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Investigation of A_{1g} phonons in $YBa_2Cu_3O_7$ by means of linearized-augmented-plane-wave atomic-force calculations

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We report first-principles frozen-phonon calculations for the determination of the force-free geometry and the dynamical matrix of the five Raman-active A_{1g} modes in $YBa_2Cu_3O_7$. To establish the shape of the phonon potentials atomic forces are calculated within the linearized-augmented-plane-wave method. Two different schemes—the local-density approximation (LDA) and a generalized gradient approximation (GGA)—are employed for the treatment of electronic exchange and correlation effects. We find that in the case of LDA the resulting phonon frequencies show a deviation from experimental values of approximately −10%. Invoking GGA the frequency values are significantly improved and also the eigenvectors are in very good agreement with experimental findings. [S0163-1829(97)01345-3]

I. INTRODUCTION

The phonons in high-temperature superconductors have been intensively studied in the last decade, where Raman scattering is the most often used experimental technique. The phonon frequencies of different symmetries are measured for a variety of high-T_c (HTSC) compounds. On the other hand, much less is known about the corresponding eigenvectors. Experimentally, information is accessible when certain atoms in the unit cell are replaced by chemically equivalent elements. By analyzing the frequency shifts from Raman measurements performed on isotope-substituted samples the composition of the normal modes can be obtained. The experimentally best investigated HTSC crystal is $YBa_2Cu_3O_{7-x}$. Raman measurements on isotope-substituted samples of this material have given insight into the coupling of atomic vibrations especially for the two A_{1g} phonons containing barium and copper oscillations.[1,2]

In the past years, *ab initio* calculations of frequencies and eigenvectors of high-symmetry phonons in $YBa_2Cu_3O_7$ have been published.[3,4] These works were carried out by the frozen-phonon technique within all-electron band-structure calculations utilizing the local-density approximation (LDA) for the treatment of electron exchange and correlations. The phonon potentials were derived from total-energy values for different ionic configurations. The so-obtained A_{1g} phonon frequencies show a tendency of being slightly too soft, lying approximately 10% below their experimental counterparts.

This deviance can be discussed in several terms. First, the sole employment of total-energy values for establishing the dynamical matrix requires self-consistent electronic-structure calculations for a huge number of atomic configurations. When only harmonic terms are taken into account this number is proportional to N^2 when N atoms are involved in the vibrations of the same symmetry class. Thus the number of actually used total-energy values hardly exceeds the minimum number of configurations. Anharmonic contributions to the phonon potentials which might change the diagonal and off-diagonal elements of the dynamical matrix could not be accounted for. Second, the strong electron correlations in high-T_c materials are known to be underestimated by LDA leading to some shortcomings in the description of the electronic density distribution.[5] This fact might also bring up certain inaccuracies in the description of structural and vibronic properties of this material.

In this paper we present frozen-phonon calculations employing the linearized augmented plane-wave (LAPW) method.[6,7] We evaluate the atomic forces acting on the ions when distorted from equilibrium.[8,9] Using these data instead of total-energy values the geometry is optimized and the phonon potentials of the five A_{1g} modes are constructed. We checked the necessity of including anharmonic terms in the description of the energy surface and the number of configurations required for a stable fit. This procedure was carried out within the local-density approximation first. Alterations of the phonon potentials when treating electron exchange and correlations via a generalized gradient approximation[10] (GGA) rather than via LDA are also investigated.

II. CRYSTAL STRUCTURE AND SYMMETRY

$YBa_2Cu_3O_7$ is an orthorhombic crystal with the space group $Pmmm$. Yttrium and the chain atoms Cu(1) and O(1) occupy sites with the full symmetry of the cell (mmm). For barium, the copper and oxygen atoms in the planes—Cu(2), O(2), and O(3)—and the bridging oxygen O(4) the site symmetry is lower (mm), with a vibrational degree of freedom along the c axis. Thus the five A_{1g} Raman-active modes are coupled c-axis vibrations of these atoms.

