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# Isotope effect in $La_{2-x}Sr_xCuO_4$ superconductors

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A "nonzero" isotope effect for $x=0.15$, and an "anomalous" isotope effect, with the oxygen isotope-effect exponent $\alpha_O$ larger than the theoretical value of 0.5 for $x=0.12$, were reported in the past for the $La_{2-x}Sr_xCuO_4$ system. In view of the importance of understanding the mechanisms of high-temperature superconductivity, a reinvestigation of the isotope effect with more precise materials synthesis and isotope characterization is called for. We synthesized in flowing $^{18}O_2$, or in flowing $^{16}O_2$, copper-rich and stoichiometric versions of the $La_{2-x}Sr_xCuO_4$ materials at $x=0.125$ and $x=0.15$. We characterized the materials with x-ray diffraction, high-sensitivity, high-temperature mass spectrometry, and magnetic measurements. We found that in the stoichiometric materials, both at $x=0.125$ and $x=0.15$, the oxygen isotope-effect exponent, $\alpha_O \simeq 0.4$. The copper-rich samples at $x=0.125$ have a larger isotope shift than the stoichiometric ones, due to a larger amount of the $La_{1.67}Sr_{0.33}Cu_2O_5$ nonsuperconducting second phase in the $^{18}O$-containing material, than in the $^{16}O$-containing material, which leaves the superconducting phase with a lower strontium concentration, which further lowers $T_c$. For the copper-rich $x=0.15$ material we found an oxygen isotope-effect exponent $\alpha_O=0.08$.

The family of high-temperature superconductors discovered by Bednorz and Müller[1] still remains the most intriguing one, due to the wealth of physics found in it. Here we report that these oxides, as judged from the isotope effect, can behave either as the conventional superconductors, or as the new, high-temperature superconductors.

According to the Bardeen-Cooper-Schrieffer[2] (BCS) model for conventional superconductors, superconductivity is a result of the electron-phonon interaction in the microscopic pairing mechanism. In the weak-coupling approximation the superconducting transition temperature $T_c$ is proportional to the Debye temperature and thus to $M^{-0.5}$, where $M$ is the mass of the atoms. A shift of $T_c$ with the isotopic mass according to

$$\frac{\delta T_c}{T_c} = -\alpha \frac{\delta M}{M} \tag{1}$$

with $\alpha=0.5$ is considered the crucial experiment to prove the existence of phonon-mediated pairing. For materials consisting of different atoms, the isotope-effect exponent $\alpha$ is summed over all the constituents with their respective masses. Since in the high-temperature superconductors it is expected that the vibrations of the lightest atom, oxygen, will make the largest contribution to $\alpha$, the isotope-effect studies concentrated on measuring the oxygen isotope-effect exponent $\alpha_O$, the others being negligible.

While no isotope effect was found in the $T_c=90$ K compounds,[3] indicating the absence of phonon-mediated pairing, a "nonzero" isotope effect was reported in the $La_{2-x}Sr_xCuO_4$ system. Here $T_c$ depends on the value of $x$, giving a domeshaped curve of $T_c$ versus $x$, that has its maximum at $x=0.15$. At this concentration $\alpha_O=0.16$ was reported by Batlogg *et al.*[4] and $\alpha_O=0.09$–$0.37$, *depending on sample*, by Faltens *et al.*,[5] implying that in this $T_c=37$ K material phonons still have some role in the superconducting pair condensation.

