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POSSIBLE MECHANISM FOR HIGH-TEMPERATURE SUPERCONDUCTIVITY IN THE Ba(Sr)-La(Y)-Cu-O SYSTEMS *

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ABSTRACT

A high-temperature mechanism of superconductivity is proposed for distorted perovskite-like structures of $Ba_xLa_{2-x}CuO_4$ type. For x close to unity it is shown that the Jahn-Teller effect of the Cu^{2+} cations might bring about an attractive pairing interaction in the wavevector space. In the opposite limit $x \sim 0$ it is argued that the Coulomb repulsion might cause a real-space electron pairing. In both cases optimal values of the concentration x are predicted above $1 - 1/\pi$ and below $1/\pi$ which agree with the experimental data. The corresponding critical temperatures are also estimated.

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1. Introduction

The high-temperature superconductivity in the recently discovered Ba(Sr)-La(Y)-Cu-O systems [1-5] seems to be related (besides the percolative, interfacial and two-dimensional fluctuation effects) to the orthorhombically distorted oxygen-deficient perovskite-like structures $Ba(Sr)_xLa(Y)_{2-x}CuO_4$ and $Ba_2YCu_3O_{6.5+1.5x}$, $0 < x < 1$, which are layered structures of the K_2NiF_4 type [6-8]. They consist of alternating Cu-oxygen and (Ba(Sr),La(Y))-oxygen layers, the former being rather well separated by an average distance of $\sim$ 6-7 A and screened by the latter. Consequently, we may take, as a first approximation, a single Cu-oxygen layer and neglect its interaction with the others. The copper cation is coordinated by four in-layer and two off-layer oxygen anions, the copper-copper in-layer average distance being a $\simeq$ 3.8 A. Substituting Ba(Sr) for La(Y) (or, equivalently, lowering the oxygen deficiency) the valence state of the copper cation changes from Cu^{2+} to Cu^{3+}, the ratio Cu^{2+}/Cu^{3+} being recognized as critical for the superconducting properties of these compounds. The average valence of the copper cation can be written as $z = 2+x$, according to the stoichiometry given above. We shall consider a square array of N copper sites labelled by i and introduce the electron occupancy variable n_i which may take two distinct values: $n_i = 0$ for Cu^{3+} and $n_i = 1$ for Cu^{2+}. The valence z_i of the i-th copper cation is then given by $z_i = 3-n_i$, and its averaging over all the i sites leads to

$$\sum_i n_i = N(1-x). \qquad (1)$$

The hamiltonian

$$t \sum_{(i,j)} c_i^+ c_j + (\alpha_M e^2/8a\xi) \sum_{(i,j)} n_i n_j \qquad (2)$$

of these localized electrons includes the electron transfer between two nearest-neighbour sites (ij) and the Coulomb repulsion which is represented, for simplicity, by a short-range interaction (α_M is the Madelung constant, e is the electron charge and ξ is the dielectric constant). A similar model has been used recently [9] for $BaPb_{1-x}Bi_xO_3$.

A strong electron-lattice coupling is expected to occur in these layered structures as a consequence of the oxygen-displacive modes [10] and low carrier concentration which is unable to shield the optical phonons [11]. This interaction has been discussed in various contexts [12] and, in fact, it can always be related to the Jahn-Teller effect [13]. Indeed, it is well-known [14], for example, that the distances between Cu^{2+} and the off-layer oxygen anions in La_2CuO_4 are much longer (2.4 A) than the in-layer copper-oxygen distances (1.9 A). The Jahn-Teller effect of the Cu^{2+} cation in such type of structures distorts the copper-oxygen bonding and lowers the electronic level of the copper cation. The energy involved in this process may be written, within a simplified model, as

$$(1/2)M\omega^2 w_i^2 - g_0 w_i n_i - g_1 w_i \sum_{(j)} n_j, \qquad (3)$$

where M is the oxygen mass, ω is its characteristic frequency, w_i is the displacement of the i-th off-layer oxygen anion and summation over (j) is restricted to the nearest-neighbours of the i-th site. The coupling constants g_0 and g_1 are such as $g_0 \gg g_1$. The lattice coordinate w_i can be eliminated from (3) by minimizing this energy with respect to w_i. One finds that (3) reaches its minimum at $w_i^0 = (M\omega^2)^{-1}(g_0 n_i + g_1 \sum_{(j)} n_j)$,

