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LETTER TO THE EDITOR

ELECTRONICALLY INDUCED ANOMALY IN LO PHONON DISPERSION OF HIGH-T_c SUPERCONDUCTORS

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Dedicated to Professor Kseno Ilakovac on the occasion of his 70$^{\mathbf{th}}$ birthday

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Strong, electronically-induced anomaly in the spectrum of the longitudinal optical (LO) phonons propagating along the main axes of the CuO_2 plane is tentatively attributed to the oxygen-oxygen charge transfer between two in-plane oxygen atoms. It is argued that this charge transfer can be large and that it is strongly coupled to the LO dimerization of the oxygens. The corresponding negative contribution to the free energy is quartic in the LO phonon amplitude, indicating the instability via the first-order phase transition, with a concomitant domain structure.

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The discovery of the electron-induced anomaly in the dispersion of the oxygen longitudinal optical (LO) phonons, which propagate along the main axes of the CuO_2 plane in $La_{2-x}Sr_xCuO_4$ (LSCO) [1, 2] and $YBa_2Cu_3O_{6+x}$ (Y123) [3], has renewed interest in the origin of this anomaly and its possible interplay with high-T_c superconductivity. Similar anomalies seem to occur in La_2CaCuO_{4+x} [4], $Pb_2Sr_2(Ca,Y)Cu_3O_8$ and $Li_{1-x}T_{2-x}O_4$ [5]. The oxygen LO phonon is anomalous even in the superconducting perovskite $Ba_{1-x}K_xBiO_3$ [6, 7]. On the other hand, structural instabilities of a somewhat different nature have been observed in $La_{2-x}Ba_xCuO_4$ [8] and $Tl_2Ba_2CaCu_2O_8$ [9], where oxygen atoms move perpendicularly to the CuO_2 planes.

Common feature observed in oxygen LO phonons of LSCO and Y123 is the occurrence of a break in the dispersion at $2\pi/a(0.25,0)$, half-way between the origin

(0,0) and the edge (0.5,0) of the CuO_2 planar Brillouin zone (BZ). This break was tentatively attributed [1] to the (quasi)static longitudinal dimerization of the in-plane oxygens with wave vector [0.5,0] shown in Fig. 1a. The latter should produce the new BZ edge at [0.25,0] and, correspondingly, a gap in the LO dispersion. However, the (quasi)static dimerization has never been observed. This led to the speculation [1] that the dimerization is highly disordered, with various, usually very low estimates of the corresponding correlation length. However, the length in question should not be shorter than a few times $4a$, if a gap of an LO phonon with a wavelength $4a$ is attributed to the $2a$ dimerization.

Although the LO phonon anomaly depends strongly on doping, the electronic mechanism that produces it has not been understood until now.

The conventional Peierls-like explanation is unlike, because it requires the appearance of strong [0.5,0] charge density fluctuations, coupled to the lattice by a linear electron-phonon coupling.

Although some phonon-induced features seem to exist [10] in the electron spectra, recent ARPES measurements [11-14] and their theoretical interpretations [15] have yielded, for the whole range of doping, Fermi surfaces of LSCO or Y123 which do not possess the nesting properties favouring [0.5,0] charge fluctuations. On the other hand, there is no apparent reason why the bare linear electron-phonon coupling would be particularly strong [16] for the LO dimerization.

The aim of this note is to examine a mechanism which can explain the LO anomaly in LSCO and Y123. When the linear electron-phonon coupling is ruled out, the natural step is to consider quadratic electron-phonon coupling and charge fluctuations which couple through it to the lattice. Such a quadratic electron-phonon coupling was already used to explain the LTO/LTT transition in $La_{2-x}Ba_xCuO_4$ [17], in which oxygen atoms move perpendicularly to the plane.

When the LO dimerization mode is involved quadratically in the electron-phonon coupling, it can only couple to the homogeneous charge distribution within the unit cell. This charge distribution can be either symmetric or antisymmetric with respect to the symmetry operation $x \rightleftharpoons y$. We will show here that the antisymmetric charge distribution is large, that it is exactly the same as the one which leads to the LTO/LTT instability in $La_{2-x}Ba_xCuO_4$ and that it explains satisfactorily the LO instability in LSCO and Y123.

