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ON THE MECHANISM OF HIGH-TEMPERATURE SUPERCONDUCTIVITY IN Ba–La(Y)–Cu–O TYPE SYSTEMS

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An extended molecular crystal model is put forward for the mechanism of high-temperature superconductivity in the typical perovskite-like structures $Ba_xLa_{2-x}CuO_4$ and $Ba_2YCu_3O_{6.5+1.5x}$, $0 < x \lesssim 0.4$. It is shown that the Jahn–Teller effect of the Cu^{2+} cation brings about an attractive pairing interaction between the hybridized $3d^9$ electron states. The critical temperature is estimated and compared with the available experimental data.

1. INTRODUCTION

ON MACROSCOPIC scale the high-temperature superconductivity in the recently discovered Ba-La-(Y)-Cu-O type systems [1–7] seems to be associated with percolative [1], superconductive-glass [8] and interfacial effects [2]. One widely agrees however that the microscopic mechanism of superconductivity is located on the perovskite-like structures $M_xLa_{2-x}CuO_4$ and $Ba_2RCu_3O_{6.5+1.5x}$, $0 < x \lesssim 0.4$, where M = Ba, Sr or Ca and R = Y or lanthanide rare-earth elements (or some of their combinations as, for example, $R = Y_{0.75}Sc_{0.25}$ or even $Ba_{1.5}Sr_{0.5}YCu_3O_{6.5+1.5x}$ [6]). For the sake of specificity we restrict the present discussion to $Ba_xLa_{2-x}CuO_4$ and $Ba_2YCu_3O_{6.5+1.5x}$, $0 < x \lesssim 0.4$, although the results hold for the whole class of compounds given above. The former is a (tetragonal or orthorhombically distorted) layered-like structure of the K_2NiF_4 type [9, 10] which consists of alternating Cu–oxygen and (corrugated) (Ba, La)–oxygen layers; the Cu–oxygen layers are rather well separated by an average distance of 6–7 Å and screened by the (Ba, La)–oxygen layers. The latter structure ($Ba_2YCu_3O_{6.5+1.5x}$) is a succession of three Cu–oxygen layered assemblies of thickness ~ 8 Å disrupted by Y layers [7, 11]; corrugated Ba–oxygen layers separate the Cu–oxygen layers within each assembly. The middle Cu–oxygen layer in each assembly could also be viewed as consisting of oxygen-deficient octahedra, separated from the adjacent Cu–oxygen layers by Ba planes. All this experimental evidence suggests a schematic one-layer model consisting of a two-dimensional network of copper cations, each copper cation being coordinated by four in-layer and two off-layer oxygen anions (not all the oxygen positions being necessarily occupied). According to the above stoichiometry the average valence of the copper cation is $z = 2 + x$. One can see that substituting Ba for La or, equivalently, lowering the oxygen deficiency the copper valence state changes from Cu^{2+} to Cu^{3+}, the ratio Cu^{2+}/Cu^{3+} being recognized as essential for the superconducting properties of these compounds.

Electronic structure studies [10, 12, 13] strongly emphasized the two-dimensional character of the electronic bands. The orbital degeneracy of the Cu^{2+}-$3d^9$ configuration is removed by the elongated Cu–oxygen octahedra in the La–compounds, the Cu–$d_{x^2-y^2}$ orbital being left as the only partially occupied orbital. This latter orbital strongly overlaps with the four surrounding p orbitals of the in-layer oxygen anions that point towards the nearest-neighbour copper cations. A similar situation occurs in the Y-compounds, although here the Cu–oxygen octahedra seems to be rather flattened than elongated along the perpendicular-to-layer axis [14]. The corresponding electronic structure can therefore be described by a tight-binding model that effectively accounts for the electron transfer between the nearest-neighbour copper cations [15]. The Hubbard hamiltonian

$$\mathscr{H}_{\mathrm{el}} = t_0 \sum_{\langle ij \rangle \sigma} c_{i\sigma}^+ c_{j\sigma} + U \sum_{i\sigma} n_{i\sigma} n_{i-\sigma}, \qquad (1)$$

is assumed to describe the in-layer electron motion, where $c_{i\sigma}^+$ ($c_{i\sigma}$) is the creation (destruction) operator of the hybridized Cu^{2+}-$3d^9$ electron state on the i-the copper site, the summation is extended to the nearest-neighbour copper cations in a two-dimensional network of N copper sites and the on-site energy is put equal to zero. The valence state of the i-th copper cation may be written as $z_i = 3 - \Sigma_\sigma n_{i\sigma}$, where $n_{i\sigma}$ is the occupation number of the electron state with spin σ located on the i-th site. Requiring the average valence to be equal to $z = 2 + x$ (according to the given stoichiometry) one obtains