so that we are left with a lattice-free electron energy

$$-(g^2/M\omega^2) \sum_{(i,j)} n_i n_j - (g_0^2/2M\omega^2) \sum_i n_i, \qquad (4)$$

where $g^2 = g_0 g_1$ and g_1^2 - contribution has been neglected. In view of (1) one may also neglect the last term in (4). Therefore, the model hamiltonian proposed for this type of compounds can be written as

$$H = t \sum_{(i,j)} c_i^+ c_j + J \sum_{(i,j)} n_i n_j, \qquad (5)$$

$J = (\alpha_M e^2/8a\xi) - (g^2/M\omega^2)$, which should be used in conjunction with the condition (1).

Among many oversimplifications of this model there is one which needs a further comment. In the dilute limit $x \sim 1$ the attractive electron-lattice interaction would prevail over the Coulomb repulsion and J would acquire a negative sign. On the contrary, in the opposite dense limit $x \sim 0$ this attractive interaction would be overridden by the Coulomb repulsion and the coupling constant J would become positive. The model hamiltonian (5) does not contain this feature (J should be x - dependent in this case) which, however, will be incorporated in the forthcoming discussion. In addition, it is worthwhile emphasizing that J affects all the available electronic states, in contrast to the usual electron-phonon interaction which is restricted to a very thin shell around the Fermi surface. The low mobility (small values of t) and carrier concentration favour such an unscreening effect which is one of the main reasons for obtaining high-values of the critical temperature.

2. The dilute limit $x \sim 1$

According to the preceding discussion the attractive electron-lattice interaction ($J < 0$) will, in this case, lead to a standard electron pairing in the wavevector space, described by the pairing hamiltonian

$$\mathcal{H} = t\sum_{\underset{\sim}{k}} v(\underset{\sim}{k}) c^{+}_{\underset{\sim}{k}} c_{\underset{\sim}{k}} - (|J|/N) \sum_{\underset{\sim}{k}\,\underset{\sim}{k'}} v(\underset{\sim}{k}-\underset{\sim}{k'}) c^{+}_{-\underset{\sim}{k}} c^{+}_{\underset{\sim}{k}} c_{\underset{\sim}{k'}} c_{-\underset{\sim}{k'}} \qquad (6)$$

where $v(\underset{\sim}{k}) = 2(\cos k_x a + \cos k_y a)$. For low occupancy we may approximate the Fermi sea by a disc of radius k_F, $a^2 k_F^2 = 4\pi(1-x)$ and $v(\underset{\sim}{k})$ by $4 - a^2k^2$. Averaging $v(\underset{\sim}{k}-\underset{\sim}{k'})$ over this Fermi sea one finds that the effective pairing strength is $4|J|(1-\tilde{\pi}+\tilde{\pi}x)/N$ which imposes a lower bound $x_0 = 1 - 1/\tilde{\pi}$ for the present approximation.

Standard calculations lead to the critical temperature

$$T_c \simeq 3.12\tilde{\pi}\, t(1-x) e^{-\alpha/(x-x_0)}, \quad \alpha = 2t/|J|, \qquad (7)$$

which has a maximum for the optimal concentration

$$x_0 = x_0 + \frac{1}{\tilde{\pi}} \frac{2\alpha}{\alpha + \sqrt{\alpha^2 + 4\alpha/\tilde{\pi}}} \qquad (8)$$

The corresponding critical temperature is given by

$$T_c^0 \simeq 3.12 t \left(1 - \frac{2\alpha}{\alpha + \sqrt{\alpha^2 + 4\alpha/\tilde{\pi}}}\right) \exp\left[-\tilde{\pi}\left(\alpha + \sqrt{\alpha^2 + 4\alpha/\tilde{\pi}}\right)\right], \qquad (9)$$

which predicts critical temperatures as high as $10^5 . t$ [eV] K in the limit $|J| \to \infty$ ($\alpha = 2t/|J| \to 0$). The most interesting prediction is, however, the existence of an optimal concentration x_0 (given by (8)) above the limit $1 - 1/\tilde{\pi} \simeq 0.68$. This is in good agreement with the value $x \simeq 0.8$ reported for $Ba_xY_{2-x}CuO_4$ [4].

