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SPECIAL TOPICS

Metal–insulator transition induced by ^{16}O – ^{18}O oxygen isotope exchange in colossal negative magnetoresistance manganites

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The effect of ^{16}O → ^{18}O isotope exchange on the electric resistivity was studied for $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ceramic samples. It was found that at $y=0.75$, the substitution of ^{16}O by ^{18}O results in the reversible transition from a ferromagnetic metal (FM) to charge ordered (CO) insulator at zero magnetic field. The applied magnetic field ($H \geq 2$ T) transformed the sample with ^{18}O again to the metallic state and caused the increase in the FM transition temperature T_C of the ^{16}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. © 1998 American Institute of Physics. [S0021-8979(98)27511-6]

INTRODUCTION

The perovskite manganites $\text{R}_{1-x}\text{M}_x\text{MnO}_3$ (Ref. 1), (R^{3+} is a rare earth cation, M is a doubly charged cation with a large ionic radius, attract considerable current interest owing to the recent discovery of colossal negative magnetoresistance (CMR). 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 are a number of factors contributing to these interactions, including the Jahn–Teller nature of Mn^{3+} ions, the strong dependence of electron transfer on the Mn–O–Mn bond angle,^{4,5} 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 Mn^{3+} and Mn^{4+} ions.^{6–8} The CO state is usually characterized by semiconductorlike and antiferromagnetic behavior and is accompanied by lattice distortions. Such an ordering, characteristic of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x=0.2$ – 0.5), was actively studied recently.^{7,8}

The significant role of electron–lattice interactions in manganites is confirmed by a pronounced isotope effect on the electrical and magnetic properties: in $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ the isotope shift of the Curie temperature was as large as 21 K.^{9,10} 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) $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ to the charge-ordered antiferromagnetic (AF) insulator $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$].^{4,11}

The isotope effect in electrical resistivity which we observed for $\text{La}_{0.175}\text{Pr}_{0.525}\text{Ca}_{0.3}\text{MnO}_3$ ($y=0.75$) 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.

EXPERIMENT

The preparation of the ceramic samples is described in Ref. 2. X-ray diffraction (XRD) showed that the $\text{La}_{0.175}\text{Pr}_{0.525}\text{Ca}_{0.3}\text{MnO}_3$ ceramic samples produced were of single phase with an orthorhombic structure [lattice parameters $a=0.5436(2)$ nm, $b=0.5461(2)$ nm, $c=0.7686(3)$ nm at 300 K].

The $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ 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 manganite was similar to that utilized for high-temperature superconductor ceramics.¹³ Two $1 \times 1 \times 8$ mm³ bars were cut from the sintered pellet of $\text{La}_{0.175}\text{Pr}_{0.525}\text{Ca}_{0.3}\text{MnO}_3$. Both samples were treated simultaneously: one sample was heated in $^{16}\text{O}_2$ atmosphere, the other sample was heated in $^{18}\text{O}_2$ (the molar fraction of $^{18}\text{O}_2$ was 85%) for 48 h at 950 °C under oxygen pressure of 1 bar. The ^{18}O content in the samples was determined by measure-

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FIG. 1. Temperature dependence of resistivity for ^{16}O and ^{18}O samples of $\text{La}_{0.175}\text{Pr}_{0.525}\text{Ca}_{0.3}\text{MnO}_3$ before and after oxygen backexchange.

ment 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.^{6–8,13}

RESULTS

The temperature dependence of resistivity $\rho(T)$ in zero magnetic field for the $\text{La}_{0.175}\text{Pr}_{0.525}\text{Ca}_{0.3}\text{MnO}_3$ samples is shown in Fig. 1. The resistivity curves for samples treated in $^{16}\text{O}_2$ and $^{18}\text{O}_2$ differ drastically. The ^{16}O sample exhibits 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 attains about $10^8 \Omega \text{ cm}$ at 50 K, below which the $\rho(T)$ 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.¹³

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

Application of the magnetic field is known to provide melting of the CO state in $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, resulting in a metamagnetic phase transition with a drastic decrease of the electric resistivity.^{4,11} This is a magnetic transition of the first order, exhibiting a pronounced temperature hysteresis.

FIG. 2. Temperature dependence of resistivity for ^{16}O and ^{18}O samples of $\text{La}_{0.175}\text{Pr}_{0.525}\text{Ca}_{0.3}\text{MnO}_3$ in different magnetic fields. The solid line is for the ^{16}O sample; the dashed line is for the ^{18}O sample.

To avoid hysteresis the samples were heated above 150 K, then cooled in the applied magnetic field.

Temperature dependencies of resistivity $\rho(T)$ in the magnetic field are shown in Fig. 2. We found that a magnetic field of 1 T was not enough to suppress the CO state in $\text{La}_{0.175}\text{Pr}_{0.525}\text{Ca}_{0.3}\text{Mn}^{(18}\text{O}_{0.85}\text{O}_{0.15})_3$ in spite of the more than 30 K upward shift of T_C in the case of $\text{La}_{0.175}\text{Pr}_{0.525}\text{Ca}_{0.3}\text{Mn}^{(16}\text{O})_3$. Nevertheless, in a field of 2 T melting of the charge-ordered state was clearly demonstrated (Fig. 2).

