Reply to "Comment on 'Axial oxygen-centered lattice instabilities in $YBa_2Cu_3O_7$: An application of the analysis of extended x-ray-absorption fine structure in anharmonic systems'"

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We assert that the one-site Cu(1)-O(4) model, suggested in the Comment by Thomsen and Cardona [Phys. Rev. B **47**, 12 320 (1993)] is inconsistent with polarized x-ray-absorption fine-structure and diffraction results. We also show that the two-site Cu(1)-O(4) distribution is not inconsistent with optical measurements, although a rigid double-well modeling of this distribution is [Phys. Rev. Lett. **68**, 3236 (1992)].

The two-site Cu(1)-O(4) distribution derived from x-ray-absorption fine-structure (XAFS) studies,[1-4] and labeled the "double well," is a subtle effect, and potentially of great importance in cuprate superconductors. It was *missed* in early structural studies (XAFS and diffraction) and remains susceptible to misinterpretation, as evidenced by the Comment of Thomsen and Cardona.[5]

First, it is essential to clearly distinguish three issues: (1) Interpretation of XAFS data in terms of a two-site Cu(1)-O(4) distribution, (2) a local model for the two-site distribution, and (3) consequences of (1) and (2) for the CuO_2 planes including possible implications for superconductivity. Reference 1 is devoted to establishing point (1). Concerning point (2), Ref. 6 is our best attempt to date to describe the two-site distribution in terms of a local dynamical-polarizability model—a microscopic description of polaron tunneling due to lattice-charge transfer coupling. Reference 6 is explicitly referenced in Ref. 1. As we point out in Ref. 6 and earlier references,[1,2] it is essential to *correlate* structural and optical observations—here we agree with Thomsen and Cardona.[5] However, our model points out that is *not* possible to predict IR and Raman mode implications on the basis of a *rigid* double-well potential. This is the major misinterpretation introduced in the Comment by Thomsen and Cardona (i.e., the difference between the inference of a two-site Cu(1)-O(4) distribution from XAFS and a *specific* rigid double-well local model for such distribution). As we discuss below, there is *no* contradiction with optical measurements to our knowledge.

Concerning point (3), we have *not* claimed that any implications for superconductivity are proved by our observations. It is natural to *speculate* on such implications. Indeed, indications in this direction have existed for several years.[7] However, additional experiments and theoretical calculations are required to determine whether anomalies in the two-site distribution are driving forces or merely spectators through superconductivity-elasticity coupling.[2] These (and several other)[8] local structural anomalies are at least as striking as any anomalies in the magnetic behavior and must be as seriously investigated. However, to date our only *quantitative* assertions have concerned points (1) and (2) above. Returning now to these points, we have the following observations:

(i) Besides our own work,[1-4] Yacoby *et al.*[9(a)] and Stern *et al.*[9(b)] also found a split axial oxygen position in $YBa_2Cu_3O_7$ using *polarized* XAFS [the use of unpolarized XAFS as in Ref. 10 does not allow us to draw quantitative conclusions on the Cu-O(4) distribution[1]], and Bianconi *et al.*[11] have concluded the existence of a split axial oxygen position in $Bi_2Sr_2CaCu_2O_8$. In *addition*, pair distribution function analysis of neutron scattering[12] in $Tl_2Ba_2CaCu_2O_8$ also yielded a split axial oxygen position, with *dynamical* fluctuations between these positions, in agreement with our original tunneling interpretation.[2] C-axis structural anomalies have also been found by ion-channeling,[13] Mössbauer,[14] and neutron inelastic scattering experiments.[15]

(ii) The possibility of interpreting our XAFS data using a *single* axial position, as proposed in the Comment by Thomsen and Cardona and Ref. 10 was extensively discussed in our paper.[1] Here, we only remark that this possibility is *inconsistent* with the XAFS data of Refs. 6 and 9, and leads to changes in the average Cu(1)-O(4) bond length, in the vicinity of T_c, in *contradiction* with diffraction measurements.[16]

(iii) The statement that our XAFS analysis included only a single Cu(1)-O(4) bond is incorrect. We explicitly stated[1,2] that both the Cu(1)-O(4), and Cu(2)-O(4) contributions were included, and contributions from further shells were shown to have very small effect. This was confirmed by Yacoby *et al.*[9(a)] and Stern *et al.*[9(b)]

(iv) The statement that the fluctuation region proposed in our work is an order of magnitude smaller than that inferred from c-parameter diffraction and expansibility measurements (~ 40 K) is also not correct. In Ref. 2, we stated that we could *not* determine the extension of this fluctuation region, since we did not have any mea-

surements at intermediate temperatures between 10 and 83 K. Subsequent measurements[9] indicate that the fluctuation region extends at least 20 K.

