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Large copper isotope effect in oxygen depleted $YBa_2Cu_3O_y$: Importance of Cu-dominated phonon modes in the pairing mechanism

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We have measured the copper isotope effect in $YBa_2Cu_3O_y$. We find a large positive copper-isotope exponent ($\alpha_{Cu} \approx 0.37$) in the underdoped plateau region ($y \sim 6.6$). The exponent decreases to zero (or slightly negative) in the optimally doped region ($y \sim 6.94$). The α_{Cu} in $YBa_2Cu_3O_{6.6}$ is similar to the α_O (oxygen-isotope exponent) in $YBa_{2-x}La_xCu_3O_y$ with the same T_c. These comparable values of α_{Cu} and α_O show that phonons which involve Cu motion as well as the (high-frequency) modes of the oxygen in the CuO_2 planes are important in the pairing mechanism. [S0163-1829(96)07333-X]

It is now well established that oxygen isotope effect is small in optimally doped cuprates (highest T_c) but large in underdoped cuprates.[1–10] This large oxygen-isotope effect points to an important role of phonons in the pairing mechanism of high-T_c superconductivity. Recently, we have observed a large oxygen-isotope shift ($\Delta T_c = -1.46$ K) in site-selective oxygen isotope substituted underdoped $Y_{0.7}Pr_{0.3}Ba_2Cu_3O_7$ samples where ^{18}O atoms are in the CuO_2 planes and ^{16}O atoms are in the apical and chain sites.[11] This shows that the phonon modes which involve the CuO_2 plane oxygen (not the apical oxygen) are responsible for most of the oxygen-isotope shift, and that these phonon modes are important in the pairing mechanism of high-T_c superconductivity.

Since the planar oxygen contributes a large isotope effect in underdoped $YBa_2Cu_3O_y$ (YBCO), one might anticipate a large copper-isotope effect in underdoped YBCO, but only if the phonon modes involve motion of the copper as well as of oxygen. Measurement of the copper-isotope effect in underdoped YBCO thus can determine whether the low-lying Cu-dominated phonon modes contribute substantially to the superconducting pairing. Here we report the measurements of the copper-isotope effect in underdoped and optimally doped YBCO.

Since the compound $YBa_2Cu_3O_y$ is a line phase, it is not difficult to ensure the same Y/Ba/Cu composition for two samples prepared separately. But it is difficult to ensure that two reduced and then quenched samples have exactly the same oxygen content, which is so sensitive to the grain size and the density of the pellets. Fortunately, in the YBCO system there exists a plateau region [$T_c \sim 58$–60 K; $y \sim 6.52$–6.67 (Ref. 12)] where the transition temperature is insensitive to the oxygen content. This provides an opportunity to obtain a reliable copper-isotope shift in oxygen-depleted YBCO if the oxygen content is in the plateau region.

The samples were prepared from high-purity Y_2O_3 (99.99%), $BaCO_3$ (99.999%), and copper oxides with different copper isotopes (^{63}Cu and ^{65}Cu). The copper isotopes were obtained as oxides from the Institute of Molecular Physics, Russian Research Center ''Kurchatov Institute.'' These copper oxides have very high chemical purities [for the ^{63}CuO:Ni=7 ppm (in weight), Zn=3, Co=3, Fe=4, Mn=1, Ca=5, Ti=1, Cr=20, Pb=20, Sn=4, Mo=2, K<10, Na<10; for the ^{65}CuO:Ni=6 ppm, Zn=4, Co=3, Fe=3, Mn=1, Ca=4, Ti=1, Cr=20, Pb=20, Sn=2, Mo=2, K<10, Na<10]. Note that the difference in chemical impurities of the copper isotopes is extremely small (<5 ppm in atom units).

The mixtures of Y_2O_3 and $BaCO_3$ were first prepared with the required stoichiometric ratio of Y and Ba. These mixtures were then combined with the stoichiometric amounts of ^{63}CuO and ^{65}CuO. They were ground in the same manner and for the same time. The well-mixed powder samples were calcined at 920 °C for 15 h in flowing oxygen (70 cc/min). The samples were then ground thoroughly, pelletized, and sintered at 920 °C for 15 h in flowing oxygen. To ensure that the samples had small grain size and enough porosity, they were reground, pelletized, and annealed at 800 °C in flowing oxygen for 10 h, and cooled to room temperature in 6 h (130 °C/h). The samples were finally annealed at 670 °C in flowing oxygen for 12 h and cooled to 120 °C in 11 h (50 °C/h). From the measured lattice constants ($a = 3.821$ Å, $b = 3.884$ Å, and $c = 11.687$ Å), the oxygen content y was determined to be 6.94 ± 0.02 (Ref. 12). Three samples with natural Cu isotope were prepared in the same way. These samples were used to check whether the transition temperatures are the same for samples prepared separately using the identical procedure and the same Cu isotope.