The preceding symmetry analysis can be specified within the tight-binding model, which distributes the holes over the Cu $3d_{x^2-y^2}$ orbital and the $O_{x,y}$ $2p_{x,y}$ orbitals. This model is widely used in the theory of high-T_c superconductors either in the small U or in the large U limit, where U is the Coulomb repulsion at the Cu site. Only four single-particle parameters are usually used in addition to U, namely, the Cu and $O_{x,y}$ site energies ε_d and $\varepsilon_p^x = \varepsilon_p^y$, the Cu-O overlap t and the O_x-O_y overlap t' [15].

The variation of the crystal-field potential of the ionic lattice, introduced by the dimerization modes with the amplitudes $u_{\pi,0}$ and $u_{0,\pi}$, leads in the first place to the variation of the site energies, i.e. to the variation of $\Delta_{pd} = \varepsilon_d + (\varepsilon_p^x + \varepsilon_p^y)/2$ and $\Delta_{pp} = \varepsilon_p^x - \varepsilon_p^y$. The variation of the oxygen site energies can be calculated in the point-charge approximation, and written in the form [18, 19]

$$\varepsilon_p^i \approx \frac{2e^2}{a}[\alpha_p^i u_Q + \beta_p^i u_Q^2 + \cdots],\ i = x, y \tag{1}$$

where $Q = (\pi, 0)$ or $(0, \pi)$, $\tilde{u}_Q = 2u_Q/a$, u_Q is the amplitude of the displacement, and $a/2$ is the distance between Cu and O_x.

The parameters α_p^i and β_p^i can be written in terms of two contributions associated with the ionic $(\pi, 0)$ displacements in even and odd CuO_2 planes defined according to Figs. 1. In general, they can also depend on the interplanar phase $\cos(\varphi_z) = \tilde{u}_Q(\text{odd})/\tilde{u}_Q(\text{even})$ (as in Y123, Fig. 1b). Previous calculations [19] estimated α_p^i and β_p^i from the crystal-field potential at the oxygen sites. The values of α_p^i and β_p^i obtained in this way for the $(\pi, 0)$ mode in LSCO and Y123 are given in Table 1. It should be noted that in LSCO (see Fig. 1a) a small linear term α_p^x

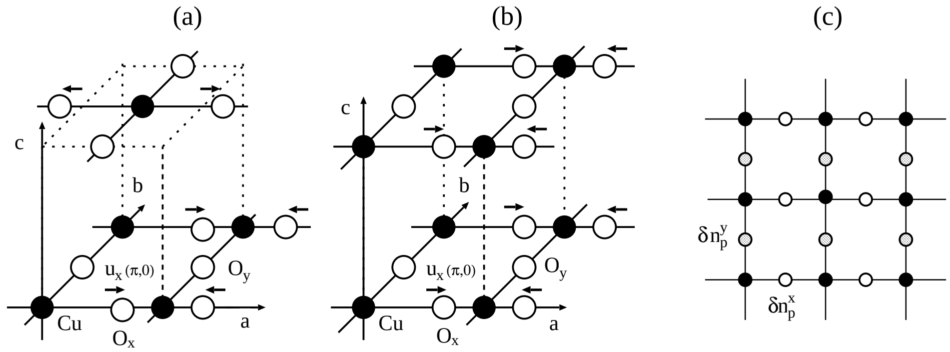

Fig. 1. The $(\pi, 0)$ oxygen LO phonons in LSCO *(a) and* Y123 *(b). Since in* Y123 *there are two* CuO_2 *planes per unit cell, the upper plane will be referred to as an odd, and the lower one as an even plane. The considered sites are placed in an even plane. (c) The homogeneous component of the charge fluctuations induced by the $(\pi, 0)$ oxygen LO phonons.*

