Electronic Structure and Excitonic-Enhanced Superconducting Mechanism in $YBa_2Cu_3O_{7-\delta}$

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On the basis of the calculated electronic structure, an excitonic-enhanced superconducting mechanism is used to explain the high-T_c superconductivity in the $YBa_2Cu_3O_{7-\delta}$ system.

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The recent discovery of high-T_c superconductivity in the La-X-Cu-O [1] and Y-Ba-Cu-O [2] systems has stimulated research activity on these materials to an unprecedented scale. Experimental measurements of all kinds known to condensed-matter physicists have been applied or are being carried out on these remarkable materials. On the other hand, the theoretical understanding of these materials is rather limited. The resonant-valence-bond model[3] and the conventional BCS theory with strong electron-phonon coupling[4] have been suggested as possible explanations for the $T_c=35$ K in the $La_{2-x}Sr_xCuO_4$ system. However, these models appear to be inadequate to explain the $T_c=92$-K mechanism in the $YBa_2Cu_3O_{7-\delta}$ system. There is experimental evidence that other superconducting phases with T_c above 100 K and even near room temperature may exist.[5,6] Thus, a reliable model capable of explaining all of these phenomena in a consistent manner is urgently needed.

In this Letter, we present a plausible model based on excitonic enhancement[7,8] of the superconducting critical temperature as the basis for interpreting the band structure of $YBa_2Cu_3O_7$. In 1968, Wong and Bajaj[7] suggested a possible high-T_c superconducting mechanism for a certain class of semimetals and semiconductors with certain features in their band structure. The theory was based on the earlier work of Jerome, Rice, and Kohn,[9] and predicted the possibility of high T_c and low current density[8] in such materials. The paper received little attention, presumably because physicists at the time were skeptical that materials with such special electronic structure could exist. Even if they did, electronic-structure calculations at that time were not developed to today's sophisticated level and were unable to give accurate enough parameters to test such a theory. The basic idea of the excitonic-enhancement mechanism depends on the Coulombic binding between holes in the valence band (VB) and electrons in the conduction band (CB) being just slightly larger than the band gap for the semiconductorlike band structures.[10] This results in the lowering of the collective ground-state energy of the electronic system by the formation of partially shielded excitoniclike charged clouds which, in turn, are coupled into Cooper pairs via phonon-induced coupling. Obviously, this idea requires an accurate band structure in order to obtain the reduced masses of the electron-hole pairs and to compare the single-exciton binding energy to the band gap.

We have calculated the electronic structure of $YBa_2Cu_3O_7$ in the orthorhombic phase[11] using the self-consistent orthogonalized linear combination of atomic orbitals (OLCAO) method. Since detailed descriptions of the procedure and the results will be presented elsewhere,[12] we only outline briefly the computational procedure involved and present those aspects of the results which are relevant to our discussion of the superconducting mechanism in $YBa_2Cu_3O_{7-\delta}$. It was demonstrated recently that the OLCAO method in the local-density-functional approximation can provide accurate, state-of-the-art results for the ground-state properties of bulk crystals.[13] In the present calculation, an extended basis of functions, including the Y $6s,5p,5d$, Ba $7s$, Cu $5s,5p,4d$, and O $3s,3p$ orbitals, was employed. The local-density-functional potential with the Wigner interpolation formula for the correlation correction was used. Self-consistency in the potential was achieved after sixteen iterations using four special $\mathbf{k}$ points in the irreducible part of the Brillouin zone (BZ). The self-consistent potential and the same basis functions were then used in the direct-space approach of the OLCAO method such that the secular equation at any $\mathbf{k}$ point could be easily solved.[14]

The band structure near the Fermi level (E_F) along the symmetry axis in the basal plane of the BZ is shown in Fig. 1. The bands in the upper plane are almost identical, with very little dispersion in the z direction. These bands are all derived from the bonding and antibonding states of Cu_1-O_1 in the linear chain, the Cu_2-O_2, Cu_2-O_3 in the two-dimensional planar units, and Cu_1-O_4 along the z axis of the orthorhombic cell.[11] The symmetry of these states has been fully analyzed.[12] This band structure is similar but not identical to that of Massida *et al.*,[15] calculated with use of the linear augmented-plane-

