Locally unstable crystal configurations and electronic superconductivity mechanism

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A superconductivity mechanism which is based on the nonmonotonic energy dependence of the repulsive Coulomb interaction potential and which leads to an effective attraction is proposed. The necessary condition for the realization of this mechanism is the proximity to the electronic instability point, whose existence is characterized by locally unstable intermediate charge states of ions.

1. Many experimental data (nonmonotonic behavior of temperature, variation of lattice parameters and of the elastic and vibrational characteristics) have suggested that high-T_c superconductors tend to be structurally unstable near T_c and above it. It would be reasonable to assume that there is a strong correlation between the superconductivity of these compounds and their structural instability. Attempts to describe this relationship in terms of the present conceptual understanding of the soft phonon mode, which leads to a renormalization of the coupling, do not seem to be able, however, to combine the large collection of experimental data or to explain the large values of T_c, $T_c \approx 100$ K. In the present letter we present a viewpoint, according to which both the structural instability and the large values of T_c are attributable to the fact that the system is close to the electronic instability of the charge transfer type or the superionic transition type. The electronic instability is associated with the interaction of two bands spaced closely apart. The proximity to an instability is characterized by the presence of a finite-energy maximum in the electron–electron-interaction amplitude in the zero-sound channel. The existence of such a maximum can, as will be shown below, give rise to a purely Coulomb superconductivity mechanism. Above the electronic-instability point there is a temperature interval in which locally unstable configurations appear in the form of short-range order regions: atoms with an "incorrect" valence. An abnormally high mobility of oxygen ions (the "oxygen flash"[1]) and of copper[2] ions is a manifestation of such unstable configurations.

2. The main features of the scenario presented above can be described on the basis of the standard semiconductor model with an interband Coulomb interaction (the exciton-dielectric model[3]) (Fig. 1). In application to copper–oxygen layers, the exciton instability was recently considered in Ref. 4. A similar spectrum (Fig. 1) can be found in the nearest-neighbor approximation[3,5] for the Cu–O plane and is described in the lattice-site representation by the Hamiltonian

$$\hat{H}_0 = \sum_{ij} (\epsilon_0 P_{i\alpha}^{+} P_{i\alpha} + \epsilon_d d_j^{+} d_j + t_{ij}^{\alpha} P_{i\alpha}^{+} d_j + \text{H.c.}), \qquad (1)$$

where P^+ (d^+) is an operator which creates an electron at O(Cu), and $\alpha = x,y$ is the index of the oxygen p-orbital. At $\epsilon_0 < \epsilon_d$ the upper band is primarily a d band, while

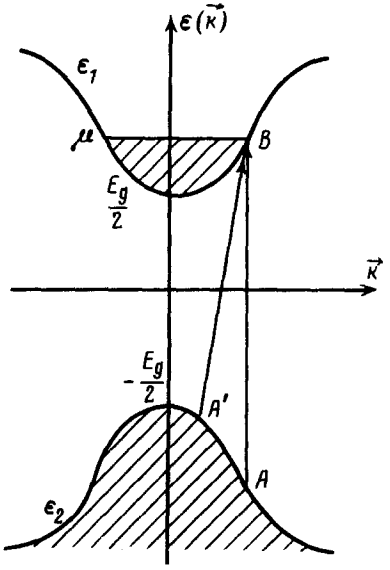

FIG. 1.

the lower one is a p band, $E_g = \epsilon_d - \epsilon_0$ [the dispersion-free branch of spectrum (1) was omitted in Fig. 1]. If we consider only the interaction at one of the adjacent sites

$$\hat{H}_{int} = \sum_{ij} u n_{jd\sigma} n_{jd-\sigma} + v_{Pd} n_{ip} n_{jd}, \tag{2}$$

then the principal scattering processes in the band system

$$v_0 c^+_{a\sigma} c^+_{a\sigma'} c_{a\sigma'} c_{a\sigma}; \quad v_1 c^+_{1\sigma} c^+_{2\sigma'} c_{2\sigma'} c_{1\sigma}; \quad \tilde{v}_2 c^+_{1\sigma} c^+_{2\sigma'} c_{1\sigma'} c_{2\sigma}; \quad v_2 c^+_{1\sigma} c^+_{1\sigma'} c_{2\sigma'} c_{2\sigma} \tag{3}$$

