Metal-insulator transition induced by $^{16}\text{O} - ^{18}\text{O}$ oxygen isotope exchange in colossal negative magnetoresistance manganites

N. A. Babushkina, L. M. Below and V. I. Ozhogin
Russian Research Center “Kurchatov Institute”, Kurchatov sq. 1, Moscow, 123182 Russia

O. Yu. Gorbenko, A. R. Kaul and A. A. Bosak
Chemistry Department, Moscow State University, Vorobievy Gory, Moscow, 119899 Russia

D. I. Khomskii
Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
Lebedev Physics Institute, Leninskii pr. 53, Moscow, 117924 Russia

K. I. Kugel
Scientific Center for Applied Problems in Electrodynamics, Izhorskaya St. 13/19, Moscow, 127412 Russia

The effect of $^{16}\text{O} \rightarrow ^{18}\text{O}$ isotope exchange on the electric resistivity was studied for $(\text{La}_{1-x}\text{Pr}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ceramic samples. Depending on $y$, this mixed perovskite exhibited different types of low-temperature behavior ranging from ferromagnetic metal (FM) to charge ordered (CO) antiferromagnetic insulator. It was found that at $y = 0.75$, the substitution of $^{16}\text{O}$ by $^{18}\text{O}$ results in the reversible transition from a FM to a CO insulator at zero magnetic field. The applied magnetic field ($H \geq 2$ T) transformed the sample with $^{18}\text{O}$ again to the metallic state and caused the increase in the FM transition temperature $T_C$ of the $^{16}\text{O}$ sample. As a result, the isotope shift of $T_C$ at $H = 2$ T was as high as 63 K. Such unique sensitivity of the system to oxygen isotope exchange, giving rise even to the metal-insulator transition, is discussed in terms of the isotope dependence of the effective electron bandwidth which shifts the balance between the CO and FM phases.

I. INTRODUCTION

The perovskite manganites $R_{1-x}M_x\text{MnO}_3$, (Ref. 1) ($R^{3+}$ is a rare earth cation, $M$ is a doubly charged cation with a large ionic radius, both $R$ and $M$ occupy A positions of the ABO$_3$ perovskite lattice) attract a considerable current interest owing to the recent discovery of colossal negative magnetoresistance (CMR). CMR in manganites stems from the semiconductor-metal transition accompanied by arising of ferromagnetic ordering, both transitions are usually interpreted on basis of the double exchange (DE) mechanism.1 However, double exchange alone is insufficient to explain the whole variety of phenomena observed in manganites. These materials are characterized by a strong interplay of structural, orbital, and spin degrees of freedom dramatically affecting their transport properties. The important role of the electron-lattice interaction was pointed out in Ref. 3. There is a number of factors contributing to these interactions, including the Jahn-Teller nature of $\text{Mn}^{4+}$ ions, the strong dependence of electron transfer on the Mn–O–Mn bond angle related to the average ionic radius at the A site, trapping of charge carriers due to the optical breathing mode, and different polaronic effects.

Another feature of the perovskite manganites is the possible formation of the charge ordered (CO) state, manifesting itself in localization of charge carriers accompanied by the regular arrangement of $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ ions.1,4 The CO state is usually characterized by semiconductor-like and antiferromagnetic behavior. The tendency towards CO is observed with a decrease in the average ionic radius in A position. Such an ordering, characteristic of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.2 - 0.5$), was actively studied recently.4,11-13 The charge ordering gives rise to lattice distortions resulting in the instability of the initial crystal lattice.

The significant role of electron-lattice interactions in manganites is confirmed by a pronounced isotope effect on the electrical and magnetic properties. The effect of $^{16}\text{O} - ^{18}\text{O}$ isotope exchange on the magnetization of $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ was first reported in Refs. 12,13. The obtained isotope shift of the Curie temperature was as large as 21 K.

