Anomaly of Phonon State of Superconducting $YBa_2Cu_3O_7$ Studied by Inelastic Neutron Scattering

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Inelastic neutron scattering measurements over a wide Q-E range have been performed on superconducting $YBa_2Cu_3O_7$. Fine structure in its phonon density of states as well as the Q dependence of excitations was revealed by means of a high-energy-resolution chopper spectrometer at a pulsed neutron source. The temperature dependence showed an anomalous behavior at T_c similar to critical phenomena, which could be due to a local distortion and an expansion of the dynamical correlation length. The distortion is associated with a $\langle 110 \rangle$ buckling structure, which is commonly observed in the orthorhombic phase of $La_{2-x}Ba_xCuO_4$ and in $Tl_2Ba_2CaCu_2O_8$ in the superconducting state.

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In the early stage of the study of the high-T_c oxide superconductors, an exotic magnetic interaction was introduced as a mechanism for the superconductivity [1]. However, a huge accumulation of experimental and theoretical work on the high-T_c superconductors has shown the importance of the electron-phonon interaction, as for BCS superconductors. In particular optical spectroscopy [2], Raman scattering and infrared reflection, and neutron scattering measurements [3,4] have revealed a strong relation between phonon states and superconductivity. As we reported in a preceding paper on $La_{2-x}Sr_xCuO_4$ (2:1:4) [4], phonon states are correlated with electron states. Raising the temperature above T_c and suppressing superconductivity by substitution of Cu^{2+} with Zn^{2+} have the same effect on the phonon states. In the superconducting state the intensity of a specific oxygen phonon mode seems to be increased. Therefore, since we are motivated to find common phenomena on phonon states among high-T_c oxide superconductors, we performed high-energy-resolution neutron scattering measurements on superconducting $YBa_2Cu_3O_7$ ($T_c \sim 93$ K).

In the case of $YBa_2Cu_3O_7$, the effect of substitution on phonon states cannot be studied directly, because the substituting atoms enter the chain site first. This is why a considerable amount of substitution is needed to suppress superconductivity, in contrast to the 2:1:4 compound, causing a structural deformation [5]. Thus the obvious way to observe an intrinsic change in phonon states related to the superconducting state, without artificial structural deformation, is by changing the temperature across T_c.

Arai *et al.* [6] demonstrated that an analysis of the Q dependence of $S(Q,E)$ provides detailed information on the local or short-range structure of a network glass, and they found that the Q dependence is very sensitive to a change in the local structural environment. This method is also applicable to crystalline materials as we will show in the following section. In contrast, the conventional diffraction technique accumulates the intensity integrated along a certain locus in Q-E space defined by the geometry of the instrument, and measurements of PDOS give the average of $S(Q,E)$ through Q space. So both techniques are essentially insensitive to local structural or local dynamical evolution.

The ceramic sample of $YBa_2Cu_3O_7$ (1:2:3-O_7) was synthesized by the usual solid state reaction. For the present neutron scattering measurement special attention was paid to sample preparation: Hydrogenous impurities were carefully excluded. The onset temperature $T_c = 93$ K was confirmed by bulk magnetization measurement. Therefore the sample is fully oxidized and the chemical formula is very close to $Y_1Ba_2Cu_3O_7$.

Neutron inelastic scattering measurements were carried out on the chopper spectrometer MARI [7] installed at the ISIS facility of Rutherford Appleton Laboratory. The spectrometer covers the wide scattering angle from 3° to 135° with 550 detectors. The employable incident energy is from 20 meV to 1 eV with an energy resolution of 1.2% of the incident energy. The measurement was done by the time-of-flight method.

The disk-shaped sample, 8 cm in diameter and 8 mm in thickness, was mounted on the cold head of a helium closed-cycle refrigerator. The neutron beam size is 5×5 cm^2 as defined by the collimation system. The unexposed area on the sample was covered by a Cd shielding plate to define the scattering volume precisely. This amount of sample gives a considerable intensity for multiple scattering. Therefore the multiple scattering was corrected for by the Monte Carlo simulation program MSCAT [8]. Also multiphonon scattering was corrected for by an analytical method [9]. We employed two different incident energies of 130 and 200 meV. The measured temperatures were 45, 50, 83, 100, and 103 K for $E_i = 130$ meV and 53, 83, 93, 103, and 113 K for $E_i = 200$ meV.