Crawford *et al.*[6] investigated the oxygen isotope effect in $La_{2-x}Sr_xCuO_4$ as a function of $x$ and found at $x=0.12$ an "anomalous" isotope-effect exponent, which was larger than the theoretical value of 0.5. The magnitude of $\alpha_O$ was *dependent on the temperature of oxygen exchange*, and reached 0.85 when the exchange was made at 700 °C. Similar "anomalous" isotope effect was found in $La_{2-x}Ba_xCuO_4$ at $x=0.10$ (Ref. 7). Since the barium-containing material undergoes a low-temperature orthorhombic (LTO) to low-temperature tetragonal (LTT) phase transformation in this doping regime,[8] it was suggested that the anomalous isotope effect is related to this phase transformation in spite of the fact, that the phase transformation was not found in the strontium-containing material.[7] Since then, the anomalous isotope effect was explained by a variety of theoretical models.[9]

In view of the importance of understanding the mechanisms of high-temperature superconductivity, a reinvestigation of the isotope effect with more precise materials synthesis and isotope characterization is called for. The chemical composition of samples is often given as the nominal value. Due to the extreme hygroscopic nature[10] of $La_2O_3$, samples made without following the process with chemical analyses are likely to be lanthanum poor, i.e., copper rich. The lanthanum oxide–copper oxide–strontium oxide ternary phase diagram is a complex one, consisting of many solid solutions[11] out of which $La_{2-x}Sr_xCuO_4$ is the poorest in copper. The other phases, which are richer in copper, are often richer in strontium than the superconducting compositions, and are metallic, but not superconducting.[12] The amounts of a nonsuperconducting phase in equilibrium with the superconducting phase may well be different for the $^{18}O$-containing material, than for the $^{16}O$-containing material. If the $^{18}O$-containing material has more of the higher strontium-containing nonsuperconducting phase, *the remaining* $La_{2-x}Sr_xCuO_4$ *will be poorer in strontium, and this results in a lower* $T_c$. No such danger exists in making the samples slightly lanthanum rich in the concentration range of interest. There will be small amounts of $La_2O_3$ precipitates at large distances from each other, exerting no influence on $T_c$.

Also of concern is the way $^{18}O$ was introduced to the samples. In all the papers referenced here, the material was synthesized in $^{16}O_2$ and $^{18}O$ was introduced subsequently by exchange in a stationary $^{18}O_2$ atmosphere at an annealing temperature ranging between 700–1100 °C. Anneal at such temperatures causes phase segregation, and may emphasize differences in the equilibrium concentrations of $^{18}O$-containing phases versus the $^{16}O$-containing phases, which will effect $T_c$ in the way discussed above. Bear in mind that the isotope effect is evaluated solely from the change in $T_c$, and anything that lowers $T_c$ is taken as the isotope effect, even if other conditions do not remain the same during the exchange. We are further concerned that the amount of $^{18}O$ exchanged was either not determined directly,[6,7] or not determined with great accuracy.[4] In all cases the fraction of $^{18}O$, estimated with sizable error, was extrapolated to 100% exchange to yield the isotope-effect exponent, an extrapolation not justified by theory.

To ensure a maximum isotope content, we synthesized the $^{18}O$-containing materials in flowing $^{18}O_2$ and used $Cu_2O$ instead of CuO in the synthesis. Due to the high cost and limited availability of $^{18}O_2$ gas, prior to working with this isotope, we made extensive process studies in $^{16}O_2$, to reduce the reaction time. For the same reason, the high purity, and reanalyzed starting materials were of a very small particle size, about 1 μm for $La_2O_3$, and a few microns for $Cu_2O$, and $SrCO_3$. The $La_2O_3$ was dried for 10 h at 1050 °C prior to weighing. The temperature cycle for all syntheses was to heat from room temperature to 800 °C in 10 min, hold at 800 °C for 2 h to oxidize the $Cu_2O$ to CuO; heat at a rate of 5 °C per min from 800 to 1050 °C, hold for 2 h at 1050 °C, cool from 1050 to 500 °C at the rate of 20 °C per min, and cool from 500 °C to room temperature in 20 min. We made materials with two different strontium contents: $x = 0.15$, where $T_c$ is the maximum, and $x = 0.125$, where the "anomalous" isotope effect was observed. Each of these strontium-containing materials we made in two different versions: (a) (in order to exaggerate the role of excess copper) with 7% excess copper, which we will refer to as copper rich, and (b), stoichiometric. Each of these four different compositions we made in twice one hundreds of the respective molecular weights, or about 8 g, divided it in two, and synthesized one half in flowing $^{18}O_2$ (EG&G Mound Applied Techn. $^{18}O_2$ typically 97%) and the other half in flowing $^{16}O_2$ (Mattheson 99.997%) at a flow rate of 10 cc per minute, having thus four isotope pairs to evaluate. The lanthanum content of the materials was determined with a volumetric chemical analysis with an accuracy of ±0.5%, the copper content also with a volumetric chemical analysis with an accuracy of ±1.0%, the strontium content was determined with inductively coupled plasma spectroscopy with an accuracy of ±3.0%. Results of the chemical analyses are given in the first column of Table I. The grain size of samples, as determined by scanning electron microscopy, is given in the second column of the table. Note that the grain size of the copper-rich samples is larger than that of the stoichiometric ones.

