PHYSICAL REVIEW B VOLUME 37, NUMBER 13 1 MAY 1988

# Frequencies, eigenvectors, and single-crystal selection rules of $\mathbf{k}=0$ phonons in $YBa_2Cu_3O_{7-\delta}$: Theory and experiment

R. Liu, C. Thomsen, W. Kress, M. Cardona, and B. Gegenheimer
*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany*

F. W. de Wette, J. Prade, and A. D. Kulkarni
*University of Texas, Austin, Texas 78712*

U. Schröder
*Universität Regensburg, D-8400 Regensburg, Federal Republic of Germany*
(Received 11 December 1987)

We have determined the components of the Raman tensor of single-crystal superconducting $YBa_2Cu_3O_{7-\delta}$ for the phonons at $\sim$500, 440, 330, and 150 $cm^{-1}$. They all correspond to the totally symmetric modes both in the tetragonal ($A_{1g}$) and orthorhombic ($A_g$) structures except for the 330-$cm^{-1}$ mode which is $B_{1g}$ tetragonal. We have also performed lattice dynamical calculations with parameters extracted from those of perovskite and other metallic oxides. The frequencies and eigenvectors obtained agree well with the experimental results. This work settles discrepancies found in the previous literature.

Many reports on vibrations of high-$T_c$ superconductors have appeared.[1-5] The disagreement between assignment of phonons by various authors have spurred measurements on single crystals.[6-9] In one case[9] incorrect experimental selection rules were obtained. Little theoretical work on phonon frequencies and eigenvectors has been published so far.[10,11] While in Ref. 10 the semiconducting $O_6$ compound was treated, Ref. 11 has adjusted the force constants to fit the experimental data. Here we present theoretical results from parameters not adjusted but taken over from known oxide perovskite and other metallic oxide potentials. We also present an unambiguous experimental determination of the Raman selection rules for single crystals and the details of the Raman tensors. The results agree with the theoretical predictions. This fact enables us to propose an assignment of the ir phonons observed in ceramic samples.

Single crystals of $YBa_2Cu_3O_{7-\delta}$ were grown from a nonstoichiometric melt by slow cooling following Ref. 12. Tetragonal platelets (maximum dimensions $2.5\times2.5\times0.08$ mm) formed and were separated from the flux; their composition was checked with an EDAX microprobe. With a single-crystal diffractometer we found the crystal studied here to be oriented with the $c$ axis perpendicular to the large surface of the platelet. The lattice constants were $a=3.869$ Å, $b=3.872$ Å, and $c=11.71$ Å, values typical for unannealed crystals.[12] These values for $a$, $b$, and $c$ indicate $\delta$ values slightly smaller than that of the tetragonal phase ($\delta\approx0.5$).[13] By measuring the shielding in a weak magnetic field, $T_c$ (onset) was found to be 40 K (at 10% of maximum shielding). The complete shielding effect was 77% while the Meissner effect was found to be 6%. The details of the Raman setup are given in Ref. 2.

The potentials for the lattice dynamical calculation were taken from least-squares fits to $BaTiO_3$,[14] SrO,[15] and NiO,[16] with the only modification that the polarizability in the $z$ direction of the Cu—O bonds was set equal to their longitudinal polarizability. This change is justified by the structural differences between the perovskites and the superconductor, as shown in the $\delta\cong1$ case.[10]

Let us first consider the case where the wave vector of the incident light $\mathbf{k}_i$ is parallel to the scattered one $\mathbf{k}_s$ and to the $c$ axis of the crystal (curves 1-6 of Fig. 1). In curve 1 both the (linear) polarization of the incident light ($\hat{\mathbf{e}}_i$) and the orientation of the (linear) analyzer ($\hat{\mathbf{e}}_s$) are along the $x$ axis. (No differences were found between the $x$ and $y$ axes since the crystal is nearly tetragonal. Even for an orthorhombic crystal no difference would be expected because of twinning.[12]) Curve 2 shows no detectable depolarized scattering to within noise. From the absence of all phonon features under cross polarization we conclude that *all* observed peaks have $A_g$ symmetry in the orthorhombic structure, i.e., $a_{ij}=0$ for $i\neq j$ where $a_{ij}$ are the components of the Raman tensor.

