Argon annealing of the oxygen-isotope exchanged manganite La$_{0.8}$Ca$_{0.2}$MnO$_{3+y}$

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We have resolved a controversial issue concerning the oxygen-isotope shift of the ferromagnetic transition temperature $T_C$ in the manganite La$_{0.8}$Ca$_{0.2}$MnO$_{3+y}$. We show that the giant oxygen-isotope shift of $T_C$ observed in the normal oxygen-isotope exchanged samples is indeed intrinsic, while a much smaller shift observed in the argon annealed samples is an artifact. The argon annealing causes the $^{18}$O sample to partially exchange back to the $^{16}$O isotope due to a small $^{16}$O$_2$ contamination in the Ar gas. Such a contamination is commonly caused by the oxygen outgas that is trapped in the tubes, connectors and valves. The present results thus unambiguously demonstrate that the observed large oxygen isotope effect is an intrinsic property of manganites, and places an important constraint on the basic physics of these materials.

An intensive research effort [1] has recently been made to study the manganese-based perovskites Ln$_{1-x}$A$_x$MnO$_3$ (where Ln is a trivalent element, A is a divalent element) due to the discovery of very large (“colossal”) magnetoresistance (CMR) in thin films of these compounds [2,3]. The physics of manganites has primarily been described by the double-exchange model [4,5]. Recent calculations [6–8] show that a strong electron-phonon interaction must be involved to explain the basic physics of these materials. Many recent experiments have provided compelling evidence for the existence of a strong electron-phonon interaction and of polaronic charge carriers in manganites [9–17].

In particular, the observed giant oxygen isotope shift of the Curie temperature [10] should provide direct evidence that lattice vibrations play an important role in the magnetic properties of these materials. However, Nagaev [18] has recently shown that the observed giant oxygen-isotope effects in manganites [10] are not caused by a strong electron-phonon coupling, but rather by an oxygen-mass dependence of excess oxygen. In addition, Franck et al., demonstrated that [19] the oxygen-isotope shift was reduced by more than 10 K after the oxygen-isotope exchanged samples of La$_{0.8}$Ca$_{0.2}$MnO$_{3+y}$ were annealed for 24 h in argon and at 950 °C. They thus argued that the giant isotope shift (21 K) reported in Ref. [10] is not intrinsic, but caused by the presence of excess oxygen in the samples.

In order to resolve the controversy concerning the isotope effect in the manganites, we perform thermogravimetry (TG) experiments on the oxygen-isotope exchanged samples of La$_{0.8}$Ca$_{0.2}$MnO$_3$, which were carried out in flowing argon gas and at 950 °C. The experiments demonstrate that the $^{18}$O sample was partially exchanged back to the $^{16}$O isotope when it was annealed in flowing argon gas and at 950 °C. This is due to the fact that the oxygen outgas trapped in the tubes, connectors and valves contaminates the argon gas although the Ar gas itself is very pure. The present experiments thus show that the oxygen-isotope effects observed in the argon annealed samples are not reliable, and that the normal isotope exchange procedure can ensure the same oxygen content for two isotope samples.

Samples of La$_{0.8}$Ca$_{0.2}$MnO$_{3+y}$ were prepared by conventional solid state reaction using dried La$_2$O$_3$, MnO$_2$ and CaCO$_3$. The well-ground mixture was heated in air at 1000 °C for 20 h, 1100 °C for 20 h with one intermediate grinding. The powder samples were then pressed into pellets and sintered at 1260 °C for 72 h, and 1160 °C for 72 h with one intermediate grinding. Two pieces were cut from the same pellet for oxygen-isotope diffusion. The diffusion was carried out for 50 h at 1000 °C and oxygen pressure of 1 bar. The oxygen-isotope enrichment was determined from the weight changes of both $^{16}$O and $^{18}$O samples. The $^{18}$O samples had $\sim$90% $^{18}$O and $\sim$10% $^{16}$O.

