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Anomalous oxygen isotope effect in $La_{2-x}Sr_xCuO_4$

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We report measurement of the oxygen isotope effect α_O in $La_{2-x}Sr_xCuO_4$ as a function of x. For values of $x < 0.15$, α_O in the expression $T_c \sim M^{-\alpha_O}$ is large (0.4–0.6) but decreases by about a factor of 5 for $x \geq 0.15$, where we obtain $\alpha_O \approx 0.1$, in good agreement with earlier results. The large values of α_O obtained for small x are reproducible when the ^{18}O,^{16}O sample pairs are cross exchanged. The maximum measured values of α_O fall outside the range of standard Bardeen-Cooper-Schrieffer theory and may imply anharmonic phonon-mediated superconductivity. The variability of α_O may be related to a nearby lattice instability, similar to that observed in $(La,Ba)_2CuO_4$. Isotope frequency shifts of the far-infrared transverse-optic phonons of A_{2u} symmetry at 240 and 500 cm^{-1} also display an anomaly between $x = 0.11$ and 0.15 and, in addition, demonstrate ^{18}O exchange for both oxygen sites.

INTRODUCTION

The isotope effect in superconductivity, first reported in 1950, was taken as evidence for phonon mediation.[1] It has since been investigated in many materials.[2] When high-temperature superconductivity was discovered in metal oxides, the oxygen isotope effects [α_O] were promptly measured.[3] In $YBa_2Cu_3O_7$, the value of α_O in the expression $T_c \propto M^{-\alpha_O}$ (where M is the oxygen mass) is apparently inconsistent with any present theory of phonon-induced superconductivity.[3] In the lower-T_c materials $Ba_{1-x}K_xBiO_3$ (Ref. 4) and $La_{2-x}Sr_xCuO_4$,[5] however, this may not be true. In the latter material, when $x = 0.15$, the measured value of α_O is consistent with a mechanism based on strong electron-phonon coupling.[5] In both the $YBa_2Cu_3O_{7-x}$ and $La_{2-x}Sr_xCuO_4$ systems, T_c can be varied by changing the carrier concentration.[6,7] Therefore, it is possible to examine the relationship between T_c and α_O within either structure. In this paper we report the determination of the isotope effect in $La_{2-x}Sr_xCuO_4$ for six values of x, over which T_c varies from 8 to 37 K. We find that the measured values of the isotope shift depend strongly on x and, in particular, α_O decreases by a factor of 5 between $x = 0.11$ and 0.15. There is no obvious correlation of α_O with T_c in this system.

EXPERIMENTAL

Samples of $La_{2-x}Sr_xCuO_4$ were prepared by standard solid-state techniques using stoichiometric quantities of La_2O_3, SrO_2, and CuO. Well-ground mixtures of the binary oxides were fired to 1100 °C in oxygen for 12 h and furnace cooled to room temperature. The samples were reground and refired under the same conditions to ensure complete reaction. Powder x-ray diffraction data were collected on each of the samples as a check of phase purity. All samples appeared to be single phase by this criterion.

Oxygen exchange was carried out on two ~300-mg samples taken from the same powder preparation at a given Sr content. The paired samples were loaded into gold pans, weighed, placed in identical reaction vessels, and attached to a vacuum manifold. Samples were evacuated to 10^{-3} Torr and heated to 700 °C in vacuum. After 30 minutes, $^{16}O_2$ or $^{18}O_2$ (95%, Cambridge Isotopes) was admitted to the reaction vessels to a pressure of 500 Torr, and both vessels were heated to 875 °C. Samples were held under these conditions for 2 h. The progress of isotope exchange was monitored by removing aliquots from the vapor above the sample and analyzing the [$^{16}O/^{18}O$] ratios by mass spectrometry. These experiments demonstrated that isotopic equilibrium among the oxygen atoms was reached within 1 h. To achieve enrichments of 80% and above, the samples were given two additional exchanges by pumping out the equilibrated vapor and refilling with fresh $^{16}O_2$ or $^{18}O_2$. The second and third exchanges were carried out at 850 °C for 2 h and 6 h, respectively. Following the third exchange, the samples were cooled to room temperature in the equilibrated gas mixture, removed from the reaction vessel and weighed. In all cases, the ^{16}O samples showed essentially no weight change (<0.02%), while the ^{18}O samples showed significant weight increases (~1.8%). ^{18}O incorporation could be determined from these weight changes as well as the $[^{16}O]/[^{18}O]$ ratio in the vapor. These two determinations were generally in good agreement. Percent exchange data for the ^{18}O sample of each experimental pair are shown in Table I.

