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LETTER TO THE EDITOR

ANHARMONIC EFFECTS AND POLARON FORMATION IN THE COPPER OXIDES

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We discuss polaron formation in anharmonic lattice. Expanding the local lattice distortion into coherent Glauber states, from the minimum energy condition we determine the hybridization amplitude renormalization and discuss its influence on polaron mobility and magnetic interactions.

The polaron concept was introduced to describe localized states in which electron and the lattice degrees of freedom are coupled together via strong electron-phonon interaction. The model of formation of two polaronic bands in copper oxides based on mixed-valent (MV) behaviour of both copper and oxygen ions was presented in Ref. 1. In this approach, however, only linear terms in lattice distortion electron-phonon coupling and harmonic lattice were taken into account. The aim of the present contribution is to study anharmonic effects associated with small polaron formation. With transition between different electronic configurations of MV ion is associated respective change in ionic volume. Provided that valence fluctuations are sufficiently slow to allow surrounding ions to relax to appropriate electronic state they generate local distortion of the lattice. The distortion can achieve significant values, for example, in the $La_{2-x}Sr_xCuO_4$ the Cu-O bond length change from 0.213 nm in case of $[\text{Cu-O}]^0$ complex Cu^{+2}-O^{-2} states to 0.194 nm in the $[\text{Cu-O}]^{+1}$ complex. The large values of local lattice distortions indicate that anharmonic effects may be of importance in polaron formation.

Let us assume that MV ion located at site R_i fluctuates between $\mid l^n >$ and $\mid l^{n-1}L >$ electronic states, where $l = d$ or f denote localized electronic state while $L = s$, p or d are the band states. The Hamiltonian of the system we assume to be given in the form [2]:

$$H_0 = \sum_k \epsilon_k \cdot c_k^+ c_k + \sum_j E_j \cdot b_j^+ b_j + \sum_{kj} [V_{kj} \cdot e^{\mathrm{i}\vec{k}\vec{R}_j} \cdot c_k^+ b_j + h.c.] \tag{1}$$

where in (1) first and second term describe energies of band and localized electronic states with c_k^+, c_k, b_j^+ and b_k being respective creation and destruction operators, while third term describes hybridization between these states.

In the copper oxides one would expect two fluid picture of Cu^{+3} and O^{-1} polarons, the one being small and heavy the latter of intermediate character between large and small polarons [1]. In the following we will focus our attention on the small polarons associated with the CuO_6 octahedron breathing modes i.e. to a case for which the anharmonic effects are of importance. In the conventional approach the linear coupling of an electron to harmonic lattice of the following form is considered [2]

$$H_1 = \sum_i \hbar\omega \cdot a_i^+ a_i + \lambda \sum_i (a_i^+ + a_i) \cdot (2b_i^+ b_i - 2n + 1) \tag{2}$$

where n-is the occupation number of $\mid l^n >$ state. The first term in (2) represents the energies of N harmonic oscillators, while the second describes the linear electron-phonon interaction. For n=1 the Hamiltonian (2) reduces to form given, e.g., in Refs. 2 and 3. In (2) we assume that the electron-phonon coupling is dominated by longitudinal optic (LO) phonons (represented by operators a_i^+ and a_i), which sense more effectively the ionic shift or size effect. Provided that both electron-phonon coupling constant λ and lattice distortion are small, Eq. (2) describes satisfactorily the elastic contribution to the energy of the system. However, since the ligand distortions in case of the above mentioned substances exceed 10 percent of the lattice spacings neither harmonic lattice nor linear electron-phonon coupling approximations can be justified. In this case the description of polaronic effects requires consideration of higher degree electron-phonon coupling as well as anharmonic contribution to the elastic energy. The aim of this paper is to study the effect of anharmonic lattice and higher-order electron-phonon coupling on polaronic effect in mixed-valent solids. The expansion of the electron lattice interaction energy in powers of local distortion will allow consideration of the higher-order terms, at least of the bilinear one of the form

$$H_2 = \Gamma_2 \sum_i (a_i^+ + a_i)^2 \cdot (2b_i^+ b_i - 2n + 1). \tag{3}$$

Similar generalization of electron-phonon coupling in polaron theory has been considered recently in Ref. 4. Let us consider a system described by the Hamiltonian:

$$H = H_0 + H_1 + H_2 = \sum_i H_i \tag{4}$$

i.e. MV ion system with local quadratic electron-phonon interaction and anharmonicity of the lattice taken into account. First of all we will find the ground states of the lattice associated with the two accessible electronic configurations. According to Ref. 5 the strain fields around the MV ion associated with the two accessible electronic states can be expanded in a unique way in terms of the the coherent Glauber states $|\alpha)_i$:

$$|\alpha)_i = \exp[\alpha \cdot (a_i^+ - a_i)] \cdot |0> . \tag{5}$$

They are the eigenstates of the phonon destruction operators a_i i.e. fulfilling the relation [5]:

$$a_i|\alpha)_i = \alpha \cdot |\alpha)_i. \tag{6}$$

In Eq. (4) $|0>$ denotes the phonon vacuum. In principle the expansion of arbitrary lattice state $|F)_i$ reads :

$$|F)_i = \frac{1}{\Pi} \cdot \int |\alpha)_i \cdot F(\alpha^*) \cdot e^{-\frac{1}{2}|\alpha|^2} \cdot \mathrm{d}^2\alpha \tag{7}$$

where

$$F(\alpha)_i = (\alpha|F)_i \cdot e^{-\frac{1}{2}|\alpha|^2} \tag{8}$$

and the integration is extended over entire area of complex plane. However, since both accessible electronic states have well defined value of local normal coordinate

$$Q_i = (\frac{\hbar}{2M\omega})^{\frac{1}{2}} \cdot (a_i^+ + a_i), \tag{9}$$

which describes distortion of local environment, only one value of α is allowed in (5) i.e. the expansion amplitude F(α^*) should be proportional to Dirac delta $\delta(\alpha - \alpha_o)$. Following Sherington and von Molnar [2] the local lattice ground state in case of $|l^n>$ ionic configuration we assume to be given by the coherent Glauber state $|\alpha_n)_i$ (5) while this of $|l^{n-1}L>$ by the $|\alpha_{n-1})_i$. The ground state eigenenergies of single site Hamitonian H_i (4) associated with these configurations are given by :

$$E_n = (\alpha_n|H_i|\alpha_n)_i \quad \text{and} \quad E_{n-1} = (\alpha_{n-1}|H_i|\alpha_{n-1}). \tag{10}$$

The values of the parameters α_n and α_{n-1} can be easily determined from the energy minimum condition

$$\frac{\partial E_n}{\partial \alpha_n} = \frac{\partial E_{n-1}}{\partial \alpha_{n-1}}. \tag{11}$$

Solving Eqs. (10-11) we obtain:

$$\alpha_n = \frac{-\lambda}{\hbar\omega + 4\Gamma_2}, \qquad \alpha_{n-1} = \frac{\lambda}{\hbar\omega - 4\Gamma_2}. \tag{12}$$

The most important effect of the local lattice distorsion is the renormalization of the hybridization amplitude V_{kj}. If we account for the lattice states the MV ions fluctuate between $|l^n, \alpha_n)$ and $|l_{n-1}, L, \alpha_{n-1})$ quantum states. Thus, the effective hybridization H_{hyb}^{eff} renormalizes according to [2]:

$$H_{hyb}^{eff} = (\alpha_n | H_{hyb}^0 | \alpha_{n-1}) \tag{13}$$

where the H_{hyb}^0 is the third term of Eq. (1). In view of Eq. (13) the effective hybridization can be written as:

$$\tilde{V}_{kj} = V_{kj} \cdot \exp(-\frac{1}{2}(|\alpha_n|^2 + |\alpha_{n-1}|^2) + \alpha_n \alpha_{n-1}) = V_{kj} \cdot \exp(-\frac{1}{2}|\alpha_n - \alpha_{n-1}|^2). \tag{14}$$

The classical current density formula in the MV system reads [8]

$$\vec{j} = -e \sum_k \frac{\partial \epsilon_k}{\partial k} c_k^+ c_k - e \sum_{jk} \frac{\partial V_{jk}}{\partial k} (b_j c_k e^{\mathrm{i}\vec{k}\vec{R}_j} + h.c.). \tag{15}$$

In the adiabatic limit, when the phonon cloud follows the electron, the second term in Eq. (15) gives us the polaron motion contribution to the current density. This allows us to estimate change in the polaron mobility. The immediate consequence of renormalization (14) is the increase of lifetime of localized state i.e., the reduction of polaron mobility and effective exchange integrals. Depending on the relation between quantities $\gamma = |\alpha_n - \alpha_{n-1}|^2$ and $\gamma^0 = |\alpha_n(\Gamma_2 = 0) - \alpha_{n-1}(\Gamma_2 = 0)|^2$ the quadratic coupling (3) can either increase (for $\gamma > \gamma^0$) or reduce ($\gamma < \gamma^0$) the renormalization (14). As one can see from (12-14), independently on the sign of coefficient Γ_2 the quadratic electron-phonon coupling reduces the renormalization below the $\Gamma_2 = 0$ value provided that $\Gamma_2^2 > (\hbar\omega)^2/8$. In the $\Gamma_2 \to \infty$ limit polaron recovers the free electron mobility. Contrary to the former case, for $\Gamma_2^2 < (\hbar\omega)^2/8$ the renormalization factor γ increases and for $\Gamma_2^2 \to (\hbar\omega)^2/16$ we have complete localization, i.e. $\tilde{V}_{kj} \to 0$.

