



# Absence of Anomalous Copper Vibrations in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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## Absence of anomalous copper vibrations in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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We find a normal temperature dependence for the Doppler broadening of the 230-eV resonance in the neutron cross section of  $^{65}\text{Cu}$  atoms in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  between 10 and 300 K. No abrupt changes in the copper momentum spectrum corresponding to vibrations in the  $ab$  plane were observed in either the superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_7$  or nonsuperconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$  compounds. This result differs from ion-channeling experiments in which sharp changes in the channeling minimum yield and width of the rocking curve indicated irregular vibrational behavior near the superconducting critical temperature.

Anomalous phonon behavior has been reported in a variety of high- $T_c$  superconductors. Several investigations including numerous Raman spectroscopy<sup>1-4</sup> and inelastic neutron scattering<sup>5-7</sup> studies indicate softening or hardening of phonons when passing from the normal to the superconducting state.<sup>8,9</sup> Two methods in particular have revealed anomalous vibration behavior associated with copper atoms: ion channeling<sup>10-12</sup> and neutron resonance absorption spectroscopy (NRAS).<sup>13</sup> Using ion channeling<sup>10,11</sup> on  $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_7$  ( $R = \text{Y, Er}$ ), two groups found large changes associated with the motions of copper atoms in the  $ab$  plane near the critical temperature  $T_c$ . However, there is a striking disagreement between these two channeling results. One of the groups concentrates on the temperature dependence of the width of a rocking curve,  $\psi_{1/2}$ , and the other group measured the minimum yield,  $\chi_{\min}$ . Qualitatively, a decrease in a vibration amplitude should result in a decrease in the channeling  $\chi_{\min}$  and an increase in  $\psi_{1/2}$ . Surprisingly, the experiments of Refs. 10 and 11 showed that both  $\chi_{\min}$  and  $\psi_{1/2}$  increase as the temperature is lowered through  $T_c$ . In addition, for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  ( $\text{Bi}2212$ ) NRAS measurements,<sup>13</sup> a dramatic decrease which begins approximately  $20^\circ$  above  $T_c$  was observed for the average kinetic energy of copper in the  $ab$  plane. This was interpreted as softening of the copper phonons. Since the mechanism of high-temperature superconductivity is not understood, any irregularities which occur in the vicinity of the phase transition, especially those associated with vibrations in the superconducting Cu-O planes, clearly deserve further study.

In this paper, we present NRAS measurements of the average kinetic energy of copper in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) as a function of temperature from 10 to 300 K. NRAS is especially useful, because using this technique one can determine the average motion due to all phonons associated with a particular atom. Other techniques like Raman spectroscopy

and inelastic neutron scattering usually probe only a few selected phonons. Raman spectroscopy, for instance, is generally used to study  $q=0$  phonons, leaving out potentially important phonons with  $q>0$ , throughout the Brillouin zone. These  $q>0$  phonons can in principle be studied by inelastic neutron scattering, but for YBCO, a large number of low-energy modes overlap, making them difficult to separate and only the high symmetry directions have been investigated. Some of the high-frequency modes involving primarily the motion of oxygen atoms have been investigated, because they are isolated from the others and a few were reported to exhibit irregular behavior.<sup>5,7</sup>

In NRAS the average kinetic energy of atoms in the high-temperature superconductors is measured by extracting the Doppler broadening component of the width of a resonance in the neutron cross section. For this work, the naturally occurring  $^{65}\text{Cu}$  isotope has a neutron resonance in the center of mass reference frame at 230 eV which is suitable for precision Doppler broadening determination. The ‘‘Doppler width’’

$$\delta = 2 \left[ \frac{m E_n k_B T}{m + M} \right]^{1/2} \equiv 2 [R k_B T]^{1/2} \quad (1)$$

for an atom in a gas was first calculated by Bethe and Plazcek<sup>14</sup> where  $m$  and  $E_n$  are the mass and energy of a neutron, respectively,  $M$  is the mass of the atom,  $k_B$  is Boltzmann's constant, and  $T$  is the sample temperature. However this calculation is not valid for an atom in a lattice, because the average energy is not proportional to  $k_B T$  as it is for a classical ideal gas. At low temperatures, the average energy for an atom in a solid is dominated by zero point motion. Lamb showed<sup>15</sup> that after neglecting multiphonon effects the average energy has the form

$$\langle E_i \rangle = \int d\omega \hbar \omega g^i(\omega) [n^i(\omega) + \frac{1}{2}], \quad (2)$$

where  $\omega$  is the phonon frequency,  $g^i(\omega)$  is the phonon density of states, and  $n^i(\omega)$  is the Bose-Einstein distribution function for atom of type  $i$ . Taking into account the differing contributions from identical atoms on inequivalent sites gives