The transition temperatures were determined by measuring the field-cooled magnetic susceptibility (Meissner effect) in a commercial superconducting quantum interference device (SQUID) susceptometer as a function of temperature. Fields with nominal values between 2 and 5 Oe were used in order to provide a good signal to noise ratio as well as a sharp, well-defined transition. Cylindrical nylon sample holders were used for the powders; pellets were suspended directly from a string. Most measurements were made on powders, which generally showed better reproducibility and sharper transitions than pellets of the same composition. ^{16}O-^{16}O sample pairs prepared and measured in this way give dc susceptibility curves which cannot be distinguished. When samples are properly stored and handled, magnetic data for a given sample can be reproduced in separate runs made weeks apart. As has been observed by others, the fraction of material that shows flux exclusion maximizes for $x=0.15$.[8] The ^{16}O and ^{18}O members of the isotope pair for each Sr concentration were measured sequentially, without altering the field, to ensure identical conditions. In order to correct the raw data for minor differences in the masses and magnetization factors of each member of a pair, the ^{18}O curve of each pair was multiplied by a constant so that the flat, low-temperature portions of the curves were matched. As can be seen from Fig. 1, the two curves for a given pair are very similar, except for the shift in T_c. The ΔT_c values were measured horizontally across the steepest portions of the paired curves (Fig. 1). These curve sections represent the bulk of the superconducting sample, and are in all cases nearly parallel. T_c for each ^{16}O sample was taken as the point at which extrapolations of the nearly vertical portion and the almost horizontal high-temperature portion of the curve intersect.

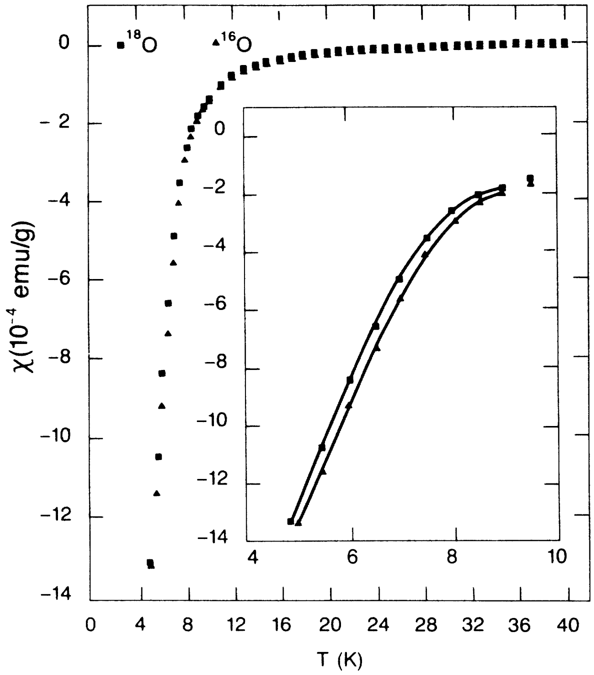

FIG. 1. Meissner data for ^{16}O and 86% ^{18}O exchanged $La_{1.74}Sr_{0.26}CuO_4$. Inset shows an expanded view.

