The 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 the two oxygens in the plane. It is argued that this charge transfer can be large and that it is strongly coupled to the zone boundary LO phonons. The corresponding negative contribution to the free energy is quartic in the LO phonon amplitude, making the LO phonon unstable through the first order phase transition, with a concomitant domain structure.

The discovery of the electron-induced anomaly in the dispersion of the oxygen LO phonons, which propagate along the main axes of the CuO$_2$ plane in La$_{2-x}$Sr$_x$CuO$_4$ \cite{1} and YBa$_2$Cu$_3$O$_{6+x}$ \cite{2}, 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$_2$CaCuO$_{4+x}$ \cite{3}, Pb$_2$Sr$_2$(Ca,Y)Cu$_3$O$_8$ and Li$_{1-x}$T$_{2-x}$O$_4$ \cite{4}. The oxygen LO phonon is anomalous even in the superconducting perovskite Ba$_{1-x}$K$_x$BiO$_3$ \cite{5,6}. On the other hand, structural instabilities of a somewhat different nature have been observed in La$_{2-x}$Ba$_x$CuO$_4$ \cite{7} and Tl$_2$Ba$_2$CaCu$_2$O$_8$ \cite{8}, where the oxygen displacements occur perpendicularly to the CuO$_2$ planes.

The common feature observed in oxygen LO phonons of La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) and YBa$_2$Cu$_3$O$_{6+x}$ (YBCO) 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 \cite{1} to the (quasi)static longitudinal dimerisation of the 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 dimerisation has never been observed. This led to the speculation \cite{5} that the dimerisation is highly disordered, with various, usually very low estimates of the corresponding correlation length. The length in question should not however be shorter than a few times $4a$, if an LO phonon gap with wavelength $4a$ is to be attributed to the $2\pi$ dimerisation.

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 unlikely, because it requires the appearance of the 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 \cite{9} in the electron spectra, recent ARPES measurements \cite{10,11,12,13,14} have however yielded Fermi surfaces of LSCO and YBCO which do not possess the nesting properties favoring $[0.5,0]$ charge fluctuations. On the other hand, there is no apparent reason why the bare linear electron-phonon coupling would itself be particularly strong \cite{15} for the LO dimerisation.

The aim of this note is to examine a mechanism which can explain the LO anomaly in LSCO and YBCO. When the linear electron-phonon coupling is ruled out, the natural next step is to consider a quadratic electron-phonon coupling and the 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$_x$CuO$_4$ \cite{16}, in which the oxygens move perpendicularly to the plane. When the LO dimerisation mode is involved quadratically in the electron-phonon coupling, it can only couple to the homogeneous charge redistribution within the unit cell. This charge redistribution can be either symmetric or antisymmetric with respect to the symmetry operation $x \leftrightarrow y$. We will show here that the antisymmetric charge redistribution is large, that it is exactly the same as the one which leads to the LTO/LTT instability in La$_{2-x}$Ba$_x$CuO$_4$, and that it explains satisfactorily the

---

*Electronic address: ivanam@phy.hr*
LO instability in LSCO and YBCO.

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 on the Cu site. Only four single particle parameters are usually used in addition to $U$, namely, the Cu and O_{x,y} site energies $\epsilon_d$ and $\epsilon_x$, the Cu-O overlap $t$ and the O_{x,y}-O_{y} overlap $t'$. [17]

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

$$\epsilon_p^i \approx \frac{2e^2}{a} [\alpha_p^i u_Q + \beta_p^i u_Q^2 + \cdots], \quad (1)$$

where $Q = (\pi, 0)$ or $(0, \pi)$. Previous calculations [19] estimated $\alpha_p^i$ and $\beta_p^i$ from the crystal field potential at the oxygen sites. The values of $\alpha_p^i$ and $\beta_p^i$ obtained in this way for LSCO and YBCO are given in Table 1.

TABLE 1: (a) The electron-phonon coupling constants $\alpha_p^i$ and $\beta_p^i$ for the $(\pi, 0)$ deformation. (b) The corresponding constants calculated for the LTT deformation of the La$_2$CuO$_4$ lattice.

|            | $\alpha_p^i$ | $\beta_p^i$ | $\alpha_p^0$ | $\beta_p^0$ |
|------------|--------------|--------------|--------------|--------------|
| YBa$_2$Cu$_3$O$_7$ | 0.0 | -0.2 | 1.5 | 0.9 |
| La$_1$Sr$_{0.3}$CuO$_4$ | 0.05 | 1.1 | 2.1 | 0.9 |
| LTT        | 0.0 | -0.9 | 0.0 | -1.8 |