$$\langle E_i \rangle = \frac{\sum_{j=1}^N \alpha_j \int d\omega \hbar \omega g_j^i(\omega) [n_j^i(\omega) + \frac{1}{2}]}{\sum_{j=1}^N \alpha_j}, \quad (3)$$

where  $j$  is the number of inequivalent sites for atom  $i$ ,  $\alpha_j$  represents site occupancy, and the subscript on  $g_j^i(\omega)$  and  $n_j^i(\omega)$  indicates that there is now a difference between identical atoms on inequivalent sites. Furthermore, for a complex material like YBCO,  $\langle E \rangle$  is anisotropic, because contributions to the Doppler-broadened width come only from motion in the neutron direction.  $\langle E_i \rangle$  will be referred to as  $\langle E \rangle$  of copper for the rest of this paper. Because of the quantum behavior of phonons in a solid,  $\langle E \rangle$  is greater than  $k_B T$  when  $T$  is less than the Debye temperature for the solid. Thus, in Eq. (1),  $\langle E \rangle$  replaces  $k_B T$  so that the effective width is now equal to

$$\delta_{\text{eff}} = 2[R\langle E \rangle]^{1/2}. \quad (4)$$

The measured width of the resonance is still strongly dependent on temperature. But more importantly,  $\langle E \rangle$  depends on the phonon spectrum of the material through  $g(\omega)$ . Therefore, any abrupt variations in the resonance width indicate changes in phonon frequency for the atom being studied.

Our neutron transmission measurements<sup>16</sup> were performed at the Oak Ridge Electron Linear Accelerator (ORELA), a pulsed neutron source. Neutrons were detected by a <sup>6</sup>Li glass scintillator optically connected to a fast timing photomultiplier tube at the end of the 18.5 m beam line, allowing energy determination by time of flight. The neutron burst repetition rate was under 1000/s in order to avoid significant overlap of the low- and high-energy neutrons produced from successive bursts. A boron filter was placed in the beam line to remove low-energy neutrons below 1 eV. Data were collected for a neutron energy range from 100 eV to 70 keV which included resonances for Y, Ba, and Cu. For a collection time of 2–3 days, more than 30 000 neutrons are counted per 16 ns ( $\sim 80$  meV) channel on either side of the <sup>65</sup>Cu, 230 eV neutron resonance. The background from all sources was small enough,  $< 1\%$  of the total counts, to be neglected for this experiment.

Our YBCO sample was prepared at General Electric by Tkaczyk and Lay.<sup>17</sup> The sample is large (40 g) and consists of oriented microcrystallites. The  $c$  axis of the microcrystallites lies perpendicular to the neutron beam direction, allowing determination of  $\langle E \rangle$  for copper in the  $ab$  plane. Neutron rocking curves for this sample have a mosaic spread of less than  $5^\circ$  in the  $c$  direction. The small deviation in the relative orientation of the microcrystallites has little effect on the  $\langle E \rangle$  determination in the  $ab$  plane, because the projection of

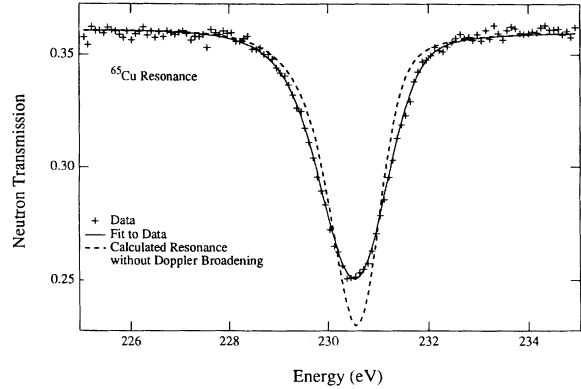


FIG. 1. Example of the 230 eV resonance in the neutron transmission spectrum from 225 to 235 eV. The line is the actual fit to the data which is used to determine  $\langle E \rangle$  of copper. The dashed line shows the calculated resonance without Doppler broadening.

the vibrational amplitude in the direction of the neutron beam varies little over a few degrees.

The fully oxygenated YBCO<sub>7- $\delta$</sub>  ( $\delta \sim 0$ ) sample was tested first. Neutron transmission spectra were collected for sample temperatures ranging from 300 to 10 K. The sample was cooled by a closed cycle, helium refrigerator and was allowed to equilibrate to the predetermined temperature for at least 6 h.

