RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 13 1 OCTOBER 1991-I

Apex-oxygen-atom tunneling as source of anomalous low-temperature specific heat in high-T_c superconductors

Marco Zoli*

Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 1000 Berlin 33, Germany

(Received 10 May 1991; revised manuscript received 19 July 1991)

A model is proposed in which the quantum tunneling of the apex oxygen atom is coupled to the quasiparticle excitations of the superconducting state. A path-integral formulation allows one to renormalize the coupling constant as a function of temperature. It is shown that such a model can account for the anomalous low-temperature specific heat observed in high-T_c $YBa_2Cu_3O_{7-\delta}$ superconductors.

Several publications have emphasized the role of electron-phonon coupling of the apex oxygen atoms in high-T_c superconductors (HTSC).[1] Pyramidal apex oxygen atoms are present in the majority of HTSC although the various cuprates have different ratios of apex to total oxygen atoms in the unit cell. Hereafter I focus on the $YBa_2Cu_3O_{7-\delta}$ systems, the most investigated among the HTSC. In $YBa_2Cu_3O_{7-\delta}$, the linear-chain oxygen atoms are particularly mobile and a percentage of the oxygen atoms may tunnel, providing the relevant low-energy excitations for this compound at low temperatures. Raman-scattering experiments[2] have shown that the coupling constants of the apex oxygen atoms are not particularly large, at least near the Γ point of the Brillouin zone. Therefore, high transition temperatures should not be ascribed solely to strong electron-phonon coupling. Tunneling systems (TS) have been observed by acoustic methods[3] in $YBa_2Cu_3O_{7-\delta}$ below 1 K. The presence of two Cu-O(4) distances, indicative of a double well, has also been detected in the experimental extended x-ray-absorption fine-structure (EXAFS) spectra of $YBa_2Cu_3O_{7-\delta}$.[4] The EXAFS spectra have been analyzed in the range $10 \leq T \leq 105$ K by using a double-well potential for the O(4) atom.[5] The best fit to the data is obtained by assuming a separation of 0.13 Å between the minima of the double well. A special role for the O(4) atom is also suggested by infrared reflectivity studies,[6] Raman scattering,[7,8] and electron-energy-loss experiments.[9] An anomalous broadening of the linewidth of the apex-oxygen-atom stretching mode has been observed[2] in the superconducting state for phonon energies larger than that of the gap. The presence of anharmonic phonons below T_c should be related to the breaking of Cooper pairs.

In this paper, a model is presented in which the low-energy excitations provided by the apex oxygen atoms are coupled to the electronic degrees of freedom involved in the superconducting transition. The model is applied to calculate the low-temperature specific heat of $YBa_2Cu_3O_{7-\delta}$ superconductors, which exhibit an anomalous finite linear contribution.[10] This unconventional behavior is common to several HTSC and it seems to be due at least partly to some intrinsic mechanism. So far, a clear explanation of this feature is still lacking. Unconventional superconductivity[11] has been invoked to explain the finite linear term, but it has been shown[12] that the resonating-valence-bond theory is also consistent with a vanishing linear term. Here, I suggest that the TS associated with the stretching vibrations of the apex oxygen atoms may account for the finite linear term in $YBa_2Cu_3O_{7-\delta}$ compounds, below 10 K.

In order to explain the physical properties of $A15$ compounds, Yu and Anderson[13] have proposed a local phonon model in which a single atom interacts strongly with a Fermi gas of spinless electrons. The strong electron-phonon coupling in the normal state of the $A15$ compounds leads to the formation of double-well potentials and anharmonic phonons. I believe that the local phonon model should be reconsidered to describe the TS that are present in the superconducting state of the HTSC. However, one has to note that the existence of TS should not be necessarily ascribed to a strong-coupling regime and so far, the origin of the TS in HTSC is not understood.[14]

