Pseudo-Jahn–Teller mechanism for the formation of a highly correlated Bose system in atomic clusters: The problem of high-T_c superconductivity

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Under certain conditions, the transition of atomic M-clusters to polar configurations, $M \rightarrow M^{\pm}$, may be accompanied by a transition from a weak pseudo-Jahn–Teller effect to a strong one and by the formation of $[M]^{\pm}_{JT}$ vibron centers which differ by an S-boson: two electrons which are paired by an interaction with an $[M]^{+}_{JT}$ vibron center and which form a completely filled shell. Hole (or electron) doping or photoexcitation of the lattice of M-clusters leads to the formation of seeds of a new phase: a system of $[M]^{+}_{JT}$ and $[M]^{-}_{JT}$ centers or an S-boson liquid in a reservoir of $[M]^{+}_{JT}$ vibron centers. The copper–oxygen high-T_c superconductors are discussed as an example of such a system.

Despite the large number of different mechanisms for the pairing of electrons (or holes) which are being discussed in connection with the problem of high-T_c superconductivity, electronic–vibrational interactions remain the most likely candidates for explaining the wide spectrum of unique properties of the high-T_c superconducting compounds.

Of primary interest here are the strong-coupling approximation, the formation of small-radius polarons, a bipolaron superconductivity,[1,2] and various versions of the Jahn–Teller (JT) effect (or the pseudo-JT effect)[3–7] in atomic clusters. Under the conditions of the strong JT effect or the pseudo-JT effect (vibron interactions), electronic–vibrational interactions might lead to strong electron correlations and to a radical change in the electronic structure of atomic clusters is solids. In several cases this restructuring would required substantial changes in our understanding of the basic organizational principles of this structure. Of particular theoretical and practical interest is the solution of the complex problem of the role played by electronic–vibrational interactions in systems with a varying number of particles N, primarily the problem of the transition to polar configurations, $M \rightarrow M^{\pm}$. Strictly speaking, the problem of seeking a many-particle adiabatic potential must be solved again in each specific case, with a definite value of N. Simplified model approaches based on a fixed adiabatic potential of the system will, obviously, lead to a satisfactory description only if two-particle interactions are completely ignored or if the dependence of the lower branch of the adiabatic potential on the number of particles, N, is clearly weak. The appearance of an electron degeneracy or quasidegeneracy (closely spaced levels) in the ground state of the system at a certain value of N will create conditions in the system for the JT effect or strong pseudo-JT effect, with a radical change in the adiabatic potential. It would become necessary to deal with some new correlation effects: a

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strong polarization interaction and a vibron reduction of electron interactions. In this case, the standard approach to the analysis of electronic-vibrational interactions in systems with a variable number of particles N is justified only if a change in N does not drive the system away from the conditions of the weak pseudo-JT effect.

1. Strong pseudo-Jahn–Teller effect in polar configurations of atomic clusters. With an eye on applications to copper–oxygen high-T_c superconductors, we consider as an example the simplest one-particle (one-hole) center. This is an atomic cluster M^h_{sp} which has only two one-particle valence shells, of s and p types (s is the orbital ground singlet, and p is a nondegenerate, doubly degenerate, or triply degenerate level) under conditions of the weak pseudo-JT effect:[8]

$$\Delta_1 = E_p - E_s > 4E_{\mathrm{JT}} = \frac{2V^2}{K}. \tag{1}$$

Here V is the constant of the electronic-vibrational interaction, and K is the stiffness of the vibrational mode Q_{sp} which is active in the JT effect. The addition of one more particle (or hole) may cause a transition of the center to the conditions of the strong pseudo-JT effect, with a radical restructuring of the adiabatic potential, even without a change in the constant of the electronic–vibrational interaction. Here it is sufficient that a quasidegeneracy arise in the ground state of the two-particle system. In particular, it is sufficient that the energies of singlet terms of the s^2 and sp configurations be close together and that the following condition hold:[8]

$$\Delta_2 = E(sp;{}^1P) - E(s^2;{}^1S) = \Delta_1 + U(sp) - U(s^2) < 4E_{\mathrm{JT}} \quad (Q_{sp}=0). \tag{2}$$