TABLE 1. (a) The electron-phonon coupling constants at the oxygen sites O_x *(α_p^x, β_p^x) and* O_y *(α_p^y, β_p^y) for the $(\pi, 0)$ deformation, with φ_z representing interplanar phase defined by $\cos(\varphi_z) = \tilde{u}_Q(\text{odd})/\tilde{u}_Q(\text{even})$. The contributions of the odd planes are given for comparison in the parentheses. (b) The corresponding constants calculated for the LTT deformation of the* La_2CuO_4 *lattice.*

		φ_z	α_p^x	β_p^x	α_p^y	β_p^y
(a)	Y123	0	0.0	1.5	2.4	0.9
		π	0.0	-0.2	1.5	0.9
	LSCO	0, π	0.05 (0.05)	1.1 (0.0)	2.1 (0.0)	0.9 (0.0)
(b)	LTT		0.0	-0.9	0.0	-1.8

comes from the interplanar contributions [i.e from α_p^x(odd)], while large linear term α_p^y is in the first place associated with the intraplanar terms [i.e. with α_p^y(even)]. Notice also that in this lattice the constants α_p^x(even) and β_p^i(odd) vanish for the symmetry reasons.

Singling out the homogeneous component of Δ_{pp}, it is found that

$$\begin{aligned} \delta\Delta_{pp}^H &\approx \tfrac{2e^2}{a}\,(\beta_p^x - \beta_p^y)(u_{\pi,0}^2 - u_{0,\pi}^2), \\ \delta\Delta_{pd}^H &\approx \tfrac{1}{2}\tfrac{2e^2}{a}\,(\beta_p^x + \beta_p^y)(u_{\pi,0}^2 + u_{0,\pi}^2). \end{aligned} \tag{2}$$

$\delta\Delta_{pp}^H$ couples to the homogeneous charge distribution between O_x and O_y, $n_{pp}^H = (n_p^x - n_p^y)^H$ shown in Fig. 1b, adding a bilinear term to the Hamiltonian H_0,

$$H = H_0 + n_{pp}^H \delta\Delta_{pp}^H. \tag{3}$$

In most of the high-T_c superconductors (Y123 is an exception) $\Delta_{pp}^H = 0$ in the non-deformed lattice and $\delta\Delta_{pp}^H$ lifts the $\varepsilon_p^x = \varepsilon_p^y$ degeneracy of the CuO_2 unit cell in a way similar to the Jahn-Teller (JT) effect. Even in the presence of the hybridizations t and t', the $\delta\Delta_{pp}^H$ JT effect leads to large energetic gains. In the conventional JT effect, charge transfer between the two levels, whose degeneracy is lifted, is described by a step function of the splitting $\delta\Delta_{pp}^H$. In general, the effects of hybridizations t and t' make this charge transfer analytic

$$\bar{n}_{pp}^H \approx \chi_{pp}\delta\Delta_{pp}^H, \tag{4}$$

where χ_{pp} is the exact charge susceptibility for the Hamiltonian (3), i.e., χ_{pp} is related to the exact correlation function $\langle n_{pp}^H n_{pp}^H \rangle$ for the Hamiltonian H_0 of (3). The JT effect is now the consequence of the possibly large χ_{pp}. Actually, singular χ_{pp} in (4) indicates nonanalytic nature of the charge transfer $\bar{n}_{pp}^H$, analogous to the conventional JT effect.

Free energy variation, corresponding to (4), is

$$\Delta F = -\frac{1}{2}\chi_{pp}\delta{\Delta_{pp}^H}^2 + \cdots. \tag{5}$$

It should be noted that, according to Eqs. (2) and (4), ΔF of the Eq. (5) is quartic (of the fourth order) in the dimerization $u_{\pi,0}$. However, when χ_{pp} is singular, ΔF should be evaluated with special care, as discussed below.

