PHYSICAL REVIEW B VOLUME 38, NUMBER 10 1 OCTOBER 1988

Calculation of the isotope effect in $La_{2-x}M_xCuO_4$ and $YBa_2Cu_3O_{7-x}$

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(Received 20 June 1988)

We have calculated the transition temperature and the isotope shift for oxygen replacement for $La_{2-x}M_xCuO_4$ (M=Sr,Ba) and $YBa_2Cu_3O_{7-x}$, based on the lattice-dynamical calculations of these compounds with shell models. It is found that the experimental value of T_c and the isotope shift ΔT_c for $La_{2-x}M_xCuO_4$ can be accounted for on the basis of McMillan's strong-coupling equation for T_c, supporting the conclusion that $La_{2-x}M_xCuO_4$ is a strong-coupling BCS superconductor. In contrast, experimental values of T_c for $YBa_2Cu_3O_{7-x}$ cannot be obtained on this basis. It is argued that expressing isotope shifts in terms of isotopic mass exponents α_i is not a useful procedure for these multi-ionic compounds.

An overwhelming amount of theoretical effort is being devoted to the question of the electron-pairing mechanism that is responsible for the high-temperature superconductivity phenomenon. Since the first discovery of the high-T_c superconductors[1,2] it has been felt that most probably novel and hitherto unknown mechanisms may be required to explain the high transition temperatures, although the "traditional" electron-phonon interaction cannot be ruled out as a contributory mechanism. Very direct evidence of the involvement of the electron-phonon interaction in the determination of T_c is the *isotope* effect, i.e., the shift in T_c resulting from isotopic substitution of certain key elements in the superconducting material. Accordingly, a search for the isotope effect in the 40-K compounds $La_{2-x}(Sr,Ba)_xCuO_4$ (Refs. 3 and 4) and the 90-K compounds $Y(Ba,Eu)_2Cu_3O_{7-x}$ (Refs. 5–7) has been one of the crucial experiments in the determination of the involvement of the electron-phonon interaction. The results of such experiments to date can be summarized as follows. (1) There exists a nonzero isotope shift ΔT_c in $La_{1.85}Sr_{0.15}CuO_4$ upon (partial) replacement of ^{16}O by ^{18}O (Refs. 3 and 4). (2) In $Y(Ba,Eu)_2Cu_3O_{7-x}$ the results are much less conclusive; they range from no measurable ΔT_c (Ref. 5) to small ΔT_c's of less than 0.2% (Ref. 6), and less than 1% (Ref. 7), respectively. These particular isotope shifts in $Y(Ba,Eu)_2Cu_3O_{7-x}$ are considered to be much too small to result from a strong-coupling BCS superconductor. Similar conclusions have been arrived at recently by Weber and Mattheiss[8] on the basis of tight-binding calculations applied to the study of the electron-phonon interaction in these compounds.

We are involved in a systematic study of the lattice dynamics of the high-T_c superconductors, with the aim of contributing to the overall physical characterization of these compounds. Of course, the most important issue involving lattice dynamics is that of the role of the electron-phonon interaction in the pairing mechamism. In this paper we study the oxygen isotope shifts, in $La_{2-x}M_xCuO_4$ (M=Sr, Ba) and $YBa_2Cu_3O_{7-x}$,[9] in the framework of McMillan's equation[10] for T_c in strong-coupling BCS superconductors, using the phonon densities of states which were obtained in our lattice-dynamical calculations for $La_{2-x}M_xCuO_4$ (Ref. 11) and $YBa_2Cu_3O_{7-x}$ (Ref. 12).

The lattice-dynamical calculations were carried out in the framework of shell models, which take into account short-range overlap and long-range Coulomb interactions, as well as ionic polarizabilities. The short-range interactions are represented by Born-Mayer potentials. This procedure has the advantage that the short-range potential parameters can be taken from known shell models that have been developed for perovskites and metal oxides for which neutron measurements of phonon dispersion curves are available. For the details of these models and the lattice-dynamical results we refer to Refs. 11 and 12.

