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SUPERCONDUCTORS**

**AUTHOR(S): A. R. Bishop
J. Mustre de Leon
M. I. Salkola**

SUBMITTED TO: Plenum Press

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POLARON TUNNELING IN HIGH-TEMPERATURE SUPERCONDUCTORS

A. R. Bishop, J. Mustre de Leon, and M. I. Salkola

Los Alamos National Laboratory
Los Alamos, NM 87545, USA

ABSTRACT

Nonlinear self-trapping effects are frequently proposed in the nonlinear science community — in contexts from excitons, magnons, and polarons in solid state materials, to molecular crystals and polypeptides, to nonlinear optics. The general phenomena of self-trapping involves the selfconsistent response of one field to one or more with which it is coupled, and provides excellent examples of coexisting influences of nonlinearity, lattice discreteness, quantum and thermal fluctuations, disorder, competing timescales, etc. Correspondingly, many approximate analytical and numerical techniques have been used to approach these complex issues. Here we consider a simple copper-oxygen cluster which appears in many high-temperature superconductors, which displays unusual structural and optical behavior, and which we model in terms of “dynamic polaron tunneling.” We introduce a Peierls-Hubbard model to describe this cluster and use exact diagonalization to evaluate its properties. We emphasize the importance of nonlinear and nonadiabatic aspects of structural measurements, inelastic neutron scattering, and phonon spectroscopy (infrared and Raman).

I. INTRODUCTION

Nonlinear phenomena characterize many aspects of high-temperature cuprate superconductors [1] — from microstructural texturing appearing as precursors to structural phase transitions and interpreted as local rotations and distortions of perovskite unit cells (twinning, tweed, etc., textures [2]); to structure, dynamics and melting of anisotropic (Abrikosov) flux lattices in the superconducting state [3]; to microscopic spin, charge or lattice configurations (polarons, bags, excitons) invoked in theories of the pairing mechanism itself [4].

Here, we will describe one specific aspect which connects directly to the phenomenon of energy or charge polaronic “self-focusing” studied widely in the nonlinear science community. Such self-focusing is typical of coupled field problems, as in magnon-phonon, exciton-phonon (Davydov-Scott [5]), or electron-phonon cases. (We will discuss the last case here.) In such problems, it is sometimes possible to make use of a separation of timescales to slave one field to the other adiabatically, leading to the nonlinear Schrödinger equation or discrete versions thereof (as in “discrete self-trapping equations” [5]). However, in general, especially for small numbers of lattice sites and physically relevant response functions, nonadiabatic effects are very important. Furthermore, it is necessary to consider coexisting (and often) competing influences of self-focusing (nonlinearity), quantum and thermal fluctuations, disorder, and lattice discreteness. Serendipitously, the complex chemistry of high-temperature-superconductors appears now to provide a clear example, where these

issues must be addressed. In view of the intense experimental focus on these materials, there is an excellent opportunity to investigate the complex problem in detail, and to develop a proper experimental and theoretical appreciation of the signatures of the dual faces of polarons — namely the two fields which are self-coupled, in our case lattice deformation and charge (electronic) density. This appreciation and development of techniques should be valuable far beyond the high-temperature superconductors themselves.

II. THE CLUSTER MODEL

The atomic structure of all high-temperature cuprate superconductors is distinguished by planar Cu-O sheets in which the superconductivity is concentrated [1]. However, careful materials preparation and experimentation over the last few years has made it clear now that the material lying *between* the Cu-O planes, as well as the c-direction [i.e., perpendicular to the (a-b) planes], are intimately involved. In particular, electronic structure calculations [6] show anomalously strong electron-phonon (charge-transfer-lattice) coupling in the c-direction involving the sensitivity of the a-b plane electronic properties to motion of the so-called O(4) axial (“bridging”) oxygen atoms lying *off* the plane. Again, optical studies [7] have shown an unusual correlation of c-axis phonon (dielectric constant) frequencies with the a-b plane frequency dependent conductivity. Many more indications are reported in Ref. [1] along with important evidence from structural probes (XAFS [8], inelastic neutron scattering [9,10], ion-channeling, etc.) for *local, dynamic* structural anomalies involving unusually large distortions of certain Cu-O bond lengths. It is not clear yet whether these distortions are primarily spectators to the superconductivity or whether they fundamentally drive the hole pairing. However, it is clear that the lattice distortions are large and anomalous at T_c (the superconductivity onset temperature) so that meaningful microscopic theories must include appropriate electron-lattice coupling (spin-phonon charge-phonon, etc.).

