

## Nonzero Isotope Effect in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$

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The effect on the superconducting transition temperature of an exchange of  $^{18}\text{O}$  for  $^{16}\text{O}$  in  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  has been studied. The concentration of the two isotopes has been determined by Rutherford backscattering spectroscopy, and Raman spectroscopy confirmed the mass-related phonon frequency shift. The  $^{18}\text{O}$  substitution is found to be the same on the two O sites. Magnetic measurements of the transition temperature reveal a nonzero isotope effect ( $\alpha=0.16\pm 0.02$ ). The exponent  $\alpha$  has also been calculated within a conventional electron-phonon interaction model and found to be significantly larger.

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The high superconducting transition temperatures of Cu-O-based compounds<sup>1-10</sup> has led to a lively discussion about the mechanism responsible for superconducting pairing. A variety of novel mechanisms have been proposed,<sup>11-17</sup> and the absence of an isotope effect in the  $T_c=90$  K compounds  $\text{Ba}_2\text{EuCu}_3\text{O}_7$ <sup>18</sup> and  $\text{Ba}_2\text{YCu}_3\text{O}_7$ <sup>18,19</sup> was taken as strong evidence in favor of nonphonon mechanisms.<sup>20</sup> Less clear is the situation with the  $(\text{LaSr})_2\text{CuO}_4$  superconductors, where strong electron-phonon interaction may account for a considerable fraction, if not all, of the observed  $T_c$  of 36–40 K. To clarify the role played by the conventional mechanism, we studied the isotope effect in  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ . In contrast to the 90-K material, we find a dependence of  $T_c$  on the oxygen mass. When expressed as  $T_x \sim M^{-\alpha}$ ,  $\alpha$  is found to be  $0.16 \pm 0.02$ .

The experimental steps are similar to the ones we adopted in Ref. 18, except for a few modifications dictated by the different crystal chemistry of the present compound. Polycrystalline samples were prepared by the technique described in Ref. 3 resulting in disk-shaped pellets of  $\approx 10$ -mm diameter and 1-mm thickness. Several small pieces ( $\approx 1 \times 1 \times 4$  mm<sup>3</sup>) were cut from this sample and heat treated either in vacuum or in oxygen atmosphere as described before. We would like to stress that these procedures guarantee the best possible control for identical treatment of sample and reference, since they are treated simultaneously in the same furnace for the same time. Whereas in  $\text{Ba}_2\text{YCu}_3\text{O}_7$  thermogravimetric studies were a guide to the treatment process in showing the ease with which O can be removed and reinserted, they showed in this case that no O is lost by heating in vacuum to 1000°C. Therefore, we relied on a nonnegligible O diffusion at high temperatures and exposed the samples to O atmosphere first at 700°C for three weeks and then at 400°C for one more week. An attempt to determine the  $^{16}\text{O}:^{18}\text{O}$  isotope ratio by a mass-spectroscopic analysis of the evolved gas failed, since no oxygen evolved under heating to 1250°C. Thus,

the  $^{16}\text{O}:^{18}\text{O}$  ratio was measured by Rutherford backscattering spectroscopy (RBS). After one treatment cycle,  $52\% \pm 5\%$  of the oxygen is present in the form of the heavy isotope.

In the  $\text{K}_2\text{NiF}_4$  structure, oxygen occupies two inequivalent sites: O2 in the Cu-O plane with Cu-O distance of 1.889 Å and O1 at the apex of the Cu-O pyramids (out of plane) at a distance to Cu of 2.412 Å. Therefore, the possibility of site-selective O exchange has to be considered whenever less than 100% of the  $^{16}\text{O}$  is replaced. The long annealing times have been adopted to facilitate equal occupation of the different O sites. For the measured  $^{16}\text{O}:^{18}\text{O}$  ratio, the frequency shift of phonons involving only O motion can be calculated to be  $\approx 3.1\%$  on the assumption of nonpreferred O exchange. In Fig. 1 we show the inelastic-light-scattering spectra for two samples. The 4880-Å laser line with  $\approx 50$  mW power was focused to a line and the scattered light was analyzed with a SPEX 1403 double monochromator. Here only the line at  $\approx 428$  cm<sup>-1</sup> is seen, which shifts by  $14.5 \pm 1.5$  cm<sup>-1</sup> to  $\approx 413$  cm<sup>-1</sup>. The agreement between predicted and observed frequency shifts ( $3.4\% \pm 0.3\%$ ) indicates uniform  $^{18}\text{O}$  distribution among the sublattices, since the observed line involves only motion of the out-of-plane oxygens. The same agreement is found for two more sets of samples with slightly higher (70%–75%)  $^{18}\text{O}$  concentrations. The superconducting transition temperature was measured magnetically and two representative sets of magnetization versus temperature curves are shown in Fig. 2. The  $^{18}\text{O}$ -rich samples have a distinctly lower  $T_c$ , and in Table I  $\Delta T_c$  is compared with the measured shift of the phonon frequency. Combining these results yields an isotope-effect exponent  $\alpha$  of  $0.16 \pm 0.02$ .