$$\sum_{i\sigma} n_{i\sigma} = N(1 - x), \tag{2}$$

which tells that the average electron occupancy per site can not exceed unity ($0 < x \lesssim 0.4$). It follows that the configurations with double electron occupancy are highly unlikely, especially if the bare Hubbard repulsion acquires large values. Consequently, we shall assume the renormalized Hubbard's U in (1) be much less effective than the covalent interactions with the oxygen anions and correlations which will be discussed below [16]. This point is further supported by the fact that there are only two valence states of the copper cation Cu^{2+}/Cu^{3+} and an antiferromagnetic ordering has been reported for these compounds [17]. The transfer integral t_0 should acquire small values in view of the low electron mobility in these systems. This is consistent with the narrow-band electron localization which is presumably responsible for the increase of electrical resistivity observed in some of these compounds just above the critical temperature. The two-dimensional character of the present one-layer model agrees with the experimentally observed ineffectiveness of the R-layers [6, 7] and anisotropy of the critical magnetic field [18].

2. EXTENDED MOLECULAR CRYSTAL MODEL

A strong electron-lattice coupling is expected in these compounds as a consequence of the oxygen-displacive modes [19], low electron mobility and carrier concentration ($\sim 10^{21-22}\,\mathrm{cm}^{-3}$) which is unable to shield the optical phonons [20]. Electron band calculations [12, 13] suggest a strong coupling between electrons and giant Kohn anomaly phonons [21] (related to a possible Peierls-type instability of the Fermi surface) corresponding to breathing modes of the in-layer oxygen anions. On the other hand the displacement of the off-layer oxygen anions, leading to elongated or flattened Cu–oxygen octahedra, is well documented in these compounds [10, 14, 22]. It is well-known [22], for example, that the distances between Cu^{2+} and the off-layer oxygen anions in La_2CuO_4 are much larger (2.4 Å) than the in-layer Cu–oxygen distances (1.9 Å). A similar situation has been reported [14] for the Y-compounds, where the copper cations located at the ends of the unit cells are surrounded by flattened oxygen octahedra while the middle copper cations are coordinated by elongated square oxygen pyramids. Distinct optical phonon activity has been associated with both in-layer and off-layer oxygen modes [23].

The strong coupling between electrons and the oxygen-displacive modes has been discussed in various contexts [24] and, in fact, it can always be related to the Jahn–Teller effect of the Cu^{2+} cation [25]. Indeed, it is well-known [26, 27] that Cu^{2+} is a typical Jahn–Teller cation which distorts the copper-oxygen bondings and lowers the electronic energy level, yielding the so-called Jahn–Teller polaron. The various types of oxygen displacements in octahedral coordination have been studied to a large extent in perovskite-like structures [28]. For the sake of simplicity the present discussion is only limited to one oxygen coordinate Q_i (conjugate momentum P_i) related to the i-th Cu–oxygen complex [29]. The extended molecular crystal model [25, 30] includes both the on-site (g_0) and nearest-neighbour (g_1) linear Jahn–Teller coupling. The dynamical oxygen-lattice modes are neglected since the corresponding coupling seems to be very weak [23]. The coupling constant g_1 is lesser than g_0 when an off-layer oxygen is involved and of the same order of magnitude as g_0 for the Cu-in-layer oxygen bond stretching modes. The corresponding model hamiltonian may be written as

$$\mathscr{H} = \mathscr{H}_{\mathrm{el}} + \sum_i (P_i^2/2M + \tfrac{1}{2} M\omega^2 Q_i^2) - g_0 \sum_{i\sigma} Q_i n_{i\sigma} - g_1 \sum_{\langle ij\rangle\sigma} Q_i n_{j\sigma}, \tag{3}$$

where $\mathscr{H}_{\mathrm{el}}$ is given by (1), M is the oxygen mass and ω is a characteristic frequency of the oxygen-displacive modes. By making use of the canonical transformation generated by

$$i(M\omega^2)^{-1}(g_0 \sum_{i\sigma} P_i n_{i\sigma} + g_1 \sum_{\langle ij\rangle\sigma} P_i n_{j\sigma}),$$

one can shift the lattice coordinates to new equilibrium positions and obtain the effective Hamiltonian