I assume the existence of a superconducting state, below a given critical temperature T_c, which can be described in the framework of the BCS theory. The interaction between the local phonon and the mates of the Cooper pair can be described by

$$H_{e\text{-ph}} = -\sum_{\mathbf{k},\mathbf{k}'} \mathbf{B}^{\dagger}(\mathbf{k}') \begin{pmatrix} 0 & \lambda Q \\ \lambda Q & 0 \end{pmatrix} \mathbf{B}(\mathbf{k}) , \tag{1}$$

where λ is the electron-phonon coupling and Q is the one-dimensional (1D) atomic displacement (along the c axis for the apex oxygen atom). $\mathbf{B}(\mathbf{k})$ is a two-component field operator,

$$\mathbf{B}(\mathbf{k}) = \begin{pmatrix} c_{\mathbf{k}\uparrow} \\ c^{\dagger}_{\mathbf{k}\downarrow} \end{pmatrix} , \tag{2}$$

with $c^{\dagger}_{\mathbf{k}}$ and $c_{\mathbf{k}}$ the creation and annihilation operators for electrons with momentum $\mathbf{k}$; a particular choice of spin indices has been made to simplify the notation. The diagonal matrix elements can be absorbed into the noninteracting Hamiltonian $H_0 = H_{\text{osc}} + H_{\text{el}}$, where H_{osc} describes a local Einstein oscillator and H_{el} represents the superconducting bath of Cooper pairs. In the normal state, it has been shown[13] that the electrons provide a double-well potential for the atom which hops back and forth between the minima of the TS. When the atom hops, the electrons tend to follow it to recover equilibrium. This implies time-retarded electron-phonon interactions and the breakdown of the adiabatic approximation. In the superconducting state, to lowest order in the coupling constant, the

partition function of the system is given by

$$Z = Z_0 \exp\left[-2\int_0^\beta d\tau\, U(\tau)\Gamma(\tau)\right], \tag{3}$$

where Z_0 is the partition function for the Hamiltonian H_0, β is the inverse temperature, and τ is the time according to the Matsubara Green-functions method;[15] $U(\tau) \equiv \lambda Q(\tau)$ and $Q(\tau)$ describes a fixed path for the atom. $\Gamma(\tau)$ is given by

$$\Gamma(\tau) = \int_{-\infty}^{+\infty} dE\, N_{SC}(E)\Gamma(E,\tau), \tag{4}$$

with

$$\begin{aligned} &E \equiv E_{\mathbf{k}} = [\xi_{\mathbf{k}}^2 + \Delta(T)^2]^{1/2}, \\ &N_{SC}(E) = N(\xi)\frac{E}{[E^2-\Delta(T)^2]^{1/2}}, \\ &\Gamma(E,\tau) = -\frac{\Delta(T)}{2E}\{e^{-E\tau}[\Theta(\tau)-f(E)] \\ &\qquad -e^{E\tau}[\Theta(\tau)-f(-E)]\}. \end{aligned} \tag{5}$$

$E_{\mathbf{k}}$ and $\xi_{\mathbf{k}}$ are the quasiparticle and electron energies, respectively; $\Delta(T)$ is the gap function of the BCS theory; $N_{SC}(E)$ and $N(\xi)$ are the densities of states in the superconducting and normal state, respectively; $\Theta(\tau)$ is the step function; and $f(E)$ is the Fermi distribution. $\Gamma(E,\tau)$ is the Fourier transform of the anomalous Green function which defines the gap function in a uniform medium.[16] In absence of applied fields, $\Gamma \equiv \Gamma^\dagger$; this justifies the factor 2 in Eq. (3), which accounts for the two possible choices of spin indices in Eq. (2).

Standard path-integral techniques[17,18] can be used to integrate out the electronic degrees of freedom. In order to evaluate the $d\tau$ integral in Eq. (3), one has to specify the function $Q(\tau)$ which describes the quantum tunneling of the atom between the two minima of the TS. I consider the class of linear hopping paths with an even number of hops. This simplifies the mathematical procedure and retains the essential physics.[13,19]

