Anomalous Isotope Effect and van Hove Singularity in Superconducting Cu Oxides

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(Received 6 August 1990)

High- T_c Cu oxides such as YBa₂Cu₃O₇ and the Bi-Sr-Ca-Cu-O systems are characterized by a nearzero oxygen-isotope effect. Recents results by Crawford *et al.* show, however, that the isotope effect in the La_{2-x}Sr_xCuO₄ system depends strongly on the doping level (x) and can significantly exceed the BCS limit. Within the framework of the BCS phonon-mediated pairing, a logarithmic (2D) van Hove singularity in the density of states can provide a basis for understanding these anomalous isotope effects and possibly the origin of high-temperature superconductivity.

PACS numbers: 74.20.Fg, 74.60.Mj, 74.65.+n

Clues to the mechanism responsible for high-temperature superconductivity in Cu oxides are presumably hidden in their unusual normal-state and superconducting properties. Early experimental findings such as the very small oxygen-isotope effect¹⁻³ (i.e., $\alpha_0 \sim 0$ to 0.2, $T_c \sim M^{-\alpha_0}$, where M is the atomic mass of oxygen) and the linear temperature dependence of the in-plane normal-state resistivity⁴ [i.e., $\rho_{\parallel}(T) \propto T$ for $T > T_c$] tend to endorse theoretical models based on non-Fermi-liquid and nonphononic superconducting pairing mechanisms. Recent experimental results, however, have altered this view significantly. Many of the superconducting-state characteristics show that the new Cu oxides are BCSlike superconductors. And evidence, mostly from experiments such as NMR⁵ and photoelectron spectroscopy,⁶ for a conventional Fermi-liquid description of the normal state is increasing. In addition, a dominant quadratic temperature dependence of $\rho_{\parallel}(T)$ above T_c was observed recently for the electron-doped Nd-Ce-Cu-O system⁷ and several relatively low- T_c hole-doped cuprates.⁸ These new resistivity data clearly show that the linear temperature dependence of $\rho_{\parallel}(T)$ is not a universal normal-state property and provide additional supporting evidence for a Fermi-liquid normal state in Cu-oxide superconductors.

The previously observed small oxygen-isotope effect (or the absence of it) in various Cu oxides has been considered as an important piece of evidence for nonphononic superconductivity. Efforts to pin down the pairing mechanism through a basic understanding of the isotope effect are, however, further complicated by the new results reported by Crawford et al.⁹ for $La_{2-x}Sr_xCuO_4$. As shown in Fig. 1, the value of α_0 for this oxide system is found to depend strongly on the concentration of Sr doping (x). Furthermore, α_0 can be significantly higher than the BCS limit of the phonon-mediated pairing (i.e., $\alpha^{BCS} = 0.5$). Another interesting feature of the data shown in Fig. 1 is that the value of α_0 first increases sharply with increasing x for $x \leq 0.12$, and then it decreases precipitously with x, while T_c still increases. The magnitude of α_0 reaches a relatively shallow minimum at $\alpha_0 \sim 0.06$, corresponding to a maximum in T_c , in keeping with earlier results that show that high- T_c Cu oxides are generally characterized by a small or nearzero oxygen-isotope effect. Recently, similar results have been reported for the 1:2:3 material by Franck *et al.*⁹

In this Letter, we wish to show that these anomalous isotope effects can be understood in terms of a van Hove-like singularity in the density of states N(E), near the Fermi energy E_F , along with a conventional BCS phonon-mediated pairing which is also responsible for the high-temperature superconductivity. Such a T_c enhancement mechanism is also consistent with other unusual superconducting and normal-state properties including the temperature dependence of $\rho_{\parallel}(T)$ and its correlation with T_c .

