LATTICE DYNAMICS OF La$_2$NiO$_4$ IN THE CHARGE FLUCTUATION MODEL

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The lattice dynamics of La$_2$NiO$_4$ is calculated in the framework of a description of the electronic density response recently applied to the high-temperature superconductors (HTSC). The local part of the density response is approximated by a proper *ab initio* ionic model of rigid ions to represent the effects of the ionic forces in the crystal. The structure parameters and the phonon dispersion curves are investigated in this model and are compared with recent interpretations of the experimental data. Additionally, nonlocal contributions to the density response in the form of charge fluctuations at the ions are considered and their influence on the dispersion is discussed. From our results we find that some corrections of the current interpretation of the experimental data may be appropriate. Finally, the importance of phonon-induced charge fluctuations for the HTSC is emphasized.

THE LATTICE dynamics of La$_2$NiO$_4$, which is isostructural to La$_2$CuO$_4$, has been investigated by neutron scattering in [1, 2], see Fig. 1. In the main symmetry directions $\Delta \sim (1, 0, 0)$, $\Lambda \sim (0, 0, 1)$ and $\Sigma \sim (1, 1, 0)$ all phonon branches were determined. The experimental data were analyzed on the basis of certain lattice dynamical models and several features of the dispersion were discussed using these models to interpolate the data [1, 2]. From such an interpretation La$_2$NiO$_4$ looks like a two-dimensional metal. In particular the LO–TO splittings for modes polarized within the xy-plane (E_u-modes) vanish, which is typical for a metal, while on the other hand a large splitting for a Γ-point mode polarized along the z-axis (A_{2u}-mode), which is typical for an ionic insulator, has been observed.

Furthermore, pronounced anomalies were found for the highest Δ_1- and Σ_1-branch which involve in-plane O–Ni stretching vibrations. There is an anomalous softening of the highest Δ_1-branch midway in the Δ-direction and the planar oxygen breathing mode at the X-point is according to the interpretation in [1, 2] very soft, i.e. thought to be strongly renormalized by coupling to the electrons. Such a behaviour was reproduced by a model description including a negative planar breathing deformability of the Ni atom and guided by a theoretical prediction [3] that La$_2$CuO$_4$ should display a breathing mode instability. However, such a characteristic feature results from a screening approach used in [3] which is suitable for conventional high-density metals but ignores the effects of long-range ionic forces, which recently have been shown to be very essential for a realistic description of the electronic density response and the phonon dispersion in the high-temperature superconductors (HTSC) [4, 5], and which are likewise expected to be important in case of La$_2$NiO$_4$.

In the meantime it is known experimentally that in case of La$_2$CuO$_4$ the X-point breathing mode is the hardest mode in the spectrum [6] rather than being the softest. This has also been confirmed by the calculations in [5] and related to the influence of the ionic forces. The calculations presented in this paper predict an analogous result also for La$_2$NiO$_4$, contrary to the current interpretation of the experimental data [1, 2].

