Phonon dispersion and electron-phonon interaction for YBa$_2$Cu$_3$O$_7$ from first-principles calculations

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We present a first principles investigation of the lattice dynamics and electron-phonon coupling of the high-$T_c$ superconductor YBa$_2$Cu$_3$O$_7$ within the framework of density functional perturbation theory using a mixed-basis pseudopotential method. The calculated phonon dispersion curves are in excellent agreement with Raman, infrared and neutron data. Calculation of the Eliashberg function $\alpha^2\lambda$ leads to a small electron-phonon coupling $\lambda=0.27$ in disagreement with earlier approximate treatments. Our calculations strongly support the view that conventional electron-phonon coupling is not an important contribution to superconductivity in high-$T_c$ materials.

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Since the discovery of superconductivity in copper oxides in 1986 many different mechanisms have been suggested to explain the high transition temperatures observed in these materials. However, even after more than 15 years of extensive research no consensus has been reached apart from the fact that conventional electron-phonon coupling alone cannot explain the observed transition temperatures. Even the much simpler question concerning the magnitude of electron-phonon coupling has not been answered conclusively due to the fact that calculations in the past treated the lattice dynamics only in a very approximate way. Recent progress in the ab initio calculation of the lattice dynamics has made it possible to overcome these limitations.

Modern bandstructure calculations together with ab initio determination of the phonon dispersion, electron-phonon coupling and solution of the Eliashberg equations have made it possible to calculate transition temperatures and study in detail the electron-phonon coupling. This has recently been done very successfully for the newly discovered superconductor MgB$_2$. For high-$T_c$ superconductors (HTSC) in the past however only a few attempts have been made to proceed along the above mentioned road map to a deeper understanding of the electron-phonon coupling. The most involved ones are those concerned with La$_2$CuO$_4$ and doped CaCu$_2$O$_2$. For La$_2$CuO$_4$ the complete phonon dispersion has been calculated however no electron-phonon coupling was determined. Complications arise from the fact that the calculations are carried out for the high-$T_c$ tetragonal phase while at low $T_c$ experimentally an orthorhombic phase is observed. More important however is the fact that for undoped La$_2$CuO$_4$ an antiferromagnetic non-metallic ground state is observed while LDA calculations find a metallic ground state which questions the reliability of the calculations. The system CaCu$_2$O$_2$, which is much simpler, also requires hole doping which has been taken into account in an average way, however only after properly doping the Fermi surface becomes similar to those of other high-$T_c$ superconductors. Thus these results are also questionable. To our knowledge so far all other ab-initio treatments are restricted to the calculation of phonon modes for the $\Gamma$-point only. In addition, even these calculations are not complete but have been restricted to modes of special symmetry classes only. Due to these limitations estimates of the coupling strength are not very accurate, thus asking for a more complete treatment of the electron-phonon coupling in the whole Brillouin zone (BZ).

To clarify the role of electron-phonon coupling in the copper oxides we have studied as a prototype YBa$_2$Cu$_3$O$_7$ along the above mentioned lines. This system has been selected since it is the best experimentally studied high-$T_c$ superconductor with detailed information available about the Fermi surface and the lattice dynamics and in addition does not have the complications of doping and/or structural phase transitions. Furthermore, bandstructure calculations based on the local-density approximation for exchange and correlation (LDA) have been successful in describing the Fermi surface and account properly for the metallic ground state. For YBa$_2$Cu$_3$O$_7$ we have carried out a systematic study of the lattice dynamics and the electron-phonon coupling using the mixed-basis pseudopotential method. For all atoms we have used well-tested potentials of BHS-type. As valence states we included Y4s, Y4p, Ba5s, Ba5p and O2s which led to fairly deep potentials, but they could be dealt with very efficiently due to the mixed-basis formulation. The wave functions were constructed from localized s,p,d functions at the yttrium and barium sites, s and p functions at the oxygen sites and d-functions at the copper sites supplemented by plane waves with an energy cut-off of 20 Ry. Detailed tests were carried out to ensure convergence with respect to the number of plane waves as well as with respect to k-point sampling. For the structural optimization 576 k-points in the BZ together with a Gaussian smearing of 0.2 eV have been used. The calculation of the phonon dispersion is based on a recently developed mixed basis perturbation approach which also allowed for the calculation of the electron-phonon coupling. Since these parts are very k-point sensitive up to 5184 k-points
in the BZ have been used here. All our calculations were carried out using the local exchange-correlation potential of Hedin and Lundqvist \[14\].

