Copper and Oxygen Isotope Effects in $La_{2-x}Sr_xCuO_4$

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The copper and oxygen isotope effects were investigated in $La_{2-x}Sr_xCuO_4$ for $x=0.15$ and $x=0.125$. It is found that the partial isotope exponents α_{Cu} and α_O are close to each other. For $x=0.15$ we find $\alpha_{Cu}=0.15$ and $\alpha_O=0.11$, while for $x=0.125$ anomalously large isotope exponents of $\alpha_{Cu}=0.93$ and $\alpha_O=0.91$ are found. The results show that large parts of the phonon spectrum influence the superconducting transition temperature.

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Investigations of the copper isotope effect in high temperature cuprate superconductors have so far been confined to fully oxygenated $YBa_2Cu_3O_7$ (YBCO). In all cases, no observable isotope effect was found [1-5]. In contrast to this, a small but observable oxygen isotope effect exists for this compound. If we define the partial isotope exponent by $\alpha_i = -\Delta \ln T_c/\Delta \ln m_i$, where m_i is the mass substituted, then the oxygen isotope exponent in YBCO has been reported in the range $\alpha_O=0.03$ to 0.17, with a probable average of $\alpha_O \approx 0.05$ [6-8]. It is now well known that this small oxygen isotope effect increases when substituted materials are investigated, reaching values of $\alpha_O \approx 0.5$, and in some cases exceeding this [9-12]. It is therefore of interest to investigate the copper isotope effect in substituted cuprate superconductors.

A particularly interesting, and somewhat anomalous case is provided by the system $La_{2-x}Sr_xCuO_4$. Crawford *et al.* [11] have shown that for a Sr concentration of $x=0.125$, the oxygen isotope effect shows a pronounced maximum of $\alpha_O \approx 0.85$, dropping to $\alpha_O \approx 0.10$ for the optimal Sr concentration of $x=0.15$. A similar situation also exists in $La_{2-x}Ba_xCuO_4$ [12]. We decided therefore to investigate the copper isotope effect in these compounds. We found that indeed a copper isotope effect is observable in this system, and that α_{Cu} is very close to the oxygen isotope exponent α_O. Our investigations so far are confined to the two Sr concentrations $x_{Sr}=0.125$ and $x_{Sr}=0.15$.

The samples were prepared from high purity La_2O_3 (99.999%), $SrCO_3$ (99.999%), and ^{63}CuO and ^{65}CuO. The copper isotopes were obtained as oxides from the isotope division of Martin Marietta Energy Systems (Oak Ridge), the copper isotopic purity is very high (99.72% ^{63}Cu and 99.61% ^{65}Cu, respectively). It was further ensured that both copper isotopes had been obtained in the same separation run, and that the overall chemical purity is high. In the spectrographic analysis, only traces of B, Mg, and Si were found, all below a concentration of 0.01%. In previous investigations [5] we have used these same ^{63}CuO and ^{65}CuO materials for the preparation of $YBa_2Cu_3O_7$. We found a transition temperature of $T_c=91.2$ K for both copper isotopes, no discernible temperature shift was found, with a sensitivity of $\Delta T_c \leq 0.04$ K. We believe, therefore, that any observed transition temperature shift in compounds using these oxides cannot be ascribed to chemical impurities.