In the following we outline our ionic *ab initio* model, more details can be found in [5]. The ionic densities $\rho_\alpha(\mathbf{r} - \mathbf{R}^A)(\mathbf{R}^A = \mathbf{R}^a + \mathbf{R}^\alpha$ denote the centers of localization of the ions and $\mathbf{a}, \alpha$, are the primitive and nonprimitive lattice indices, respectively) have been calculated with a modified version of the Herman–Skillman program [7] where the Slater exchange potential has been replaced by the exchange potential of local density-functional theory and a correlation potential according to [8] has been taken into account. The unstable O^{2-}-ion is treated with the help of the Watson-sphere method [9]. Given these ionic densities, the interactions between the ions are
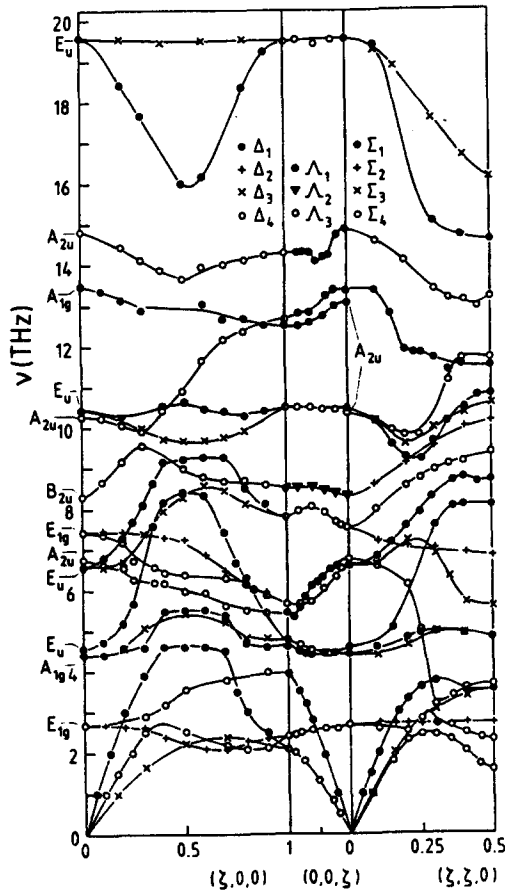
Fig. 1. Experimentally determined phonon dispersion curves of La$_2$NiO$_4$ as published in [1].
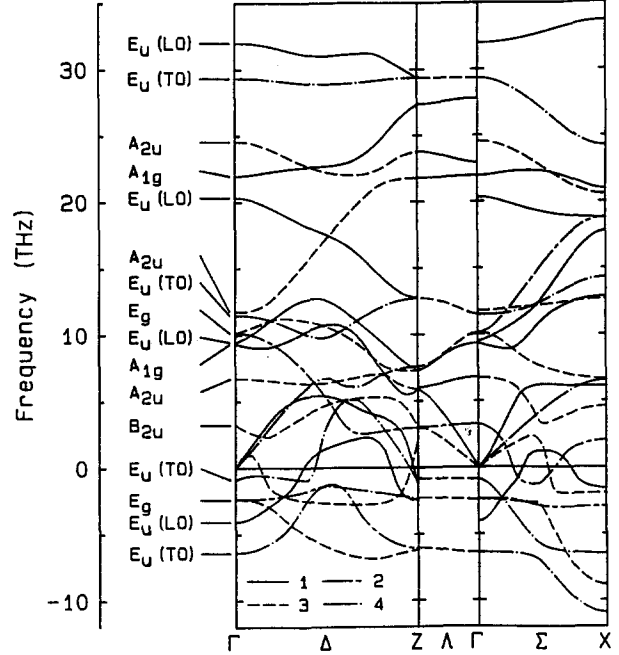

Fig. 2. Calculated phonon dispersion of La$_2$NiO$_4$ for the ionic reference model in the main symmetry directions $\Delta \sim (1, 0, 0)$, $\Lambda \sim (0, 0, 1)$ and $\Sigma \sim (1, 1, 0)$. The classification of the phonon branches by irreducible representations (with symmetry labels 1–4) has been brought about in the figure by using different line types. Imaginary frequencies are represented as negative numbers.

calculated using the approach of [10]. This results in pair potentials $\Phi_{\alpha\beta}(R)$ between ions of type α and β with distance R, respectively:

$$\Phi_{\alpha\beta}(R) = \frac{Z_\alpha Z_\beta}{R} + \tilde{\Phi}_{\alpha\beta}(R). \tag{1}$$

Z_α, Z_β denote the ionic charges, and the long-range Coulomb part has been separated from the short range contribution $\tilde{\Phi}$. The latter is calculated numerically for different values of the distance R between the ions and the results are fitted to a two-

exponential form

$$\tilde{\Phi}(R) = \alpha_+ \, e^{-\beta_+ R} - \alpha_- \, e^{-\beta_- R} \tag{2}$$

Differentiating $\Phi_{\alpha\beta}$ twice with respect to the ion coordinates yields the force constants from which the dynamical matrix is obtained by Fourier transformation. Finally, the energy of the ionic system

$$E = \frac{1}{2}\sum_{b,\alpha,\beta}' \Phi_{\alpha\beta}(|\mathbf{R}_\beta^b - \mathbf{R}_\alpha^a|) \tag{3}$$

is minimized with respect to the structure parameters a (lattice constant), c/a (ratio of c axis to lattice constant), $z(\text{La})$, $z(\text{O}_Z)$ (positions of La and O$_Z$ in the elementary cell).

