

Comments

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Comment on "Axial oxygen-centered lattice instabilities in $\text{YBa}_2\text{Cu}_3\text{O}_7$: An application of the analysis of extended x-ray-absorption fine structure in anharmonic systems"

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(Received 6 March 1992; revised manuscript received 20 August 1992)

We argue that the multiparameter-based analysis of the temperature-dependent extended x-ray-absorption fine-structure data in $\text{YBa}_2\text{Cu}_3\text{O}_7$ leads to conclusions about a possible double-well potential of the apical oxygen that are in contradiction with results from Raman and infrared spectroscopy.

In their recent paper Mustre de Leon *et al.*¹ conclude from an analysis of their extended x-ray-absorption fine-structure (EXAFS) data that the apical oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_7$ occupies a split position. The separation of the two potential minima is 0.13 Å and decreases by 0.02 Å inside a narrow fluctuation region $83 \text{ K} \leq T \leq 86 \text{ K}$. The corresponding energy separation of the ground state and first excited state shows a singularity in the fluctuation region, represented by two data points in Ref. 1. Aside from the possible non-uniqueness of a ten-parameter fit to data previously subjected to normalization and Fourier-filtering procedures, there is a discrepancy with results of optical measurements. We would like to point out here that it is impossible to reconcile the interpretation of the EXAFS data in terms of an asymmetric double-well potential for the apical oxygen given in Ref. 1 with Raman and infrared measurements. The model of Ref. 1 requires, except in the narrow region around T_c , a lowest excitation energy for the apical oxygen vibrations along c below 150 cm^{-1} , the next one being 1000 cm^{-1} . These are incompatible with both Raman and ir data.

Mustre de Leon *et al.* point out that as "EXAFS measures the *average* environment around an absorbing atom" their analysis in terms of a single bond [Cu(1)-O(4)] may not be fully realistic. In addition, they state that a symmetric (Raman-active) vibration should not exhibit any anharmonic behavior, while the observation of an anomalous behavior of the antisymmetric (ir-active) mode is consistent with the double-well potential.¹

The vibrations of the apical oxygen belong to the best studied lattice properties of $R\text{Ba}_2\text{Cu}_3\text{O}_7$ (R = rare earth). Both Raman^{2,3} and ir^{4,5} phonon frequencies show modest changes at T_c in frequency ($\sim 1\%$) and in linewidth ($\sim 10\text{--}30\%$). We show in Fig. 1 the parameters of the 565 cm^{-1} ir-active vibration of the apical oxygen.⁶ The atomic displacement is in the z direction in this mode; the softening amounts to 0.5%, the

linewidth broadening to 20% in the case of $R = \text{Er}$ with similar values for $R = \text{Tm}$. The increase in the oscillator strength is about 30% for $R = \text{Er}$ between 100 and 10 K.⁷ Raman measurements of the symmetric vibration have frequency variations² of 2% ($R = \text{Tm}$), linewidth variations³ of 15% ($R = \text{Tm}$), and an anomalous intensity increase⁸ below T_c of 25% ($R = \text{Y}$). The absolute electron-phonon coupling constants of these modes have been determined experimentally and theoretically⁹

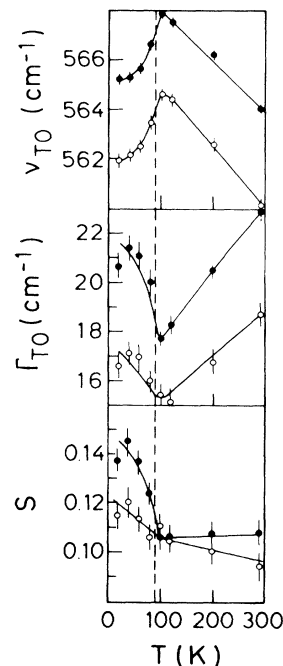


FIG. 1. Temperature dependence of the frequency, linewidth, and oscillator strength of the ir-active vibration of apical oxygen in $R\text{Ba}_2\text{Cu}_3\text{O}_7$. Note the steplike discontinuities near T_c .

and lie around 0.01 (in terms of contributions to λ); they are hence in the weak-coupling regime. Furthermore, the coupling constants of the x - and y -direction Raman-active vibrations were found to be zero to within experimental error ($\Delta\lambda = \pm 0.02$ for the x direction, $\Delta\lambda = \pm 0.003$ for the y direction).¹⁰

The changes in the parameters of the Raman-active phonons at T_c have been understood in some detail and originate from resonant electron-phonon interaction effects in the superconducting state. The explanation of the effects for the ir-active phonons involves more difficult processes due to the complicated nature of the transverse charge (see, for instance, Ref. 11). In all cases of phonon anomalies reported to date, the general observation is a steplike change of the phonon energy in the percent range at T_c and a somewhat larger change in their width. In contrast, the energy parameter determined from the EXAFS data almost doubles in a narrow, singularitylike interval at T_c . (See points at 83, 86, and 88 K in Fig. 9 of Ref. 1 obtained for two different models of the double well. Unfortunately the next points to lower T 's are at 9 and 10 K. More measurements between 10 and 83 K are thus highly desirable.) From this qualitative difference a relation between the two sets of data appears unlikely. Similarly, the c parameter determined by x-ray diffraction¹² and the thermal expansivity of the c axis¹³ in $\text{YBa}_2\text{Cu}_3\text{O}_7$ do not have a discontinuity across T_c , but rather a change in slope. The possible anomalous region in the x-ray experiment is ~ 40 K wide, one order of magnitude larger than suggested in Ref. 1, and again qualitatively incompatible with the interpretation

of Mustre de Leon *et al.*

Furthermore, if the ir-active mode at 565 cm^{-1} breaks the symmetry due to the supposed asymmetric double-well potential, it should become Raman active; similarly, the Raman-active mode should become ir active. Neither of these two predictions have been observed experimentally. It should be noted that the classification of being exclusively Raman or ir active is based on the existence of inversion symmetry for the primitive cell of a crystal. A symmetry breaking for the asymmetric double-well potential as Mustre de Leon *et al.* conclude from their data has as a consequence, without further assumptions, the breakdown of the optical selection rules.

We conclude from the optical data that there is no evidence for the asymmetric double-well potential derived from the EXAFS data.¹ The variations in the energy levels in the double well have singular character near T_c and are one to two orders of magnitude larger than energy changes in Raman- and infrared-active phonons, which have small steplike changes at T_c . Moreover, the asymmetric nature of the double-well potential should lift the Raman and ir selection rules, in clear contrast to the spectroscopical results. A possible reason for the apparent discrepancy of the double-well potential of Ref. 1 may lie in the analysis of the authors; Röhler, Larisch, Schäfer,¹⁴ e.g., starting from unoriented powder EXAFS data, conclude that there is *no* evidence for such large anharmonicities or a double-well potential from EXAFS data (one may argue, however, that the data of Ref. 1 are more precise since they are taken on c -axis-aligned powder samples and polarized x rays).

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