McMillan[10] was the first to develop a parametrized expression for the superconducting transition temperature T_c, based on the Eliashberg theory of strong-coupling superconductors. His expression, which is similar in structure to the original BCS expression for T_c [cf. Eq. (8) below], has the form

$$T_c = X \exp\left[-\frac{1+\lambda}{\lambda-\mu^*[1+\lambda(\langle\omega\rangle/\omega_0)]}\right]. \tag{1}$$

Here, λ is the electron-phonon coupling constant defined by

$$\lambda = 2\int_0^{\omega_0} \frac{\alpha^2(\omega)F(\omega)}{\omega}\,d\omega\,, \tag{2}$$

where $\alpha^2(\omega)F(\omega)$ is the Eliashberg function and $F(\omega)$ the phonon density of states; ω_0 is the maximum phonon frequency. Further,

$$\langle\omega\rangle = \frac{2}{\lambda}\int_0^{\omega_0} \alpha^2(\omega)F(\omega)\,d\omega\,, \tag{3}$$

$$\omega_{\log} = \exp\left[\frac{2}{\lambda}\int_0^{\omega_0} \frac{\alpha^2(\omega)F(\omega)}{\omega}\ln\omega\,d\omega\right], \tag{4}$$

and μ^* is the screened electron-electron Coulomb coupling constant. Finally, for the prefactor X of the exponential, various choices have been suggested: $X = \omega_0$ or $X = \langle\omega\rangle$ by McMillan,[10] and $X = \omega_{\log}$ by Allen.[13] The function $\alpha^2(\omega)$ in the Eliashberg function is unknown, but for metals it appears that α^2 is more or less constant over the range of phonon frequencies (cf. Ref. 13). Equation (1) is considered to be a reasonable approximation in the range $1 \le \lambda \le 2$. For $\lambda \approx 3$ the exponential in Eq. (1) levels off and begins to approach its asymptotic value, so that the expression begins to underestimate T_c.

In Fig. 1 we display the phonon density of states $F(\omega)$ for $\mathrm{La}_{2-x}M_x\mathrm{CuO}_4$ and $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{7-x}$ as they follow from our best lattice-dynamical models. In each case the full curve represents the density of states for the compound in which all oxygen ions are the $^{16}\mathrm{O}$ isotope, whereas the dashed curve is the density of states for the compound in which all oxygen ions are $^{18}\mathrm{O}$. Notice the expected isotope shift of about 6% in the upper two-thirds of the density of states,[3,6] which represents predominantly oxygen vibrations. However, the isotope shift is also evident in the lower reaches of the density of states.

