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Transition from Fermi liquid to charged Bose liquid: A possible explanation of the isotope shift in high-T_c oxides

A. S. Alexandrov*

Institut für Theoretische Physik, Rheinisch-Westfälische Technische Hochschule Aachen, 5100 Aachen, Germany

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Three puzzling features of the oxygen isotope shift in the superconducting transition of metal oxides: large values ($\alpha > 0.5$) in "low-T_c" oxides, an overall trend to lower values for α as T_c increases, and a negative α in Bi 2:2:2:3 at $T_c = 108$ K, are explained by the polaron theory of high-T_c superconductivity.

A charged Bose liquid, which was proposed by Schafroth[1] as a phenomenological explanation of superconductivity and later derived microscopically from the Fröhlich electron-phonon interaction (bipolaronic superconductivity[2]) is an intriguing possibility for high-T_c metal oxides.[3]

Such characteristic features of high-T_c superconductors as the curious absence of coherence effects and of the Korringa law in the nuclear spin relaxation rate, the unexpected "coherence" peak of low-frequency conductivity, linear in T resistivity, and the unusually short coherence length are indicative of charged bosons—small bipolarons.[4] There is other convincing evidence for small (bi)polarons in high-T_c compounds:[5] the local lattice deformation measured in photo-induced infrared and photo-modulation experiments,[6] the x-ray-absorption fine-structure results on the radial distribution function of apex oxygen ions, and their corresponding vibrational mode, which is both infrared- and Raman-active,[7,8] the temperature dependence of the vibration energy of certain atoms engaged in polaron formation.[9] The fine structure of the normal-state angle-resolved photoemission spectra[10] (ARPES) shows a superposition of multiphonon excitations in accordance with the polaron theory of ARPES.[11] One should add here the heat capacity, which is reminiscent of He-4 and unusual temperature dependencies of lower and upper critical fields as well as of the sound attenuation and velocity which, however, can be expected for charged bosons.[12]

Nevertheless, a reduced isotope effect (practically zero in initial experiments) led Anderson and Abrahams[13] to suggest that phonons and bipolarons could not be responsible for high T_c.

Recent advances in the fabrication of isotope-substituted oxides have changed the situation: a sizable isotope effect, $\alpha = -d \ln(T_c)/d \ln M \geq 0.1$, has been measured in many high-T_c materials, including 1:2:3,[14] several compounds have shown $\alpha > 0.5$ BCS value,[15,17] and recently a negative $\alpha = -0.013$ in Bi 2:2:2:3 ($T_c = 108$ K) has been found.[18]

It is argued[19] that some of these striking variations in α, including its large values, do not necessarily imply a large phonon contribution to the T_c value and do not invalidate the electronic mechanisms with a small phonon contribution, of course. Within the BCS theory there is no reason at all for α not to become negative, when the Coulomb psuedopotential μ is comparable with the electron-phonon coupling constant λ. However, if the two mechanisms (the phonon-mediated and the exotic nonphonon interaction) both make a contribution, then as the nonphonon interaction dominates with increasing T_c, α should decrease and approach zero at the highest T_c. But in this case α would not go negative as was found in Bi 2:2:2:3.[18] It is also impossible to obtain a negative value of α within the orthodox BCS theory for T_c as high as 100 K. In all conventional superconductors with anomalously low or negative α, T_c is 1 K or smaller.

As far as large values of $\alpha > 0.5$ are concerned several possible explanations have been suggested including anharmonic effects,[20] the inhomogeneous structure,[21] the energy dependence in the electronic density,[19,22,23] and the structural phase transition.[15] However, the large value of $\alpha \geq 1$ (Ref. 24) seems hardly explicable by the usual BCS-like schemes[19,22,23] for a reasonable range of parameters and is, on the contrary, characteristic for small bipolarons.[25] There is no indication of the low-temperature phase transition in $La_{2-x}Ca_xCuO_4$ with the most unusual α.[15] As for the apex oxygen anharmonicity, it is due to the polaronic effect as has been demonstrated recently.[26]

In this paper I show that the common puzzling features of the oxygen isotope effect might be explained by the small-polaron theory of high-T_c metal oxides.[27]

