

Oxygen isotope effect in $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3+\delta}$ and its dependence on oxygen stoichiometry

J. P. Franck, I. Isaac, and D. D. Lawrie

Department of Physics, University of Alberta, Edmonton AB, Canada T6G 2J1

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The oxygen isotope effect of the ferromagnetic transition temperature was investigated in various samples of the manganite $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3+\delta}$, as a function of sintering conditions. Sintering at 1200 °C and above leads to oxygen-stoichiometric comparison samples with an isotope exponent of $\alpha_{\text{O}}=0.41\pm 0.02$, and transition temperatures $T_C(16)=189\pm 2$ K and $T_C(18)=180\pm 2$ K. Samples sintered at 1000 °C, and below, always have oxygen excess. The oxygen excess leads to vacancies at the *A* (La,Ca) and *B* (Mn) sites, leading to a decrease in unit cell volume. The unit cell volume is identical for both isotopes, and this implies equal oxygen content for the isotopic comparison samples. The isotope exponent α_{O} for oxygen excess samples is much larger than 0.4. Its value, as well as the transition temperatures T_C , depends on the Mn^{4+} concentration, as well as the defect structure induced by *A* and *B* sites vacancies.

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I. INTRODUCTION

Very large oxygen isotope effects of the Curie temperature have been observed in the CMR system $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$ for a range of calcium concentrations.¹⁻³ Very large isotope effects have also been published for the metal-insulator transition in $\text{La}_{0.175}\text{Pr}_{0.525}\text{Ca}_{0.3}\text{MnO}_3$,⁴ and in the charge ordering transition in $\text{La}_{0.58}\text{Ca}_{0.42}\text{MnO}_3$.⁵ In general the oxygen isotope exponent $\alpha_{\text{O}}=-\Delta \ln T_C/\Delta \ln m$, where T_C is the ferromagnetic Curie temperature for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$, decreases with increasing calcium concentration² x . An exceptionally large isotope exponent in the range 0.85 to 1.0 was published¹ for a calcium concentration of $x=0.2$. It was shown later^{2,3} that this effect is due to oxygen excess above 3.0, $\delta>0$, and that an oxygen isotope exponent near $\alpha_{\text{O}}=0.4$ represents the value for samples with oxygen stoichiometry 3.0. Theoretically it has also been claimed⁶⁻⁸ that ^{16}O and ^{18}O substituted samples have different oxygen excess based on thermodynamical equilibrium calculations. Such differences could lead to spuriously large isotope exponents, not only because the Curie temperature T_C is a strong function of oxygen excess at $x=0.2$, but also because of possibly different diffusion rates of ^{16}O and ^{18}O in the comparison samples. In a recent paper it was stated, however, that the making conditions of the $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3+\delta}$ samples have no bearing on T_C , and the isotope exponent.⁹ In particular, samples made by sintering at 800 °C or 1260 °C in an atmosphere of $^{16}\text{O}_2$ (1 atm) were shown to have the same transition.

In this paper we present experiments, which show that the total oxygen content is indeed a function of preparation conditions. At low temperature sintering conditions (T substantially lower than 1200 °C) oxygen excess always exists. This leads to a large isotope exponent and this isotope effect for oxygen excess is apparently an equilibrium effect. The only possibility of observing an intrinsic isotope effect in this system is to prepare both ^{16}O and ^{18}O compounds such that $\delta=0$.

II. EXPERIMENT

The experiments described here were conducted on a variety of samples with $x=0.2$. We prepared these samples by

the usual method of repeated sintering of stoichiometric mixtures of La_2O_3 , CaCO_3 , and MnO_2 in air at temperatures up to 1200 °C. For the isotopic exchange, the air and $^{16}\text{O}_2$ treated samples were cut into two and gas-exchanged in flowing clean $^{16}\text{O}_2$ and $^{18}\text{O}_2$ in the apparatus previously described.¹⁰ Isotopic exchange was always performed in 1 atm of oxygen gas to facilitate the exchange. Under these conditions it is important at which temperature the exchange is carried out. It is well known that $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$ can contain excess oxygen, particularly when processed at lower temperatures (somewhat below 1200 °C).¹¹⁻¹⁶ Since the perovskite structure has no room for additional oxygen, the nominal oxygen excess in fact represents vacancies at the *A* (La,Ca) site and the *B* (Mn) site. In the end member $\text{LaMnO}_{3+\delta}$ the vacancies occur approximately equally at these two sites.^{17,18} Excess oxygen leads to disproportionation of Mn^{3+} into Mn^{2+} and Mn^{4+} , increasing the carrier concentration, and usually the Curie temperature T_C .¹⁸ Oxygen deficiencies below 3.0 can also be obtained by sintering at very low oxygen partial pressures. The oxygen deficiencies are accommodated through oxygen vacancies surrounded by Mn^{2+} ions.¹⁹ Oxygen excess at given sintering temperatures in 1 atm of oxygen increases rapidly with lower Ca concentrations, and therefore larger distortions of the perovskite structure, and is serious for $x=0.2$ for sintering temperatures of 1000 °C and below. In order to obtain comparison samples with δ approximately zero, one has two choices. If one prefers to work at 1 atm of oxygen, one has to sinter at temperatures of 1200 °C or above, and maintain the equilibrium composition during cool down. We did this by fast quenching. The samples at the end of the sintering period were quenched to room temperature, still in the gas atmosphere. Because of the small size of the samples, the cool down through the sensitive temperature interval above 700 to 800 °C took only 5 to 10 sec. A second approach is to work at lower oxygen partial pressure, e.g., in argon, or by gettering oxygen with tantalum. These experiments are less well controlled as to the exact oxygen partial pressure, and can also lead to oxygen deficiency (particularly for tantalum gettering). We performed for this reason all of the experiments described here in 1 atm of oxygen and controlled the oxygen

