Formation, Motion, and High-Temperature Superconductivity of Large Bipolarons

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Although small (spatially compact) bipolarons readily localize, large bipolarons (like large polarons) can be mobile. As such, large bipolarons are a suitable basis for bipolaronic superconductivity. However, large bipolarons can only form in multidimensional ionic solids if the static dielectric constant greatly exceeds twice the optical dielectric constant. The formation and normal-state and superconducting properties of large bipolarons appear consistent with observations of the high-temperature superconductors.

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The discovery of very-high-temperature superconductors[1-3] has rekindled interest in the idea of bipolaronic superconductivity.[4] In this approach, carriers are presumed to bind together in singlet pairs within the potential wells produced by the atomic displacements that the carriers' presence stabilizes. A necessary condition for bipolaronic superconductivity is that the bipolarons be mobile.

The energy of a carrier generally depends upon the positions of the atoms with which it has contact. This effect produces a short-range electron-lattice interaction. It has been shown that with a short-range electron-lattice interaction, the polaronic ground state is always *small* in electronic systems of two or three dimensions.[5,6] That is, the local states from which a Bloch-type small-polaronic band is composed are severely localized. The coherent motion of polaronic carriers requires the collateral tunneling of the electronic carriers and their atomic displacement patterns.[7] As a result of the large atomic displacements that typify severely localized states, small (bi)polarons are very massive. The coherent motion of such small and heavy particles is easily disrupted by even very modest disorder. Therefore, consistent with empirical evidence, *small* polaronic states are generally viewed as *localized* rather than mobile.[8-11] Thus, although small bipolarons can be formed with a short-range electron-lattice interaction, small bipolarons do not provide a suitable basis for bipolaronic superconductivity.

In ionic systems, an additional component of the electron-lattice interaction arises from the electrostatic interaction of an electronic carrier with the relative displacements of the solid's anions and cations. Being of Coulombic origin, this component of the electron-lattice interaction is of long range. Considering only the effect of this long-range electron-lattice interaction, one finds that the (Fröhlich) polaron is *large* rather than small.[6,12] Concomitantly, large polarons are generally quite mobile. However, classically, the long-range atomic displacements of the large polaron just reduce the effective Coulomb repulsion between a pair of large polarons with charge e separated by the distance s from $e^2/\epsilon_\infty s$ to $e^2/\epsilon_0 s$, where ϵ_∞ and ϵ_0 are the high-frequency and static dielectric constants, respectively. Thus, large polarons will not classically bind to form large bipolarons.

Large bipolarons are not formed with either a short-range or a long-range electron-lattice interaction. Nonetheless, we have now shown that large bipolarons *can* be formed with the *combined* presence of sufficiently strong short- and long-range components of the electron-lattice interaction.[13] In essence, the extra binding provided by the short-range component of the electron-lattice interaction when the charge distributions of two large polarons overlap stabilizes the *large bipolaron.* In this Letter only the essential physics of the formation, motion, and superconductivity of large bipolarons is described since a lengthy and detailed account has been prepared.[13] Here, in addition, it is noted that a number of the normal-state and superconducting properties of high-temperature superconducting materials can be understood as manifestations of a collection of large bipolarons.

The formation of a *large* bipolaron requires an exceptional confluence of circumstances. First, the coupling constant associated with the long-range component of the electron-lattice interaction, α, must be sufficiently large, $\alpha \gg 1$. This means that the high-frequency dielectric constant must be modest enough that the long-range Coulombic fields are not strongly screened by the electronic polarization. A more demanding (rarely satisfied), but still not sufficient, condition is that the displaceability of the solid's ions be sufficiently large that a large bipolaron with two carriers centered at the same site be a bound state, $\epsilon_0 \gg 2\epsilon_\infty$.[13] In insulating La_2CuO_4 the static dielectric constant is ≈ 50.[14] The high-frequency dielectric constants in the CuO_2-based materials are about 4.[15] With the bare electronic mass being the free-electron mass and an optical-phonon temperature of even 900 K, $\alpha \approx 5$. Clearly, $\epsilon_0 \gg 2\epsilon_\infty$. Thus, there are indications that these dielectric criteria are satisfied in high-temperature superconducting materials.

The remaining conditions for the formation of a large singlet bipolaron impose constraints on the strength of

the short-range component of the electron-lattice interaction and on the electronic transfer energy J. If the short-range component of the electron-lattice interaction is too weak, the interpolaron repulsion of the Fröhlich large polarons will prevail. Alternatively, if the short-range component of the electron lattice is too strong, the large bipolaron will collapse to be an immobile small bipolaron. Thus, bipolaron formation requires that the electronic parameters fall within a bracketed domain.