[here c_a is the electronic operator in the band $a = 1,2$ (Fig. 1)] are characterized by the following amplitudes:

$$v_0 = v_1 \approx u + v_{pd}; \qquad v_2 = \tilde{v}_2 \approx u - v_{pd}. \tag{4}$$

The model in Fig. 1 differs from the standard model[3] in that it has doping (the filled states are hatched). Formally, a half-filled conduction band corresponds to the compounds La_2CuO_4 and $YBa_2Cu_3O_6$, which are known to be antiferromagnetic insulators. An increase in doping suppresses antiferromagnetic order and exposes the Fermi surface, creating a situation illustrated in Fig. 1. In this case the interband interaction becomes important (the fact that short-range antiferromagnetic order and a pseudogap may be present in the spectrum[6] does not change qualitatively the picture we are considering). While the instability threshold in the model of Ref. 3 corresponds to the case in which the following condition is satisfied $E_{ex} = E_g$, where E_{ex} is the exciton binding energy, this threshold in the model of Fig. 1 shifts toward higher

interaction energies (the analog of the Burshsteĭn shift):

$$E_{ex} = E_g + 2\mu_c . \tag{5}$$

The instability in this case can evolve into the inhomogeneous phase, since the excitation energy of the AB transition (Fig. 1) with zero total momentum of the electron and hole ($q = 0$) is higher than that of the $A'B$ transition with $q \neq 0$. The maximum in $\mathbf{q}(\mathbf{q} = \mathbf{q}_{\max})$ is determined with allowance for the effective phase-space volume which decreases upon transition from the state A to the ceiling of the valence band. In contrast with Ref. 3, the screening of the effective interaction potential due to the presence of the free charge carriers should also be taken into account.

Under unstable conditions we must get away from the pure states in zones *1* and *2* and their superposition

$$\psi = U\varphi_1 + V\varphi_2 . \tag{6}$$

In the mean-field approximation the phase which is modified below the critical temperature is characterized by the order parameter $\Delta \sim \langle UV \rangle$. In model (1) the manifestation of $\Delta \neq 0$ means that the charge moves either from center to center (e.g., $O^{--}Cu^{++} \rightarrow C^{-}Cu^{+}$)

$$\hat{H}_{int} \rightarrow \hat{H}_{\Delta s} = \sum_{ij} \Delta (n_{pi} - n_{dj}), \tag{7}$$

or from link to link (the charge is centered between the atoms):

$$\hat{H}_{int} \rightarrow \hat{H}_{\Delta B} = \sum_{ij} \Delta p_i^{+} d_j ; \tag{8}$$

here the p nature of the oxygen orbitals is taken into account. In the strong-coupling approximation $u \gg t$, the mean-field approximation for the seed electronic operators (2) and (4) cannot be used. A more suitable approach is the one which is based on the introduction of auxiliary bosons (see, e.g., Ref. 7), which takes into account the strong repulsion of the charge carriers at the center. It can be shown, however, that the physical picture (6)–(8) of the interband instability does not change even in this approach. The charge-transfer amplitude in this case is the density of the boson field condensate[7] $\langle b^{+} \rangle$. The intermediate value of the interaction, $u \sim t$, apparently corresponds to an actual situation in a high-T_c superconductor, as has been frequently noted.

If the interaction is strong, then the instability point is preceded by a broad temperature interval of developed fluctuations. It has been reliably established[8] that in this interval the interelectronic correlations form a short-range order [$\langle UV \rangle = 0$, $\langle (UV)^2 \rangle \neq 0$], which implies, on the basis of model (1) which is being considered, the existence of long-lived local charge fluctuations (the local change in valence). The characteristic size of the region of short-range order for a strong interaction is determined by the atomic spacing.[8] A change in the charge state of the ion means that the nature of its interaction with the surroundings changes radically. When the valence changes by two digits, for example, the radii of the O and Cu ions change by a factor of

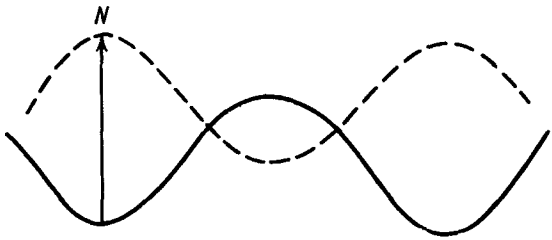

FIG. 2.

