Evidence for Large Static and Dynamic Distortions in High T_c Superconducting $YBa_2Cu_3O_{7-\delta}$ Crystals over a Wide Temperature Range

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Large deviations from the expected atomic thermal vibrational amplitude in Cu-O rows in a $YBa_2Cu_3O_{7-\delta}$ ($T_c = 92.5$ K) crystal have been observed in a wide temperature range (300–30 K) by ion channeling. In contrast, Y-Ba as well as Cu-O rows in nonsuperconducting deoxygenated $YBa_2Cu_3O_{6.2}$ specimens show a normal decrease in the atomic vibrational amplitude as the sample temperature is lowered. These anomalous results in the YBCO superconductor provide a clear indication of uncorrelated static and dynamic distortions associated with Cu-O rows. Possible implications of these structural changes are discussed. [S0031-9007(96)01720-6]

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Extensive studies on the role of phonons and other structural displacement of atoms associated with the superconducting phase transition have been conducted in high T_c materials using a variety of techniques. Raman measurements [1] have shown softening of one of the phonon modes at 340 cm^{-1} and hardening of another at 440 cm^{-1} associated with the out-of-phase and in-phase motion of O_{II} and O_{III} atoms in the superconducting state of $YBa_2Cu_3O_{7-\delta}$. Evidence for structural changes at T_c have been observed in dilatation [2] and precision inelastic neutron scattering [3] measurements. The infrared spectroscopy measurements [4] have indicated the role of chains in this system. However, all of these, as well as the isotope effect [5], the specific heat [6], elastic constant [7], and neutron diffraction measurements [8], have not been able to provide a definite answer to the behavior of phonons in high T_c materials.

In the present work the ion channeling technique, which provides a direct real space probe of displacements as small as 1 picometer, is used to investigate the phonon behavior and other atomic displacements related to static or dynamic distortion (such as Jahn-Teller distortions) in $YBa_2Cu_3O_{7-\delta}$. The critical angle for channeling to occur depends on the incident ion energy, the atomic numbers of the projectile and target, the interatomic spacing, electron screening potential, and, most important for the present study, any displacements (dynamic or static) of the atoms from their regular lattice sites [9]. It is important to note that neutron and x-ray diffraction are relatively insensitive to local uncorrelated atomic displacements in the sample due to the fact that the diffraction data are analyzed within the constraints of a particular model based on the symmetry of the crystal space group. Random displacements from the ideal atom positions, whether static or thermal, contribute only to diffuse scattering, which is not included in the model.

Two different sets of high quality [001] $YBa_2Cu_3O_{7-\delta}$ crystals, seven of each set, made at Argonne National Laboratory by the same method, one superconducting ($T_c = 92.5$ K) and the other made nonsuperconducting by deoxygenation, have been used in the present measurement. One of the two sets of samples was annealed a second time for 184 h at 500 °C in 0.0093% O_2/N_2 ambient and then quenched in liquid nitrogen to reduce the oxygen stoichiometry to $\delta = 0.77$, thus making it nonsuperconducting. These samples were 4 to 5 mm^2 in area and ~ 100 μm thick. The superconducting set of crystals had $\delta < 0.1$, $T_c = 92.5$ K with $\Delta T_c = 1$ K.

Ion channeling measurements were carried out using a well-collimated beam (0.5 mm diameter and $<0.01°$ divergence) of 1.5 MeV He^+ ions. The sample was suitably mounted on a precision five axis goniometer having an angular resolution $<0.01°$. The target holder was thermally insulated from the goniometer and could be cooled down to 33 K via a flexible Cu braid attached to a closed-cycle refrigeration unit. The target system was surrounded by two coaxial copper cryoshields; the outer one was cooled to 87 K while the inner one was maintained at 25 K. In this way, the effective pressure of condensable gases was reduced to a negligible level ($\sim 3 \times 10^{-11}$ Torr) at the target surface; the background pressure in the target chamber was maintained at $\sim 2 \times 10^{-8}$ Torr. The specimen temperature could be varied by a small 25 W heater mounted on the back of the target holder, and could be maintained to within ± 2 K at any desired temperature between 30 and 300 K.

The backscattered He^+ particles were analyzed using an annular silicon surface barrier detector of 300 mm^2 active area with a 4 mm diameter central hole which was mounted along the beam axis at a distance of ~ 5 cm from the target. This arrangement provided good statistics ($\sim 10^4$ counts in the gate at each angular setting in a random direction) for backscattered (170°) particles at a

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dose of only 3 nC of the incident He ions in a channeling angular scan. Since $YBa_2Cu_3O_{7-\delta}$ single crystals are very susceptible to radiation damage, it was important to keep the incident beam dose as low as possible. The 0.5 mm diameter beam spot was shifted to a new position on the specimen after every incident ion dose of 300 nC. It was possible to use three or four nonoverlapping spots on the specimen.