The isotope effect should be even more pronounced in the vicinity of lattice instability related to the charge ordering. Bearing this in mind, we studied the effect of oxygen isotope substitution on the electrical resistivity of a mixed compound $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. By varying the relative contents of Pr and La (i.e., changing the average radius of the rare earth ion) it is possible to obtain the different types of low-temperature behavior [from the ferromagnetic metal
(FM) La$_{0.7}$Ca$_{0.3}$MnO$_3$ to the charge-ordered antiferromagnetic insulator Pr$_{0.7}$Ca$_{0.3}$MnO$_3$.

The isotope effect in electrical resistivity which we observed for La$_{0.175}$Pr$_{0.525}$Ca$_{0.3}$MnO$_3$ ($y = 0.75$) samples appeared to be far in the excess of our expectations since the $^{16}$O – $^{18}$O exchange resulted not only in the significant lowering of the Curie temperature, but also in the metal-insulator transition.

II. EXPERIMENT

To prepare the ceramic samples, water solutions of La(NO$_3$)$_3$, Pr(NO$_3$)$_3$, Ca(NO$_3$)$_2$, and Mn(NO$_3$)$_2$ were mixed together in proper ratios. Then ash-free paper filters were soaked with the solution. Dried at 120°C, the powder residue was pressed into the form of pellets that were sintered at 1200°C for 12 h in air. X-ray diffraction (XRD) showed that the La$_{0.175}$Pr$_{0.525}$Ca$_{0.3}$MnO$_3$ ceramic samples produced were of single phase with an orthorhombic structure (lattice parameters $a = 5.436(2)$ nm, $b = 5.461(2)$ nm, $c = 7.686(3)$ nm at 300 K).

The (La$_{1-y}$Pr$_y$)$_{0.7}$Ca$_{0.3}$MnO$_3$ system appeared to be convenient for oxygen isotope substitution since its oxygen stoichiometry depends only slightly on variations in the thermal treatment conditions (temperature and partial pressure of O$_2$).

The method used for oxygen isotope substitution $^{16}$O – $^{18}$O in the selected manganese was similar to that utilized for high-temperature superconductor ceramics. Two 1 × 1 × 8 mm$^3$ bars were cut from the sintered pellet of La$_{0.175}$Pr$_{0.525}$Ca$_{0.3}$MnO$_3$ and placed in alumina boats which were then mounted in the furnace inside two quartz tubes. The quartz tubes were parts of two identical closed loops with forced circulation of gas. Both samples were treated simultaneously: one sample was heated in $^{16}$O$_2$ atmosphere, the other sample was heated in $^{18}$O$_2$ (the molar fraction of $^{18}$O$_2$ was 85%). The diffusion annealing was carried out for 48 h at 950°C under oxygen pressure of 1 bar. The $^{18}$O content in the samples was determined by measurement of the weight change of the samples after the isotope enrichment. As a result, the completeness of the isotope exchange was verified.

The electric resistivity was measured by the standard four-probe technique at temperatures down to 4.2 K. The highest resistance that could be measured with the experimental setup was 1 GΩ. The resistivity measurements in the magnetic field applied along the bar sample were performed only during the cooling stages. The magnetic properties were not measured in the current study, thus the assignment of the magnetic states was qualitative and based on experimental data for similar compounds published earlier.

III. RESULTS

The temperature dependence of resistivity ρ(T) in zero magnetic field for the La$_{0.175}$Pr$_{0.525}$Ca$_{0.3}$MnO$_3$ samples is shown in Fig. 1. The resistivity curves for samples treated in $^{16}$O$_2$ and $^{18}$O$_2$ differ drastically. For both the $^{16}$O and $^{18}$O samples a semiconductor-like activation behavior is observed at high temperature and the resistivity increases dramatically with decreasing temperature. Then the $^{16}$O sample exhibited a clearly pronounced resistivity peak at $T_C = 95$ K associated with transition to the FM state. This value of $T_C$ is in good agreement with Ref. 4. For the $^{18}$O sample the resistivity increases monotonically with decreasing temperature and reaches about 10$^7$ Ω·cm at 50 K, below which the ρ(T) value is so large that it exceeds our measuring limit. This behavior can be attributed to the charge-ordered state which is usually responsible for such an increase in the resistivity.