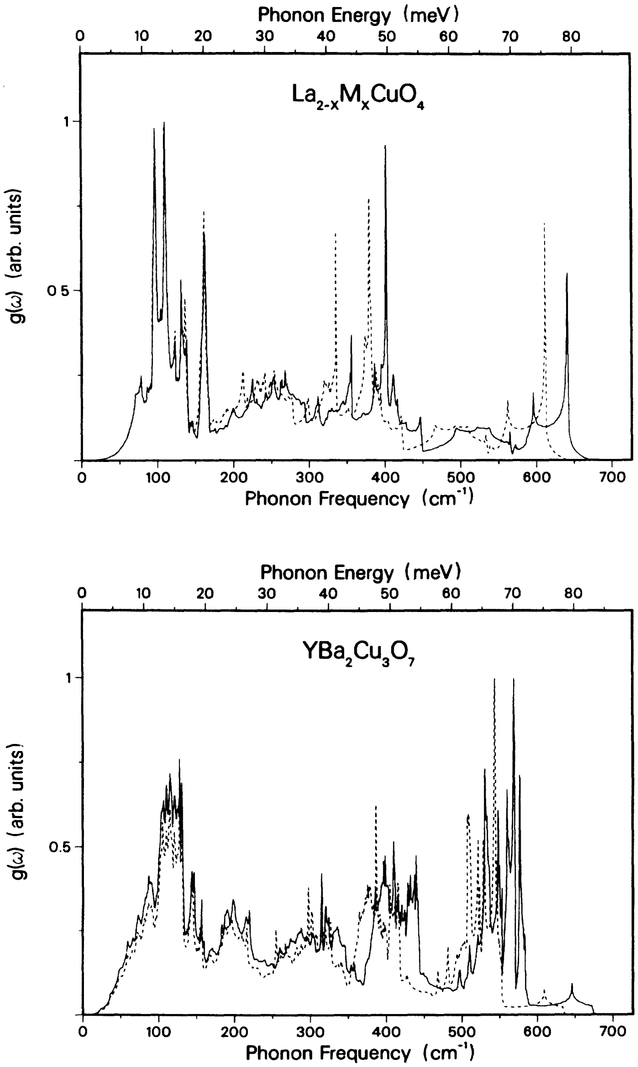

FIG. 1. Phonon densities of states $F(\omega)$ for $\mathrm{La}_{2-x}M_x\mathrm{CuO}_4$ and $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{7-x}$. Solid line for $^{16}\mathrm{O}$, dashed line for $^{18}\mathrm{O}$.

In Fig. 2 we plotted T_c as a function of α, for constant α in the integrals (2)-(4) and for the "canonical" choice of $\mu^* = 0.13$ (cf. Ref. 13). The expressions for T_c with the prefactors ω_0, $\langle\omega\rangle$, and $\omega_{\log}$ [$T_c(\omega_0)$, $T_c(\langle\omega\rangle)$, and $T_c(\omega_{\log})$] were evaluated with the density of states for $\mathrm{La}_{2-x}M_x\mathrm{CuO}_4$. In the figure we have indicated the band of T_c's (30-40 K) for the $\mathrm{La}_{2-x}M_x\mathrm{CuO}_4$ compounds and for comparison, also the band (90-100 K) for the $\mathrm{Y(Ba,Eu)}_2\mathrm{Cu}_3\mathrm{O}_{7-x}$ compounds. The vertical band between $\lambda = 1$ and $\lambda = 2$ indicates the strong-coupling regime of the McMillan theory. Notice that the curves for $T_c(\langle\omega\rangle)$ and $T_c(\omega_{\log})$ begin to saturate for values of α larger than ~2.5, whereas the correct asymptotic behavior shows a $\lambda^{0.5}$ dependence (Ref. 13). However, it is evident that the $T_c(\langle\omega\rangle)$ and $T_c(\omega_{\log})$ curves give T_c values for $\mathrm{La}_{2-x}M_x\mathrm{CuO}_4$ in the correct temperature range, for $1 \le \lambda \le 2$, i.e., well within McMillan's strong-coupling regime for BCS superconductors, supporting the conclusion that the electron-phonon interaction can account for the superconductivity in these compounds. In contrast, because of its limited validity, McMillan's equation cannot make a statement about the role of the electron-phonon interaction in the determination of T_c in the $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{7-x}$ compounds.

These conclusions can be made more firm by evaluating the isotope effect on the basis of McMillan's equation. The isotope effect is most directly expressed in the shift in the transition temperature, ΔT_c, although frequently it is expressed in terms of the isotopic mass exponent α_i (not to be confused with α^2 in the Eliashberg function), which expresses the dependence of T_c on the mass M_i of the ion species i. In analogy with the original BCS expression $T_c \propto M^{-\alpha}$ (where, in principle, $\alpha = \frac{1}{2}$ for a monatomic material), one writes

$$T_c \propto M_i^{-\alpha_i}, \qquad (5)$$

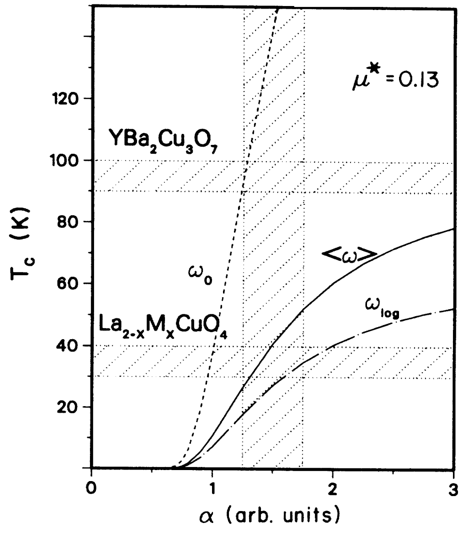

FIG. 2. $T_c(\omega_0)$, $T_c(\langle\omega\rangle)$, and $T_c(\omega_{\log})$ evaluated for $\mathrm{La}_{2-x}M_x\mathrm{CuO}_4$ as a function of α, using McMillan's equation (1) for T_c. The function $\alpha^2(\omega)$ in the averaging integrals is taken to be constant. For $\alpha \gtrsim 2.5$ the curves saturate and do not show the correct asymptotic behavior.