The reduced samples were obtained by annealing the above samples in flowing mixed gas (0.1% O_2 and 99.9% N_2) for 40 h at 400, 450, or 500 °C, followed by rapid cooling to room temperature in ~2 min. The oxygen content of each reduced sample was determined by thermogravimetric analysis (TGA), while heating to 520 °C in flowing oxygen. The TGA apparatus was calibrated using the Curie temperatures of three standard ferromagnets (Ni, Perkalloy, and

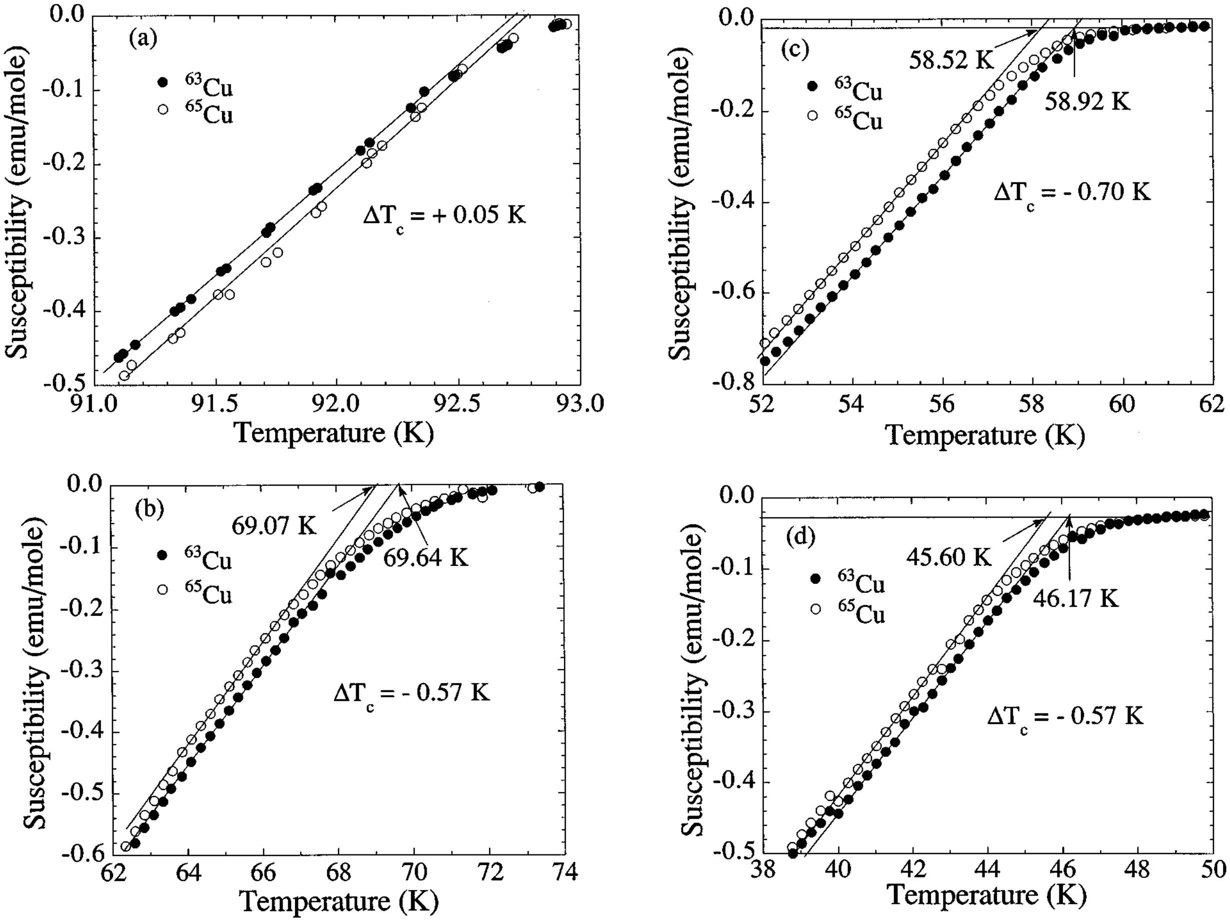

FIG. 1. Copper-isotope shift of T_c in $YBa_2Cu_3O_y$: Susceptibility data near T_c for the ^{63}Cu and ^{65}Cu samples of pair I with different oxygen contents: (a) $y \sim 6.94$; (b) $y \sim 6.75$; (c) $y \sim 6.63$; (d) $y \sim 6.48$. The slopes of the linear portions on the transition curves are similar for the ^{63}Cu and ^{65}Cu samples (a), indicating that they have nearly the same grain size (see text).