The results from the minimization of the energy of the ionic model are collected in the first row of Table 1 and are compared with the experimental results [11]. Compared to the experiments, the model leads to a slightly enhanced planar lattice constant and to a (c/a) ratio, which is about eight percent too small. The theoretical values are closer to the experimental data than in case of La$_2$CuO$_4$ [5]. The agreement of the internal structure parameters $z(\text{O}_Z)$ and z (La)

Table 1. Comparison of the structure parameters of La$_2$NiO$_4$ for the minimum of energy of the ionic reference system (first row) with the experimental results from [11]

	a (Å)	c/a	$z(\text{O}_Z)$	z (La)
Model	3.974	3.023	0.190	0.363
Expt.	3.876	3.272	0.180	0.363

HTSC electron correlations and long-range ionic forces should also play an important role in La$_2$NiO$_4$. A direct manifestation of such correlations are for example the magnetic correlations in the material. Neutron scattering experiments [14] have shown antiferromagnetic order at $T_N = 70$ K with T_N depending very strongly on oxygen stoichiometry. Thus we assume as in [4, 5] charge fluctuations at the ions as the dominant electronic screening mechanism.

For a detailed description of the density response and the electron–phonon interaction in terms of charge fluctuations and for a derivation how these fluctuations enter the dynamical matrix we refer to [4, 5]. Here we list only the key-elements of such a formulation and give their physical meaning. These are the change in energy $C_{\kappa\kappa'}^{ab}$, in case unit charge fluctuations with form factors $\rho_\kappa^a, \rho_{\kappa'}^b$ are excited at the positions $\mathbf{R}_\kappa^a, \mathbf{R}_{\kappa'}^b$, in the solid (a, b specify the elementary cells, and κ numbers the localization centers of the charge fluctuations in a certain elementary cell) and the quantities $B_i^{b\kappa A}$ which express the "force" on the charge fluctuation with form factor ρ_κ^b if ion A is displaced in the i direction or, equivalently, the "force" on ion A in i direction if the charge fluctuation bκ is excited by a unit excitation. Using density functional theory we obtain

$$B_i^{b\kappa A} = \int dV \rho_\kappa(\mathbf{r} - \mathbf{R}_\kappa^b) V_i^\alpha(\mathbf{r} - \mathbf{R}^A) \qquad (4)$$

with

$$V_i^\alpha(\mathbf{r} - \mathbf{R}^A) = \frac{\partial}{\partial R_i^A} V_\alpha(\mathbf{r} - \mathbf{R}^A). \qquad (5)$$

$V_\alpha(\mathbf{r} - \mathbf{R}^A)$ is the ionic potential.

$$C_{\kappa\kappa'}^{ab} = \int dV \, dV'$$
$$\times \rho_\kappa(\mathbf{r} - \mathbf{R}_\kappa^a) F''(\mathbf{r}, \mathbf{r}') \rho_{\kappa'}(\mathbf{r}' - \mathbf{R}_{\kappa'}^b), \qquad (6)$$

with

$$F''(\mathbf{r}, \mathbf{r}') = T_s''(\mathbf{r}, \mathbf{r}') + v(\mathbf{r} - \mathbf{r}') - v_{xc}(\mathbf{r}, \mathbf{r}'), \qquad (7)$$

where v is the Coulomb interaction and T_s'' and $(-v_{xc}) = E_{xc}''$ are the second functional derivatives with respect to the density ρ of the kinetic energy and the exchange-correlation energy.

Introducing the inverse polarizability π^{-1} of the electronic system by the relation $\pi^{-1}(\mathbf{r}, \mathbf{r}') = T_s''(\mathbf{r}, \mathbf{r}')$, we can express C in equation (6) in compact notation as

$$C = \pi^{-1} + \tilde{V}, \qquad \tilde{V} \equiv V - V_{xc}. \qquad (8)$$

The contribution of the kinetic energy enters C via the polarizability π. The latter quantity is approximated by the same tight-binding model as described in detail in [5], allowing for charge fluctuations on the Ni- and O$_{x,y}$ ions in the plane.