The fermion-boson interaction of the Fröhlich type:

$$H_{f\text{-}b} = (1/\sqrt{2N}) \sum_{\mathbf{k},\mathbf{q}} \gamma(\mathbf{q}) \omega(\mathbf{q}) c^{\dagger}_{\mathbf{k}+\mathbf{q}} c_{\mathbf{k}} (b_{\mathbf{q}} + b^{\dagger}_{-\mathbf{q}}) , \quad (1)$$

where γ is a dimensionless interaction constant, ω is a boson frequency ($\hbar = c = 1$), and $c_{\mathbf{k}}, b_{\mathbf{q}}$ are fermionic and bosonic operators correspondingly, leads to the familiar polaron collapse of the electron band [28] at some critical value of the coupling:[29]

$$\lambda \geq \lambda_c = 1/\sqrt{2z} \quad (2)$$

with $\lambda = (1/2DN) \sum_{\mathbf{q}} \gamma^2(\mathbf{q}) \omega(\mathbf{q})$ and z being a coordination lattice number.

Starting from this critical value of the interaction, fermions prefer tunneling in a narrow polaronic band having the reduced half-bandwidth:

$$W = D \exp(-g^2) , \quad (3)$$

where D is a bare half-bandwidth in a rigid lattice and

$$g^2 = (1/2N) \sum_{\mathbf{q}} \gamma^2(\mathbf{q}) \coth[\omega(\mathbf{q})/2T][1 - \cos(\mathbf{q}\mathbf{m})] \quad (4)$$

is the number of bosons in a small polaron cloud, $\mathbf{m}$ being the nearest-neighbor lattice vectors and N a total number of cells.

From a more general viewpoint an instability of the bo-

son vacuum develops in the system and results in a polaron collapse of the band, Eq. (3). Depending on the ratio of the polaron-polaron attraction $V=2D(\lambda-\mu)$ to the polaron half-bandwidth W, the many-polaron system may be a polaronic Fermi liquid with the Cooper-like polaronic pairs[30] at low temperatures if $V \leq W$ or a bipolaronic superfluid Bose liquid[2] if $V \gg W$. In the first case the critical temperature of the superconducting transition is determined by the BCS-like formula but with W instead of ω because of nonadiabaticity of polarons, $W<\omega$, and with the renormalized density of states (DOS) $N_p=N(0)\exp(g^2)$ (for details see Refs. 27 and 30):

$$T_c=Df(n)\exp\{-[g^2+\exp(-g^2)/(\lambda-\mu)]\} \tag{5}$$

with $\mu=V_c/2D$, V_c being the Coulomb repulsion, and $f(n)$ being a smooth function of the atomic concentration of fermions n, $f(n)=1.14\sqrt{n(2-n)}$ for the energy-independent DOS. The first term in the argument of the first exponent describes the effect of the bandwidth renormalization on the energy range of attraction while the second exponent is due to an enhancement of DOS. This enhancement is responsible for the maximum in T_c as a function of the interaction g, and possibly for high values of T_c in metal oxides as discussed in Ref. 27.

In the case of a large attraction, real-space local pairs—small bipolarons form, the tunneling is two-particle, and[2]

$$T_c=t\phi(n)\ , \tag{6}$$

where t is the bipolaronic half-bandwidth:

$$t \leq D\exp(-2g^2)/(\lambda-\mu) \tag{7}$$

and ϕ is a smooth function of the concentration, $\phi(n)\sim n^{2/3}$ for a three-dimensional (3D) dilute Bose-liquid and $\phi(n)\sim n$ for quasi-2D bosons. Equation (7) describes the tunneling of on-site pairs. If bipolarons are intersite as they are in Ti_4O_7 or $M_xV_2O_5$,[31] they can tunnel by a one-particle hopping (a "crablike" motion) and

$$t \simeq D\exp(-g^2)\ . \tag{8}$$

The latter possibility is more realistic for copper-based oxides because of the large on-site Coulomb repulsion on copper.

It was argued[27] that high-T_c oxides belong to the transition region from the polaronic BCS-like superconductors, Eq. (5), to the charged bipolaronic Bose liquid, Eq. (6) (see also Ref. 32). A description of this region is a challenging problem, which was discussed by Nozières and Schmitt-Rink[33] and more recently by Randeria, Duan, and Shieh,[34] Sofo, Balserio, and Castillo,[35] as well as by van der Marel and Mooij[36] within a phenomenological U-negative Hubbard model. The bipolaronic Hamiltonian cannot be mapped on the U-negative one because of the drastic renormalization of the one-particle spectrum, Eq. (3), and the cumbersome dependence of the bipolaronic hopping t on g^2 (Ref. 37). However, the problem of the interpolation between two different many-particle states, being much more complicated in case of small polarons, may be settled for intersite pairs. In a wide region of concentration, $n \sim 1$, the functions f and ϕ are of the order of unity and one can take $f \approx \phi$ in this region. Then one can see from the comparison of Eq. (5) and Eqs. (6) and (8) that the weak-coupling formula for T_c, Eq. (5), interpolates perfectly well between two extreme limits of the polaron-polaron attraction. According to Ref. 33 the transition from the BCS ground state to the Bose liquid should be continuous, so I adopt

