Giant isotope effect and spin state transition induced by oxygen isotope exchange in $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$

G. Y. Wang, X. H. Chen and T. Wu, G. Wu, X. G. Luo and C. H. Wang

Hefei National Laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People’s Republic of China

(Dated: March 23, 2022)

We systematically investigate effect of oxygen isotope in $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ which shows a crossover with x from ferromagnetic metal to the insulator with spin-state transition. A striking feature is that effect of oxygen isotope on the ferromagnetic transition is negligible in the metallic phase, while replacing $^{16}O$ with $^{18}O$ leads to a giant up-shift of the spin-state transition temperature ($T_s$) in the insulating phase, especially $T_s$ shifts from 36 to 54 K with isotope component $\alpha_S = -4.7$ for the sample with $x=0.175$. A metal-insulator transition is induced by oxygen isotope exchange in the sample $x=0.172$ being close to the insulating phase. The contrasting behaviors observed in the two phases can be well explained by occurrence of static Jahn-Teller distortions in the insulating phase, while absence of them in the metallic phase.

PACS numbers: 75.30.-m, 71.38.-k, 31.30.Gs

Cobaltites with CoO$_6$ octahedra have recently attracted much attention because they exhibit various intriguing physical properties as magnetoresistance,[1] enormous Hall effect,[2] superconductivity,[3] and large thermoelectric effect.[4] Prosvskite-related cobalt oxides show their unique feature: temperature-induced spin state transition (SST).[5] Such spin state transition, which is extremely sensitive to composition and pressure,[2] is closely connected with electrical conductivity. The Co$^{3+}$ ion, which contains six 3d electrons, often exhibits a SST from the low spin (LS, $t_{2g}$) ground state to the intermediate spin (IS, $t_{2g}^2e_g^1$) or to the high spin (HS, $t_{2g}^3e_g^2$) state with increasing temperature. The most important character of the SST in perovskite-type cobalt oxides is often accompanied by the metal-insulator transition (MIT).

Experimental and theoretical works indicated that the spin-state transition in cobaltites is from LS to IS below room temperature.[5, 6, 8, 10] The IS state is expected to be strong Jahn-Teller (JT) active due to the partially filled $e_g$ level, creating monoclinic distortions of CoO$_6$ octahedra. Actually, elastic and inelastic neutron scattering showed that spin activation of Co$^{3+}$ ions in $La_{1-x}Sr_xCoO_3$ system induces local static JT distortions in the paramagnetic insulating phase for all x, while the static JT distortions are absent in the ferromagnetic metal phase.[11] Understanding the characteristics of Jahn-Teller instability can help elucidate the nature of metal-insulator transition, magnetoresistance, and even superconductivity.[12] The IS-JT state is stabilized with doping in the insulating phase for perovskite cobalt oxides.[6, 13] However, charge dynamics interfere with orbital JT ordering resulting in a new state and the JT distortions can lose their long-range coherency with increasing charge mobility in the ferromagnetic metal phase. JT interactions in perovskite oxides often result in quite intriguing physical phenomena through the coupling between orbital and spin degrees of freedom with lattice.[14] Coupling of JT modes to the lattice results in formation of small JT polars, so that coupling of the charge carrier to the JT lattice distortions leads to a giant oxygen isotope effect, and the JT distortions play an essential role in $La_{1-x}Ca_xMnO_3+y$.[15] Especially, a metal-insulator transition was induced by oxygen isotope exchange in $La_{0.175}Pr_{0.525}Ca_{0.3}MnO_3$.[16] To investigate JT physics and its role played in cobaltites, here we systematically study effect of oxygen isotope in perovskite $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ system with different x. This system is suitable to study the JT physics by oxygen isotope effect since it shows a crossover at $x\sim0.175$ from a ferromagnetic metal phase to an insulating phase with SST with increasing x.[17, 18] Therefore, it is expected that effect of oxygen isotope should be quite different in the ferromagnetic metal phase from the insulating phase because the static JT distortions are observed in the insulating phase, while absent in the metallic phase.

Polycrystalline samples $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with different x were prepared by conventional solid-state reaction. Proper molar ratios of $Pr_6O_{11}$, $Sm_2O_3$, $CaCO_3$ and $CoO_4$ were mixed, well ground and then calcined at 1000 °C and 1100 °C for 24 h with intermittent grinding. The pellets pressed from the powder were sintered at 1200 °C in the flowing oxygen for 48 h. All samples were characterized by X-ray diffraction and found to be single phase. One pellet for the samples with different x obtained above was cut into two pieces for oxygen-isotope diffusion. The two pieces for each composition were put into an alumina boat which were sealed in a quartz tube filled with oxygen pressure.
of 1 bar (one for $^{16}O$ and another for $^{18}O$) mounted in a furnace, respectively. The quartz tubes formed parts of two identical closed loops. They were heated at 1000 °C for 48 h and then slowly cooled to room temperature. The obtained samples were re-examined by X-ray diffraction to confirm them single phase. The oxygen-isotope enrichment is determined from the weight changes of both $^{16}O$ and $^{18}O$ samples. The $^{18}O$ samples have about 70% $^{16}O$ and 30% $^{18}O$. 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. Magnetic susceptibility measurements were performed with a SQUID magnetometer in a magnetic field of 1000 Oe. Resistance measurements were performed using the ac four-probe method with an ac resistance bridge system (Linear Research Inc. LR-700P).