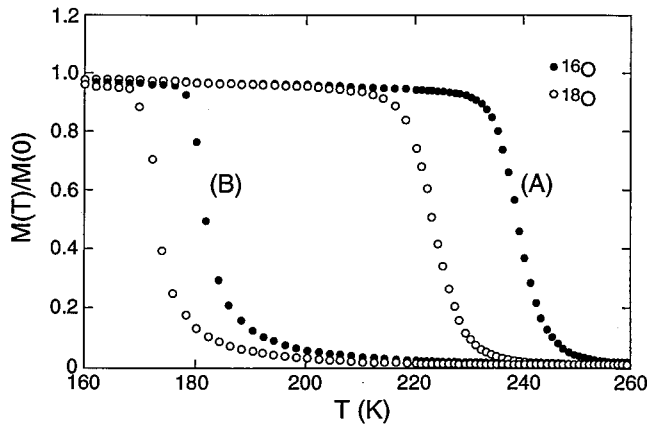


FIG. 1. The magnetic transition (50 G, FC) in two isotopic comparison samples. (a) Sintering in 1 atm of $^{16}\text{O}_2$ or $^{18}\text{O}_2$ at 900°C for 90 h, slow cooled. (b) Sintering in 1 atm of $^{16}\text{O}_2$ or $^{18}\text{O}_2$ at 1225°C for 42 h, fast quench.

excess through the sintering temperature, and quenching. A comparison between the structure for the oxygen stoichiometric samples (obtained by either quenching from 1225° in oxygen, or annealing in argon at 950°) and oxygen excess samples will also be presented.

III. RESULTS

The first set of experiments were carried out on a pair of samples which had previously been gas-exchanged in $^{16}\text{O}_2$ and $^{18}\text{O}_2$ (1 atm) at 950°C , and, following this, sintered in an atmosphere of argon (1 atm) at 950°C for 24 h twice. The results of these treatments were published previously,^{2,3} they were $\alpha_0 = 0.83$ after sintering in 1 atm of oxygen, and $\alpha_0 = 0.34$ after the argon sintering. Argon annealing did not substantially affect the $^{18}\text{O}_2$ concentration in the ^{18}O exchanged samples, a possibility suggested recently.²⁰ From Raman analysis, we found an $^{18}\text{O}_2$ concentration of at least 75% [J. C. Irwin (private communication)]. These samples were then re-ground and pressed into pellets of 3 mm diameter and sintered at 1000°C in $^{16}\text{O}_2$ for 24 h to remove ^{18}O . This was followed by sintering in $^{16}\text{O}_2$ respectively $^{18}\text{O}_2$ (1 atm) at 900°C for 90 h. This resulted in an ^{18}O content of 88.5% and a large increase in the Curie temperature T_C , the ^{16}O sample had an increase in T_C of 43.66 K, and the ^{18}O sample of 36.18 K; see Fig. 1. The samples were quite dense, with a density of about 90% of x-ray density. The increase in T_C is no doubt due to excess oxygen. The isotopic shift is $\Delta T_C = 15.48$ K, with $\alpha_0 = 0.55$. A further sintering at 900°C for 120 h did not change these results substantially. The samples were then sintered at 950°C for 24 h, 1050°C (24 h), and 1100°C (48 h), always followed by a slow cool down ($1^\circ\text{C}/\text{min}$). The results after the 1100°C sintering led to severely nonparallel transitions; see Fig. 2. The ^{16}O transition is quite broad, and its onset is the same as in the ^{18}O sample. The ^{18}O transition has sharpened, with little change in T_C . It appears that at this temperature the ^{16}O sample is starting to lose its oxygen excess leading to a very broad transition due to regions of various oxygen excess. No mean-

