Conductivity of $La_{1-x}Ca_xMnO_3$ under magnetic resonance of Mn ions

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Change of the electrical conductivity, σ, is observed in the manganese perovskite $La_{1-x}Ca_xMnO_3$ with $x = 0$ and 0.3 under saturation of the magnetic resonance transitions of Mn ions. This effect has the maximum in the temperature range of the magnetic phase transition of the compounds. Two contributions to the change of σ are found. The first, dominating in $LaMnO_3$, is an increase of σ caused by heating of the sample under magnetic resonance. The second is a σ decrease due to reorientation of the Mn spins, observed in $La_{0.7}Ca_{0.3}MnO_3$.

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Recently, much interest has been devoted to properties of the mixed valence compound $La_{1-x}Ca_xMn^{3+}_{1-\delta}Mn^{4+}_{\delta}O_3$ (LCMO) due to appearance of "colossal" magnetoresistance at the paramagnetic-ferromagnetic (PM/FM) transition. The ferromagnetic coupling is strongest at $x \approx 0.3-0.4$, which gives the maximum Curie temperature $T_C \approx 250$ K [1]. The correlation between conductivity and magnetic ordering of Mn ions has been attributed to the double–exchange mechanism [2–4] with association of the Jahn–Teller interaction to take into account the electron–lattice interaction [5] and the formation of lattice polarons [6,7]. Recently it was shown [8,9] that the sharp decrease of the resistance of $La_{1-x}Ca_xMnO_3$ ($0.15 < x < 0.4$) near T_C can be explained by collapse of the carrier density due to the tendency of polarons to form immobile bound pairs in the PM phase and dissociation of the pairs in the FM phase.

As follows from all the presented models, the resistivity, $\rho(T)$, of the manganese perovskites depends strongly on the average spin projection $\langle S_z \rangle$ of Mn ions. EPR investigations in the PM phase of LCMO [10–13] show that all Mn^{3+} and Mn^{4+} ions contribute to a broad unresolved EPR line, characterized near room temperature with a g-factor about 2 and a linewidth $\Delta B_{pp} = 10-20$ mT. The shape and width of this line depend on the Ca doping (x), on the temperature, and on the sample preparation. Accurate measurements of the EPR line intensity show that the magnetic susceptibility is proportional to $\langle S_z \rangle$ and coincides with the susceptibility of the Mn system determined by dc-magnetometry [12]. When the temperature is lowered towards the PM/Fm transition the amplitude and the width of the EPR line increase gradually. Upon passing T_C the EPR line broadens remarkably attaining the width of $\Delta B_{pp} = 100-200$ mT. An additional broad line with $g > 2$ attributed to the FM phase [13] is usually observed below the PM/FM transition.

In the PM phase ($T > T_C$), where the EPR line of the Mn ions is well detectable, the value of $\langle S_z \rangle$ can be changed by a resonant microwave field strong enough to saturate the EPR transitions. A consequent change can be observed in $\rho(T)$ using electrical contacts on the sample. This technique of electrical detection of magnetic resonance (EDMR) gives direct information about the relation between transport properties and the average spin projection of Mn ions and allows us to detect the contribution of the magnetic field to the conductivity of LCMO in relatively weak magnetic fields $B < 1$ T. So far the EDMR method has been used only for investigation of paramagnetic centers in semiconductors. In this Letter we report the first observation of a change of $\rho(T)$ induced by microwave resonance field in manganese oxide perovskites.

Ceramic samples of $La_{1-x}Ca_xMnO_3$ with $x = 0$ and 0.3 were synthesized by mixing stoichiometric amounts of high-purity oxides La_2O_3, $CuCO_3$, MnO_2 and heating them for 35 h at 1320°C with intermediate grindings. Then the powder was pressed into a pellet, sintered for 22 h at 1375°C in air and finally annealed for 13 h at 1520°C. For the EDMR investigations samples of the size $0.5 \times 0.5 \times 0.5$ mm were cut from the pellet and provided with electrical contacts soldered with In on two opposite ends. The magnetic properties of the samples were investigated by rf-SQUID magnetometer.

The EDMR experiments were performed with an EPR spectrometer at the microwave frequency of 9.024 GHz and powers up to $P \cong 400$ mW, employing 100 kHz field modulation with the amplitude of $B_m \approx 1$ mT. The spectrometer allows simultaneous observation of the usual EPR spectra and changes of σ under scanning the magnetic field B. To establish a stable measurement current of $I = 0.1-20$ mA, in the geometry of $\mathbf{I} \parallel \mathbf{B}$, a dc-voltage, V, was applied to the contacts through a load resistor $R_L > 10R_S$, where R_S is the resistance of the sample. The amplitude of the voltage oscillating between the ends of the sample at the 100 kHz field modulation frequency was detected by a lock-in amplifier, allowing us to observe only the field-dependent part of R_S. The temperature of the sample was varied between $70-300$ K in a helium gas-flow cryostat.