X-ray diffraction revealed that the second phase in the

TABLE I. Characterization of the materials investigated.

| Composition | Grain size μm | $La_{1.67}Sr_{0.33}Cu_2O_5$ $I_{rel}$ | $La_2O_3$ $I_{rel}$ | $^{18}O$ at. % | Diamag. shield % | Trap. flux emu/cm$^3$ | $T_c$ K | $\alpha_O$ |
|---|---|---|---|---|---|---|---|---|
| $La_{1.87}Sr_{0.125}Cu_{1.07}O_4$ | 2–4 | 6.9 | | | 10.7 | 1.39 | 28.8 | 0.65 |
| $La_{1.87}Sr_{0.125}Cu_{1.07}O_4$ | 2–4 | 11.9 | | 89.4<br>90.9 | 10.8 | 0.74 | 26.4 | |
| $La_{1.88}Sr_{0.125}Cu_{0.97}O_4$ | 1 | | 4.2 | | 2.7 | 0.23 | 30.1 | 0.44 |
| $La_{1.88}Sr_{0.125}Cu_{0.97}O_4$ | 1 | | 3.5 | 92.2<br>91.6 | 2.4 | 0.20 | 28.4 | |
| $La_{1.85}Sr_{0.15}Cu_{1.07}O_4$ | 2–4 | 9.5 | | | 14.5 | 1.95 | 36.6 | 0.08 |
| $La_{1.85}Sr_{0.15}Cu_{1.07}O_4$ | 2–4 | 9.4 | | 86.8<br>85.2 | 13.5 | 1.74 | 36.3 | |
| $La_{1.85}Sr_{0.15}Cu_{0.97}O_4$ | 1 | | | | 4.6 | 0.434 | 33.25 | 0.36 |
| $La_{1.85}Sr_{0.15}Cu_{0.97}O_4$[a] | 1 | | | 97.8<br>98.7 | 4.2 | 0.416 | 31.75 | |

[a] Because the $T_c$ curves crossed, after one heat treatment, we synthesized this material by applying twice the heat-treatment program given in the text, and used 99% $^{18}O$.

copper-rich samples is $La_{1.67}Sr_{0.33}Cu_2O_5$, a metallic but not superconducting perovskite compound built from corner-sharing $CuO_6$ octahedra, $CuO_5$ pyramids, and $CuO_4$ square planar groups.[13] The intensity of the most intense peak of the second phase is given in the table relative to the intensity of the most intense (103) tetragonal phase diffraction peak of $La_{1.85}Sr_{0.15}CuO_4$, which we take as 100. Notice, that comparing the two different isotope containing versions of the copper-rich $x = 0.125$ material, the intensity of the second phase, $La_{1.67}Sr_{0.33}Cu_2O_5$, is larger in the $^{18}O$ material than in the $^{16}O$ material indicating a larger concentration. Here we have the first evidence in our experiments that phase equilibria in copper-rich $x = 0.125$ materials are different for the $^{18}O$- than for the $^{16}O$-containing materials. Small difference is seen in the copper-rich $x = 0.15$ materials, where the intensities of the metallic second phase are similar for the different isotope-containing versions. We see small amounts of $La_2O_3$ in the $x = 0.125$ stoichiometric sample because one heat treatment does not drive the reaction to completion in the stoichiometric material.