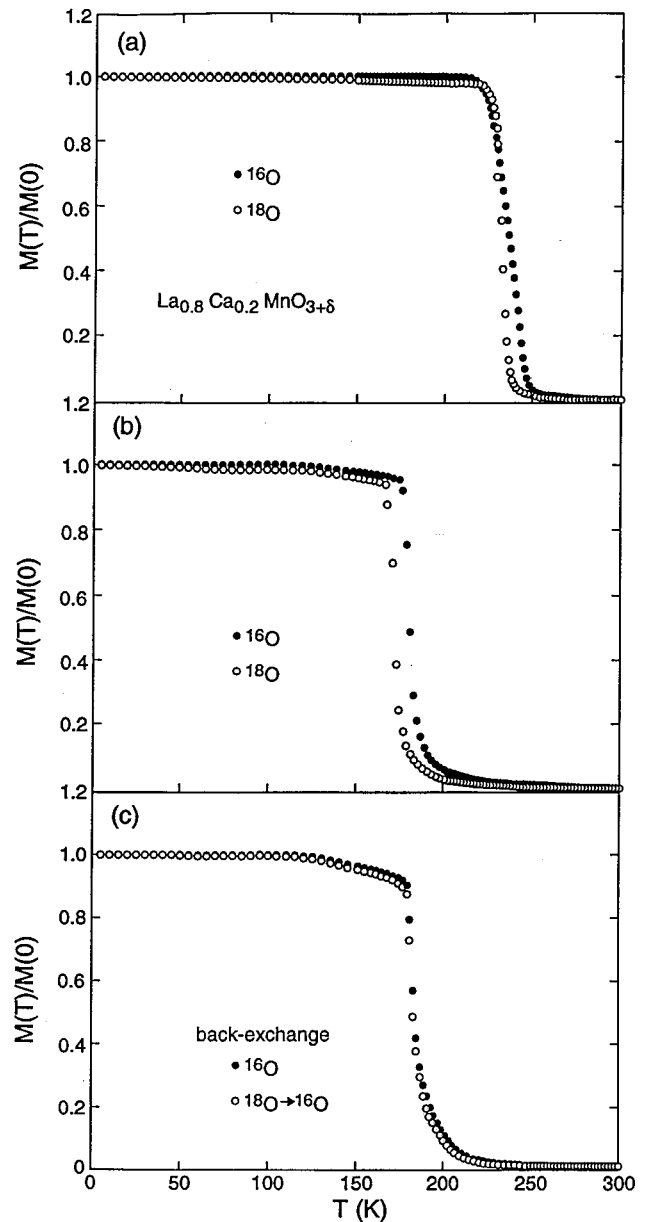


FIG. 2. The approach to excess oxygen loss, magnetic transitions (50 G, FC). (a) Sintering in 1 atm of $^{16}\text{O}_2$ or $^{18}\text{O}_2$ at 1100°C for 48 h, slow cool. (b) Sintering at 1225°C , fast quench. (c) Back-exchange in 1 atm at $^{16}\text{O}_2$ at 1225°C for 25 h, fast quench.

ingful isotope effect can be obtained for this sintering. Finally, the sample pair was sintered at 1225°C for 42 h and quenched to room temperature (5–10 sec). We recovered much lower transition temperatures, $T_C(16) = 187.2$ K and $T_C(18) = 178.30$ K; see Fig. 1. Apparently the samples have lost most of the oxygen excess, and we have an isotopic shift of $\Delta T_C = 8.9$ K, and $\alpha_0 = 0.41$. Following those various sinterings we back-exchanged the samples in $^{16}\text{O}_2$ (1 atm) at 950°C (30 h), 1050°C (30 h), and 1225°C (25 h), followed by a quench to room temperature. The transitions for both samples coincided, and were very close to the previous 1225°C (quench) result for ^{16}O . In order to remove the ^{18}O at 1225°C , we had to regrind both pellets. The results of this

TABLE I. Transition temperatures of $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3+\delta}$. Samples sintered at high temperatures and quenched to room temperature.

Sample	T_{sinter} (°C)	$T_C(16)$ (K)	$T_C(18)$ (K)	ΔT_C (K)	α_O
G2,H2	1175	194.3	184.3	10.0	0.45
G3,H3	1195	191.20	182.36	8.84	0.40
G4,H4	1200	188.90	179.98	8.92	0.41
E1,E2	1225	187.05	177.70	9.35	0.43
E1,E2 ^a	1225	189.0	189.0 ^a		
DRRA ^b	1225	190.91	182.00	8.91	0.40

^aAfter back-exchange in $^{16}\text{O}_2$ (1 atm).

^bSample made at University of Maryland (Ref. 21).

series of experiments are given in Table I as series E.

Our interpretation of these experiments is that sintering at temperatures of 1000 °C, or below, introduces both ^{16}O and ^{18}O oxygen excess. For sintering at higher temperature, the samples lose this excess, but for sintering temperatures near 1100 °C at different rates (the ^{16}O is more mobile). Finally, for sintering at a temperature of 1200 or 1225 °C, the excess oxygen is essentially removed in both isotopic samples. Fast quenching is essential to retain this situation at room temperature. Even so-called oven-quench (obtained by switching the furnace off and cooling at initial rates of 8 to 10 K/min) is not sufficient. In this case we observed the same onset as for fast quench but followed by a much larger tail due to regions of various degrees of oxygen excess. We estimated the oxygen excess of the ^{16}O sample through weight comparisons between the 950 °C sinter, and the 1225 °C sinter. We found that the ^{16}O sample had lost $\delta_{16}=0.092$, so that the 950 °C sintered sample is $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3.092}$, assuming that a sintering temperature of 1225 °C we have $\delta=0$. The rate of change in T_C with oxygen excess for these samples is $\Delta T_C/\Delta\delta=475$ K for the ^{16}O sample.

