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Effect of pressure and magnetic field on the phase transitions in lanthanum-deficient manganites

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ABSTRACT

We report on the pressure, field and temperature dependencies of magnetization and resistance in manganites of \((La_{1-x}Ca_x)_{1-y}Mn_{1+y}O_3\) type. The \(M(T)\) dependencies is established to exhibit the following peculiarities: the first is connected with the paramagnet (PM) - ferromagnet (FM) transition at 267 K; the peak of \(M(T)\) dependence at 263 K is presumably due to an existence of AFM clusters; an anomaly in magnetization (as well as in susceptibility) is connected with the FM - canted phase transition at 42 K and the large irreversibility in the field-cooled and zero field-cooled magnetization. As field is increased above 200 Oe, the sign of the \(M(T)\) anomaly changes, namely, the \(M(T)\) magnetization increases with increasing field at 42 K. The character of \(M(T)\) dependencies does not change under pressure. However, both the Curie temperature, \(T_c\), and the resistance peak (\(T_{\text{res}}\)) corresponding to metal-insulator transition shift in the direction of high temperatures with increasing pressure. A pressure stabilizes the ferromagnetic metallic phase. The temperature of the FM - cantiing phase transition does not change under pressure. The magnetoresistance effect increases by 15\% under pressure of 12.6 kbar. The linear increasing of \(T_c\) with the derivatives of \(dT_c/dP \approx +1.5 \text{ K} / \text{ kbar}\) in \((La_{0.7}Ca_{0.3})_{1-x}Mn_{1+y}O_3\) and \(dT_c/dP = +1.9 \text{ K} / \text{ kbar}\) in \(La_{0.6}Mn_{1.4}O_3\) ceramics was observed at pressure up to 10 kbar. The \(T_{\text{res}}(P)\) dependencies display a nonmonotonic behaviour with a peculiarity at \(P = 5 \text{ kbar}\).

Keywords: pressure, magnetic transition, magnetization, resistance, manganite, canted phase.

1. INTRODUCTION

The hole-doped manganites \(La_{1-x}A_xMnO_3\) where La is the lanthanide and A is the alkaline-earth ion were in fact extensively studied in the 1950s for their remarkable magnetic and electrical behaviour. Among the perovskites, the La-Ca-Mn-O system has been explored mostly these last years owing to both the colossal magnetoresistance (CMR) effect and occurrence both ferromagnetic (FM) and metal-insulator (MI) transitions at rather high temperatures. The \(La_{1-x}Ca_xMnO_3\) compounds with \(0.1 \leq x \leq 0.3\) transform from an antiferromagnetic (AFM) insulator to a FM metal. In these compounds AFM and FM interactions are competing to give the complicated magnetic structures when not only FM and AFM, but canted structure (for certain compositions and temperatures) can be exist.

The magnetic behavior of the lanthanum-manganese oxides is determined by several factors such as the kind of cation (trivalent or divalent or monovalent) substitution for La and the percentage of the n-valent doped ions. The substitution of the Mn ions by other transition metal ions gives also rise to important modifications in the magnetic properties.

In this paper, to modify the \(\text{Mn}^{3+}\) / \(\text{Mn}^{4+}\) ratio less traditional method, namely, the method connected with the provision of superfluous manganese content was used. As a result of Mn-doping, the optimum conditions for the double exchange interaction also take place what corresponds to the higher temperature of FM and MI transitions.

It should be noted that the magnetic properties of the La-deficient compounds have so extensively been not investigated including under high pressure. Therefore, the main purpose of this paper is to report the effect of magnetic field and pressure on the character of magnetic phase transitions in the perovskites with superfluous manganese content of \((La_{0.7}Ca_{0.3})_{1-x}Mn_{1+y}O_3\) type. These experiments is expected to provide new information to understand magnetic properties of these materials.

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2. SAMPLE PREPARATION AND CHARACTERIZATION

The \((\text{La}_{0.7}\text{Ca}_{0.3})_{1-x}\text{Mn}_{1.2+x}\text{O}_3\) samples were prepared by a ceramic technology using the double synthesizing annealing (at 900 - 950°C) and sintering in air at 1150°C with the subsequent slow cooling. All specimens were examined by X-ray diffraction with CuKα radiation. The room temperature X-ray diffraction patterns show that the samples are single-phase with close to cubic structure (the lattice parameter of \(a = 3.8674 \text{ Å}\)). The Mn-doping does not change the structural symmetry and leads to a decrease in the \(a\) parameter in comparison with the parent oxide \(\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3\). Magnetization, \(M(T,H)\), measurements were performed using a vibrating sample magnetometer over a temperature range of 4.2-300 K. The zero-field-cooled (ZFC) and field-cooled (FC) magnetization was measured in magnetic fields from 2 to 10 kOe. Real and imaginary parts of the ac susceptibility were measured employing a mutual induction method with an excitation field \(h_{ac} = 5.0 \text{ Oe}\) at various frequencies. The magnetic measurements were carried out on pressed powder pellets of cylindrical shape \((d = 3 \text{ mm, } l = 6 \text{ mm})\). Resistance of the epitaxial films as a function of temperature, pressure and magnetic field was measured using the conventional Dc four-probe method. For magnetic measurements under hydrostatic pressure (10 GPa) was used the specially constructed microcontainer of the piston-cylinder type \((d_{int} = 1.4 \text{ mm, } d_{ext} = 4 \text{ mm, } l = 60 \text{ mm})\). Similar container \((d_{ext} = 6 \text{ mm, } d_{ext} = 30 \text{ mm, } l = 120 \text{ mm})\) was used for study of transport properties up to 21 kbar. The pressure was tested at low temperature measuring the \(T_c\) change of Sn-probe placed near the sample inside the channel of pressure cell.