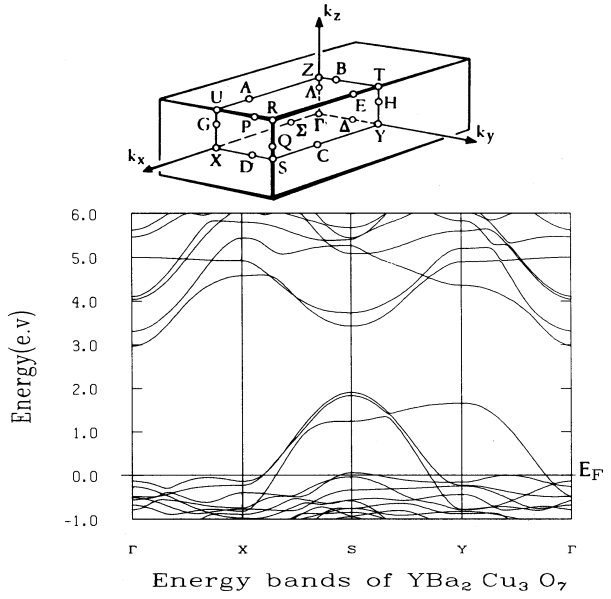

FIG. 1. Energy bands of $YBa_2Cu_3O_7$ in the vicinity of the Fermi energy, and the "semiconductor" gap. Inset: The orthorhombic BZ.

wave method, and is slightly different from that of Mattheiss and Hamann,[16] who use the same linear augmented-plane-wave method. The density of states (DOS) shown in Fig. 2 was calculated with use of the tetrahedron method based on eigenvalues at 147 *ab initio* **k** points (432 tetrahedrons) in the $\frac{1}{8}$ part of the BZ. The accuracy of BZ integration was checked by our using different ways of cutting the cubes to obtain the tetrahedrons and monitoring the shift in E_F (less than 0.0001 eV). The E_F cuts at a very sharp edge of the DOS, with an $N(E_F)$ value of 6.0 states/eV-cell. A shift in E_F as small as 0.05 eV reduces the $N(E_F)$ value to 3.8 states/eV-cell. The presence of oxygen defects, or the replacement of O with F, will raise E_F and reduce $N(E_F)$ significantly, in better agreement with experiment. A Mulliken charge analysis gives the effective charges on Cu_1 and Cu_2 as 9.8 and 9.9 electrons, respectively. A special feature of this DOS and band structure is that the empty hole region above E_F accommodates exactly four holes. Had this region been filled by exactly four additional electrons, the material would be a typical multivalley semiconductor with the top of the VB at S and the bottom of the CB at Γ. In such a scenario, the indirect gap would be 1.06 eV and the direct gap 1.54 eV at S. The electron effective masses (EM) at Γ and S are $0.49m$ and $1.17m$ (m is the free-electron mass), respectively, while the hole EM at S is $-0.57m$. The top VB at Y is very flat, resulting in a large EM of $-8.49m$ at Y. In the true superconducting phase $YBa_2Cu_3O_{7-\delta}$, we expect that the hole region is slightly reduced as the Fermi level is raised. Because of the presence of a gap immediately above the unfilled VB which contains a hole region, this metallic oxide has properties qualitatively different from normal metals which generally have an unfilled CB extending into the continuum. This means that the conduction in this material is mostly by holes instead of electrons, in agreement with Seebeck measurements on this system.[17] Such an unusual semiconductor-like multivalley band structure favors the excitonic mechanism, thereby enhancing the conventional type-I superconductivity.

In order to interpret the band structure for $YBa_2Cu_3O_7$ according to the excitonic-enhancement mecha-