$$T_c=\mathfrak{D}(n)\exp[-g^2-(\lambda-\mu)^{-1}\exp(-g^2)] \tag{9}$$

for the whole range of the interaction g. Here $\mathfrak{D}=Df(n)$ depends smoothly on the concentration, $\mathfrak{D} \leq D$.

Because λ, μ and f,ϕ are isotope mass independent, the explicit forms of $\mathfrak{D}$ as well as of λ and μ are irrelevant in our analysis of the isotope effect. On the other hand, g^2 strongly depends on the oxygen mass M, Eq. (4), being proportional to $1/\omega$:

$$g^2=\text{const}\times\sqrt{M}+g_s^2\ , \tag{10}$$

where g_s^2 is a possible contribution to the fermion-boson interaction from the vibrations of other ions and spin fluctuations ("magnons").

Differentiating Eq. (9) with Eq. (10) one obtains

$$\alpha=(\beta/2)g^2[1-(\lambda-\mu)^{-1}\exp(-g^2)] \tag{11}$$

with $\beta=(1-g_s^2/g^2)$ being a relative contribution of oxygen to the small polaron cloud. It is convenient to introduce a relative maximum T_c^* of T_c as a function of g^2, Eq. (9), keeping $(\lambda-\mu)$ constant:

$$T_c^*=\mathfrak{D}\times(\lambda-\mu)/e\ , \tag{12}$$

and express T_c in units of $\mathfrak{D}$:

$$\begin{aligned} T_c&=\exp[-g^2-a\exp(-g^2)]\ ,\\ \alpha&=(\beta/2)g^2[1-a\exp(-g^2)]\ . \end{aligned} \tag{13}$$

Equation (13) allows an analysis of the correlation between α and T_c with a minimum set of parameters: β and $a=\mathfrak{D}/eT_c^*$.

Figures 1 and 2 show the dependence of T_c and α on g^2 correspondingly for two different values of T_c^* and β. The value of $\beta=1$ corresponds to a zero contribution to the boson cloud from other bosonic excitations, except oxygen vibrations. $\beta=\frac{1}{3}$ corresponds to the relative weight of oxygen ions in the CuO_2 in-plane unit cell. Fig-

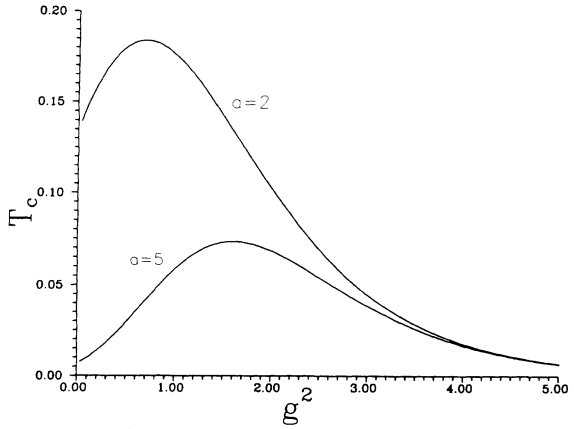

FIG. 1. The dependence of the critical temperature (in units of $\mathfrak{D}$) on the fermion-boson interaction constant g^2 for two different values of the polaron-polaron attraction: $a=(\lambda-\mu)^{-1}=2,5$.

ure 3 gives $\alpha(T_c)$ for $\beta=1$ and $a=5$ so one can see all three remarkable features, which have been mentioned above: (1) α exceeds the BCS value 0.5 for "low-T_c" bipolaronic superconductors:

$$\alpha=(\beta/2)\ln(1/T_c) \tag{14}$$

if $g^2\gg 1$ (see also Refs. 25 and 29); (2) there is an overall trend to a lower value for α as T_c increases; and (3) α becomes negative for high-T_c polaronic superconductors with $g^2\approx 1$.