The [001] single crystal of $YBa_2Cu_3O_{7-\delta}$ was precisely aligned parallel to the incident beam direction. Angular channeling scans were made by measuring the Rutherford backscattering (RBS) yield as a function of the tilt angle about the [001] axis of the sample at sixteen different temperatures in the range 300 to 30 K. At each angular setting the complete RBS spectrum was recorded. Examples of [001] axial channeling angular scans made with the RBS yield, as a function of specimen tilt angle for the superconducting sample at temperatures of 100, 80, and 33 K, are shown in Fig. 1. Five sets of measurements have been made using seven high quality YBCO crystals. Each time a 5%–6% increase in FWHM is seen, while cooling through T_c between 100 and 80 K and no appreciable change between 80 and 33 K. A standard deviation of $<1\%$ is determined in these measurements. It is important to note that the RBS yield contains the signals emanating from the three constituents, Cu, Y, and Ba, of the superconducting sample and cover a depth of $\sim$400 nm from the sample surface for the Cu signal. Thus the information from both the Cu-O and Y-Ba rows is mixed in the data collected. Similar scans from a nonsuperconducting sample are shown in Fig. 2. In this case, no abrupt change is seen in the FWHM between 80 and 100 K. The observed variation of FWHM seems to follow the normal trend of decrease in thermal vibrational amplitude as a function of decreasing temperature. The large reduction in counts, to $<3\%$ of the random yield when the [001] axis of the specimen is aligned with the incident beam direction, demonstrates a very high-quality, single crystal specimen (both superconducting and nonsuperconducting). The observed step across T_c is in accordance with our earlier results [10].

The plots of the FWHM of the channeling angular scans made with Cu-Y-Ba signals from the respective superconducting and nonsuperconducting samples as a function of temperature, 300 down to 33 K, are shown in Figs. 3(a) and 3(c). Also shown in this figure is a similar plot obtained with the signals only from Y-Ba rows of the superconducting sample [Fig. 3(b)]. It is evident that there is a gradual increase in the value of the FWHM as the temperature is lowered in the nonsuperconducting sample [Fig. 3(a)] as well as for the Y-Ba rows in the superconducting case, indicating that the thermal vibration amplitude is decreasing with temperature as expected. However, for the Cu-Y-Ba signals in the superconducting sample, there are anomalies in the variation of the FWHM as a function of temperature [Fig. 3(c)] and seem to be associated with the Cu-O rows. In Fig. 3(c), three main points are to be noted: (1) a faster increase in FWHM as the sample is cooled from room temperature down to 220 K; (2) practically no variation between 220 and 180 K followed by a smaller increase in FWHM down to 100 K; (3) an abrupt increase of 5%–6% between 100 and 80 K, i.e., across T_c followed by practically no

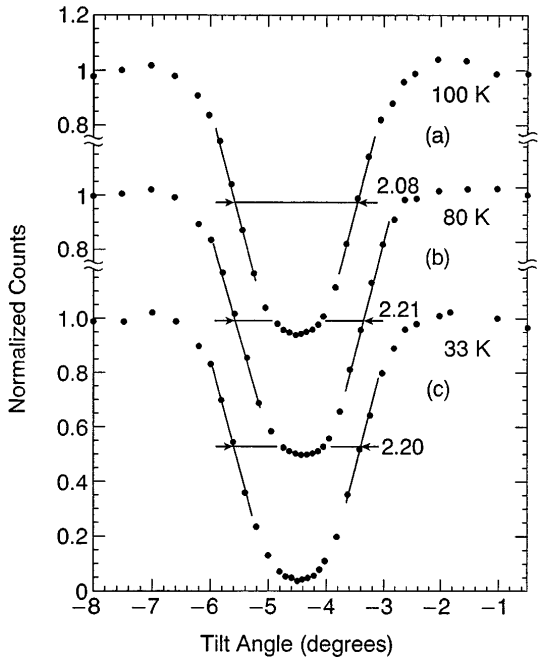

FIG. 1. The [001] channeling angular scans (a) 100 K, (b) 80 K, and (c) 33 K in $YBa_2Cu_3O_{7-\delta}$ crystal ($T_c = 92.5$ K). A $\sim$5%–6% increase in the FWHM is seen across T_c between 100 and 80 K, with practically no change between 80 and 33 K.

