Isotope effect as an *experimentum crucis* for identifying the mechanism for high-T_c superconductivity

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The anomalous decrease in the oxygen isotope effect with increasing transition temperature T_c, with the index of the isotope shift of T_c dropping to vanishingly low values and even going negative, is characteristic of a plasmon mechanism for superconductivity. A direct experiment is proposed for identifying this mechanism for high-T_c superconductivity.

1. Recent measurements of the oxygen isotope effect in $YBa_2Cu_3O_{7-\delta}$ during a partial replacement of Y by Pr and Ca (Refs. 1 and 2), of Cu by Zn (Ref. 3), and of Ba by La and Sr (Ref. 4), at a constant oxygen content (δ=const) in all cases, unambiguously confirm a tendency which had been seen earlier.[5–7] The isotope-shift index $\alpha_O = (\Delta T_c/T_c)(M_O/\Delta M_O)$ (ΔT_c is the change in T_c when ^{16}O is replaced by ^{18}O, M_O is the mass of the ^{16}O atom, and ΔM_O is the mass difference between the oxygen isotopes) decreases with increasing T_c. Furthermore, when Ba was replaced by Sr, it was found[4] that the oxygen isotope effect becomes vanishingly small and even goes slightly negative, with an accompanying decrease in T_c.

In this letter we show that such anomalies of the isotope effect are characteristic of a plasmon mechanism for superconductivity.[8] In this mechanism, the Cooper pairing of "light" (l) carriers in a broad band (of width $W_l > 1$ eV) results primarily from an exchange of virtual quanta of collective excitations of the charge density of nearly localized "heavy" (h) carriers in a narrow band (of width $W_h < 0.1$ eV). These virtual quanta are "acoustic plasmons,"[9,10] which hybridize with polar optical phonons,[11,12] in particular, with dipole-active of O^{2-} oxygen ions in the CuO_2 layers in the metal-oxide cuprates. A preliminary discussion of this question was published in Ref. 13, but some new experimental data[2,3] now make it possible to analyze the problem of the isotope effect in the metal-oxide cuprates in more detail.

2. The plasmon mechanism for superconductivity may be vastly more effective in the layered metal-oxide cuprates than in transition metals[10,14,15] or in degenerate semiconductors and semimetals,[8,16] for the following reasons: (a) The electron spec-

trum is quasi-two-dimensional, promoting a Cooper pairing in momentum space and the formation of bound pairs in real space.[17] (b) There is a region of electron–electron attraction by virtue of an electron–plasmon coupling throughout the Brillouin zone in the case of nearly localized h carriers in a narrow 2D band.[18] (c) The crystal is ionic, and there is a hybridization of acoustic plasmons with optical oxygen modes.[11–13] (d) Local-field effects[19] renormalize the Coulomb vertex (they increase the effective charge) by virtue of many-body correlations, and they almost completely cancel the nonadiabatic renormalization of the coupling constant due to the electron–plasmon interaction.[8–16] (e) The cuprates $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ and $Tl_mBa_2Ca_{n-1}Cu_nO_x$ ($m=1,2$) have a multilayer packet structure, with a proximity effect operating between the superconducting CuO_2 layers, at a distance $d_0 \approx 3$ Å from each other, in a packet. The contribution of these layers to the density of states is nearly additive, so the electron-phonon coupling constant is[20]

$$\lambda_{pl}(n) \approx \frac{\alpha_l}{2} n; \quad \alpha_l = m_l^* e^2/\epsilon_\infty k_{Fl}. \tag{1}$$

Here $k_{Fl} = \sqrt{2\pi N_l}$ is the Fermi momentum of the degenerate l carriers in the two-dimensional CuO_2 layers, with an density N_l (per unit area of the layer), m_l^* is the effective mass of these carriers (it is on the order of the mass of a free electron, m_0), and ϵ_∞ is the optical dielectric constant of the crystal.

The electron–plasmon coupling constant, which is directly responsible for the Cooper pairing of the l carriers, can be estimated from the following formula,[16,20] which incorporates local-field corrections:[19]

$$\tilde{\lambda}_{pl}(n) \approx \lambda_{pl}(n)[1+\lambda_{pl}(n)]. \tag{2}$$

To describe the electron–plasmon and electron–phonon interactions, we work from the Einstein model of a vibrational spectrum with two δ-function peaks.[21] One of these peaks is at the frequency of hybrid phonon-plasma vibrations $q_\parallel \approx 2k_{Fl}$ and $\omega_{LO} \gg \omega_{TO}$,

$$\tilde{\Omega}_+(n) \approx \left[\frac{n^2\Omega_h^2 k_{Fl} d + \omega_{LO}^2}{1+\alpha_l n^2}\right]^{1/2}, \tag{3}$$

where $\Omega_h = \sqrt{4\pi e^2 N_h/\epsilon_\infty m_h^* d}$ is the plasma frequency of the h carriers, with a two-dimensional density N_h and an effective mass $m_h^* = 4/a^2 W_h \gg m_l^*$ (a is the lattice constant in the plane of the layer), and ω_{LO} and ω_{TO} are the frequencies of longitudinal and transverse optical vibrations of the O^{2-} oxygen ions in the CuO_2 layers. The second peak is at the frequency Ω_O, of the higher-frequency vibrations of oxygen atoms lying outside the cuprate layers ($\Omega_O > \omega_{LO}$).