The thermal stability of the $La_{2-x}Sr_xCuO_4$ powders was studied by Knudsen Effusion Mass Spectrometry.[14] The instrumentation of this high-temperature mass spectrometer exhibiting unique high sensitivity is described elsewhere.[15] Samples, 250 mg in size, were heated at 4 K per minute from 300 to 1160 K, then down to 960, and finally up to the maximum temperature of 1500 K. The purpose for retracing the temperature interval from 960 to 1160 K was to completely remove the $O_2$ overlap due to the release of either doping-induced excess oxygen, or oxygen due to the second phase. The molecular beam from the Knudsen cell was modulated at 20 Hz, followed by ionization using 30-eV electrons. The ion currents (counts/s), which are proportional to the gas flux through the orifice, were measured for the significant vapor species ($H_2O$, $O_2$, $CO_2$, and their $^{18}O$ analogues, and Cu), with an automated quadrupole mass spectrometer. After heating, the samples were reweighed and the weight loss used for calibration of the integrated ion signals. The percentage of $^{18}O$ exchange in each of the samples was determined from the binomial distribution of the $^{16}O$ and $^{18}O$ in the $O_2$ molecule ($m/z$ 32, 34, and 36). The precision of this calculation is better than 1% for the low, and 0.2% for the high temperature regions.

Figure 1 shows the rate of oxygen release from the stoichiometric, $x = 0.125$, $^{18}O$- containing sample measured at $m/z$ 36 ($^{18}O$-$^{18}O$) as a function of temperature. The peak centering at around 1300 K represents oxygen release during the decomposition of $La_2CuO_4$ to $LaCuO_2$ (in which copper is monovalent), $La_2O_3$ and free oxygen. This we call the high-temperature peak. The release in the temperature range between 800 and 1100 K, which is almost 2 orders of magnitude smaller (note the logarithmic scale), than the release at the high-temperature peak, is due to oxygen introduced by the strontium doping, and is absent in undoped $La_2CuO_4$. This we call the low-temperature slope. The rate of oxygen release from the copper-rich, $x = 0.125$, $^{18}O$-containing sample measured at $m/z$ 36 ($^{18}O$-$^{18}O$) as a function of temperature is shown in Fig. 2. When comparing the stoichiometric (Fig. 1) and the copper-rich (Fig. 2) samples, we see that while the high-temperature peaks are similar, in the low temperature regime the copper-rich sample shows a peak superposed on the slope representing the stoichiometric sample. The low temperature peak can be fitted by a zeroth-order reaction, characteristic of the thermal decomposition of a compound. The low temperature peak in the copper-rich sample is due to the decomposition of the $La_{1.67}Sr_{0.33}Cu_2O_5$ second phase present in this sample. In Fig. 3 we compare the rate of low-temperature oxygen release for the copper-rich, $x = 0.125$, $^{18}O$-containing sample (also shown in Fig. 2) and for its $^{16}O$-containing equivalent, and see that the low-temperature peak, representative of the decomposition of the $La_{1.67}Sr_{0.33}Cu_2O_5$ second phase is considerably higher for the $^{18}O$-containing sample than for the $^{16}O$-containing sample, indicating that there is more of the second phase in the $^{18}O$ material. This is the second re-

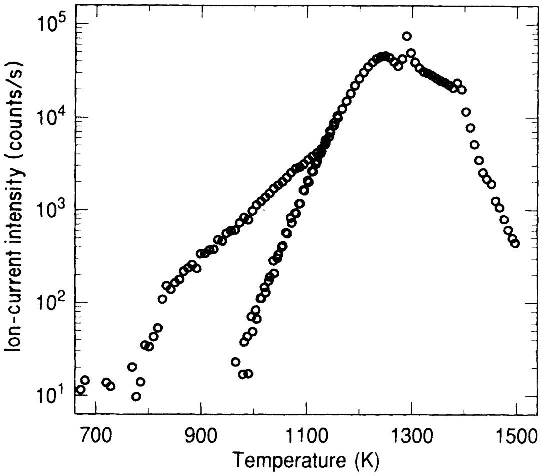

FIG. 1. The rate of oxygen release from the stoichiometric, $x = 0.125$, $^{18}O$-containing sample measured at $m/z$ 36 ($^{18}O$-$^{18}O$) as a function of temperature.