which leads to

$$\alpha_i = -\frac{d\ln T_c}{d\ln M_i} = -\frac{M_i}{T_c}\frac{\Delta T_c}{\Delta M_i} . \qquad (6)$$

Below we give reasons why α_i is at best a rather ambiguous measure of the isotope effect, especially when it is used to compare the effects of isotope replacement of different elements.

In Table I we list, for various choices of $\alpha^2(\omega)$, the values of $T_c(\langle\omega\rangle)$ and $T_c(\omega_{\log})$ for ^{16}O and ^{18}O and the corresponding values of ΔT_c. The first two rows are for constant $\alpha^2(\omega)=2.5$ and 3.0, respectively, while in the third and fourth rows $\alpha^2(\omega)$ is taken to be a decreasing linear function of ω with its values at 0 and 690 cm^{-1} as indicated in the first column. The last choice $\alpha^2(\omega)=4 \rightarrow 0.4$ is meant to represent in some way the ω^{-1} dependence which enters α^2 through the electron-phonon matrix element (cf. Ref. 13). Moreover, the M^{-1} dependence of the electron-phonon matrix element has been taken into account in the ^{18}O case by reducing the density of states above 300 cm^{-1} (roughly the onset of the oxygen vibrations) by a factor $\frac{16}{18}$. We point out that the values for T_c and ΔT_c obtained in the last two rows (diminishing α^2) are in the range of the experimental values, namely $\alpha_i=0.16$ of Ref. 3, and $-1.0<\Delta T_c<-0.3$ K and $0.15<\alpha_i<0.35$ of Ref. 4. We also note that the corresponding values of λ are, of course, well within the McMillan's strong-coupling regime. This supports the conclusion that the electron-phonon interaction is sufficient to account for the transition temperatures of the $La_{2-x}M_xCuO_4$ compounds. A similar conclusion has been reached by Weber[14,15] and Mattheiss.[15]

As noted above, McMillan's equation fails to give valid results for the $YBa_2Cu_3O_{7-x}$ compounds. This can be seen in a qualitative way by referring to Fig. 1. We see that the density-of-states curves, which are plotted on the same horizontal scale, have about the same maximum frequency and are rather similar in overall appearance, although there are differences in detail. On this basis one can expect the results for λ, T_c, and ΔT_c for $YBa_2Cu_3O_{7-x}$ to be quite comparable to the results for $La_{2-x}M_xCuO_4$; and this is indeed the case. In other words, making the same choices for $\alpha^2(\omega)$ as was done for $La_{2-x}M_xCuO_4$ (cf. Table I), the computed T_c values for $YBa_2Cu_3O_{7-x}$ fall in the same range, namely between 30 and 50 K, instead of in the range 90 to 100 K, as needed. It is thus evident that McMillan's equation does not allow us to draw conclusions about the role of the electron-phonon interaction for T_c in the $YBa_2Cu_3O_{7-x}$ compounds. Many investigators feel that a different mechanism is responsible for the superconducting state in these compounds (even including the $La_{2-x}M_xCuO_4$ compounds).[16] On the other hand, recent work by Zeyher and Zwicknagl[17] indicates that the electron-phonon coupling mechanism can account for the transition temperatures in the $YBa_2Cu_3O_{7-x}$ compounds. Irrespective of how these questions will be settled in the end, the correct theory should explain why the isotope effect is present in $La_{2-x}M_xCuO_4$—if the mechanism is *not* electron-phonon coupling, or why it is *not* present in $YBa_2Cu_3O_{7-x}$—if the mechanism *is* electron-phonon coupling. Finally, a different pairing mechanism in $YBa_2Cu_3O_{7-x}$ nevertheless does not preclude the electron-phonon interaction from making a significant contribution to the transition temperature.