To calculate T_c we use the approximate exponential expression derived in Ref. 21. In the case at hand that expression becomes

$$T_c \approx \tilde{\omega}_0 \exp\{-1/\tilde{\Lambda}\}, \tag{4}$$

where

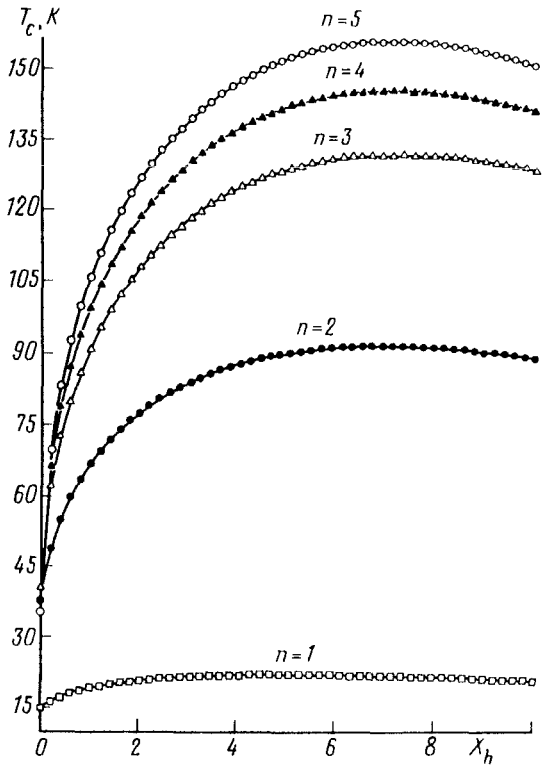

FIG. 1.

$$\tilde{\Lambda}=\frac{\tilde{\lambda}_{pl}+\lambda_{ph}-\tilde{\mu}_C^*(1+\tilde{\lambda}_\infty)}{1+\lambda_{pl}+\lambda_{ph}+\tilde{\lambda}_0}, \tag{5}$$

$$\tilde{\lambda}_0=\tilde{\lambda}_{pl}\ln(1+\tilde{\omega}_0/\tilde{\Omega}_+)+\lambda_{ph}T\ln(1+\tilde{\omega}_0/\Omega_O), \tag{6}$$

$$\tilde{\lambda}_\infty=\tilde{\lambda}_{pl}\ln(1+\tilde{\Omega}_+/\tilde{\omega}_o)+\lambda_{ph}\ln(1+\Omega_0/\tilde{\omega}_0), \tag{7}$$

$$\tilde{\mu}_C^*=\tilde{\mu}_C\,[1+\tilde{\mu}_C\ln(E_{Fl}/\tilde{\omega}_0)]^{-1}, \quad \tilde{\mu}_C\approx\tilde{\lambda}_{pl}, \tag{8}$$

$$\tilde{\omega}_0=[(\tilde{\lambda}_{pl}\tilde{\Omega}_+^2+\lambda_{ph}\Omega_O^2)/(\tilde{\lambda}_{pl}+\lambda_{ph})]^{1/2}, \tag{9}$$

and E_{Fl} is the Fermi energy of the l carriers in the wide 2D band.

We write the electron–phonon coupling constant as $\lambda_{pl}=\kappa\lambda_{ph}$; with $\kappa<1$ we have a polar interaction with the high-frequency oxygen mode Ω_O, weakened by the remoteness of the oxygen ions in the insulating oxide layers from the conducting CuO_2 layers, in which the l carriers are localized.

