Lattice dynamics of the high-$T_c$ superconductor HgBa$_2$CuO$_4$

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Abstract

A lattice dynamical study of the phonon dispersion relation and one phonon density of states is presented in the framework of the shell model for the first member of the high-temperature superconductor HgBa$_2$CuO$_4$. This is complemented with a frozen-phonon first-principles determination of frequencies and eigenvectors of the Raman-active modes. The results are compared with recent Raman and neutron-scattering data.

1. Introduction

The members of the family of mercury compounds which belong to the series HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+\delta}$ $(n = 1-6)$ denoted by Hg-$12(n-1)n$, have the highest superconducting transition temperatures for known layered copper-oxide superconductors. The $n = 3$ member has the record $T_c = 135$ K [1-4], and under pressure $T_c$'s above 150 K have been achieved [5,6].

At present there is interest in understanding their structural and physical properties. We have recently studied the electronic structure of the Hg family with $n = 1-5$ within the local density approximation (LDA), for the stoichiometric ($\delta = 0$) compounds [7-10]. Agreement has been obtained with the results of other authors [11-15].

The crystal structure for the whole series has recently been determined by neutron powder diffraction techniques [16,17]. From these studies it was shown that the oxygen composition near optimal doping corresponded to $\delta = 0.06$ in Hg-1201, $\delta = 0.2$ in Hg-1212 and $\delta = 0.41$ in Hg-1223. Oxygen takes the position in the large open space surrounded by Hg and Ba in the Hg plane. In the case of the one layer compound only, substitution of some Hg atoms by Cu was observed.

Phonons are important in the understanding of the physical properties. In particular so is the study of the electron–phonon interaction in order to establish their role in the mechanism of superconductivity.

As a first step towards this goal, we present in this paper a lattice dynamical study of the phonon dispersion relation for the first member of the Hg-family, Hg-1201, in the framework of the shell model. This study is complemented with a first-principles determination of frequencies and eigenvectors of the Raman-active modes. The results are compared with recent experimental work. The importance of this theoretical study lies in the possible clarification of the mode assignment made in the experimental work due to the difficulties that appear because of the rather low purity of the polycrystalline samples used presently and sets the

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starting point for future work on the electron-phonon coupling.

2. Method of calculation

Part of our calculations of the lattice dynamics of the HgBa$_2$CuO$_4$ are carried out in the framework of the shell model which takes into account short-range and long-range Coulomb interactions, as well as ionic polarizabilities. In this model every ion is represented by a shell coupled to a core through a harmonic force constant $K$, and the short-range interactions between the ions are represented by Born–Mayer potentials: $V(r) = ae^{-br}$.

For the ab-initio frozen-phonon calculation of the Raman active modes in the framework of the LDA, we used a fast and precise full-potential linear muffin-tin orbital (FP-LMTO) technique which makes no shape approximation for the charge density or for the potential [18,19]. Details of the method as applied to Hg-1201 can be found in Ref. [7]. The calculations needed to be carried out in two panels. The following orbitals were taken as valence band electrons: Ba 5p and 6s, Hg 5d and 6s, Cu 3d and 4s, Ca 4s and 3p, and O 2s and 2p. The Cu 3s and 3p, Ba 5s, Ca 3s and Hg 5s and 5p were included as semi-core. We have chosen to modify our sphere radii and empty spheres included from those in our previous work and used those of Ref. [20] with the necessary decreased sphere-radii modifications so as to allow for displacements of atoms. In this way detailed comparisons could be made since the same FP-LMTO implementation is used. The basis set included 172 LMTO’s per cell and 30 and 65 irreducible points were used (plus linear tetrahedral interpolation) to sample the Brillouin zone for the $A_{1g}$ and $E_g$ modes, respectively. For the frozen-phonon calculation to be presented we used the experimental equilibrium volume and $c/a$ ratio.

