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Magnetoresistance effect in the fluctuating-valence $BaSmFe_2O_{5+w}$ system

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The occurrence of negative magnetoresistance (MR) in semiconductive $BaSmFe_2O_{5+w}$ double-perovskite samples is demonstrated. A peak in the MR value was observed at the Verwey-type transition temperature. The transition signifies the charge separation of the $Fe^{2.5+}$ fluctuating mixed valence state into high-spin Fe^{2+} and Fe^{3+}. The samples were ferrimagnetic with a Curie temperature of ~ 710 K. Upon oxidizing/reducing the samples the size of the MR peak and the temperature at which the peak occurred varied. The largest MR value observed was 1.4% at 7 T. © *2000 American Institute of Physics.* [S0003-6951(00)03837-7]

The double-perovskite cuprate $BaY(Cu_{0.5}Fe_{0.5})_2O_5$ was first discovered by Er-Rakho *et al.*[1] Despite many attempts superconductivity has not been induced in this phase, due to the fact that 30%–50% Fe is needed to stabilize the phase.[2] However, this so-called 0112 phase was successfully synthesized with 100% Fe at the transition metal site and Sm or Nd at the rare-earth site.[3] Also the pure Co-based phase $BaRECo_2O_{5+w}$ has been obtained.[4] Furthermore, oxidized samples of the Co-based 0112 phase exhibit intragrain colossal magnetoresistance (CMR) at temperatures where the magnetic ordering competes between ferro- and antiferromagnetism.[5] In the samples exhibiting the optimal magnetoresistance (MR) properties the Co valence was reported to be close to 3+, as judged by the oxygen content. Recently a Verwey-type mixed-valence or valence-fluctuation state, formally expressed as $Fe^{2.5+}$, was observed in the $BaSmFe_2O_{5+w}$ oxygen-deficient double-perovskite system.[6] In samples with a reduced oxygen content $w \approx 0$ equal amounts of Fe atoms adopt valence states of 3+ and 2+ on a single lattice site. ^{57}Fe Mössbauer spectra recorded at room temperature were nevertheless dominated by a single magnetic component which formally can be assigned to the valence state $Fe^{2.5+}$. Upon cooling the samples down below the Verwey-type transition temperature, T_V (~ 200 K) charge separation occurs and expected amounts of divalent and trivalent iron were found in the Mössbauer spectra.[6] The fluctuating $Fe^{2.5+}$ valence state was recently observed in the Sr_2FeMoO_{6-u} system as well.[7] This double-perovskite phase is better known for its spin-polarized giant tunneling magnetoresistance (TMR).[8] In the following the experimental evidence for a new kind of MR effect related to the $Fe^{2.5+}$ state in the $BaSmFe_2O_{5+w}$ phase is presented.

The preparation of the $BaSmFe_2O_{5+w}$ samples is reported elsewhere.[9,10] In brief, high-purity powders of $BaCO_3$, Sm_2O_3, and Fe_2O_3 were mixed and calcined twice at 900 °C for 15 h in argon with an intermediate grinding. The calcined powders were pelletized and encapsulated in evacuated fused-quartz ampoules containing Fe grains. The Fe grains were used as getters realizing the expected oxygen partial pressure of 7.6×10^{-16} atm[11] during the 40 h heat treatment at 985 °C. In addition to the as-synthesized sample a reduced sample was synthesized. This was done by annealing as-synthesized powder for 5 h in a reducing 5% H_2/Ar atmosphere at 600 °C. The annealing was carried out using a thermobalance (MAC Science TG/DTA 2000S).

The phase purity of the samples was confirmed by x-ray diffraction. According to the TG results the portion of excess oxygen corresponds to $w \approx 0.0$ and 0.1, for the reduced and as-synthesized samples, respectively. For the reduced sample no weight loss was seen in TG, indicating a complete removal of excess oxygen, whereas an earlier Mössbauer study revealed the presence of some excess oxygen atoms, the amount of which was estimated to $w \approx 0.04$.[10] This oxygen content value is henceforth used for the reduced sample. The amount of excess oxygen for the as-synthesized sample, as determined by Mössbauer spectroscopy was in accordance with the TG value.

For the four-probe resistivity measurements the samples were pelletized under a pressure of 10 MPa. Afterwards they were ground into the shape of oblong parallelepipeds with a cross section of $2-5$ mm^2. Gold electrode pads were deposited directly on the sample surface. During the deposition the spacing between the electrodes was controlled by wrapping a Teflon film around the sample. The distance between the pads was set to be 0.1–0.3 mm. Ag leads were attached to the Au pads with Ag paste. The actual measurements were carried out using a standard four-probe technique. The measurement was performed using a physical property measurement system (Quantum Design PPMS). The measurements were repeated several times both in field- and temperature-scan mode. The detection limit of magnetoresistance was estimated to at least 0.05%, for the current semiconductive samples. The external magnetic field was varied from -7 to $+7$ T. The field direction was perpendicular to the direction of current flow.