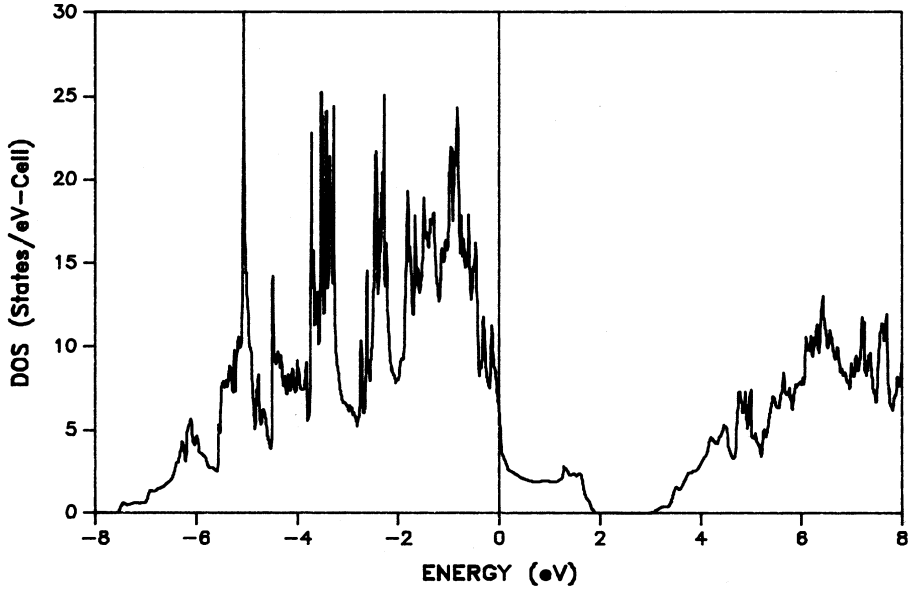

FIG. 2. Total density of states of $YBa_2Cu_3O_7$.

nism, let us go over some of the excitonic phase arguments. If we ignore phonon coupling, the excitonic wave equation[9] is given by

$$[(E_g+k^2/2\mu^*)^2+4|\Delta_{ex}|^2]^{1/2}\phi_{\mathbf{k}} = \sum_{\mathbf{p}} V(\mathbf{k}-\mathbf{p})\phi_{\mathbf{p}}, \quad (1)$$

where E_g is the band gap for a simple two-band model, μ^* is the reduced EM of the electron-hole pair, and $V(k)$ is the Coulomb potential. (The indirect-gap case has been carefully considered by Jerome, Rice, and Kohn,[9] and the result is essentially equivalent.) Now, by comparison with the elementary single-exciton wave equation

$$[k^2/2\mu^* + |E_B|]\chi_{\mathbf{k}} = \sum_{\mathbf{p}} V(\mathbf{k}-\mathbf{p})\chi_{\mathbf{p}}, \quad (2)$$

where E_B is the single-exciton binding energy, we find that the excitonic gap Δ_{ex} given by (1) vanishes when $E_g > |E_B|$. This means that the excitonic mechanism is present in the semiconductorlike structure when $|E_B| > E_g$. Kozlov and Maksimov[10] had obtained the phase diagram for both semimetallike and semiconductorlike structures. Lo and Wong[8] had further shown that if $|E_B|$ is substantially larger than E_g, the system becomes an insulator. In fact, $|E_B|$ cannot be much larger than E_g, because this will cause E_F to be lowered into the high-DOS region (see Fig. 2), raising the energy of the system which induces lattice instability. In other words, $|E_B|$ will be pinned close to but slightly less than E_g. Thus, a superconducting phase is possible in such materials *if and only if* $|E_B|$ is *slightly* larger than E_g, which is approximately given by[10]

$$|E_B| \approx hc(\mu^*/m)(1/\epsilon_0^2)\mathcal{R}, \quad (3)$$

where $\mathcal{R}$ is the Rydberg constant and ϵ_0 is the interband part of the static dielectric constant of the material. From Fig. 1, the reduced EM for the multibands ranges from $0.27m$ to $1.1m$. The positive band gaps between CB valleys and VB tops range from 1.1 to 2 eV. The larger VB EM at Y should dominate the reduced excitonic EM because the bands along YS and YT are rather flat. Hence, we can safely say that the reduced EM in $YBa_2Cu_3O_7$ ranges from $0.47m$ to $1.1m$. Requiring $|E_B|$ to be of the order E_g, so that it can have a chance to override the band gap, we can easily obtain from (3) the range of values for ϵ_0. This is illustrated in Fig. 3 where we plot μ^*/E_g vs ϵ_0. The presence of O defects or the replacement of O by F in $YBa_2Cu_3O_{7-\delta}$ will flatten the bands and increase the EM even further; thus a realistic estimation of ϵ_0 for $YBa_2Cu_3O_{7-\delta}$ ranges from 3 to 7. On the basis of the band structure and wave function of $YBa_2Cu_3O_7$, we have evaluated the interband optical-absorption curve[18] and have obtained, from the appropriate sum rule, a value of 5.43 for ϵ_0 for the case of Y being the top of the VB. The dielectric constants for Cu_2O and CuO are from 7.5 to 10, while that of ZnO is about