The isotope shift of T_C was as large as 63 K in a field of 2 T and 54 K in a field of 3 T, which is considerably larger than isotope effects ever reported for $\text{R}_{1-x}\text{M}_x\text{MnO}_3$. It is of note that T_C grows significantly with the increase of the applied magnetic field for both samples. The $\rho(T)$ curves at higher temperature are nearly independent of the isotope exchange (Fig. 2).

Under an external field of 2 T, the resistivity drops by more than seven orders of magnitude to $\rho_{2\text{T}} = 1.5 \Omega \text{ cm}$ at 50 K, exhibiting one of the largest magnitudes of CMR (10^7). For the ^{18}O sample the large decrease in ρ , and thus CMR, can be related to the field-induced melting of the CO state. For the ^{16}O sample the magnitude of the CMR is much less (10^4 for $H = 2$ T).

Note the striking difference between the results for CMR in the ^{16}O and ^{18}O samples. In the ^{16}O sample metallic conduction and ferromagnetism occur spontaneously below the Curie temperature T_C . CMR arises from the abrupt increase in electron hopping via DE at the onset of the spontaneous FM ordering. Sizable CMR exists in the vicinity of T_C . In the ^{18}O sample neither metallic conduction nor ferromagnetism is observed in zero field. CMR originates from the field-induced simultaneous semiconductor-metal and AF-FM transitions.

DISCUSSION

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_{eff} . The CO state is favored in the situation when t_{eff} is small enough.^{4,5} One can show this for a simple case of one electron per two sites using the model initially formulated for magnetite,^{14,15} which takes into account the Coulomb repulsion V of electrons at neighboring lattice sites. Its Hamiltonian has the form

$$H = t \sum_{\langle i,j \rangle} a_i^\dagger a_j + \frac{V}{2} \sum_{\langle i,j \rangle} n_i n_j, \quad (1)$$

where $a_i^\dagger$ and a_i are creation and annihilation operators for an electron at the i th site, $n = a^\dagger a$, and $\langle \dots \rangle$ means the summation over the nearest neighbors. On-site Coulomb interaction U is assumed to be the largest parameter, $U \rightarrow \infty$.

The standard mean-field treatment shows¹⁵ that the CO state occurs if the hopping integral t is less than a certain critical value, $t < t_c = Vz/2$ (z is the number of nearest neighbors). The CO critical temperature is given by the expression

$$T_{\text{CO}} \approx Vz \sqrt{1 - (t/t_c)^2} \quad (2)$$

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_{eff} value is 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

$$t_{\text{eff}} = \langle t \rangle = t_0 \left(1 + \frac{1}{2} \alpha^2 \langle u^2 \rangle \right), \quad (3)$$

where the interatomic distance $r = r_0 + u$, $t_0 = t(r_0)$, and $\alpha \propto 1/r_0$. The mean-square displacement $\langle u^2 \rangle$, and hence t_{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

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

where B is the bulk modulus. Thus

$$\delta t_{\text{eff}} \approx -t_0 (\langle u^2 \rangle / r_0^2) (\delta M / M). \quad (4)$$

The corresponding change in t_{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 follows from Eq. (2),

$$\delta T_{\text{CO}} \propto \delta t / \sqrt{1 - (t/t_c)^2}. \quad (5)$$

Note that in Eq. (2) the typical values of the intersite Coulomb repulsion $Vz \approx 1$ eV (10^4 K), while $T_{\text{CO}} \sim 10^2$ K; hence the square roots in (2) and (5) are of the order of 10^{-2} . Thus, $\delta T_{\text{CO}} \propto \delta t \times 10^2$, and it is not surprising $\delta T_{\text{CO}} \propto \delta t \times 10^2$ that even a relatively small variation of t_{eff} caused by isotope substitution leads to such a drastic change in properties.

The effect discussed above may be strongly enhanced if the charge carriers have polaronic nature. In this case the polaronic band narrowing gives

$$t_{\text{eff}} = t_0 \exp(-E_{\text{pol}}/\omega) \propto t_0 \exp(-\text{const}/\sqrt{M}) \quad (6)$$

and in the specific case considered here it is the oxygen mass that enters Eq. (6).¹⁶

Another factor which may play a role in this effect is possible change of the Mn–O–Nm angle which can also influence t_{eff} .

CONCLUSIONS

The electric resistivity of $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ceramics demonstrates very high sensitivity to the oxygen isotope exchange. At $y=0.75$, the samples with ^{16}O are metallic at low temperatures, while substitution of ^{16}O by ^{18}O results in the insulatorlike behavior. 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.

We argue that this 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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