We prepared as a first step mixtures of La_2O_3 and $SrCO_3$ with the required stoichiometric ratio of Sr to La. These mixtures were then combined with the stoichiometric amounts of ^{63}CuO or ^{65}CuO. We ensured therefore that in both isotopic copper samples the La:Sr ratio was identical. The calcining and sintering procedure for the $x=0.125$ samples was as follows: 900 °C in air for 19 h, 950 °C in air for 19 h, 1125 °C in air for 24 h, 1130 °C in air for 28 h, and 1000 °C in air for 75 h. After this the samples were introduced into the oxygen isotope exchange apparatus described previously [8]. The samples were held in pure $^{16}O_2$ for 12 h at 1000 °C, 12 h at 850 °C, and 48 h at 700 °C, and then oven cooled. After this treatment the transitions were determined in a SQUID magnetometer, and a copper isotope shift of $\Delta T_c(Cu) \approx 0.7$ K was found. After this the samples were split into equal halves, and again gas exchanged. The ^{63}Cu sample was gas exchanged in $^{16}O_2$, and the ^{65}Cu sample in $^{18}O_2$. These and the following gas exchanges were carried out at 650 °C. After this the transitions were again observed, and we found an oxygen isotope effect, in addition to the copper isotope effect. Following this, we gas exchanged the ^{63}Cu-^{16}O sample in $^{18}O_2$, and the ^{65}Cu-^{18}O sample in $^{16}O_2$. The backexchange from ^{65}Cu-^{18}O to ^{65}Cu-^{16}O reproduced the original ^{65}Cu-^{16}O transition. After these steps we have transitions for all combinations, i.e., ^{63}Cu-^{16}O, ^{63}Cu-^{18}O, ^{65}Cu-^{16}O, and ^{65}Cu-^{18}O. We found four different and closely parallel transition curves, from which the isotope exponents were determined.

For the $x=0.15$ samples the powders were calcined for 4 h at 750 °C, and for 11 h at 900 °C, in air. The sintering was performed again in pure $^{16}O_2$, for 4 h at 700 °C, 11 h at 1050 °C, and 24 h at 650 °C. After this the transitions were observed in the SQUID magnetometer, and a smaller copper isotope shift of $\Delta T_c(Cu)=0.15$ to 0.2 K was observed. Following this, the samples were reground and gas exchanged in $^{18}O_2$ at 650 °C for 30 h, a larger oxygen isotope shift of about $\Delta T_c(O)=0.5$ K was ob-

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served. After this, the samples were backexchanged with $^{16}O_2$, and again with $^{18}O_2$. We found that the oxygen isotope shift is reversible on backexchange.

The making conditions for $x=0.125$ and $x=0.15$ were adopted after extensive preliminary studies with natural copper isotopes showed that these procedures give reasonably sharp transitions, and parallel transition curves for ^{18}O substitution. In the case of $x=0.15$ it was necessary necessary to regrind the pellets before gas exchange with ^{18}O in order to obtain high oxygen substitution levels (as observed by weighing). In all cases the samples were parallel processed either by side by side mounting in platinum gauze when the same gas atmosphere was used or by using the parallel-processing system previously described for $^{16}O_2$ and $^{18}O_2$ exchange [8].

The transitions were observed by field-cooled magnetization measurements in a Quantum Design SQUID magnetometer (Meissner effect) in various fields between 1 and 150 G, the observed shifts in T_c were essentially independent of the measured field. The magnetization curves were normalized so that they coincided in the flat low temperature region (5.6 K). It was found that the larger mass isotope always showed a slightly smaller volume susceptibility at low temperature, this effect amounted to (5–8)% for ^{16}O-^{18}O exchange, and to (8–14)% for ^{63}Cu-^{65}Cu exchange. This finding is similar to that of Crawford *et al.* [12]. The reasons for this difference are presently not understood. The isotopic shifts of the transition temperature were determined at the approach to $M=0$, in order to eliminate effects due to demagnetization, and particle size. We used two methods. In the first, the steep part of the magnetization is extrapolated to $M=0$, and the transition temperatures so obtained used for the isotopic shifts. This is shown in Fig. 1. In the second method, we obtained the shifts in T_c at the level of 1% of the Meissner effect at $T \rightarrow 0$ K. This is shown in Fig. 2. Both methods give similar shifts. In Table I we give the transition temperature shifts obtained at the 1% level of the total Meissner effect at $T \rightarrow 0$ K, the error limits quoted for the partial isotope exponents α_{Cu} and α_O represent variations due to determinations of ΔT_c by the two methods mentioned, and determinations in various fields. Because of the dependence of T_c on different masses, $T_c = T_c(m_i)$, the total temperature change is given by