(v) We stated in Refs. 1 and 4 that a *rigid* double-well modeling of the split axial oxygen position was a convenient phenomenological description of the XAFS structural observations, but that one *cannot* draw any conclusions regarding excited states *not* accessible at the temperatures used in the experiment (in this case $T < 105$ K). In order to interpret the optical data we considered the microscopic model presented in Ref. 6 and mentioned Refs. 1 and 4. Here we summarize the main conclusions: (a) The IR mode develops a distinct two-site behavior, while the Raman mode does not, consistent with the XAFS observation of a symmetric radial distribution function (RDF); (b) the calculation of the IR absorption shows that the tunneling frequency derived from XAFS *cannot* be identified with the measured Raman (505 cm^{-1}) or IR (585 cm^{-1}) modes. The arguments in the Comment by Thomsen and Cardona on the relative percentage changes of the IR and Raman frequencies thus do *not* apply. We also emphasize that this two-site distribution cannot be obtained within homogeneous local-density-approximation (LDA) calculations, unless specific correlation effects are included.[17]

(vi) The IR spectrum in Fig. 1(a) shows the tunneling at very low frequencies (~60 cm^{-1}), a main peak at ~620 cm^{-1}, and a smaller side peak at ~510 cm^{-1}. Experimental data[18] [Fig. 1(b)] indeed show a marked asymmetry of the "585 cm^{-1}" peak with a structure similar to the calculation. Clearly, an experimental search for the low-frequency tunneling mode and its correlation with the 585 cm^{-1} mode is desirable. The smaller side peak in the calculation corresponds to a Raman-active excitation, which arises from the breaking of the symmetry, as stated in the Comment by Thomsen and Cardona. We note, however, that in order to discard evidence of a symmetry breaking from experimental data, it is necessary to quantify such an effect. As shown in Fig. 1 in this case the experimental data are actually *consistent* with the breaking of the selection rules within our model.

(vii) Although the effect of the superconducting transition is not included in the model,[6] by changing the electron-phonon coupling (these are electronic degrees of freedom within the cluster, and *not* those representing holes in the plane) to reproduce the split separation determined by XAFS we can estimate changes in the frequencies observed in the IR spectrum. The changes in the tunneling frequency are ~70–80 %, consistent with the XAFS estimates.[1] However, the changes in the fundamental IR-active peak and its satellite are only ~2–5 %; these changes are *not* inconsistent with the results from optical spectroscopy.[18–20]

(viii) We note that the temperature dependences of the

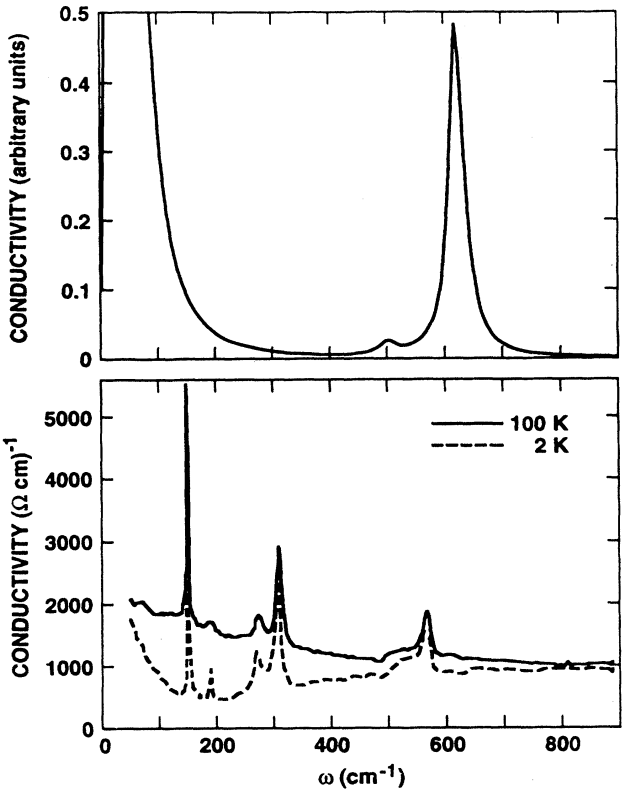

FIG. 1. (a) Calculated IR spectrum using the model of Ref. 1 and (b) imaginary part of the conductivity obtained from IR-absorption measurements (Fig. 4) in Ref. 18. Note the asymmetry (or side lobe) of the "585 cm^{-1}" mode.