After subtraction of multiple scattering and multiphonon scattering, single-phonon vibrational densities of states (PDOS) were calculated by keeping the total area of $G(E)$ equal to 1.0. Figure 1 shows $G(E)$ for $E_i = 130$ meV observed at 50 K (circles) and 100 K (line). There

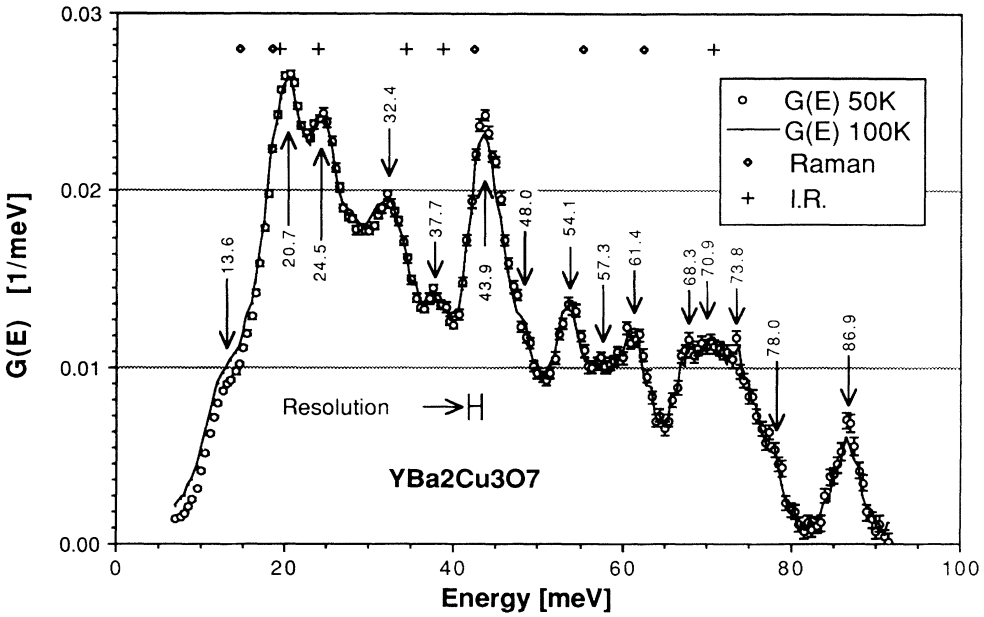

FIG. 1. Generalized phonon density of states (PDOS) at 50 and 100 K for $E_i = 130$ meV.

is considerably more detail than in the results published previously by Renker *et al.* [3]. At the top in Fig. 1 the observed peak positions from Raman [5] and infrared [10] spectroscopy are also plotted. Overall we could recognize every peak observed by optical spectroscopy. Furthermore there are many additional peaks. In Fig. 1 the possible peak positions are marked with arrows. The prominent peak at 87 meV was newly observed in the present work. An experiment from a single crystal [11] did not observe dispersion for this energy mode. Thus we may expect that the mode at 87 meV is an incoherent mode, i.e., a localized mode or short-range mode. We found weak peaks around 120 meV, but the statistical precision is not sufficient enough to allow discussion of the details at this moment. Further experiments should elucidate this point.

As shown in Fig. 1, the intensity of $G(E)$ shows prominent increases at 44 and 87 meV below T_c, which are assigned to the modes related to the out-of-plane displacement of planar oxygen O(2) and O(3) and the stretching motion in the plane. This phenomenon in $G(E)$ is very similar to the results on the 2:1:4 compound [4], for which the assignment was a sharpening of a phonon mode. In the previous paper, we did not apply the multiphonon correction. We have confirmed that after the multiphonon correction the sharpening turns into an intensity increase. Therefore we recognize that the increase in $G(E)$ below T_c may be a common feature in the phonon states of 1:2:3 and 2:1:4 compounds. In Fig. 2 the integrated intensity, from 40 to 50 meV, of the peak at 44 meV is plotted for $E_i = 130$ and 200 meV by normalizing to the intensity at 100 K. The intensities for the two incident energies, for which multiple scattering and multiphonon scattering contribute quite differently, agree with each other very reasonably. Therefore we believe that these corrections have been done properly and the increase in $G(E)$ below T_c is an intrinsic property of this material. The intensity starts to increase at T_c and then grows steadily below T_c. The intensity at 87 meV has a similar temperature dependence.

The peak at 44 meV was fitted with a Gaussian function and the width (FWHM) is plotted in Fig. 3. The FWHM increases almost linearly at T_c and broadens by 15% at 50 K. The calculated results under a strong electron-phonon coupling by Zeyher and Zwichnagl [12] are plotted as the line. The agreement between the obser-