In curve 3 we have rotated $\hat{\mathbf{e}}_i$ and $\hat{\mathbf{e}}_s$ by 45° so that they are both parallel to either [110] or [$\bar{1}$10]. We find the same spectrum for orientations along either direction and thus display only one of them. In the spectrum taken under crossed polarization ($\hat{\mathbf{e}}_i\perp\hat{\mathbf{e}}_s\|[110]$, curve 4) we see that the peak at $\sim$330 $cm^{-1}$ has recovered the strength of that in curve 1, while the other peaks continue to be weak or absent. From this observation we conclude that the Raman polarizability must have components $a_{xx}=-a_{yy}$. Furthermore, from the absence of the peak at 330 $cm^{-1}$ in curve 8, taken for $\hat{\mathbf{e}}_i\|\hat{\mathbf{e}}_s\|z$, we infer that $a_{zz}\cong0$. We have thus specified all Raman tensor components of this mode. They are consistent with the measurement with circularly polarized light (curves 5 and 6). The absence of the peak at 330 $cm^{-1}$ for equal angular momenta of incident and scattered light (in an absolute

 

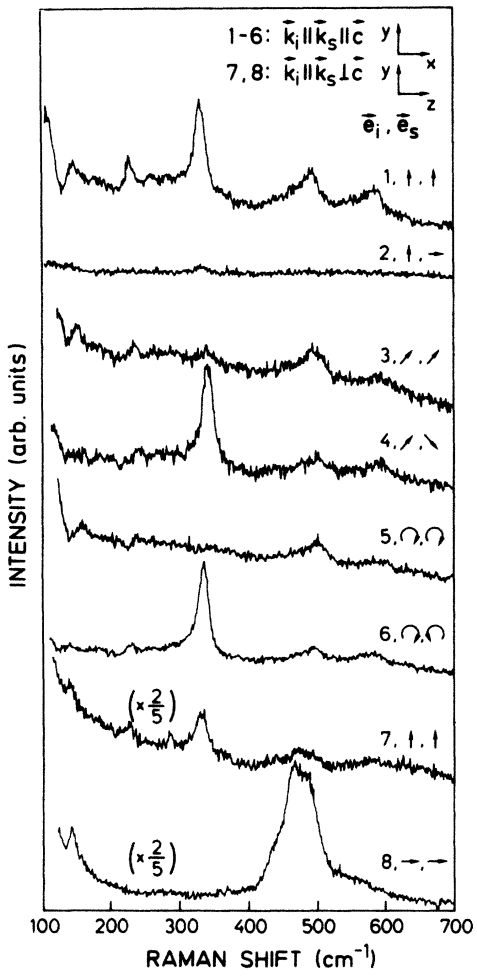


FIG. 1. Polarization-dependent Raman spectra of single-crystalline $YBa_2Cu_3O_{7-\delta}$. All curves were obtained in the backscattering geometry ($\mathbf{k}_i \| \mathbf{k}_s$); the orientations of the polarization vectors with respect to the crystal axes are indicated in the figure.

frame; opposite if we take the direction of propagation $\mathbf{k}_{i,s}$ as the quantization axis) shows that $\alpha_{xx} = -\alpha_{yy}$ to good accuracy.

The connection between this peak and the superconducting mechanism of these compounds has been shown to lie in an anomalous temperature dependence.[17,18] When the ceramic samples of $YBa_2Cu_3O_{7-\delta}$ are cooled below the superconducting transition temperature this peak lowers its frequency (softens), whereas all other Raman peaks are observed to stiffen. In the nonsuperconducting compound $YBa_2Cu_3O_6$ where this mode is also present (with tetragonal $B_{1g}$ symmetry), no anomalous temperature dependence has been found.[10] Closest in frequency in our lattice dynamical calculation for $\delta = 0$ lies an O(II)-O(III) ($z$) out-of-phase mode (347 $cm^{-1}$, Fig. 2) with the O(II)-O(III) motion required for the Raman tensor; we thus assign it to the experimental peak at 330 $cm^{-1}$. There is hence an anomaly related to superconductivity for vibrations in the so-called "planes" of $YBa_2Cu_3O_{7-\delta}$. We have also searched for this anomaly in the single crystals studied here, but found it to be weaker than in high-oxygen-content ceramic samples. The reason for that is found in curve 8 of Fig. 1, where $\mathbf{k}_i \| \mathbf{k}_s \perp c$ axis. The broad, large peak centered at $\sim$475 $cm^{-1}$ corresponds[4] to a distribution of O contents between 6.0 and 6.6. A distribution like this is characteristic for those of our single crystals which were not oxygen treated after preparation. We also note that the peak at 330 $cm^{-1}$ has resonant behavior;[19] when the spectra in Fig. 1 were taken with the 4880-Å $Ar^+$ laser line, this peak decreased by a factor of 5–10.