$$\Delta \ln T_c = -\sum_i \alpha_i \Delta \ln m_i , \tag{1}$$

where the partial isotope effects exponents α_i are given by

$$\alpha_i = -(\Delta \ln T_c / \Delta \ln m_i)_{m_{j\neq i}} . \tag{2}$$

For the calculation of α_{Cu} from $\Delta T_c(\text{Cu})$ no adjustment for full isotopic exchange is necessary, because the isotopic enrichment is close to 100%. The oxygen isotopic enrichment was determined by weighing before and after gas exchange. The oxygen isotope exponents α_O were adjusted to 100% ^{18}O concentration, assuming a linear relationship between α_O and oxygen concentration, as is common in investigations of this type. The partial isotope exponents determined in this way are given in Table I.

As mentioned above, the oxygen isotope shifts could be reversed by backexchanging at 650 °C. This can, therefore, be taken as evidence that these shifts are indeed true isotope shifts. For the copper isotope shifts this is, of course, not possible. Apparent shifts can obviously be caused by an imbalance in chemical impurity between the ^{63}CuO and ^{65}CuO used. We guarded against this by using high purity compounds, as mentioned. Experimentally, one can point to the fact that the copper isotope shift for the $x=0.125$ samples is more than 3 times larger than the shift observed for the $x=0.15$ samples. We are certain, therefore, that the anomalously large copper isotope shift for $x=0.125$ is a true isotope shift, and cannot be caused by chemical imbalances. The smaller copper isotope shifts for $x=0.15$ is also believed not to be caused by chemical imbalances, because of the null result ob-

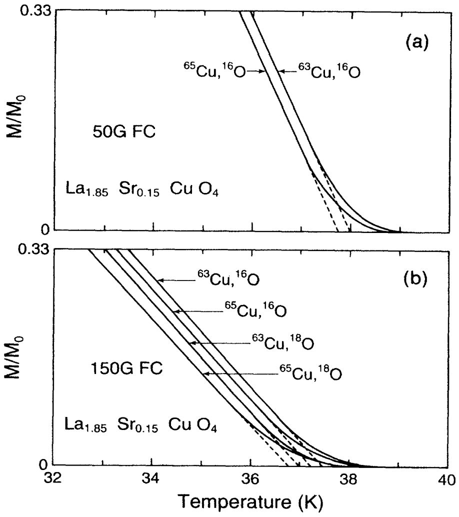

FIG. 1. The reduced field-cooled magnetization for parallel-processed $La_{1.85}Sr_{0.15}CuO_4$ samples. (a) Samples made with ^{63}Cu and ^{65}Cu. The magnetization was measured on the sintered pellets, in a field of 50 G. (b) Samples after recrushing and ^{16}O and ^{18}O gas exchange. Measurements were made on powders, in a field of 150 G.

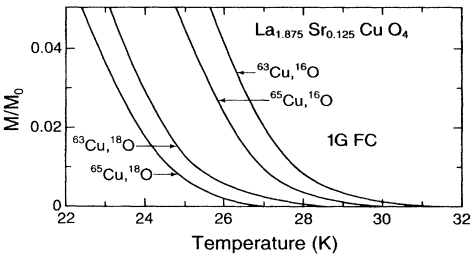

FIG. 2. The reduced field-cooled magnetization for $La_{1.875}Sr_{0.125}CuO_4$. All measurements were made on parallel-processed sintered pellets, in a field of 1 G.

TABLE I. Copper and oxygen isotope effect in $La_{2-x}Sr_xCuO_4$.

		T_c [a]	ΔT_c(Cu)		ΔT_c(O)		α_{Cu}		α_O [b]	
x	%^{18}O	(K)	(^{16}O)	(^{18}O)	(^{63}Cu)	(^{65}Cu)	(^{16}O)	(^{18}O)	(^{63}Cu)	(^{65}Cu)
0.125	86	27.84	0.84	0.69	2.51	2.36	0.98	0.88 ± 0.16 [c]	0.93	0.90 ± 0.07
0.15	92	37.94	0.14	0.20	0.41	0.47	0.12	0.17 ± 0.03	0.10	0.12 ± 0.03

[a] Transition temperature for ^{63}Cu, ^{16}O.