2 and 1–1/2, respectively.[9] Such a change of the local state may lead to the loss of local stability. In configuration space this corresponds to various shapes of the potential well for the states with different valences (Fig. 2). With $\langle (UV)^2 \rangle \neq 0$ the ion spends part of the time in an unstable state (the point N in Fig. 2), which accounts for the abnormally high mobility. It is well known that such phenomena occur under nonequilibrium conditions (radiation-accelerated diffusion) when the local charge state changes as a result of laser bombardment.[10]

3. Superconductivity model. The two-component, energy-dependent, superconducting order parameter forms the basis of the suggested superconductivity mechanism. One component (Δ_1) describes the superconducting condensate formed by the charge carriers in the states near the Fermi level. The second component (Δ_2) pertains to the states in band 2 which participate in the interband interaction that is responsible for the electronic instability. If the characteristic dimension L of the region of the short-range order which determines the structural instability is smaller than the correlation length of the superconducting order parameter ξ_0 [the ion spends only a short time in the wrong charge state: $\langle (UV)^2 \rangle \to 0$], the renormalization of the interaction can, because of the coherence factors,[11] be ignored in the self-consistency equation for the superconducting order parameter. Restricting the analysis to the two indicated groups of states and ignoring the frequency dispersion of the interaction (it will be described elsewhere), we find that T_c is determined by solving the following system of equations:

$$\Delta_1(\mathbf{k}) = -\hat{\Gamma}_0 \Delta_1(\mathbf{k}') - \hat{\Gamma}_2 \Delta_2(\mathbf{k}'); \qquad \Delta_2(\mathbf{k}) = -\hat{\Gamma}_0 \Delta_2(\mathbf{k}') - \hat{\Gamma}_2 \Delta_1(\mathbf{k}'), \tag{9}$$

where

$$\hat{\Gamma}_a \Delta_b(\mathbf{k}') = \sum_{\mathbf{k}'} \Gamma_a(\mathbf{k},\mathbf{k}') \frac{\Delta_b(\mathbf{k}')}{\mu - E_b(\mathbf{k}')} \tanh \frac{\mu - E_b(\mathbf{k}')}{2T_c};$$

$\Gamma_a(\mathbf{k},\mathbf{k}')$ is the total amplitude of the Coulomb scattering which corresponds to the bare potential v_a (3). It is easy to show that if the sign of the component Δ_1 is opposite to that of Δ_2, the system of equations (9) may have a nontrivial solution at T_c, despite the fact that each interaction $\Gamma_a(\mathbf{k},\mathbf{k}')$ corresponds to a repulsion. Let us consider the following model problem. We replace in the integral operators (9) all the quantities by their values averaged over the energy and angles:

$$\Delta_a(\mathbf{k}) \to \Delta_a = \text{const}, \quad \hat{\Gamma}_a \Delta_1(\mathbf{k}') \to \Gamma_a \ln \frac{\tilde{\omega}}{T_c} \Delta_1 \quad , \quad \tilde{\omega} \sim \mu \ .$$

$$\hat{\Gamma}_a \Delta_2(\mathbf{k}') \to \frac{\Gamma_a}{E} \ , \qquad \frac{1}{\tilde{E}} \approx \int \frac{d\mathbf{k}'}{|E_2(\mathbf{k}')| + E_{g/2} + \mu} \ . \tag{10}$$

The parameter values $v_1/\tilde{E} \approx 1$ correspond to the electronic instability point (5).

We see from (9) and (10) that a solution for T_c ($T_c = \tilde{\omega} e - 1/g_{\text{eff}}$) exists only for the positive values of the effective interaction constant g_{eff}

$$g_{eff} = \frac{\Gamma_2^2 - \tilde{\Gamma}_0^2}{\tilde{E} + \Gamma_0} > 0 \qquad \tilde{\Gamma}_0^2 = \Gamma_0(\Gamma_0 + \tilde{E}) \ . \tag{11}$$

Analysis of (11) reveals that superconductivity at the repulsive bare interaction in our model occurs at $\Gamma_2 > \tilde{\Gamma}_0$. At the electronic instability point the vertex Γ_2 has a singularity at the momentum transfer $\mathbf{q} = \mathbf{q}_{\max}$. In Eqs. (9) the integration is over the momentum transfer ($\mathbf{q} = \mathbf{k} + \mathbf{k}'$), which removes the singularity. Near the instability point, however, the amplitude Γ_2 remains large and condition (11) holds. In the model we are considering the temperature interval most suitable for the realization of superconductivity is therefore near the electronic instability point and above it (below the instability point the singularity in Γ_2 is further suppressed by the change in the electronic spectrum).