This situation is completely realistic if the repulsion of s and p particles is smaller than that of two s particles. The possibility of a transition from a weak pseudo-JT effect to a strong one in this system upon the change $N=1 \rightarrow N=2$ clearly implies a significant electrostatic repulsion of the particles in valence shells. The reaction in which a hole attaches to an M^h_{sp} center, forming a center with a strong dynamic pseudo-JT effect, can be written symbolically as

$$M^h_{sp} + h = [M^{hh}_{sp}]_{\mathrm{JT}} = [M^h_{sp}]^+_{\mathrm{JT}}. \tag{3}$$

The adiabatic potential of such a center is complex, with diverse and unique properties:[8]

1) There is a JT stabilization energy E_{JT}, which in the case at hand acts as a sort of energy of the pairing of two fermions to form a quasiboson formation: a vibron shell.

2) There is a strong s^2-sp hybridization of vibron origin involving an active vibrational mode (or modes) Q_{sp}, and stationary states described by correlation functions—vibron biorbitals—form.

3) A new scale of ultralow energies arises, in connection with the energy of a "free" or "retarded" rotation of the displacement field (respectively the energy of a rotational quantum or of a tunneling splitting):[8]

$$\delta \sim \left(\frac{\hbar\omega_0}{4E_{\mathrm{JT}}}\right)\hbar\omega_0 \tag{4}$$

($\hbar\omega_0$ is the energy scale of the phonon of the Q_{sp} vibrational mode).

4) There is an anomalously large (and generally temperature-dependent) electric polarizability.

5) There is redistribution of the intensity of the s^2–sp allowed electric-dipole transition ($\hbar\omega=\Delta_2$ at the point $Q_{sp}=0$) over the broad spectral range, from the band at $\hbar\omega\simeq 4E_{JT}$ (corresponding to a transition between lower and upper branches of the adiabatic potential) to the bands corresponding to transitions between tunneling states ($\hbar\omega\sim\delta$) within the lower branch of the adiabatic potential.

6) There is softening of vibrational modes which are active in the pseudo-JT effect, and there is an intensification of the corresponding IR bands.

7) There is an anomalous manifestation of an orbital magnetism of a JT center, which has both an electron contribution (if the orbital angular momentum of the doubly or triply degenerate p level is not frozen) and, in general, an ion contribution, associated with a possible "revolution" of cluster ions in "orbits".[8]

8) There is the possibility of introducing a quasispin of orbital nature to describe the lower tunneling states of a center with an anisotropic g-factor and an effective spin Hamiltonian

$$H_S=D\hat{S}_z^2+E(\hat{S}_x^2-\hat{S}_y^2)+..., \tag{5}$$

where the parameters of the "quasispin" anisotropy, D, E, . . ., are determined by the magnitude of the tunneling splittings.

In contrast with ordinary paramagnetic centers, in this case one will observe the following: a) an electric–dipole nature of the resonant transitions; b) an anomalously strong quasispin–lattice coupling; c) an ultrahigh sensitivity with respect to small low-symmetry electrical or mechanical external perturbations, which can convert a dynamic JT center into a static one with a "freezing" of the quasispin and magnetic moment; d) an anomalously weak coupling with the surrounding magnetic spin system, because of the orbital nature of the magnetic moment and effects stemming from the vibron reduction of the electronic interactions. Particularly noteworthy is the circumstance that a dynamic JT center with an anomalously high polarizability is the source of a strong pairing potential of a polarization nature and a center for the condensation of fermion pairs (quasibosons).

