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Oxygen stoichiometry and isotope effect in $La_{1-x}Ca_xMnO_{3+\delta}$

K. Conder*
Laboratory for Neutron Scattering, ETH Zürich & Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

Guo-meng Zhao
Department of Physics and Texas Center for Superconductivity, University of Houston, Houston, Texas 77204

R. Khasanov
Physik-Institut der Universität Zürich, CH-8057 Zürich and Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

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Oxygen stoichiometry in the colossal magnetoresistive $La_{1-x}Ca_xMnO_{3+\delta}$ has been measured using hydrogen reduction on thermobalance. With a thoughtful measurement procedure, the excess oxygen content can be determined with an uncertainty of $\Delta\delta = \pm 0.003$. Applying this method to the oxygen-isotope exchanged samples, we find that the oxygen stoichiometries of the ^{16}O- and ^{18}O-substituted samples are the same. This leads us to conclude, that the observed giant oxygen-isotope effect on the Curie temperature T_C in the ferromagnetic manganites is intrinsic and is not caused by a difference in the oxygen contents of the two isotope samples.

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In the colossal magnetoresistance (CMR) materials, an unexpected large oxygen-isotope effect (OIE) on the Curie temperature T_C was observed.[1–3] Upon replacing ^{16}O with ^{18}O, the T_C for $La_{0.8}Ca_{0.2}MnO_{3+\delta}$ was lowered by about 20 K.[1] Such a giant oxygen-isotope effect on the Curie temperature is not expected from conventional theories of magnetism, where the atoms can usually be considered as infinitely heavy and static. The observation of the giant oxygen-isotope effect, thus, indicates that electron-lattice coupling in the CMR manganites should be very strong. This is consistent with several theoretical studies[4–6] and many independent experiments.[7] Soon, several isotope-effect experiments performed by Franck *et al.*[8,9] gave evidence for a strong correlation of the isotope effect with the oxygen stoichiometry. However, the importance of the observed isotope effects and the role of electron-phonon coupling in manganites were discounted by the theoretical studies by Nagaev.[10,11] In particular, Nagaev claimed that the measured OIE's in the manganites are not caused by strong electron-phonon coupling, but simply arise from a difference in the oxygen stoichiometries of the ^{16}O- and ^{18}O-substituted samples due to their different oxygen-oxide thermodynamic properties.[11] His claim has already been undermined by studies of the lattice parameters for both ^{16}O- and ^{18}O-substituted manganites.[12,13] Although these studies[12,13] suggest that there is only a negligible difference in the oxygen contents of both isotope samples, direct and precise measurements of the oxygen contents for the isotope-exchanged manganites are essential to finally resolve this controversial issue.

Oxygen stoichiometry in manganites could be determined by thermogravimetric (TG) removal of the access oxygen (over three) at high temperatures.[14] This method, however, cannot be used for ^{18}O-substituted samples, as the isotope back exchange will take place, which will strongly influence the weight of the sample. Here, we directly determine the oxygen stoichiometries for both ^{16}O and ^{18}O samples of $La_{0.8}Ca_{0.2}MnO_{3+\delta}$ using hydrogen reduction on thermobalance.

$La_{0.8}Ca_{0.2}MnO_{3+\delta}$ sample were prepared using La_2O_3, $CaCO_3$, and MnO_2. The sample was calcinated at temperatures 1000–1350 °C for 120 h with several intermediate grindings. It was characterized using powder x-ray diffraction method (SIEMENS D500). The ^{18}O sample was obtained via the oxygen-isotope exchange, which was performed in a closed apparatus[15] under controlled oxygen $^{18}O_2$ pressure slightly above 1 bar and at 1000 °C for 35 h and cooled with a rate 300 °C/h. A reference ^{16}O sample was obtained by annealing in the natural oxygen environment with the condition same as the one for the ^{18}O sample. The exchange apparatus was equipped with a mass spectrometer (BALZERS Prisma), which allows determination of the progress of the isotope exchange. During the oxygen-isotope exchange between the gas ($^{18}O_2$) and the solid phase (containing ^{16}O) the gas phase will be enriched in $^{16}O_2$ and $^{16}O^{18}O$ molecules. Therefore, the following parameter β describes the progress of the exchange reaction:

$$\beta = \frac{[^{18}O] + 0.5[^{16}O^{18}O]}{[^{16}O] + [^{16}O^{18}O] + [^{18}O]},$$

where $[^{16}O]$, $[^{16}O^{18}O]$, and $[^{18}O]$ are concentrations of the gas components proportional to the ionic currents for the masses $m/e = 32$, 34, and 36, respectively. Thermogravimetric hydrogen reduction measurements have been performed using NETZSCH Jupiter STA 449C system combined with mass spectrometer ThermoStar Pfeiffer Vacuum. Samples of about 50 mg were used for the experiments. NETZSCH TG sample holder and alumina crucibles were used in all the experiments. Before starting each measurement, the system was evacuated for three times and filled again with protective (and purge) gases. In order to decrease the reproducibility errors caused by the buoyancy power, helium and He $+10\%H_2$ were used as the protective and purge gases, respectively. All the measurements were performed with a base line correction. Magnetization measurements were per-