Fe). The oxygen content of the samples after equilibration at 520 °C in 1 bar oxygen was taken to be 6.82 (Ref. 12). The oxygen contents of the samples annealed at 400, 450, and 500 °C were calculated as 6.75±0.03, 6.63±0.03, and 6.48 ±0.03, respectively.

The susceptibility was measured with a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The field-cooled, measured-on-warming susceptibility was measured in a field of ~10 Oe. For the optimally doped samples (in which the isotope shift is very small), the temperature measurements were performed with a platinum resistance thermometer (Lakeshore PT-111) placed in direct contact with the sample and driven by microprocessor controlled ac bridge in the SQUID. The resolution was 2.5 mK and reproducibility 10 mK at 77 K after cycling to room temperature.[7] For the other samples, the temperatures were directly measured from the internal thermometer of the SQUID magnetometer, which shows reproducibility of ±0.05 K from repeated measurements on the same sample. The magnetic-field was kept unchanged throughout each series of measurements.

In Figs. 1(a)–1(d), we show the susceptibility near T_c for the ^{63}Cu and ^{65}Cu samples of pair I with different oxygen contents: (a) $y \sim 6.94$; (b) $y \sim 6.75$; (c) $y \sim 6.63$; (d) $y \sim 6.48$. Since there is a room-temperature annealing effect for the reduced samples, we measured the samples one week after they had been prepared. The isotope shifts of the transition temperature are determined from the linear portion of the susceptibility data extended to the base line (as indicated in the figures), in order to eliminate effects due to possible differences in demagnetization factor, particle size, and superconducting fraction of the ^{63}Cu and ^{65}Cu samples. Near T_c, the effects due to intragrain flux trapping and intergrain weak link will be small in our porous samples. Under these conditions, the slope of the linear portion near T_c on the transition curve is proportional to R^2 (where R is the average radius of the grains).[13] The ^{63}Cu and ^{65}Cu samples show nearly identical slopes of the linear portion [Fig. 1(a)], indicating that the two samples have nearly the same grain size. Since the samples are very porous, and the grain sizes of both samples are nearly the same, the diffusion of oxygen into and out of the two samples is the same. This ensures that, after they are subject to the same heating and cooling schedule, they will have the same oxygen content.

The copper-isotope exponent is defined as $\alpha_{\mathrm{Cu}} = -d \ln T_c / d \ln M_{\mathrm{Cu}}$. If we take T_c as the diamagnetic onset temperature, we obtain $\alpha_{\mathrm{Cu}} = -0.017$ and $T_c \sim 93.0$ K for $y \sim 6.94$; $\alpha_{\mathrm{Cu}} = +0.25$ and $T_c \sim 73.0$ K for $y \sim 6.75$; $\alpha_{\mathrm{Cu}} = +0.37$ and $T_c \sim 60.0$ K for $y \sim 6.63$; $\alpha_{\mathrm{Cu}} = +0.37$ and $T_c \sim 48.5$ K for $y \sim 6.48$. The uncertainty of the α_{Cu} has two main sources: (a) determination of T_c (± 0.05 K); (b) a pos-

