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Oxygen isotope effect on the spin-state transition in $(Pr_{0.7}Sm_{0.3})_{0.7}Ca_{0.3}CoO_3$

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Oxygen isotope substitution is performed in the perovskite cobalt oxide $(Pr_{0.7}Sm_{0.3})_{0.7}Ca_{0.3}CoO_3$ with a sharp spin state transition from the intermediate spin (IS) state to the low spin (LS) state at a certain temperature. The transition temperature (T_s) of the spin state up-shifts with the substitution of ^{16}O by ^{18}O from the resistivity and magnetic susceptibility measurements. The up-shift value is 6.8 K and an oxygen isotope exponent (α_S) is about −0.8. The large oxygen isotope effect indicates strong electron-phonon coupling in this material. The substitution of ^{16}O by ^{18}O leads to a decrease in the phonon frequency and an increase in the effective mass of electron (m^*), so that the bandwidth W decreases and the energy difference between the different spin states increases. This is the reason why the T_s is shifted to high temperature with oxygen isotopic exchange.

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I. INTRODUCTION

Perovskite-related cobalt oxides have attracted much interest recently because of the spin state transition induced by temperature. In a cubic crystal field, the fivefold 3*d* orbitals will be split into two parts: twofold e_g orbitals and threefold t_{2g} orbitals. The Co^{3+} ion, which contains six 3*d* electrons, often exhibits a spin state transition from the low spin (LS, t_{2g}^6) ground state to the intermediate spin (IS, $t_{2g}^5e_g^1$) or to the high spin (HS, $t_{2g}^4e_g^2$) state with increasing temperature.[1–12] This indicates that the energy difference δE between these spin states is rather small, and the crystal field splitting energy Δ_C and the Hund coupling energy J_H are comparable.

In the study of $R_{1-x}A_xCoO_3$ (R=Y and various rare earth elements, A=Ba, Sr, and Ca), Tsubouchi *et al.*[10,11] found an abrupt metal-insulator (*M-I*) transition and a spin state transition from IS state to LS state at 90 K with decreasing temperature in $Pr_{0.5}Ca_{0.5}CoO_3$, which is accompanied with a decrease of Co-O-Co bond angle. The temperature at which the spin state transition occurs is defined as T_S. They believe that the decrease of Co-O-Co bond angle results in a reduction of covalency and thus unstabilizes the itinerant IS state. The volume contraction induced by the decrease Co-O-Co bond angle can enlarge the splitting of crystal field, which also stabilizes the LS state. Fujita *et al.*[12] studied the *T-x* phase diagram of $Pr_{1-x}Ca_xCoO_3$ under various external pressures and found that this transition is not an order-disorder transition. They also studied other materials,[12–14] but only the Pr(Ca) cobalt oxides show this transition. Based on the *x* dependence of unit cell volume V_u, and CoO_6 octahedra volume V_o and the Co-O-Co bond angle, they found that the Co-Co transfer energy *t* is also important to determine δE in this kind of material.[12] But it is still unclear why only the materials contain Pr and Ca show this transition. In order to give more experimental evidence for this question, we investigate the oxygen isotope effect of $(Pr_{0.7}Sm_{0.3})_{0.7}Ca_{0.3}CoO_3$ with a spin state transition.[14] The reason we choose this material is that its oxygen content is not sensitive to the heat treatment compared to $Pr_{0.5}Ca_{0.5}CoO_3$.[12]

Isotope substitution is an effective tool to study the lattice dynamical and electronic properties of solids.[15] In perovskite manganites, the study on the effect of substitution of ^{16}O with ^{18}O in $La_{0.8}Ca_{0.2}MnO_3$ shows a large decrease in Curie temperature.[16] This result indicates much larger isotopic effect on magnetic and electronic phase transitions than that in the other earlier studied oxides such as high-temperature superconductors, suggesting a strong coupling of charge carriers to the Jahn-Teller lattice distortions in manganites. It gives a direct evidence for the existence of polaron in manganites. More interesting is that a metal-insulator (*M-I*) transition induced by oxygen isotope substitution was reported in $(La_{0.5}Nd_{0.5})_{0.67}Ca_{0.33}MnO_3$ (Ref. 17) and $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$.[18,19] In cobalt oxides, electron-phonon coupling is also important to affect the transport and magnetic properties.[1–3,9–14] The Co^{3+} in IS state is also a Jahn-Teller active ion just like Mn^{3+}. Therefore, the interesting phenomenon ought to be expected when ^{16}O is substituted by ^{18}O. In the present work, we find an up-shift of T_S about 6.8 K in $(Pr_{0.7}Sm_{0.3})_{0.7}Ca_{0.3}CoO_3$, and the isotope exponent is about −0.8. To our knowledge, this is the first report to study oxygen isotope effect on spin state transition in cobalt oxides. The result is discussed in the framework of electron-phonon coupling.