$$\tilde{\mathscr{H}} = t \sum_{\langle ij\rangle\sigma} c_{i\sigma}^{+} c_{j\sigma} - J \sum_{\langle ij\rangle\sigma\sigma'} n_{i\sigma} n_{j\sigma'} + \tilde{U} \sum_{i\sigma} n_{i\sigma} n_{i-\sigma} - 3E_{\mathrm{JT}} \sum_{i\sigma} n_{i\sigma} + \sum_i (P_i^2/2M + \tfrac{1}{2} M\omega^2 Q_i^2), \tag{4}$$

where $t = t_0 \exp[-3(1 + zg_1^2/g_0^2)\,(E_{\mathrm{JT}}/\omega)]$ (z being the nearest-neighbour number), $J = 6(g_1/g_0)E_{\mathrm{JT}}$, $\tilde{U} = U - 3E_{\mathrm{JT}}$ and $E_{\mathrm{JT}} = g_0^2/6M\omega^2$ is the Jahn–Teller stabilization energy [27]. An additional term of the order $(g_1^2/g_0^2)E_{\mathrm{JT}}$ has been neglected in (4); it represents an attractive interaction between the electron states of the first coordination sphere and, depending on the particular two-dimensional lattice, its effect is a further increase of J, reduction of $\tilde{U}$ and an additional next-nearest-neighbour attractive interaction. The "dressed" electron-transfer integral t has been obtained by averaging over the phonon vacuum, a satisfactory approximation for a wide range of temperatures. A complete decoupling of the electron and lattice degrees of freedom has thereby been obtained in the effective Hamiltonian (4). It follows that the main effect of the electron-lattice interaction included in (3) is a narrowing of the electron band (as in the case of the small polaron [30]) and an attractive interaction between the electron states which could lead to superconductivity.

It is worth emphasizing that the canonical transformation which takes (3) into (4) acts in a close manner, *i.e.* $\tilde{H}$ is not a perturbation series in the coupling constant. This means that one may use (4) even for rather larger values of the coupling parameter J/t without resorting to a "strong-coupling" approach to the original Hamiltonian (3). Actually, such an attempt would turn out to be improper since the present theory does not possess a natural perturbation parameter m/M as the usual electron–phonon coupling does. The retardation and damping effects should be treated within a perturbational approach starting directly with the two-body interaction given by (4). It is also noteworthy that the attractive interaction J affects almost all of the available electron states, in contrast to the usual electron–phonon interaction which is restricted to a very thin shell around the Fermi surface. The low mobility and carrier concentration favour such an unscreening effect which is one of the main reasons for obtaining high values of the critical temperature. One can also see that the electron-lattice interaction lowers the Hubbard repulsion U to $\tilde{U} = U - 3E_{\mathrm{JT}}$. According to the previous discussion the renormalized $\tilde{U}$ is highly ineffective on account of the unlikelihood of the double occupancy configurations. Consequently, the $\tilde{U}$ contribution to (4) will be neglected in what follows. A careful estimation of U as well as the general Coulomb repulsion as compared with the attractive J would provide an interesting superconductivity criterion for these narrow-band electron systems.

3. RESULTS AND DISCUSSION

There is still a great deal of uncertainty regarding the crystalline structure of the high-temperature superconducting compounds. A tetragonal structure (with one copper site per unit cell) would imply a metallic behaviour for La_2CuO_4 in contrast to the experimental evidence [31]. An orthorhombic distortion may have such a particular pattern as to leave all the copper sites equivalent and, therefore, preserve the metallic character [10, 12, 13, 21]. Evidence for a Mott–Hubbard correlation gap has recently been pointed out [32]. More probably an antiferromagnetic order would set up [17], in which case the two-dimensional network would be a square one with two inequivalent copper sites per unit cell. A standard BCS pairing Hamiltonian

$$\mathscr{H}_{\text{pair}} = t \sum_{\mathbf{k}\sigma} v(\mathbf{k}) c^{+}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} - (2J/N) \sum_{\mathbf{k}\mathbf{k}'\sigma} v(\mathbf{k} - \mathbf{k}') \times c^{+}_{\mathbf{k}\sigma} c^{+}_{-(\mathbf{k}\sigma)} c_{-(\mathbf{k}'\sigma)} c_{\mathbf{k}'\sigma}. \tag{5}$$

can be derived in this case from (4) in the weak coupling regime [33], where $v(\mathbf{k}) = 4\cos(ak_x/2)\cos(ak_y/2)$, a being the lattice spacing. The Brillouin zone is almost completely filled, according to (2), the (hole) Fermi wavevector being given by $a^2k_F^2 = 4\pi x$ in an isotropic, spherical approximation. Averaging the pairing interaction over the (hole) Fermi sea one obtains $(8J/N)(1 - \pi x/2)$ for the pairing strength of the singlet superconductivity, valid for $0 < x \lesssim 0.4$. The critical temperature is readily obtained as