We earlier discussed reaction (3), the capture of a hole or the ionization of an M_{sp}^h cluster, resulting in the formation of a dynamic JT center $[M_{sp}^{hh}]_{JT}$. The capture of an electron by an M_{sp}^H center in the standard simplified approach leads to the trivial result

$$M_{sp}^h+e=M_0 \quad (Q_{sp}=0), \tag{6}$$

where M_0 represents the core of the completely filled shells. However, the possible formation of a new hybrid vibron shell with $Q_{sp}\neq 0$ in a reaction like (3) contributes one more channel for reaction (6):

$$M_{sp}^h+e=M_{sp}^h+h+2e=[M_{sp}^{hh}]_{JT}+(s^2;{}^1S)_0=[M_{sp}^h]_{\overline{JT}}. \tag{7}$$

This process is accompanied by the formation of a bound state of the JT center $[M_{sp}^{hh}]_{JT}$ and of two electrons, paired by the interaction with a vibron shell, under the condition that they must form a completely filled shell $(s^2;{}^1S)_0$ with localization at the point $Q=0$ of the adiabatic potential (an S-boson). The addition of a completely filled shell under these conditions does not lead to any fundamental change in the adiabatic potential for the vibron shell or to destruction of the JT center.

The binding energy of an S-boson is determined by the mechanism for the polarization pairing with account of the vibron reduction of the electrostatic interaction of the S-boson and vibron shell which are localized at different points in configurational Q-space. Although the binding energy E_b of the S-boson is complex, it is very simple to estimate: $E_b \simeq E_{JT}^-$, where E_{JT}^- is the energy of the JT stabilization of the $[M_{sp}^h]_{JT}^-$ center. This circumstance is another indication of a correlation nature of the S-boson and the vibron shell.

Reactions (3) and (7) also make it possible to describe a new channel for the known disproportionation reaction accompanied by the formation of two polar JT centers:

$$M_{sp}^h + M_{sp}^h = (M_{sp}^h + h) + (M_{sp}^h + e) = [M_{sp}^{hh}]_{JT} + ([M_{sp}^{hh}]_{JT} + (s^2;{}^1S)_0) = [M_{sp}^h]_{JT}^+ + [M_{sp}^h]_{JT}^-. \quad (8)$$

The polar JT centers $[M_{sp}^h]_{JT}^{\pm}$ differ only in that the $[M_{sp}^h]_{JT}^-$ center has an additional completely filled s^2 shell: an S-boson. Both highly polarized centers, in the lattice of M_{sp}^h clusters, can serve as catalysts for the disproportionation reaction for M_{sp}^h clusters in the nearest neighborhood. In other words, the lattice of M_{sp}^h centers, which are unstable with respect to a transition from a weak pseudo-JT effect to a strong one upon doping with an electron or a hole, is unstable with respect to the disproportionation reaction and the formation of a nucleation center of a new phase: a strongly correlated Bose system, which is a system of $[M_{sp}^h]_{JT}^+$ and $[M_{sp}^h]_{JT}^-$ vibron centers differing by one S-boson. A similar situation can be observed during photoexcitation of a lattice of original centers. The new phase may be thought of as a lattice of $[M_{sp}^h]_{JT}^+$ JT centers, half of whose sites are filled by S-bosons with a charge of $2e$, or as a lattice of $[M_{sp}^h]_{JT}^-$ centers, half of whose sites are filled with hole S-bosons with a charge of $2e$. This system may be thought of as a sort of Bose liquid which cannot exist without its own reservoir: a lattice of JT centers. Among its possible states are metallic, superfluid (superconducting), charge-ordering, and mixed.[2] Along the one-particle fermion band approach, the new phase can be described as a Fermi system with a conduction band and a valence band, separated by a gap $E_g \approx E_{JT}^+ + E_{JT}^-$. Generally speaking, the energies of the JT stabilization of the $[M_{sp}^h]^{\pm}$ centers $(E_{JT}^{\pm})$ are different. In "boson" terms, the size of the gap E_g is the sum of the binding energies of two quasiboson formations: a vibron shell and an S-boson.