The importance of the lattice and especially the c-axis is evident in all high-temperature cuprate superconductors [1]. Here we consider only the case of $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($T_c \sim 93$ K), whose atomic structure contains “O(4) - Cu(1) - O(4)” structural units in the c-direction bridging symmetrically between active Cu-O planes [1]. It is for these 3-site O-Cu-O clusters that a “polaron-tunneling” model of the local chemistry has been recently developed [11,12] to interpret anomalous structural and optical data.

The cluster Hamiltonian used is

$$H = H_{\text{cl}} + H_{\text{ph}} + H_{\text{el-ph}} \quad (1)$$

with

$$\begin{aligned}
H_{\text{el}} &= \sum_n \epsilon_n \rho_n + \sum_{\langle nn' \rangle \sigma} t_{nn'} (c_{n\sigma}^\dagger c_{n'\sigma} + \text{h.c.}) \\
&\quad + U \sum_n \rho_{n\uparrow} \rho_{n\downarrow} + \sum_{\langle nn' \rangle} V_{nn'} \rho_n \rho_{n'} , \\
H_{\text{el-ph}} &= -\lambda_{IR} (a_{IR} + a_{IR}^\dagger) (\rho_1 - \rho_3) \\
&\quad - \lambda_R (a_R + a_R^\dagger) (\rho_1 + \rho_3 - \rho_o) , \\
H_{\text{ph}} &= \hbar \omega_{IR} a_{IR}^\dagger a_{IR} + \hbar \omega_R a_R^\dagger a_R .
\end{aligned}$$

Here, $c_{n\sigma}^\dagger$ creates an electron of spin σ at site n , $\rho_{n\sigma} = c_{n\sigma}^\dagger c_{n\sigma}$ (electron density operator), and $\rho_n = \sum_\sigma \rho_{n\sigma}$. The 3 sites are labelled $n = 1, 3$ for O(4), and $n = 2$ for Cu(1); $t_{nn'} = t$ for the electron transfer matrix element between O(4) and Cu(1) sites and $t_{nn'} = t'$ for the effective matrix element connecting O(4) sites through parts of the unit cell not explicitly included in the cluster; ρ_o is chosen to fix the average cluster size. The Coulomb interaction is described by the on-site potential U and longer-range terms $V_{nn'}$. In the absence of el-ph interactions, the cluster has just two phonon modes which are assumed to be harmonic, consistent with local density frozen phonon calculations. The symmetric phonon is Raman active and the antisymmetric one is infra-red active — these are described by creation operators $a_R^\dagger$ and $a_{IR}^\dagger$ with bare frequencies ω_R and ω_{IR} , respectively. The term $H_{\text{el-ph}}$ contains linear electron coupling to each of these phonons, with strength λ_R and λ_{IR} , respectively. Parameter values in Eq. (1) appropriate to $\text{YBa}_2\text{Cu}_3\text{O}_7$ are discussed in Refs. [11,12] based on available electronic structure and experimental data. For the present purposes we assume representative values only and concentrate on the basic phenomenon of “polaron tunneling” below.

III. POLARON TUNNELING

Polaron tunneling occurs in our problem by introducing two holes (i.e. removing two electrons) from the elemental cluster. In the ground state, one hole is predominantly located at the Cu(1) site and the second fluctuates between the O(4) sites. This is a fundamentally quantum-mechanical effect and exact diagonalization (Lanczos) numerical techniques have been used [11] to represent it accurately — including all the electronic degrees-of-freedom and a large number of IR and R phonon states in the basis set for our cluster. Approximation techniques (slaving, adiabatic, antiadiabatic, coherent states, etc.) can be appropriate in weak or strong el-ph coupling limits but not in the intermediate coupling regime which turns out to be relevant in the present context — nonadiabatic, multiphonon, symmetry-mixing effects are a central part of the behaviour.