TABLE I. Summary of isotope effect and FIR data for $La_{2-x}Sr_xCuO_4$.

x	T_c	ΔT_c	% ^{18}O Exchange	240 cm^{-1} $\nu(^{18}O)/\nu(^{16}O)$	500 cm^{-1} $\nu(^{18}O)/\nu(^{16}O)$	α_O[a]
0.038	NSC		85	0.967	0.959	
0.0750	21.2	0.84	90	0.966	0.957	0.40
0.113	29.7	1.91	88			0.64
	29.6	1.82	86	0.970	0.961	0.60
	29.6	1.90	87			0.64
0.150	37.8	0.32	87	0.958	0.952	0.08
	38.3	0.36	82			0.10
	35[b]					0.16
	34.5–37[c]					0.09–0.37
	35[d]					0.14
0.188	34.4	0.21	84	0.955	0.954	0.06
0.225	23.0	0.23	88	0.954	0.953	0.10
0.263	8.0	0.22	86	0.955	0.956	0.12

[a] Uncertainties in the determination of T_c, combined with the reproducibility errors shown, for example, in the three data sets for $Sr=0.113$ suggest error limits of $+-0.03$ in calculated values of α_O.

[b] First part of Ref. 5.

[c] Second part of Ref. 5.

[d] Reference 21.

Near normal incidence far-infrared reflectance spectra were measured using a Fourier-transform infrared spectrometer, a Si composite bolometer, and a Helitran sample cryostat. Samples were not polished, but were coated with ~1000 Å of Al after the first infrared measurement and were then measured again. The latter spectrum was used as a reference to correct for geometric scattering. Far-infrared spectroscopy directly demonstrates that the samples have been efficiently ^{18}O exchanged. In contrast to Raman measurements, for which only the axial oxygen, O(2), is active, infrared spectroscopy is able to probe both oxygen sites (in-plane and axial). Some typical pairs of spectra are shown in Fig. 2. The phonons which appear in these spectra are *c* axis polarized (*ab* plane polarized phonons are screened by the free charge carriers) and, despite the orthorhombic symmetry of some of the samples, only three modes ($3A_{2u}$) are consistently observed. Apparently the small orthorhombic distortion is not sufficient to give the 6 B_{1u} modes which one would expect for Abma-D_{2h}^{18} symmetry. The transverse optic (TO) phonon at 500 cm^{-1} is primarily due to Cu-O(2) stretching, whereas the 240 cm^{-1} TO mode is a Cu-O sheet bending vibration.[9] Both modes show substantial (3–5%) isotope shifts for all experimental sample pairs (Table I).

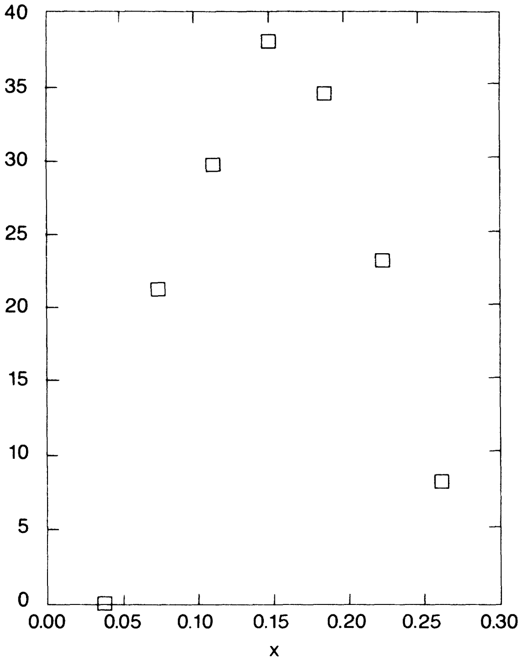

FIG. 3. T_c vs x for $La_{2-x}Sr_xCuO_4$.