Let us define τ_0, the time for hopping between the two minima $-Q_0$ and $+Q_0$, then

$$Q(\tau) = -Q_0 + \frac{2Q_0}{\tau_0}(\tau - t_i), \tag{6}$$

where t_i is the instant at which the ith hop starts. The condition $Q(\beta) = Q(0)$, ensures that each path has an even number of hops. To obtain the full partition function (Z_T) one has to integrate over the times t_i and sum over all possible even number of hops. Finally, by increasing τ_0 or, equivalently, by decreasing the temperature, the short scale fluctuations are cut off and the dominant path (atom sitting in a well) is approached. The scaling techniques allow one to renormalize electron-phonon coupling and hopping probability as a function of temperature. Details of the method are given elsewhere.[20] The partition function which I have derived is

$$Z_T = Z_{el}\exp\left[-\frac{\beta M\omega^2 Q_0^2}{2}\right]\left[\frac{\Delta(T)\beta}{2}\right]^{\tilde{\lambda}}\left[1-\frac{\tilde{p}^2}{2-\tilde{\lambda}}\right], \tag{7}$$

where M is the apex-oxygen-atom mass and ω is the frequency of the local phonon; $\tilde{\lambda}$ and $\tilde{p}$ are the renormalized coupling constant and hopping probability, respectively:

$$\begin{aligned} &\tilde{\lambda} = 2\lambda Q_0 N_0 \Delta(T)\beta, \\ &\tilde{p} = \{4e/[\Delta(T)\beta]^2\}^{\tilde{\lambda}/2}\exp\{-\tfrac{1}{2}M\omega^2 Q_0^2 \\ &\qquad \times[\beta^{-1}(2/\hbar\omega)^2 - 2\beta/3]\}. \end{aligned} \tag{8}$$

N_0 is the unrenormalized electron density of states at the Fermi energy and e is the Euler number. Z_{el} is the partition function for the system of Cooper pairs described by H_{el}. The contributions associated with H_{osc} appear in the exponential functions of Eqs. (7) and (8). The physics of the model is contained in Eqs. (8). In the superconducting state, the local phonon vibrations are coupled to the Cooper pairs and the temperature dependence of the coupling is governed by $\Delta(T)\beta$. By decreasing the temperature the coupling increases and the hopping probability is slightly reduced. Physically, it means that the vibrational mode hardens because of the interactions with the quasiparticle excitations of the surrounding superconducting bath. However, the tendency to hop is still present at low temperatures (below 10 K) where the TS provide the relevant low-energy excitations of the system. This picture may be of interest also in connection with the mechanism of breaking of the Cooper pairs. Pair-breaking effects offer additional decay channels for the vibrational mode and the local phonon becomes anharmonic. A detailed description of $\tilde{\lambda}$ and $\tilde{p}$ as a function of the input parameters will be reported on in a next paper.[20] Here, consistent with the experimental indications, I assume that the apex oxygen phonon mode has an energy $\hbar\omega \simeq 40$ meV (Ref. 1) and that $N_0 \simeq 2$ states/eV atom.[21] The minimum of the double-well potential is chosen at $Q_0 = 0.065$ Å (Ref. 8) and the unrenormalized electron-phonon coupling is $\lambda = 7.35$ meV Å^{-1}. These parameters yield, for the O(4) stretching vibration, a dimensionless coupling constant $\Lambda \simeq 0.01$ as determined by Raman-scattering experiments.[3] Such a value lies in the relatively weak coupling range and therefore justifies the use of low order perturbation theory in Eq. (3).

From Eq. (7), one can calculate the constant-volume specific heat $C_v = C_{el} + C_{lph}$, where C_{el} is the well-known result of the BCS theory and C_{lph} originates from the local phonon and from its coupling to the superconducting bath. So far, the existence of a single Einstein oscillator has been assumed. Therefore, to allow a comparison with experimental data, a lattice contribution $C_{latt} \simeq bT^3$ should be realistically added to C_v. The coefficient b determines the zero-temperature Debye temperature $\Theta_D(0)$ of the system.[22] I fix $b = 0.02$ mJ K^{-4} g-at.$^{-1}$ which yields $\Theta_D(0) = 459.8$ K for $YBa_2Cu_3O_7$. This value is among the largest measured[23] for $YBa_2Cu_3O_{7-\delta}$ samples.