III. METHOD

A. Energy surface

Within the frozen-phonon approach potentials underlying lattice vibrations are traditionally constructed through polynomial fitting of total-energy values calculated at selected frozen-in distortions of the crystal. If N denotes the number of coupled degrees of freedom in a certain phonon symmetry, the minimal number of total-energy calculations necessary for the harmonic approximation of the potentials scales with N^2. This scaling behavior in conjunction with the formidable computational effort of self-consistent band-structure calculations for polyatomic structures limits the feasibility of this approach when applied to $\mathrm{YBa_2Cu_3O_7}$. Thus, in past publications,[3,4] the number of actually calculated energy values hardly exceeded the minimal number necessary for the quadratic energy surface. In this way, neither anharmonic effects in the phonon potentials can fully be taken into account nor is it possible to perform a reliable check on the stability of the fitting parameters. These limitations can be overcome by evaluating the forces acting on atoms when they are displaced from equilibrium. Atomic-force formalisms[8,11] have proved to give an accurate description of the total-energy gradient with respect to ionic positions and thus enlarge the information on the shape of the energy surface obtainable from each frozen-phonon calculation. In fact, for the harmonic approximation it suffices to consider a number of distortion patterns scaling with N rather than N^2. The additional numerical effort required for the evaluation of atomic forces is not significant.

B. Atomic forces

If the electronic density distribution $\rho(\mathbf{r})$ in a crystal is precisely known, the Hellmann-Feynman theorem[12,13] states that the atomic force $\mathbf{F}_\alpha^{\mathrm{at}}$ (defined as the negative derivative of the total energy E_{tot} with respect to the nuclear coordinate $\mathbf{R}_\alpha$) is exactly described by the electrostatic force exerted on the nucleus α by all other charges of the system:

$$\mathbf{F}_\alpha^{\mathrm{at}} \equiv -\frac{dE_{\mathrm{tot}}}{d\mathbf{R}_\alpha} = -q_\alpha \sum_{\beta\neq\alpha} q_\beta \frac{(\mathbf{R}_\alpha-\mathbf{R}_\beta)}{|\mathbf{R}_\alpha-\mathbf{R}_\beta|^3} + q_\alpha \int_\Omega \rho(\mathbf{r}) \frac{(\mathbf{R}_\alpha-\mathbf{r})}{|\mathbf{R}_\alpha-\mathbf{r}|^3} d^3\mathbf{r} \tag{3.1}$$

with q_β denoting the nuclear charge at site $\mathbf{R}_\beta$. This electrostatic force is called the Hellman-Feynman force and is denoted $\mathbf{F}_\alpha^{\mathrm{HF}}$ in the following. In practical *ab initio* calculations charge densities are never exact and so correction forces have to be added to the HF force to obtain an accurate description of the total-energy gradient.[14] The calculation of these forces requires an analytic treatment of the first-order change of the energy expression when the ionic positions $\mathbf{R}_\alpha$ are displaced by a small amount $\delta\mathbf{R}_\alpha$. The energy expressions depend on the approximations made when simplifying the many-body crystal Hamiltonian. In the case of the all-electron band-structure method LAPW,[6] which is based on density-functional theory and a local exchange-correlation potential, this results in two corrective force-terms so that the atomic force can be written as

$$\mathbf{F}_\alpha^{\mathrm{at}} = \mathbf{F}_\alpha^{\mathrm{HF}} + \mathbf{F}_\alpha^{\mathrm{core}} + \mathbf{F}_\alpha^{\mathrm{IBS}}. \tag{3.2}$$

$\mathbf{F}_\alpha^{\mathrm{core}}$ is due to the simplifications made for the core elctrons' wave functions. The core states are assumed to be nondispersive in $\mathbf{k}$ space and are obtained by solving the Schrödinger equation neglecting the nonspherical part of the effective crystal potential $V_{\mathrm{eff}}(\mathbf{r})$. It was shown in Ref. 8 that $\mathbf{F}_\alpha^{\mathrm{core}}$ can explicitly be calculated by

$$\mathbf{F}_\alpha^{\mathrm{core}} = -\int_\Omega \rho_{\mathrm{core}}^\alpha(r) \nabla V_{\mathrm{eff}}(\mathbf{r}) d^3\mathbf{r}. \tag{3.3}$$