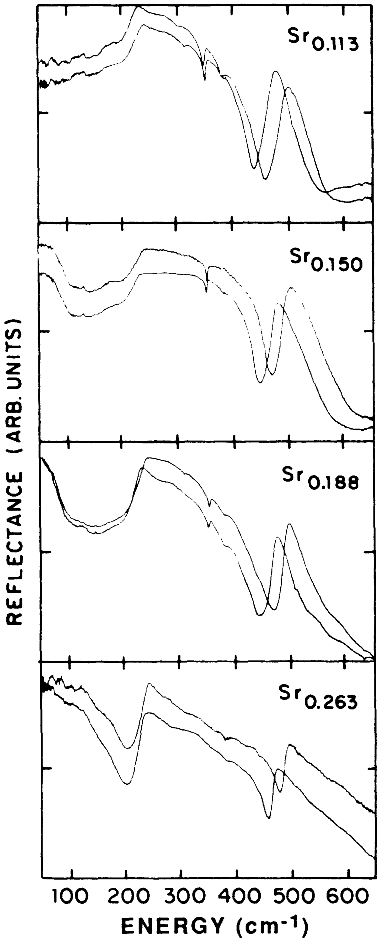

FIG. 2. FIR reflectance spectra for $La_{2-x}Sr_xCu^{16}O_4$ and $La_{2-x}Sr_xCu^{18}O_4$ at four values of x at 10 K. Fractional frequency shifts for the 240 cm^{-1} and 500 cm^{-1} phonons are given in Table I.

RESULTS

T_c and ΔT_c values obtained as already described for six different values of x in $La_{2-x}Sr_xCuO_4$ are given in Table I. The variation of T_c with x is shown in Fig. 3. The variation of α_O calculated from these data is shown in Fig. 4. The T_c values that we have obtained as a function

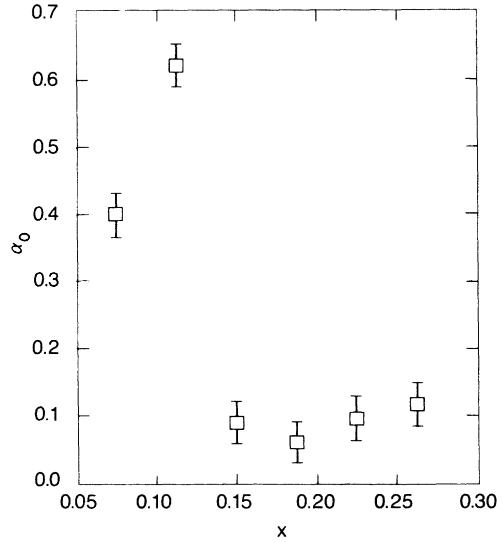

FIG. 4. The ^{18}O isotope effect, α_O, in $La_{2-x}Sr_xCuO_4$ vs x. Error bars are estimated from the spread in values obtained for different sample pairs with $x=0.113$ (three pairs) and $x=0.150$ (two pairs).

of x, and our measured value of α_O at $x=0.15$ (Fig. 5), are in good agreement with previously published work.[5,7,10]

ΔT_c for two sample pairs prepared with the same Sr content and the same oxidation treatment in two different synthetic batches is identical. This is explicitly demonstrated for the $x=0.113$ sample in Table I. Entries one and two ($x=0.113$) represent two different preparations. Both show α_O values in excess of 0.60. One $x=0.113$ sample pair has also been cross exchanged; that is, the ^{18}O member of the pair had its oxygen replaced with ^{16}O, while the ^{16}O member was reexchanged with ^{18}O. Figure 6 shows the data for this sample pair before and after the cross exchange (first and third entries for $x=0.113$ in Table I). This explicitly demonstrates the reversible nature of the oxygen exchange process. Tarascon *et al.* have shown that T_c can vary with differences in oxygen annealing conditions in this system.[10] However, the cross-exchange experiment also clearly demonstrates that small variations in our exchange process must make a relatively insignificant contribution to the measured ΔT_c values.

DISCUSSION

Our results are surprising for two reasons. First, the ^{18}O isotope effect, expressed as α_O or ΔT_c, does not correlate in any simple way with T_c. Previous measurements on high-T_c superconductors suggested that smaller α_O correlated with higher T_c. Our results suggest a more complex relationship. Second, the value of α_O exceeds 0.5 over some region of the superconducting phase diagram. To date, α's have been observed to vary between 0.5 and -2.2 in other superconducting materials, but substantiated values of $\alpha > 0.5$ have apparently not been reported.[3] We will discuss two possible explanations for our unusual results.