In full notation it can be written as

$$\pi_{\kappa\kappa'}(\mathbf{q}) = -\frac{2}{N} \sum_{\substack{n,n' \\ \mathbf{k}}} \frac{f_n(\mathbf{k}) - f_{n'}(\mathbf{k} + \mathbf{q})}{E_n(\mathbf{k}) - E_{n'}(\mathbf{k} + \mathbf{q})}$$

$$\times [C_{\kappa n}^*(\mathbf{k}) C_{\kappa n'}(\mathbf{k} + \mathbf{q})]$$

$$\times [C_{\kappa' n}^*(\mathbf{k}) C_{\kappa' n'}(\mathbf{k} + \mathbf{q})]^*. \qquad (9)$$

The f's, E's and C's represent the occupation numbers, the electronic bandstructure and the expansion coefficients of the Bloch-functions in terms of tight-binding functions. For the calculation of $\pi_{\kappa\kappa'}(\mathbf{q})$ we use the same two-dimensional tight-binding model for the bandstructure as in [5]. With the above restrictions for the centers of the charge fluctuations this yields a 3×3 matrix for $\pi_{\kappa\kappa'}(\mathbf{q})$.

The important long-range Coulomb contributions of B and C can be separated, i.e.

$$[B_i^{b\kappa A}]_c = \frac{\partial}{\partial R_i^A} \left[\frac{Z_\alpha}{|\mathbf{R}^A - \mathbf{R}_\kappa^b|} \right], \qquad (10)$$

$$[C_{\kappa\kappa'}^{ab}]_c = \frac{1}{|\mathbf{R}_{\kappa'}^b - \mathbf{R}_\kappa^a|}, \qquad (11)$$

and can be dealt with exactly using the Ewald method. The short-range contribution to the charge-fluctuation-ion coupling B and to the potential energy part $\tilde{V}$ of C are calculated approximately using for the form factors the Ni-d and O-p orbital densities. The most important contribution to $\tilde{V}$ is given by the on-site repulsion terms $\tilde{V}_{\kappa\kappa}^{aa}$. In such a procedure it is assumed that the charge fluctuation at an ion corresponds in a first approximation to a change of the occupation of its outmost shell and the $\tilde{V}$'s and B's can be estimated by calculating the occupation-dependent Hartree- and XC-energy of an ion (in the local-density approximation) or the occupation-dependent pair potential $\tilde{\Phi}_{\alpha\beta}(R)$ of a pair of ions, respectively.

In Fig. 3 we have displayed the phonon dispersion of La$_2$NiO$_4$ taking these charge fluctuations into account. We find that the LO–TO splittings are reduced in comparison with the results from the ionic reference model (Fig. 2) because electronic charge fluctuations are now possible within the plane leading to a certain amount of screening. In accordance with experiment the highest Δ_1 branch is decreased below Δ_4 and now shows the characteristic dip of the experimental dispersion midway in the Δ direction.

with the experimental values is in case of La perfect and also satisfying for O$_Z$ confirming the validity of the ionic description of these ions, with the minor restriction that O$_Z$ might be considered to be slightly more covalent than La in these compounds.

In Fig. 2 the phonon-dispersion curves of the ionic reference model for the tetragonal phase of La$_2$NiO$_4$ are displayed for the $\Delta \sim (1, 0, 0)$, $\Lambda \sim (0, 0, 1)$ and $\Sigma \sim (1, 1, 0)$-direction. The results are very similar to those found for La$_2$CuO$_4$ [5]. As discussed in [5] important qualitative features of the ionic model dispersion also can be found in the experimental results for La$_2$CuO$_4$ [6], and we think the same facts to be true in case of the phonon dispersion of La$_2$NiO$_4$.