The effective mass of the S-boson is determined by only two-particle interactions of a polarization nature:

$$m_{\text{eff}}^{-1} \sim \langle \phi_s(\mathbf{r}_1)\phi_3(\mathbf{r}_2) \,|\, U_{\text{pol}} \,|\, \phi_s(\mathbf{r}_1-\mathbf{R})\phi_s(\mathbf{r}_2-\mathbf{R}) \rangle \sim \langle \phi_s(\mathbf{r}) \,|\, \phi_s(\mathbf{r}-\mathbf{R}) \rangle^2. \quad (9)$$

Here $U_{\rm pol}$ is the effective two-particle potential of the polarization interaction, and $\langle \phi_s(\mathbf{r}) | \phi_s(\mathbf{r}-\mathbf{R}) \rangle$ is the overlap integral of the s-orbitals for the nearest centers. The JT centers making up the lattice constitute a reservoir for the S-bosons which are interacting with each other. The result of this interaction may be one form or another of a low-temperature cooperative JT ordering of the static or dynamic ordering of electric dipoles. An S-boson liquid will be stable, within certain limits, with respect to changes in the nature of the ordering of the lattice of Jahn–Teller centers, at least up to certain critical values of the local polarizability of the lattice. Accordingly, for a lattice of M^h_{sp} centers, in addition to the known phase states--an antiferromagnetic insulating state (large values of U, high threshold for the disproportionation reaction) and a Fermi-liquid state (small values of U), we need to consider yet another possible state: a highly correlated Bose system with a strong pseudo-JT effect (moderate values of U).

2. Relationship with the copper–oxygen high-T_c superconductors. The role of the M^h_{sp} center in the copper–oxygen high-T_c superconductors is played by the one-hole CuO_4^{6-} cluster with D_{4h} symmetry. The s-like ground state of this cluster is of a hybrid $Cu3d_{x^2-y^2}-O2p_\sigma$ nature with symmetry b_{1g}. Analysis of the optical properties of a wide range of copper oxides with CuO_4^{6-} clusters[9] leads to the assertion that the fundamental absorption band peaking at $\Delta_1 = 1.5$–2.0 eV is, according to its intensity and polarization properties, related to an $b_{1g}-e_u$ charge–transfer transition. It thus becomes possible to identify the first excited state of the CuO_4^{6-} cluster with the purely oxygen p-wave e_u orbital doublet of p type. Clearly, the predominantly "copper" nature of the b_{1g} state and the purely oxygen nature of the e_u state promote satisfaction of the condition $U(b_{1g}b_{1g}) > U(b_1e_u)$, required for quasidegeneracy or proximity of $^1A_{1g}$ and ^1E_u terms of the two-hole configurations b^2_{1g} and $b_{1g}e_u$, respectively. The onset of absorption bands in mid-IR range, $\hbar\omega \sim 0.1$–0.5 eV, upon the introduction of holes in the CuO_2 planes of copper oxides[10] directly indicates a quasidegeneracy in two-hole CuO_4^{5-} clusters and thus the possibility of a transition weak pseudo-JT effect to a strong one upon the addition of a hole to the original CuO_4^{6-} cluster. In this case the introduction of additional holes or electrons in a CuO_2 plane leads to the formation of $[CuO_4^{5-}] \equiv [M^h_{sp}]_{JT+}$ or $[CuO_4^{7-}] \equiv [M^h_{sp}]^-_{JT}$ JT centers and nucleation centers (micrograins) of a new phase: a strongly correlated Bose liquid. In this phase, S-bosons consisting of paired electrons in a completely filled b^2_{1g} shell, $^1A_{1g}$, move through the lattice of $[CuO_4^{5-}]_{JT}$ JT centers. The increase in the number of nucleation centers and the growth of these centers suppress the original antiferromagnetic insulating phase. When a percolation threshold is reached, the stage is set for a transition of the system to a metallic state and a superconducting resistive transition at the condensation temperature of the S-bosons. A further increase in the concentration of dopant holes (or electrons) can lead to a strong electrostatic screening and a transition of the system into a "Fermi-liquid" regime.