Large χ_{pp} is found every time when the Fermi level falls close to the two groups of the quasi-degenerate electronic states associated with the a and b axes of the CuO_2 plane, which are split by finite $\delta\Delta_{pp}^H$. This is particularly the case when Fermi level falls close to the van Hove singularities at (0.5,0) and (0,0.5) points of the two-dimensional Brillouin zone, associated with single-electron propagation in the CuO_2 planes. The single-particle picture can safely be used in two limits of the Hamiltonian H_0 in (3), namely for free fermions ($U = 0$) and for infinite

U (U larger than $\Delta_{pd}, \Delta_{pp}, t$ and t'). In this case, for $T \approx 0$ K, the real part of the generalized susceptibility, given in terms of the vertex functions $g(\mathbf{k})$ and $h(\mathbf{k})$, reads

$$\mathrm{Re}\{\chi_{g,h}(\varepsilon_F)\} \quad = \quad \frac{1}{V}\sum_{\mathbf{k}\sigma} g(\mathbf{k})h(\mathbf{k})\frac{\partial f[\varepsilon_L(\mathbf{k})]}{\partial \varepsilon_L(\mathbf{k})}. \tag{6}$$

Here $f[\varepsilon_L(\mathbf{k})]$ is the Fermi function and $\varepsilon_L(\mathbf{k})$ is the energy of the lowest occupied band [15]. The case $g(\mathbf{k}) = h(\mathbf{k}) = 1$ describes the density of states at the Fermi level, n_F, averaged appropriately over k_BT, and $g(\mathbf{k}) = h(\mathbf{k}) = 2\partial\varepsilon_L(\mathbf{k})/\partial\Delta_{pp}$ the real part of the intraband pp susceptibility, χ_{pp}. Although it has been shown [15] that interband effects might also be important in high-T_c materials, for the sake of simplicity, we retain here only the intraband contributions to χ_{pp}.

For $|\varepsilon_F - \varepsilon_{vH}| \gg \delta\Delta_{pp}$, and assuming that $\Delta^H_{pp} = 0$ at the outset, the susceptibility in Eqs. (4) and (5) takes the form

$$\chi_{pp} = -c \cdot n_F. \tag{7}$$

For the logarithmic van Hove singularity, with the electron-hole symmetry [15] with respect to ε_{vH}

$$n_F \approx \frac{1}{\varepsilon_0}\log\frac{\varepsilon_0}{\max[k_BT, |\varepsilon_F - \varepsilon_{vH}|]}, \tag{8}$$

and c is close to 1/5, as illustrated in Fig. 2. In the opposite limit [15] of the extended van Hove singularity, the electron-hole symmetry with

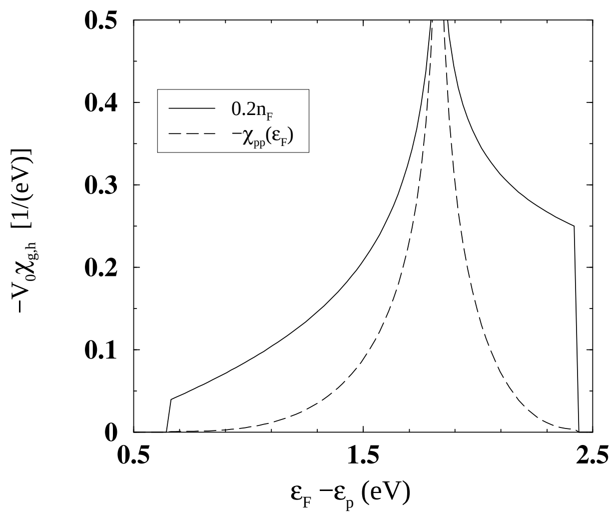

Fig. 2. The density of states and the intraband pp susceptibility as functions of the Fermi energy ε_F, for the simplest case, $\Delta_{pd} = 0.66$ eV, $t = 0.73$ eV and $t' = \Delta_{pp} = U = 0$.

respect to ε_{vH} is entirely broken. At $T = 0$,

$$n_F \approx \frac{1}{\sqrt{\varepsilon_0(\varepsilon_F - \varepsilon_{vH})}} \tag{9}$$

for $\varepsilon_F > \varepsilon_{vH}$, with the appropriate scale ε_0 [15]. The extension of Eq. (9) to $k_B T > (\varepsilon_F - \varepsilon_{vH})$ is straightforward [20].

