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Absence of isotope effect in Mn⁴⁺-rich CMR manganites Sm_{1-x}Ca_xMnO₃ ($x \sim 0.85$ – 0.88)

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Abstract

The oxygen isotope effect has been studied in the Sm_{1-x}Ca_xMnO₃ system in the vicinity of a phase boundary at $x = 0.85$ and 0.88 . Resistivity $\rho(T)$ and ac magnetic susceptibility $\chi'(T)$ measurements did not demonstrate any significant change in transport and magnetic properties of the system as a result of the ¹⁶O–¹⁸O isotope substitution, as opposed to the hole-doped manganites of the Ln_{1-x}A_xMnO₃ system, where an enormous oxygen isotope effect has been reported.

Introduction

Use of oxygen ¹⁶O–¹⁸O isotope exchange as a tool to study properties of the colossal magnetoresistive manganites has recently attracted great attention due to the discovery of an enormous isotope effect, and even a metal–insulator transition induced by ¹⁶O–¹⁸O isotope substitution in the hole-doped manganites of the Ln_{1-x}A_xMnO₃ system, where A is an alkaline cation corresponding to $x < 0.5$ [1–3]. The existence of such an extraordinary effect proved that electron–phonon interactions play a very significant role in the properties of this system, which undoubtedly made a large impact on the explanation of the behavior of these compounds. In hole-doped La_{0.8}Ca_{0.2}MnO₃ manganites a pronounced isotope effect was indeed obtained with a large shift of the transition temperature $\Delta T_C = 21$ K [3] after ¹⁶O–¹⁸O isotope substitution. Moreover, it was found that isotope substitution results in a metal–insulator transition in the mixed system (La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO₃ for $y = 0.75$ in the vicinity of the charge-ordered state [1, 2].

The recent investigation of Mn⁴⁺-rich manganites [4, 5], such as Sm_{1-x}Ca_xMnO₃ ($x > 0.50$), showed that these compounds also exhibit CMR properties for $x \approx 0.83$ – 0.85 . However, the magnetotransport properties are very different from the hole-doped ones. One observed a metal-like behaviour with unsaturated ferromagnetism in a very narrow range of concentrations $x = 0.83$ – 0.85 . It was found that this state was not really ferromagnetic, but had a more complicated magnetic order [6]. But starting with $x = 0.85$ the Sm_xCa_{1-x}MnO₃ compound demonstrated antiferromagnetic ordering with insulating behaviour and by applying magnetic field, one could induce a ferromagnetic component and colossal magnetoresistance.

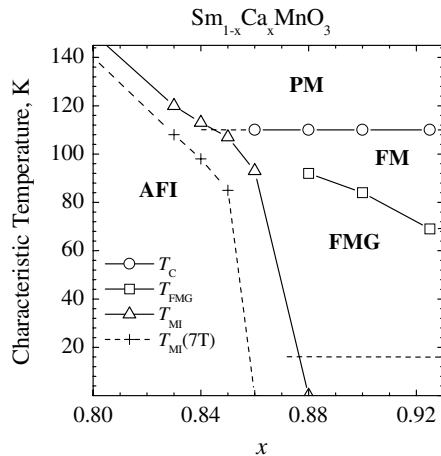


Figure 1. Phase diagram reconstructed from [4] and [5]. Abbreviations denote: PM—paramagnetic, FM—ferromagnetic, FMG—ferromagnetic glass, AFI—antiferromagnetic insulating phases. T_C —Curie temperature, T_{FMG} —temperature of the transition into a ferromagnetic glass phase, T_{MI} —metal–insulator transition temperature.

This great difference between hole-doped and electron-doped CMR manganites is also observed in their structural behaviour. In the first ones, the insulator to metal transition is accompanied by a structural transition involving a significant variation of the Jahn–Teller distortion [7], whereas in the electron-doped manganites, close to CaMnO_3 in the CMR region, the Jahn–Teller distortion is not detected [8]. These observations suggest that the electron–phonon interactions cannot influence the magnetotransport properties of the hole-doped and electron-doped manganites in the same way.