It should be noted that the sturcture of problem (9)–(11), which accounts for the superconducting solution in the case of bare repulsion, is formally similar to the structure of the phonon model for superconductivity with a Coulomb repulsion.[12] In the latter case the interaction amplitudes, which correspond to various energy scales have, as we know, different strengths, and the sign of the order parameter above the Debye energy is opposite to that below it.[12] The formal transition to the phonon model in (9) corresponds to the following transformation:

$$\hat{\Gamma}_1 \Delta_1 \to (-v_{ph} + u_c) \ln \frac{\theta_D}{T_c} \Delta_1 ; \quad \hat{\Gamma}_2 \Delta_2 = \hat{\Gamma}_1 \Delta_2 \to u_c \ln \frac{\mu}{\theta_D} \Delta_2 ;$$

$$\hat{\Gamma}_2 \Delta_1 \to u_c \ln \frac{\theta_D}{T_c} \Delta_1 , \tag{12}$$

where v_{ph} is the attractive potential due to the electron–phonon interaction, and u_c is the Coulomb repulsive potential. For the effective coupling constant in this case we find the standard expression $g(ph/\text{eff}) = -v_{ph} + u_c/(1 + u_c \ln \mu/\theta_D)$, which contains a weakened Coulomb pseudopotential. In the model under consideration the physical mechanism, which accounts for the effective attraction, differs markedly, however, from that of the model with electron-phonon interaction. While in the phonon model (12) the relative increase in the interaction amplitude with increasing energy ($u_c > u_c - v_{ph}$) is caused by the attraction ($-v_{ph}$) and the reduction of the amplitude at low energies, in the model (9)–(11) this process is caused by an increase

in the interaction at high energies near the instability point ($\Gamma_2 > \Gamma_0$). The extent to which the repulsion can be suppressed in the phonon model is determined by the parameter μ/θ_D. In our model such a role is played by the strength of the peak Γ_2, which determines the softness of the system.

The mechanism we have proposed here is amenable to a formal comparison with the mechanism which is responsible for the effective attraction for the higher-order harmonics ($l \geqslant 1$) of the superconducting order parameter (see, e.g., Ref. 13). A change in the Hartree–Fock potential Γ as a function of the energy in the self-consistency equation for Δ plays the same role as the change in the harmonic with $l \geqslant 1$: the change in the interaction potential as a function of the angle.

[1]B. Ya. Sukharevskiĭ *et al.*, Izv. Akad. Nauk SSSR, ser. fiz., **53**, 1345 (1989).
[2]A. M. Prokhorov *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **51**, 132 (1990) [JETP Lett. **51**, 148 (1990)].
[3]A. M. Kozlov and L. A. Maksimov, Zh. Eksp. Teor. Fiz. **48**, 1184 (1965) [Sov. Phys. JETP **21**, 790 (1965)].
[4]P. B. Littlewood *et al.*, Phys. Rev. **B39**, 12371 (1989).
[5]L. F. Mattheiss and D. R. Hamann, Solid State Commun. **63**, 395 (1988).
[6]A. Kampf and F. R. Schrieffer, Preprint, Los Alamos, 1989.
[7]C. Castellani and G. Kotliar, Phys. Rev. **B39**, 2876 (1989).
[8]T. Moriya, *Spin Fluctuations in Magnetic Materials with Collectivized Electrons*, Mir, Moscow, 1988.
[9]W. E. Pickett, Rev. Mod. Phys. **61**, 433 (1989).
[10]M. Lannoo and J. Bourgoin, *Point Defects in Semiconductors I*, Springer–Verlag, New York, 1981.
[11]A. A. Gorbatsevich, Pis'ma Zh. Eksp. Teor. Fiz. **51**, 39 (1990) [JETP Lett. **51**, 46 (1990)].
[12]N. N. Bogolyubov *et al.*, *New Method in the Superconductivity Theory*, Academy of Sciences of the USSR, 1958.
[13]M. T. Beal-Monod *et al.*, Phys. Rev. **B34**, 7716 (1986).

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