Singling out the homogeneous component of $\Delta_{pp}$, it is found that

$$\delta \Delta_{pp}^H \approx (\beta_x^p - \beta_y^p)(u_{x,0}^2 - u_{0,x}^2),$$
$$\delta \Delta_{pd}^H \approx \frac{1}{2}(\beta_x^p + \beta_y^p)(u_{x,0}^2 + u_{0,x}^2). \quad (2)$$

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

$$H = H_0 + n_{pp}^H \delta \Delta_{pp}^H. \quad (3)$$

In most of the high-$T_c$ superconductors(YBCO is an exception) $\Delta_{pp}^H = 0$ in the undeformed lattice and $\delta \Delta_{pp}^H$ lifts the $\epsilon_x^p = \epsilon_y^p$ degeneracy of the CuO$_2$ unit cell, in a way similar to the Jahn-Teller (JT) effect. Even in the presence of the hybridisation $t$ and $t'$, the $\delta \Delta_{pp}^H$ JT effect leads to large energetic gains. In the conventional JT effect the charge transfer between the two levels, whose degeneracy is lifted, is a step function of the splitting $\delta \Delta_{pp}^H$. In general, the effect of hybridisations $t$ and $t'$ is however to make this charge transfer analytic

$$\hat{n}_{pp}^H \approx \chi_{pp} \delta \Delta_{pp}^H, \quad (4)$$

where $\chi_{pp}$ is the exact charge susceptibility for the Hamiltonian [3], i.e. $\chi_{pp}$ is related to the exact correlation function $\langle \hat{n}_{pp}^H \hat{n}_{pp}^H \rangle$ for the Hamiltonian $H_0$ of [3]. The JT effect is now associated with the expectation that $\chi_{pp}$ is large. Actually, a singular $\chi_{pp}$ in [4] indicates a nonanalytic nature of the charge transfer $\hat{n}_{pp}^H$, i.e. recovery of the conventional JT effect, with $\Delta F$ linear in $\Delta_{pp}^H$.

The free energy variation, corresponding to [4], is

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

It should be noted that, according to Refs.[2] and [4], $\Delta F$ of the equation [3] is quartic in the dimerisation $u_{\pi,0}$. However, when $\chi_{pp}$ is singular, $\Delta F$ is to be taken linear in $\delta \Delta_{pp}^H$, i.e. quadratic in dimerisation.

Large $\chi_{pp}$ is found every time when the Fermi level falls close to the two groups of the quasi degenerate electronic states respectively associated with the $a$ and $b$ axes of the CuO$_2$ plane, which get split by the finite $\Delta_{pp}^H$. This is in particular the case when the 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 the single electron propagation in the CuO$_2$ planes. The single particle picture can be used with some confidence in two limits for 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 $g(k)$ and $h(k)$, reads as

$$\text{Re}\{\chi_{g,h}(\varepsilon F)\} = \frac{1}{V} \sum_{k\sigma} g(k)h(k) \frac{\partial f(\varepsilon_L(k))}{\partial \varepsilon_L(k)}. \quad (6)$$

Here $f(\varepsilon_L(k))$ is the Fermi function and $\varepsilon_L(k)$ is the energy of the lowest occupied band [17]. The case $g(k) = h(k) = 1$ describes the density of states at the Fermi level, $n_F$, averaged appropriately over $k_B T$, and $g(k) = h(k) = \varepsilon_L(k)/\partial \Delta_{pp}$ the real part of the intraband pp susceptibility, $\chi_{pp}$. Although it has been shown [17] that interband effects might also be important in high-$T_c$ materials, for the sake of simplicity we shall retain here only the intraband contribution to $\chi_{pp}$. Assuming that $\Delta_{pp}^H = 0$ at the outset and for $\varepsilon_F \approx \varepsilon_{cH}$, it follows than straightforwardly that

$$-\chi_{pp} \approx c \cdot n_F \approx c \cdot \log \frac{\varepsilon_0}{\max[k_B T, |\varepsilon_F - \varepsilon_{cH}|]} \quad (7)$$

with the constant $c$ typically of order 1/5, as illustrated in Fig. 2. $\varepsilon_0$ is the energy scale which characterizes the van Hove singularity at $\varepsilon_{cH}$, assumed two-dimensional, logarithmic, rather than extended one-dimensional, i.e. more singular than the logarithm. $\chi_{pp}$ of Eq. (6) is
singular at low temperatures for $\varepsilon_F \approx \varepsilon_{vH}$, when the expansion (3) breaks down and $\Delta F$ becomes linear in $\delta \Delta^H_{pp}$, i.e. quadratic in the dimerisation displacement $u$. This reasoning can be applied to YBCO by the replacement $\Delta^H_{pp} \rightarrow \Delta^H_{pp} + \delta \Delta^H_{pp}$ in Eqs. (4) and (5), assuming that the value of $\Delta^H_{pp}$ in the undeformed lattice is sufficiently small.