Bearing in mind that the CMR effect appears in both systems, n- and p-type manganites, in compositional regions where FM and AF components are competing, we have investigated the isotope effect of the electron-doped CMR manganites at the boundary between FM metallic and AF insulating states, i.e. for $x = 0.88$ and 0.85 (figure 1). We demonstrate herein that, in contrast to hole-doped manganites, the CMR electron-doped manganites do not show any isotope effect. We explain this different behaviour, by the absence of charge ordering in these electron-doped regions, so that the electron–phonon interactions are weak.

1. Experiment

The $\text{Sm}_{1-x}\text{Ca}_x\text{MnO}_3$ system was studied in the present research for Sm concentrations $x = 0.88$ and 0.85 . Bulk ceramic $2 \times 0.7 \times 6.5 \text{ mm}^3$ bar samples were used. Series of measurements were carried out including ac magnetic susceptibility and electrical resistivity in magnetic fields up to 4.5 T. Ac susceptibility ($\chi'(T)$) measurements were carried out in the temperature range $T = 4.5\text{--}300 \text{ K}$ with a frequency of 667 Hz and a driving field of 0.1 Oe. Electrical resistivity ($\rho(T)$) measurements were performed by a standard four-probe method in the temperature range $T = 4.5\text{--}300 \text{ K}$ in the cooling cycles.

Oxygen $^{16}\text{O}\text{--}^{18}\text{O}$ isotope exchange was carried out both in $\text{Sm}_{0.12}\text{Ca}_{0.88}\text{MnO}_3$ and $\text{Sm}_{0.15}\text{Ca}_{0.85}\text{MnO}_3$ samples. Pairs of samples were annealed simultaneously at 950°C for 72 hours in $^{16}\text{O}_2$ and $^{18}\text{O}_2$ atmosphere under an oxygen pressure of 1 bar with enforced gas circulation. Oxygen atmosphere was replaced after the first 24 hours of annealing.

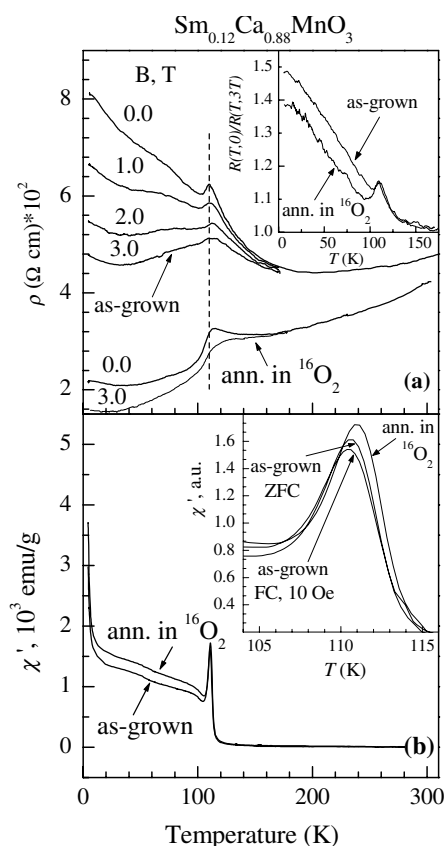


Figure 2. Temperature dependences of (a) resistivity in different magnetic fields and (b) ac magnetic susceptibility of $\text{Sm}_{0.12}\text{Ca}_{0.88}\text{MnO}_3$. Dependences for as-synthesized samples and samples annealed in $^{16}\text{O}_2$ are shown. In the inset on (b) ZFC indicates zero-field cooling, FC—cooling in field of 10 Oe.

Completeness of isotope exchange was determined by measuring the weight change of the samples. Isotope enrichment in the sample with ^{18}O was estimated at 70% (3% mass change of the sample). The annealed samples were subsequently studied.

2. Results

2.1. Preliminary study: as-synthesized and oxygen treated samples

Series of measurements were performed on the samples of $\text{Sm}_x\text{Ca}_{1-x}\text{MnO}_3$ before and after annealing. To separate the effect of oxygen heat treatment from the isotopic effects we first compared the conductivity and magnetic susceptibility data of as-synthesized samples and samples annealed in natural oxygen (^{16}O samples).