A van Hove singularity in N(E) has been proposed in the past as a T_c -enhancement mechanism for the conventional A15 superconductors¹⁰ and more recently for the high- T_c Cu oxides.¹¹⁻¹⁴ Although one-electron bandstructure calculations¹⁵ have shown that the Cu oxides are characterized by some 2D Fermi surface nesting, the idea of achieving high-temperature superconductivity with the aid of a sharp peak in N(E) at E_F along with a phonon-mediated pairing has not been widely accepted. The main objections to this high- T_c mechanism mostly stem from the fact that there is no convincing direct experimental evidence for a N(E) singularity near the Fermi level and from the consideration that a sharp peak of



FIG. 1. Experimental results of T_c (**•**) and α_0 (**0**) as a function of doping concentration for La_{2-x}Sr_xCuO₄ [the data were taken from the paper by Crawford *et al.* (Ref. 9)].

N(E) can be easily smeared out by disorder due to doping and various structural defects. Furthermore, the effectiveness of a van Hove singularity in enhancing the T_c is supposed to diminish greatly if there is a slight shift of E_F from the singularity. This high- T_c mechanism has been resurrected recently on the basis of the recent observation of a correlation of T_c with the degree of linearity of $\rho_{\parallel}(T)$, and other experimental findings.⁸ It is suggested that the proximity of the van Hove singularity to the Fermi level determines the dependence of $\rho_{\parallel}(T)$, i.e., $\rho_{\parallel}(T) \sim T$ or T^2 , and the magnitude of T_c . It is estimated that, even with a modest electron-phonon interaction $(\lambda \leq 1)$, a T_c of the order of 100 K can be achieved with the aid of a logarithmic singularity in N(E) near E_F . And it is shown that, although T_c can be limited by various N(E) broadening effects (as mentioned above) on the scale of $k_B T_c$, these effects are not sufficient to invalidate this high- T_c mechanism for Cu oxides. Furthermore, a recent slave-boson mean-field band-structure calculation¹⁶ for CuO₂-layered systems indicates that the Fermi level is pinned very close to the nearly logarithmic van Hove singularity. The singularity does not occur at the half-filling point, as in the Hubbard model, but corresponds to a finite doping level of x = 0.15 - 0.35 for the high- T_c Cu-O systems, depending on the long-range interactions in the model. These results are shown to be consistent with the experimentally observed $N(E_F)$ and the angle-resolved photoemission data.

To see the role of a two-dimensional van Hove singularity in determining the magnitude of T_c and the isotope effect, one could start with the full-fledged Eliashberg equations¹⁷ and assume a logarithmic density of states,

$$N(E) = N_0 \ln \left| E_F / (E - E_F) \right|, \tag{1}$$

in order to take into account the effects of strong electron-phonon interaction λ and the effective Coulomb coupling constant μ^* on T_c , where N_0 is the density of states normalized to a flat band with a bandwidth of $2E_F$. For the essence of the van Hove-singularity effects on T_c and the isotope effect, it will suffice to recall the standard BCS gap equation:

$$\frac{2}{V} = \int_{E_F - \hbar\omega_c}^{E_F + \hbar\omega_c} \tanh\left(\frac{E - E_F}{2k_B T_c}\right) N(E) \left(\frac{dE}{E - E_F}\right), \quad (2)$$

where ω_c is the cutoff frequency $(\hbar \omega_c \sim k_B T_{co})$, T_{co} is the phonon cutoff temperature, and V is a measure of the electron-phonon interaction strength.

From Eqs. (1) and (2), an expression for T_c can be obtained if the tanh $[(E - E_F)/2k_BT_c]$ in Eq. (2) is approximated by two tangents: One is tanh $[(E - E_F)/2k_BT_c] = (E - E_F)/2k_BT_c$ for $|E - E_F| \le 2k_BT_c$, the other is tanh $[(E - E_F)/2k_BT_c] = 1$ for $E - E_F > 2k_BT_c$:

$$T_c = 1.36T_F \exp\left\{-\left[\frac{2}{N_0 V} + \left(\ln\frac{k_B T_F}{\hbar \omega_c}\right)^2 - 1\right]^{1/2}\right\}.$$
 (3)