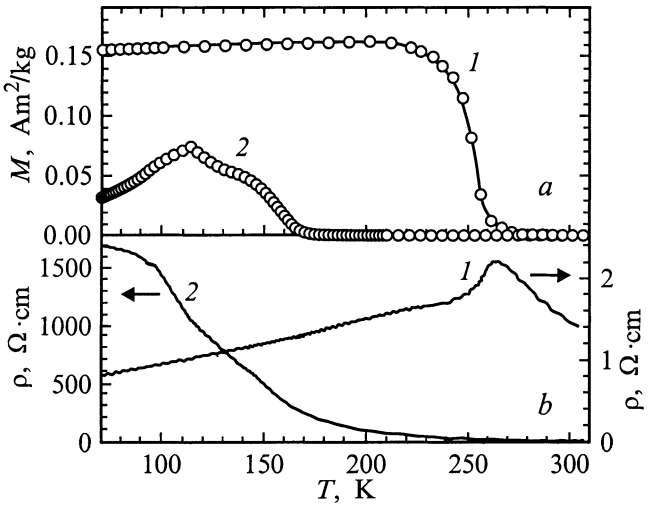

Figure 1. Temperature dependences of the magnetic moment M (a) and the resistivity ρ (b) for $La_{0.7}Ca_{0.3}MnO_3$ (*1*) and $LaMnO_3$ (*2*).

Fig. 1, *a* shows the temperature dependence of the magnetic moment, $M(T)$, for the $La_{0.7}Ca_{0.3}MnO_3$ and $LaMnO_3$ samples, measured in the field $B = 0.2$ mT after zero field cooling. From these data the PM/FM transition with $T_C \approx 250$ K can be clearly observed for LCMO with $x = 0.3$. The magnetic anomaly observed in $LaMnO_3$ below $T \cong 170$ K and the decrease of $M(T)$ for $T < 120$ K can be attributed to antiferromagnetic ordering. The temperature dependences of ρ measured directly in the cavity of the EPR spectrometer at $B \cong 0$ are plotted in Fig. 1, *b*. These measurements were made by two point contact method and the resistivity of the contacts can give the contribution to the measured values. The resistivity of $La_{0.7}Ca_{0.3}MnO_3$ has a drop below $T \cong 250$ K corresponding to the PM/FM transition. The resistivity of $LaMnO_3$ shows semiconductor like behavior for $T < 300$ K.

The change of ρ under magnetic resonance was found in $La_{0.7}Ca_{0.3}MnO_3$ for microwave powers $100 < P < 400$ mW. The EDMR signals observed at $T = 275$ and 250 K for opposite directions of the current I are shown in Fig. 2, *b, c, e, f*. The shape of these signals repeats that of the EPR line of Mn ions with $g \approx 2$ (curves *a* and *d*). The change of the sign of the EDMR signal, S, when I is reversed, can be explained simply by 180° phase shift of the alternating (100 kHz) voltage appearing over the sample. This confirms that the EDMR signal really originates from a change of ρ under saturation of the EPR transitions. The sign of this change was established independently in the same installation by comparing the sign of the EDMR signal with the sign of the resonance change of the photoconductivity by spin-dependent recombination in irradiated silicon [14]. According to this experiment the resistivity of $La_{0.7}Ca_{0.3}MnO_3$ increases under magnetic resonance.

The amplitudes of the EPR and EDMR signals increase when the temperature decreases from 300 to 250 K. Below T_C the EPR and EDMR lines are considerably broadened and disappear below $T \cong 220-230$ K. The amplitude of the EDMR line, S, increases roughly linearly with the square root of the microwave power up to $P \cong 400$ mW whereas the EPR line exhibits usual saturation behavior [15] already above $P \cong 20$ mW. Under saturation of the EPR transitions the ratio of Mn ions with spin-up and spin-down orientations decreases. This leads to a decrease of $\langle S_z \rangle$ and, consequently, to the decrease of σ, in accordance with the proposed models [2–9]. Relative change of the resistance of the sample under magnetic resonance, $\Delta R_S/R_S$, is $\sim 10^{-3}$ which is surprisingly low taking into account the much larger change of $\Delta\langle S_z \rangle/\langle S_z \rangle \sim 0.1-0.3$ estimated from the saturation of the EPR line.

As can be seen from Fig. 2 (traces *e, f*) an additional change of the background signal, G, depending on the magnetic field, is observed at $T = 250$ K. This is the contribution of the magnetoresistance to the total resistivity of the sample. The electrically detected signals S and G show different dependences on the value of I (Fig. 3). While S exhibits a saturation at $I \cong 5$ mA, G has no saturation up to $I = 50$ mA. This suggests that different physical mechanisms are responsible for the EDMR line S and for the magnetoresistance signal G. The limitation of S when I increases, as well as the low value of $\Delta R_S/R_S$ can be attributed to scattering of carriers by localized magnetic moments of Mn ions. This interaction can strongly reduce the Mn spin relaxation time and higher microwave power is needed to saturate the EPR transitions. It is equivalent to reduction of $\Delta\langle S_z \rangle/\langle S_z \rangle$ at fixed microwave power. This can