Of course, the calculated dispersion displays the characteristics of an ionic insulator and not those of a two-dimensional metal as reported in [1, 2]. A striking feature of the dispersion is the LO–TO splitting of the E_u modes and the discontinuity of the A_{2u} vibrations at the Γ point when approaching from the Λ- or Σ-direction, respectively. The splitting of the E_u vibration with the highest and lowest frequency is relatively small while that of the two other optical E_u modes is large. The largest splitting (discontinuity) of all modes is found for the A_{2u} mode with highest LO-frequency ("ferroelectric mode"). Nearly no splitting is observed for the lowest optical A_{2u} mode. Concerning the disagreement of the E_u-splittings with the results found in [1, 2] it seems very likely, that a conductivity induced by defects has caused the behaviour observed in the experiments [12].

The stability of the ferroelectric mode found for La$_2$NiO$_4$ in this work and for La$_2$CuO$_4$ in [5] is mainly due to the strong short-range overlap repulsions between the ions. On the other hand it is tempting to think about microscopic mechanisms which would favour the tendency towards a ferroelectric instability in general. We find within our model essentially two sources which would favour a softening of the ferroelectric mode. One source is the reduction of the overlap repulsion by covalent hybridization and the other reason are dipolar fluctuations of the electronic density at the apex oxygen ion in the z-direction modulating dynamically the covalent bond between copper and the apex oxygen. When we implement the latter mechanism in our density response description we find a very strong decrease of the ferroelectric mode-frequency together with the appearance of a "rotonic" minimum in the corresponding transverse acoustic mode in the Δ-direction. We would like to mention that a possible occurrence of such a minimum for example in SrTiO$_3$ would be helpful

for an interpretation of the phase-transition-like feature showing up in this material in the quantum paraelectric regime as discussed in [13].

The highest Σ_1-branch shows an increasing dispersion in the ionic model with the result that the planar oxygen breathing mode at the X-point is the hardest mode in the spectrum and we see no hint pointing to a breathing instability. The other characteristic feature of the high-frequency oxygen-vibrations in the experiments namely the pronounced softening of the highest Δ_1-branch, is only very weakly developed in the ionic model. However, such a behaviour can be understood by taking into account electronic screening effects in terms of charge-fluctuations at the Ni and O$_{x,y}$ ions, see below.

As far as the unstable modes in the ionic model are concerned, these modes indicate physical properties like instabilities and/or anharmonicities in the system related to the very important ionic component of the forces, see also [5]. For example the imaginary frequency of the tilt-mode (second lowest "frequency" at the X-point) means that this mode is unstable because of the ionic forces in the tetragonal phase of La$_2$NiO$_4$ or La$_2$CuO$_4$, respectively, considered in our calculations and also for the interpretation of the experiments in [1, 2]. In the sample used in [1, 2] this mode has the lowest frequency in the spectrum and is only marginally stable. Note that stoichiometric La$_2$NiO$_4$ shows a tetragonal to orthorhombic phase transition at $T \approx 240$ K [14]. Also La$_2$CuO$_4$ has an orthorhombic low-temperature structure and the instability of the tilt mode correctly announces the phase transition form the tetragonal to the orthorhombic phase. Indeed, the tilt mode is stabilized in our ionic model in case the orthorhombic structure is considered. Thus, our calculations clearly relate the tetragonal to orthorhombic transition to the ionic forces. Actually, we have done this calculation in case of La$_2$CuO$_4$ in context with our investigations in [5], but we think the same to be true in case of La$_2$NiO$_4$ because of the great similarity of the calculated dispersions in both materials.