II. EXPERIMENT DETAILS

Polycrystal samples $(Pr_{0.7}Sm_{0.3})_{0.7}Ca_{0.3}CoO_3$ were prepared by conventional solid-state reaction. Proper molar ratios of Pr_6O_{11}, Sm_2O_3, $CaCO_3$ and Co_3O_4 were mixed, well ground and then calcined at 1000 and 1100 °C for 24 h with intermittent grinding. The powder was pressed into pellets and sintered at 1200 °C in the flowing oxygen for 24 h.

One pellet of the as-synthesized samples was picked out and cut into two pieces for oxygen-isotope diffusion. Each piece was put into an alumina boat which was sealed in a quartz tube filled with 1 bar oxygen (one for ^{16}O and another for ^{18}O) mounted in a furnace. The quartz tubes formed parts of two identical closed loops. They were heated at 1000 °C

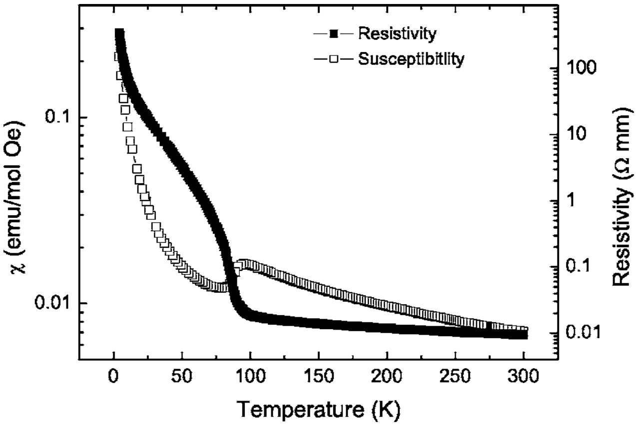

FIG. 1. The temperature dependence of the magnetic susceptibility and resistivity for the as-synthesized $(\mathrm{Pr}_{0.7}\mathrm{Sm}_{0.3})_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$ sample. The spins state transition can be seen in both curves.

for 24 h and then slowly cooled to room temperature. No impurity phase was found in powder x-ray diffraction patterns. The oxygen-isotope enrichment is determined from the weight changes of both ^{16}O and ^{18}O samples. An electronic microbalancer (Mitteler-Telado XL26) with 1 μg precision was used for sample weighting. The ^{18}O sample has $70\% (\pm 1\%)$ ^{18}O and $30\% (\pm 1\%)$ ^{16}O. To make sure the isotope exchange effect, back exchange of ^{18}O sample by ^{16}O was carried out in the same way and the weight change showed a complete back exchange. The resistivity and magnetic susceptibility of all the samples were measured. Resistivity measurements were performed on a ac resistance bridge (Linear Research, Inc., Model LR700) by the standard four-probe method. Magnetic susceptibility measurements were performed in a superconducting quantum interference device (SQUID) magnetometer (MPMS-7XL, Quantum Design) under the magnetic field of 1000 Oe.

III. RESULT AND DISCUSSION

Figure 1 shows the temperature dependence of resistivity and magnetic susceptibility for the as-synthesized $(\mathrm{Pr}_{0.7}\mathrm{Sm}_{0.3})_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$ sample. A sharp decrease around 96 K in susceptibility curve is found with decreasing temperature, indicating a spin state transition from IS to LS state for Co^{3+}.[14] T_S is defined as the spin state transition temperature corresponding to the maximum of susceptibility for $(\mathrm{Pr}_{0.7}\mathrm{Sm}_{0.3})_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$. A sharp increase appears in the resistivity curve at T_S. It is consistent with those reported by another group.[14] Co^{3+} in IS state has one e_g electron which can hop from one site to another site via the Co^{3+}-O^{2-}-Co^{4+} double exchange mechanism, and the $e_g$electron can be regarded to be itinerant. Co^{3+} in LS state has no e_g electron and its t_{2g} orbitals are fully occupied, and the charge is localized. Therefore, the resistivity may jump several orders when the Co^{3+} ion abruptly change from IS to LS state.