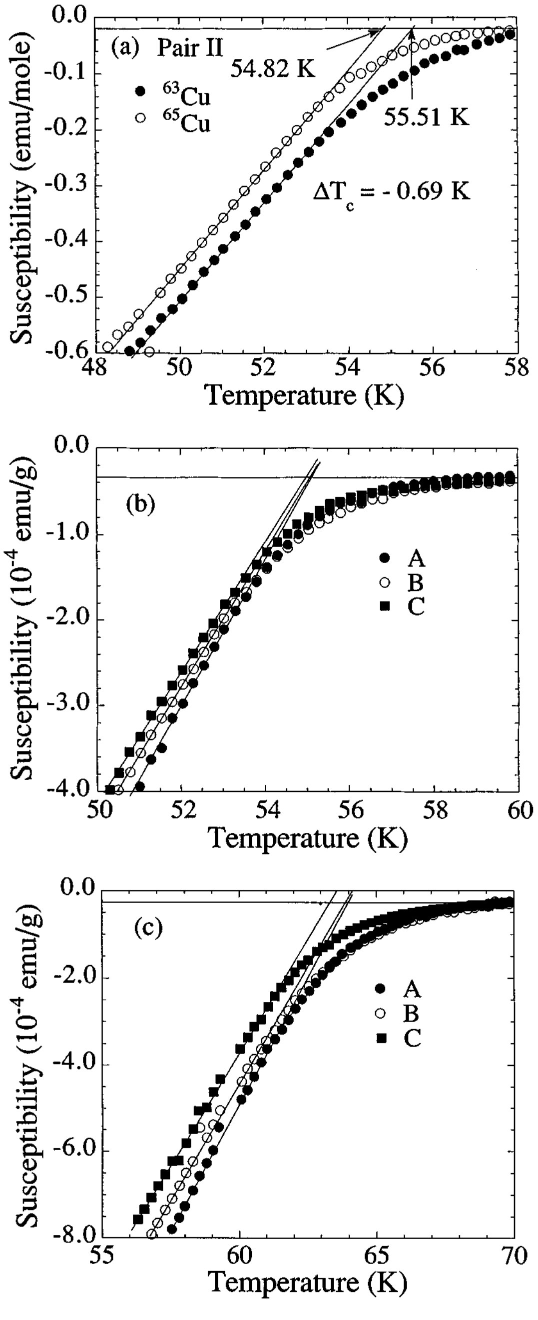

FIG. 2. Susceptibility data near T_c for (a) the ^{63}Cu and ^{65}Cu samples of pair II with $y \sim 6.60$; (b) three samples separately prepared with the same natural copper isotope (and reduced to $y \sim 6.6$); (c) three samples separately prepared with the same natural copper isotope (and reduced to $y \sim 6.7$). The T_c difference between sample A and C is ~ 0.12 K in the plateau region, but increases to ~ 0.7 K outside the plateau region.

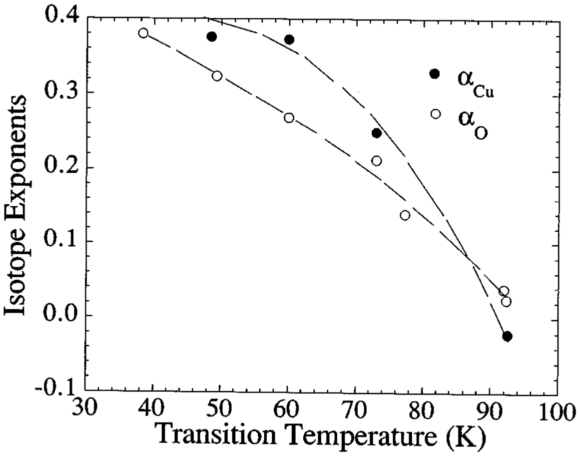

FIG. 3. The T_c dependence of α_{Cu} in $YBa_2Cu_3O_y$ and of α_O in $YBa_{2-x}La_xCu_3O_y$ (Ref. 7). The copper-isotope exponent α_{Cu} in the optimally doped $YBa_2Cu_3O_{6.94}$ is very small. It increases when T_c is reduced by oxygen depletion which causes underdoping. α_{Cu} has a similar T_c dependence as the oxygen-isotope exponent α_O in $YBa_{2-x}La_xCu_3O_y$, and with comparable magnitude ($\alpha_{Cu}/\alpha_O \sim 1.2$–$1.4$).

sible difference in the oxygen contents of the two isotope samples (ruled out for sample pair I, as discussed in the previous paragraph).

In Fig. 2(a), we show the susceptibility data for sample pair II with $y \sim 6.6$. The copper-isotope shift for sample pair II is the same as that for sample pair I within the uncertainty [see Figs. 1(c) and 2(a)] although the two sample pairs were prepared independently by different authors of this paper. This confirms that the observed large copper-isotope shift in the underdoped plateau region has good reproducibility and is not an artifact. The accuracy of the measured copper-isotope shift was also checked by preparing samples with the same Cu isotope and measuring the T_c variation.