$$T_0 \simeq 12.4\, tx \exp[\alpha(x - 2/\pi)^{-1}],\ \alpha = t/2J, \tag{6}$$

for the weak coupling case $\alpha \gtrsim 0.8$. In spite of the simplifications featured by the present model Hamiltonian one might expect the x-dependence of the critical temperature (6) be preserved for the more realistic cases, providing the electronic band structure is not changed. Equation (6) is fitted to the experimental x-dependence of the critical temperature for the Y-compounds [6, 11, 32] with $\alpha \simeq 0.92$ and $t \simeq 330\,\mathrm{K}$; a maximum critical temperature of $\simeq 99.5\,\mathrm{K}$ is obtained for $x \simeq 0.2$. One obtains also $E_{\mathrm{JT}} \simeq 6\,\mathrm{meV}$ (for $g_1/g_0 = 0.5$) in fair agreement with the typical values of the Jahn–Teller stabilization energy of the Cu^{2+} cation [27] and the characteristic frequency $\omega \simeq 13\,\mathrm{meV}$ ($t_0 \simeq 0.5\,\mathrm{eV}$ [12]) in agreement with the low-frequency optical modes estimated for these compounds [21, 23]. For the La-compounds [1, 3, 10, 34] one obtains $\alpha \simeq 1$, $t \simeq 150\,\mathrm{K}$ and $E_{\mathrm{JT}} \simeq 12\,\mathrm{meV}$, $\omega \simeq = 10\,\mathrm{meV}$ for $g_1/g_0 \simeq 0.1$.

As the α values are rather close to the validity limit of (6) ($\alpha \simeq 0.8$) one may suggest that an intermediate coupling regime is rather effective instead of a weak coupling one. The same conclusion is reached starting from the extreme strong coupling limit. As it is well-known [33] a bipolaron-type superconductivity might be expected for $\alpha \ll 1$ with, however, a too low critical temperature as compared with the experimental data. For reasonably small values of α the usual BCS gap equation gives an anisotropic gap $\Delta_{\mathbf{k}} \sim \cos(ak_x/2)\cos(ak_y/2)$ in agreement with the experimental data [35] and a critical temperature

$$T_0 \simeq 2J[x + \sqrt{x/\pi}\, J_1(4\sqrt{\pi x}) + \sqrt{x/8\pi}\, J_1(4\sqrt{2\pi x})], \tag{7}$$

where J_1 is the first-order Bessel function. From the experimental data one obtains $J \simeq 180\,\mathrm{K}$ for the Y-compounds and $J \simeq 70\,\mathrm{K}$ for the La-compounds. With $\omega \simeq 10\,\mathrm{meV}$ a rather larger value $\alpha > 0.4$ is obtained which again points out the tendency towards an intermediate coupling regime. A proper treatment of this case would require, beside the competition between the BCS – and bipolaron-type superconductivity, an accurate knowledge of the crystalline structure and electronic energy levels. It is also highly desirable to have a direct experimental estimation of the Jahn–Teller stabilization energy E_{JT} as well as a detailed knowledge of the oxygen-displacive modes involved in the present mechanism of superconductivity. It is interesting to note in the present context that the foregoing discussion favours an electron-lattice coupling with the rather low-frequency optical modes, $\omega \simeq 10\,\mathrm{meV}$. This estimation is based on $t_0 = 0.5\,\mathrm{eV}$ [12] for the bare electron-transfer integral. However, a stronger electron localization recently reported [32] would reduce this value and allow for the high-frequency optical models coupling as well. Preliminary calculations suggest the same conclusion when the Coulomb repulsion is taken into account.

Let us conclude by noting that for a standard $M^{-0.5}$-dependence of the frequency ω the coupling constant $J = g_1 \cdot g_0/M\omega^2$ of the present model does not depend on the oxygen mass M and, consequently, no appreciable isotope effect will occur (for the intermediate-coupling regime the M-dependence of the bandwidth parameter t is very weak). Recent experimental data [36] show that for an average relative mass variation $\delta M/M \simeq (9.3 \pm 1)\%$ a relative frequency shift $\delta\omega/\omega \simeq -(4.3 \pm 0.4)\%$ is obtained, which corresponds to an $\omega \sim M^{-0.4} - M^{-0.56}$ dependence. The experimentally reported absence of the isotope effect [36] suggests, within the present model, the standard $M^{-0.5}$-dependence for the characteristic frequency ω.

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