So far the local part of the electronic density response and electron–phonon interaction has been accounted for in La$_2$NiO$_4$ by the ionic *ab initio* model. Using such a model, likewise as in [4, 5] for the HTSC, as a reference system for the ionic forces we incorporate additionally nonlocal contributions to the density response in the form of charge fluctuations on the ions. This type of nonlocal screening has been shown in [4, 5] to be adequate for the highly correlated electrons in these anisotropic mixed ionic-metallic (covalent) compounds. Similarly, as for the
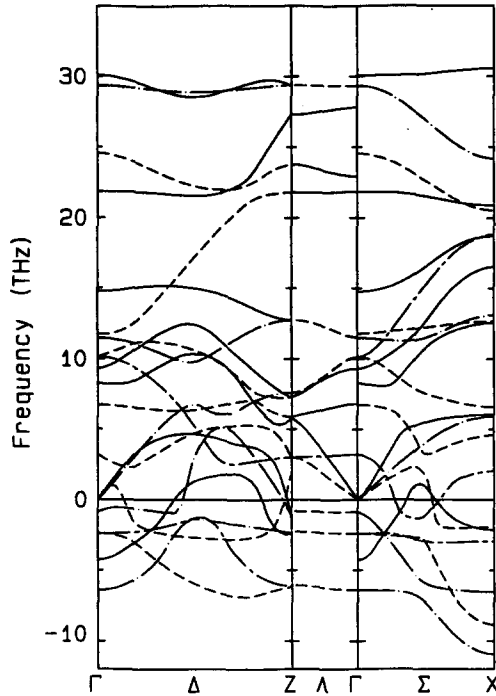
Fig. 3. Phonon dispersion of La$_2$NiO$_4$ taking charge fluctuations at the nickel and oxygen in the plane into account. The labeling of the curves is the same as in Fig. 2.

(Note that labels Δ_3 and Δ_4 as well as Σ_3 and Σ_4 are exchanged in the experimental curves in Fig. 1 as compared with the theoretical results). Also the highest Σ_1 branch is decreased relative to the ionic model but still has an increasing dispersion towards the X point leading to a stable planar oxygen breathing mode as a consequence of the strong ionic forces screened by the electrons in a highly correlated way in our model. The discontinuities of the A_{2u} modes at Γ do not change at all and the highest Λ_1 branch, including the axial symmetric apex oxygen breathing mode at the Z-point (O$_z^z$) remains practically unchanged from the ionic model. The reason for such a behaviour is related to the two dimensional electronic structure and a detailed discussion, which will not be repeated here, is given in [5] in case of La$_2$CuO$_4$, where the same features appear in the insulating phase.

In context with the O$_z^z$ mode we would like to point out the drastic changes of the charge fluctuation patterns accompanying this mode owing to an insulator–metal transition. In [4, 5] we have investigated this problem using La$_2$CuO$_4$ as an example. We have shown that in the *metallic* phase of La$_2$CuO$_4$ the O$_z^z$ and to a lesser extent the La$_z^z$ vibrations induce charge fluctuations at the Cu and O$_{x,y}$ ions that have

the *same* sign in the *whole* plane and alternating signs in consecutive planes ("interplane charge transfer"). This provides an effective screening of the Coulomb interactions, being responsible for the high frequency of O$_z^z$ in the insulating and ionic models. The large difference in frequency between O$_z^\Gamma$ and O$_z^z$ (endpoints of the second highest Δ_1 branch) in La$_2$NiO$_4$ as well as in insulating La$_2$CuO$_4$ [5] is related to the fact that the Coulomb interaction between nearest neighbour apex oxygen ions in different planes acts destabilizing in case of O$_z^\Gamma$ (counterintuitive) where these ions are vibrating in opposite directions while they are vibrating in the same direction in O$_z^z$. In the *metallic* phase the interplane charge transfer leads to a strong renormalization of O$_z^z$ and a reinforcement of the phonon mediated contribution to the pairing mechanism of superconductivity can be expected via long-range nonlocal electron–phonon interactions as discussed in [4, 5]. Such a kind of coupling between z-axis phonons, like O$_z^z$, and charge fluctuations, if strong enough, will also favour an increase of the amplitude of vibration and this could be a source for possible anharmonicities (here the amplitude of the two apex oxygens vibrating against the CuO-plane is increased and the frequency decreased by the destabilization of the direct Coulomb interaction between these ions in the presence of the charge fluctuations in the plane). In the *insulating* phase there is virtually no decrease in frequency for O$_z^z$ because the charge fluctuations are confined locally within the plane and are of different sign on the Cu(Ni) and O$_{x,y}$ compensating each other. This is less effective for screening.

From the discussion above and from the detailed considerations presented in [4, 5] we recognize the important role played by certain charge fluctuation patterns induced by certain significant phonon modes, like O$_z^z$ in case of La$_2$CuO$_4$, for phonon renormalization and nonlocal electron–phonon interaction effects strengthening phonon mediated pair binding. Having these facts in mind it is very important to look for similar significant phonon modes in the other HTSC generating similar favourable charge fluctuation patterns. Possibly, there is more than one significant mode contributing via nonlocal electron–phonon interaction to the pairing mechanism. This seems to be the case as our preliminary investigations indicate.