2.1.1. $\text{Sm}_{0.12}\text{Ca}_{0.88}\text{MnO}_3$. Resistivity measurements (figure 2(a)) for the as-synthesized sample demonstrated a monotonically growing temperature dependence with lowering of temperature, with a smeared peak at $T = 110$ K. When magnetic field was applied, the low-temperature insulating behaviour was suppressed, thus demonstrating large negative

magnetoresistance. The temperature of the peak slightly shifted towards higher temperatures with increase of the field. These features testify that the ferromagnetic metallic state develops in this compounds at $T < 110$ K in accordance with the phase diagram (figure 1). Note that all this phenomenon occur on the pronounced semiconducting background, which is a specific feature of the compound with $x \leq 0.86$ or $x \geq 0.90$ [4]. Such a behaviour is probably a consequence of the large contribution of the intergranular weak links to resistivity of ceramic.

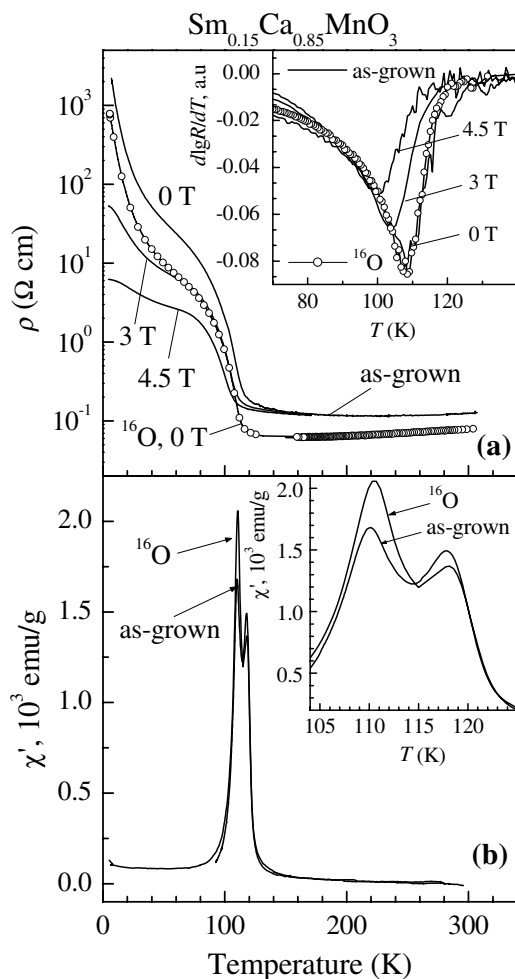


Figure 3. Temperature dependences of (a) resistivity in different magnetic fields and (b) ac magnetic susceptibility of $\text{Sm}_{0.15}\text{Ca}_{0.85}\text{MnO}_3$. Dependences for as-synthesized samples and samples annealed in $^{16}\text{O}_2$ (marked as ^{16}O) are shown.

The susceptibility measurements (figure 2(b)) revealed that the samples displayed a sharp transition at $T_{FM} = 110$ K. This pronounced peak has been associated in [4] and [5] with a ferromagnetic transition. We do not observe any significant difference in susceptibility registered in the zero-field-cooled (ZFC) or field-cooled (FC) process, as it was pointed out in [5]. A pronounced increase in $\chi'(T)$ was observed at $T = 10$ K, which corresponds to the second magnetic transition of unknown nature.

In comparison with as-synthesized sample the $\rho(T)$ curves indicated that ^{16}O sample had metallic temperature dependence in the whole temperature range with a well defined transition to ferromagnetic metallic state at about 110 K (figure 2(a)). The magnetic susceptibility of the ^{16}O sample in the ferromagnetic phase is a little higher than that in as-synthesized ceramic. Both resistivity and ac-susceptibility data show that transition temperature in ^{16}O sample shifts to higher temperature by about 1 K. It is interesting that magnetoresistance and susceptibility are similar in both samples, even though resistivity curves differ significantly. This may confirm the assumption that the large semiconducting background is not an intrinsic property of the material, but the effect of granularity. As a result we conclude that annealing in natural oxygen favours the formation of the ferromagnetic state.