As a starting point in our shell model calculations for HgBa$_2$CuO$_4$ we have transferred the Ba–O, Cu–O and O–O potentials from pairs of ions in similar configurations in compounds for which phonon dispersion curves have been measured. By these Born–Mayer type potentials one has been able to describe the lattice dynamics of several high-$T_c$ superconductors: YBa$_2$Cu$_3$O$_7$ [21], Bi$_2$CaSr$_2$Cu$_2$O$_8$ [22], Pb$_2$Sr$_2$YCu$_3$O$_8$ [23], Tl$_2$CaBa$_2$CuO$_8$ [24] and related Tl based compounds [25,26]. However, in our case the Cu–O interaction poses a special problem because of the strong structural anisotropy. In HgBa$_2$CuO$_4$ the intraplanar Cu–O distance (1.9 Å) is significantly smaller than the Cu–apex O distance (2.8 Å). As a matter of fact, the Cu–apex O distance in HgBa$_2$CuO$_4$ is the largest of all high-$T_c$ compounds. As a consequence, in order to obtain a stable acoustic branch near the Brillouin zone boundary, we had to introduce different Born–Mayer potentials for interplanar and intraplanar interactions which produce little effects on the other phonon frequencies. As a Hg–O potential we tested a Tl–O potential previously used in the Tl based compounds [25,26]. However, the apex-oxygen $A_{1g}$ mode acquired a too high frequency compared with the experiments. In addition an $E_g$ Hg–apex O mode and an acoustic branch became unstable. These problems could not be overcome with physically reasonable values of a Born–Mayer potential. Therefore, to determine the Hg–O interaction, we have fitted the longitudinal and the transversal force constants. The former has been fitted to obtain a frequency of 591 cm$^{-1}$ for the apex oxygen $A_{1g}$ mode, as has been observed in Raman experiments [27–30] and the latter so as to obtain a stable acoustic branch near the zone center. Here, the transverse acoustic branch with polarization along the $c$-axis has a strong tendency to instability. The eigenvector for this mode presents also a component of apex O displacement perpendicular to the $c$-axis. This is the reason why the transversal Hg–O force constant is able to stabilize these modes. But, values of the Hg–O force constants needed to obtain this lead to unphysical values of the Born–Mayer potential parameters. This suggests that this interaction reflects a high degree of covalency in the Hg–O bond. This picture is supported by a relatively high electron density along this bond, as obtained from LDA calculations as seen in Fig. 1. The model parameters used are listed in Table 1.

3. Results and discussion

The ionic displacements for the modes at $q=0$, as obtained from the shell model are qualitatively shown in Fig. 2. The frequencies of the TO stretching and bending $E_{2u}$ modes in the CuO$_2$ plane have values comparable with those of the corresponding modes in...
Hg

O

Cu

O

Fig. 1. Contours of constant valence charge density in Hg-1201 in the (100) plane. Lowest contour and spacing are 0.01 and 2.5 × 10^{-3} electrons/bohr³, respectively.

Tl₂Ba₂CuO₆, 563 cm⁻¹ and 326 cm⁻¹ [25], respectively. On the other hand, for the breathing and quadrupolar zone boundary modes we obtain the values 553 cm⁻¹ and 383 cm⁻¹, respectively, comparable with 598 cm⁻¹ and 347 cm⁻¹ for YBa₂Cu₃O₇.

In Table 2 we compare our shell-model frequencies of the Raman active A₁g and Eₘ modes with the corresponding experimental values. Except for the apex-oxygen Eₘ mode, the agreement is reasonable. In a Raman measurement on a polycrystalline sample a peak at 108 cm⁻¹ [29] was observed which is closer to our value for the Ba Eₘ mode. We obtain a rather high value of the apex oxygen Eₘ frequency. A similar difference between theory and experiment was found in YBa₂Cu₃O₇ [31]. Even with the mentioned Tl–O potential, this mode has a frequency above 200 cm⁻¹, higher than the value obtained by Raman scattering.