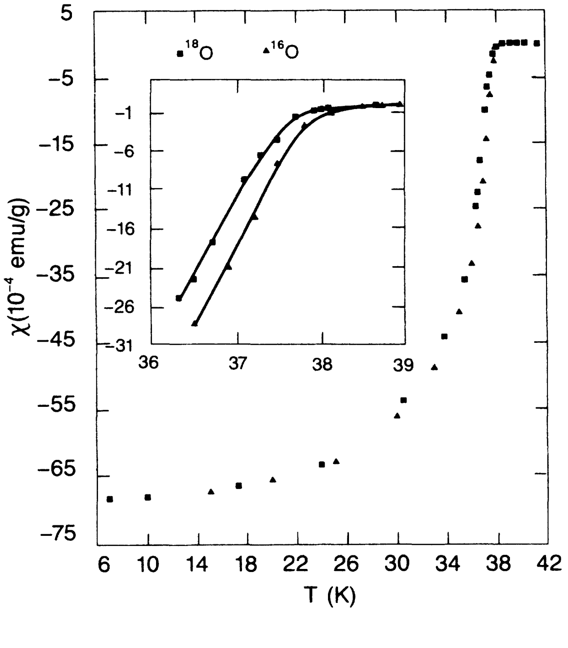

FIG. 5. Meissner data for ^{16}O and 82% ^{18}O exchanged $La_{1.85}Sr_{0.15}CuO_4$. Inset shows an expanded view.

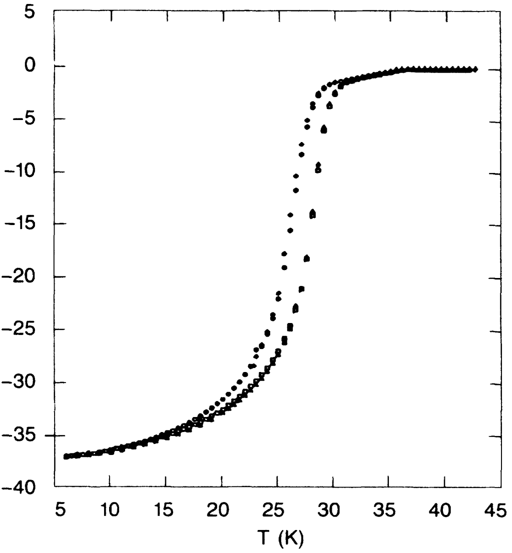

FIG. 6. Data sets for a $La_{1.87}Sr_{0.113}CuO_4$ sample pair before and after cross exchange.

A striking observation has been made recently in a systematic study of the related $La_{2-x}Ba_xCuO_4$ system.[11–13] This material goes from semiconducting and antiferromagnetic at $x=0$ to superconducting with $T_c \approx 30$ K at $x=0.09$. As x increases still further, however, the T_c first decreases to a minimum ($T_c \leq 5$ K) for $x=0.12$, then increases again to a second maximum near $x=0.15$ ($T_c \approx 30$ K), and the material finally transforms into a nonsuperconducting metal as x increases beyond this value. Structural studies indicate the minimum in T_c near $x=0.12$ is associated with a phase transition at ~ 65 K in which the structure converts from $Abma\text{-}D_{2h}^{18}$ (the low-temperature orthorhombic or LTO phase in the nomenclature of Ref. 12) to $P4_2/ncm$ (low-temperature tetragonal, LTT) space-group symmetry.[11,12] This phase transition involves a soft Cu-O octahedra tilting optic phonon, similar to the soft mode identified to drive the well-known phase transition from $I4/mmm$ (high-temperature tetragonal, HTT) to $Abma\text{-}D_{2h}^{18}$ (LTO) in La_2CuO_4.[14] In the $La_{2-x}Ba_xCuO_4$ system the LTO→LTT phase transition is accompanied by marked changes in transport properties, in contrast to the HTT→LTO transition.[13,15] In fact, the LTT structure may not superconduct.[12] One possible explanation for these observations is that the zone-boundary tilting mode is strongly coupled to the charge carriers near the LTO-LTT phase transition (lattice instability), and it is this interaction which leads to high-temperature superconductivity.