To make sure that the effect is due precisely to the isotope exchange, we carried out an isotope back-exchange. The completeness of the exchange was proved again by change of the sample weight. The sample, which had been first saturated by $^{18}$O and was insulating thereafter, became metallic below 95 K after subsequent annealing in $^{16}$O$_2$. Correspondingly, the sample, that had been first treated in $^{16}$O$_2$ and was metallic below 95 K thereafter became an insulator after the subsequent treatment in $^{18}$O$_2$ (Fig. 1).

Application of the magnetic field is known to provide melting of the CO state in (La$_{1-y}$Pr$_y$)$_{0.7}$Ca$_{0.3}$MnO$_3$ resulting in a metamagnetic phase transition with a drastic decrease of the electric resistivity. This is a magnetic transition of the first order, exhibiting a pronounced temperature hysteresis. To avoid hysteresis the samples were heated above 150 K, then cooled in the applied magnetic field.
zero field. CMR originates from the field-induced simultaneous semiconductor-metal and AF–FM transitions.

IV. DISCUSSION

Let us discuss qualitatively the possible mechanisms of the observed isotope effect. Note that $^{16}$O – $^{18}$O exchange stabilizes the high-resistivity charge-ordered state at zero magnetic field and at the same time shifts toward lower temperatures the onset of the ferromagnetic metal phase at sufficiently high applied field. The samples studied in current research lie close to the FM–CO phase boundary and a relatively small influence can in principle transform one state into another, this can be achieved even by isotope substitution.

The relative stability of different phases is determined mainly by the electron bandwidth, or the effective hopping integral $t_{\text{eff}}$. The CO state is favored in the situation when $t_{\text{eff}}$ is small enough. One can show this for a simple case of one electron per two sites, using the model initially formulated for magnetite [12] which takes into account the Coulomb repulsion $U$ of electrons at neighboring lattice sites. Its Hamiltonian has the form

$$H = t \sum_{<i,j>} a_i^+ a_j + \frac{V}{2} \sum_{<i,j>} n_i n_j,$$

where $a_i^+$ and $a_i$ are creation and annihilation operators for an electron at the $i$th site, $n_i = a_i^+ a_i$, and $< ... >$ means the summation over the nearest neighbors. On-site Coulomb interaction $U$ is assumed to be the largest parameter, $U \to \infty$.

The standard mean-field treatment shows [3] that the CO state occurs if the hopping integral $t$ is less than a certain critical value, $t < t_c = V z/2$ ($z$ is the number of nearest neighbors). The CO critical temperature is given by the expression

$$T_{CO} \approx V z \sqrt{1 - (t/t_c)^2}$$

and is reduced with the increase of $t$, especially strongly for $t \approx t_c$. Thus, the increase of the hopping integral $t$ destabilizes the CO phase.

The $t_{\text{eff}}$ value can be determined by averaging $t$ over corresponding lattice vibrations that, in turn, depend on the isotope composition of the material. In the simplest case: $t(r) \propto \exp(-\alpha r)$ and

$$t_{\text{eff}} = t_0 \left(1 + \frac{1}{2} \alpha^2 <u^2> \right),$$

where the interatomic distance $r = r_0 + u$, $t_0 = t(r_0)$, and $\alpha \propto 1/r_0$.

The mean-square displacement $<u^2>$, and hence $t_{\text{eff}}$, depend on the ionic mass $M$ (even at $T = 0$ due to the zero-point vibrations).
In case of dominant contribution of zero-point vibrations, we have:

\[
\langle u^2 \rangle = \frac{\hbar}{2M\Theta_D} = \frac{\hbar}{2(BM)^{1/2}}
\]

where \( B \) is the bulk modulus. Thus

\[
\delta t_{\text{eff}} \approx -t_0 \left( \langle u^2 \rangle / r_0^2 \right) (\delta M/M).
\]

The corresponding change in \( t_{\text{eff}} \) is generally not large, especially taking into account that we have to use the reduced mass instead of the pure ionic mass. But this change may still be sufficient to shift our system from one state to another if we are close to the phase boundary at the phase diagram, which is apparently the case in our system. In this situation \( t \approx t_c \) and, as it follows from Eq. (2),

\[
\delta T_{CO} \propto \sqrt{1 - (t/t_c)^2}.
\]

Note that in Eq. (2) the typical values of the intersite Coulomb repulsion \( V_z \approx 1 \text{ eV} \left(10^4 \text{ K} \right) \), while \( T_{CO} \approx 10^8 \text{ K} \); hence the square roots in Eq. (2) and Eq. (3) are of the order of \( 10^{-2} \). Thus, \( \delta T_{CO} \propto \delta t \cdot 10^2 \) and it is not surprising that even a relatively small variation of \( t_{\text{eff}} \) caused by isotope substitution leads to such an important change in properties.