Apart from these experiments, we investigated a number of different samples, the results are also included in Table I. The sample series G,H refers to another sample pair with $x=0.2$. Sintering at temperatures from 1175 to 1200 °C in 1 atm of $^{16}\text{O}_2$ or $^{18}\text{O}_2$, and quenching to room temperature, leads again to much reduced isotope exponents, close to $\alpha_O=0.4$. The difference between sintering at 1175 °C and 1225 °C show that sintering temperatures of at least 1200 °C are necessary to obtain oxygen-stoichiometric samples. In Ref. 9 it has been claimed that the isotope shifts and the Curie temperatures are independent of sintering conditions, either at 800 °C or at 1260 °C/min followed by a 5 °C/min cool down. We decided to repeat this experiment closely. We used for this a sample of $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3+\delta}$ obtained from the University of Maryland.²⁰ This sample is quite open, its density was 63% of the x-ray density. Comparison samples were sintered several times at 950 °C, and 1200 °C in 1 atm of $^{16}\text{O}_2$ or $^{18}\text{O}_2$, with an estimated ^{18}O content near 94%. We then sintered the samples at 1225 °C (35 h), followed by a fast quench to room temperature (5–10 sec), and, following this, by treatment at 1225 °C (36 h) followed by a 5 °C/min cool down. The results are shown in Fig. 3(a). The difference

between the two sintering conditions is obvious. For the fast quench we have an isotopic shift of 8.91 K, and $\alpha_O=0.40$, whereas the 5 °C/min cool down results has an isotopic shift of 15.54 K, and $\alpha_O=0.66$. We find that the slow (5 °C/min) cool down results in an increase of $T_C(16)$ of 15.54 K, and of $T_C(18)$ of 8.91 K, i.e., a ratio of 1.7. After this we sintered the quenched samples at 800 °C for 92 h followed by

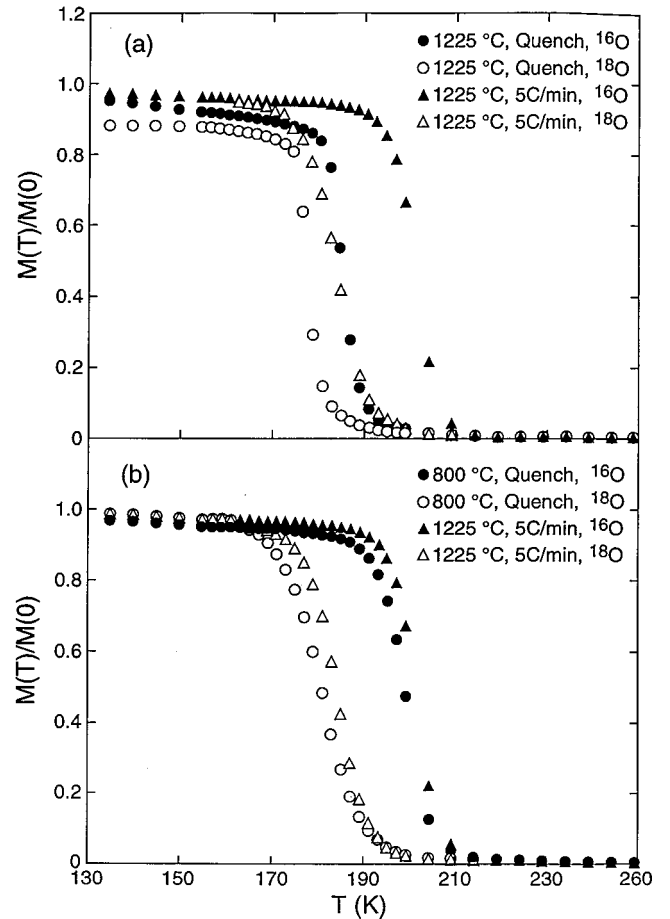


FIG. 3. Comparison of slow cool down and fast quench. (a) Sintering in 1 atm of $^{16}\text{O}_2$ or $^{18}\text{O}_2$ at 1225 °C, followed by fast quench (triangles), or by a cool down at 5 °C/min (dots). (b) The transition for sintering at 800 °C in 1 atm of $^{16}\text{O}_2$ or $^{18}\text{O}_2$ for 92 h, followed by fast quench, compared with sintering at 1225 °C, cooled at 5 °C/min.

quenching. The transitions are practically undistinguishable from the slow cool results; see Fig. 3(b). We further found that the 800 °C sintering increases δ_{16} by 0.026. These results again point to the importance of fast quenching to retain the high temperature oxygen stoichiometry. The results of these various experiments are given in Table I.