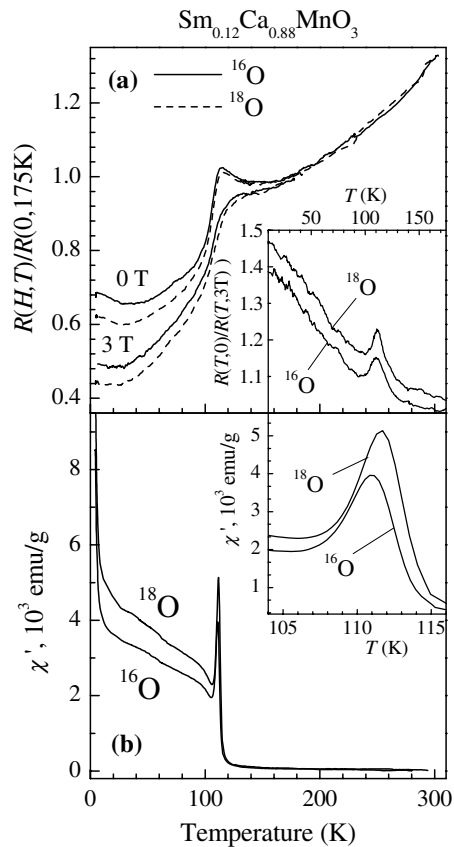


Figure 4. Temperature dependences of (a) normalized resistivity in different magnetic fields and (b) ac magnetic susceptibility of $\text{Sm}_{0.12}\text{Ca}_{0.88}\text{MnO}_3$ with ^{16}O and ^{18}O .

2.1.2. $\text{Sm}_{0.15}\text{Ca}_{0.85}\text{MnO}_3$. As the temperature decreased the resistivity (figure 3(a)) unambiguously demonstrated a metal–insulator transition at $T_{MI} = 110$ K. When magnetic field was applied, the low-temperature semiconducting behaviour was somewhat suppressed though even a relatively high magnetic field, $H = 4.5$ T, was not enough to turn the samples into the metallic state. Nevertheless, the negative magnetoresistance $R(0 \text{ T})/R(4.5 \text{ T})$ achieved a rather high value of 10^2 at the lowest temperature. The temperature of metal–insulator transition, defined as the minimum of logarithmic derivation $-\text{d} \lg R/\text{d}T$, diminished with

magnetic field (figure 3(a)). The value $dT_{MI}/dH = 1.6 \pm 0.2 \text{ K T}^{-1}$ appears to be about half that estimated in [5] at $H = 7 \text{ T}$.

The susceptibility measurements (figure 3(b)) revealed an antiferromagnetic behaviour with two pronounced peaks: at 110 K and 120 K. The first peak coinciding with T_{MI} one may associate with the temperature of the antiferromagnetic transition T_{AF} .

The annealing in ^{16}O induced the increase of absolute value of conductivity in the metallic state ($T > T_{MI}$) with higher slope $d\rho/dT$, than that in as-synthesized samples (figure 3(a)). At $T < T_{MI}$ temperature dependence $\rho(T)$ did not change significantly, so the $d\lg R/dT$ stayed almost the same. The T_{MI} was also not affected by annealing in oxygen.

The position of the magnetic susceptibility peak was slightly changed and the height of the low-lying peak became relatively higher in comparison with the as-grown sample (figure 3(b)).

As a result we conclude that oxygen heat treatment might have improved the contacts between crystallites in ceramic and did not modify the bulk properties of material.

2.2. Isotope exchange

2.2.1. $\text{Sm}_{0.12}\text{Ca}_{0.88}\text{MnO}_3$. The enrichment of the sample with ^{18}O caused only minimal (if any) effect on the resistivity and magnetic susceptibility. We did not observe any shift of the ferromagnetic temperature determined from the resistivity curve (figure 4(a)) and about 1 K increase of T_{FM} in the ^{18}O sample extracted from the susceptibility peak (figure 4(b)). One can notice the general tendency arising under enrichment. The ^{16}O – ^{18}O exchange is favourable to the formation of a metallic ferromagnetic state: the value of the conductivity and susceptibility at $T_C < T_{FM}$ is higher in the ^{18}O sample. The magnetoresistance $\rho(T, H = 0)/\rho(T, H = 3 \text{ T})$ in ^{18}O sample is also higher, but this is not the case because it is merely reflects the higher value of zero-field conductivity $\rho(T, H = 0)$ in the ^{18}O sample, whereas $R(H)$ curves are identical in both compounds (see the inset in figure 4(a)).