The magnetization measurements were performed using a direct-current (dc) superconducting quantum interference device (SQUID) (Quantum Design MPMS-5S) in the temperature range 5–300 K. For dc susceptibility measurements the external field was set at 1000 Oe. The $M-H$ property

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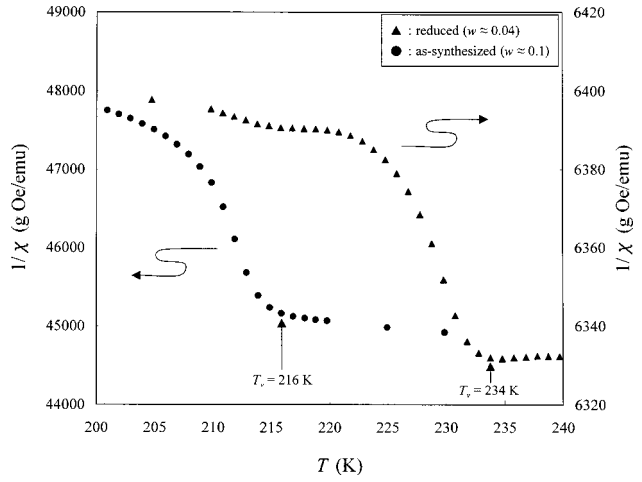

FIG. 1. Inverse magnetic dc susceptibility of the reduced and as-synthesized samples. The Verwey–type transition temperature is indicated in the plots.

was measured at 5 K with an external applied field ranging from 0 to 3.5 T. Additionally the saturation magnetization of the samples was measured in the temperature range 5–300 K using an external field of 1.5 T. A magnetic-balance apparatus based on the Faraday method was used for checking the dc magnetization in the temperature range 300–1000 K.

The Verwey-type transition is clearly observed in the susceptibility curves of both samples (Fig. 1). The discontinuity in the susceptibility curves corresponds well to the transition temperature of the charge-separation reported previously.[6] In particular the shift of T_V as a function of the oxygen content agrees with the earlier results. The saturation magnetization of the reduced sample was estimated at $0.14\,\mu_B$ by extrapolating to $H=0$ on the M vs H curve. Both samples were attracted to a permanent magnet, indicating ferrimagnetic ordering. Judging by the magnetic-balance data the Curie temperature of the samples is ~ 710 K.

In Fig. 2 the results from the resistivity vs temperature measurements of the two $BaSmFe_2O_{5+w}$ samples are shown using a logarithmic y scale and inverse temperature. At $T \approx T_V$ there is a change in the activation energy, E_a, which results in a strong increase in the slope of the curves. An estimate of the activation energy can be obtained using the following expression for the sample resistivity, ρ:

$$\rho = \rho_0 \exp(E_a / k_B T), \tag{1}$$

where ρ_0 is a constant and k_B Boltzmann's constant. In the temperature region above T_V the plot appears to be linear as expected for a semiconductor. The slopes correspond to activation energies of 0.18 and 0.33 eV for the as-synthesized and reduced samples, respectively. Below T_V the dependence deviates from a linear one, but at least for the as-synthesized sample the activation energy is higher than above the transition temperature. The deviation from a linear dependence at $T<T_V$ may suggest that the charge carriers propagate by a hopping mechanism. Additionally a hysteretical behavior in the region around the transition temperature is observed, which could be related to a frustration effect caused by the charge separation.[6]

The magnetoresistance effect is clearly visible in the resistivity curves of Fig. 2. In particular in the transition region the external field of 7 T served to reduce the resistivity value, Fig. 2. In order to obtain the magnitude of the MR effect the samples were measured at fixed temperatures by scanning the field. The MR value is defined as

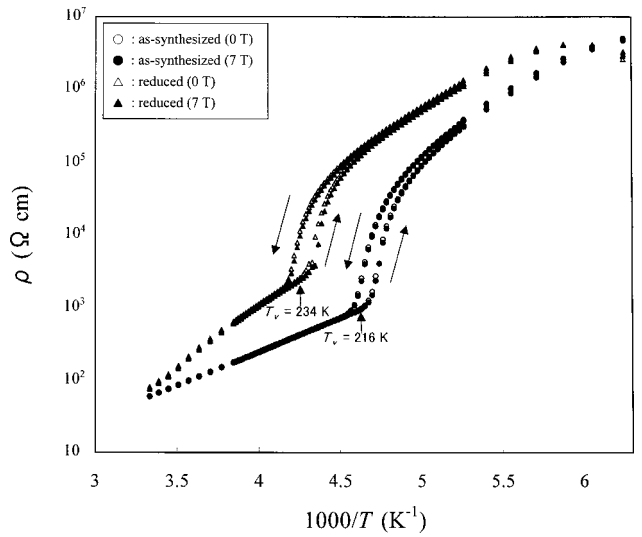

FIG. 2. Sample resistivity vs inverse temperature for the reduced and as-synthesized samples, recorded in external fields of 0 and 7 T.