In $La_{2-x}Sr_xCuO_4$ there is no evidence in the literature for an LTO→LTT phase transition. It is, however, conceivable that for $x \approx 0.12$, where the LTO→LTT phase transition occurs at 65 K for $La_{2-x}Ba_xCuO_4$, the $La_{2-x}Sr_xCuO_4$ system approaches a similar lattice instability, but the optic mode softens less and a structural phase transition does not occur. Other evidence for such a lattice instability in this system includes elastic[16] and ultrasonic anomalies,[17] and upturns in the low-temperature resistivity.[9,18] The latter may arise from increased electron-phonon scattering due to partial mode softening near the lattice instability. We do not know how the ^{18}O isotope effect on T_c will be affected by such a situation, but we speculate that the unusual isotope effects we observe near $x = 0.11$ may be related to such a lattice instability. The soft mode in the LTO→LTT phase transition in $La_{2-x}Ba_xCuO_4$ is an essentially pure oxygen vibration and an instability of this kind should be sensitive to the oxygen mass. We are not aware of any theoretical models which describe the isotope effect for this situation. We suggest as a possible explanation, then, for the large α_O values (> 0.5) that we measure, coupling of charge carriers by the highly anharmonic oxygen vibrations which should be present near such a phase transition.

Even if anharmonic oxygen vibrations are not the source of the variable isotope effects on T_c, the temperatures at which the HTT→LTO and LTO→LTT phase transitions occur should be oxygen-isotope (mass-) dependent. We are presently studying this effect. In contrast to this expected large sensitivity to oxygen mass, the effect of copper isotope substitution upon superconducting T_c and phase transition temperatures should be quite small [i.e., $\alpha(\mathrm{Cu}) \ll 0.5$] if the zone-boundary tilting vibrations are responsible for the superconducting pairing, since the copper atoms have small (or zero) vibrational amplitude during these vibrations.

As discussed earlier, the far-infrared spectra of ^{16}O and ^{18}O $La_{2-x}Sr_xCuO_4$ exhibit isotope frequency shifts which demonstrate ^{18}O substitution in both O(1) and O(2) sites. There is, however, an interesting dependence of this shift upon x, which we display in Fig. 7. There we plot the ^{18}O fractional frequency shifts for the 240 cm^{-1} and 500 cm^{-1} TO phonons, normalized to the specific amount of ^{18}O substituted for each value of x. There is an anomaly in the shifts which occurs at the same x values for which the α_O values change. The source of this correlation within a soft-phonon picture is not clear. If the α_O values were driven by the zone-boundary lattice dynamics, as seems likely, then it is at first sight somewhat surprising that zone center A_{2u} phonons would also be affected as these observations imply. It may be that the vibrational potentials for the zone center (A_{2u}) modes become more anharmonic or the vibrational amplitude for oxygen varies with x, causing the anomalies we observe in Fig. 7. It should be noted that there are also zone-center ultrasonic anomalies.[17]

Although we are intrigued by the possibility that the unusual α_O values reflect an incipient phase transition in these materials, there is a possible complication in these experiments that may affect the interpretation of our isotope effect measurements. If one measures α_O in a region of the phase diagram where the superconducting transition temperature is varying rapidly with hole content, then small differences in oxygen content for the ^{16}O and ^{18}O samples can yield misleading α_O values. The required oxygen content differences are quite small. For example, we estimate that if the ^{18}O sample at $x = 0.11$ contained .005 fewer oxygen atoms per formula unit than the ^{16}O sample, then a decrease of roughly 1.8 K in T_c would be expected. We cannot measure oxygen contents this accurately. Iodometric titrations of ^{16}O, ^{18}O sample pairs, however, yield identical hole contents for each member of the pair within the experimental accuracy ($+/-0.02$ hole per formula unit), and for samples where $x = 0.2$ or less the measured hole contents are equal to the nominal Sr^{2+} stoichiometries. Furthermore, the large variations of α_O which we observe for $0.1 < x < 0.15$, where the previously described phase transition occurs in $La_{2-x}Ba_xCuO_4$, in addition to the approximately constant α_O for $0.15 < x < 0.26$, where T_c is again varying strongly with x, and our infrared data argue in favor of a lattice dynamical or structural interpretation of the x dependence of the isotope effect in $La_{2-x}Sr_xCuO_4$.