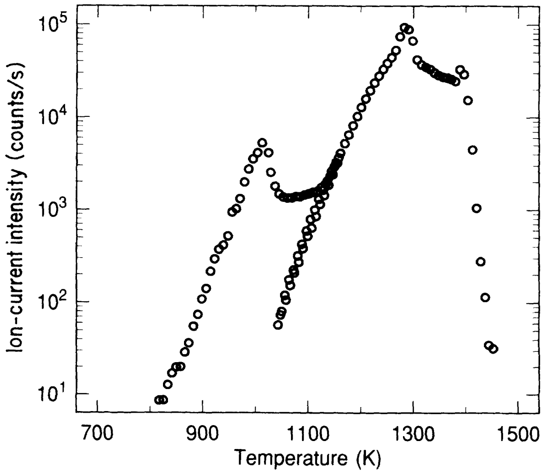

FIG. 2. The rate of oxygen release from the copper-rich, $x = 0.125$, $^{18}O$-containing sample measured at $m/z$ 36 ($^{18}O$-$^{18}O$) as a function of temperature.

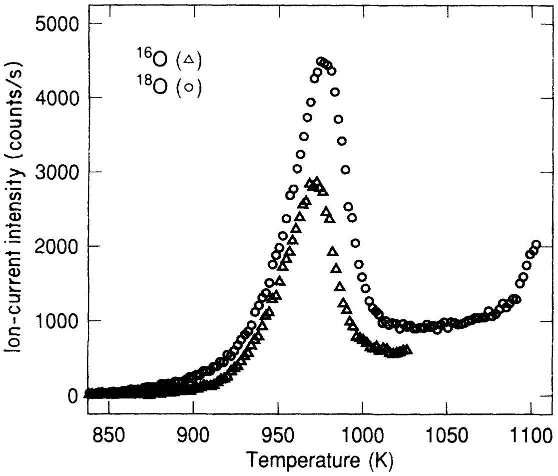

FIG. 3. Comparison of the rate of low-temperature oxygen release for the copper-rich, $x=0.125$, $^{18}$O-containing sample (also shown in Fig. 2), and for its $^{16}$O-containing equivalent.

sult, which proves that phase equilibria at the copper-rich, $x=0.125$ composition are different in the $^{18}$O-containing materials than in the $^{16}$O materials.

The atomic percents of $^{18}$O, determined by mass spectrometry in the relevant materials are given in the fifth column of the table. For every $^{18}$O-containing material two numbers are given, the first gives the $^{18}$O concentration from oxygen release in the low-temperature regime, the second number for the high-temperature regime. We see that the isotope concentration in the two regimes is similar, indicating a fairly uniform distribution of $^{18}$O.

Magnetic measurements were made using a Quantum Design SQUID magnetometer. The scan length of the measurement was adjusted to a distance of 3 cm, to keep gradient-field effects at a minimum. Powder samples approximately 500 mg in weight were used in each measurement, where the powder was in a gelatine capsule. For the purposes of calculating magnetic parameters, the particles were treated as spheres with a demagnetization coefficient of $3/8\pi$, thus $M\simeq 0.12H$ for perfect shielding by superconducting currents.