The transmission spectra from 225 to 235 eV were analyzed using SAMMY,<sup>18</sup> a data analysis program utilizing Bayesian methods to determine the best theoretical fits to the data. Given the known resonance parameters, SAMMY calculates the theoretical cross section using  $R$ -matrix formalism.<sup>19</sup> In order to determine the temperature broadening of the resonance, the instrument-broadened cross section is convoluted with a temperature-dependent Gaussian function to obtain the Doppler-broadened cross section. From the width  $\delta_{\text{eff}}$  of the Gaussian which gives the best fit to the data, we can extract the average kinetic energy  $\langle E \rangle$ , see Eq. (4). The sum of the intrinsic linewidth and instrument broadening of the resonance is of the same order as the Doppler broadening term,  $\sim 0.5$  eV. We also compared our results for  $\langle E \rangle$  with those obtained using a nonlinear least-squared fitting routine<sup>20</sup> and found close agreement.

An example of a calculated fit to the 230 eV resonance is shown in Fig. 1. Figure 2(a) shows the extracted  $\langle E \rangle$  for the <sup>65</sup>Cu atoms versus sample temperature.  $\langle E \rangle$  increases with temperature as anticipated although it seems to saturate to its zero point value at an unexpectedly high temperature. There is no indication of any abrupt changes in  $\langle E \rangle$ , which implies that the temperature dependence of the thermal vibrations increases smoothly.

The sample was then deoxygenated to determine whether there was a change in the Doppler broadening which could be attributed to the phase transition in the superconducting compound. The oxygen was removed by heating the sample up to 700 K and cooling it in an oxygen environment with a pressure of approximately 200 mTorr. The resulting stoichiometry was YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.2</sub> as determined by gravimetric analysis. Meissner susceptibility measurements confirmed that the sample was not superconducting above 25 K. The resulting values for the average kinetic energy versus tem-

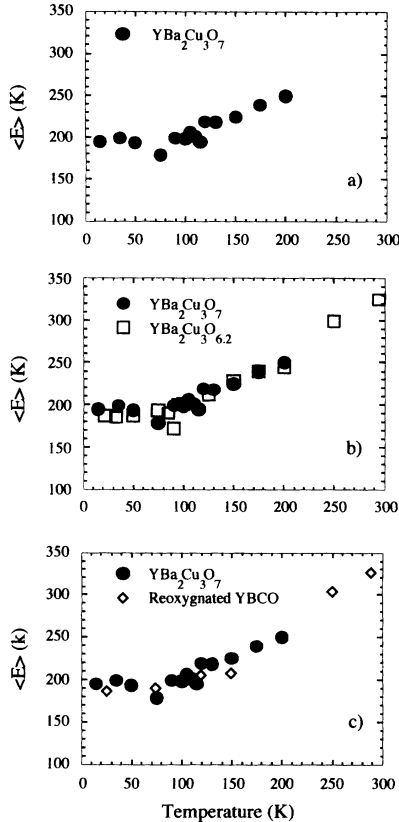


FIG. 2. Average kinetic energy vs temperature of copper in the  $ab$  plane for (a)  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , (b)  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$ , and (c)  $\text{YBa}_2\text{Cu}_3\text{O}_7$  before and after deoxygenation. Uncertainties are indicated by the size of the data points.

perature for the nonsuperconducting compound are shown in Fig. 2(b). Notice that within experimental error there is no difference in the Doppler broadening between the superconducting and nonsuperconducting compounds.

We might have anticipated a very small change in the  $\langle E \rangle$  of copper simply because of the oxygen removal, but we expect that it should be insignificant especially for copper in the Cu-O planes. Most of the oxygen is removed from the O(1) site located in the chains and a small amount from the O(4) site between the chains and the planes.<sup>21</sup> The O(4) site will have little effect on  $ab$  plane vibrations. O(1) removal will affect Cu(1) vibrations, but our NRAS results, which show that there is no difference between the two compounds, indicate that the change is minimal.

The sample was then reoxygenated to take transmission spectra with better statistics at a few select temperatures. Magnetic susceptibility measurements on the reoxygenated YBCO showed an abrupt superconducting transition above 90 K with a narrow width of  $\sim 1$  K. The results of the new  $\langle E \rangle$  determination are overlaid with the original measurements in Fig. 2(c).

These NRAS results for copper motion within the  $ab$  plane of YBCO are quite different from those determined for copper in Bi2212 (Ref. 13) by Mook *et al.* For vibrations along the  $c$  axis of the Bi2212 sample, they found that the temperature dependence of  $\langle E \rangle$  is similar to that of YBCO. However, for copper vibrations in the  $ab$  plane,  $\langle E \rangle$  dramati-

cally decreases when cooling through 100 K. Eventually,  $\langle E \rangle$  levels off below  $T_c$  to its zero point limiting value. The unusual behavior of  $\langle E \rangle$  in the vicinity of  $T_c$  indicates softening of the copper phonon modes in Bi2212. Such a large softening in copper vibrations within the  $ab$  plane was not seen for YBCO.