A second peak associated with the planes in the superconductor is usually observed in ceramic materials around 435 $cm^{-1}$.[2,6,20] In Fig. 1 it is only seen in curve 8 as a shoulder. Its Raman tensor must hence be of the form $\alpha_{xx} = \alpha_{yy} = 0$: only $\alpha_{zz}$ is nonzero. This peak corresponds to the O(II)-O(III) in-phase vibration along $z$ (373 $cm^{-1}$, Fig. 2).

At low frequencies in Fig. 1 we find a peak at 145 $cm^{-1}$ in curves 1, 3, 5, and 7 with roughly equal amplitude and in curve 8 with 1.5 times that amplitude. The peak is absent in curves 2, 4, and 6. The opposite selection rule of this peak compared to the peak at 330 $cm^{-1}$ for circular polarizations implies $\alpha_{xx} = \alpha_{yy}$, and the ratio of the peak amplitudes for $z^2$ and $x^2$ geometry (curve 8) sets the magnitude of the $\alpha_{zz}$ component to $|\alpha_{zz}| \cong 1.2|\alpha_{xx}|$. In our lattice dynamical calculation this peak corresponds to the Cu(2) vibration (159 $cm^{-1}$, Fig. 2). The Ba ($z$) mode below that (132 $cm^{-1}$ in Fig. 2) is not clearly seen in Fig. 1, but it has been reported[6] to lie near 116 $cm^{-1}$. The peak with the largest amplitude in (single-phase) ceramic material[2,6,20] and also in the single-crystal data of Fig. 1 is centered here at 475 $cm^{-1}$. It appears only in curve 8 (except through leakage in some of the other curves), hence it also has the Raman tensor components $\alpha_{xx} = \alpha_{yy} \cong 0$. This mode has been associated, rather conclusively and by many groups,[1,2,5,6,8,10] with the O(IV)-Cu(1) $A_g$ mode calculated at 515 $cm^{-1}$ (Fig. 1).

There has been controversy[21] about Raman features with frequencies $>550$ $cm^{-1}$. The selection rules of Fig. 1 can help identify impurity phases that do not have the same symmetry as the superconducting crystal or are randomly oriented. We conclude from arguments such as those used above that the Raman tensors of the broad peak at $\sim$580 $cm^{-1}$ and the feature at 220 $cm^{-1}$ are not compatible with the crystal symmetry. While diagonal, according to the data for the polarizations parallel to the crystal axes, the data for circular polarization and those for polarizations parallel to the base diagonals ($x+y$, $x-y$) require that the $\alpha_{xx}$ and $\alpha_{yy}$ components be *incoherent*. The data for polarizations along $z$ show that $\alpha_{zz} \cong 0$. Incoherent components suggest defect-induced scattering. Thus one possible assignment of the 220- and 580-$cm^{-1}$ modes is to the $x$- and $y$-polarized TO modes calculated to be at 130 and 576 $cm^{-1}$. O(I) defects, which exist to a great deal for $\delta \cong 0.5$, may induce the Raman scattering. The defect-induced nature and the twinning would cause the incoherence of $\alpha_{xx}$ and $\alpha_{yy}$.

Having discussed all the observed Raman peaks we now propose an assignment of the corresponding ir Davydov partners. Detailed far-infrared data on single crystals are