3. The dense limit $x \sim 0$

For small values of x almost all of the sites are occupied by electrons and, consequently, the Coulomb repulsion will prevail over the attractive electron-lattice interaction. The coupling constant J in (5) acquires positive values in this case. We argue that in this limit the real-space electron pairing is favoured via "virtual" electron exchange processes between two neighbour sites. Indeed, suppose that for $x = 0$ an electron is destroyed on the i-th site; at the next moment the Coulomb repulsion will prompt an electron placed on the neighbour j-th site to replace it, and the i-th electron may well occupy this latter emptied site. It follows that the Coulomb repulsion correlates these two inter-changed electrons in "virtual" pairs, named so as long as the two partners are "flying" between the (i,j)-th sites. Moreover, one may observe in addition that, as far as the many-exchange processes are neglected (which would involve more than two sites), the wavevectors of the two partners (viewed as wavepackets) should be equal in magnitude and opposite in direction. The correction to the electron energy levels owing to these "virtual" real-space electron-pairs could be estimated by means of a standard second-order perturbation calculation. However, the problem is whether these electrons could bound together in pairs. If such "virtual" electron-pairs are to exist in the real space the ground-state of the system would contain a superposition of states with a variable number of electron-pairs (the partners in a missed pair "flying"

continuously between two neighbour sites), the average number of electrons being, of course, constant. This fluctuation effect in the total number of electrons might well be ennanced by the two-dimensional geometry of the problem. The consequence of this pair-number fluctuating ground-state is that the quantity $\Delta_{ij} = \langle c_i c_j \rangle$ may be taken as an order parameter.

The problem can be looked at from a slightly different point of view, with the same conclusion. Suppose that two neighbour electrons in a completely filled system are squeezed out of their equilibrium positions against one another. They will oscillate around these equilibrium positions with an off-site probability which is sensibly large in low-dimensional systems. These oscillations are nothing else but the fluctuations in the electron positions of a two-dimensional Wigner crystal [15]. As long as two neighbour electrons are off their (i,j) - positions they may be viewed as forming a "virtual" pair; the corresponding ground-state will then contain a state with one pair lesser and the parameter $\Delta_{ij} = \langle c_i c_j \rangle$ will acquire non-vanishing values. If the interaction favours (as it seems to do) such a pairing, then the ground-state energy of the system would lower and the "virtual" electron-pair in the real space would be bound. The point is, as it will be easily to see, that the hamiltonian (5) with $J > U$ actually possesses such a ground-state.

Within a mean-field approximation the hamiltonian (5) can be written as

$$h = t \sum_{(i,j)} c_i^+ c_j - (J/2) \sum_{(i,j)} (\Delta_{ij} c_i^+ c_j^+ + \text{h.c.}) \qquad (10)$$

which becomes

$$h = t \sum_{\underset{\sim}{k}} v(\underset{\sim}{k}) c_{\underset{\sim}{k}}^+ c_{\underset{\sim}{k}} - (J/2N) \sum_{\underset{\sim}{k}\,\underset{\sim}{k}'} (\Delta_{\underset{\sim}{k}\underset{\sim}{k}'} c_{\underset{\sim}{k}}^+ c_{\underset{\sim}{k}'}^+ + \text{h.c.}) \qquad (11)$$

in an extended-orbital representation, where

$$\Delta_{\underset{\sim}{k}\underset{\sim}{k}'} = \sum_{(i,j)} \Delta_{ij} e^{-i\underset{\sim}{k}\underset{\sim}{r}_i - i\underset{\sim}{k}'\underset{\sim}{r}_j}, \qquad (12)$$

$\underset{\sim}{r}_i$ being the i-th site position vector. In the high-density limit, when practically all the N sites are occupied, one may expect Δ_{ij} not depending on i. In this case $\Delta_{\underset{\sim}{k}\underset{\sim}{k}'} = \Delta_{\underset{\sim}{k}} \delta_{\underset{\sim}{k},-\underset{\sim}{k}'}$ and one can see that only single-exchange processes contribute, in agreement with the previous qualitative discussion. Within this approximation (11) acquires the form

$$h = t \sum_{\underset{\sim}{k}} v(\underset{\sim}{k}) c_{\underset{\sim}{k}}^+ c_{\underset{\sim}{k}} - (J/2N) \sum_{\underset{\sim}{k}\,\underset{\sim}{k}'} [v(\underset{\sim}{k}+\underset{\sim}{k}') \langle c_{-\underset{\sim}{k}}^+ c_{\underset{\sim}{k}}^+ \rangle c_{\underset{\sim}{k}'} c_{-\underset{\sim}{k}'} + \text{h.c.}] \qquad (13)$$