frequencies of all observed Raman- and IR-active peaks, *except* the 585 cm^{-1} mode, have been explained by the authors of the Comment by Thomsen and Cardona by assuming a superconducting gap $2\Delta \sim 400$ cm^{-1}.[21,22] Softening of the 585 cm^{-1} mode was postulated as evidence for the existence of a second gap around $\sim 500 - 550$ cm^{-1} (p. 273 of Ref. 22). So far no conclusive evidence for a second gap at those high energies has appeared. Our interpretation is that the different temperature dependence of the Raman (505 cm^{-1}) and IR (585 cm^{-1}) modes reflects the different nature of these modes.[6]

In conclusion, we assert that the evidence for a two-site Cu(1)-O(4) distribution in $YBa_2Cu_3O_7$ and other cuprate superconductors is strong and growing. It is indeed crucial that it be correlated with optical spectroscopy. Available optical data are *not* inconsistent with a two-site distribution, originating in polaron tunneling, but certainly more experiments are called for. Finally, the consequences for coupling to electrons in the CuO_2 planes are tantalizing, but we are not in a position to draw conclusions on the basis of current XAFS data.

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[1] J. Mustre de Leon *et al.*, Phys. Rev. B **45**, 2447 (1992).
[2] J. Mustre de Leon *et al.*, Phys. Rev. Lett. **65**, 1675 (1990); J. Mustre de Leon *et al.*, in *Electronic Structure and Mechanisms of High-Temperature Superconductivity*, edited by J. Ashkenazi *et al.* (Plenum, New York, 1991), p. 425.
[3] J. Mustre de Leon *et al.*, Phys. Rev. B **44**, 2422 (1991).
[4] P.G. Allen *et al.*, Phys. Rev. B **44**, 9480 (1991).
[5] C. Thomsen and M. Cardona, preceding paper, Phys. Rev.

B **47**, 12 320 (1993).
[6]J. Mustre de Leon, I. Batistić, A.R. Bishop, S.D. Conradson, and S.A. Trugman, Phys. Rev. Lett. **68**, 3236 (1992).
[7]A.R. Bishop, R.L. Martin, K.A. Müller, and Z. Tesanović, Z. Phys. B **76**, 17 (1989).
[8]See, e.g., *Proceedings of the Workshop on Lattice Effects on High Temperature Superconductors*, Santa Fe, New Mexico, 1992, edited by Y. Bar-Yam, T. Egami, J. Mustre de Leon, and A. R. Bishop (World Scientific, Singapore, to be published).
[9](a) Y. Yacoby *et al.*, Bull. Am. Phys. Soc. **36**, 989 (1991); (b) E.A. Stern *et al.*, *Lattice Effects in High-T_c Superconductors*, edited by Y. Bar-Yam *et al.* (World Scientific, Singapore, 1992).
[10]J. Röhler, A. Larisch, and R. Schäfer, Physica C **191**, 57 (1992).
[11]A. Bianconi *et al.*, in *Lattice Effects in High-T_c Superconductors*, edited by Y. Bar-Yam *et al.* (World Scientific, Singapore, to be published).
[12]T. Egami *et al.*, Physica C **185-189**, 867 (1991).
[13]R.P. Sharma *et al.*, Phys. Rev. Lett. **62**, 2869 (1989).
[14]Y. Wu, S. Pradhan, and P. Boolchand, Phys. Rev. Lett. **67**, 3184 (1991).
[15]J. Rossat-Mignod *et al.*, Physica C **185-189**, 86 (1991); M. Arai *et al.*, Phys. Rev. Lett. **69**, 359 (1992); H. A. Mook *et al.*, *ibid.* **69**, 2272 (1992).
[16]J.J. Capponi *et al.*, Europhys. Lett. **3**, 301 (1987); W. Schäfer *et al.*, Mater. Res. Bull. **23**, 1439 (1988).
[17]V.I. Anisimov, M. A. Korotin, J. Zaanen, and O.K. Andersen, Phys. Rev. Lett. **68**, 345 (1992).
[18]D. A. Bonn *et al.*, Phys. Rev. B **37**, 1574 (1988).
[19]K. F. McCarty *et al.*, Phys. Rev. B **43**, 13 751 (1991).
[20]H. S. Obhi and E. K. Salje, Physica C **171**, 547 (1990); B. Güttler *et al.*, J. Phys. Condens. Matter **2**, 8977 (1990).
[21]C. Thomsen, M. Cardona, B. Friedl, C.O. Rodriguez, I.I. Mazin, and O.K. Andersen, Solid State Commun. **75**, 2 (1990); B. Friedl, C. Thomsen, and M. Cardona, Phys. Rev. Lett. **65**, 915 (1990).
[22]A.P. Litvinchuk, C. Thomsen, and M. Cardona, Solid State Commun. **80**, 257 (1991).