# Identification of the 1250-cm$^{-1}$ Raman feature in $YBa_2Cu_3O_6$

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We have resolved the controversy over the origin of a feature in the Raman spectra of semiconducting $YBa_2Cu_3O_6$ near 1250 cm$^{-1}$. We find that, upon isotopic replacement of oxygen $^{16}O$ by $^{18}O$, the feature softens by about 5%, thus identifying it as of phononic origin.

The high-energy Raman spectra of semiconducting $YBa_2Cu_3O_6$ have been of interest mainly in connection with light scattering by magnons. Lyons *et al.*[1] first identified a broad peak (linewidth $\Gamma \approx 1300$ cm$^{-1}$) centered at 2600 cm$^{-1}$ and having predominantly $B_{1g}$ symmetry as originating from the two-magnon density of states. Similar results were found in other semiconducting modifications of the high-$T_c$ superconductors, such as $La_2CuO_4$,[2,3] $Nd_2CuO_4$,[4] and $TlYBa_2Cu_2O_7$.[5] These observations, confirmed and complemented by neutron scattering[6] have stimulated the discussion about the possible coexistence of magnetism and superconductivity and about magnetic interactions as a possible mechanism for the pairing of charge carriers in the superconducting state.

*Two-magnon* Raman scattering in antiferromagnets is typically much stronger than *one-magnon* scattering. This is because the mechanism involved is not the direct magnetic interaction of the photon with the spin but rather two subsequent spin flips; in the case of the two-dimensional planes of the high-$T_c$ superconductors the process may be described by a three-step process: an electric-dipole transition of Cu $d$, an interaction via oxygen (superexchange) to a neighboring copper, and a second electric-dipole transition emitting a photon. This explains the relative strength of the two-magnon scattering process. Because the wave vectors of two particles can add up to zero throughout the Brillouin zone, the resulting peak in the Raman spectra reflects the density of states of magnons, which peaks at the zone boundary and thus occurs at relatively large Raman shifts. In addition, magnon-magnon interactions broaden the pure density-of-states contribution to a peak centered at a frequency lower than twice the zone-boundary frequency.[7]

While the identification of the two-magnon peak in $YBa_2Cu_3O_6$ is generally accepted, there are some features above the one-phonon region (i.e., $\omega \geq 700$ cm$^{-1}$) which have not been uniquely interpreted. Most authors report a feature near 1200 cm$^{-1}$ (near 1500 cm$^{-1}$ in $La_2CuO_4$), which is attributed either to a *one-magnon*[1,5,8] or a *two-phonon*[3,4,8] process. In the former interpretation it would have to be a zone-boundary magnon next to a vacancy or defect causing the scattering. Alternatively, a zone folding may be possible through a magnetic superlattice, but there is no independent evidence that this exists. Either process, however, appears unlikely in view of the fact that the two-magnon scattering peak extends to frequencies far beyond twice 1250 cm$^{-1}$.

The two-phonon interpretation of the 1250 cm$^{-1}$ peak, on the other hand, is supported by the fact that the experimentally observed feature is broad and density of states like and occurs at roughly twice the high end of the one-phonon spectrum. In fact, in $La_2CuO_4$ it has been claimed[9] that the entire one-phonon spectrum is repeated at higher frequencies in two-phonon form. In order to decide which of the interpretations is correct for $YBa_2Cu_3O_6$, we have performed an isotope-shift experiment.

Since the electronic properties of various isotopes do not differ, the force constants of the vibrations involving isotopically replaced atoms are the same. The difference in frequency of vibration for two isotopes is thus solely determined by their atomic mass. In particular in the high-$T_c$ superconductors, Raman scattering has been employed to verify the isotopic replacement of oxygen when determining the isotopic dependence of the transition temperature $T_c$.[10,11] (For a small, possible influence of the isotopic mass on electronic band structure, see, e.g., the comment of Ref. 12. It may for the present purpose be neglected.) The isotopic replacement of copper has resolved the controversy in the literature over the assignment of the eigenfrequency in the Raman spectra.[13]