Apart from the weighing method, one can also obtain the amount of oxygen excess by careful determination of the unit cell volume through powder x-ray analysis. This was shown for $\text{LaMnO}_{3+\delta}$ by van Roosmalen *et al.*²² and for a range of Ca concentrations in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$ by Dabrowski *et al.*¹³ These authors give for a Ca concentration of 20% and stoichiometric oxygen content ($\delta=0.00$) a formula unit cell volume of $58.62 \pm 0.04 \text{ \AA}^3$, or a lattice constant of $3.8846 \pm 0.009 \text{ \AA}$ of the effective cubic unit cell. For the samples DRRA, quenched from 1225 °C, we find $a=3.8865 \pm 0.0019 \text{ \AA}$ (^{16}O sample) and $a=3.8860 \pm 0.0026 \text{ \AA}$ (^{18}O sample). The measured lattice constant is therefore identical for both isotopes, and agrees with the value for stoichiometric oxygen content. This is an independent confirmation that the quenching process produces isotopic comparison samples with equal, and stoichiometric oxygen content. For oxygen excess, the unit cell volume decreases slowly because of the formation of A and B site vacancies and Mn^{4+} formation. This is shown in Fig. 4, where the (110) and (002) reflections are shown, for the DRRA samples, both for the quench from 1225 °C and the quench from 800 °C. The increase in 2θ corresponding to the unit cell decrease is clearly seen in both reflections, and is indeed visible throughout the spectrum. The (002) reflection shows, in addition, a large increase in splitting due to the increase in lattice distortion associated with increased effective oxygen content. It is further obvious that the lattice constant, and therefore the unit cell volume, is the same within experimental accuracy for both isotopic samples. For the 800 °C quenched samples, we find lattice constants of $3.8755 \pm 0.0021 \text{ \AA}$ (^{16}O) and $3.8752 \pm 0.0015 \text{ \AA}$ (^{18}O). The shift corresponds to a decrease of formula unit cell volume of -0.4970 (^{16}O) and -0.4834 (^{18}O), practically identical. The experimentally determined dependence of unit cell volume, and therefore lattice constant, as function of oxygen excess, δ , by Dabrowski *et al.*¹³ is given by

$$V = 58.62[1 - \gamma\delta] \text{ \AA}^3, \quad (1)$$

$$\gamma = 0.197 \pm 0.060.$$

From this one would estimate an oxygen excess in the 800 °C quench sample of $\delta=0.042 \pm 0.015$. This agrees quite well with the estimate from the weight method of $\delta = 0.026$, considering the uncertainty in $dV/d\delta$ (about 10%), and the uncertainty of the weight method. In Fig. 5 we show the (110) and (002) reflections for the DRRA samples cooled at 5 °C/min from 1225 °C. The lines show some difference between the isotopes, with the ^{18}O sample showing the larger shift, or smaller volume. This shows that the quench process is inherently superior. Differences in volume between the two isotopes, even for a cool down rate of 5 °C/min depend on the kinetics of the excess in oxygen content between the

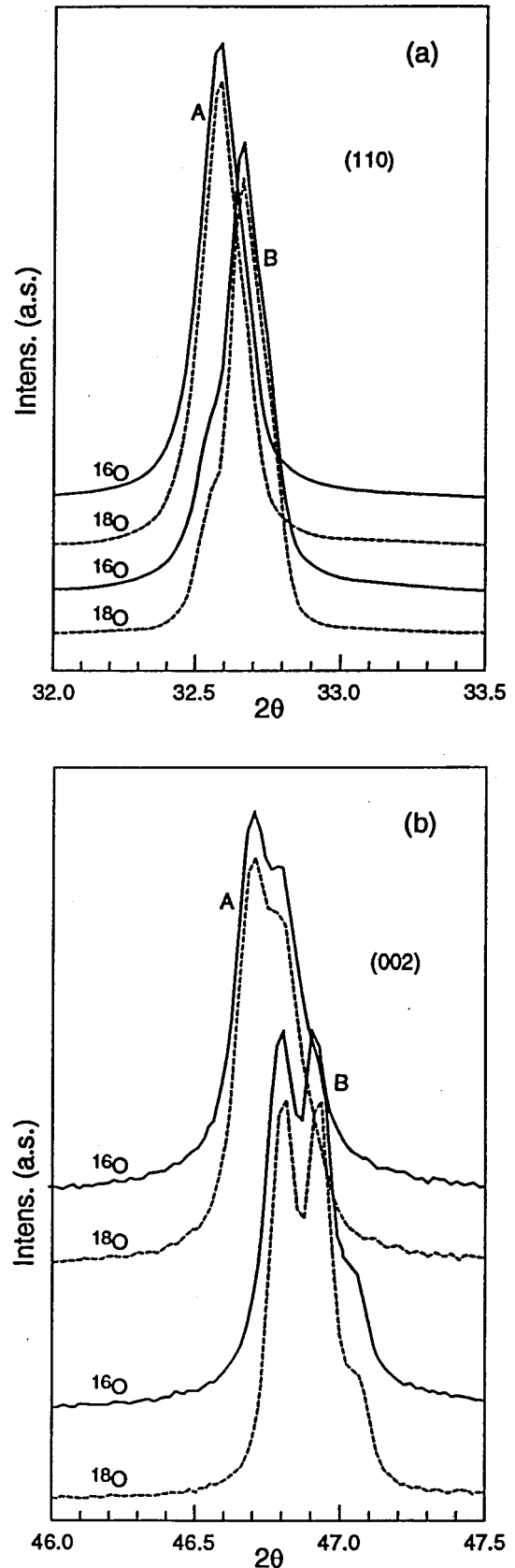


FIG. 4. Comparison of two x-ray reflections representative of the total x-ray spectrum, A for samples quenched from 1225 °C, and B quenched from 800 °C. (a) (110) reflection; (b) (002) reflection. The (002) line shows the largest split due to lattice distortion.