$\mathbf{F}_\alpha^{\mathrm{IBS}}$ is related to the fact that only a finite number of basis functions can be taken into account when solving the eigenvalue problem for the valence electrons by a variational scheme. In our particular case, the wave functions are linear combinations of *linearized augmented plane waves* (LAPW's). Since these LAPW's depend on the atomic positions the incompleteness of the set of basis functions (IBS) leads to one part of the correction force $\mathbf{F}_\alpha^{\mathrm{IBS}}$. A further contribution termed $\mathbf{D}_\alpha$ stems from the discontinuity of the second derivative of the wave functions at the atomic-sphere boundaries. The total $\mathbf{F}^{\mathrm{IBS}}$ is given by[8]

$$\mathbf{F}_\alpha^{\mathrm{IBS}} = -\sum_i w_i \left[\left\langle \frac{d\psi_i}{d\mathbf{R}_\alpha} \right| \hat{T} + V_{\mathrm{eff}} - \varepsilon_i | \psi_i \rangle + \langle \psi_i | \hat{T} + V_{\mathrm{eff}} - \varepsilon_i \left| \frac{d\psi_i}{d\mathbf{R}_\alpha} \right\rangle \right] - \mathbf{D}_\alpha \tag{3.4}$$

with

$$\mathbf{D}_\alpha = \sum_i w_i \oint_{MT_\alpha} [\psi_i^*(\mathbf{r}) \hat{T} \psi_i(\mathbf{r})|_{MT_\alpha} - \psi_i^*(\mathbf{r}) \hat{T} \psi_i(\mathbf{r})|_{\mathrm{int}}] d\mathbf{A}_\alpha. \tag{3.5}$$

ψ_i denotes the wave function of a valence state, w_i is the respective occupation number, and ε_i is the corresponding eigenvalue. The integration in the term $\boldsymbol{D_\alpha}$ runs over the surface of the atomic sphere around the nucleus α. $\psi_i(\mathbf{r})|_{MT_\alpha}$ is the eigenstate expressed in terms of the local basis functions within the atomic sphere. $\psi_i(\mathbf{r})|_{\mathrm{int}}$ is the interstitial part of the wave function where the basis set consists of plane waves.

IV. CALCULATIONS

A. Energy surface and dynamical matrix

The zone-center A_{1g} Raman-active modes in $\mathrm{YBa_2Cu_3O_7}$ are coupled c-axis vibrations of Ba, Cu(2), O(2), O(3), and O(4). Using experimentally determined lattice constants[15] ($a=3.8231$ Å, $b=3.8864$ Å, $c=11.6807$ Å) atomic forces acting on these atoms were calculated for 19 different distortion patterns in the vicinity of the force-free geometry. Ten patterns corresponded to single-atom displacements, in the remaining nine configurations two atoms were distorted simultaneously. The maximum amplitude of displacement from equilibrium was approximately 0.05 Å. This yielded a set of 95 values for establishing a least-squares fit of the energy surface with respect to the five coupled degrees of freedom. To optimize this fit anharmonic coefficients supplemented the linear and quadratic terms where necessary. On the basis of the 15 independent harmonic force constants of the resulting polynomial function we set up the dynamical matrix for calculating phonon frequencies and eigenvectors. Additionally, the stability of the fit parameters was tested by repeating the fitting procedure on the sole basis of the ten single-atom displacement patterns. The resulting change in

TABLE I. Force contributions in mRy for a mixed distortion [$-$O(2), $-$O(4)].