This domain of electronic parameters opens and grows progressively as $\epsilon_0/2\epsilon_\infty$ increases beyond unity. In particular, for given values of the dielectric constants and the short-range component of the electron-lattice interaction, these restrictions impose upper and lower limits on J, $J_{\max}$ and $J_{\min}$. Furthermore, the regime of acceptable values of J is wider for electronically quasi-two-dimensional systems than for three-dimensional systems. In particular, $J_{\max}$ is less for a three-dimensional electronic system than for a quasi-two-dimensional electronic system. For example, with comparable strengths for the long- and short-range components of the electron-lattice interaction, $J_{\max}$ is reduced in half in passing from a quasi-two-dimensional system to a three-dimensional electronic system. Furthermore, in such a two-dimensional system, $J_{\max}=4E_b(1+f)$, where E_b is the small-polaron binding energy (a measure of the strength of the short-range component of the electron-lattice interaction) and f is a function of the dielectric constants.[13] Assuming a two-dimensional system (four nearest neighbors), $E_b=0.2$ eV, and (with $\epsilon_0/\epsilon_\infty=5$) $f=0.6$, one has a maximum bandwidth of $8J_{\max}=10$ eV. Thus, systems that have $\epsilon_0/2\epsilon_\infty \gg 1$ and are electronically quasi-two-dimensional systems are prime (but not exclusive) candidates for the formation of large singlet bipolarons.

One hallmark of a large bipolaron is its large effective mass, $M_{\rm bp}$. Furthermore, because of its large size and large mass, a large acoustic bipolaron is not effectively scattered by the long-wavelength acoustic phonons with which it interacts. Thus, a large bipolaron is also characterized by a long scattering time τ.[16] The long scattering time and the large effective mass compensate one another to yield mobilities that are often smaller though comparable to those of nonpolaronic carriers.[16] In addition, the scattering rate τ^{-1} for a large bipolaron is simply proportional to the temperature, provided that the thermal energy exceeds the energy of an acoustic phonon with a wavelength comparable to twice the large bipolaron's diameter.[16] Thus, the mobility of a large bipolaron is inversely proportional to temperature except at very low temperatures. A further indication of the charge carriers having a polaronic character is the collateral decrease in the carrier's effective mass and scattering time at frequencies in excess of acoustic-phonon frequencies. Such effects have been reported in the normal state of the superconducting materials.[17]

Introducing polarons into a solid typically alters the solid's vibrational properties. Induced ir absorption has been observed to accompany the (optically induced) production of charge carriers in insulating La_2CuO_4 and $YBa_2Cu_3O_{6.25}$.[18] These observations, along with inferred carrier-induced local structural transitions and large estimated carrier masses ($24m_e$ and $11m_e$ per elementary electronic charge, respectively, in these two materials), indicate that the carriers form either large polarons or large bipolarons.[18]

The superconducting transition temperature for bipolaronic superconductivity is the temperature of the Bose-Einstein condensation.[4] Even for a gas of noninteracting bosons of isotropic effective mass $M_{\rm bp}$ and density $n_{\rm bp}$ one can readily envision a high transition temperature, $T_c=3.3\hbar^2 n_{\rm bp}^{2/3}/M_{\rm bp}k_B$, where k_B is the Boltzmann constant.[19] For example, if $M_{\rm bp}\approx 20m_e$ and $n_{\rm bp}=10^{21}$ cm^{-3}, then $T_c=117$ K.

It is important to note that, while isolated carriers may pair to form large bipolarons, bipolaron formation will be precluded if the carrier density becomes too large. In particular, with a sufficiently large carrier density (1) atomic-displacement patterns surrounding different bipolarons will interfere with (and tend to cancel) one another, and (2) the carriers will screen out the long-range portion of the electron-lattice interaction.[13] Thus, the bipolarons will tend to be destabilized as the carrier density rises. Ultimately, the density of bipolarons $n_{\rm bp}$, and concomitantly T_c, will fall with increasing carrier density. This dependence of T_c on carrier density has been reported in the high-temperature superconductors.[20]

For definitiveness, a more detailed view of the CuO_2-based materials and their large bipolarons is now adopted. First, the CuO_2-based materials are modeled as a three-dimensional deformable medium. Second, the large bipolaron is taken to have a morphology that depends upon the number of contiguous CuO_2 planes. Specifically, a quasi-two-dimensional singlet large bipolaron on an isolated CuO_2 sheet has a disklike morphology with an in-plane radius $R_{\rm bp}$ that exceeds several interatomic separations and a thickness equal to the extent of the electronic wave function perpendicular to the CuO_2 sheet. Moreover, if several CuO_2 sheets are contiguous (as are pairs of sheets in the 1:2:3 materials), the thickness of the bipolaron, t, is the net width of the contiguous CuO_2 sheets. A disklike morphology prevails provided that $t<2R_{\rm bp}$. Third, the carrier density of this material is viewed as sufficiently small to support a collection of large bipolarons. For example, in $La_{1.85}Sr_{0.15}CuO_4$ one hole is nominally found within 15% of the unit cells. With half of the oxygen atoms of a unit cell lying within a CuO_2 sheet and with holes pairing to form bipolarons, less than 4% ($\approx \frac{15}{4}$%) of the oxygen sites in the CuO_2 sheets are centers for a large bipolaron. Finally, with the holelike carriers primarily occupying bonding orbitals on oxygen atoms,[21] the short-range component of the electron-lattice interaction is taken to primarily involve displacements of the Cu atoms that are the