There are also other factors affecting \( t_{\text{eff}} \), such as a possible change of the Mn–O–Mn angle, polaronic effects, and lattice anharmonicity, especially in the vicinity of the lattice instability that manifests itself in the system under study. They should be taken into account in a more detailed analysis.

The experimental results obtained correlate with relationships (4) and (3) indicating that \( t(M) \) is a decreasing function of \( M \) since the charge-ordered state becomes stable for the heavier isotope. The behavior of \( T_C \) at nonzero magnetic fields does not contradict the character of the \( t(M) \) dependency. In fact, if the ferromagnetism stems from the double exchange (i.e., \( t < J_H \), where \( J_H \) is the intraatomic exchange coupling giving rise to the Hund rule), then \( T_C \) is proportional to \( t \). For decreasing \( t(M) \), we have \( T_C (18\text{O}) < T_C (16\text{O}) \), in agreement with our results and with earlier experiments on the isotope effect in manganites. However, it is not quite clear why the isotope effect for \( T_C \) is so large. In Ref. [12] this fact is related to manifestations of the Jahn-Teller effect which can enhance the unharmonic contribution to polaronic narrowing of \( t \). In the vicinity of lattice instability caused by the possibility of charge ordering this effect can be even more pronounced. An additional contribution to the isotope shift of \( T_C \) may be due to the isotope mass dependence of the fraction of Mn–O–Mn linkages involved in the double exchange. This fraction is determined by the quantity \( \omega_R \exp (-\varepsilon_p/t) \), where \( \omega_R \) is the frequency of the optical breathing mode that traps a carrier at a single cation site and \( \varepsilon_p \) is the characteristic energy of manganese clusters participating in the double exchange.

We have \( \omega_R \sim M_O^{-1/2} \) (\( M_O \) is the oxygen atomic mass), hence this contribution results in the additional \( T_C \) lowering at the \( 18\text{O} \to 16\text{O} \) exchange.

\[ \text{V. CONCLUSIONS} \]

The electric resistivity of La_{0.175}Pr_{0.525}Ca_{0.3}MnO_3 ceramics demonstrates very high sensitivity to the oxygen isotope exchange. The samples with \( 18\text{O} \) are metallic at low temperatures, while substitution of \( 18\text{O} \) by \( 16\text{O} \) results in the insulator-like behavior. This transition is completely reversible and the sample returns to the original metallic state after backsubstitution \( 18\text{O} \to 16\text{O} \). The magnetic field exceeding 1 T restores the metallicity, but the isotope shift of the resistivity peak is very large, 63 and 54 K at \( H = 2 \) and 3 T, respectively. Moreover, the CMR is much more pronounced in the case of \( 18\text{O} \) (the resistivity drops for \( 18\text{O} \) and \( 16\text{O} \) differ by a factor attaining the value of \( 10^5 \) at \( H = 2 \) T).

We argue that this enormous isotope effect is caused by modification of the effective hopping integrals and the resulting electron bandwidth due to isotope substitution, which shifts the relative stability of the CO versus FM states and leads to a transition between these phases. Simple model considerations suggest a significant enhancement of the isotope effect near the onset of the charge-ordered state and the corresponding lattice instability. To analyze this problem quantitatively we must take into account a whole set of competing mechanisms: electron-phonon interaction, polaronic band narrowing, the Jahn-Teller effect, double exchange, intersite Coulomb repulsion of electrons, etc. Nonetheless, we think that our simple arguments correctly describe the main physics of the phenomenon observed.

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* Electronic mail: belova@imp.kiae.ru

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