In the standard BCS treatment, N(E) is assumed to be independent of energy, N_0 , and Eq. (2) will lead to the well-known BCS formula for T_c in the weak-coupling limit:

$$T_c = 1.13T_{\rm co} \exp(-1/N_0 V)$$
 for $N_0 V \ll 1$. (4)

Estimates of T_c values based on Eqs. (3) and (4), using realistic parameters for the coupling constant, T_{co} , and T_F are listed in Table I. For comparison purposes, a coupling constant λ for states near the Fermi level may be defined by averaging the density of states over the energy range up to the phonon cutoff: $N_{av} = N_0 \omega_c^{-1}$ $\times \int_0^{\omega_c} \ln(E_F/E) dE$. The coupling constant may then be taken as $\lambda = N_{av}V$. Relatively low λ values are used in these T_c estimates: 0.25 in the first and 0.36 in the second row of Table I (for BCS with van Hove singularity). These results are in line with direct experimental measurements, ^{18,19} which suggest that λ is small for high- T_c Cu oxides in spite of the fact that they are all characterized by a large energy-gap to T_c ratio $[2\Delta(0)/k_BT_c \sim 5-7]$. As pointed out recently in Ref. 8 the lack of correlation between λ and $2\Delta(0)/k_BT_c$ can be understood in terms of a strong energy-dependent density of states near E_F . We have taken a large value of the phonon cutoff frequency because we have in mind as a specific mechanism pairing via the apical oxygen modes²⁰ which lie near the upper cutoff of the phonon frequency spectrum.²¹ It should be emphasized that although one should not attach too much numerical significance to the T_c estimates listed in Table I, they do underscore that a T_c of the order of 100 K can be realized in low-dimensional systems with only modest electron-phonon coupling and a logarithmic N(E) singularity close to the Fermi level.

The effect of the van Hove singularity on the isotope mass exponent α as defined in the expression $T_c \sim M^{-\alpha}$ can be calculated from the following expression:

$$\alpha = -\frac{\partial \ln T_c}{\partial \ln M} \,. \tag{5}$$

Based on Eq. (3), the BCS standard value for α (i.e., $\frac{1}{2}$) should be corrected according to the following equation, if the Fermi level is located right at the van Hove singularity:

$$\alpha_{s} = \frac{1}{2} \left[\ln \left(\frac{T_{F}}{T_{co}} \right) / \ln \left(\frac{1.36T_{F}}{T_{c}} \right) \right].$$
(6)

If the Fermi level is slightly off the singularity, then the

TABLE I. T_c estimates based on Eqs. (3) and (4).

	N_0V	$T_{\rm co}$ (K)	T_F (K)	T_c (K)
BCS with van Hove	0.081	754	5800	40
singularity [Eq. (3)]	0.12	754	5800	92
Standard BCS	0.081	754		0.004
[Eq. (4)]	0.12	754		0.2

 T_c formula Eq. (3) becomes

$$T_{c} \simeq 1.36 T_{F} \exp\left\{-\left[\frac{2}{N_{0}V} + \left(\ln\frac{T_{F}}{T_{co}}\right)^{2} - 1 + \frac{\delta^{2}}{2k_{B}^{2}}\left(\frac{1}{4T_{c}^{2}} + \frac{1}{T_{co}^{2}}\right)\right]^{1/2}\right\},\tag{7}$$

and Eq. (6) is modified as

$$\alpha \approx \frac{1}{2} \left[\left\{ \ln \left(\frac{T_F}{T_{co}} \right) + \frac{\delta^2}{2k_B^2 T_{co}^2} \right\} \right] \left\{ \ln \left(\frac{1.36T_F}{T_c} \right) - \frac{\delta^2}{8k_B^2 T_c^2} \right\} \right], \tag{8}$$

where δ is the E_F shift from the singularity and it is assumed that $\delta < 2k_BT_c$.