When $n_F$ of (3) is finite, i.e. the negative contribution to the free energy $\Delta F$ can be taken as quartic in $u$. As discussed previously (10), the activation of the negative contribution to $\Delta F$ quartic in $u$ occurs through first order phase transition. 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 dimerisation because the electron-phonon coupling constants of Table I are large and because the corresponding susceptibility (3) is large. The disadvantage that the electron-phonon coupling is quadratic rather than linear in $u$ is set off by satisfactory consequence that the resulting phase transition is of first order, providing a possible explanation of the LO anomaly observed in LSCO and YBCO. Further experimental and theoretical investigations are however required to explain unambiguously the origin of the LO anomaly in the high-$T_c$ superconductors.

Acknowledgments

Useful discussions with Lev Gor’kov, Jacques Friedel and Robert Comes are gratefully acknowledged.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2}
\caption{The density of states and the intraband $pp$ susceptibility as functions of the Fermi energy $\varepsilon_F$, for the simplest case, $\Delta_{pd} = 0.66$ eV, $t = 0.73$ eV, and $t' = \Delta_{pp} = U = 0$.}
\end{figure}

[1] R. J. McQueeney, Y. Petrov, T. Egami, M. Yethiraj, G. Shirane and Y. Endoh, Phys. Rev. B 82 (1999) 628;
[2] L. Pinchovius and M. Braden, Phys. Rev. B 60 (1999) R15039;
[3] Y. Petrov, T. Egami, R. J. McQueeney, M. Yethiraj, H. A. Mook and F. Dogan, cond-mat 0003414 (2000);
[4] L. Pinchovius and M. Braden, J. Low Temp. Phys. 105 (1996) 813;
[5] F. Gompf, B. Renker and H. Mutka, Physica 180B - 181B (1992) 459;
[6] M. Braden, W. Reichardt, A. S. Ivanov and A. Y. Rumiantsev, Europhys. Lett. 34 (1996) 531;
[7] M. Braden, W. Reichardt, W. Schmidbauer, A. S. Ivanov and A. Y. Rumiantsev, J. Supercond. 8 (1995) 1;
[8] J. D. Axe, A. H. Moudden, D. Hohlwein, D. E. Cox, K. M. Moharnty, A. R. Moodenbaugh and Youwen Xu, Phys. Rev. Lett 62 (1989) 2751;
[9] B. H. Toby, T. Egami, J. D. Jorgensen and M. A. Subramanyam, Phys. Rev. Lett. 64 (1990) 2414;
[10] A. Lanzara, P. V. Bogdanov, X. J. Zhou, S. A. Kellar, D. L. Peng, E. D. Lu, T. Yoshida, H. Eisaki, A. Fujimori, K. Kishio, J.-I. Shimoyama, T. Noda, S. Uchida, Z. Hussain, Z.-X. Shen, Nature 412 (2001) 510;
[11] M. C. Shabel, C. -H. Park, A. Matsuura, Z.-X. Shen, D. A. Bonn, Ruixing Liang and W. N. Hardy, Phys. Rev. B 57 (1998) 6090;
[12] M. C. Shabel, C.-H. Park, A. Matsuura, Z.-X. Shen, D. A. Bonn, Ruixing Liang and W. N. Hardy, Phys. Rev. B 57 (1998) 6107;
[13] A. Ino, C. Kim, T. Mizokawa, Z.-X. Shen, A. Fujimori, M. Takaba, K. Tamasaku, H. Eisaki and S. Uchida, J. Phys. Soc. Jpn. 68 (1999) 1496;
[14] A. Ino, C. Kim, M. Nakamura, T. Yoshida, T. Mizokawa, Z.-X. Shen, A. Fujimori, T. Kakeshita, H. Eisaki and S. Uchida, cond-mat/0005374 (2000);
[15] D. Mihailović and V. V. Kabanov, Phys. Rev. B 63 (2001) 4505;
[16] S. Barisić and J. Zelenko, Solid State Commun. 74 (1990) 367;
[17] I. Mrkonjić and S. Barisić, cond-mat 0103057 (2001);
[18] S. Barisić and I. Batistić, Int. J. Mod. Phys.B 1 (1988) 291;
[19] S. Barisić, I. Kupčić and I. Batistić, Int. J. Mod. Phys. B 3 (1989), 2051; I. Kupčić, S. Barisić and E. Tutiš, Phys. Rev. B 57 (1998) 8590.