A first logical step is to examine the situation for the orthorhombic phase of La$_2$CuO$_4$. Here our current investigations show that as a consequence of the orthorhombic tilt at least four A_g modes appear at the Z point inducing charge fluctuations at the Cu and O$_{x,y}$ with the *same* sign in the *whole* plane

whose magnitude depends on the tilt angle. Among those in particular a second O_z^z-like mode emerges generating strong fluctuations if the tilt is sufficiently large. This points to a possible relationship between the occurrence of superconductivity and the structure of this compound. Such a relationship has been reported quite recently [15]. In [15] arguments are given from the experimental side that a disappearance of superconductivity in doped La$_{2-x}$Sr$_x$CuO$_4$ is associated with an orthorhombic to tetragonal structural phase transition near $x = 0.2$.

Next we turn to the situation in YBa$_2$Cu$_3$O$_7$ here the (orthorhombic) structure and the presence of the CuO double layer may enhance the favourable charge fluctuation effects. An additional enhancement should occur when three CuO layers are present as in Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$. From our quantitative calculations in [4, 5] we have learned, taking O_z^z as an example, that the Coulomb interaction favours charge separation in consecutive planes in the *metallic* phase of La$_2$CuO$_4$ in this mode. An essential aspect supporting such a possibility for charge rearrangement is that screening should be relatively poor along the z-axis. This is not possible if conventional high-density electron gas screening is assumed for the HTSC, while on the other hand the highly correlated screening mechanism of our approach, dominated by charge fluctuations on the ions in the planes, is more adequate and we believe our model to be a fair compromise between perfect rigour and oversimplification.

As compared to La$_2$CuO$_4$ in YBa$_2$Cu$_3$O$_7$ two facts favour the charge separation by Coulomb interaction in consecutive planes (the double layer in this case). Firstly, the CuO$_4$-plaquettes of the two consecutive layers are not shifted with respect to each other as in La$_2$CuO$_4$ enhancing the Coulomb attraction and secondly, the distance within the double layer of YBa$_2$Cu$_3$O$_7$ is much smaller than between the layers in La$_2$CuO$_4$ also favouring the decrease in energy by Coulomb attraction. There is another important factor increasing the charge fluctuations in the plane and thus the nonlocal electron–phonon interaction effects namely a shorter distance of the apex oxygen from the plane. In this context it is interesting to remember that the critical temperature for superconductivity T_c increases if the apex oxygens move towards the plane with increasing hydrostatic pressure [16]. Such a movement can also be achieved by oxidizing YBa$_2$Cu$_3$O$_{6+x}$ to YBa$_2$Cu$_3$O$_7$ [17]. In the latter case of course the total hole concentration is also increased.

Finally, from our current calculations in YBa$_2$Cu$_3$O$_7$ we get the message that there are indeed more, and may be even more favourable charge fluctuation patterns induced by certain phonon modes than in La$_2$CuO$_4$. The following short summary can be offered at the moment. For example in the O_4^z (A_g), $O_{2,3}^z$ (A_g) and certain B_{1u}-modes at the Γ point (2, 3 denote the oxygens in the plane and 4 denotes the apex oxygen, Γ, Z denote vibrations at the Γ- and Z-point, respectively; all modes are polarized along the z-axis) the charge fluctuations in the individual CuO planes of the double layer have different sign. However, there are also modes O_4^z (B_{1u}) and O_4^Γ (A_g) where charge fluctuations of the same sign are generated in the whole CuO double layer. Here the O_4^z (B_{1u}) charge fluctuation pattern is energetically supported by corresponding charge fluctuations of different sign at the O$_4$-ions, while O_4^Γ (A_g) is supported by corresponding charge fluctuations of different sign at the O$_4$ ions and the CuO chains. A complete study of the phonon dispersion and the charge fluctuation behaviour in YBa$_2$Cu$_3$O$_7$ will be given elsewhere [18].

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