The experiment reported here was performed with the 530.9-nm line of a krypton-ion laser as an exciting source, a Dilor-XY triple monochromator in subtractive mode and a Photometrics charge-coupled device (CCD) camera cooled to $-110\,^{\circ}$C as detector. The laser power was 20 mW, focused to a point of $\sim$40-$\mu$m diameter and the spectra were analyzed by appropriate binning of the CCD detector. A special computer program was utilized to suppress the spikes typical of a CCD. The resolution of

 

the monochromator was 7 $cm^{-1}$ at 100 $cm^{-1}$ and varied by ~10% throughout the spectral range studied. The spectra shown in this study have not been corrected for spectral sensitivity of the system, since it is not relevant to the point discussed here. Accumulation times for the enlarged spectra in Fig. 1 were 40 min. The complete spectrum was obtained by splicing together eight individual ones, each having accumulated for 200 sec. Samples were held in vacuum at room temperature.

The ceramic samples used in this study were obtained from regular pellets by the exchange of $^{16}O$ in several steps, which were monitored thermogravimetrically.[11] First, an $^{16}O$ unit was removed from the pellet by heating the sample at 650 °C in vacuum. Then, after replacing vacuum by an $^{18}O_2$ atmosphere at a pressure of 0.2 bar the pellet was annealed at 480 °C for 40 h. This treatment led to a substitution of 55% $^{16}O$ by $^{18}O$. Finally, 90% of the initial $^{16}O$ was exchanged after removing about one oxygen unit by heating at 700 °C in vacuum and subsequent annealing of the sample at 550 °C in an $^{18}O_2$ atmosphere at 0.2 bar for 26 h.

In Fig. 1 we show the Raman shifts in a spectral range of 100 – 1500 $cm^{-1}$. The oxygen content of the sample shown has been determined by thermogravimetry to be 6.2. Similar spectra have been obtained for an oxygen content of 6.0. In the low-energy region we find the usual phonon peaks of $YBa_2Cu_3O_{6.2}$ at 140 (Cu), 339 (O II,III), 450 (O II,III), and 477 $cm^{-1}$(O VI). The barium vibration is not seen in this spectrum; it is normally found near or somewhat below 100 $cm^{-1}$ in semiconducting $O_6$ material. The shift in the 339-$cm^{-1}$ mode in the oxygen replaced sample to 319 $cm^{-1}$ (6.1%) confirms the nearly complete replacement of $^{16}O \rightarrow {}^{18}O$ in the $CuO_2$ planes.

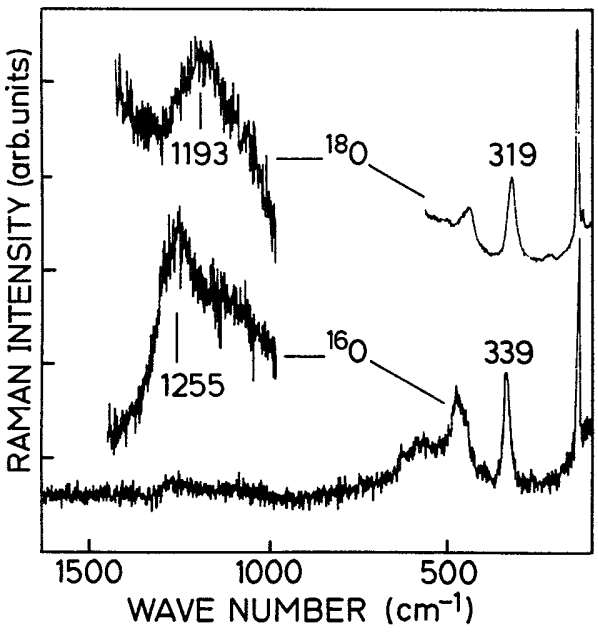


FIG. 1. Raman spectra of $YBa_2Cu_3O_{6.2}$ for two different oxygen isotopes. The feature at 1250 $cm^{-1}$ is identified as of phononic origin through the dependence of its frequency on the isotopic mass.