Figure 2(b) shows the susceptibility curves for three separately prepared samples with $y \approx 6.6$ made from natural Cu isotope. The measured transition temperatures of these samples were the same within ± 0.06 K. This shows that, in the plateau region, T_c is closely repeatable. Outside the plateau region, T_c is an order of magnitude more sensitive to the oxygen content so a slight difference in oxygen content could give a spurious "isotope shift." This is clearly seen in Fig. 2(c), which shows the susceptibility for three samples separately prepared using the same natural Cu isotope, but with $y \sim 6.7$ (outside the plateau region). The T_c difference between sample A and C is ~ 0.7 K [see Fig. 2(c)] vs only ~ 0.12 K in the plateau region [see Fig. 2(b)].

The above results indicate that if the samples are not in the plateau region, a small difference in oxygen content could lead to a substantial difference in T_c. Franck and Lawrie[14] reported a large negative copper isotope effect ($\alpha_{Cu} \sim -0.34$ for samples with $T_c \sim 69.5$ K, and $\alpha_{Cu} \sim -0.15$ for samples with $T_c \sim 64$ K). Since their samples have $T_c > 60$ K they probably are outside the plateau region ($58 \leq T_c \leq 60$ K).[12] Their observation of apparent negative copper-isotope shifts may arise from slight differences in the oxygen contents of their two isotope samples. From the magnitude of dT_c/dy given in Ref. 12, it appears that Franck and Lawrie's data[14] can be explained by a slightly larger (~ 0.005) oxygen content in their ^{65}Cu samples.

In Fig. 3 we show the T_c dependence of the α_{Cu} for $YBa_2Cu_3O_y$ and for comparison, the α_O of $YBa_{2-x}La_xCu_3O_y$ (Ref. 7). The copper-isotope exponent α_{Cu} in the underdoped $YBa_2Cu_3O_y$ shows a similar T_c dependence as the oxygen-isotope exponent α_O in $YBa_{2-x}La_xCu_3O_y$. This result agrees with that reported for $La_{2-x}Sr_xCuO_4$ (Ref. 15).

Attempts have been made to avoid the importance of the phonons in high-temperature superconductivity by explaining the large oxygen-isotope effect in the underdoped HTSC region as due to a dependence of the hole concentration on the mass of the apical oxygen.[16] If such a model were correct, one would not expect both the O and Cu in the CuO_2 planes to contribute substantially to the total isotope shift. An important role for the apical oxygen mass is also contradicted by the large oxygen-isotope shift ($\Delta T_c = -1.46$ K), which we observed in the site-selective $Y_{0.7}Pr_{0.3}Ba_2Cu_3O_7$ samples where the ^{18}O atoms are in the CuO_2 planes and the ^{16}O atoms in the apical and chain sites.[11] The large copper-isotope shift in the underdoped region which is reported here is even more difficult to explain by the charge-transfer mechanism[16] which is specific to the apical oxygen.

The large copper-isotope effect in the underdoped YBCO, in conjunction with our previous measurements of oxygen-isotope effects, suggests that phonon modes involving Cu and O both play an important role in the superconducting pairing. This is consistent with theoretical calculations of the electron-phonon coupling in YBCO by Cohen, Pickett, and Krakauer[17] who found large coupling constants to Cu- (and Ba-) dominated modes. Furthermore, tunneling experiments in the cuprate superconductors $Bi_2Sr_2CaCu_2O_8$ (Refs. 18 and 19) and $Na_{1.85}Ce_{0.15}CuO_4$ (Ref. 20) have clearly shown strong-coupling features in the tunneling conductance with an average excitation energy of ~30 meV. These results also indicate that low-lying phonon modes such as Cu-dominated modes have a strong coupling to the electronic continuum, in agreement with our results.

The large copper- and oxygen-isotope effect in underdoped cuprates lead us to suggest that the phonons are important in the pairing mechanism. However, we believe that the very small isotope effect observed in several optimally doped cuprates cannot be explained by the conventional phonon-mediated mechanism, but are consistent with modified phonon mechanisms involving the anharmonicity of the phonon modes[21] and/or polaronic nature of the conducting carriers.[22]

In summary, we have measured the copper isotope effect in the optimally and underdoped $YBa_2Cu_3O_y$. We find a very small negative or null copper-isotope effect in the optimally doped region, and a large positive copper-isotope effect in the underdoped region. The copper-isotope exponent α_{Cu} in underdoped $YBa_2Cu_3O_y$ has a similar T_c dependence as the oxygen-isotope exponent α_O in $YBa_{2-x}La_xCu_3O_y$ with comparable magnitude. These results, in conjunction with our previous work, show that both Cu- and O-dominated phonon modes in the CuO_2 planes play an important role in the pairing mechanism of high-T_c superconductivity.

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