From Eqs. (3), (6), (7), and (8), one concludes that a logarithmic van Hove singularity in N(E) at or very close to the Fermi level can indeed significantly decrease α from its standard BCS value. In particular, Eqs. (7) and (8) show that α is at its minimum when T_c is maximum. This is qualitatively in agreement with the α data shown in Fig. 1. It should be pointed out that, in principle, a van Hove singularity in N(E) can lead to the absence of the isotope effect in a weak-coupled BCS superconductor. In other words, a vanishingly small α is not necessarily evidence for nonphonon pairing. This is clear from Eq. (3); one obtains

$$T_c \sim T_F \exp[-(2/N_0 V)^{1/2}], \qquad (9)$$
provided that

 $2/N_0 V \gg [\ln(k_B T_F/\hbar\omega_c)]^2,$

or $k_B T_F \sim \hbar \omega_c$. Here $\hbar \omega_c$ could be the energy of certain phonon mode(s). Based on Eq. (9), α is obviously zero and this is a possible explanation for observed nearly zero α_0 in high- T_c oxide superconductors such as the YBa₂Cu₃O₇ and Bi₂Sr₂Ca₁Cu₂O₈ systems.

If the Fermi level is far away from the singularity [i.e., the E_F shift $\delta = (E_s - E_F) > \hbar \omega_c$ or $k_B T_{co}$, where E_s is the energy at the singularity], one can expand the logarithmic energy-dependent N(E) around E_F ; then N(E)can be expressed by

$$N(E) = N(E_F) \left[1 + \sum_{n=1,2,3,\ldots} C_n \left(\frac{E - E_F}{\delta} \right)^n + \cdots \right],$$
(10)

where $C_n = [n \ln(E_s/\delta)]^{-1}$. From Eqs. (2) and (10), one obtains an expression for T_c and α :

$$T_{c} \sim \hbar \,\omega_{c} \exp\left[-\frac{1}{N(E_{F})V} + \sum_{n=2,4,\dots} \frac{C_{n}}{n} \left(\frac{\hbar \,\omega_{c}}{\delta}\right)^{n} + \cdots\right], \qquad (11)$$

$$\alpha = \frac{1}{2} \left\{ 1 + \sum_{n=2,4,\dots} C_n \left(\frac{\hbar \omega_c}{\delta} \right)^n \right\}.$$
 (12)

From Eqs. (11) and (12), one can see that, for $\delta > \hbar \omega_c$, both T_c and α increase with decreasing δ because the coefficients C_n (n=2,4,...) are always positive and increase with decreasing δ . It is important to note that, away from the singularity, α is always increasing

with increasing T_c and can be much larger than the BCS standard value of $\frac{1}{2}$. Again, these results roughly describe the experimental data (Fig. 1) for x < 0.12. On the other hand, according to Eqs. (7) and (8), α should decrease with increasing T_c near the singularity where the T_c peaks. In short, from these predicted opposite variations of α with T_c as a function of the Fermi-energy shift from the singularity (δ), one expects that α should be at a minimum and T_c at a maximum when $\delta = 0$, and α should increase with increasing δ and reach a peak (at $\delta \sim \hbar \omega_c$) in α with the peak value of α much greater than $\frac{1}{2}$.

A numerical calculation based on Eqs. (1) and (2) to incorporate the effects of a logarithmic N(E) singularity at and near the Fermi level has yielded results in good agreement with what is concluded from Eqs. (7), (8), (11), and (12). In Fig. 2, the calculated values for T_c and α are plotted as a function of δ . A quantitative comparison with the experimental results (Fig. 1) in terms of the doping concentration (x) is not possible because the conversion of δ from x may be nonlinear and is not known at the present time. However, the essential features of the data in Fig. 1 can be reproduced by this calculation, whose qualitative features do not depend on parameters such as the phonon cutoff frequency, and for example could be obtained by identifying the phonon