The band at 1250 $cm^{-1}$ is the feature under discussion here. We have determined its depolarization ratio, i.e., the ratio of scattered light perpendicular and parallel to the incident light, to be 30 ± 5%. The inset, spectra taken separately from the large scan, shows the dependence of the peak on isotopic mass of the oxygen. While for $^{16}O$ the maximum of the Raman feature is at 1255 ± 5 $cm^{-1}$, it is seen to shift down to 1193 ± 5 $cm^{-1}$ for the $^{18}O$ sample. The difference in frequencies upon replacement is thus $\Delta\omega = 62 \pm 10$ $cm^{-1}$, i.e., $\Delta\omega/\omega = 5.1 \pm 0.8\%$. *The dependence on isotopic mass thus identifies the origin of the Raman feature at 1250 $cm^{-1}$ in $YBa_2Cu_3O_6$ as a vibrational process.*

In order to understand the detailed origin of this feature, one is led to look at second-order phonon processes. The large shift $\Delta\omega/\omega = 5\%$ is only consistent with oxygen being the predominantly vibrating atom with some admixture from heavier atoms. This admixture is expressed in a reduction of the isotopic shift from its ideal value of 6.1%. At the zone center, this admixture is required for ir-active (odd-parity) modes to keep fixed the center of mass of the unit cell during a vibration. Lattice-dynamical calculations correspondingly predict shifts of 4.0% to 5.9% for oxygen-related vibrations in $YBa_2Cu_3O_7$ (see Table III of Ref. 11). At the $X$ point, on the other hand, the center of mass is conserved automatically even without admixture of heavier atoms. (There should, however, be some admixture at the $R$-point, i.e., the edge of the Brillouin zone along the [110] direction, and at other points at the edge of the Brillouin zone.) The expected shift from $X$-point phonon contributions to the feature at 1250 $cm^{-1}$ should, just like for the even-parity Raman-active phonons, be the full 6.1%. In view of the somewhat lower shift determined from Fig. 1 we conjecture that the $X$-point and Raman-active phonons are secondary contributors to the 1250 $cm^{-1}$ peak. The highest observed Raman mode[14] of $A_{1g}$ symmetry is at ~480 $cm^{-1}$; a corresponding overtone process at the zone center does not even have high enough frequency. Infrared-active, zone-center modes in $YBa_2Cu_3O_6$, on the other hand, have been observed[15] at ~650 $cm^{-1}$ and, through a large density of phonon states or Fröhlich interaction coupling,[16] may contribute to the feature under discussion here. Also, one should consider the Raman-active modes, which are usually not seen in the first-order spectra ($E_g$ symmetry in the $D_{4h}$ point group); they may contribute to second-order processes although the corresponding density of states is expected to be small. Recently, those modes were claimed to have been observed in $YBa_2Cu_3O_7$ at frequencies of up to 526 and 555 $cm^{-1}$ (zone center), too low to account for the observed two-phonon peak.[17] Finally, the second-order phonon scattering should have a contribution proportional to the two-phonon density of states (TPDOS), to which zone-edge critical points should con-

tribute most. In neutron-scattering spectra taken on ceramic material[18] such a (weighted) TPDOS is provided, and the first-order phonon spectra in $YBa_2Cu_3O_6$ have a peak at 640 $cm^{-1}$ in good agreement with the values found here for the single phonons, which contribute to the observed two-phonon Raman spectrum under the assumption of overtone scattering. A confirmation of the existence of such high-frequency vibrational modes is found in the calculated TPDOS, see, e.g., Refs. 18 and 19. We note that there is a change in line shape of the feature discussed, which deserves further investigations.

Without reliable information about the phonon dispersion curves it is not possible to decide precisely which branch point or regions contribute most to the peak at 1250 $cm^{-1}$ in the Raman spectra. From the isotopic shift of the peak, however, we have identified its phononic origin and shown that it is most likely a two-phonon density-of-states scattering of oxygen atoms. Certainly, a direct connection to magnons may be ruled out on the basis of the results presented here.

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