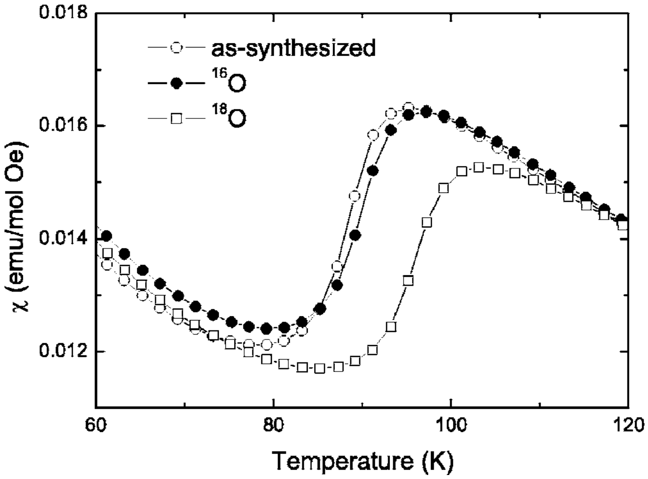

FIG. 2. The temperature dependence of magnetic susceptibility for different samples. Open square for as-synthesized sample, closed circle for ^{16}O sample, and open circle for ^{18}O sample. A positive shift of T_S for ^{18}O sample can be seen in this figure.

Figure 2 shows the magnetic susceptibility of the three samples: as-synthesized, ^{16}O, and ^{18}O ones. All samples show a sharp decrease in susceptibility. A very slight difference in T_S between as-synthesized sample and ^{16}O sample is observed, this could arise from the slight change of oxygen content or oxygen distributing induced by 1000 °C heat treatment. In addition, the very slight change in T_s suggests that the oxygen content is robust in this system. The ^{18}O and ^{16}O samples should have the same oxygen content due to the same heat treatment at the same oxygen pressure. As shown in Fig. 2, the T_S is 97.1 K for the ^{16}O sample and 103.9 K for the ^{18}O sample, respectively. An up-shift of T_S is about 6.8 K with the substitution of ^{16}O by ^{18}O. The oxygen isotope exponent $\alpha_S = -d \ln T_S / d \ln M_{\mathrm{O}}$ (where M_{O} is the oxygen isotope mass) is about -0.8. This is a negative value as is the exponent for charge-ordered temperature in $\mathrm{La}_{0.57}\mathrm{Ca}_{0.43}\mathrm{MnO}_3$.[21] The α_S is comparable to that in other oxides such as CMR materials and high-T_C superconductors. In $\mathrm{La}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$, the exponent for Curie temperature T_C is $\alpha_c \approx 0.85$ for $x=0.2$ and 0.7 for $x=0.1$,[16] $\alpha_c \approx 0.57$ for $x=0.1$, 1 for $x=0.2$, 0.55 for $x=0.25$, 0.32 for $x=0.33$, and 0.28 for $x=0.4$,[20] respectively; while the exponent for charge-ordered temperature is $\alpha_{co} \approx -0.41$ for $x=0.43$.[21] In $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_3$, the exponent for Curie temperature T_C: $\alpha_c \approx 0.19$ for $x=0.10$, 0.14 for $x=0.15$, and 0.07 for $x=0.3$, respectively.[16] In other materials, a crossover from metal to insulating phase[17–19,22] induced by the substitution of oxygen isotope are reported. The large oxygen isotope exponent indicates a strong electron-phonon coupling in this material. The temperature dependence of resistivity for as-synthesized ^{16}O and ^{18}O samples $(\mathrm{Pr}_{0.7}\mathrm{Sm}_{0.3})_{0.7}\mathrm{Ca}_{0.3}\mathrm{CoO}_3$ are shown in Fig. 3. All the samples show a *M*-*I* transition at T_s with decreasing temperature. An up-shift of the *M*-*I* transition temperature by about 7 K is observed in ^{18}O sample relative to the ^{16}O, being consistent with the magnetic susceptibility results.