Given the nonzero isotope effect, we compare it with calculations of the electron-phonon interaction, extending the work of Weber.<sup>21</sup> These calculations are based on one-electron energy-band structures,<sup>22</sup> and are therefore of limited applicability if many-body effects are

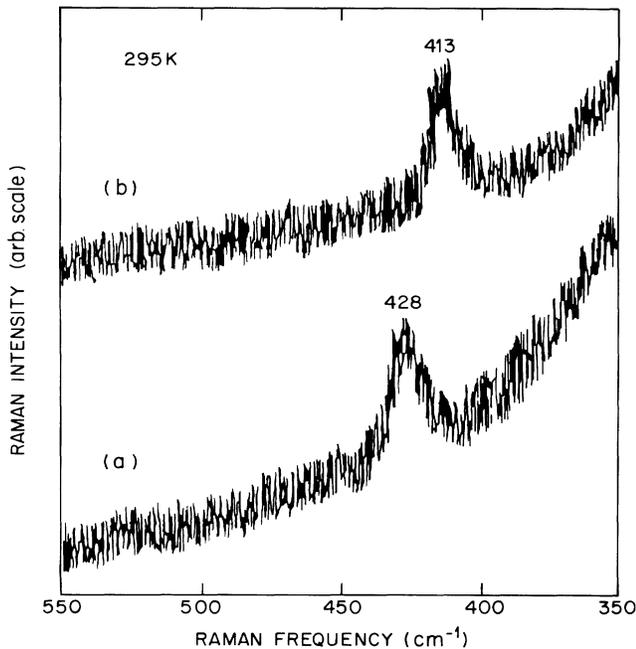


FIG. 1. Raman spectra of  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  at room temperature. (a) Sample containing  $^{16}\text{O}$  isotope. (b) Sample containing 50%–55%  $^{18}\text{O}$ . Excitation was with the 488-nm Ar-laser line at a power of  $\approx 100$  mW using line focusing.

essential in describing the electronic properties of the Cu-O superconductors. Also, anharmonic effects are not considered. Within this framework the isotope-effect exponents  $\alpha_i$  were calculated for the various atoms in  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ . Here  $\alpha_i$  is defined in the usual way as  $T_c \sim M_i^{-\alpha_i}$ , where  $M_i$  is the mass for the  $i$ th atom in the compound. Such a decomposition of  $\alpha$  into  $\alpha_i$  simply reflects the fact that it is vibrations of not just one species of atoms, say oxygen, that contribute to the overall coupling strength  $\lambda$ . The magnitudes of the various  $\alpha_i$  depend on details of the phonon spectrum and were calculated for two cases, which differ only in the choice of the force constant  $f_2$  between Cu and the in-plane O2 (see Table II). A smaller  $f_2$  leads to a more pronounced softening of the strong-coupling breathing-type modes of the O2 atoms in the Cu-O planes, and to increased contributions of these modes to  $\lambda$ . Note that the individual  $\alpha_i$  add up to  $\approx 0.5$ , and the deviation from 0.5 is caused by finite  $\mu^*$ , which was set to 0.13. Reasonable estimates of the mass dependence of  $\mu^*$  (see Morel and Anderson<sup>23</sup>) lead only to minor corrections on  $\alpha$ , as the present calculations are in the limit of  $\mu^* \ll \lambda$  ( $=0.96$  and  $2.56$ , respectively). Two points are particularly noteworthy. First, only  $\alpha$  for Cu and for oxygen are dominant and their relative weights depend on  $f_2$ , which determines  $\lambda$  and  $T_c$ . Second, the in-plane O2 has an  $\alpha$  which is about 10 times larger than the out-of-plane O1. The big difference between  $\alpha_{\text{O1}}$  and  $\alpha_{\text{O2}}$  requires the dis-

