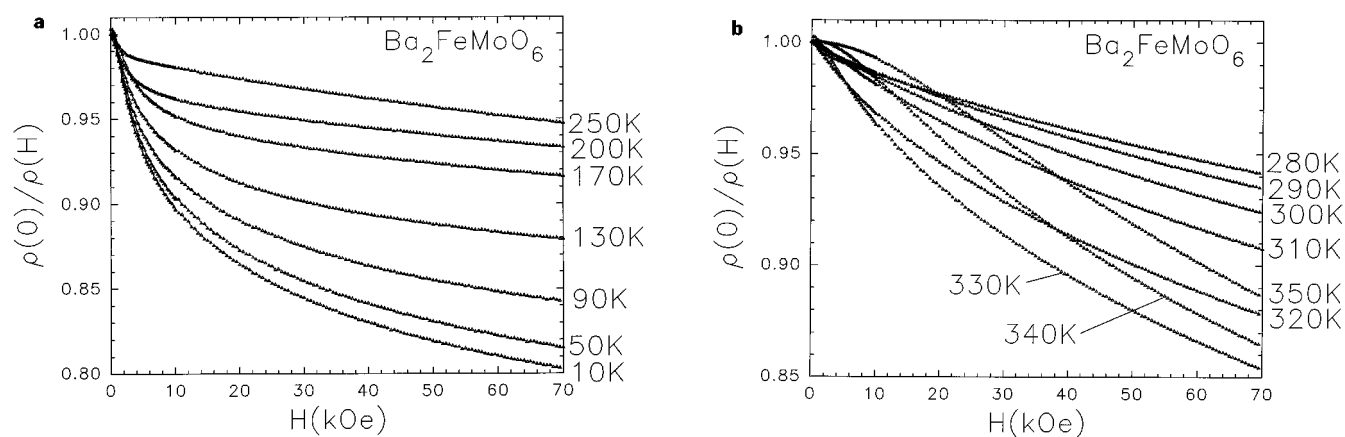


FIG. 2. Magnetic field (H) dependence of the resistivity ratio $\rho(0)/\rho(H)$. T values are labeled on the graph. (a) $10 \leq T \leq 250$ K; (b) $280 \leq T \leq 350$ K.

T increases from 280 to 330 K and then decreases again rapidly as T further increases, to 350 K. The drop in resistance at 1 T is maximal at 330 K, close to T_C . The large MR of this phase under 7 T, of 15% at 330 K (Fig. 2b), is quite remarkable compared to the 9% value at 300 K for $\text{Sr}_2\text{FeMoO}_6$ in the same magnetic field (7). These results, and especially the abrupt disappearance of MR just above T_C , i.e., at 350 K strongly suggest that this second kind of MR is correlated with T_C , and consequently appears inside the grains, arising from the DE-like mechanism described above.

The $M(H)$ curves of this compound (Fig. 3) show that far below T_C , the ferromagnetic state is easily reached. If a type of DE mechanism holds in this double-perovskite, the core spins are aligned at these temperatures, and since the carriers are not scattered, the kinetic energy of the carriers is maximal (11). However, close to T_C , large magnetic fields are required to align the spins (Fig. 3) so that the carrier kinetic energy is gradually increased with the magnetic field, leading to a progressive resistivity decrease.

In order to check the hypothesis of bulk MR based on DE mechanism, we have also plotted the temperature dependence of the normalized magnetoresistance in 0.2 and 1 T (Fig. 4). The constant decrease of the MR as T increases is consistent with intergranular magnetoresistance of these polycrystalline materials (7) in low magnetic field, as shown for the 0.2 T curve, which decays roughly as the square of magnetization (Fig. 4, right y axis). However, this intergranular MR cannot explain the magnitude of the MR peak exhibited at T_C , which increases as the magnetic field is increased from 0.2 to 1 T. This clearly demonstrates that the MR maximum observed at T_C is a direct consequence of the