The numerically exact many-body ground-state wave-function of our model is shown in Fig. 1, plotted as a function of the IR and R displacement coordinates, and after summing over all electronic degrees-of-freedom. We see that, as λ_{IR} increases the wave-function shape deviates from a Gaussian, a double-peak structure begins developing at intermediate λ_{IR} , and the two peaks are completely separated for large λ_{IR} . In contrast, no double-well structure develops as λ_{IR} increases. This behavior is quite intuitive since the configuration *short* Cu(1) - upper O(4) bond and *long* Cu(1) - lower O(4) bond is

expected to be degenerate with the reversed short- and long-bond lengths configuration. Anharmonic effects only, not double-well nonlinearity, are found in the Raman coordinate [12].

Careful investigation of the many-body eigenstates, including both phonon and electron degrees of freedom, leads to the following interpretation as λ_{IR} is increased [11]. For small values of λ_{IR} , the tunneling of holes between the equivalent O(4) sites occurs on a time scale faster than the ionic motion, allowing the use of adiabatic approximations, and yielding simple quasiharmonic phonon frequency shifts and phonon expectation values $\ll 1$. As λ_{IR} increases to intermediate strength, the motion of the hole couples strongly to the phonons, and *dynamically* generates tunneling between two equilibrium positions depending on the location of the O(4) hole. Correspondingly, the O(4) position follows the hole tunneling, leading to the double Cu-O bond-length distribution shown in Fig. 1(b). This correlation of structure and hole density is what is referred to as polaron self-localization. Since the O(4) is now dressing the hole (the phonon expectation value is significant), the tunneling rate for the composite object is slow — the prediction in high-temperature superconductors is $\lesssim 100 \text{ cm}^{-1}$ — and the difference between short and long Cu-O bond lengths can be large ($\gtrsim 0.1 \text{ \AA}$). It is of course very interesting that the experimental situation in YBaCu₂O₇ and many related high-temperature superconductors appears to place us [11] in this polaron-tunneling crossover regime with a tunneling energy $\sim k_B T_c$! For very large values of λ_{IR} , the polaron tunneling rate becomes very slow, i.e. the holes are nearly “frozen” in one or the other distorted states, and the ions oscillate harmonically with respect to the shifted equilibrium positions. Coherent states built from phonons defined with respect to the shifted equilibrium (displaced harmonic oscillators) are useful in this regime, which may be viewed as nearly frozen ferroelectricity, i.e. a permanent dipole.

The polaron tunneling frequency is calculated technically as the difference between the first excited-state and ground-state energies; see Fig. (2). This, and the higher lying excited states, control the anticipated IR optical absorption — the imaginary part of the dielectric constant — shown in the inset of Fig. (2). Note that the IR absorption contains a low-frequency (tunneling) component plus a high-frequency mode with a lower energy “shoulder” due to nonlinear mixing of the R and IR symmetries of the uncoupled limit ($\lambda_{IR} = 0$) [11,12]. Note also that the “phonon” frequency is a severe renormalization of the bare phonon frequency. Indeed, lattice dynamics modeling in a static bare potential is in general qualitatively inadequate in the tunneling regime because timescales cannot be separated and it would be necessary to allow the potential to change self-consistently with the charge distribution.

Detailed comparisons with experimental data in YBa₂Cu₃O₇ are given in Refs. [11,12] and will not be repeated here. Rather, we emphasize that polaronic models can only be meaningfully tested if they make experimentally verifiable predictions regarding *both* of the coupled fields — in this case the distortion of the O(4) ions *and* the associated nonlinear, nonadiabatic optical signatures. At the same time, it is essential that experimental techniques are developed which can probe local, slow cluster dynamics, and that interpretation of experiments fully respects the possibility of accompanying anharmonic, nonadiabatic effects. In this respect, conventional IR or R spectroscopy is not optimal since it probes zone-center or boundary responses in wave-vector space, not local zone-interior wavelengths. In principle, recent advances in inelastic neutron scattering resolution (using time-of-flight techniques on pulsed sources [10]), may hold the most exciting prospects. However, here also it is essential to appreciate the possibility of effects far beyond harmonic, adiabatic interpretations such as traditional Debye-Waller analysis.

Figure 1. Squared many-body ground-state wave function of the cluster as a function of the Raman (u_R) and infrared (u_{IR}) coordinates for (a) $\lambda_{IR} = 0.10$ eV, (b) $\lambda_{IR} = 0.12$ eV, and (c) $\lambda_{IR} = 0.15$ eV (in all cases $\lambda_R = 0.10$ eV) for the Hamiltonian given in Ref. [11]. When the phonon coordinate is at the left bump, the extra hole is predominantly on the leftmost oxygen, and vice versa. The scale of the coordinates is fixed to be 3 times the root-mean-square fluctuation of the wave function, and therefore it is different for the three panels.