nearest neighbors of the oxygen atoms of the CuO_2 sheets. Since the Cu atoms are the heavy atoms of the sheet, this interaction is essentially with acoustic phonons.

The mass of these large bipolarons can be calculated within the adiabatic approach. That is, electronic carriers can only move when the atomic-displacement pattern associated with their self-trapping changes. Thus, the effective mass of the large bipolaron is dependent on the mass of the solid's atoms and the extent to which the atoms must move to shift the carrier a given distance. An especially interesting situation arises when the dominant contribution to the large bipolaron's effective mass comes from its (deformational-potential-like) short-range interaction with acousticlike atomic displacements. Then the effective mass of a disklike large bipolaron is isotropic but dependent on the bipolaron's shape,[13]

$$M_{\rm bp} \propto c_s^{-2} E_b (a/R_{\rm bp})^2 (a/t) , \quad (1)$$

where c_s is the speed of sound and a is an interatomic separation.

This effective mass of the bipolaron then depends upon the mass of the solid's atoms only through the dependence of the bipolaron's effective mass on the square of the material's sound velocity c_s: $M_{\rm bp} \propto c_s^{-2}$.[13,16] Since c_s^{-2} is proportional to the solid's density, its fractional change with isotropic substitutions is simply the fractional change of the mass of the atoms of a unit cell, $\Delta M_{\rm uc}/M_{\rm uc}$. Then, even for complete replacement of ^{16}O by ^{18}O in the CuO_2-based materials, the bipolaron's effective mass, and hence T_c, will only be weakly affected by isotopic substitutions for the solid's oxygen atoms; i.e., then $\Delta T_c/T_c = -\Delta M_{\rm bp}/M_{\rm bp} = -\Delta M_{\rm uc}/M_{\rm uc} \approx -0.02$.

The effective mass of such a large bipolaron also varies inversely as the volume of the large bipolaron: $M_{\rm bp} \propto 1/R_{\rm bp}^2 t$. Therefore, the maximum T_c increases with the thickness of a disklike bipolaron (comparable to the net width of contiguous CuO_2 sheets), so long as $t < R_{\rm bp}$. When $t \approx 2R_{\rm bp}$, the morphology of the large bipolarons becomes more like a spheroid than a disk. Then, depending on the electronic parameters, further additions of contiguous CuO_2 sheets will produce either no further increase in the maximum T_c or a loss of superconductivity.

Summarizing, it has been shown that *large* singlet bipolarons can exist. However, their formation is contingent on a sufficiently strong long-range component of the electron-lattice interaction and on a static dielectric constant that greatly exceeds the high-frequency dielectric constant. Furthermore, the formation of large bipolarons is favored in systems of low electronic dimensionality.

Large bipolarons have distinctive normal-state transport properties. Namely, large bipolarons are characterized by itinerant-type mobilities, albeit with large effective masses and long scattering times. The effective masses and scattering times fall as the frequencies of ac fields reach acoustic-vibrational frequencies. The resulting itinerant mobility for an (acoustic) bipolaron is proportional to temperature except at very low temperatures.

Reasonable values of the mass and density of large bipolarons yield transition temperatures for the superconductivity of *large* bipolarons (Bose-Einstein transition temperatures) that are comparable to the high observed values of T_c. Furthermore, with the bipolaron's effective mass being dominated by the short-range electron-lattice interaction with acoustic phonons, the superconducting transition temperature has only a weak dependence on isotopic substitutions for the oxygen atoms. In addition, the disklike large singlet bipolarons envisioned to characterize the CuO_2-based materials will have a mass that varies inversely with the net thickness of contiguous CuO_2 sheets. As a result, the maximum T_c should rise with the number of contiguous CuO_2 sheets until the bipolarons begin to resemble spheroids, at $t \simeq 2R_{\rm bp}$. Finally, superconductivity will be lost when the carrier density becomes too great to support bipolaron formation. All these features are in general accord with observations on the CuO_2-based materials.

Finally, it should be mentioned that, although systems of lower electronic dimensionality are favorable for the formation of large bipolarons, three-dimensional electronic systems are still possible. The superconductors based on $BaBiO_3$ may be examples of these.

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