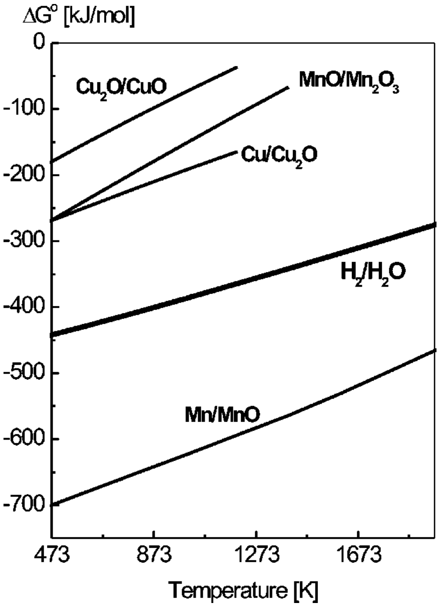

FIG. 1. Ellingham plot for water and manganese and copper oxides. The plot shows a change of a Gibbs free energy $\Delta G°$ for the reactions of oxidation in which one mole of oxygen is bounded. Only the oxides for which the lines are lying above those for H_2/H_2O can be reduced with hydrogen, as the total Gibbs free energy will decrease after the mutual reaction.

formed using Physical Property Measurement System PPMS (Quantum Design) at the field of 1000 Oe. The samples were cooled to 10 K in the field. After waiting for 30 min at this temperature, the measurements were performed upon warming to room temperature.

Thermogravimetric hydrogen reduction is commonly used for the determination of the oxygen contents in cuprates. Under reaction with hydrogen at elevated temperatures metallic copper and Y_2O_3 and BaO are obtained in the case of $YBa_2Cu_3O_{7-\delta}$.[16] Thus, one can easily calculate the oxygen content in the starting sample when the weight change during reduction reaction is recorded. As can be shown in Ellingham plot (Fig. 1), only Mn^{2+} (as well as La^{3+} and Ca^{2+}; for La_2O_3/La and CaO/Ca the appropriate lines are lying much below that for Mn/MnO) are thermodynamically stable in hydrogen atmosphere. Thus, products of the reduction reaction should be strictly oxygen stoichiometric, i.e., an end point (weight plateau) for the reaction should be obtained. Figure 2 shows TG runs (heating and cooling rate 20 °C/min) obtained during hydrogen reduction of both ^{18}O- and ^{16}O-substituted samples in a stream of He with 8% of H_2 in the gas mixture. The reduction starts at about 400 °C and is completed at about 1000 °C. Figure 3 shows an enlarged part of the curves around the end point of the reduction. As one can see no plateau can be obtained in the case of $La_{0.8}Ca_{0.2}Mn^{18}O_{3+\delta}$ sample. The reason for that is the oxygen-isotope exchange, which proceeds with the traces of oxygen in the purge gas. This effect was confirmed in an experiment in which, after 1100 °C was reached, the sample was additionally kept at this temperature for 1 h. A continuous decrease of the weight of the sample (about 0.25%/h) was achieved. The change of the mass of the sample caused by the isotope exchange can be minimized by using gases of very high purity and with a high heating rate, but cannot be completely avoided. Therefore, the correction for this effect is essential. The correction is based on the assumption that the rate of the exchange depends only on the amount of oxygen in the purge gas, and thus can be estimated from the mass change observed during cooling of the sample. For the experiments performed in this work, this correction was 0.02% (see Fig. 3) for the oxygen-isotope exchange at temperatures below 1000 °C. Thus, from the mass changes obtained in reduction experiments in the case of ^{18}O- substituted samples, 0.02% had to be subtracted. It has to be stressed that this correction depends mainly on the experimental conditions, e.g., purity of the gases used, heating rates, temperature range at which the reaction takes place, and the isotope content in the sample.