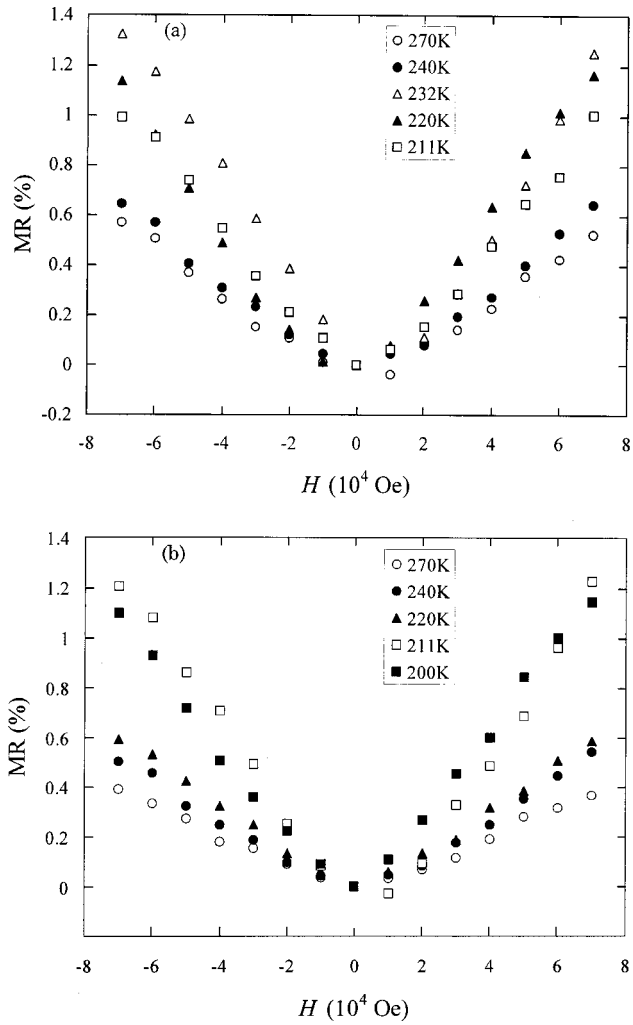

FIG. 3. MR vs external field H curves obtained at various fixed temperatures for the (a) reduced and (b) as-synthesized samples.

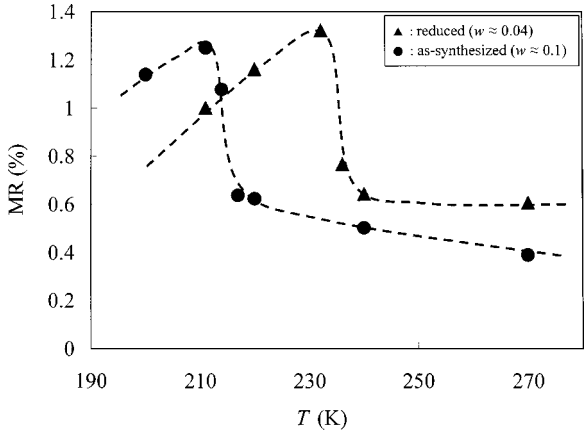

FIG. 4. The maximal MR values obtained at 7 T vs temperature, for the reduced and as-synthesized samples. Lines are drawn as guides for the eye.

$$\mathrm{MR}(T,H)=\frac{\rho(T,0)-\rho(T,H)}{\rho(T,H)}\cdot 100\%, \tag{2}$$

where H denotes the external field. In Fig. 3 the resulting MR curves are presented for various temperatures. For both samples a peak in the MR value occurs at $T\approx T_V$. The peak at T_V becomes evident in a plot of the MR values (recorded for $H=7$ T) versus temperature. The result is given in Fig. 4, and the data of Fig. 3 was used for plotting it.

The origin of the current MR effect, *albeit* small, is believed to be different from that of the CMR[12] and TMR[13] systems. In the former the MR effect is closely connected to a magnetic transition, e.g., competition between ferro- and antiferromagnetism,[14] or between ferro- and paramagnetism. In addition to this the conductivity is substantially different for the competing phases and the location of the transition point itself is sensitive to the external field. Therefore the sample resistance also depends on the applied magnetic field. Materials exhibiting TMR effects are half-metals, i.e., the charge carriers are spin polarized. The scattering of charge carriers at grain/domain boundaries is therefore tunable by an external magnetic field, thus leading to a magnetic field-dependent sample conductivity. The magnetization data of the present samples exhibit an increase of $\sim 1\%$ when T_V is passed from below, otherwise there is no sign of competition between various types of magnetic ordering. Contrary to the CMR and TMR systems the origin of magnetoresistance in the present case is likely to be directly connected to the charge–separation transition itself. Half-metallic features may indeed be present, but the occurrence of a peak at $T=T_V \ll T_C$ is not expected for half-metallic systems. On the contrary, the MR values for half-metals are found to decrease as a function of increasing temperature.[8]

The highest MR value obtained thus far for the $BaSmFe_2O_{5+w}$ system was 1.4%, in the reduced sample. From earlier studies on the Verwey transition, it is known that the oxygen content w strongly affects the Verwey-type transition temperature.[6] Future endeavors will therefore focus on the influence of oxygen content and transition metal/rare earth site doping on the value of MR. Due to the fact that the present system has a Curie temperature of ~ 710 K, it may be possible to increase the Verwey–type transition temperature and thus the temperature regime in which the magnetoresistance shows a peak.

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