Figure 1 shows temperature dependence of resistivity for the samples $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with $x=0.175, 0.20, 0.25$ and 0.30 treated in $^{16}O$ and $^{18}O$, respectively. The samples $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with various $x$ treated in $^{16}O$ shows a very weak semiconductive behavior at the high temperatures, while a sharp metal-insulator transition is observed at certain temperatures ($T_S$) for different $x$ with decreasing temperature. $T_S$ increases with increasing $x$. As shown in Fig.1, substitution of $^{18}O$ for $^{16}O$ leads to an enhancement of $T_S$ for all samples. The up-shift of $T_S$ decreases with increasing $x$. A giant isotopic shift is observed in the sample with $x=0.175$. $T_S$ shifts from 36 to 54 K after replacing of $^{16}O$ by $^{18}O$. The oxygen isotope exponent $\alpha_s = -\frac{\text{dln}T_S}{\text{dln}M_O}$ (where $M_O$ is the oxygen isotope mass) is about -4.7, which is much larger than $\alpha_c = 0.8$ observed in $La_{1-x}Ca_xMnO_3+y$.[14] However, the up-shift of $T_S$ is about 7 K for the sample with $x=0.30$ and the isotope component $\alpha_s$ is about -0.8. To make sure that the effect arises from the oxygen isotope exchange, we carried out the isotope back-exchange. The transport properties completely return to that observed in the samples previously treated in $^{16}O$ and $^{18}O$ after the isotope back-exchange, respectively. Such metal-insulator transition has been believed to arise from the spin-state transition. Therefore, the susceptibility was measured for the samples above.

Temperature dependence of susceptibility measured in the field-cooled process with magnetic field of 1000 Oe is shown in Fig.2 for the same samples used in resistivity measurements. All samples show a sharp SST from IS state to LS state with decreasing temperature, respectively. $T_s$ increases with increasing $x$. Replacing of $^{16}O$ with $^{18}O$ makes $T_s$ shift to high-temperature. This is consistent with metal-insulator transition observed in resistivity as shown in Fig.1. It should be pointed out that $T_s$ is exactly the same as that of metal-insulator transition observed in Fig.1. The sample with $x=0.175$ treated in $^{16}O$ and $^{18}O$ show a sharp SST from IS state to LS state with decreasing temperature at 36 and 54 K, respectively. It further supports that the metal-insulator transition arises from the SST. It has been noted that there exists a thermal hysteresis for the phase transition. Therefore, all measurements were carried out in the cooled process to keep the consistency.

Figure 3 shows temperature dependences of resistivity and susceptibility for the $^{16}O$ and $^{18}O$ samples $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with $x=0.172$. The sample treated in $^{16}O$ shows a very weak semiconductive be-

![FIG. 1: Temperature dependence of resistivity for the $^{16}O$ and $^{18}O$ samples $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with $x=0.175, 0.20, 0.25$ and 0.30. The data denoted by the solid and open symbols are taken from the samples treated in $^{16}O$ and $^{18}O$, respectively.](image)

![FIG. 2: Temperature dependence of susceptibility for the $^{16}O$ and $^{18}O$ samples $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with $x=0.175, 0.20, 0.25$ and 0.30. The data denoted by the solid and open symbols are taken from the samples treated in $^{16}O$ and $^{18}O$, respectively.](image)
The reversibility of the metal-insulator transition induced by about 39 K after the treatment in while a sharp metal-insulator transition is observed at about 60 K, while the ferromagnetic transition disappears and a sharp spin-state transition at about 42 K. The remarkable feature is that the replacement of Pr with Sm content x in (Pr1−xSmx)0.7Ca0.3CoO3 with x=0.172 treated in 18O suppresses the ferromagnetic transition and leads to a down-shift of the Curie temperature (Tc), being similar to that observed in manganites although the down-shift of Tc is much less relative to La1−xCaxMnO3+y.17 The down-shift of Tc slightly increases with increasing x. However, the shift of Tc is very small compared to that of TS. It suggests that the effect of oxygen isotope on ferromagnetic transition is negligible.