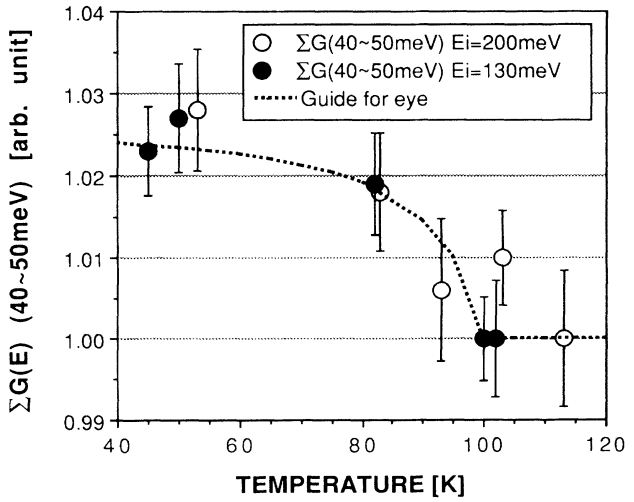

FIG. 2. Temperature dependence of integrated peak intensity between 40 and 50 meV for $E_i = 130$ meV (closed circles) and 200 meV (open circles). The dotted line is a guide for the eye.

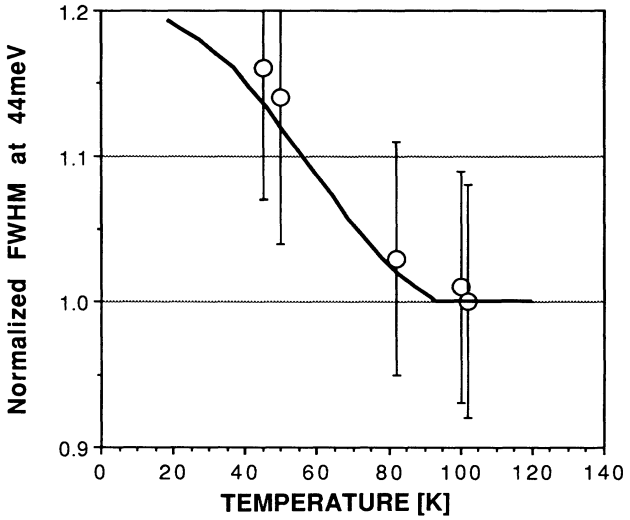

FIG. 3. Temperature dependence of FWHM of the peak at 44 meV. The solid line is the theoretical result by Zeyher and Zwichnagl [12]. All widths are normalized to the 100-K results.

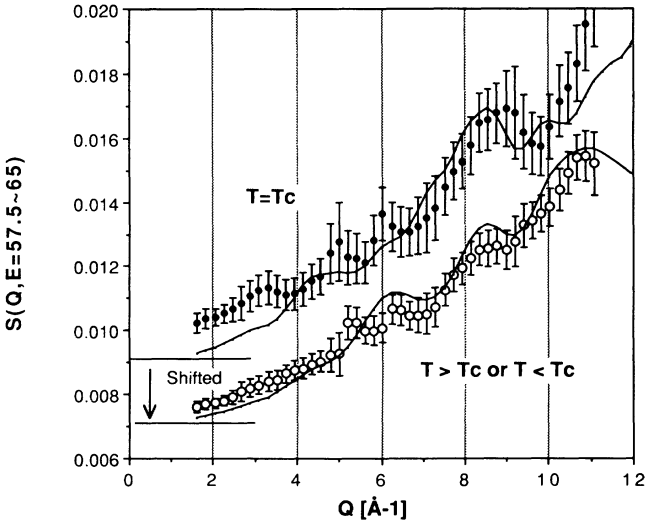

FIG. 4. Q dependence of peak intensity at 61.4 meV integrated between 57.5 and 65 meV. The solid lines are model calculations explained in the text. Incident energy is $E_i = 200$ meV.

vation and the calculation is quite good without any mutual scaling between them. The only assumption is that the ratio between the peak energy $\omega_0 = 44.0$ meV and superconducting gap energy 2Δ is $\omega_0/2\Delta = 1.08$, i.e., $2\Delta = 40.7$ meV. This is very close to the results of $2\Delta = 39.67$ meV for $T_c = 93$ K by Friedl *et al.* [13].

Raman scattering showed an energy shift at 41.8 meV (337 cm^{-1}) by about 1.2 meV [14] at 5 K; however, we were unable to resolve this shift in our observation because of insufficient energy resolution ($\Delta E \sim 1.56$ meV).

In Fig. 4 the Q dependence of the peak at 61.4 meV, which is a very strong peak in the Raman spectrum [5], is plotted. The integration range is from 57.5 to 65 meV. The Q dependence is very similar above and below T_c and the oscillating feature is smoother than for $T = T_c$. Therefore in Fig. 4 the data above and below T_c are represented by the average of the data at 53 and 83 K. The Q dependence changes considerably at T_c and the amplitude of the oscillation dramatically increases. In Fig. 5, for instance, we show the temperature dependence of $S(Q,E)$ for $Q = 7.5$–10 $Å^{-1}$ at $E = 57.5$–65 meV, where there is an obvious increase at T_c. From the figure it is very clear that the phonon state has some kind of critical behavior at T_c. We found that a larger change in $S(Q,E)$ occurs at higher energy transfer at T_c. The evolution of $S(Q,E)$ seems to be very enhanced compared to $G(E)$. We should note that $G(E)$ is an averaged value of integration of $S(Q,E)$ in some extent of Q space, for which the change in the oscillation behavior in $S(Q,E)$ cancels out.