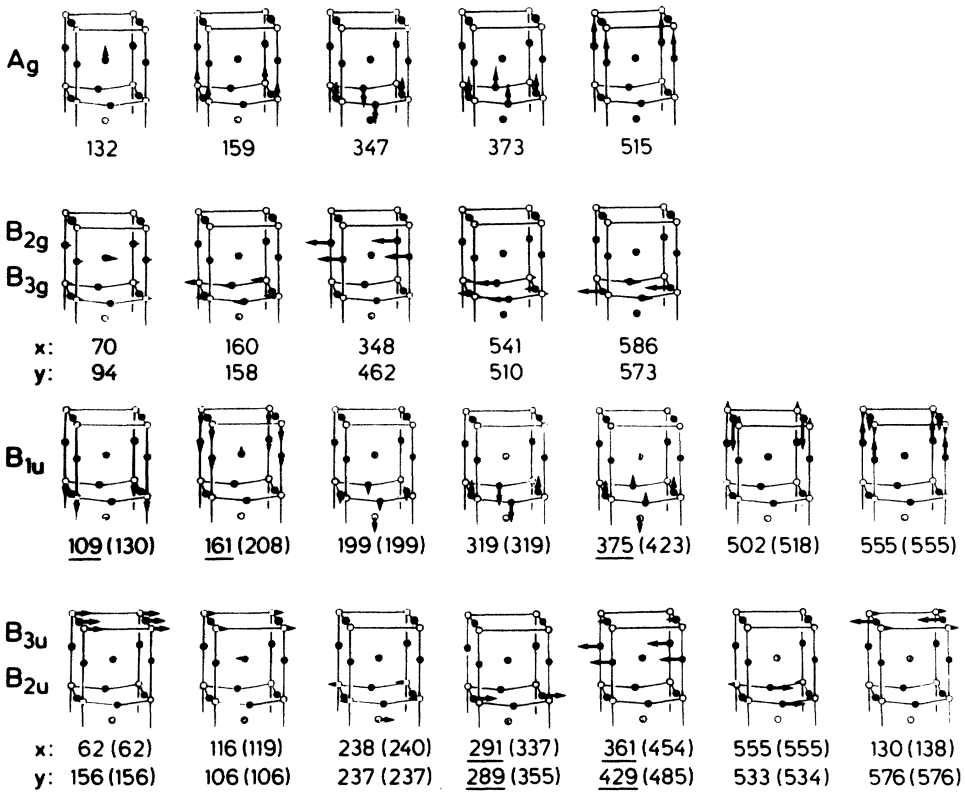


FIG. 2. Eigenvectors of all 36 optical modes of $YBa_2Cu_3O_{7-\delta}$ in the upper half on the unit cell. The displacements for the lower part can be simply obtained from the upper ones. The frequencies are below each mode; for the odd modes the TO (LO) frequencies are given outside (inside) parentheses. (Filled circles—O; open circles—Cu; hatched circles—Ba; dotted circles—Y.) In the text, O(II), O(III), and Cu(2) refer to atoms in the Cu-O planes adjacent to Y; O(I) and Cu(1) are atoms in the chains of the superconductor.

not available so we turn to measurements on ceramic materials.[2,18] Here we find peaks at 115, 150, 193, 275, 320, and 575 $cm^{-1}$. The three lowest frequencies have been suggested to belong to Ba and Y vibrations; the latter assignment is evidenced by the shift in frequency when Y is replaced by a rare earth.[2] We suggests that the weak peak at 115 $cm^{-1}$ corresponds to the mode at 109 $cm^{-1}$ (Fig. 2), while 150 and 193 $cm^{-1}$ are the Ba ($B_{1u}$) frequency and the Y ($B_{1u}$), calculated at 161 and 199 $cm^{-1}$, respectively. The next two peaks in the doublet at 275 and 320 $cm^{-1}$, also possess an anomalous temperature dependence,[18,22] and we find five likely frequencies in Fig. 2: the $B_{3u}$ and $B_{2u}$ in-plane movements (290, 361, and 429 $cm^{-1}$), and two $B_{1u}$ out-of-plane vibrations (319 and 375 $cm^{-1}$). We assign the 290-$cm^{-1}$ in-plane vibration to the experimental peak at 275 $cm^{-1}$. In the tetragonal material, the mode at 319 $cm^{-1}$ (Fig. 2) is exactly silent since it has no net dipole moment: it is indeed not seen in $YBa_2Cu_3O_6$,[10] and is probably too small to be detected in ir measurements of $YBa_2Cu_3O_{7-\delta}$. The calculated eigenmode at 375 $cm^{-1}$ (Fig. 2) shows a large shift upon the replacement of Y by a rare earth which is not observed in the experiment. Thus, we assign the peak at 320 $cm^{-1}$ to the remaining mode ($B_{2u}$ and $B_{3u}$ symmetries; 361 and 429 $cm^{-1}$) which has a large $x$-$y$ anisotropy. The two frequencies may be smeared out in polycrystalline material and not observed separately in spite of their rather large TO-LO splitting. The peak at 575 $cm^{-1}$ could correspond to the bond stretching O(I) vibration which has already appeared, defect induced, in the Raman spectra. A definitive assignment, however, must come from single-crystal ir measurements.

In conclusion, we have determined the Raman tensor elements of four of the phonons of superconducting $YBa_2Cu_3O_{7-\delta}$ by polarization-dependent Raman scattering on single crystals. We have also presented a calculation of the eigenvectors and frequencies of all phonons obtained in a lattice dynamical calculation. The agreement between theory and experiment is good. The phonons with the temperature anomaly observed below $T_c$ have been shown to be related to the CuO planes in the superconductor.