[b] α_O has been adjusted for partial ^{18}O substitution.

[c] The isotopic temperature shifts were obtained at the 1% level of the normalized Meissner effect. Error limits reflect uncertainties due to different methods of determining ΔT_c (see text).

tained for $YBa_2Cu_3O_7$ using the same isotopic copper oxides [5].

The results can then be summarized as follows: (i) The copper and oxygen partial isotope effects in the $La_{2-x}Sr_xCuO_4$ system are numerically very close to each other. Small deviations, indicating that possibly α_{Cu} is somewhat larger than α_O, are still within the uncertainties of the experiment. (ii) At the strontium concentration $x=0.125$ anomalously large copper and oxygen isotope exponents near 0.9 are found. Our results confirm therefore the anomalously large oxygen isotope exponent for $x=0.125$, found by Crawford *et al.* [11], and show that an equally large and anomalous copper isotope exponent exists at this concentration. It has been sometimes suggested that incomplete oxygen exchange might explain these anomalous shifts. In Ref. [13] it was suggested that a second phase, $La_{1.67}Sr_{0.33}Cu_2O_5$, might be present as an impurity, its concentration depending on the transition enthalpy ΔH and entropy ΔS with $La_{1.875}Sr_{0.125}CuO_4$. Since ΔH and ΔS are mass dependent, a spuriously large isotope effect could result. These explanations can be effectively ruled out by the present results, since for the copper isotope effect no exchange is needed, and the differences in the transition enthalpy and entropy are much smaller for the copper isotopes due to the much smaller relative mass change.

Our results show that large parts of the phonon spectrum influence the transition temperature, not only oxygen dominated vibrations, whose significance was shown in the recent work on partially ^{18}O substituted YBCO by Nickel, Morris, and Ager [14]. de Wette *et al.* [15,16] have published lattice dynamical calculations of the phonon spectrum of $La_{2-x}Sr_xCuO_4$, both for the normal isotopic species of oxygen and copper and for substitution of the ^{16}O mass by ^{18}O, and the ^{63}Cu mass by ^{65}Cu. Upon ^{18}O substitution they find that the upper two-thirds of the spectrum is shifted in the expected way, but oxygen isotope shifts are also observable in the low energy range due to hybridization of copper and oxygen vibrations. Based on these spectra, and the Eliashberg theory formalism, they obtained both the oxygen [15] and the copper isotope effect [16]. The authors choose coupling constants $\alpha^2(\omega)$ (not to be confused with the isotope exponent) that lead to transition temperatures in the observed range. With an electron phonon coupling constant λ in the range 1.7 to 2 they find transition temperatures between 43 and 51 K. The isotope exponents were obtained for various assumptions about the frequency dependence of $\alpha^2(\omega)$. Estimated values for α_O lie in the range 0.10 to 0.39, and for α_{Cu} in the range 0.21 to 0.29. They find, in particular, that coupling to high frequency oxygen vibrations alone leads to unacceptably large isotope effects. The best fit to the experimental data is given by an $\alpha^2(\omega)$ which is somewhat increased in the low frequency range. Similar calculations were also given by Batlogg *et al.* [17]. Theoretical determinations of the electron-phonon coupling in YBCO by Cohen, Pickett, and Krakauer [18] have also found large coupling constants to Cu (and Ba) dominated modes. These calculations agree therefore essentially with our finding that α_{Cu} and α_O are numerically close, a more detailed comparison is not possible because we do not know the electron-phonon coupling constant variation. These methods, however, cannot explain the anomalously large isotope exponents observed at $x=0.125$. In the original work by Crawford *et al.* [11,12] it was suggested that this anomaly might somehow be connected with the known low temperature orthorhombic (LTO) to low temperature tetragonal (LTT) lattice transition observed in $La_{1.875}Ba_{0.125}CuO_4$, and possibly present in incipient form in the corresponding strontium compound [19]. A more detailed analysis of this suggestion was given by Pickett, Cohen, and Krakauer [20]. They find that the carrier density of states near the Fermi energy is decreased by about a factor of 2 near the critical Ba or Sr concentration $x=0.12$. They further show that the amount of transformation is strongly oxygen mass dependent because of large anharmonicities of the oxygen motion; in this way the structure becomes oxygen mass dependent and an anomalously large oxygen isotope effect might result. The present results on the copper isotope effect cast some doubt on this explanation, since the structure dependence on copper mass should be much less than for oxygen. One would therefore expect a copper isotope effect much smaller than the oxygen isotope effect at this concentration, contrary to observations. Phillips and Rabe [21] have suggested an explanation of the anomalous properties of $La_{2-x}Ba_xCuO_4$ near $x=0.125$ in terms of a two band model involving a very narrow dopant band. They suggest that in $La_{2-x}Sr_xCuO_{4-y}$ composition dependent short range order may make y (i.e., the total oxygen content) isotopic mass dependent, and in this way lead to an