FIG. 2. Calculated results of T_c and α based on Eqs. (1) and (2) as a function of the Fermi-energy shift δ normalized to the cutoff phonon frequency $\hbar \omega_c$. The parameters used in the numerical calculation are $\hbar \omega_c = 0.065 \text{ eV}$, $k_B T_F = 0.5 \text{ eV}$, and $N_0 V = 0.084$.

cutoff with the Debye frequency. Of particular interest to note is that α is indeed at a minimum where T_c peaks, and off the T_c maximum, α reaches a peak. The minimum value $\alpha \sim 0.15$ and the peak value of $\alpha \sim 0.9$ are in fair agreement with the experimental findings, although the calculated peak value of the isotope shift is likely to depend on details of the model beyond the minimal one considered here, such as coupling to the phonon modes responsible for the $Abma \rightarrow P4_2/ncm$ structural phase transition,⁹ occurring near the doping 0.12. The observed peak value of $\alpha \sim 0.8$ is indeed significant in terms of the following considerations: (1) Apart from uncertainties due to structural phase instability,⁹ α can be determined with an accuracy of $\Delta \alpha$ $=\pm 0.02$ (see Refs. 1 and 2, for example). Therefore, an experimentally determined value for $\alpha = 0.77$ at x = 0.12 is quite significant and deserves a fundamental interpretation. (2) The isotope mass exponent α as defined in the expression $T_c \sim M^{-\alpha}$ implicitly contains contributions to the isotope shift in T_c from all the constituent elements, $\alpha = \sum_{i} \alpha_{i}$, where α_{i} is the partial isotope exponent for element *i*. In this sense, it is quite remarkable for the α value from oxygen alone to exceed significantly the standard BCS limit for α .

As demonstrated by Eq. (12) and also the numerical results shown in Fig. 2, a logarithmic N(E) at E_F , or any concave upward energy-dependent N(E),²² can produce an α value greater than $\frac{1}{2}$. Without including such an effect, a conventional Eliashberg (or McMillan) treatment cannot account for any α that is significantly different from the BCS value, despite the inclusion of strong Coulomb correlation.^{23,24} As pointed out by Faltens *et al.*,¹ the McMillan formula for α can allow $\alpha = 0.15$, for example, but only at the expense of physically unreasonable parameters such as $\lambda = 21$ and $\mu^* = 0.43$.

There is apparently no other model that can provide a mechanism for enhancing α over the BCS limit and explaining the strong composition dependence of α as observed in the La_{2-x}Sr_xCuO₄ system. It should also be pointed out that nearly all of the nonphononic models predict a zero isotope effect independent of oxide composition. If these models are correct, it would mean that the basic mechanisms for superconductivity in the Cu oxides such as La_{2-x}Sr_xCuO₄ and YBa₂Cu₃O₇ are quite different in spite of the fact that these Cu oxides share many structural, electronic, and magnetic characteristics.

The origin of the asymmetry in $\alpha_0(x)$ with respect to $x \sim 0.15$ as shown in Fig. 1 is not well understood, although we have some preliminary results of numerical calculations that indicate that if the density-of-states function N(E) is not symmetrical with respect to the singularity, one of the α peaks in Fig. 2 can be significantly suppressed.

Finally it is important to mention that the van Hove-singularity idea is not merely a concept invoked to explain the isotope shift and T_c data, but it also leads to natural explanations for many other normal-state and superconducting properties of the Cu-oxide superconductors. ^{7,8,14,16}

The authors wish to thank J. E. Demuth and D. H. Lee for useful discussions.

¹B. Batlogg et al., Phys. Rev. Lett. **59**, 912 (1987); T. A. Faltens et al., Phys. Rev. Lett. **59**, 915 (1987).

²B. Batlogg et al., Phys. Rev. Lett. **58**, 2333 (1987); L. C. Bourne et al., Phys. Rev. Lett. **58**, 2337 (1987).

³H. Katayama-Yoshida et al., Physica (Amsterdam) 156C, 481 (1989).