To further study the JT physics by oxygen isotope effect in the ferromagnetic metallic phase, the susceptibility is systematically studied on the 16O and 18O samples (Pr1−xSmx)0.7Ca0.3CoO3 with x=0.05, 0.10, 0.15 and 0.17. Temperature dependence of susceptibility for these samples are shown in Fig.4. Actually, substitution of 18O for 16O suppresses the ferromagnetic transition and leads to a down-shift of the Curie temperature (Tc), being similar to that observed in manganites although the down-shift of Tc is much less relative to La1−xCaxMnO3+y.17

The effect of oxygen isotope on ferromagnetic transition is negligible.
competition between ferromagnetic transition and SST. As shown in Fig. 5, a maximum isotope component \( \alpha \) is observed in the boundary between ferromagnetic metal and insulating phases. A intriguing phenomenon is that the substitution of \( ^{18}O \) by \( ^{16}O \) leads to a disappearance of ferromagnetic transition and induces the SST accompanied by the metal-insulator transition in the sample \((Pr_{0.82}Sm_{0.172})_{0.7}CaO_3CoO_3\) system, which is in the ferromagnetic metal phase close to the crossover boundary.

In the insulating regime (\( x > 0.175 \)), the up-shift of \( T_S \) induced by oxygen isotope exchange can be explained to originate from that substitution of \( ^{16}O \) by \( ^{18}O \) leads to a decrease in frequency of phonon, and consequently enhances effective mass of electron \( (m^* ) \) through strong electron-phonon coupling. The enhancement of \( m^* \) leads to a decrease of bandwidth \( \Gamma \), resulting in an increase of energy difference \( \Delta E \) between IS and LS states and consequently an up-shift of \( T_S \). The increase of Sm-doping leads to a decrease in the ionic radius of A site \((Pr_{1-x}Sm_x)_{0.7}CaO_3\) in the \((Pr_{1-x}Sm_x)_{0.7}CaO_3CoO_3\) system, so that volume of the CoO\(_6\) octahedra decreases. The decrease in volume of the CoO\(_6\) octahedra results in an increase of crystal field splitting energy \( \Delta C \) and \( \Delta E \), causing an increase in \( T_S \). Therefore, decrease of the isotope component \( \alpha \) with increasing \( x \) could be due to the increase of \( T_S \). In contrast to the giant oxygen isotope effect in the insulating phase, a negligible oxygen isotope effect occurs in the ferromagnetic metal phase. Beyond the expectation, substitution of \( ^{16}O \) by \( ^{18}O \) leads to a phase transition from a ferromagnetic metal to an insulator in the sample with \( x = 0.172 \) which lies in the ferromagnetic metal phase close to the crossover boundary. These contrasting behaviors are in support of the observation that static JT distortions occur in the insulating phase, while are absent in the ferromagnetic metal phase. It provides a direct demonstration of the important of lattice vibrations in these materials.

**Acknowledgement:** This work is supported by the Nature Science Foundation of China, and by the Ministry of Science and Technology of China (973 project No:2006CB601001), and by the Knowledge Innovation Project of Chinese Academy of Sciences.

---

* Corresponding author; Electronic address: chenxb@ustc.edu.cn

[1] G. Brépège, H. Y. Chang, S. D. Sun, P. G. Schultz and X. D. Xiang, Science 270, 273(1995).

[2] A. V. Samoilov, G. Beach, C. C. Fu, N. C. Yeh, and R. P. Vasquez, Phys. Rev. B 57, R14032(1998).

[3] K. Takada et al., Nature 422, 55(2003).

[4] T. Terasaki et al., Phys. Rev. B 56, R12685(1997).

[5] M. A. Senaris-Rodriguez and J. B. Goodenough, J. Solid State Chem. 116, 224(1995).

[6] S. Tsuobuchi et al., Phys. Rev. B 66, 052418(2002).

[7] K. Asai et al., J. Phys. Soc. Jpn 66, 967(1997).

[8] S. Yamaguchi, Y. Okimoto and Y. Tokura, Phys. Rev. B 55, R8666(1997).

[9] T. Saitoh et al., Phys. Rev. B 56, 1290(1997).

[10] M. A. Korotin et al., Phys. Rev. B 54, 5309(1996).

[11] D. Louca and J. L. Sarrao, Phys. Rev. Lett. 91, 155501(2003).

[12] I. B. Bersuker, Chem. Rev. 101, 1067(2001).

[13] D. Louca et al., Phys. Rev. B 60, R10378(1999).

[14] J. B. Goodenough, Mater. Res. Bull. 6, 967(1971).

[15] G. M. Zhao, K. Conder, H. Keller, and K. A. Miller, Nature 381, 676(1996).

[16] N. A. Babushkina et al., Nature 391, 159(1998).

[17] T. Fujita et al., J. Phys. Soc. Jpn 73, 1987(2004).

[18] T. Fujita et al., J. Phys. Soc. Jpn 74, 2294(2005).