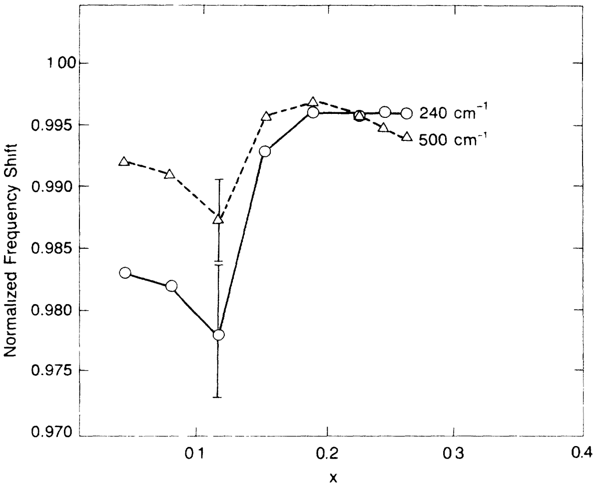

FIG. 7. ^{18}O frequency shifts for the 240 cm^{-1} and 500 cm^{-1} TO phonons, normalized to the amount of ^{18}O in the lattice (i.e., divided by [mass (^{18}O exchanged)/16]$^{1/2}$), as a function of x($T = 10$ K). The sample with $x = 0.038$ was not superconducting.

Finally, we briefly address certain aspects of how the electronic and lattice-dynamical properties of $La_{2-x}Sr_xCuO_4$ vary with composition. It has been claimed that the only electronically homogeneous composition of this material which can support superconductivity has $x = 0.15$.[19] In this point of view, superconductivity is observed at nominally different compositions only due to electronic inhomogeneity. We instead suggest that the *lattice dynamical properties* vary across the phase diagram in such a way as to give rise to superconductivity only in a certain composition range; doping beyond about $x = 0.3$ moves the lattice away from the instability region, leading to a loss of superconductivity. Support for this contention lies in the observation that α_O varies with composition (reflecting the changing lattice dynamics), and the fact that the structural, lattice dynamical, and superconducting properties of the related $La_{2-x}Ba_xCuO_4$ system also correlate with x. In contrast, the normal-state electronic properties, e.g., resistivity, vary smoothly with x.[20] Furthermore, the superconducting transitions we measure are sharp and well defined for all values of x and, in all cases, the ^{16}O and ^{18}O curves are parallel. These observations indicate that these materials are not electronically multiphase, but rather that the charge carrier pairing is affected by the local lattice dynamics.

CONCLUSIONS

In summary, we have observed a strong dependence of the oxygen isotope effect in $La_{2-x}Sr_xCuO_4$ upon the Sr concentration. This is the first example of a high-T_c system where the isotope effect has been examined as a function of doping level. At low Sr concentrations the measured isotope effect exceeds 0.6, greater than the BCS limit of 0.5. This may be a result of anharmonic phonon mediated charge carrier pairing. Our results imply that the oxygen isotope effect is sensitive to subtle variations in lattice vibrational or electronic structure. The isotope effect, like T_c and flux exclusion volume, varies across the compositional phase diagram of this material. It is possible that this is true for the phase diagrams of other high-T_c materials as well. This sensitivity to composition may explain some of the variability that has appeared in the isotope effect literature concerning many of the new materials. The discrepancy in the reported values[4] for α_O in $Ba_{1-x}K_xBiO_3$ may arise from considerations similar to those we have discussed here since nominally different values of x were used in the two independent α_O determinations.

Note added in proof. Since the submission of this manuscript we have measured α_O at $x=0.12$, 0.13, and 0.14. We find the maximum, $\alpha_O \sim 0.77$, to occur at $x=0.12$. Furthermore, we observe α_O to vary in a similar manner in $La_{2-x}Ba_xCuO_4$. These results will be reported in a subsequent publication.

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