Earlier it had been suggested by Mattheiss[18] and Weber[14] that the so-called oxygen breathing mode could be playing a key role in the electron-pairing mechanism. If this were the case then one would expect the function $\alpha^2(\omega)$ to be such, that it selects only the appropriate part of the spectrum in the averages. To see what the result of such an averaging procedure would be, we have repeated calculations with an $\alpha^2(\omega)$ of Gaussian shape, namely

$$\alpha^2(\omega) = A_0 \exp\left[-\left(\frac{\omega-\omega_0}{\sigma}\right)^2\right] . \qquad (7)$$

In the calculation for $La_{2-x}M_xCuO_4$ we have centered the Gaussian on the oxygen vibrations by making the following choices: $\omega_0=500$ cm^{-1} and $\sigma=160$ cm^{-1}. Our choices of A_0 have been guided by the requirement to obtain $T_c(\langle\omega\rangle)$ and $T_c(\omega_{\log})$ approximately in the correct temperature range. This procedure leads to values of the isotope shifts ΔT_c in the range -8 to -12 K, which are totally unrealistic in view of the experimental results for ΔT_c quoted above. On the basis of these results we conclude that averaging with a function $\alpha^2(\omega)$ which selects only a limited part of the density of states is not a correct procedure, even for $La_{2-x}M_xCuO_4$.

We now discuss the reasons why we consider the isotopic mass exponent α_i [cf. Eq. (6)] to be an inappropriate and possibly confusing basis for a discussion of the isotope effect in multi-ionic superconducting compounds. The historical reason for expressing the isotopic mass depen-

TABLE I. Computed values of $T_c(\langle\omega\rangle)$ and $T_c(\omega_{\log})$ for $La_{2-x}M_xCuO_4$, and corresponding values of ΔT_c for oxygen isotope replacement, for four different choices of $\alpha^2(\omega)$. The values of α_i are included for comparison with the measurements (Refs. 3 and 4).

$\alpha^2(\omega)$[a] for ω (cm^{-1}) =			$T_c(\langle\omega\rangle)$ (K)				$T_c(\omega_{\log})$ (K)			
0	690	$\lambda(^{16}O)$	^{16}O	^{18}O	ΔT_c (K)	α_i	^{16}O	^{18}O	ΔT_c (K)	α_i
2.5	2.5	1.69	44.9	43.0	−1.9	0.38	30.0	29.2	−0.8	0.23
3.0	3.0	2.02	51.5	49.2	−2.3	0.39	34.4	33.5	−0.9	0.23
3.0	2.0	1.84	45.8	44.2	−1.6	0.30	30.9	30.3	−0.6	0.17
4.0	0.4	2.03	43.4	42.9	−0.5	1.10	30.2	30.2	0.0	0.00

[a] Results for diminishing α^2 are in good agreement with the measurements.

dence of the transition temperature as

$$T_c \propto M^{-\alpha} \tag{8}$$

is that in the original BCS expression for a monatomic material

$$T_c = \omega_0 \exp\left[-\frac{1}{N(0)V}\right], \tag{9}$$

the maximum vibrational frequency ω_0 has the simple mass dependence $M^{-\alpha}$ ($\alpha \approx 0.5$), while the value of the exponential, containing the electron density of states $N(0)$ and the electron-phonon interaction strength V, is independent of isotope mass. However, to replace Eq. (8) by Eq. (5) for a multiatomic material, and to use α_i as a measure for the isotope effect resulting from isotopic substitution of species i is not useful and, in fact, confusing. First of all, in McMillan's equation (1) for T_c, the simple exponential prefactor ω_0 of the original BCS expression (8) has been replaced by an average over the phonon spectrum, so that there no longer exists a simple scaling of T_c with a particular isotopic mass as implied by Eq. (5). Moreover, if there is doubt about the basic pairing mechanism, as in the case of the high-T_c superconductors, the meaning of the quantity α_i becomes very doubtful, as can be seen from Eq. (6). Remember that (6) implies the assumption that the electron-phonon interaction is the basic pairing mechanism. Thus if Eq. (6) is used to derive a value of α_i connected with a *measured* isotope shift ΔT_c, what value should one substitute for T_c if T_c is *not*, or only partially, the result of electron-phonon coupling? As noted, our calculations show that on the basis of calculated density of states for both $La_{2-x}M_xCuO_4$ and $YBa_2Cu_3O_{7-x}$, T_c is at most of the order of 40-50 K, so that the use of the *measured* T_c for $YBa_2Cu_3O_{7-x}$ is inconsistent with the basis on which Eq. (6) was derived.