In Fig. 1, C_{latt} and C_v are separately plotted as a function of temperature. At 15 K, C_{el} is 3 orders of magnitude smaller than C_{lph} so that C_v can be identified with C_{lph} in the low-temperature range which is here considered. Three curves are shown for C_{lph} corresponding to three choices of the zero-temperature gap $\Delta(0)$. By increasing $\Delta(0)$, C_{lph} is lowered. This can be understood by noting that large gaps tend to decrease the hopping probability in Eq. (8) and therefore discourage the apex-oxygen-atom

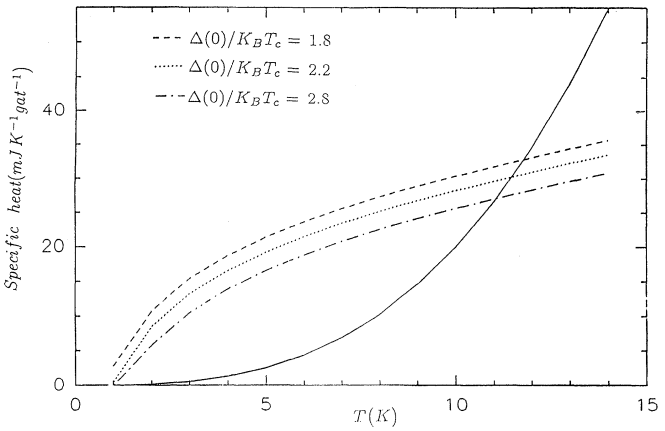

FIG. 1. Specific heat vs temperature in $YBa_2Cu_3O_{7-\delta}$ superconductor. The solid line refers to the lattice term C_{latt}. The tunneling systems contribution C_{lph} is plotted for three selected values of the zero-temperature gap $\Delta(0)$.

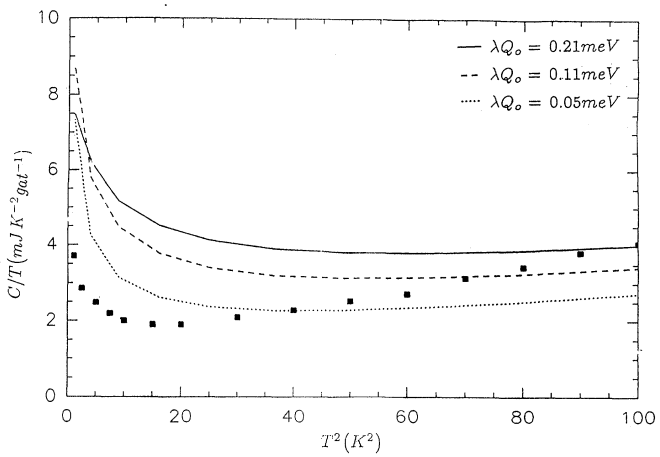

FIG. 2. Sommerfeld parameter C/T vs T^2 in $YBa_2Cu_3O_{7-\delta}$ superconductor, for three values of the input parameter λQ_0. The ratio $\Delta(0)/K_BT_c = 1.8$ is assumed. The experimental data (■) are taken from Ref. 24.

motion; the effectiveness of the tunneling systems is reduced accordingly and their contribution to the specific heat is lowered. Here I see the connection between TS and pair-breaking effects: the TS are effective in breaking Cooper pairs whose energy is comparable with a typical tunneling energy, say 10–20 meV. A fraction of electronic states may be recovered in the low-temperature superconducting state as a consequence of pairs breaking.

In this picture, BCS gap values emphasize the role of the TS but also larger gaps (see Fig. 1) may be consistent with this model. Below 10 K, the lattice term is negligible and the TS are the relevant low-energy excitations which determine the total specific heat. In Fig. 2, the ratio $\Delta(0)/K_BT_c = 1.8$ is assumed and the Sommerfeld parameter C/T ($C = C_{lph} + C_{latt}$) vs T^2 is presented for three different choices of the input parameter λQ_0. The experimental data, referring to sample *Jo* 136 of $YBa_2Cu_3O_{7-\delta}$ in Ref. 24, are also reported in Fig. 2. Although the measured specific-heat values are sample dependent and increased by impurity phases, all the $YBa_2Cu_3O_{7-\delta}$ superconductors exhibit a linear low-temperature specific heat and the majority of them also shows an upturn in C/T at very low temperatures.[23] For the moment, the available experimental data scatter too much and quantitative comparisons between theory and experiment are therefore premature. Nonetheless, it is interesting that the proposed model accounts for the size of the linear term, for realistic values of the input parameters. Also the upturn in C/T emerges at low temperatures as a result of the TS contribution.