Once we know the individual atomic motion, i.e., atomic displacement vector for a mode, we can calculate the Q dependence of $S(Q,E)$ for such an optical mode if the phonon dispersion is flat enough [6]. Burns *et al.* [5] assigned the peak at 62.5 meV as an A_g mode, which is the O(4) (apical oxygen) mode parallel to the c axis (here we call it A_g 5). The calculated Q dependences are drawn as lines in Fig. 4. The calculation and the observed data above and below T_c agree very well in absolute intensity scale without any adjustment except that the participation of only the upper half O(4) atoms in a unit cell is enough for obtaining the Q dependence in Fig. 4. If we take all O(4) atoms in a unit cell for the calculation, the periodicity of the Q dependence becomes too fine and very different from the observation. There are two possible explanations for this: (1) The phonon dispersion is not flat and goes out of the energy range where the energy integration gives a Q dependence. In this case the Q dependence would become smoother as shown in Fig. 4. (2) For some reason the dynamical correlation length is essentially shortened. Since at very high energy at 87 meV, where the phonon dispersion would be very flat, we

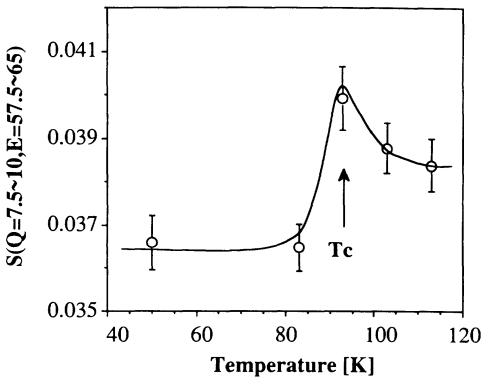

FIG. 5. Temperature dependence of $S(Q,E)$ for $Q = 7.5$–10 $Å^{-1}$ and $E = 57.5$–65 meV.

definitely found that the Q dependence can be explained by a short correlation length, we therefore conclude that a short dynamical correlation length is intrinsic for this system, even if we take condition (1) into account. Thus we recognize from the calculation that the O(4) motion in A_g 5 has a very short dynamical correlation length ($\sim$6 Å) in the a-b plane and is decoupled from the lower part of the unit cell over the Y atom.

From this point of view the dramatic change in Q dependence at T_c can be explained by an expansion of the dynamical correlation length associated with a local structural distortion. The expansion occurs in the a-b plane for A_g 5, i.e., neighboring O(4) motion couples with the A_g 5 mode in a unit cell, and needs to be enough to produce the sharp rise in the Q dependence at T_c as shown in Fig. 4. The best result can be obtained by shifting apical O(4) atoms in the neighboring unit cell in the $\langle 110 \rangle$ direction by 14% of the a and b lattice constants from the original position in a random fashion. The shift of the apical O(4) of the O(4)-Cu(2)-O(2,3) pyramid likely creates a $\langle 110 \rangle$ buckling structure or motion; a similar distortion was observed in the orthorhombic phase of $La_{2-x}Ba_xCuO_4$ [15] and in $Tl_2Ba_2CaCu_2O_8$ [16] in the superconducting state. Furthermore recent work also showed a local structural distortion even in an n-type superconductor $Nd_{2-x}Ce_xCuO_{4-y}$ [17].

Toby *et al.* reported an anomalous increase at T_c in the pair correlation function contributed by the buckling motion in $Tl_2Ba_2CaCu_2O_8$ [16]. This is an indirect method of obtaining the inelastic intensity from the total scattering. Our results are a direct observation of an anomaly in the dynamical aspect of $S(Q,E)$ for the first time. Thus we may conclude that the anomaly in phonon states in the short-range region, associated with a local structural distortion, is a common aspect of the high-T_c oxide superconductors at T_c. The anomalous behavior of $S(Q,E)$ seems to be enhanced for higher-energy excitations. This is not expected from the well known behavior of a conventional BCS superconductor. A Peierls-type Fermi-surface instability was proposed [18] as the mechanism of high-T_c superconductivity, which helps to induce a short-range $\langle 110 \rangle$ buckling motion [19]. This theoretical suggestion is very similar to our observation, but we cannot confirm this suggestion conclusively before further detailed study.

It is, however, evident from our experimental results that phonon states have a strong relation with electron states and may have an important role in the mechanism for the high-T_c oxide superconductivity.

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