Second, if Eq. (6) is used to derive an α_i value for a *calculated* value of ΔT_c, it should be kept in mind that through the averages over the density of states, the value of ΔT_c can be strongly dependent on the particular way in which $\alpha^2(\omega)$ depends on the masses M_i of the various ions, and this is basically unknown. For example, our calculations show that there is no shift in the density of states of $La_{2-x}M_xCuO_4$ upon replacement of ^{139}La by ^{138}La. Hence, if $\alpha^2(\omega)$ was strictly independent of the lanthanum mass, there would be zero isotope shift. However, if we assume $\alpha^2(\omega)$ to be proportional to $M_{La}^{-0.5}$ for $\omega \leq 300$ cm^{-1}, where most of the lanthanum vibrations occur, then we find $\Delta T_c \approx +0.13$ K which leads to $0.38 \leq \alpha_{La} \leq 0.52$, owing to the large value of M_{La} entering in Eq. (6). Incidentally, for the replacement of ^{16}O by ^{18}O, which leads to a 6% downward shift in the upper part of the density of states, the T_c values of Table I lead to $0.10 \leq \alpha_O \leq 0.40$. In other words, oxygen replacement could lead to smaller values of α_i than lanthanum replacement.

This discussion should make it clear that the procedure of deriving α_i values from measured or calculated isotope shifts ΔT_c contains too many uncertainties, especially for the high-T_c superconductors, to lead to useful quantities on which to base a meaningful assessment of the isotope effect. We therefore feel that future discussions of the isotope effect should be based strictly on ΔT_c, which is the primary quantity anyway.

To summarize, we have our lattice-dynamical results for $La_{2-x}M_xCuO_4$ and $YBa_2Cu_3O_{7-x}$ to evaluate the transition temperatures T_c, and the isotope shifts ΔT_c on the basis of McMillan's equation for strong-coupling BCS superconductors. For $La_{2-x}M_xCuO_4$ the measured values of T_c and ΔT_c can indeed be obtained with McMillan's equation. This result supports the conclusion that $La_{2-x}M_xCuO_4$ is a strong-coupling BCS superconductor. However, the T_c values of $YBa_2Cu_3O_{7-x}$ lie outside the validity range of McMillan's equation. This and the apparent absence of the isotope effect in these compounds does not, however, unequivocally warrant the conclusion that the electron-phonon interaction is *not* the primary pairing mechanism in these compounds.

The high transition temperatures in $YBa_2Cu_3O_{7-x}$ (and in later discovered compounds) have given rise to an intense search for an alternative pairing mechanism. In particular, the occurrence of Cu-O planes in all these compounds, and their apparent role in the superconducting phenomenon, supports the assumption of a common pairing mechanism in all these compounds. However, if the pairing mechamism in $La_{2-x}M_xCuO_4$ would be this new mechanism rather than the electron-phonon interaction, one would have to explain why the isotope effect is nevertheless present. Finally, we have argued that in the search for the isotope effect in the high-temperature superconductors, the experimental results should be discussed strictly in terms of ΔT_c. There are too many uncertainties in trying to express experimental results in terms of a mass exponent α_i to make this a meaningful procedure.

This work was supported by the National Science Foundation through Grant No. DMR-8505747, by the Robert A. Welch Foundation through Grant No. F-433, and by a grant from the Deutsche Forschungsgemeinschaft. A NATO grant for international collaboration is also gratefully acknowledged.

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