For $\delta\Delta_{pp} \gg (\varepsilon_F - \varepsilon_{vH}), k_B T$, and in the symmetric case, it is easy to show that Eq. (5) should be modified by the replacement

$$\chi_{pp} \to -\frac{1}{\varepsilon_0} \log \frac{\varepsilon_0}{\delta\Delta_{pp}}\,, \tag{10}$$

making ΔF resemble to the Peierls $T = 0$ result. However, on the contrary to the Peierls' linear case, here $\delta\Delta_{pp}$ is quadratic in u. In the opposite limit of the extended van Hove singularity [15], ΔF becomes linear [21] in $\delta\Delta_{pp}$, just like in the conventional JT effect. Hence the linearity of ΔF for sufficiently large $\delta\Delta_{pp}$ is related to the breakdown of the electron-hole symmetry at ε_{vH}.

This reasoning can be applied to Y123 by the replacement $\delta\Delta_{pp}^H \to \Delta_{pp}^H + \delta\Delta_{pp}^H$ in Eqs. (4) and (5), assuming that the value of Δ_{pp}^H in the non-deformed lattice is sufficiently small.

The physical situation in the high-T_c superconductors is probably closer to the symmetric limit of Eqs. (8) and (10) than to the asymmetric limit of Eq. (9) and its extension to the larger values of $\delta\Delta_{pp}$. In the former case, ΔF is quartic (or quartic Peierls-like) in u. Negative quartic terms are expected to lead to the first-order phase transition, as already found in Ref. [17] for the LTO/LTT transition in $La_{2-x}Ba_xCuO_4$. The compelling feature of such explanation is that the two phases with $u = 0$ and a finite u mix, i.e. the (disordered) domains of the dimerised phase are expected to condense in the $u = 0$ phase. This might explain the difficulty in the experimental observation of the dimerised domains, provided that the latter turns out to be small. The theoretical discussion of the domain size requires the insight into the gradient terms quadratic and/or perhaps quartic in u, which is, however, beyond the scope of the present paper.

Here, we only wanted to stress that the homogeneous charge transfer couples appreciably to the LO dimerization because the electron-phonon coupling constants of Table 1 are large and because the corresponding susceptibility (7) is large. The disadvantage that the electron-phonon coupling is quadratic rather than linear in u is set off by the possibility that the above phase transition is of first order, with the domain structure expected at low temperatures. In this particular respect, the advantage of the O-O charge transfer mechanism proposed here is that it does not activate long-range repulsive Coulomb forces, since each unit cell remains neutral. In contrast to that, long-range Coulomb forces are involved in energy balance of the charged stripes, associated recently [22] with the explanation of LO phonon anomaly. This repulsive Coulomb energy is adverse to the formation of the charge stripes [23], but not to the O-O (or Cu-O) charge transfer stripes.

Further investigations should, therefore, be focused on the nature of the low-temperature lattice and charge patterns, including in particular the charge-transfer stripes since they gain JT energy and do not loose long-range Coulomb energy.

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ELEKTRONSKI INDUCIRANA ANOMALIJA U DISPERZIJI LONGITUDINALNIH OPTIČKIH FONONA VISOKOTEMPERATURNIH SUPRAVODIČA

Jaku, elektronski induciranu anomaliju u spektru longitudinalnih optičkih (LO) fonona, koji se šire uzduž glavnih osi ravnina CuO_2, pokušavamo objasniti prijenosom naboja kisik-kisik između dvaju kisikovih atoma u istoj ćeliji. Tvrdimo da taj prijenos naboja može biti velik te da je snažno vezan s LO dimerizacijom kisikovih atoma. Negativni doprinos energiji je četvrtog reda u dimerizacijskoj amplitudi, što ukazuje na nestabilnost sustava putem faznog prijelaza prvog reda s popratnom domenskom strukturom.