Since \(\text{YBa}_2\text{Cu}_3\text{O}_7\) crystallizes in the orthorhombic crystal structure optimization requires the determination of 8 parameters (the length of the axis a, b, c and 5 internal positions)(see Fig. 1). In table I our results are summarized and compared to all-electron results \[6\] as well as experimental data \[15, 16\].

The two calculations give very similar results and the differences are well within the limit of numerical accuracy. The calculated equilibrium volume turns out to be 4% to 5% smaller than the experimental one in agreement with previous calculations \[2, 6\] and general trends observed for LDA-calculations.

Having determined the equilibrium structure we now proceed to the calculation of phonon modes. For comparison with other calculations as well as experimental studies we concentrate first on the \(\Gamma\) point. Here, besides neutron scattering studies also Raman and infrared data are available. Table II summarizes the even symmetry modes and compares our results with those of an all-electron study \[9\](full potential linearized augmented plane-wave calculations (FLAPW)) which is to our knowledge the most extensive phonon study available up to now as well as with experimental data \[17, 18\].

| Mode | Theory | Neutron | IR |
|------|--------|---------|----|
| \(A_{1g}\) Ba | 14.8 | 15.3 | 14.4-14.8 |
| Cu(2) | 18.8 | 18.2 | 18.0-18.6 |
| O(2)-O(3) | 42.1 | 41.9 | 41.5 |
| O(2)+O(3) | 50.4 | 52.3 | 53.9-54.6 |
| O(4) | 58.6 | 60.4 | 61.1-62.0 |
| \(B_{2g}\) Ba | 8.0 | 8.1 | 8.7 |
| Cu(2) | 17.4 | 17.6 | 17.6 |
| O(4) | 27.8 | 27.5 | 26.0 |
| O(3) | 47.9 | 48.2 | 45.9 |
| O(2) | 71.4 | 73.5 | 71.8 |
| \(B_{3g}\) Ba | 9.8 | 9.8 | 10.3 |
| Cu(2) | 17.4 | 17.5 | 17.4 |
| O(4) | 36.6 | 36.3 | 37.6 |
| O(2) | 45.3 | 46.1 | 46.9 |
| O(3) | 65.2 | 67.7 | 65.2 |

TABLE III: Calculated and measured odd symmetry modes for the \(\Gamma\) point in meV.

| Mode | Theory | Neutron | IR |
|------|--------|---------|----|
| \(B_{1u}\) Y/Ba | 10.3 | 10.2 | - |
| Cu(1) | 20.7 | 19.4 | 19.2 |
| Y/Cu(2) | 23.8 | 23.9 | 23.9 |
| O(2)-O(3) | 27.0 | - | silent |
| O(3) | 44.6 | 44.0 | 44.9 |
| O(2) | 42.6 | - | 42.7 |
| O(4) | 33.5 | 35.0 | 34.7 |
| O(2)+O(3) | 40.3 | 37.2 | 37.2 |
| O(4) | 68.2 | 68.1 | 70.3 |
| \(B_{2u}\) Y/Ba | 10.1 | 10.1 | - |
| O(1) | 16.4 | 15.6 | - |
| Cu(1) | 19.0 | 19.5 | - |
| Y/Cu(2) | 21.8 | 24.0 | 23.5 |
| O(2) | 71.9 | 74.3 | 74.0 |
| O(4) | 33.5 | 35.0 | 34.7 |
| O(3) | 44.6 | 44.0 | 44.9 |
| O(2) | 42.6 | 44.5 | 44.9 |
| O(4) | 68.2 | 68.1 | 70.3 |
| \(B_{3u}\) Y/Ba | 10.0 | 10.1 | - |
| Cu(1) | 19.7 | 19.5 | - |
| Y/Cu(2) | 21.2 | 23.4 | 23.4 |
| O(2) | 42.6 | 44.5 | 44.9 |
| O(1) | 61.4 | 59.4 | 59.2 |
| O(3) | 65.6 | 68.0 | 67.6 |