⁴M. Gurvitch and A. T. Fiory, Phys. Rev. Lett. **59**, 1337 (1987).

⁵H. Alloul, T. Ohno, and P. Mendels, Phys. Rev. Lett. **63**, 1700 (1989).

⁶C. G. Olson et al., Phys. Rev. Lett. 64, 2308 (1990).

 7 C. C. Tsuei, A. Gupta, and G. Koren, Physica (Amsterdam) **161C**, 415 (1989).

⁸C. C. Tsuei, Physica (Amsterdam) 168A, 238 (1990).

⁹M. K. Crawford, M. N. Kunchur, W. E. Farneth, E. M. McCarron, III, and S. J. Poon, Phys. Rev. B **41**, 282 (1990); J. P. Franck, J. Jung, M. A. K. Mohamed, S. Gygax, and I. G. Sproule (to be published).

 10 J. Labbe, S. Barisic, and J. Freidel, Phys. Rev. Lett. **19**, 1039 (1967); G. Kieselmann and H. Rietschel, J. Low Temp. Phys. **46**, 27 (1982); J. E. Hirsch and D. J. Scalapino, Phys. Rev. Lett. **56**, 2732 (1986), and the references therein.

¹¹P. A. Lee and N. Read, Phys. Rev. Lett. **58**, 2691 (1988); A. Virosztek and J. Ruvalds, Phys. Rev. B **42**, 4064 (1990).

¹²J. E. Dzyaloshinskii, Pis'ma Zh. Eksp. Teor. Fiz. **46**, 97 (1987) [JETP Lett. **46**, 118 (1987)]; Zh. Eksp. Teor. Fiz. **93**, 1487 (1989) [Sov. Phys. JETP **66**, 848 (1989)].

¹³J. Labbe and J. Bok, Europhys. Lett. **3**, 1225 (1987); J. Friedel, J. Phys. **48**, 1787 (1987); **49**, 1435 (1988); J. Phys. Condens. Mater **1**, 7757 (1989).

¹⁴R. S. Markiewicz, J. Phys. Condens. Matter 2, 665 (1990);
R. S. Markiewicz and B. C. Giessen, Physica (Amsterdam) 160C, 497 (1989).

¹⁵A. J. Freeman, J. Yu, and C. L. Fu, Phys. Rev. B **36**, 7111 (1987); H. Krakauer and W. E. Pickett, Phys. Rev. Lett. **60**, 1665 (1988); S. Massidda, J. Yu, and A. J. Freeman, Physica (Amsterdam) **152C**, 251 (1988), and the references therein.

¹⁶D. M. Newns, P. C. Pattnaik, and C. C. Tsuei, Phys. Rev. B (to be published); (to be published).

¹⁷P. B. Allen and B. Mitrovic, Solid State Phys. 37, 1 (1982).

¹⁸Z. Schlesinger, R. T. Collins, F. Holtzberg, C. Feild, N. E. Bickers, and D. J. Scalapino, Nature (London) **343**, 242 (1990).

¹⁹S. D. Brorson *et al.*, Solid State Commun. **74**, 1305 (1990).
 ²⁰K. Alex Müller, Z. Phys. B **80**, 193 (1990).

²¹B. Renker, F. Gompf, E. Gering, G. Roth, W. Reichardt, D. Ewert, H. Rietschel, and H. Mutka, Z. Phys. B **71**, 437 (1988).

²²J. P. Carbotte, in *Superconductivity in d- and f-band Metals*, edited by W. Buschel and W. Weber (Kernforschungszentrum, Karlsruhe, 1982), p. 487; E. Schachinger, M. G. Greeson, and J. P. Carbotte, Phys. Rev. B **42**, 406 (1990).

²³Jun Kondo, Prog. Theor. Phys. **29**, 1 (1963).

²⁴P. G. de Gennes, *Superconductivity of Metals and Alloys* (Addison-Wesley, Reading, 1989), p. 125.