The introduction of holes (electrons) in the copper–oxygen high-T_c superconductors is accompanied by a partial charge and structural disorder outside the CuO_2 planes, which leads to some disorder of the lattice of JT centers: the reservoir of S-bosons in CuO_2 planes. This disordered state of the JT lattice (of the dipole-glass type) in CuO_2 planes may be involved in many examples of a "pseudoimpurity"

behavior of copper–oxygen high-T_c superconductors (low-temperature anomalies in specific heat, observation of paramagnetic centers both in susceptibility and in resonance, features of Raman spectra, etc.). Confirmation that nucleation centers of a new phase arise as system of two types of JT (CuO_4^{5-} and CuO_4^{7-}) upon the introduction of holes (or electrons) in CuO_2 planes comes from the results of a study of the absorption in the mid-IR range for a long list of high-T_c superconductors.[10,11] These results demonstrate the following: (a) For both hole and electron doping, two absorption bands appear. These bands are identified with transitions of the lower branch of the adiabatic potential to the upper branch at $\hbar\omega \sim 4E_{JT}^{\pm}$ in $[CuO_4^{5-}]_{JT}$ and $[CuO_4^{7-}]_{JT}$ centers, respectively. (b) The integrated intensity of the absorption bands induced by doping indicates that the number of active centers is much greater than the concentration dopant holes (electrons). As expected, the Hall effect at a low doping level[11] detects only the excess number of CuO_4^{5-} or CuO_4^{7-} centers, i.e., effectively, the deviation of the concentration of S-bosons in nucleation centers from $n_b=0.5$. The faster growth of the intensity of the low-energy (LE) absorption band in the mid-IR range in comparison with the high-energy (HE) band with increasing concentration of holes in LaSrCuO and YBaCuO systems makes it possible to unambiguously link the LE band with $[CuO_4^{5-}]_{JT}$ clusters and the HE band with $[CuO_4^{7-}]_{JT}$ clusters. Two absorption bands in the mid-IR range are also observed upon photoexcitation of LaSrCuO and YBaCuO systems.[12] Upon photoexcitation at a low concentration of dopant holes (electrons), the absorption in the mid-IR range is a superposition of two clearly distinct LE and HE bands. This result is probably evidence of a localization of S-bosons in nucleating regions (a charge-order state). As the concentration of S-bosons in nucleating regions deviates from the value $n_b=0.5$ with increasing concentration of dopant holes (or electrons), the charge-order state gives way to a "mixed"state with delocalized S-bosons and a possible condensation of these entities accompanied by the formation of a superfluid (superconducting) state. In the mid-IR absorption, this circumstance is reflected in a gradual transformation of the LE and HE bands into a single wide band with a simultaneous growth of Drude absorption in the IR range. Independent confirmation that polar JT centers of two types form during both hole and electron doping comes from (in particular) the results of an analysis of EELS spectra of p-type and n-type high-T_c superconductors.[13] Those results indicate p-type states of the same nature near the Fermi level in the two cases.

In conclusion, we note that this model of a new phase is actually a two-band model, including a band of localized vibron biorbitals as centers of a pairing potential and a band of S-bosons, which can be described by an extreme version of the Hubbard model with negative U.[2] This model has the advantage that it combines many physical effects (a Jahn–Teller effect, a variable valence, local pairing, charge transport, excitonic and electronic–vibrational mechanisms for high-T_c superconductivity, etc.) which have previously been discussed, in one way or another, in connection with the problem of high-T_c superconductivity. The two-band nature of this model makes it possible to clearly distinguish physical properties of high-T_c superconductors which are associated with one band or the other, although in several cases it also indicates an unusual origin for the physical effect. Within the framework of this model, it is thus not possible to unambiguously distinguish an electronic–vibrational or excitonic mechanism as the primary mechanism for the high-T_c superconductivity. Finally, we note

that the approach taken in this work can easily be generalized to "copperless" high-T_c superconductors such as $Ba_{1-x}K_xBiO_3$.

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