TABLE II: Calculated and measured Raman modes. Besides the frequency (in meV) also the dominant eigenvector character is given.

| Mode | this work | FLAPW \[9\] | Exp. \[17\] |
|------|-----------|-------------|--------|
| \(A_{1g}\) | Ba | 14.8 | 15.3 | 14.4-14.8 |
| Cu(2) | 18.8 | 18.2 | 18.0-18.6 |
| O(2)-O(3) | 42.1 | 41.9 | 41.5 |
| O(2)+O(3) | 50.4 | 52.3 | 53.9-54.6 |
| O(4) | 58.6 | 60.4 | 61.1-62.0 |
| \(B_{2g}\) | Ba | 8.0 | 8.1 | 8.7 |
| Cu(2) | 17.4 | 17.6 | 17.6 |
| O(4) | 27.8 | 27.5 | 26.0 |
| O(3) | 47.9 | 48.2 | 45.9 |
| O(2) | 71.4 | 73.5 | 71.8 |
| \(B_{3g}\) | Ba | 9.8 | 9.8 | 10.3 |
| Cu(2) | 17.4 | 17.5 | 17.4 |
| O(4) | 36.6 | 36.3 | 37.6 |
| O(2) | 45.3 | 46.1 | 46.9 |
| O(3) | 65.2 | 67.7 | 65.2 |

connection with the FLAPW-study structure optimization has an important effect on phonon frequencies. This has also been found in our study. The agreement between both theoretical treatments and the Raman data is very satisfactory. The pseudopotential treatment is of equal quality as the FLAPW-method, in addition it is computationally less demanding and allows thus the calculation of odd modes as well which are given in table III together with neutron- and IR-data \[18, 19\].

So far, we have discussed \(\Gamma\)-point modes only, however, a reliable calculation of electron-phonon coupling requires the knowledge of the complete phonon disper-
sion throughout the BZ. Results for different directions in the BZ obtained using our mixed basis perturbation approach \[12\] are presented in Figs. 2 and 3. The modes are classified according to symmetry. For comparison also experimental data points are indicated. The dispersion curves were obtained by determining the dynamical matrix on a (4,4,2) reciprocal lattice grid in the BZ. Keeping in mind the complexity of the system the results are in excellent agreement with the available neutron data.

A number of points are worth mentioning in connection with the dispersion curves. The strong renormalization in respect to YBa$_2$Cu$_3$O$_6$ of the top-most mode of $\Delta_1$-symmetry along [100] shows up quite naturally in these calculations while model studies had extreme difficulties in reproducing this behavior. The eigenvector shows that it is an oxygen bondstretching mode in the Cu-O plane.

For experimentalists one of the major obstacles in the past has been the lack of untwinned single crystals of YBa$_2$Cu$_3$O$_7$ which made sometimes the assignment of a measured phonon to the (100) or (010)-direction very difficult. Some of these ambiguous cases have been re-assigned in view of the calculations and in agreement with very recent experimental studies \[20\]. Concerning the role of the Cu-O chains we found that most of these modes are in the range between 10 and 20 meV and only oxygen modes along the bond direction are high-lying ones with frequencies around 60 meV. No indication of a possible instability of the bond-bending chain modes (as proposed by earlier calculations \[2\]) was found in agreement with experiment. Consistent with the expectation of weak coupling perpendicular to the Cu-O-planes the dispersion in (001) direction is very small.