Thermogravimetry (TG) experiments were performed using PERKIN ELMER TGA7 Instrument. The investigated samples were heated in a stream (50 cm$^3$/min) of very pure Ar (99.998%). The weights of the $^{16}$O and $^{18}$O samples used for TG experiments were 71.833 mg and 46.145 mg, respectively. Before each experiment, the balance (with the sample inside) was flushed with the pure Ar at room temperature for at least 40 h.

Fig. 1 shows the TG data for both $^{16}$O and $^{18}$O samples of La$_{0.8}$Ca$_{0.2}$MnO$_3$. The weight was renormalized to that at 500 °C to eliminate the error due to adsorption of water and CO$_2$ in the samples. From the figure, one can see that the weights of both isotope samples start to decrease when the temperature reaches 950 °C. However, there is a substantial difference in the weight loss for the two isotope samples. After argon annealing at 950 °C for 150 minutes, the weight of the $^{16}$O sample decreases by about 0.20% while the weight of the $^{18}$O is reduced...
by 1.60%. After argon annealing at 950 °C for 24 hours, the weight of the \(^{16}\text{O}\) sample decreases by about 0.25\% while the weight of the \(^{18}\text{O}\) is reduced by 2.50\%. The extra weight decrease for the \(^{18}\text{O}\) sample is due to the fact that the \(^{18}\text{O}\) sample was partially exchanged back to the \(^{16}\text{O}\) isotope because of the \(^{16}\text{O}\) contamination in the Ar gas. Such a contamination is commonly caused by the oxygen outgas that was trapped in the tubes, connectors and valves. Without heating these elements in the system, it is hard to get rid of the trapped outgas, and the contamination is unavoidable. From the weight changes, we can estimate that the \(^{18}\text{O}\) content of the \(^{18}\text{O}\) sample became about 40\% after annealing for 150 minutes, and about 5\% after annealing for 24 h.

FIG. 1. Thermogravimetry (TG) data for both \(^{16}\text{O}\) and \(^{18}\text{O}\) samples of \(\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3\). The short-dash line and solid line are for the weights of the \(^{16}\text{O}\) and \(^{18}\text{O}\) samples (left scale), respectively. The long-dash line is for the temperature profile of both isotope samples (right scale). The investigated samples were heated in a stream (50 cm\(^3\)/min) of pure Ar (99.998\%). The weights of the \(^{16}\text{O}\) and \(^{18}\text{O}\) samples used for TG experiments were 71.833 mg and 46.145 mg, respectively. Before each experiment, the balance (with the sample inside) was flushed with the pure Ar at room temperature for at least 40 h.

In order to check the influence of the argon annealing on the ferromagnetic transition temperature \(T_C\), we performed magnetization measurements for these samples. Field-cooled magnetization was measured with a Quantum Designed SQUID magnetometer in a field of 5 mT. The samples were cooled directly to 5 K, then warmed up to a temperature well below \(T_C\). After waiting for 5 minutes at that temperature, data were collected upon warming to a temperature well above \(T_C\). In Fig. 2, we plot the temperature dependence of the low-field magnetization (normalized to the magnetization well below \(T_C\)) for the \(^{16}\text{O}\) and \(^{18}\text{O}\) samples of \(\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3\) (a) before the argon annealing; (b) after the argon annealing at 950 °C for 24 h. It is clear that before the argon annealing, the oxygen-isotope shift of \(T_C\) is about 21 K, while the shift becomes very small (about 1 K) after the annealing. As shown above, the \(^{18}\text{O}\) sample contains only about 5\% \(^{18}\text{O}\), so the isotope shift should be about 1 K, as observed. The result clearly shows that a very small isotope shift observed in the present argon annealed samples is due to a small \(^{16}\text{O}\) contamination in the argon gas, which is sufficient to exchange the \(^{18}\text{O}\) back to the \(^{16}\text{O}\) isotope.