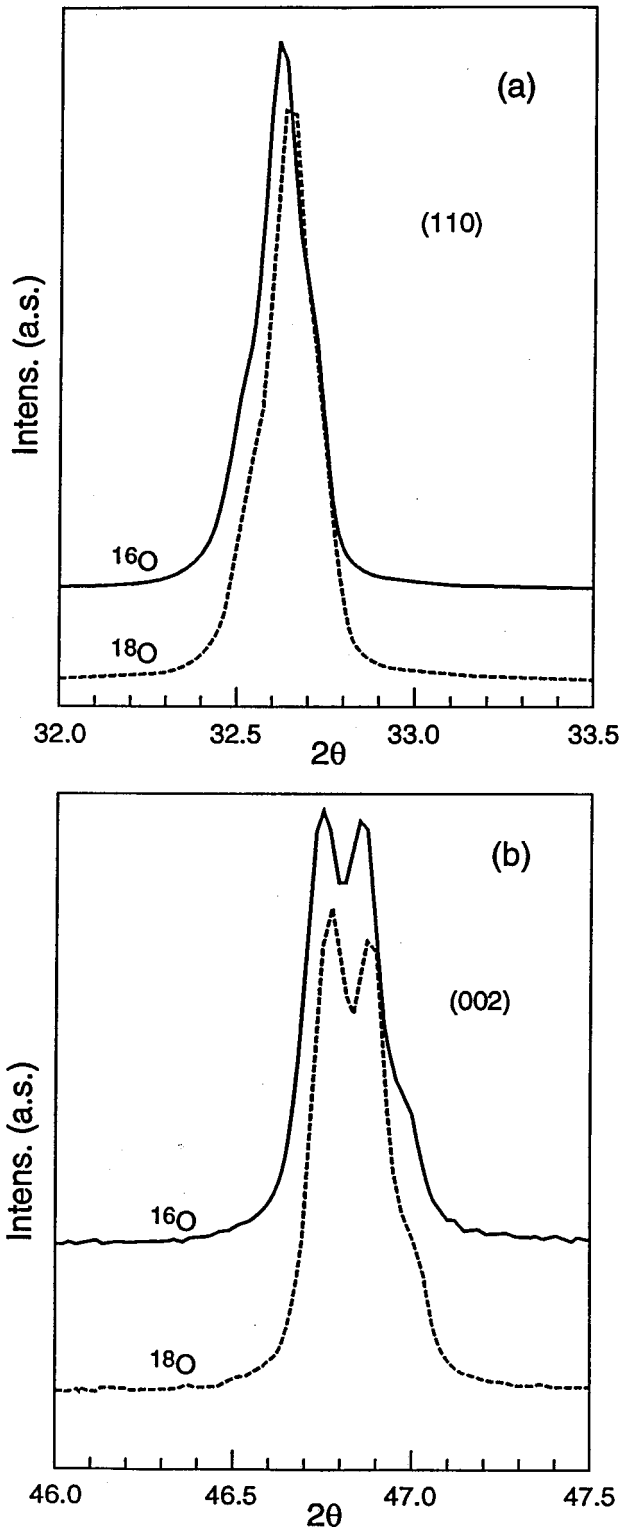


FIG. 5. Comparison of the x-ray reflections for an isotopic pair sintered at 1225 °C, and cooled at 5 °C/min. (a) (110) reflection; (b) (002) reflection.

two samples. The (002) reflection again shows the increase in distortion for both samples.

We finally addressed the question, whether the change in structure in the oxygen stoichiometric samples obtained by

quenching is due to the quench process, or an equilibrium property. We prepared therefore a number of ^{16}O comparison samples and treated them as follows: Two samples were prepared by sintering at 950 °C for 30 h, followed by cooling to room temperature at a rate of 1 °C/min. One sample was sintered in oxygen (1 atm), the second in high purity argon (1 atm). A third sample was prepared by sintering in O_2 (1 atm) at 1225 °C followed by rapid quenching to room temperature. High resolution powder x-ray data were taken, particularly for the (110) and (002) peaks. We used a scanning resolution of 0.01° in 2θ (Cu $K\alpha$). The results are shown in Fig. 6. One observes the shift to larger reflection angles 2θ , i.e., smaller lattice constant and unit cell volume, for the low temperature oxygen annealed sample, and the increased split of the (002) peak. In comparison to this, oxygen anneal at 1225 °C followed by quenching, or argon anneal at 950 °C and slow cool, show essentially the same structure. The peaks are also situated at the predicted position (Ref. 13) for oxygen stoichiometry ($\delta=0$). This shows that either method for obtaining oxygen stoichiometry leads to the same structure as seen in the x-ray spectrum.

IV. DISCUSSION

The results show not only that the isotope exponent settles around $\alpha_{\text{O}}=0.4$ for sintering near 1200 °C, but also that the Curie temperatures for both isotopes are very close for all samples, $T_C(16)$ near 189 K, and $T_C(18)$ near 180 K. When sintering is carried out at temperatures of 1000 °C or below, in 1 atm of oxygen, one always finds a larger isotope exponent, which can exceed 1.0. We have shown already that this effect is connected with an isotope-dependent oxygen excess, but it is not clear whether this is an equilibrium effect, or whether it is due to different diffusion rates for the two isotopes. Long annealing times should rule out any differences due to this cause. The fact that in our first series of experiments no difference was observed for 92 and 92+120 h sintering times also speaks against this. We have further checked this by quenching samples after sintering at 1000 °C, or below, instead of the usual slow-cooling. We have never observed differences between quenched or slow-cooled samples for sintering at 1000 °C or below. Both procedures (i.e., long annealing times, or quenching) suggest that the oxygen excess is an equilibrium property.