In the upper panel of Fig. 4 we show the generalized phonon density-of-states which should be compared with the neutron-scattering results presented in Refs. \[21, 22\]. Peaks and even shoulder positions agree quite well, as also the frequency cut off of 75 to 80 meV. The ratio of peak intensities differs substantially between the two measurements which is most likely due to the sensitivity of intensities to the background corrections. This prohibits comparison with our calculation.

To address the superconducting properties we have calculated the so-called Eliashberg function $\alpha^2 F(\omega)$ \[23\], using a very fine (24,24,4) k-point grid in performing the Fermi-surface average of the electron-phonon matrix elements \[24\]. Extensive tests have shown that this grid is sufficient for our calculations. Results are presented in Fig. 4 (lower panel). Comparing the phonon density of states $F(\omega)$ and $\alpha^2 F(\omega)$ we find a substantial shift of weight for $\alpha^2 F(\omega)$ to higher frequencies.
From the Eliashberg function we calculate the electron phonon coupling constant \( \lambda = 2 \int_0^\infty d\omega \omega^2 F(\omega)/\omega \) which gives \( \lambda = 0.27 \). For the logarithmically averaged phonon frequencies as defined in Ref. \[25\] we find 27.7 meV. After solving the isotropic gap equation for \( \mu^s = 0 \) we obtain only a \( T_c \) of \( \sim 2 \) K. Any realistic \( \mu^s \) suppresses superconductivity completely.

The very small value of \( \lambda \) is in substantial disagreement with earlier estimates based on \( \Gamma \)-point results only. Analyzing the behavior of \( \lambda \) throughout the BZ we find it to be varying by a factor of two only, however, variation as function of individual modes for given \( q \) is much larger. For the \( \Gamma \)-point for example modes of \( A_g \) and \( B_{1u} \)-symmetry account for 80\% of \( \lambda \). The largest contributions come from modes in the copper-oxygen planes as expected. Previous estimates of \( \lambda \) assumed that all modes at \( \Gamma \) contribute with similar strength as the \( A_g \)-modes. This elucidates why \( \lambda \)-values of the order of 1 or even larger have been obtained. However, this is a pure artefact of the unjustified assumption.

Raman measurements at \( \Gamma \) allowed for the determination of the anomalous frequency shifts of lattice vibrations occurring when cooling a superconductor below \( T_c \) \[56\]. Based on a theory by Zeyher and Zwicknagl for the phonon-self energy it could be shown that values of \( \lambda_1 = 0.02 \) for the \( A_g \) mode around 42 meV and \( \lambda_2 = 0.01 \) for the \( A_g \) mode around 54 meV, as determined by an LMTO-calculation \[3\], are consistent with the observed experimental frequency shifts. Our calculation give slightly larger values of \( \lambda_1 \approx 0.06 \) and \( \lambda_2 \approx 0.02 \) which are equally consistent with the measurements due to the approximations inherent in the calculation of the phonon self energy \[25\].

So far we have discussed only \( s \)-wave pairing, however many experimental facts support \( d \)-wave pairing \[23\]. In the much simpler system \( \mathrm{CaCuO}_2 \), the influence of \( s \)- versus \( d \)-pairing has been studied \[2\] and it has been found that both channels give very similar results for \( \lambda \) which should also hold for \( \mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_7 \). One other question which has not been discussed so far is the influence of correlations beyond LDA. Here the strongest argument in favor of our calculations is the fact that the calculated phonon dispersion is in very good agreement with experiment. If the electron-phonon coupling would be very strongly dependent on correlations this should show up in significant discrepancies between calculated and measured phonon modes. The good agreement supports the claim that correlation effects are of minor importance for electron-phonon coupling.

In summary, we have presented here ab-initio results for the lattice dynamics of \( \mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_7 \) which are in excellent agreement with available Raman, infrared and neutron data. Based on the knowledge of the complete phonon spectrum the electron-phonon coupling has been calculated. The electron-phonon coupling constant turns out to be very small. These calculations strongly support the view that in high-\( T_c \) materials conventional electron-phonon coupling is not an important contribution to superconductivity.

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