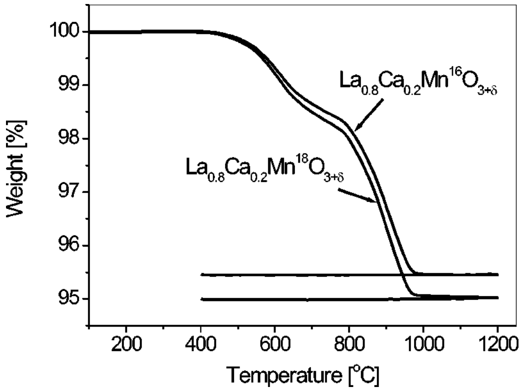

FIG. 2. Thermogravimetric investigations of the hydrogen reduction of ^{18}O- and ^{16}O-substituted $La_{0.8}Ca_{0.2}MnO_{3+\delta}$ samples (heating and cooling rate: 20 °C/min and gas mixture: He with 8% of H_2).

For the determination of the oxygen content on the base of the weight change during hydrogen reduction, the crucial information is the isotope enrichment: $100\%[^{18}O]/([^{18}O]+[^{16}O])$ in the ^{18}O sample. This could be determined using

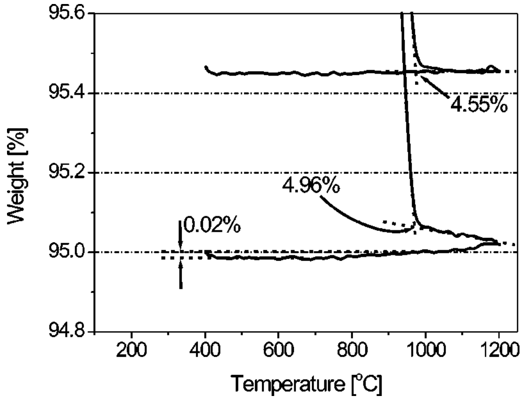

FIG. 3. An enlarged part of the curves of Fig. 2 around the end point of the reduction. In the case of $La_{0.8}Ca_{0.2}Mn^{16}O_{3+\delta}$ the weight change can be simply calculated as an onset of the curve. In the case of $La_{0.8}Ca_{0.2}Mn^{18}O_{3+\delta}$ a correction for oxygen-isotope exchange with traces of oxygen in the purge gas has to be made (see text).

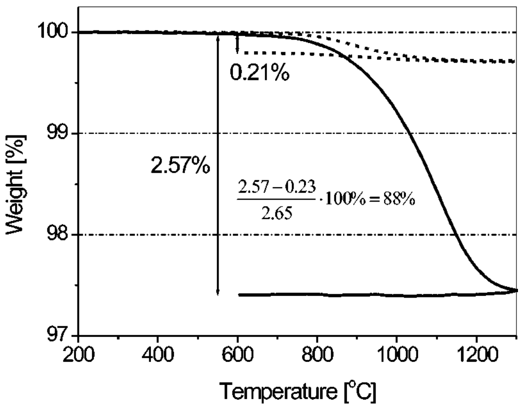

FIG. 4. Thermogravimetric investigations of the oxygen exchange in $La_{0.8}Ca_{0.2}Mn^{18}O_{3+\delta}$ (solid line) and $La_{0.8}Ca_{0.2}Mn^{16}O_{3+\delta}$ (broken line) samples. Heating and cooling rate 10 °C/min and gas mixture: He with 15% of O_2.

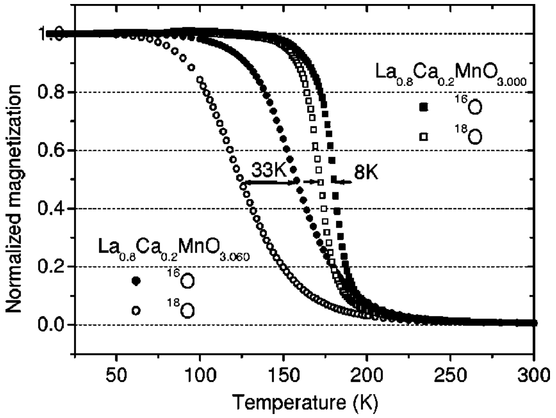

FIG. 5. Temperature dependence of the normalized magnetization for the $La_{0.8}Ca_{0.2}Mn^{18}O_{3+\delta}$ (open points) and $La_{0.8}Ca_{0.2}Mn^{16}O_{3+\delta}$ (solid points).

three methods: (1) *in situ* measurements of the β parameter during the exchange process, (2) mass increase of the sample after the light ^{16}O isotope was exchanged with the heavy ^{18}O, (3) a back exchange of the heavy isotope with a light one (there is 99.8% of the ^{16}O isotope in natural oxygen) on the thermobalance. For the $La_{0.8}Ca_{0.2}Mn^{18}O_{3+\delta}$ investigated in this work, 85% and 83% were obtained by the first and the second methods, respectively.