	Ba	Cu(2)	O(2)	O(3)	O(4)
Position (c)	0.1815	0.3530	0.3740	0.3787	0.1540
$\mathbf{F}^{\mathrm{HF}}$	46.66	123.82	0.76	-8.77	290.52
$\mathbf{F}^{\mathrm{core}}$	-36.08	-88.30	6.45	0.75	-188.87
$\mathbf{F}^{\mathrm{IBS}}$	-13.03	-35.22	6.50	7.91	-75.75
$\mathbf{F}^{\mathrm{at}}$	-2.45	0.30	13.71	-0.11	25.90

the phonon frequencies was very small (less than ± 2 cm^{-1}) indicating a high reliability of the polynomial coefficients.

B. Computational details

The self-consistent band-structure calculations for each frozen-in distortion were done using the full-potential LAPW method as implemented in the WIEN95 code.[7] Valence states and semicore states (Y-4s, Y-4p, Ba-5s, Cu-3p) were treated in the same energy window by using local orbitals[16] as an extension to the LAPW basis set. The expansion of the wave functions included 1950 LAPW's (RK_{max}=7.1). The sphere radii were chosen to be 2.5 a.u. for Y and Ba, 1.8 a.u. for Cu(1), 1.9 a.u. for Cu(2) and 1.55 a.u. for O(1), O(2), O(3), and O(4). Charge densities and potentials in the atomic spheres were represented by spherical harmonics up to $L=6$, whereas in the interstitial region these quantities were expanded in a Fourier series with 3500 stars of **K** in the LDA case and 5000 stars of **K** in the GGA case. The radial functions of each LAPW were calculated up to $l=12$ and the nonspherical potential contribution to the Hamilton matrix (Gaunt coefficients) had an upper limit of $l=6$. For Brillouin-zone (BZ) integrations a $12\times12\times4$ **k**-point mesh was used yielding 72 **k** points in the irreducible wedge.

C. Correction terms

The unreliability of the pure HF force for calculating the atomic force within the LAPW method has been demonstrated by Yu *et al.*[8] for phonons in simple systems as Mo and Si. In the case of $YBa_2Cu_3O_7$ we can confirm the importance of the corrective force terms for an accurate description of the total-energy gradient. In Table I we list the various contributions to the atomic forces when the two atoms O(2) and O(4) are displaced simultaneously from equilibrium. With the exception of O(2), $\mathbf{F}^{\mathrm{IBS}}$ and $\mathbf{F}^{\mathrm{core}}$ are of the same magnitude as $\mathbf{F}^{\mathrm{HF}}$ but of different signs. Due to this cancellation the resulting total force (3.2) is one or even two orders of magnitude smaller than its constituents. Thus a very precise calculation is required in order to obtain reliable results.

V. RESULTS

A. LDA results

For the case, where the electronic exchange and correlation effects are treated by LDA, the energy surface is well described by harmonic terms plus a cubic term in the O(4) coordinate. The minimum energy positions of this polynomial function are $z_{\mathrm{Ba}}=0.1812\ c$, $z_{\mathrm{Cu(2)}}=0.3530\ c$, $z_{\mathrm{O(2)}}=0.3789\ c$, $z_{\mathrm{O(3)}}=0.3783\ c$, and $z_{\mathrm{O(4)}}=0.1586\ c$, which agree well with the experimental structure parameters ($z_{\mathrm{Ba}}=0.1843\ c$, $z_{\mathrm{Cu(2)}}=0.3556\ c$, $z_{\mathrm{O(2)}}=0.3772\ c$, $z_{\mathrm{O(3)}}=0.3789\ c$, and $z_{\mathrm{O(4)}}=0.1584\ c$). The eigenvalues and eigenvectors of the corresponding dynamical matrix are displayed in Table II. The two low-lying modes are governed by hybridized Ba-Cu motions. Further we observe an appreciable admixture of O(2), O(3), and O(4) oscillations in the 330, 387, and 452 cm^{-1} modes. The importance of the anharmonic term in the O(4) coordinate is reflected in the fact, that its exclusion from the fitting procedure leads to a lowering of the corresponding apex mode (452 cm^{-1}) by 8 cm^{-1}. The introduction of other diagonal or off-diagonal anharmonic terms had the maximum effect of ± 1 cm^{-1} on the phonon frequencies.