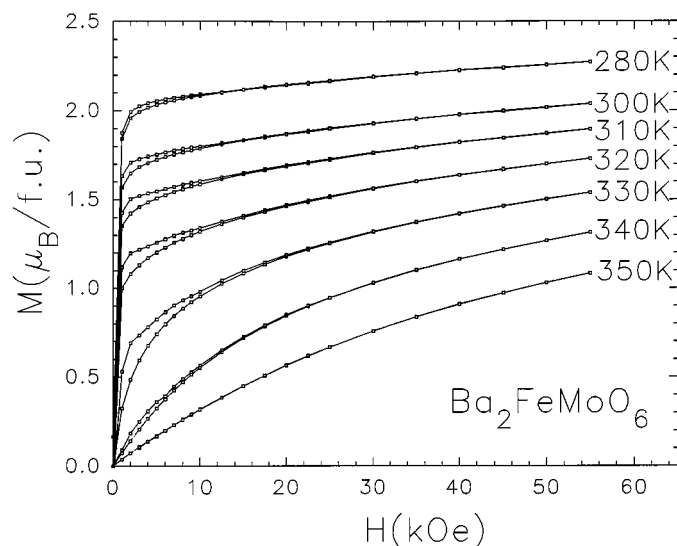


FIG. 3. $M(H)$ curves. T values are labeled on the graph.

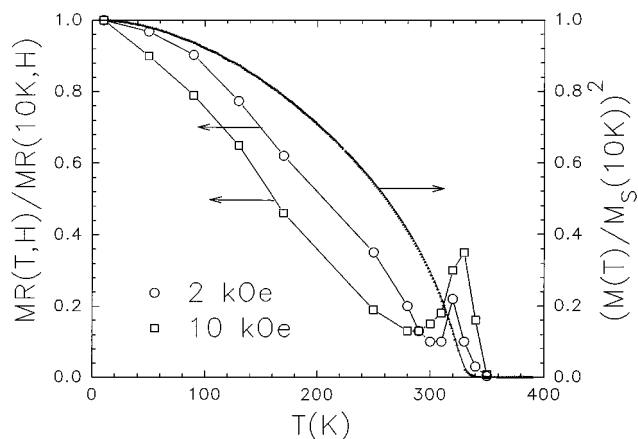


FIG. 4. Temperature T dependent normalized magnetoresistance $\text{MR}(T, H)/\text{MR}(10 \text{ K}, H)$ curves for $H = 0.2 \text{ T}$ and $H = 1 \text{ T}$ (left y axis). The square of the reduced magnetization $M(T, 0.2)/M_S$ is also given (right y axis).

reduction in intragrain carrier scattering as the local moments tend to align in a magnetic field.

Taking into consideration such a coexistence of intergranular and intragranular MR in this phase, it should be possible to change the intergranular MR without affecting the intragranular effect near T_C . Postannealing treatments in Ar/H_2 at 1000°C have thus been performed in order to modify the intergranular connections. The $\rho(T)$ curves after annealing (Fig. 5) show a large increase of the resistivity compared to the as-synthesized material, with a maximum corresponding to T_C , leading to semiconducting behavior above T_C , due to the deterioration of the grain boundaries. More importantly, the ρ_0/ρ_{7T} resistivity ratio (compare Fig. 5 and Fig. 1b) shows that a large increase of MR is achieved far below T_C due to grain boundary effect, whereas by contrast the MR is slightly decreased at T_C by postannealing.

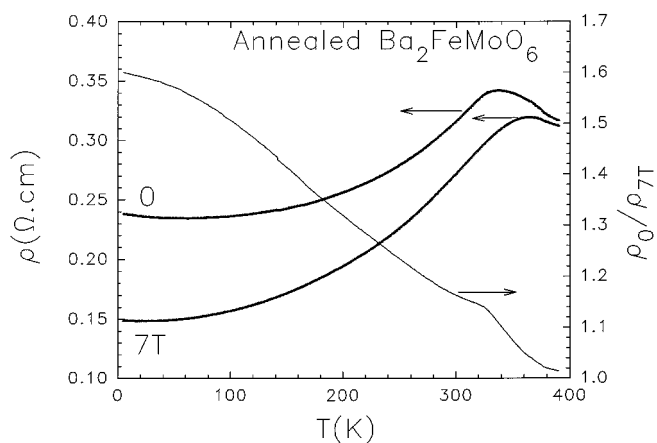


FIG. 5. $\rho_0(T)$, $\rho_{7T}(T)$ and $\rho_0(T)/\rho_{7T}(T)$ curves for the postannealed $\text{Ba}_2\text{FeMoO}_6$ oxide.