Unlike the Bi2212 compound, there are two inequivalent sites for copper in YBCO. These two sites, Cu(1), in chain, and Cu(2), in plane, atoms have different Doppler broadening contributions to the width of the neutron resonance; see Eq. (3). However, there is no indication that the softening of  $\langle E \rangle$  seen for the Bi2212 compound ( $\langle E \rangle$  decreasing  $\sim 25$  K between 100 and 80 K) is present for YBCO. Over the same temperature range,  $\langle E \rangle$  drops less than 15 K in YBCO. This is approximately the size of the expected normal decrease due to a change in phonon occupation. Since we cannot distinguish between the two copper sites, it is possible that the Cu(1) atoms behave normally in YBCO, while those on the Cu(2) positions contribute to the type of anomalous behavior measured using NRAS on Bi2212. If this was the case, we would have anticipated an averaged drop in  $\langle E \rangle$  of approximately 20 K, weighting the  $\langle E \rangle$  of the two coppers in the plane with the normal  $\langle E \rangle$  of the one in the chain. No decrease of this size was seen either. With our limits set by statistical uncertainty, we place an upper bound for a superconductivity dependent change of  $\langle E \rangle$  of 15 K if both copper sites contribute and 20 K ( $\sim 2$  meV) if only the Cu(2) atoms do.

The normal temperature dependence of the  $\langle E \rangle$  for copper in the  $ab$  plane of YBCO does not support the results by Sharma *et al.* and Haga *et al.* Naively, any abrupt changes in the amplitude of atomic vibrations should be observable as changes in the average kinetic energy. This is because  $\langle E \rangle$  measured by NRAS and the ion-channeling vibrational amplitude,  $[\langle u^2 \rangle]^{1/2}$ , are related by the density of states,  $g(\omega)$ . A more careful analysis of the two experimental techniques reveals that the frequency dependence of  $\langle E \rangle$  and  $[\langle u^2 \rangle]^{1/2}$  may make one of the techniques more sensitive to anomalous vibrations than the other.  $\langle E \rangle$  is dominated by high-frequency phonons, because these phonon energies are weighted by  $\omega$  in the frequency integral. This emphasis on large  $\omega$  phonons is quite different from the ion-channeling measurements in which the weighting factor in the  $[\langle u^2 \rangle]^{1/2}$  integral makes the low-frequency acoustic phonons the main contributors to the average displacement of the atom:

$$\begin{aligned} [\langle u_1^2 \rangle]^{1/2} &= [\langle 2E/m\omega^2 \rangle]^{1/2} \\ &= \left( \int d\omega \frac{2\hbar}{m\omega} g(\omega) \left\{ n(\omega) + \frac{1}{2} \right\} \right)^{1/2}. \end{aligned} \quad (5)$$

Therefore, it is possible that the size of an anomalous change in the average energy would be much smaller than those suggested by ion channeling.

However, a very recent ion-channeling measurement of YBCO thin films grown on MgO substrates has been reported<sup>22</sup> for which no anomalous behavior was observed. In this experiment,  $\chi_{\min}$  and  $\psi_{1/2}$  for all elements in the film were measured in a 30 K temperature range around  $T_c$ . Both parameters were shown to change smoothly with temperature

indicating that there are no abrupt variations in vibrations of all the elements in the film. These ion-channeling results strongly support our conclusions that the  $\langle E \rangle$  of copper in YBCO does not behave anomalously especially near  $T_c$ . In addition the temperature dependence of the atomic mean square displacements in YBCO using neutron diffraction, which is also sensitive to the low-frequency phonons, was studied by Schweiss *et al.*<sup>23</sup> Their calculations and data can be accurately fitted using a harmonic model of the lattice implying that no anomalous hardening or softening of the phonon spectrum occurs.

In conclusion, we have measured  $\langle E \rangle$  of copper in YBCO from 10 to 300 K using NRAS. We limit any anomaly in the average kinetic energy of copper in YBCO to less than 20 K if only Cu(2)—in plane—contribute and below 15 K if both

in-plane and in-chain coppers atoms behave irregularly. Moreover, there is little difference in the temperature dependence of the copper average kinetic energy between the superconducting and nonsuperconducting YBCO. Finally, the large softening of copper phonons seen in Bi2212 does not appear to the same degree in YBCO. This suggests that the anomalous behavior in Bi2212 associated with the onset of the phase transition is not essential for superconductivity.

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