Three sets of measurements were made on each sample. In the first measurement $M$ versus $H$ is determined for 10-Oe intervals up and down 0 to 100 Oe. The measurements were made at 5 K, and the samples were cooled in approximately zero field to start. In all cases a reversible magnetization was observed. The slope of $M$ versus $H$ is the diamagnetic shielding, which gives a measure of the fraction of superconductivity in the sample, when compared to the theoretical value given above. These values are given in percent in the sixth column of the table. The diamagnetic shielding is about 3% of the ideal in the stoichiometric samples. Recall, that for grains of 1-$\mu$m diameter, the majority of the volume is occupied by the London penetration depth ($\lambda$), leading to a greatly reduced diamagnetic signal. The volume fraction of a spherical grain not penetrated is $(r-\lambda)^3/r^3$, and for $\lambda\simeq 0.3$ $\mu$m in this system,[16] it is 6.4% for 1-$\mu$m diameter grains, and 34.3% for 2-$\mu$m diameter grains. This assumes that the material is 100% superconducting. We obtained about half of these values depending on composition and in agreement with previous reports.

In the second type of characterization we took partial hysteresis loops of the samples at 5 K. We increased the field to 40 000 Oe, and than reduced it to zero. The remanent moment found at $H=0$ is the trapped magnetic flux given in the seventh column of the table. Comparing the numbers for the $^{16}$O- and $^{18}$O-containing members of an isotope pair we notice that in the copper-rich $x=0.125$ samples the magnitude of the trapped flux is about twice as large for the $^{16}$O-containing material than for the $^{18}$O-containing material. This means that the two materials are different, and the reduction of trapped flux can well be explained by a larger amount of nonsuperconducting phase at the grain boundaries. This is the third result, which indicates, that the equilibrium concentration of the nonsuperconducting $La_{1.67}Sr_{0.33}Cu_2O_5$ phase is larger in the $^{18}$O-containing material than in the $^{16}$O-containing material at the copper-rich $x=0.125$ composition. The difference in trapped flux between the different isotope containing materials is considerably smaller at the copper-rich $x=0.15$ composition, though not negligible. Small difference in trapped flux is observed between the stoichiometric samples made with the different isotopes.

From the $M$ versus $H$ plot the position of zero field can be determined. It is necessary to determine $H=0$ in this way, because there is always a small remanent field (about 15 Oe) from the superconducting coil in the SQUID magnetometer. The applied field was then set to overcome the remanent field and give an actual field of about +3 Oe to make a temperature-dependent measurement of $M$ versus $T$. This is shown in Fig. 4, where data were taken at every degree up to 40 K. A sharp drop is seen at the superconducting transition temperature. To compare two samples, the data points are normalized by taking $M$ at each value of $T$ and dividing by $M$ at 5 K, which is the starting point of the measurement. It is now a simple matter to compare the temperature dependence of the isotope pairs. Figure 4 shows the normalized diamagnetism of the $^{16}$O- and $^{18}$O-containing pairs as a function of temperature; (a) for copper-rich $x=0.125$; (b) for stoichiometric $x=0.125$; (c) for copper-rich $x=0.15$; and (d) for stoichiometric $x=0.15$ materials. Note, that the shape of the curves is different for the copper rich, than for the stoichiometric samples because of the difference in grain size.

For the superconducting transition temperature, $T_c$, we took the intersection of the extrapolations of the steepest parts, and the near-horizontal, high-temperature parts, of the curves. This definition of $T_c$ means a "bulk onset." Because of differences in grain size between stoichiometric and copper-rich materials, we cannot define $T_c$ at midpoint because this would confuse the issue of $T_c$ with the percentage of the superconducting phase. The normalized susceptibility versus temperature curves for the $^{16}$O- and $^{18}$O-containing samples run fairly parallel to each other. The $T_c$'s of the various materials are given in the next to last column of the table. At

$x=0.125$ the stoichiometric samples have a larger $T_c$, than the copper-rich ones, where the strontium-rich second phase reduces the strontium concentration of the superconducting phase, and thus $T_c$. In contrast to this, at $x=0.15$ the copper-rich samples have a higher $T_c$ than the stoichiometric ones. As a result of this, the doping dependence of $T_c$ is significantly smaller in the stoichiometric samples—going from 30.1 to 33.25 K, when the doping is changed from $x=0.125$ to $x=0.15$—than in the copper-rich samples, where for the same change in doping, $T_c$ changes from 28.8 to 36.6 K. (We compared the $^{16}O$-containing samples.) It seems, that all previous reports on the doping dependence of $T_c$ were made on copper-rich materials.