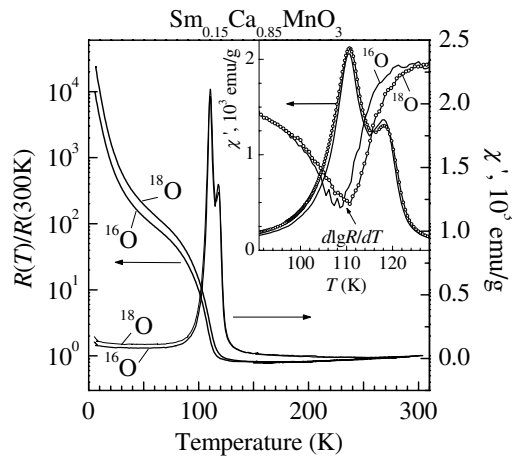


Figure 5. Temperature dependences of normalized resistivity and ac magnetic susceptibility of $\text{Sm}_{0.15}\text{Ca}_{0.85}\text{MnO}_3$ with ^{16}O and ^{18}O .

2.2.2. $\text{Sm}_{0.15}\text{Ca}_{0.85}\text{MnO}_3$. We did not find any significant changes in the properties of enriched material in comparison with the sample with natural oxygen (figure 5). It is worth noting that in the ^{18}O sample T_{MI} , determined by the position of the minimum of the logarithmic

derivative, slightly shifted up. But this is not confirmed by susceptibility measurements, where the positions of the peaks are the same in ^{16}O and ^{18}O samples.

3. Discussion and conclusion

This absence of an isotope effect in the electron-doped manganites can be explained by considering the recent structural results obtained from neutron powder diffraction data and electron microscopy [6–8].

$\text{Sm}_{0.15}\text{Ca}_{0.85}\text{MnO}_3$, which exhibits a metal–insulator transition at 115 K, is also characterized by a structural transition at the same temperature from orthorhombic paramagnetic to monoclinic antiferromagnetic with the C type. Thus for this CMR composition there exists a strong correlation between orbital ordering, spin ordering and structure distortion. However, electron microscopy shows that this oxide does not exhibit any charge ordering [9], in contrast to CMR hole-doped manganites. Consequently, it is now clear that for this phase the electron–phonon interaction is weak or absent, due to the absence of charge ordering, so that no isotope effect can be observed.

$\text{Sm}_{0.12}\text{Ca}_{0.88}\text{MnO}_3$, which is characterized by metal–metal transition, exhibits a G-type AF structure at low temperature similar to $\text{Sm}_{0.10}\text{Ca}_{0.90}\text{MnO}_3$ [8], and shows coexistence of G-type and FM domains, but in any case does not show any significant electron–phonon interactions, in agreement with the absence of isotope effect.

References

- [1] Babushkina N A, Belova L M, Gorbenko O Yu, Kaul A R, Bosak A A, Ozhogin V I and Kugel K I 1998 *Nature* **391** 159
- [2] Babushkina N A, Belova L M, Ozhogin V I, Gorbenko O Yu, Kaul A R, Bosak A A, Khomskii D I and Kugel K I 1998 *J. Appl. Phys.* **83** 7369
- [3] Zhao G, Keller H, Hofer J, Shengelaya A and Müller K A 1997 *Solid State Commun.* **104** 57
- [4] Martin C, Maignan A, Damay F, Hervieu M and Raveau B 1997 *J. Solid State Chem.* **134** 198
- [5] Maignan A, Martin C, Damay F, Raveau B and Hejtmanek J 1998 *Phys. Rev. B* **58** 2758
- [6] Martin C, Maignan A, Hervieu M, Raveau B, Jirak Z, Kurbakov A, Trounov V, André G and Bourée F 1999 *J. Magn. Magn. Mater.* **205** 184
- [7] Caignaert V, Suard E, Maignan A, Simon Ch and Raveau B 1995 *C.R. Acad. Sci., Paris* **321** 515
- [8] Martin C, Maignan A, Hervieu M, Raveau B, Jirak Z, Savosta M M, Kurbakov A, Trounov V, André G and Bourée F 2000 *Phys. Rev. B* **62** 6442–9
- [9] Hervieu M, Barnabé A, Martin C, Maignan A, Damay F and Raveau B 1999 *Eur. Phys. J. B* **8** 31