We would like to thank K. Peters for the crystallographic data, H. Hirt, M. Siemers, and P. Wurster for technical help, and M. Gehrke for the magnetic measurements. One of us (F.W. de W.) acknowledges research support from the National Science Foundation (DMR-8505747), and the Robert A. Welch Foundation (F-433). J.P. acknowledges support from the Deutsche Forschungsgemeinschaft.

[1]M. Stavola, D. M. Krol, W. Weber, S. A. Sunshine, A. Jayaraman, G. A. Kourouklis, R. J. Cava, and E. A. Rietman, Phys. Rev. B **36**, 850 (1987).

[2]M. Cardona, L. Genzel, R. Liu, A. Wittlin, Hj. Mattausch, F. García-Alvarado, and J. M. García-Gonzalez, Solid State Commun. **64**, 727 (1987).

[3]H. Rosen, E. M. Engler, T. C. Strand, V. Y. Lea, and D. Bethme, Phys. Rev. B **36**, 726 (1987).

[4]C. Thomsen, R. Liu, M. Bauer, A. Wittlin, L. Genzel, M. Cardona, E. Schönherr, W. Bauhofer, and W. König, Solid State Commun. **65**, 55 (1988).

[5]Z. Iqbal, S. W. Steinhauser, A. Bose, N. Cipollini, and H. Eckhardt, Phys. Rev. B **36**, 2283 (1987).

[6]R. Bhadra, T. O. Brun, M. A. Beno, B. Daborowski, D. G. Hinks, J. Z. Liu, J. D. Jorgensen, L. J. Novicki, A. P. Paulikas, Ivan K. Schuller, C. U. Segre, L. Soderholm, B. Veal, H. H. Wang, J. M. Williams, K. Zhang, and M. Grimsditch (unpublished).

[7]D. M. Krol, M. Stavola, W. Weber, L. F. Schneemeyer, J. V. Wasczcak, S. M. Zahurak, and S. G. Konsinski, Phys. Rev. B **36**, 8325 (1987).

[8]A. Yamanaka, F. Minami, K. Watanabe, K. Inoue, S. Takekawa, and N. Iyi, Jpn. J. Appl. Phys. **26**, L1404 (1987).

[9]R. J. Hemley and H. K. Mao, Phys. Rev. Lett. **58**, 2340 (1987). A phonon of $xy$ symmetry, which does not exist for these structures, was reported at 338 $cm^{-1}$ in this work.

[10]C. Thomsen, M. Cardona, W. Kress, R. Liu, L. Genzel, M. Bauer, E. Schönherr, and U. Schröder, Solid State Commun. **65**, 1139 (1988).

[11]F. E. Bates and J. E. Eldridge, Solid State Commun. **64**, 1435 (1987).

[12]L. F. Schneemeyer, J. V. Waszczak, T. Siegrist, R. B. van Dover, L. W. Rupp, B. Batlogg, R. J. Cava, and D. V. Murphy, Nature **328**, 601 (1987).

[13]P. K. Gallagher, H. M. O'Bryan, S. A. Sunshine, and D. W. Murphy, Mater. Res. Bull. **22**, 995 (1987).

[14]W. Kress, U. Schröder, J. Prade, A. D. Kulkarni, and F. W. de Wette (unpublished).

[15]K. H. Rieder, R. Migoni, and B. Renker, Phys. Rev. B **12**, 3374 (1975).

[16]W. Reichardt, V. Wagner, and W. Kress, J. Phys. C **8**, 3955 (1975).

[17]R. M. Macfarlane, H. Rosen, and H. Seki, Solid State Commun. **63**, 831 (1987).

[18]A. Wittlin, R. Liu, M. Cardona, L. Genzel, W. König, W. Bauhofer, Hj. Mattausch, A. Simon, and F. García-Alvarado, Solid State Commun. **64**, 477 (1987).

[19]R. Liu, C. Thomsen, M. Cardona, and B. Gegenheimer (unpublished).

[20]M. Cardona, R. Liu, C. Thomsen, M. Bauer, L. Genzel, W. König, A. Wittlin, U. Amador, M. Barahona, F. Fernández, C. Otero, and R. Sáez, Solid State Commun. **65**, 71 (1988).

[21]See, e.g., S. Blumenröder, E. Zirngiebel, H. Schmidt, G. Güntherodt, and H. Brenten, Solid State Commun. **64**, 1229 (1987).

[22]C. Thomsen, R. Liu, A. Wittlin, L. Genzel, M. Cardona, W. König, M. V. Cabañas, and E. García, Solid State Commun. **65**, 219 (1988).