To compare with experiments[14–18] I choose the pessimistic value of $T_c^*=125$ K so far achieved in Tl-based cuprates and take $\mathfrak{D}=680$ K ($a=2$) for all compounds, which, of course, is a very simplified approximation. With this approximation one takes into account the strong exponential dependence of T_c on the interaction (g^2) only and neglects the smooth concentration dependence. The result is shown in Fig. 4. To fit the absolute value of α one should take $\beta=\frac{1}{3}$. It is clear that Eq. (13) describes rough feature of α discussed above. However, there is a persistent discrepancy: The experimental decrease of α with the T_c increase is more pronounced than the theoretical one for each type of cuprates. This discrepancy may be explained by different values of $\mathfrak{D}$ for different values of doping. The nonmonotonic behavior of α in Ba- and Sr-doped La-based cuprates might be due to the global structural transition in these compounds, as discussed in Ref. 15.

This structural phase transition and the nonmonotonic behavior with doping of the isotope shift in La-Sr-Cu-O as well as in La-Ba-Cu-O might be due to the Van Hove singularity of DOS as discussed by Newns and collaborators.[38] I would like to note that the polaronic band narrowing in the strong-coupling electron-phonon system leads to a sharpening of the Van Hove singularity. This is just opposite to a smearing of it due to the electron-phonon scattering in the weak-coupling regime.

The only condition for the applicability of the polaron theory of superconductivity is a sizable value of λ, Eq. (2). This imposes some restrictions on the value of the bare adiabatic parameter D/ω, where $\omega=\lambda D/g^2$ is the characteristic phonon frequency, $\omega\approx 1.7\omega_0$ for dispersionless optical phonons with the frequency ω_0 (see, for example, Ref. 29). To obtain mobile bipolarons with a

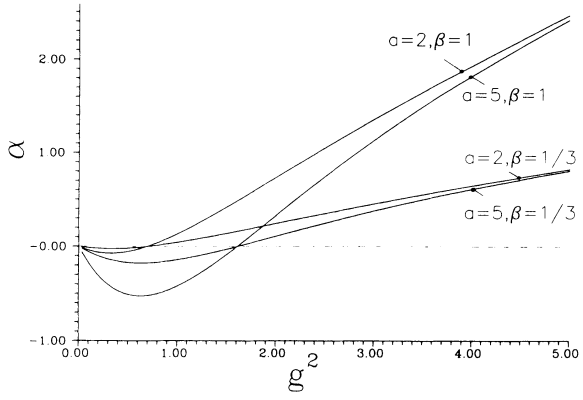

FIG. 2. The dependence of the isotope shift α on g^2 for $a=2,5$ and the relative oxygen contribution to the polaron cloud $\beta=1,\frac{1}{3}$.

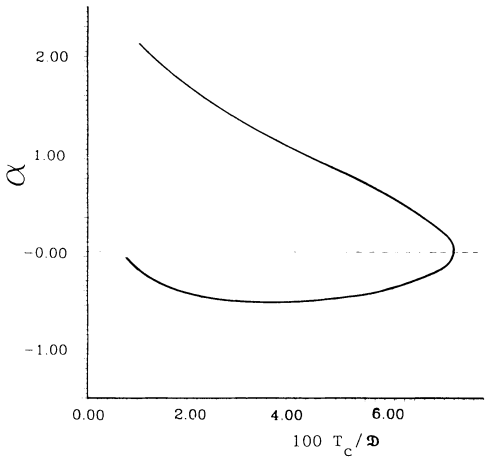

FIG. 3. α as the function of T_c for $a=5,\beta=1$.

reasonably large mass one should assume $g^2\simeq 1-3$, which gives according to Eq. (2)

$$D/\omega\leq 3-10 \tag{15}$$

for a square lattice. With $\omega_0\simeq 0.06$ eV (oxygen modes) this means $D\leq(0.3-1.0)$ eV, which lies in the experimentally determined range of the bare half-bandwidth for metal oxides.