Figure 1 shows T_c versus the dimensionless parameter $x_h=\Omega_h^2/\omega_{LO}^2$ for various values $n=1$–5 and the following parameter values, which are typical of the cuprates:

$a=4$ Å, $\epsilon_\infty=4$, $m_l^*=1.8m_0$, $\omega_{LO}=300$ K, $\Omega_O=600$ K, and $\kappa=0.2$. We assume that the density of l carriers is constant at $\bar{n}_l=8\times10^{21}$ cm^{-3}, since there is a "pinning" of the narrow band ($E_{Fl}\approx$const) when there is a narrow 2D band with a high density of states. Doping raises the density of primarily the h carriers. Accordingly, the dependence of T_c on $x_h\sim N_h$ actually corresponds to the experimental dependence of T_c on the dopant or oxygen concentration, i.e., on the number of doped holes in the primitive cell per CuO_2 layer.[22] We see a completely satisfactory qualitative and quantitative agreement between theory and experiment for $YBa_2Cu_3O_{7-\delta}$ with $n=2$. On the other hand, numerical calculations show that if there is no narrow 2D band, if there are no h carriers ($N_h=0$, $\Omega_h=0$), and if we consider only the polar electron–phonon coupling with the oxygen vibration modes ω_{LO} and Ω_O, then the dependence of T_c on the density ($\bar{n}_l$) of doped l carriers in the broad 2D band agrees neither quantitatively ($T_c<40$ K) nor qualitatively with experimental data on the cuprates.

3. Working from (4)–(9), we find the following expression for the index of the isotope shift of T_c for use in analyzing the oxygen isotope effect:

$$\alpha_O\equiv-\frac{\partial\ln T_c}{\partial\ln M_O}$$
$$\approx\frac{1}{2\tilde{\omega}_0^2(\tilde{\lambda}_{pl}+\lambda_{ph})}\left[\frac{\tilde{\lambda}_{ph}\omega_{LO}^2}{1+\alpha_l n^2}+\lambda_{ph}\Omega_O^2\right]$$
$$\times\left\{1-\frac{1+\tilde{\lambda}_\infty}{1+\lambda_{pl}+\lambda_{ph}+\tilde{\lambda}_0}(\tilde{\mu}_C^*/\tilde{\Lambda})^2\right\}. \qquad (10)$$

It follows that even under the condition $\lambda_{ph}\ll\tilde{\lambda}_{pl}$ the contribution of the electron–phonon coupling to the isotope effect can be extremely important, by virtue of the inequality $\Omega_O^2\gg\omega_{LO}^2(1+\alpha_l n^2)^{-1}$.

Figure 2 shows α_O versus T_c as calculated from (4)–(10) and the data in Fig. 1. Descending $\alpha_O(T_c)$ curves of this type have in fact been found[1] experimentally for $YBa_2Cu_3O_{7-\delta}$ upon a partial substitution of Pr for Y, upon a replacement of Cu by Zn (in Ref. 3), and upon a replacement of Ba by La (in Ref. 4; Fig. 3). In the mixed compound $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$, for example, Zn at a concentration of only 9% suppresses the superconductivity,[3] and the index of the oxygen isotrope effect decreases with decreasing x, from $\alpha_O\approx0.3$ at $x=0.08$ and $T_c\approx7$ K to $\alpha_O\approx0.03$ at $x=0.01$ and $T_c\approx80$ K (curve *1*).

According to Refs. 1–3, the decrease in α_O in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ from its maximum value $\alpha_O\approx0.55$ at $x=0.5$ and $T_c\approx30$ K to $\alpha\approx0.02$ at $x=0$ and $T_c=92$ K in pure $YBa_2Cu_3O_{7-\delta}$ (curve *2* in Fig. 3) results primarily from an increase in the density of doped holes with decreasing Pr content. The effective valence of the Pr is $z^*=3.8$ and is nearly independent of the magnetic moment of the Pr atoms.

These conclusions are also supported by experiments[4] on the replacement of Ba by La and Sr, i.e., by atoms which have no magnetic moment. A partial replacement of Ba by La in $Y(Ba_{1-x}La_x)_2Cu_3O_{7-\delta}$ results in a suppression of superconductivity (a lowering of T_c) because of a decrease in the density of mobile holes (primarily in the narrow 2D band). These holes localize at the La^{3+} ions replacing Ba^{2+} ions in the