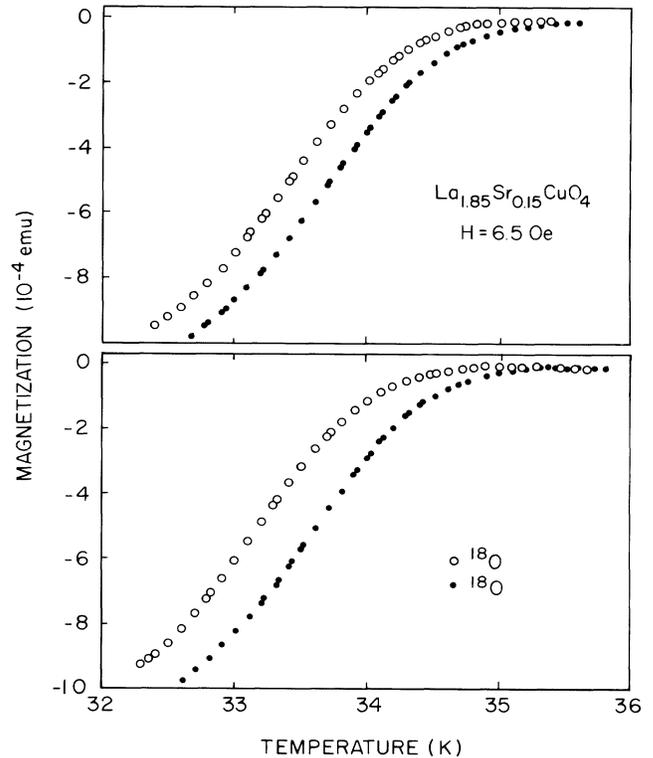


FIG. 2. Temperature-dependent magnetization near  $T_c$  for two sets of samples.

tribution of the  $^{18}\text{O}$  isotopes on the two O sites to be known. As discussed above, we find, within experimental limits, the same  $^{18}\text{O}$  occupation on the two O sites. Thus, the measured value of  $\alpha$  is found to be significantly smaller than the calculated one.

Two reasons may account for this discrepancy. First, the calculations do not include any anharmonicities, which are likely to reduce the isotope effect, PdH-PdD is a well-known example. Second, additional unconventional coupling mechanisms may contribute to  $T_c$  in  $(\text{La,Sr})\text{CuO}_4$  and would dominate in the 90-K  $T_c$  superconductors, where no isotope effect has been found.<sup>24</sup>

In conclusion, the present results of a nonzero isotope

TABLE I. Summary of the experimental results for two sets of samples with different  $^{18}\text{O}$  concentration. Compared are the measured frequency shift  $\Delta\omega$  of the  $428\text{-cm}^{-1}$  Raman line with the average change in oxygen mass  $\Delta m$ . The isotope effect exponent  $\alpha$  is defined as  $T_c \sim M^{-\alpha}$ .

$^{18}\text{O}$ (%)	$(\Delta m/m)^{1/2}$ (%)	$\Delta\omega$ ( $\text{cm}^{-1}$ )	$\Delta\omega/\omega$ (%)	$\delta T_c$ (K)	$\alpha$
$52 \pm 5$	3.1	$14.5 \pm 1$	3.4	$0.39 \pm 0.03$	$0.16 \pm 0.02$
$73 \pm 5$	4.3	$18 \pm 1$	4.2	$0.46 \pm 0.04$	$0.16 \pm 0.02$

TABLE II. Calculated isotope exponents  $\alpha_i$  for  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ .  $\alpha_i$  is defined as  $T_c \sim M_i^{-\alpha_i}$ , with  $M_i$  being the mass of the  $i$ th atom. The two cases differ in the choice of a force constant, resulting in different  $T_c$ 's and  $\lambda$ 's for fixed  $\mu^*$ . Values of  $\alpha$  given in parentheses include an approximation of the  $M$  dependence of  $\mu^*$ .

Case	$T_c$	$\lambda$	$\mu^*$	$\alpha_{\text{tot}}$	$\alpha_{\text{Cu}}$	$\alpha_{\text{O}}$	$\alpha_{\text{O2}}$	$\alpha_{\text{O1}}$	$\alpha_{\text{La}}$
1	36	2.56	0.13	0.49(0.48)	0.165	0.305	0.275	0.03	0.02
2	19	0.96	0.13	0.48(0.44)	0.27	0.18	0.16	0.02	0.01

effect demonstrate that the superconducting pairing in  $(\text{La,Sr})_2\text{CuO}_4$  is at least partly caused by conventional electron-phonon interaction.

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