The Coulomb repulsion (intersite) μ should be correspondingly suppressed, $\mu\leq\lambda$, to ensure pairing which is quite feasible due to a large value of the high-frequency dielectric constant $\epsilon\geq 5$. I should also mention that the enhancement of the low-frequency effective mass in metal oxides is now well established. Possibly one can see it most directly and avoiding ambiguity (in the determination of the carrier concentration) in the difference between the optically measured plasmon frequency

$$\Omega_p=\sqrt{4\pi ne^2/m\epsilon} \tag{16}$$

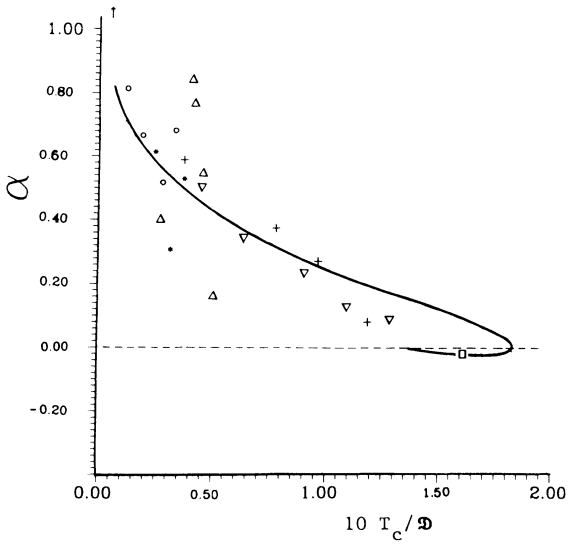

FIG. 4. α as the function of T_c for $\mathfrak{D}=680$ K, $T_c^*=125$ K ($a=2$), and $\beta=\frac{1}{3}$ and the experiment: (○) $La_{2-x}Ca_xCuO_4$ (Ref. 15), (△) $La_{2-x}Sr_xCuO_4$ (Ref. 15), (*) $La_{2-x}Ba_xCuO_4$ (Ref. 15), (▽) $Y_{1-x}Pr_xBa_2Cu_3O_{6.92}$ (Ref. 16), (+) $YBa_2Cu_{4-x}Ni_xO_8$ (Ref. 17), (□) $Bi_{1.6}Pb_{0.4}Ca_2Sr_2Cu_3O_{10}$ (Ref. 18), and (↑) $La_{2-x}Ba_xCuO_4$ from Ref. 24.

and that determined through the London penetration depth λ_L:

$$\omega_p = c/\lambda_L = \sqrt{4\pi n e^2/m^*} \ . \quad (17)$$

The ratio of the low-frequency mass m^* to the high-frequency $m \simeq m_e$:

$$m^*/m = (\Omega_p/\omega_p)^2 \epsilon \quad (18)$$

happens to be of the order of 10 in "1:2:3" [$\Omega_p = 3$ eV, $\omega_p = 1.4$ eV (Ref. 39)] or higher. This corresponds to $g^2 \simeq 2$.

In conclusion, with the formula for T_c which interpolates between the polaronic (BCS-like) and the bipolaronic superconductivity (Schafroth-like) I have described the main puzzling features of the oxygen isotope effect in high-T_c oxides: $\alpha > 0.5$ in "low-T_c" oxides, the overall trend to lower values of α as T_c increases and the negative α in Bi 2:2:2:3 at $T_c = 108$ K. For $\lambda > \lambda_c$ I propose a classification of phonon (any boson) -mediated superconductors into two different types: polaronic ($\alpha < 0$) with Cooper-like small polaronic pairs and bipolaronic ($\alpha > 0$) with preformed charged bosons. In the bipolaronic superconductor T_c is controlled by the effective mass of bosons; in the polaronic superconductor T_c is determined mainly by the exponential enhancement of the one-particle density of states. It follows from our consideration that the isotope shift can distinguish the Fermi-liquid polaronic superconductivity from the charged Bose liquid. The increase of the ion mass in bipolaronic superconductors raises the mass of a bipolaron and decreases T_c according to the classical formula for the Bose-condensation temperature of a Bose gas. On the contrary, in polaronic superconductors it leads to the band narrowing and to the increase of DOS and T_c. The pressure (p) dependence of T_c should be correspondingly different: $dT_c/dp > 0$ in the bipolaronic regime and $dT_c/dp < 0$ in the polaronic one. The comparison with the experimental data, Fig. 4, shows that more than 30% of the bosonic cloud, surrounding the small polaron, comes from oxygen vibrations, the rest is due to vibrations of other ions and (or) due to spin-fluctuations, as proposed by Mott.[40]

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*Permanent address: Moscow Engineering Physics Institute, Moscow, Russia. Present address: IRC in Superconductivity, University of Cambridge, Madingley Road, Cambridge CB3 0HE, U.K.

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