Let us now analyze the ab-initio predictions for the Raman active A₁g and Eₘ modes which displace the apex oxygen and Ba atoms in the c direction and x (or y) direction, respectively.

In order to determine the z-equilibrium positions of the two atoms (the x (or y) are zero due to symmetry) and the dynamical matrix, we calculated total energies for 12 and 9 different displacement patterns (which include individual atoms as well as mixed displacements) for the A₁g and Eₘ modes, respectively. Atomic displacements extended up to 4% of the experimental lattice constant (a = 3.875 Å).

The total energies were least squares fitted to polynomial quadratic in the displacements. The equilibrium z-positions obtained were in very good agreement with the experiments (errors less than 0.5%).

The phonon frequencies ωᵣ and eigenvectors eᵣ obtained by diagonalizing the dynamical matrix are shown in Table 2. The agreement with the experimentally determined frequencies from Ref. [30] is rather good for both A₁g modes and Eₘ apex-oxygen mode (10% softer for the well established apex-oxygen frequency). A rescaling of the dynamical matrix to the theoretical equilibrium volume gives the calculated frequency in better agreement with experiment. Ref. [30] predicts a 75 cm⁻¹ mode, assigned to Ba Eₘ, while our prediction is 104 cm⁻¹ which coincides with the shell-model predictions and the peak observed in the Raman work of Ref. [29] as already mentioned.

From the eigenvectors listed in Table 2 we see that for the A₁g modes the Ba and apex-oxygen movements are nearly decoupled. We then analyzed in more detail anharmonic effects in the energy versus z-displacement curve for pure apex oxygen. When cubic and quartic terms were included our calculated frequency increased to 573 cm⁻¹. This is not the same for the Eₘ modes where the 165 cm⁻¹ mode is predominantly of apex-oxygen character, but with an out-of-phase Ba move-

| Interaction | a (eV) | b (Å⁻¹) | Ion | Z (|e|) | Y (|e|) | K (e²/Åₙ) | Interaction | A (e²/Åₙ) | B (e²/Åₙ) |
|-------------|-------|---------|-----|-------|-------|-----------|-------------|------------|-----------|
| Ba–O        | 3225  | 2.9     | Hg  | 1.6   | 2.0   | 650       | Hg–O(2)    | 235.3     | 9.3       |
| Cu–O(1)     | 1260  | 3.35    | Ba  | 2.0   | 2.32  | 130       | Cu–O(1)    | 211.5     | -32.5     |
| Cu–O(2)     | 1260  | 3.0     | Cu  | 2.0   | 3.22  | 800       | Ba–O(1)    | 98.1      | -12.3     |
| O–O         | 1000  | 3.0     | O(1)| -1.9  | -2.7  | 200       | Ba–O(2)    | 63.7      | -7.6      |
|             |       |         | O(2)| -1.9  | -2.7  | 200       | Cu–O(2)    | 25.9      | -3.0      |
|             |       |         |     |       |       |           | O–O        | 1340      | -2.9      |
Fig. 2. Phonon frequencies (in cm⁻¹) and schematic representation of the polarization vectors of the zone center optical modes. The values of the LO frequencies are given in parentheses.
Table 2
Frequencies and eigenvectors of Raman active zone center mode. SM and LDA refer to the shell model and the full potential LMTO method in the local density approximation, respectively. EXP refers to the experimental data from Ref. [30].

<table>
<thead>
<tr>
<th>Mode</th>
<th>( \omega ) (cm(^{-1}))</th>
<th>LDA eigenvectors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EXP</td>
<td>SM</td>
</tr>
<tr>
<td>( A_{1g} )</td>
<td>592</td>
<td>591</td>
</tr>
<tr>
<td>( A_{1g} )</td>
<td>161</td>
<td>124</td>
</tr>
<tr>
<td>( E_{g} )</td>
<td>168</td>
<td>322</td>
</tr>
<tr>
<td>( E_{g} )</td>
<td>75</td>
<td>102</td>
</tr>
</tbody>
</table>

ment, while the 104 cm\(^{-1}\) consists of Ba linked to apex oxygen moving in phase. These eigenvectors correspond to ionic displacements which are in good agreement with those predicted by the shell model shown in Fig. 2.