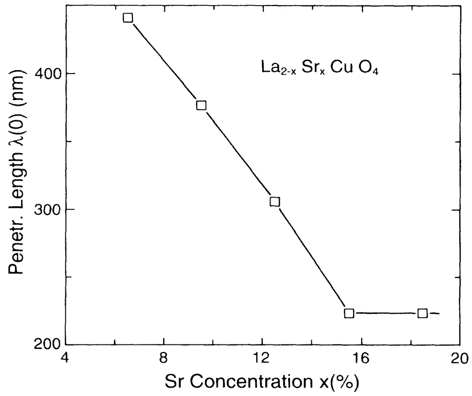

FIG. 3. The penetration length at $T=0$ K for several samples of $La_{2-x}Sr_xCuO_4$, obtained by muon spin relaxation (μSR). The measurements were performed on sintered pellets (2.5 cm diameter) fabricated separately from the isotopic samples.

anomalously large apparent oxygen isotope effect. It is difficult to see how copper isotopic substitution should produce an equally large α_{Cu}, the present results therefore do not support this suggestion.

The results suggest to us that the anomalous oxygen and copper isotope effects near $x=0.125$ are primarily due to the anomalous electronic properties at this concentration. We decided therefore to study the penetration length by μSR on a number of samples of $La_{2-x}Sr_xCuO_4$ for x varying between $x=0.065$ and 0.185. The samples were prepared by methods which were similar, but not identical to those used in the isotope studies. The results are shown in Fig. 3. We find that the penetration length below $x=0.15$ increases sharply, indicating a rapidly declining carrier concentration. A comparison between $x=0.15$ and $x=0.125$ shows that the mobile carrier concentration is reduced by almost a factor of 2. Indications of such a sharp drop have also been seen previously [22]. The reasons for this behavior are not fully understood. It has been suggested that at this concentration spin density waves might exist due to Fermi surface nesting [21]. Evidence for magnetic structure was indeed seen in our μSR data at $x=0.125$ for temperatures below 10 K, but were absent for the $x=0.15$ sample. Similar observations were already earlier published by Luke *et al.* [23]. It appears, therefore, that the anomalously large α_{Cu} and α_O for $x=0.125$ are in some way connected with the drastically reduced carrier density. We observe again that the isotope exponent becomes large when the carrier concentration is doped away from its optimal value. Such a relation was previously pointed out by us [24,25], as well as by Bornemann *et al.* [26]. It is possible that an isotope exponent larger than 0.5 might be caused by an energy-dependent density of states near the Fermi energy, possibly due to van Hove singularities. This was pointed out by Tsuei, Newns, and Pattnaik [27], and by Schachinger, Breeson, and Carbotte [28].

In conclusion, we observe in $La_{2-x}Sr_xCuO_4$ for $x=0.125$ and $x=0.15$ both a copper and an oxygen isotope effect, with α_{Cu} very close to α_O. At $x=0.125$ we find that both α_{Cu} and α_O are anomalously large, near 0.9. The results indicate that large parts of the phonon spectrum influence the transition temperature. The anomalously large isotope exponents for $x=0.125$ may be connected with a sharply reduced carrier concentration.

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