In contrast to the results obtained for sintering at 1200 °C and above (followed by quenching), results for sintering at lower temperatures (1000 °C, and below), show large differences both in the absolute Curie temperature T_C , and in the isotopic shift and exponent. This is seen, e.g., by comparing Fig. 1 and Fig. 3. It has sometimes been claimed, that the transition temperature itself can be used as an indication for the presence or absence of oxygen excess. This neglects the fact that T_C can be also be influenced by other properties, in particular lattice disorder. This was shown by the work of Stroud *et al.*^{23,24} for $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3.0}$, where lattice disorder was deliberately introduced through radiation damage. T_C decreases rapidly at this given calcium concentration from 270 K to below 150 K with increasing disorder. Dabrowski *et al.*¹⁴ showed that oxygen excess above 0.008 in

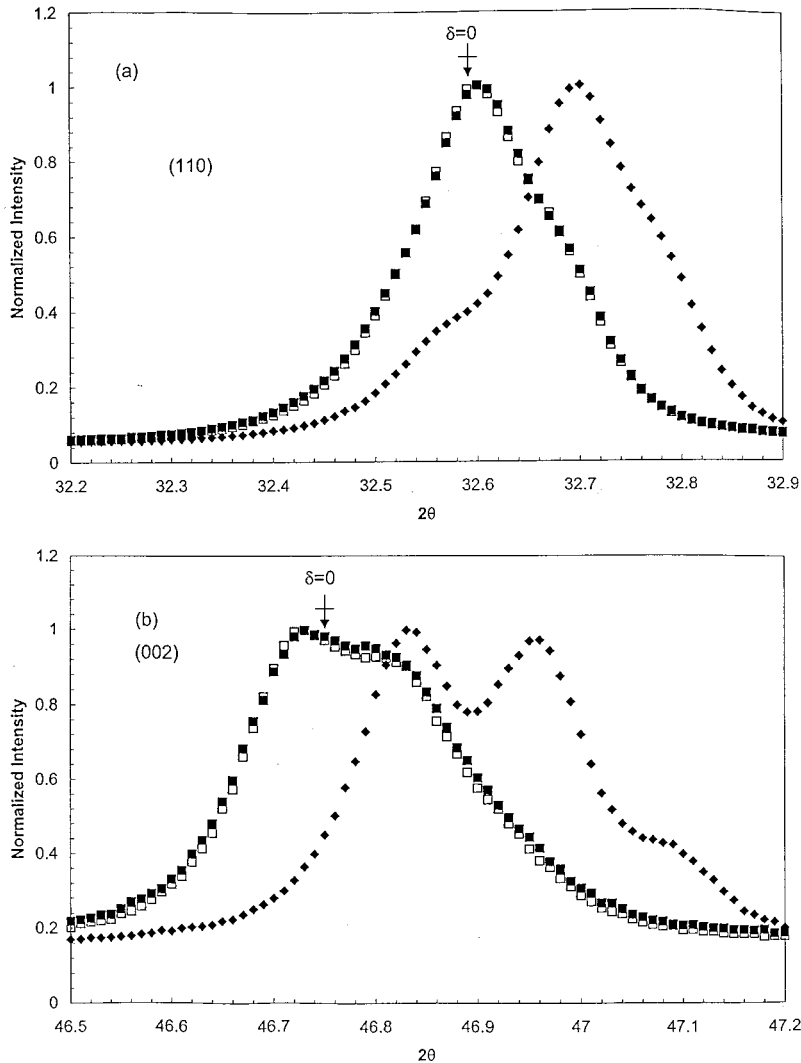


FIG. 6. Comparison of (a) the (110) and (b) the (002) reflections of $\text{La}_{0.3}\text{Ca}_{0.2}\text{MnO}_{3+\delta}$ (^{16}O) for different sintering conditions. Solid diamonds: sintering at $950\text{ }^\circ\text{C}$ in 1 atm of O_2 for 30 h, cooled at $1\text{ }^\circ\text{C}/\text{min}$. Solid squares: sintering at $950\text{ }^\circ\text{C}$ in 1 atm of Ar for 30 h, cooled at $1\text{ }^\circ\text{C}/\text{min}$. Open squares: sintering at $1225\text{ }^\circ\text{C}$ in 1 atm of O_2 for 18 h, followed by rapid quench to room temperature. The position of these lines for oxygen stoichiometry ($\delta=0$) from Ref. 13 is indicated.

$\text{La}_{0.74}\text{Ca}_{0.26}\text{MnO}_{3+d}$ can also lead to a decrease in Curie temperature. Lattice disorder can be present in samples of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ due to inherent disorder, e.g., in loosely packed samples where grain boundaries dominate, or through slight deviations from cation stoichiometry. Apart from this, oxygen excess always introduces disorder through vacancies at the A and B sites. In the latter case, the transition temperature is influenced by two different effects. Increased Mn^{4+} concentration will lead to an increase in T_C , and disorder to a decrease. In particular for large amounts of disorder, T_C will be low.