The oxygen isotope-effect exponent, $\alpha_O$ was calculated according to Eq. (1), and was not extrapolated to 100% $^{18}O$ exchange. The values of $\alpha_O$ are given in the last column of the table for the four isotope pairs. We see that $\alpha_O$ for the stoichiometric samples is 0.44 for $x=0.125$ material, and 0.36 for the $x=0.15$ material, near the theoretical value of $\alpha=0.5$ predicted by the BCS model for phonon-mediated pairing.

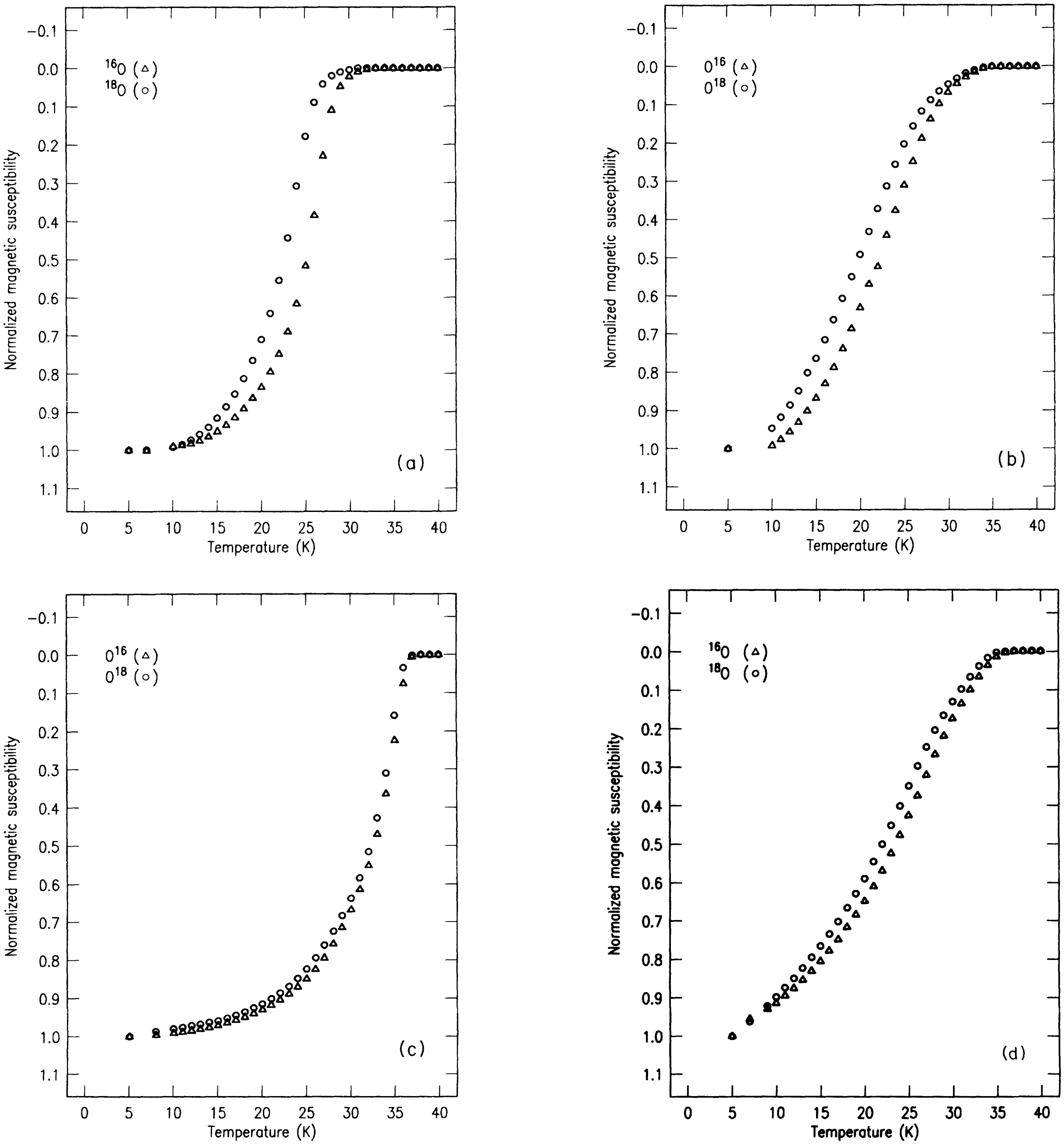

FIG. 4. (a) The normalized diamagnetism of the $^{16}O$- and $^{18}O$-containing pairs as a function of temperature for (a) the copper-rich $x=0.125$ material. (b) The stoichiometric $x=0.125$ material. (c) The copper-rich $x=0.15$ material. (d) The stoichiometric $x=0.15$ material.

We found the isotope-effect exponent for the copper-rich $x=0.125$ material to be 0.65. This apparently larger than 0.5 exponent is caused by the lower $T_c$ of $^{18}$O-containing material related to a larger equilibrium concentration of the strontium-richer nonsuperconducting $La_{1.67}Sr_{0.33}Cu_2O_5$ phase, as was amply demonstrated in this paper. The reason for this difference between the $^{18}$O-, and $^{16}$O-containing materials is, that the thermodynamic stability parameters $\Delta H$ and $\Delta S$, where $H$ is enthalpy and $S$ entropy, of the $La_{2-x}Sr_xCuO_4$ and of the $La_{1.67}Sr_{0.33}Cu_2O_5$ phases are probably very similar at the strontium concentration of 0.125. The $La_{1.67}Sr_{0.33}Cu_2O_5$ structure is possibly stabilized by the entropy contribution. The $^{18}$O version of this phase has excess entropy over the $^{16}$O version, due to the larger mass of $^{18}$O, which results in smaller vibrational frequencies. This