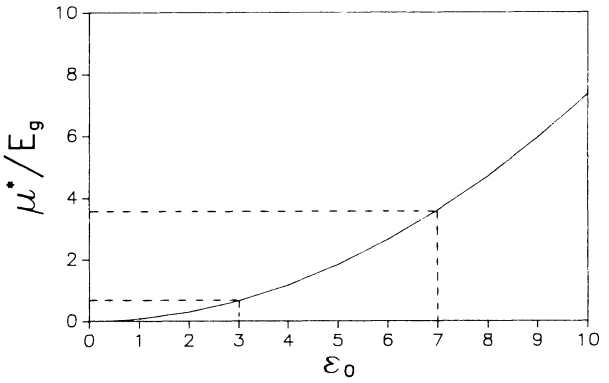

FIG. 3. Relationship of μ^*/E_g (in units of $hc/m\mathcal{R}$) to ϵ_0 for the excitonic superconductivity mechanism to work. The region within the dashed lines corresponds to the estimated value for $YBa_2Cu_3O_{7-\delta}$.

8,[19] and the value of ϵ_0 needed for the excitonic mechanism to be operational in $YBa_2Cu_3O_7$ is, therefore, not out of line. Assuming that $|E_B|$ satisfies the excitonic-mechanism requirement, Wong and Lo[7] showed that as long as a phonon-induced BCS coupling is present in such a material and a reasonably large carrier density is present (in this case the carriers are confirmed to be p-type holes), the total elementary excitation gap is given by[8]

$$\Delta_T^2 = \Delta_{BCS}^2 + \Delta_{ex}^2 = \Delta_{BCS}^2 + [|E_B|^2 - E_g^2]/4. \quad (4)$$

If $|E_B|$ and E_g are of order of 1 eV and $|E_B|$ is larger than E_g by 10^{-4} (10^{-3}) eV, an enhancement of the total excitation gap over the BCS gap of the order of 80 K (260 K) is expected. Thus, it is possible to obtain room-temperature T_c with such an enhancement mechanism. The possible price to pay is a reduction in the critical current, because on the basis of a self-consistent field formalism, one finds[7] that the current for such a superconducting system is reduced by a factor roughly proportional to $[\Delta_{BCS}/\Delta_T]^2$.

Now let us review some recent experimental evidence which supports the excitonic-enhancement model presented above: (1) The experimental fact that there exists a somewhat large and varying range of T_c in these superconducting materials is related to the sensitive dependence of T_c on $|E_B| - E_g$. (2) A recent positron-lifetime measurement[20] on various $YBa_2Cu_3O_{7-\delta}$ samples clearly indicates an increased annihilation rate below T_c. This result supports our model because below T_c excess electrons are available in the excitonic-superconducting composite state, while above T_c no such electrons are present. (3) The excitonic mechanism is also applicable to the $La_{2-y}X_yCuO_4$ system. In that case, the material has a semimetallike electronic structure[21] and the excitonic mechanism is present even when $|E_B|$ does not override the band overlap E_g.[10] Since the band overlap in semimetals decreases with an increase of

pressure,[9] we expect Δ_{ex} and, hence, T_c to be increased with increased pressure, in agreement with experiment.[22] In $YBa_2Cu_3O_{7-\delta}$, a semiconductorlike gap exists and so very little pressure effect on T_c should be observed.[23] (4) Since the bands near the gap are all derived from Cu and O orbitals with no component from Y or Ba, replacement of Y by other rare-earth elements R will not change T_c. This is in agreement with extensive measurements on $RBa_2Cu_3O_{7-\delta}$ systems.[24] (5) The absence of an isotope effect in the Y-Ba-Cu-O system[25] renders a nonphonon mechanism, such as the one suggested in this Letter, extremely attractive. (6) Far-infrared reflectance data[26] show a plasmon-type edge (starting at 60 cm^{-1}) which completely disappears at high temperature. This is indicative of the possible existence of excitonic-related energy levels of the order of $|E_B| - E_g$. (7) The recent discovery of superconductivity at 155 K in the Y-Ba-Cu-F-O system[6] further supports our argument. Evidently, the replacement of O by F raises E_F, makes the band structure more semiconductorlike, and further increases the exciton EM, thus favoring the excitonic-enhancement mechanism. The role of the O vacancy in the Y-Ba-Cu-O system may be similar.

In conclusion, we have attempted to explain the high-T_c superconductivity by using an excitonic-enhancement model based on parameters obtained from accurate electronic-structure calculations. We further speculate that materials with T_c near room temperature should have a semiconductorlike band structure with a band gap of order of 1 eV and large electron and hole effective masses. The interband portion of the static dielectric constant should be in the range of 2–10 with a substantial density of charge carriers in its normal phase.

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