3. RESULTS

3.1. Effect of magnetic field on the phase transitions in \((\text{La}_{0.7}\text{Ca}_{0.3})_{0.8}\text{Mn}_{1.2}\text{O}_3\) manganite

The measurements of zero field cooled (ZFC) magnetization were performed after cooling of the sample from room temperature to 4.2 K in zero magnetic field, and then warming at the given magnetic field. The field cooled (FC) magnetization of the sample cooled was measured during slow cooling in the applied magnetic field from 300 to 4.2 K. It was observed that the low-temperature magnetization depends on the sample FC 0.5 kOe cooling conditions. In Fig. 1, the temperature dependencies of \(M_{ZFC}\) and \(M_{FC}\) magnetization measured in fields of 100 and 500 Oe are presented. A spontaneous magnetization appears below \(T_c = 270\) K. The FM - paramagnetic (PM) phase transition determined as an inflection point of the \(M\) vs \(T\) curve occurs at \(T_c \approx 263\) and 258 K, respectively. These values are above \(T_c\) of related compound \(\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3\) which is equal to 245K. The FC curve indicates that the ZFC ferromagnetism extends slowly below 250 K. It should be noted a clear irreversibility of \(M_{FC}(T)\) magnetization. A difference between \(M_{FC}(T)\) and \(M_{ZFC}(T)\) curves is almost constant at \(T\) temperatures below 250 K.

The ZFC and FC magnetization drop appears in magnetic fields of \(H < 200 \text{ Oe}\) at \(\sim 42\) K. Thus, a part of the spins is excluded from participation in an establishment of the FM long-range ordering. The competition of AFM interplanar superexchange energy and kinetic energy of electrons in FM planes at very low temperatures is apparently responsible for this magnetization behaviour. In magnetic fields more than 200 Oe (up to 1 T), the FC magnetization increases at \(\sim 42\) K. The ZFC magnetization shows a similar behavior at these fields. When the field is increased, a hysteresis between ZFC and FC magnetization becomes less pronounced than that in low fields. The magnetization isotherms have the typical FM character. An increase of the Mn content above the stoichiometric one leads to a decrease in magnetization of sample.

The temperature dependence of in-phase, \(\chi'(T)\), susceptibility indicates that the FM state rapidly develops below 270 K and depends slightly on temperature below 250 K. The out-of-phase, \(\chi''(T)\), susceptibility abruptly increases reaching a maximum at about 260 K and rapidly decreases to zero. The temperature of maximum in the \(\chi''(T)\) susceptibility coincides...
with inflection point of the $\chi'(T)$ and $M(T)$ curves which corresponds to the PM-FM phase transition. The ac susceptibility
versus temperature, $\chi'(T)$, has a jump at ~ 42 K which coincides with anomaly in the ZFC and FC magnetization at the same
temperature indicating a change in magnetic ordered state of the compound studied. It should be noted that the $\chi'(T)$ and
$\chi''(T)$ susceptibilities display no frequency dependence up to 2000 Hz.

Thus, an observable $M(T,H)$ dependencies reflect peculiarities connected with both ferromagnetic ordering and
phase transition at 42 K as well as the large irreversibility in the FC and ZFC magnetization.

An absence of the frequency and field dependencies in ac susceptibility as well as a cusp in ZFC magnetization
indicates that the large irreversibility in the FC and ZFC magnetization has no relation to spin-glass states. The ZFC
magnetization remains almost constant between 4.2 and 250 K that can be connected with freezing of some magnetic
domains below $T_c$ when the sample is cooled at zero or very low fields. It may be supposed that the large irreversibility
arises due to the blocking of cluster magnetic moment which complicate a movement of domain walls at magnetization
process and promote a manifestation of relaxation effects. When the compound is cooled under an applied field, the latter
help some weakly interacting domains to overcome the freezing and to flip to the direction of magnetic field. In result, a
more and more domains will tend to align along field which gives a larger magnetization values and a hysteresis between
ZFC and FC magnetization becomes less pronounced than that in low fields.

Analysis of the low temperature peculiarities in $M(T,H)$ and $\chi(T)$ dependencies suggests that these are most
probably a result of a FM to canted spin state transition taking into account also that, in theory, an average magnetization of
canted spin structure is approximately less on 10'-15% than one in FM saturated structures as it is observed in experiment.