larger vibrational entropy[17] may shift the equilibrium toward more $La_{1.67}Sr_{0.33}Cu_2O_5$ in the $^{18}$O-containing material. This explains the "anomalous" isotope effect. Scanning-Auger-electron-spectroscopy measurements showed[18] that the segregation of a Sr-rich phase at the grain boundary with a Sr concentration twice that of the grain interior is the most pronounced after an anneal at 700 °C. This is the same temperature used by Crawford *et al.* for isotope exchange to obtain the largest anomalous isotope effect, $\alpha=0.85$. This effect may still be there to a small extent in the copper-rich $x=0.15$ materials, which may cause a small increase in the measured value of $\alpha_O$.

The great surprise is the behavior of the $La_{2-x}Sr_xCuO_4$ material at $x=0.15$, where the stoichiometric material gives an oxygen isotope-effect exponent of 0.36, while the copper-rich material exhibits an isotope-effect exponent approaching zero, just as in the higher-$T_c$ materials. We are currently studying these materials with low-temperature x-ray diffraction, looking for a structural reason which may explain this dramatic change in behavior.

We reproduced the results of previous studies on the "anomalous" isotope effect[6,7] at $x=0.125$ with the copper-rich material. We also reproduced the "nonzero" isotope effect at $x=0.15$ of Ref. 5, where $\alpha_O=0.09-0.37$ was reported, showing that this range of values is bound by $\alpha_O=0.36$ for the stoichiometric material, and $\alpha_O=0.08$ for the very copper-rich material. Previous studies on the isotope effect in the $La_{2-x}Sr_xCuO_4$ system were apparently made on copper-rich materials.

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