In conclusion, a model has been formulated in which the tunneling states due to the apex-oxygen-atom motion are coupled to the order parameter of the superconducting state. The partition function of the system has been derived by using a path-integral formulation and the specific heat has been calculated for $YBa_2Cu_3O_{7-\delta}$ compounds in the low-temperature limit. A finite linear term has been found in agreement with the experimental indications. This result suggests that the low-energy excitations due to the TS may be effective in breaking a fraction of the Cooper pairs in the superconducting state. The TS can therefore be responsible for the observed linear specific heat in $YBa_2Cu_3O_{7-\delta}$ compounds. However, the relation between apex oxygen atoms and the finite linear term also should be investigated for the other families of HTSC.

Financial support from CNR (National Research Council, Italy) is acknowledged.

*On leave from Institut für Theoretische Physik, Universität Hamburg, 2000 Hamburg 36, Germany.

[1]K. A. Müller, Z. Phys. B **80**, 193 (1990), and references therein.

[2]B. Friedl, C. Thomsen, E. Schönherr, and M. Cardona, Solid State Commun. **76**, 1107 (1990).

[3]B. Golding, O. Birge, W. Haemmerle, R. J. Cava, and E. Rietman, Phys. Rev. B **36**, 5606 (1987).

[4]S. Conradson, I. Raistrick, and A. R. Bishop, Science **248**, 1394 (1990).

[5]J. Mustre de Leon, S. D. Conradson, I. Batistic, and A. R. Bishop, Phys. Rev. Lett. **65**, 1675 (1990).

[6]L. Genzel, A. Wittlin, M. Bauer, M. Cardona, E. Schönherr, and A. Simon, Phys. Rev. B **40**, 2170 (1989).

[7]R. Zamboni, G. Ruani, A. J. Pal, and C. Taliani, Solid State Commun. **70**, 813 (1989).

[8]E. Altendorf, J. Chrzanowski, J. C. Irwin, and J. P. Franck, Phys. Rev. B **43**, 2771 (1991).

[9]B. N. J. Persson and J. E. Demuth, Phys. Rev. B **42**, 8075 (1990).

[10]S. E. Stupp and D. M. Ginsberg, Physica C **158**, 299 (1989).

[11]P. W. Anderson, Science **235**, 1196 (1987).

[12]H. Fukuyama, Y. Hasegawa, and Y. Suzumura, Physica C **153–155**, 1630 (1988).

[13]C. C. Yu and P. W. Anderson, Phys. Rev. B **29**, 6165 (1984).
[14]An attempt to understand the origin of the tunneling states in HTSC has been made by Y. Bar-Yam (unpublished) in the framework of his two-component theory of superconductivity. Y. Bar-Yam, Phys. Rev. B **43**, 359 (1991); **43**, 2601 (1991).
[15]G. D. Mahan, *Many Particle Physics* (Plenum, New York, 1981).
[16]A. L. Fetter and J. D. Walecka, *Quantum Theory of Many Particle Systems* (McGraw-Hill, New York, 1971).
[17]G. Yuval and P. W. Anderson, Phys. Rev. B **1**, 1522 (1970).
[18]D. R. Hamann, Phys. Rev. B **2**, 1373 (1970).
[19]M. Sassetti, E. Galleani D'Agliano, and F. Napoli, Nuovo Cimento Soc. Ital. Fis. D **9**, 361 (1987).
[20]M. Zoli, Physica C **178**, 390 (1991).
[21]R. J. Cava *et al.*, Phys. Rev. Lett. **58**, 1676 (1987).
[22]F. W. de Wette, A. D. Kulkarni, J. Prade, U. Schröder, and W. Kress, Phys. Rev. B **42**, 6707 (1990).
[23]F. Junod, in *Physical Properties of High Temperature Superconductors II,* edited by D. M. Ginsberg (World Scientific, Singapore, 1990).
[24]D. Eckert, F. Junod, A. Bezinge, T. Graf, and J. Muller, J. Low Temp. Phys. **73**, 241 (1988).