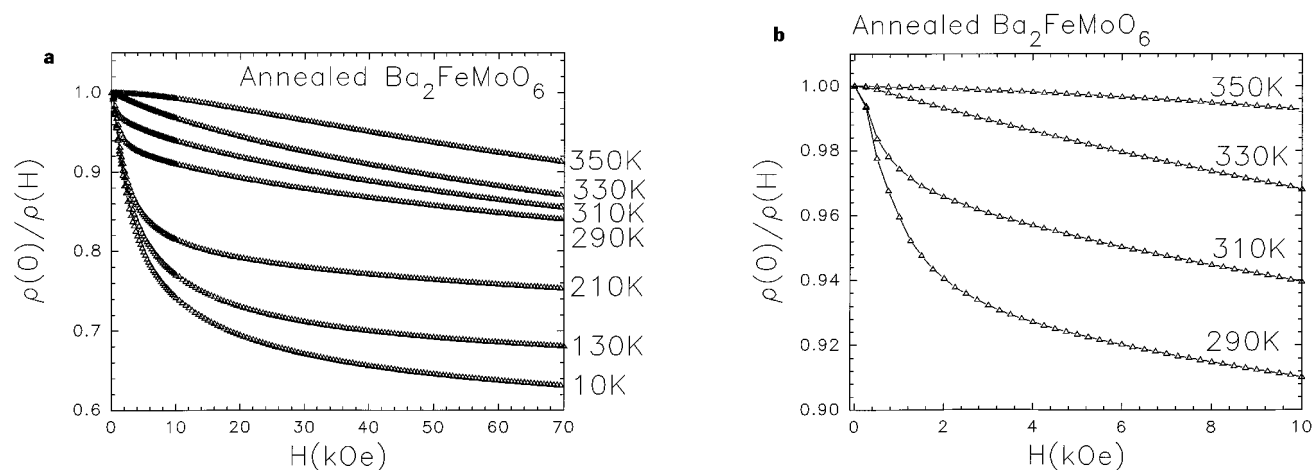


FIG. 6. (a) MR ratio $\rho(0)/\rho(H)$ for the Ar/H₂ flow annealed sample. (b) Expansion of low magnetic field region for the 290 K curve showing the large intergranular MR at low fields.

This confirms that the MR at T_C is mainly intragranular. It is worth pointing out that the low field MR of the intergranular regions (Fig. 6a) is significantly increased in comparison with the as-prepared sample (Fig. 2), as shown from the respective $\rho(0)/\rho(H)$ sets of data. The negative MR in 7 T of 20% for the as-prepared sample increases to 37% after annealing, i.e., reaches a value higher than that of Sr₂FeMoO₆ at 4.2 K (30%) (7) even though the T_C of the latter is higher, by 100 K. More importantly from the application point of view, the MR value of the annealed Ba₂FeMoO₆ reaches 4% in only 0.1 T at 290 K (Fig. 6b).

In conclusion, we have shown that the double perovskite Ba₂FeMoO₆ ceramic exhibits two types of magnetoresistance: low field tunneling magnetoresistance due to grain boundary which takes place rather far below T_C , and intragrain magnetoresistance which appears close to T_C , in the present case above room temperature. Both effects are large and should be combined for applications. It is most probable that the results obtained here for Ba₂FeMoO₆ could be extended to other ferrimagnetic double perovskites, suggesting that optimization should be reached by tuning the T_C of solid solutions of these compounds.

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