In the comparison of the calculated phonon frequencies with their experimental counterparts it can be noticed that the discrepancies lie in the range of -10%. The only exception is the out-of-phase motion of O(2) and O(3) where the agreement with the experimental frequency is excellent. These findings are close to the results of Rodriguez *et al.*[4] based on linear-muffin-tin orbital total-energy calculations but reveal larger differences to LAPW frozen-phonon calculations by Cohen *et al.*[3] particularly for the three modes dominated by the motions of the oxygens. They find a frequency of 513 cm^{-1} for the apex mode, 12% above our calculated value. For the O(2)-O(3) mode and the O(2)+O(3) mode their values are 312 and 361 cm^{-1}, whereas our results are 335 and 387 cm^{-1}, respectively. As little information is given on the computational details in the paper of Cohen et al.[3] we cannot give a definit explanation for the discrepancies. We can state that the influence of anharmonicities neither on the diagonal nor on the off-diagonal elements of the dynamical matrix is strong enough to account for the different values. Parts of the differences might be connected to the fact that Cohen *et al.* used experimental equilibrium positions to optimize each coordinate separately. It should be noted that in a recent

TABLE II. LDA phonon frequencies in cm^{-1} and eigenvectors of the five A_{1g} modes in $YBa_2Cu_3O_7$ at $q=0$ compared to experimental data (Refs. 1 and 17).

Expt.	Theory	Rel. Deviation	Ba	Cu(2)	O(2)	O(3)	O(4)
116,118	103	$-11\%,-13\%$	0.85	0.52	0.05	0.05	0.00
150,145	130	$-13\%,-10\%$	0.53	-0.84	-0.08	-0.07	0.06
335	327	$-$ 2%	0.00	0.02	-0.81	0.59	-0.05
440	387	-12%	0.02	0.09	-0.51	-0.74	-0.43
500	452	-9%	0.03	-0.11	0.28	0.32	-0.90

TABLE III. GGA phonon frequencies in cm^{-1} and eigenvectors of the five A_{1g} modes in $YBa_2Cu_3O_7$ at $q=0$ compared to experimental data (Refs. 1 and 17).

Expt.	Theory	Rel. Deviation	Ba	Cu(2)	O(2)	O(3)	O(4)
116,118	115	−1%,−3%	0.91	0.40	0.05	0.02	0.02
150,145	144	−4%,−1%	0.41	−0.91	−0.06	−0.04	0.03
335	328	−2%	0.01	0.04	−0.81	0.60	−0.02
440	405	−8%	0.02	0.07	−0.56	−0.77	−0.30
500	452	−9%	0.02	−0.04	0.20	0.23	−0.95

refinement[18] of their work the frequency of the apex oxygen mode is in much better agreement with our results.

B. GGA results and discussion

It is well known that the correlation effects between the electrons in Y-Ba-Cu-O compounds seem to play an important role for the electronic properties of these materials: Measurements of the electric-field gradient in $YBa_2Cu_3O_7$ have revealed that band-structure calculations on the basis of LDA show certain inaccuracies in the description of the materials' electronic charge distribution.[5] In addition, such calculations fail completely in reproducing the insulating and antiferromagnetic ground state of $YBa_2Cu_3O_6$.[19] This raises the question if correlation effects also influence the structural properties of $YBa_2Cu_3O_7$ and thus might account for the theoretical underestimation of the A_{1g} phonon frequencies. To obtain an insight into the shortcomings of LDA concerning vibronic properties, we used a generalized gradient approximation proposed by Perdew *et al.*[10] for the treatment of the exchange-correlation energy and potential which is now calculated from the local electronic density as well as from its gradient. We established the energy surface of the A_{1g} phonons following the same procedure as in the LDA case.