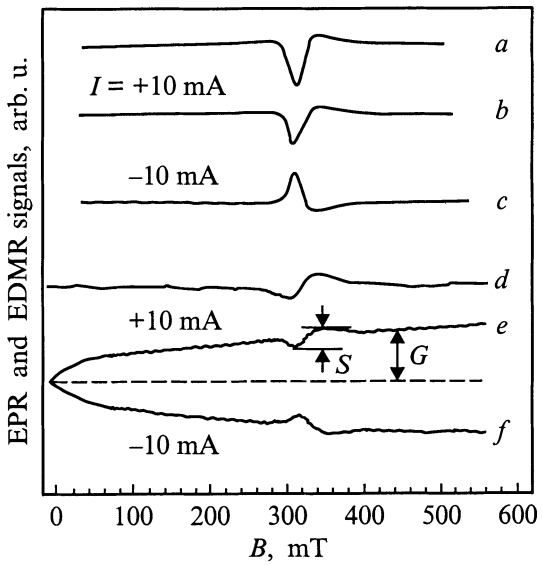

Figure 2. EPR (a, d) and EDMR (b, c, e, f) signals observed in $La_{0.7}Ca_{0.3}MnO_3$ at $T = 275$ (a, b, c) and 250 K (d, e, f) for the currents I obtained by application of a positive and a negative voltage V over the sample. All measurements are made at $P = 400$ mW, sufficient to saturate the Mn EPR transitions.

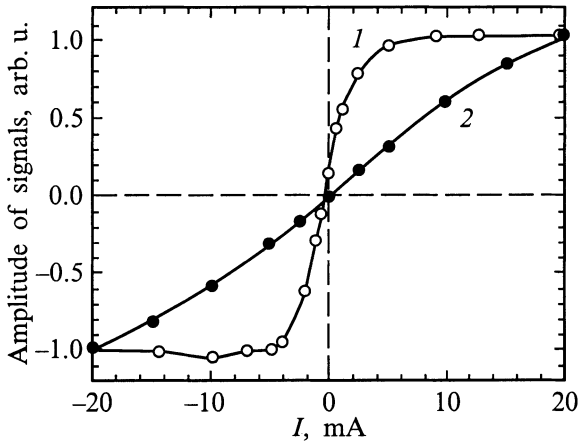

Figure 3. Dependences of the amplitudes of the S (*1*) and G (*2*) signals (Fig. 2) on the value of the *dc*-current I through the $La_{0.7}Ca_{0.3}MnO_3$ sample at $T = 250$ K.

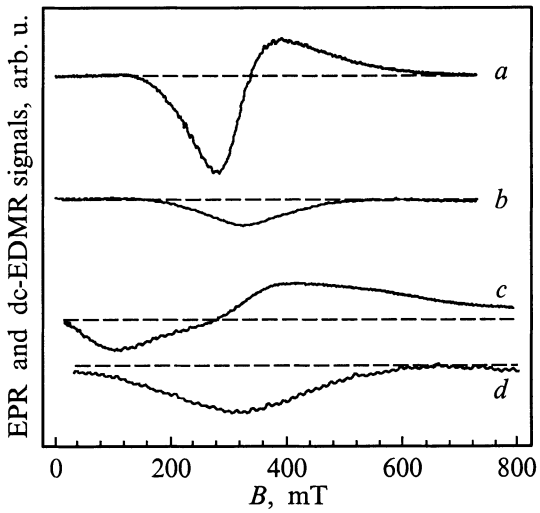

Figure 4. EPR (a, c) and *dc*-EDMR (b, d) signals detected in $LaMnO_3$ at $T = 190$ and 140 K.

explain the saturation of S when I is increased. The G signal does not depend on the microwave resonance condition and is therefore independent on the Mn relaxation time.

The S and D signals, observed at the 100 kHz modulation frequency of B, were not found in $LaMnO_3$. Instead, a strong change of σ was detected between $100 < T < 200$ K when measuring the *dc*-component of I under magnetic resonance. The recorded traces of the EPR signal and the *dc*-resistivity of $LaMnO_3$ are shown in Fig. 4. The resistivity decreases under EPR whereas the EDMR signal in $La_{0.7}Ca_{0.3}MnO_3$ corresponds to an increase of ρ. Taking into account the high sensitivity of ρ on temperature (Fig. 1, b) the EDMR signals in $LaMnO_3$ can be explained with heating of the sample by the microwave field under magnetic resonance of Mn ions.

In conclusion, we have applied for the first time the EDMR method for investigation of the manganese oxide perovskites $La_{0.7}Ca_{0.3}MnO_3$ and $LaMnO_3$. Two contributions leading to EDMR signals of opposite signs are found. The decrease of ρ observed in $LaMnO_3$ is related to heating of the sample by the microwave field under magnetic resonance. Instead, in $La_{0.7}Ca_{0.3}MnO_3$ the increase of ρ is caused by the magnetic resonance reorientation of the Mn spins, in agreement with the DE mechanism [2–4]. Saturation of the EDMR signal when increasing the *dc*-current through the sample and an additional nonresonant change of ρ, related to magnetoresistance, are observed in $La_{0.7}Ca_{0.3}MnO_3$. All these signals have the maximum amplitude near the magnetic phase transitions of the samples.

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