Figure 4 presents TG results obtained by the back exchange of the oxygen isotope in $La_{0.8}Ca_{0.2}Mn^{18}O_{3+\delta}$ (solid line). Identical experiment has been performed using $La_{0.8}Ca_{0.2}Mn^{16}O_{3+\delta}$ sample (broken line). As it can be seen, at high temperatures, also for the ^{16}O sample there is a mass loss observed. This is caused by the oxygen stoichiometry change.[14] Thus, it is evident that the mass change obtained for the ^{18}O sample (Fig. 4) is a sum of these caused by the change of the oxygen stoichiometry and by the oxygen-isotope exchange. Therefore, to calculate isotope content in the sample, from the obtained mass change (2.57%) the appropriate value for ^{16}O sample (recalculated for the heavy isotope ^{18}O) has to be subtracted, and the result should be divided by the theoretical mass change for 100% substituted sample (see Fig. 4).

Calculations of the oxygen stoichiometry were performed assuming that the following balance reaction takes place during hydrogen reduction:

$$La_{0.8}Ca_{0.2}MnO_{3+\delta}+2(0.6+\delta)H_2$$
$$\rightarrow 0.8LaO_{1.5}\cdot 0.2CaO\cdot MnO+(0.6+\delta)H_2O.$$

As a result of this reaction the sample will lose $(0.6+\delta)$ of oxygen atoms from the formula and therefore, $(0.6+\delta)16.00$ g from a mole. In the case of ^{18}O sample, the oxygen molecular weight was assumed to be 17.7 g/mole (85% of the isotope enrichment) instead of 16.00 for the natural oxygen.

The oxygen content determination of the ^{16}O and ^{18}O samples were made five times for each of them and the error were calculated statistically. With the experimental setup at our disposal, the weight loss during reduction can be measured with an absolute error of about ±0.02% which correspond to the $\Delta\delta=\pm 0.003$. For the $La_{0.8}Ca_{0.2}Mn^{18}O_{3+\delta}$ sample $\delta=0.036\pm 0.003$ and for $La_{0.8}Ca_{0.2}Mn^{16}O_{3+\delta}$ sample $\delta=0.033\pm 0.003$ have been obtained. The oxygen-isotope shift determined at midpoint of the transitions was −20 K. This is in an excellent agreement with −21 K reported in our previous works.[1–3]

In order to estimate an influence of the oxygen content to the OIE, from the existing ^{16}O and ^{18}O material two other pairs of substituted samples were prepared. The first one, after an additional oxygen exchange was performed, was reduced in Ar at 1100 °C during 2 h. The process was performed in a closed apparatus in which the gas was exchanged several times. In the case of the second pair, the oxygen exchange process was performed slightly longer as usual (50 h, at 1000 °C) and accomplished with a slow cooling (20 °C/h). The magnetization measurement results are shown in Fig. 5. For the first pair, oxygen index 3.000 ±0.003 and for the second pair 3.060±0.003 (^{18}O content ≈93%) were obtained. The OIE in T_C, again determined as a temperature shift of the midpoint of the transitions, for the $La_{0.8}Ca_{0.2}Mn^{18}O_{3.000}$ and $La_{0.8}Ca_{0.2}Mn^{18}O_{3.060}$ pairs of the samples were −8 K and −33 K consequently (see Fig. 5). The results obtained support the previous findings of Franck *et al.*[8,9] that the isotope effect increases with oxygen index being in the order of −9 K for the oxygen stoichiometric samples.

In summary, we have demonstrated that samples annealed at the same pressure and temperature in respective $^{18}O_2$ and $^{16}O_2$ environment, have the same oxygen stoichiometry within the determination error of $\Delta\delta=\pm 0.003$. Even if the difference in oxygen stoichiometries were twice as much as the estimated determination error, the corresponding difference in the Curie temperature would be about 2 K.[17] Therefore, one can conclude that although OIE observed in $La_{1-x}Ca_xMnO_{3+\delta}$ is strongly dependent on oxygen stoichiometry it is *intrinsic* and not caused by a difference in the oxygen contents of both isotope samples.

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[*] Electronic address: kazimierz.conder@psi.ch

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