The data presented here suggest isotopic comparison samples of $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3+d}$ can be prepared with stoichiometric oxygen content, $\delta=0$. In this case, the isotopic shift in T_C is about 8.8 K, with a corresponding oxygen isotope exponent $\alpha_O=0.41\pm 0.02$. The transition temperatures are $T_C(16)=189\pm 2\text{ K}$ and $T_C(18)=180\pm 2\text{ K}$. These data were obtained for both densely packed, and loosely packed samples, including a sample prepared at the University of Maryland.

Comparison samples prepared at $1000\text{ }^\circ\text{C}$ or less, have always oxygen excess. Results for very long sintering times as well as independence of the results for quenching or slow-

cooling suggest that this oxygen excess is a thermodynamical equilibrium property for a given sample pair. The oxygen excess leads to a decrease in unit cell volume, which is the same for both isotopes. From this it can be concluded that equilibrium oxygen excess is also the same for both isotopes. For this deduction, one needs a comparison of the V vs δ dependence for both isotopes, which was determined only for the ^{16}O compound [Eq. (1)].¹³ The V vs δ relation can actually be estimated using the independence of the x-ray density on oxygen excess for the system $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$, $x=0,0.15,0.30$ shown by Van Roosmalen and Cordfunke.¹⁷ Combined with the assumption that equal amount of (La, Ca) and Mn vacancies are present in oxygen excess samples, one finds

$$V = 58.62[1 - \gamma\delta] \text{ \AA}^3, \quad (2)$$

where

$$\gamma = 0.2613, \quad ^{16}\text{O},$$

$$\gamma = 0.2544, \quad ^{18}\text{O}.$$

This assumes that the $\delta=0$ volume is the same for both isotopes, as shown experimentally by us. The ^{16}O calculated value is in good agreement with the experimental data of Dabrowski *et al.*¹³ This shows that the assumption of equal vacancy occupation in the *A* and *B* sites is justified. The difference in “ γ ” between the two isotopic compounds is too small to be significant. As a consequence, equal volume also implies equal oxygen excess for both isotopes.

Nagaev^{6–8} calculates from thermodynamics the number of cation vacancies under equilibrium conditions, this is equal to the oxygen excess. In Ref. 4 he calculates a difference in ^{16}O and ^{18}O excess given by

$$\frac{\delta_{16} - \delta_{18}}{\delta_{16}} = \frac{5}{32} + \frac{\omega_{16}}{36T}, \quad (3)$$

where ω_{16} is a typical frequency of the ^{16}O compound. In order to estimate this ratio we approximate ω_{16} by a Debye temperature²⁵ of 400 K and use $T=800$ K. We obtained an estimate of $\delta_{16} - \delta_{18} = 0.16\delta_{16}$. If there are differences due to the isotopic composition, one would therefore expect a difference in lattice constant, and therefore in 2θ , of about 16% for the two isotopic oxygen excess samples. The observed total shift of the (110) line from the stoichiometric case is 0.1 to 0.12°, and we would expect therefore an isotopic difference of at most 0.02°. The detailed comparison of ^{16}O and ^{18}O samples x-ray spectrum does not support this difference. The situation for samples with oxygen excess (both prepared by quenching) is then that the unit cell volume and the oxygen excess are the same for both samples within experimental accuracy. The large isotope effects for oxygen excess are related to the increased lattice distortions around *A* and *B* site vacancies, and become important for $x=20\%$, where already large distortions exist. They are not representative of oxygen stoichiometric samples.

We finally wish to comment on the situation for optimally doped $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_{3+\delta}$. Here an isotope exponent of 0.30 ± 0.01 is observed by us² and by Zhao *et al.*²⁶ We also showed already in Ref. 2 that sintering at 950 °C or 1200 °C leads to the same results. This is due to the fact that at this

calcium concentration one is much closer to the ideal oxygen stoichiometry at both temperatures, see Ref. 14. This was also independently investigated on the samples of Ref. 2 by Heilman *et al.*²⁷ through thermoelectric power measurement. It was found that in those samples, the oxygen stoichiometry was close to 3.00, and well balanced for both isotopic samples.

V. CONCLUSIONS

In conclusion, we have shown that the preparation conditions of $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3+\delta}$ have a strong influence on the nonstoichiometric oxygen excess, δ . Physical properties, such as Curie temperature T_C and isotope exponent α_O , strongly depend on the oxygen excess. Oxygen stoichiometric samples ($\delta=0$) can be obtained by sintering above 1200° in 1 atm of oxygen and preserving the stoichiometry by fast quenching. Alternatively, they can also be obtained by sintering in argon at 950 °C, and slow cool down. In this case, the transition temperatures are very close for all samples, near 189 K for the ^{16}O samples and 180 K for the ^{18}O samples. The isotope exponent α_O is found at 0.41 ± 0.02 . When oxygen excess is present because of sintering conditions, vacancies are created at the *A* (La, Ca) and *B* (Mn) sites in equal concentration, leading to a decrease in unit cell volume identical for both isotopic samples. Transition temperatures and isotopic shifts for non-oxygen-stoichiometric samples differ; they depend both on Mn^{4+} concentration and lattice disorder and distortion, the very large isotope shifts in these samples are dependent on the defect structure.

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