It is also important to see how sensitively the \(T_C\) depends on the argon annealing. In Fig. 3, we show the temperature dependence of the low-field magnetization for the \(^{16}\text{O}\) sample before and after 24 hour argon annealing. The argon annealing does not cause a decrease
in the $T_C$ of the $^{16}$O sample. This is in contrast to the result shown in Ref. [19] where the argon annealing leads to a decrease of $T_C$ by about 10 K. The discrepancy is possibly due to the fact that our present $^{16}$O sample is nearly stoichiometric. From the TG data shown in Fig. 1, one can see that the oxygen content of the $^{16}$O sample decreases by about 0.04 per unit cell after the argon annealing. This implies that the $T_C$ is very insensitive to the oxygen content in the present sample where the oxygen content is nearly stoichiometric. The present result is consistent with Ref. [20] where it was shown that the $T_C$ of the stoichiometric sample of La$_{0.8}$Ca$_{0.2}$MnO$_3$ is reduced by about 3 K when introducing about 0.05 oxygen vacancies per cell. This would imply that the oxygen content of the $^{18}$O sample must be smaller by 0.35 per cell than the $^{16}$O sample in order to produce the observed oxygen isotope shift of 21 K. In fact, it was shown that the difference in the oxygen content of the $^{16}$O and $^{18}$O samples of (La$_{0.25}$Pr$_{0.75}$)$_{0.7}$Ca$_{0.3}$MnO$_3$ is less than 0.002 per cell, while the isotope shift is larger than 100 K [21]. Moreover, our normal oxygen-isotope exchange procedure has been extensively used for the isotope effect experiments in cuprates [23][24]. Both indirect [22][23] and direct [24] measurements on the oxygen content consistently show that the oxygen contents of two isotope samples are the same within 0.0003 per cell. Therefore, the observed large oxygen-isotope shift cannot be caused by a negligible difference in the oxygen stoichiometries of the two isotope samples.

Our present result, together with some isotope-effect results from other groups, can strongly argue against the theoretical model proposed by Nagaev [18]. According to his model, the $^{16}$O sample always has more oxygen content than the $^{18}$O sample if the samples are nonstoichiometric. The more nonstoichiometric the samples are, the more difference in the oxygen contents of two isotope samples, and thus the larger the isotope effect is. This is in contradiction with experiment. The stoichiometric (La$_{0.25}$Pr$_{0.75}$)$_{0.7}$Ca$_{0.3}$MnO$_3$ compound shows a very large isotope effect [21], while the very nonstoichiometric (LaMn)$_{0.945}$O$_3$ material has a rather small isotope effect [11]. As a matter of fact, the isotope exponent is proportional to the pressure-effect coefficient, and simply depends on $T_C$ [25]. Furthermore, this theoretical model would predict a negative oxygen isotope effect (i.e., the $^{18}$O sample has a higher $T_C$) for the overdoped regime where $dT_C/dx < 0$. In reality, one has always found positive isotope effects [19][25]. Thus, we must conclude that the theoretical explanation to the observed isotope effects by Nagaev [18] is not correct.

In summary, our present TG experiments clearly demonstrate that the argon annealing on the oxygen-isotope exchanged samples causes the $^{18}$O sample to partially exchange back to the $^{16}$O isotope due to a small $^{16}$O contamination in the Ar gas. Such a contamination is commonly caused by the oxygen outgas that is trapped in the tubes, connectors and valves. The present result clearly shows that the oxygen-isotope effect observed in the argon annealed samples may not be intrinsic, and that the normal isotope exchange procedure can ensure the same oxygen content for two isotope samples and thus produce an intrinsic isotope effect. The observed large oxygen isotope effect which is an intrinsic property of manganites places an important constraint on the basic physics of these materials.

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FIG. 3. Temperature dependence of the low-field magnetization for the $^{16}$O sample of La$_{0.8}$Ca$_{0.2}$MnO$_3$ before (solid circle) and after (solid triangle) argon annealing for 24 h. The argon annealing does not cause a significant change in the $T_C$ of the $^{16}$O sample.

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