which, as one can easily see, corresponds formally to a pairing hamiltonian of the type (6). It follows that the "virtual"-pair exchange-processes discussed above actually lead to a pairing of electrons in the real space, described by the order parameter Δ_{ij}. In the present high-density approximation these real-space pairs of electrons amount to pairs in the wavevector space. For high-occupancy ($x \sim U$) one may further approximate $v(\underset{\sim}{k}+\underset{\sim}{k}')$ by its average $4(1-\tilde{\pi}(x)$ over the Fermi disc which sets up an upper bound $x_0 = 1/\tilde{\pi}$ for the effective pairing strength $4J(1-\tilde{\pi}\, x)/N$. Standard calculations led to the optimal concentration

$$x_0 = x_0 - \frac{1}{\tilde{\pi}} \frac{2\alpha}{\alpha + \sqrt{\alpha^2 + 4\alpha/\tilde{\pi}}} \qquad (14)$$

and the same critical temperature as that given by (9). The existence of optimal concentrations below $1/\tilde{\pi} \simeq 0.32$ agrees with the experimental data $x \simeq 0.15$, 0.2 [1-3] and $x \simeq 0.25$ [8].

4. Conclusions

A simple model has been put forward in the present paper for the high-temperature superconducting phases $Ba(Sr)_xLa(Y)_{2-x}CuO_4$ and $Ba_2YCu_3O_{6.5+1.5x}$ in the recently discovered Ba(Sr)-La(Y)-Cu-O systems. The salient features incorporated by this model are the two-dimensional geometry of the copper-oxygen layers, the oxydizing function of the Ba(Sr) concentration (or,equivalently, the reducing function of the oxygen deficiency) controlled by the x parameter ($0 < x < 1$), the mixed-valence state Cu^{2+}/Cu^{3+} of the copper cations and the attractive (copper) electron - (oxygen) lattice interaction brought about by the Jahn-Teller effect of the Cu^{2+} cations. The model has been treated approximately in two limiting cases: the dilute limit $x \sim 1$ and the dense limit $x \sim 0$. In both cases optimal values have been obtained for the concentration x, placed above $1-1/\pi \simeq 0.68$ and below $1/\pi \simeq 0.32$, which agree with the experimental data. It is concluded that the superconductivity in the dilute range $x \sim 1$ arises by electron pairing in the wavevector space, owing to the strong attractive electron-lattice interaction which prevails over the Coulomb repulsion. In the opposite limit $x \sim 0$ it has been argued that an electron pairing in the real space would be favoured by the Coulomb repulsion, via the exchange processes between the "virtual" electron pairs. It has been shown that, in both cases, the high values of the critical temperature come from the strong interaction which affects almost all of the available electron states.

It is worthwhile noting that the electron spin does not play any role within the present model in view of the fact that there are only two valence states of the copper cation and therefore, we are in the situation of a "half-filled" band. Hubbard's Coulomb repulsion term is, consequently, much less effective, as compared with the present intersite Coulomb repulsion. Another point of importance that should be noted is the almost complete

decoupling between the magnetic activity (as when Gd is substituted for Y) and superconductivity, as a consequence of the layered structure of these compounds, in agreement with the experimental data.

In spite of its great simplifications the present model could provide the right way towards understanding the high-temperature superconductivity in this class of materials. The model could be improved by carefully treating the long-range character of the Coulomb interaction as well as its dependence on the filling factor x. This is likely to provide us with the desired x - dependence of J, which should be so as $J < 0$ for $x \to 1$ and $J > 0$ for $x \to 0$. A more careful treatment also needs the electron-lattice interaction by refining its form as to include the dynamics of the oxygen-displacive modes and the inertial effects of the oxygen anions.

As regards the mathematical treatment of the model it should be emphasized that the pairing hamiltonian requires a deeper analysis in the range of strong coupling. The role of the two-dimensional fluctuations of the pair-number in the real-space pairing regime should also be further investigated in close connection with the Wigner electron-lattice picture, allowance being made for the site dependence of the order parameter Δ_{ij}. Although interesing technical problems will occur (such as the transient regime between low and high electron occupancy, which, however is not likely to be related to any significant superconducting properties) the physical picture outlined above is not likely to be drastically altered.

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