To ensure the up-shift of the spin state transition temperature from the oxygen isotope effect, a back exchange of ^{18}O sample by ^{16}O was performed. The resistivity data are also shown in Fig. 3. The resistivity almost completely return to the ^{16}O sample, and its T_s is the same as the ^{16}O sample. This result indicates that the oxygen isotope effect in

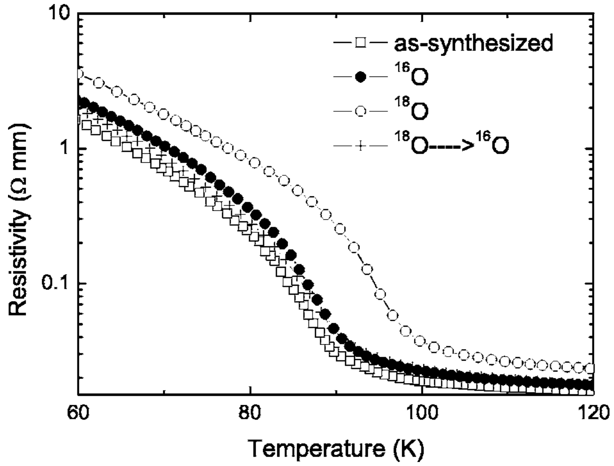

FIG. 3. Temperature dependence of resistivity for different samples. Open square for as-synthesized sample, closed circle for ^{16}O sample, open circle for ^{18}O sample, and the plus symbol for the back-exchange sample, respectively. A up shift of *M-I* transition temperature for ^{18}O sample can be clearly seen.

$(Pr_{0.7}Sm_{0.3})_{0.7}Ca_{0.3}CoO_3$ is intrinsic. It further confirms our explanation for the different T_S between as-synthesized sample and ^{16}O sample.

The substitution of ^{16}O with ^{18}O leads to an unusual large change in T_s determined by the magnetic and transport properties in $(Pr_{0.7}Sm_{0.3})_{0.7}Ca_{0.3}CoO_3$. We have checked the x-ray diffraction patterns of ^{16}O and ^{18}O samples, no obvious difference is found and almost same lattice parameters are obtained [$a=5.349(3)$ Å, $b=7.554(5)$ Å, $c=5.332(3)$ Å for the ^{16}O sample; $a=5.348(3)$ Å, $b=7.555(5)$ Å, $c=5.327(3)$ Å for the ^{18}O sample, respectively]. Therefore, the oxygen isotope exchange does not change Δ_C and J_H, which directly affect δE. The change of spin state transition caused by the substitution of ^{16}O with ^{18}O should arise from the phonon behavior. It suggests that there must be strong electron-phonon coupling in this system since large change in resistivity and magnetic susceptibility is induced. The substitution of ^{16}O by ^{18}O reduces the frequency of phonon, and consequently enhances the effective mass of electron (m^*) through the strong electron-phonon coupling. In tight-binding approximation, the bandwidth W is proportional to $1/m^*$. Therefore, the enhancement of m^* leads to a decrease of W. The slight increase in high-temperature resistivity for ^{18}O sample compared to the ^{16}O sample also indicates a decrease of W. In other words, a decrease in kinetic energy of electrons. When $\triangle_C$ and J_H remain unchanged, the decrease of W leads to an increase δE, and consequently causes an up-shift of T_S. On the other hand, Fujita *et al.* have proved that the Co-Co transfer energy t is important to determine δE.[12,14] When t decreases, δE increases and the LS state will be stabilized. In Hubbard model, W is proportional to $2zt$, z is the coordinate number. Therefore, the decrease of W leads to a decrease in t, and the increase of T_S. Our result gives direct evidence to support the opinion of Fujita *et al.*[12,14] Based on the observation of the *M-I* transition induced by oxygen isotope exchange in $(La_{0.5}Nd_{0.5})_{0.67}Ca_{0.33}MnO_3$ (Ref. 17) and $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$ (Refs. 18 and 19) whose compositions are in the boundary between metallic and insulating phases in the phase diagram, an IS-LS spin state transition induced by oxygen isotope effect should be expected in a special y for $(Pr_{1-y}Sm_y)_{0.7}Ca_{0.3}CoO_3$, that is, the low-temperature phase changes from metal to insulator with isotope exchange. This work is under investigation.

IV. CONCLUSION

An up-shift by about 6.8 K in T_S is observed in $(Pr_{0.7}Sm_{0.3})_{0.7}Ca_{0.3}CoO_3$ when ^{16}O is substituted by ^{18}O. The isotope exponent (α_S) is about -0.8. A strong electron-phonon coupling is responsible for this large oxygen isotope effect. The effective mass of electron is enhanced by the substitution, leading to a decrease in the bandwidth and an increase in δE. Therefore, the increase in δE results in the up-shift of T_S.

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