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Direct evidence for the quantum interlayer defect-assisted percolation model of cuprate high-T_c superconductivity

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Recent Raman and infrared data are used to argue that in $YBa_2Cu_3O_7$ metallic paths are not confined to Cu planes but must cross Ba planes at some points, possibly because of the presence of defects such as oxygen vacancies near those points.

I. INTRODUCTION

Many theoretical mechanisms have been proposed to explain the anomalously high T_c's found in layered cuprate superconductors. Many of these involve exotic models, in contrast to the conventional BCS theory based on attractive retarded electron-phonon exchange. In some cases phonons are replaced by other bosons such as magnons or excitons, while in still more exotic models only static repulsive interactions are invoked. In almost all models the superconductivity is supposed to be a characteristic feature of metallic CuO_2 planes.

In a recent book[1] I have argued that all the exotic (magnon, exciton, etc.) models are inconsistent with experiment, and that only the attractive electron-phonon interaction deserves close attention. However, because self-consistent field calculations show[2] that given the electronic structure of the ideal crystal the electron-phonon interaction does not yield sufficiently high T_c's, some modification of standard BCS theory is required. I argued that this modification occurs primarily in the Bloch description of the normal metallic state at high T. While the BCS theory correctly describes the phase transition from the normal state to the superconducting state, when the normal state itself is quite different from that of a normal metal (such as Pb), standard procedures for calculating electron-phonon interactions are no longer adequate.

The feature of the electronic normal state of these layered compounds, which distinguishes them from ordinary metals, is that the electrons are confined to cuprate planes. One of the central conjectures of localization theory[1,3-5] is that in the presence of disorder provided by random point defects (such as oxygen vacancies), all one-dimensional ($d=1$) systems are insulating, while $d=3$ systems can be metallic. The case $d=2$, appropriate to cuprate planes, is marginal and I assume not metallic in the absence of interplanar interactions.

While it is possible in principle that tunneling is responsible for interplanar currents, in practice it seems almost certain that in these highly defective crystals the Fermi energy will be pinned by defect states,[6] and that some of these defect states will function as interplanar electrical connectors. These points are discussed at greater length in my book.[1]

II. FANO INTERFERENCE IN RAMAN SCATTERING: LOW-FREQUENCY MODES

It might seem that there is no way to trace out, on an atomic scale, the paths followed by metallic electrons at the Fermi energy. This is certainly true if we confine ourselves to magnetoelectrical measurements. However, Raman scattering and infrared absorption provide extremely powerful probes which can identify metallic electrons interacting with atoms dominating specific optically active normal modes of vibration. The most interesting of these interactions is the Fano effect, which is an interference effect involving electron wave-function amplitudes of definite symmetries. Nearly always, a discrete mode interferes with a continuum background. For the most part the details of the Fano effect are completely understood only in the case of atomic spectra,[7] but similar effects have been recognized in the optical spectra of semiconductors where exciton resonances interfere with an interband continuum.[8]

In the present case the discrete state is provided by a phonon, while the continuum states are probably the metallic states themselves. In simple models where metallic conductivity occurs in the $Cu(2)O_2$ planes only, observation of a Fano effect then enables one to assign a phonon band to a normal mode centered on either Cu(2) or the oxygen atoms in the $Cu(2)O_2$ plane. This was the procedure followed by Cooper *et al.*[9] when they observed Fano interference between phonon bands at 116 and 340 cm^{-1} and a background continuum. Identification of these bands is made easier because of symmetry considerations and because a remarkably successful lattice vibration model is available.[10] The 340-cm^{-1} band is confidently assigned to z-polarized vibrations of the O atoms in the $Cu(2)O_2$ plane, while the 116-cm^{-1} band is assigned either to z-polarized Cu(2) modes or to z-polarized Ba modes. Because of Fano interference the former was selected.[9] There is, however, another band at 140 cm^{-1}, which was, therefore, assigned to the latter.

These assignments of the low-frequency modes can be tested[11] by replacing Ba by Sr. The result is that the 140-cm^{-1} band broadens, but does not move. This means that it cannot be associated with the Ba site, because it should shift to higher frequencies with decreasing mass in

Sr compared to Ba. The 116-cm^{-1} band "disappears," or more likely, shifts to form a single unresolved but broadened band at 140 cm^{-1}. Thus the original 116-cm^{-1} band, with its Fano interference, must be assigned to the Ba mode.