We find that the GGA scheme enhances the diagonal terms in the dynamical matrix by approximately 15% (Ba), 10% (Cu), 3% [O(2)], 5% [O(3)], and 4% [O(4)], respectively, in comparison to the LDA results. On the other hand, the coupling between the copper and the three oxygen atoms is significantly decreased. The same applies to the force constants coupling the apex vibration to the motion of the other two oxygens. The GGA approach neither changes the anharmonic cubic term in the O(4) coordinate noticeably, nor does it cause further anharmonicities in the energy surface. Resulting phonon frequencies and eigenvectors are displayed in Table III. We observe a significant improvement for the Ba and Cu dominated modes, bringing their frequency values in excellent agreement with their experimental counterparts and also reproducing the mode admixture very accurately. From isotopic substitution experiments on the copper sites the values for all three independent elements of the dynamical matrix of the Ba-Cu subsystem could be extracted.[1] It can be observed (Table IV) that the LDA calculations underestimate both diagonal terms by 15% whereas the off-diagonal term lies within the experimental uncertainty. The respective values from GGA calculations exhibit perfect agreement with the experiment.

With regard to the oxygen modes, we find that the frequency of the in-phase O(2)+O(3) mode is increased ranging approximately 8% below the experimental value, whereas the phonon frequencies of the out-of-phase O(2)-O(3) mode remains basically unaltered accurately reflecting the experimental value. The increase in the diagonal force constant of the apex oxygen is not accompanied by a corresponding increase in the frequency of the O(4) mode. This is due to the changes in the coupling between O(4) and the other atoms. Concerning the mode admixtures, no experimental data are available to fully determine the off-diagonal elements of the O(2)-O(3)-O(4) subsystem. Nevertheless, site-selective isotope substitution experiments[20] indicate that the apex mode is largely dominated by the O(4) vibration and that the hybridized O(2)+O(3) mode has a small but noticeable admixture of the apex oscillation. On contrary, the O(2)-O(3) mode is decoupled from the O(4) motion. Our calculations confirm this picture.

VI. CONCLUSIONS

We have determined phonon frequencies and eigenvectors of the five Raman-active A_{1g} modes in $YBa_2Cu_3O_7$ employing frozen-phonon calculations on the basis of the full-potential LAPW method. Atomic-force values were used to establish the atomic equilibrium positions and to map out the phonon potentials. When treating the electronic exchange and correlations by LDA, the calculated phonon frequencies display deviations from the measured values by approximately 10%. The only exception is the out-of-phase O(2)-O(3) mode where the agreement with experiment is excellent. Going beyond LDA by invoking a GGA exchange-correlation functional leads to an overall improvement of the frequencies. The two low-lying Ba-Cu modes as well as the O(2)-O(3) mode are in perfect agreement with experimental values whereas the frequency of the O(2)+O(3) mode is enhanced but still 8% too small. In comparison to LDA calculations only the O(4) frequency remains unaltered ranging 10% below its measured counterpart. Regarding the mode admixtures we find that our GGA results for the two Ba-Cu modes very accurately reproduce the diagonal and off-diagonal force constants which have been determined by iso-

TABLE IV. Force constants in N/m for the sublattice vibrations of Cu and Ba compared to measured values (Ref. 1). k_{11} and k_{22} denote the diagonal force constants, k_{12} denotes the coupling term.

	LDA	GGA	Expt.
k_{11}	101	119	118.6 (−5.3/+5.0)
k_{22}	69	77	81.3 (−2.2/+2.5)
k_{12}	−17	−15	−16.3 (−3.3/+5.6)

topic substitution experiments. Additionally, our calculations show that the O(2)-O(3) mode is completely decoupled from the O(4) oscillation, whereas there is a finite contribution of the O(4) vibration to the O(2)+O(3) mode. The domination of the O(4) displacement in the apex mode is also revealed. These findings are compatible with Raman measurements performed on site-selective substituted samples. In summary, these results indicate that first-principles calculations based on density-functional theory are an appropriate tool for the investigation of structural and vibronic properties of HTSC cuprates, where the treatment of exchange and correlation effects is an important issue for this task.

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