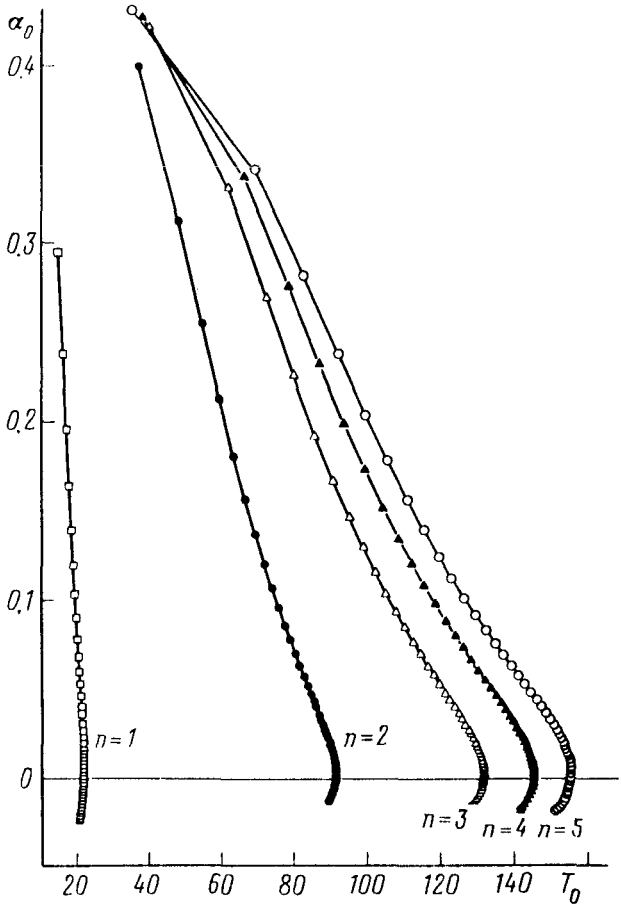

FIG. 2.

lattice. As the La content is reduced, α_O is observed to decrease from $\alpha_O \approx 0.4$ at $x=0.5$ and $T_c \approx 40$ K to $\alpha_O \approx 0.01$ at $x=0$ and $T_c \approx 90$ K (curve *3* in Fig. 3), in qualitative agreement with Fig. 2 [see the $\alpha_O(T_c)$ curve for $n=2$].

In addition, Bornemann and Morris[4] have observed a vanishingly small or even negative oxygen isotope effect, with a decrease in T_c, in $Y(Ba_{1-x}Sr_x)_2Cu_3O_{7-\delta}$ as x is increased. It would seem that the replacement of Ba by isovalent Sr would have no effect at all on T_c or α_O. However, the ionic radius of Sr^{2+} is smaller than that of Ba^{2+}, and this difference appearently creates conditions favoring a supersaturation of the cuprate with oxygen and a shift toward higher hole densities, at which T_c begins to decrease after going through a maximum (Fig. 1), and at which the oxygen isotope effect has a value $\alpha_O < 0$ (Fig. 2).

We would like to stress that the dependence of α_O on T_c in the absence of a

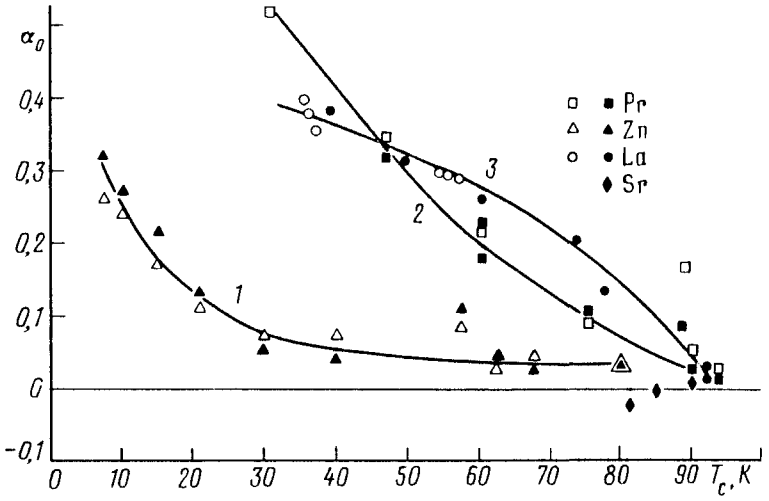

FIG. 3.

narrow two-dimensional band near the Fermi level and thus in the absence of h carriers ($N_h=0$), and also in the absence of an acoustic-plasmon branch ($\Omega_h=0$), is exactly the opposite: α_O increases with increasing T_c, going from negative values at low T_c's to positive values $\alpha_O \approx 0.4$–0.5 at the highest T_c's. This behavior is typical of a phonon mechanism for superconductivity,[7,23] but it contradicts the experimental data on the cuprates.[1–7]

An experiment to determine the magnitude and sign of α_O, in the region in which T_c goes through a maximum and decreases, might provide a direct answer to the question of the mechanism for high-T_c superconductivity (it would be a plasmon mechanism if $\alpha_O \leqslant 0$ or a phonon mechanism if $\alpha_O > 0$). The "cleanest" such experiment would be to replace some of the Y by Ca (this replacement was made in Ref. 2 in the presence of 20% Pr) or some of the Ba by K in YBa_2Cu3O_7 and to carefully measure α_O as the oxygen content or the dopant concentration was varied near the T_c maximum in multilayer cuprates of the BiSrCaCuO and TlBaCaCuO types.

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