Provided that the lattice distortion associated with the polaron formation is sufficiently large, it is reasonable to account for anharmonic contribution to the elastic energy. We take the anharmonic contribution to the elastic energy in the form of double-well potential, i.e. in the Hamiltonian we should account for a contribution H_A given by:

$$H_A = \sum_i \delta \cdot (a_i^+ + a_i)^4. \tag{16}$$

To study the effect of anharmonic term in elastic energy we add the term (16) to the Hamiltonian (4) and determine anew the ground state of the lattice associated with respective ionic configurations. Repeating the procedure performed in (10-12), with anharmonic contribution (16) included in (4), we find the ground state eigenenergies associated with both electronic configurations of an ion:

$$E_n = (\hbar\omega + 4\Gamma_2) \cdot |\alpha_n|^2 + 2\lambda \cdot |\alpha_n| + 16\delta \cdot |\alpha_n|^4$$

$$E_{n-1} = (\hbar\omega - 4\Gamma_2) \cdot |\alpha_{n-1}|^2 - 2\lambda \cdot |\alpha_{n-1}| + 16\delta \cdot |\alpha_{n-1}|^4. \tag{17}$$

The minimization procedure (11) enables us to find the values of α_n and α_{n-1}. The positive 4th term (16) will supress the lattice distorsion and therefore further increase the polaron mobility. From (17) one obtains that for some values of parameters Γ_2 and δ, the quantity $\gamma = |\alpha_n - \alpha_{n-1}|^2$ can be smaller compared to the case $\Gamma_2 = \delta = 0$.

Let us consider the bipolaron binding effect on the mobility. The local lattice distortion, associated with the polaron formation, is a source of atomic level stresses [7]. Two polarons associated with different ionic centers couple to each other via long-range components of these stresses [6,7].

The Cu^{3+} polaron coupling via long-range nonsymmetric strains can be written as [6,7]

$$H_{LR} = \sum_{ij\mu\nu} \Delta_{ij}^{\mu\nu} \cdot (Q_{i\mu}^+ + Q_{i\mu})(Q_{j\nu}^+ + Q_{j\nu}). \tag{18}$$

The coupling constants Δ_{ij} depend on relative separation of polarons as r_{ij}^{-3}, thus it suffices to limit the elastic interaction (18) to nearest neighbours. Let us evaluate the ground state eigenenergy of the lattice system with one pair of polarons, located at neighbouring sites, bound by interaction (18). The elastic energy correction is given by [7]:

$$\delta E_{corr} = \tilde{\Delta} \cdot \alpha_{n-1}^i \alpha_{n-1}^j \approx \tilde{\Delta} \cdot \alpha_{n-1}^2. \tag{19}$$

Repeating the minimization procedure with the term (19) taken into account, in the case $\delta = 0$ we receive the respective formulae for α_{n-1}^* and α_n^* as:

$$\alpha_{n-1}^* = \frac{\lambda}{\hbar\omega + \tilde{\Delta} - 4\Gamma_2}, \quad \alpha_n^* = \frac{-\lambda}{\hbar\omega + 4\Gamma_2}. \tag{20}$$

Since the polaron binding requires $\tilde{\Delta} < 0$ the polaron binding constant acts in the same way as the phonon mode softening. Provided that Γ_2 has the value, for wich the polaron mobility increases with respect to the $\Gamma_2 = 0$ case, the bipolaron binding energy strengthnes this effect. This means, in view of Eq. (12), that with anharmonic contribution to elastic energy accounted for, the Cu^{+3} like polarons are not neccessarily localized. Its mobility can be further increased by bipolaron formation. Thus, along with the oxygen centered polaron band the copper-like polaron band can contribute to formation of superconducting state.

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ANHARMONIČKI EFEKTI I TVORBA POLARONA U BAKRENIM OKSIDIMA

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Razmatra se tvorba polarona u anharmoničkoj rešetki. Razvojem lokalnog izobličenja rešetke u Glauberova stanja, postavljanjem uvjeta minimalne energije renormalizirana je amplituda hibridizacije i razmotren njezin utjecaj na pokretnost polarona i magnetska djelovanja.