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Published in:
Applied Physics Letters

DOI:
10.1063/1.1310170

Published: 01/01/2000

Please cite the original version:
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Citation: Appl. Phys. Lett. 77, 1683 (2000); doi: 10.1063/1.1310170
View online: http://dx.doi.org/10.1063/1.1310170
View Table of Contents: http://aip.scitation.org/toc/apl/77/11
Published by the American Institute of Physics
Magnetoresistance effect in the fluctuating-valence BaSmFe$_2$O$_{5+w}$ system

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(Received 12 May 2000; accepted for publication 17 July 2000)

The occurrence of negative magnetoresistance (MR) in semiconductive BaSmFe$_2$O$_{5+w}$ 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 ferromagnetic with a Curie temperature of $\sim 710$ 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.

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The double-perovskite cuprate BaY(Cu$_{0.5}$Fe$_{0.5}$)$_2$O$_5$ was first discovered by Er-Rakho et al. 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. 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. Also the pure Co-based phase BaCo$_2$Fe$_2$O$_6$ has been obtained. 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. 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$_2$O$_{5+w}$ oxygen-deficient double-perovskite system. In samples with a reduced oxygen content $w = 0$ equal amounts of Fe atoms adopt valence states of 3+ and 2+ on a single lattice site. 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. The fluctuating Fe$^{2.5+}$ valence state was recently observed in the Sr$_2$FeMoO$_6$ system as well. This double-perovskite phase is better known for its spin-polarized giant tunneling magnetoresistance (TMR). In the following the experimental evidence for a new kind of MR effect related to the Fe$^{2.5+}$ state in the BaSmFe$_2$O$_{5+w}$ phase is presented.

The preparation of the BaSmFe$_2$O$_{5+w}$ samples is reported elsewhere. In brief, high-purity powders of BaCO$_3$, Sm$_2$O$_3$, and Fe$_2$O$_3$ 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 $7.6 \times 10^{-10}$ atm 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 $w \approx 0.04$. 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 parallelepips 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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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. 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 \( \sim 710 \) K.

In Fig. 2 the results from the resistivity vs temperature measurements of the two BaSmFe\(_2\)O\(_5\)\(_{1+w}\) samples are shown using a logarithmic \( y \) scale and inverse temperature. At \( T = T_V \) 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, \( \rho \):

\[
\rho = \rho_0 \exp\left(\frac{E_a}{k_B T}\right),
\]

where \( \rho_0 \) 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.

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
The highest MR value obtained thus far for the BaSmFe$_2$O$_{5+\delta}$ system was 1.4%, in the reduced sample. From earlier studies on the Verwey transition, it is known that the oxygen content $\delta$ strongly affects the Verwey-type transition temperature.\textsuperscript{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 $\sim$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.

Professor Shunri Oda is gratefully acknowledged for allowing the authors to use his equipment in the magnetoresistance measurements. Useful discussions with Professor A. Kjekshus and Professor P. Karen of University of Oslo concerning the mixed-valence state of iron are gratefully acknowledged. The present work was supported by a Grant-in-Aid for Scientific Research (Contract No. 11305002) from the Ministry of Education, Science, and Culture of Japan, and also by an International Collaborative Research Project Grant-1999 of the Materials and Structures Laboratory, Tokyo Institute of Technology. Two of the authors acknowledge kind support from the Japan Society for the Promotion of Science (I. L.) and the Academy of Finland (M. K.; decision No. 46039).

\begin{equation}
\text{MR}(T,H) = \frac{\rho(T,0) - \rho(T,H)}{\rho(T,0)} \cdot 100\%, \tag{2}
\end{equation}

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, \emph{albeit} small, is believed to be different from that of the CMR\textsuperscript{12} and TMR\textsuperscript{13} systems. In the former the MR effect is closely connected to a magnetic transition, e.g., competition between ferro- and antiferromagnetism,\textsuperscript{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 $T = T_V \leq T_C$ 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.\textsuperscript{8}

\begin{table*}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Sample & MR value & Transition temperature & Remarks \\
\hline
Reduced & 1.4\% & $T_V \approx 710$ K & \textsuperscript{6} \\
As-synthesized & 1.0\% & $T_V \approx 680$ K & \textsuperscript{6} \\
\hline
\end{tabular}
\caption{Summary of measured MR values and transition temperatures.}
\end{table*}

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