Figure 2. Energies of the first four infrared allowed transitions as a function of λ_{IR} for the Hamiltonian given in Ref. [11]. The Raman coupling is $\lambda_R = \lambda_{IR}$ for $\lambda_{IR} \leq 0.10$ eV, and $\lambda_R = 0.10$ eV for $\lambda_{IR} \geq 0.10$ eV. There is an avoided crossing of the highest two levels. Inset: $\text{Im } \epsilon(\omega)$ (i.e. infrared absorption) for $\lambda_R = 10$ eV and $\lambda_{IR} = 0.13$ eV (i.e. the crossover double-well regime). The height of peak A is ~ 10 times larger than that of peak C [11].

Inelastic neutron scattering gives information about the system by measuring the dynamic structure factor:

$$S(q, \omega) = \sum_{nn'} v_{nn'} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle e^{-iq\mathbf{r}_n(0)} e^{iq\mathbf{r}_{n'}(t)} \rangle, \quad (2)$$

where $\mathbf{r}_n(t)$ is the position operator of n th scattering nucleus in the Heisenberg picture and $v_{nn'}$ is a cross-section coefficient determined by the scattering lengths of individual nuclei.

Examples of the dynamic structure factor calculated [12] within our cluster model in the tunneling regime are shown in Fig. 3. These illustrate: (a) unconventional Debye-Waller broadening with contributions from the O(4) - O(4), Cu(1) - O(4), and Cu(1) - O(4) splitting lengths; and (b) the need for (and value of) frequency-dependent pair-distribution function analysis [10,12] — appropriate choice of the energy range over which integration is made can pick out subtle effects such as the Cu-O bond length splitting, whereas inappropriate choices introduce timescales which obscure these effects because of quantum fluctuations. These lessons will become increasingly important as advances in structural analysis techniques allow us to probe local, dynamic effects in many contexts such as microstructure in elastic materials and precursor cluster dynamics at structural phase transitions.

IV. SUMMARY

In summary, we have seen how electron-phonon coupling, coupling lattice vibrations to charge-transfer, can generate a “dynamic double-well” which *correlates* structural distortion of specific Cu-O bonds with charge (hole) density in a polaronic sense, including quantum-mechanical tunneling of the composite charge-lattice distortion between equivalent states. In the 3-site cluster considered here, the physical manifestations are a slow oscillation of the Cu-O bond length between two limiting values accompanied by correlated optical (IR, R) absorptions which have distinctly nonadiabatic and multiphonon character. The relation of these dynamic charge-transfer effects to superconductivity in the plane are still under debate. However, these focus around (a) multiphonon mechanisms coupling the c-axis optical phonon to buckling distortions in the a-b plane; and (b) nonlinear excitonic pairing induced by the oscillating dipole field supplied by the dynamic polaron.

Finally, we note the conceptual similarity of the present polaron model to discussions of Davydov-Scott solitons [5] in lattice-vibrational exciton coupled systems. In both cases, quantum lattice effects must be treated adequately to restore translational symmetry which is broken in semiclassical and adiabatic approximations. Restoring this symmetry leads to polaron “band structures” with wave-vector labeling of Bloch states [5]. For the small cluster here, the band structure is very simple and the most important Bloch state describes the polaron tunneling. Clearly, such systems are excellent vehicles with which to study [12]; (i) effects of temperature and disorder, both of which can compete with the polaron’s tunneling and its particle-like bound phonon coherence; and (ii) physically relevant manifestations of complex dynamics, including chaos, in a truly quantum system — evident in the complex dependence of excited state energies as a function of electron-phonon coupling constants [12].

(a)

(b)

Figure 3. The dynamic structure factors (a) $S(q, \omega_T)$ and (b) $S_T(q) \equiv \int_0^{\omega_T} d\omega S(q, \omega)$, as a function of momentum transfer $\hbar q$. The insets show corresponding spatial Fourier transforms (in units of $\text{\AA}^{-1}$) as a function of distance r . The parameters are $\lambda_{IR} = 0.156$ eV and $\lambda_R = 0.156$ eV (ie., the crossover double-well regime) [12].

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