III. PARADOXICAL FANO INTERFERENCE

Thus, we have arrived at the paradoxical result that the metallic electrons, supposedly confined to the $Cu(2)O_2$ and possibly the Cu(1)O planes, interfere strongly with a normal mode centered on the Ba atom. However, this result loses it paradoxical character, and actually becomes a natural result, in the context of the quantum percolation model discussed in Ref. 1, p. 150. Briefly, in this model most of the states near the Fermi energy in the Cu planes are not metallically conductive. (They may still exhibit hopping conductivity.) A few are metallic, but this is the case only because of the existence of interplanar electrical connections associated with defects. [As a concrete example, these defects could be oxygen vacancies $O^{\square}$ in Cu(1)-O chains. An even more interesting possibility, already mentioned in Ref. 1, is that some of the Ba^{2+} sites might be occupied by $Y^{(2+\delta)+}$, where $\delta < 1$. In this case the partial density of states at these sites $N_{Ba}(E)$ would certainly have $N_{Ba}(E_F) > 0$.] One could also imagine that because of disorder there are Tauc-Nagel gaps[12] at E_F for the Cu planar states, except for a few states near E_F which follow three-dimensional paths which pass through Ba atoms associated with the defects.

This percolation model has some very useful features. When there are only a few defects, there are also only a correspondingly few metallic states. Thus, it is possible to have a large Fano interference, as is actually observed,[9] with an antiresonance canceling approximately half of the (probably quite weak) continuum background near 125 cm^{-1}. (Ideally the antiresonance is perfect, but in real solids inhomogeneous broadening and sources of damping other than decay into the continuum always produce background absorption or scattering.[8] Thus, an interference effect which reduces the background by a factor of 2 at the minimum is indeed large.)

IV. OTHER EVIDENCE FOR INTERLAYER METALLIC PATHS

The Fano interference of the Ba-centered 116-cm^{-1} mode is not the only evidence for interlayer metallic paths. While much attention has been paid to the 5-cm^{-1} softening of the 340-cm^{-1} Raman band because of its certain assignment to the $Cu(2)O_2$ planes, below T_c there is also a 10-cm^{-1} (that is, twice as large) softening of the 320-cm^{-1} infrared-active mode.[13] The assignment of this mode is much less certain, but in the highly successful theoretical model[10] it is assigned to x-polarized vibrations of the O atoms coplanar with Ba. These are the oxygen atoms bridging the Cu(1) and Cu(2) atoms.

Reproducible phonon fine structure has been observed[14] in the tunneling characteristics of $Bi_2Sr_2CaCu_2O_8$-GaAs junctions. This structure is accompanied by weaker but also reproducible multiphonon fine structure, which is explained as due to interlayer multiphonon interactions.[15] The present model provides an explicit microscopic mechanism for such interlayer interactions. If they are indeed mediated by $Y_{Ba}^{(2+\delta)+}$, as mentioned above, then the small size of Y compared to Ba should automatically produce a strongly anharmonic, flat-bottom atomic vibrational potential.[16]

Some materials scientists may be disturbed by the idea that defect-mediated interplanar coupling should be essential to high-T_c superconductivity. Would this not produce substantial variations in T_c depending on sample processing? In fact, such variations are observed, and often only data on samples with the highest T_c's are reported. In addition, percolative high-T_c dendritic paths embedded in a lower-T_c matrix are necessary to explain many experiments, as discussed in Chap. X of Ref. 1. Thus, the present model is fully consistent with experiment, and in this respect is to be preferred greatly over exotic models of hypothetically homogeneous materials.

In conclusion, Raman and infrared spectra show that the metallic electron paths are not confined to the Cu planes, but instead must cross the Ba planes as well. In the ideal crystal, however, these planes are semiconductive[17] with an energy gap of order 2 eV. Therefore, we conclude that the observed behavior results from defects which generate metallic states in some parts of the Ba planes. These Ba-plane metallic states appear to be essential to forming metallic and superconductive states in $YBa_2Cu_3O_{7-x}$.

Note added. After the bulk of this paper was completed, softening of the 464-cm^{-1} mode in $Bi_2CaSr_2Cu_2O_8$ was reported.[18] This mode is assigned to O_z atoms not in the CuO_2 planes which are somewhat similar to the O atoms coplanar with Ba mentioned above in connection with infrared-mode softening. Thus, while there are some similarities between phonon softening in $YBa_2Cu_3O_7$ and $Bi_2CaSr_2Cu_2O_8$ (the 340 cm^{-1} and 280 cm^{-1} modes, respectively), there are also differences. The differences appear to involve atoms *not* in the CuO_2 planes, and are thus exactly the kind of differences predicted by the present model.

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