The magnetisation behaviour below 42 K strongly depends on value of an applied magnetic field. Therefore, we
also do not exclude that the peculiarities of $M(T,H)$ and $\chi(T)$ dependencies at very low temperature in magnetic field can be
connected with the AFM ordering of Mn in the 2+ valence state, which according to the NMR data presents in the
La$^{2+}$A$^{3+}$MnO$_3$ systems and is likely to locate in the (Mn$^{2+}$ - Mn$^{4+}$) clusters. Therefore, the changes in sign of the ZFC and
FC magnetization with increasing magnetic field indicate that these are related to a change in the spin configuration and are
most probably a result of both the FM to canted phase transition and the presence of AFM ordered (Mn$^{2+}$ - Mn$^{4+}$)
clusters.

3.2. Pressure effect on the phase transition and resistance in (La$_{0.7}$Ca$_{0.3}$)$_{1-x}$Mn$_{1+x}$O$_3$ manganites

![Magnetization vs Temperature](image1.png)

![Resistivity vs Temperature](image2.png)

In Fig. 2, the temperature dependencies of $M_{ZFC}$ magnetization in (La$_{0.7}$Ca$_{0.3}$)$_{0.8}$Mn$_{1.2}$O$_3$ at different pressures are
presented. It is seen that the character of $M(T)$ dependencies does not change under pressure. The temperature of the FM
canting phase transition also does not change practically with increasing pressure. However, the Curie temperature, $T_c$,
shifts in the direction of high temperatures with increasing pressure. Analogous the pressure effect on the temperature of the
PM - FM phase transition is observed in La$_{0.6}$Mn$_{1.4}$O$_3$. This testifies about increase of the double exchange interaction
between multivalency ions. The linear increasing of $T_c$ with the derivatives of $dT_c/dP = +1.5$ K / kbar in (La$_{0.7}$Ca$_{0.3}$)$_{0.8}$Mn$_{1.2}$O$_3$ and $dT_c/dP = +1.9$ K / kbar in La$_{0.6}$Mn$_{1.4}$O$_3$ ceramics was observed at pressure up to 10 kbar.

Fig. 3. presents the $R(T)$ dependence for the epitaxial La$_{0.7}$Sr$_{0.3}$MnO$_3$ film at pressure $P = 0$ and 21 kbar. It is seen
that the resistance peak corresponding to metal-insulator transition shifts towards higher temperatures with increasing
pressure. A pressure stabilizes and expands the ferromagnetic metallic phase. Under pressure and in magnetic field, the value of $R(T,H)$ decreases in comparison with one at $P = 0$ in zero field. Thus, the pressure and magnetic field effect on resistance of the film is analogous. At low and very high temperatures, the pressure does not influence practically on magneto resistive effect ($\Delta R/R$). The magneto resistance effect increases by 15% under pressure of 12.6 kbar near the phase transition temperature only. The pressure dependencies $T_{\text{mag}}(P)$ at $H = 0$ and 4.2 kOe is detected to display a nonmonotonous behaviour with a peculiarity at $P = 5$ kbar. It can be evidence of an existence of the structural phase transition. To date, there do not exist the publications on the structural phase transitions in these materials under the pressure.

4. CONCLUSIONS

In this paper, the magnetic phase transitions and transport properties in compounds with superfluous manganese content has been studied in magnetic fields and under pressure. The dc magnetization and ac susceptibility in the $La_{0.56}Ca_{0.4}Mn_{1.2}O_3$ ceramic were investigated. It was shown that, despite the constant $La/Ca$ ratio, there are essential changes in the magnetic properties of the system as the Mn content is increased above the stoichiometric one. Magnetization of the sample studied decreases and the Curie temperature increases. Peculiarities in $M(T,H)$ and $\chi(T)$ dependencies observed at temperatures of $T_C \approx 260$ and 42 K are connected with a PM to FM phase transition and a FM to canted spin state transition, respectively. A presence of AFM clusters, in parallel with an canted spin state, is responsible for the change of sign in magnetization in applied fields of $H > 200$ Oe below 42 K. An absence of the frequency and field dependencies in ac susceptibility as well as a cusp in ZFC magnetization allow to propose that the large irreversibility in the FC and ZFC magnetization arises due to the random freezing of domain walls. The character of $M(T)$ dependencies does not change under pressure. However, both the Curie temperature, $T_C$, and the resistance peak corresponding to metal-insulator transition shift in the direction of high temperatures with increasing pressure. A pressure stabilizes and expands the ferromagnetic metallic phase. The temperature of the FM - canting phase transition does not change practically with increasing pressure. The maximal increase of the magneto resistive effect by 15% under pressure of 12.6 kbar takes place near the phase transition temperature. The linear increasing of $T_C$ with the derivatives of $dT_C/dP \approx +1.5$ K/kbar in $(La_{0.9}Ca_{0.3})_0.8Mn_{1.2}O_3$ and $dT_C/dP \approx +1.9$ K/kbar in $La_{0.6}Mn_{1.4}O_3$ ceramics was observed in the interval pressure up to 10 kbar.

ACKNOWLEDGMENTS

This work was partially supported by the Polish Government Agency KBN under contract N 2 P03B 139 18.