The shell model allows us to obtain the phonon frequencies in the whole Brillouin zone, which can serve as a guide for further experimental investigations. The calculated phonon dispersion curves in the main symmetry directions are shown in Fig. 3. It can be seen that the phonon frequencies are stable in the whole Brillouin zone. It is interesting to observe the strong coupling between the low-lying acoustic and optical modes in the [100] and [110] directions. A similar feature is found in thallium-based compounds [26], where the repelling of modes has been speculated to cause the onset of curvature in the acoustic branch at very low frequencies.

The one-phonon density of states (DOS) is shown in Fig. 4. A small gap is seen above 370 cm\(^{-1}\), and the very small density above this gap corresponds to the branch observed in the [100] direction above 380 cm\(^{-1}\) in Fig. 3. Another gap appears from 130 cm\(^{-1}\) to 150 cm\(^{-1}\). The structure below it corresponds to Hg modes. A similar feature is observed by inelastic neutron time-of-flight measurements [32]. At high frequencies, however, the measured DOS consists of a broad structureless band. On the other hand, the authors remark that their sample might contain additional amorphous material.

In the Raman spectra a noticeable shoulder is observed at 570 cm\(^{-1}\), in the low-frequency side of the oxygen \( A_{1g} \) peak [27–30]. There are two speculations made in Ref. [30] on this peak. One of them is that the oxygen occupation of the Hg planes breaks the sym-

![Fig. 3. Phonon dispersion curves in the main symmetry directions \([q, 0, 0]\), \([q, q, 0]\) and \([0, 0, q]\) of the Brillouin zone.](image-url)
metry of the CuO$_2$ planes and allows a Cu(1) ion to be Raman active and could modify the apex-oxygen frequency (these authors rule out the possibility of assigning it directly to the motion of oxygen defects in the Hg planes while in Refs. [27] and [28] and this shoulder peak is assigned to vibrations of interstitial oxygen). The other ascribes it to the consequences of the identified [3] substitution of some Hg ions by Cu. As for this last possibility, it has been argued that a Jahn–Teller distortion or an elastic instability could appear [30]. In order to test qualitatively the effect of the Cu replacement at the Hg site, we calculated the phonons for an hypothetical CuBa$_2$CuO$_4$ crystal. For the interaction of the replaced Cu with the apex oxygen, we take the same Cu–O(1) potential, since the distances are very similar. As a result of this, the frequency of the mentioned A$_{1g}$ mode decreased to 557 cm$^{-1}$. This reduction is simply produced by the decrease in the longitudinal force constant (see Table 1), which is reinforced by the slightly larger Hg–O(2) than Cu–O(1) distance. Moreover, the weakening of the Hg–O(2) bending force constant produces the acoustic instability mentioned above. This effect is shown in Fig. 5. The already explained form of the eigenvectors for these modes makes feasible a local distortion of the O(2) neighbors of a Cu defect, rather than an elastic instability.

In summary, we have presented the calculated phonon dispersion relation and one phonon density of states for Hg-1201 ($\delta = 0$) as predicted from the shell model. Using first principles total energies the two A$_{1g}$ and two Eg Raman active zone center modes (which involve motion of apex oxygen and Ba atoms) were analyzed. The results were compared with Raman and neutron-scattering experimental results and give insight for a possible clarification of mode assignment. A discussion of the origin of the 570 cm$^{-1}$ shoulder to be apex oxygen A$_{1g}$ peak was given although an unambiguous assignment of this defect mode is not possible at present.

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