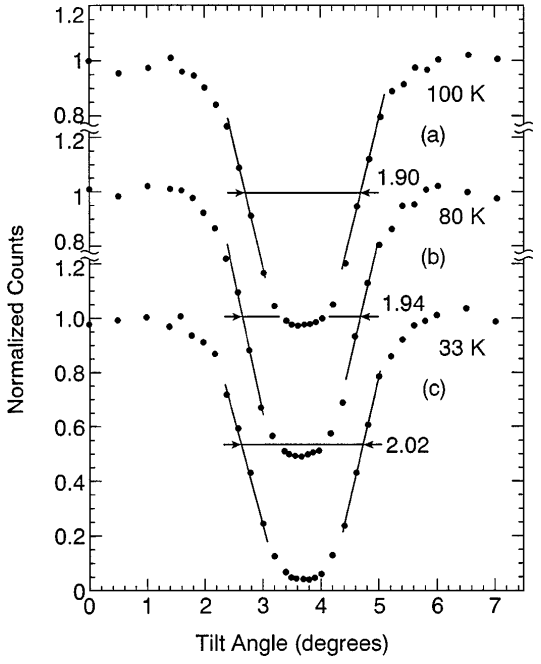

FIG. 2. Same as Fig. 1, except the sample is nonsuperconducting. No abrupt change in the FWHM is seen, instead there is a small increase throughout the temperature range as expected from a normal Debye-like behavior.

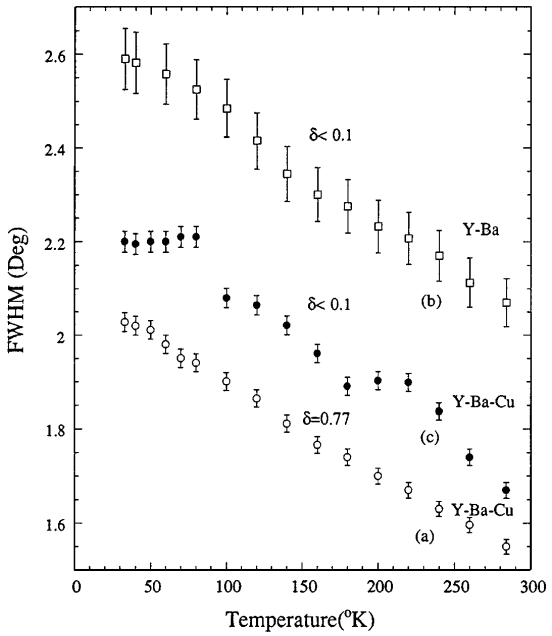

FIG. 3. FWHM of channeling angular scans versus temperature in $YBa_2Cu_3O_{7-\delta}$ samples: (a) nonsuperconducting ($\delta = 0.77$) with Y-Ba-Cu signals; (b) superconducting ($\delta < 0.1$) for Y-Ba signals only; (c) same as (b) but with Y-Ba-Cu signals.

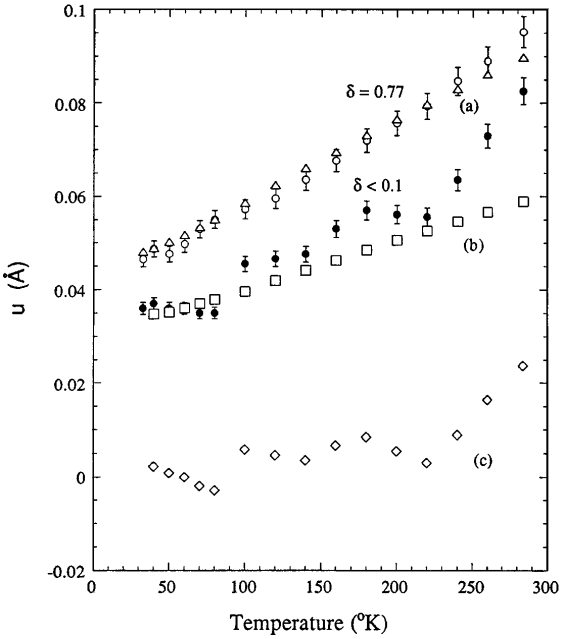

FIG. 4. The u vs T as obtained from the measured FWHM in YBCO. (a) Experimental (∘) and calculated (Δ) in the nonsuperconducting case. (b) Experimental (•) and calculated (□) in the superconducting case. (c) The difference between experimental and calculated u values as shown in (b).

change in FWHM in the wide temperature range 80 to 33 K available in the superconducting state of the sample.

The lattice vibration amplitude or the atomic displacements (u) as extracted from the measured FWHM of the channeling angular scans, using the continuum model [9] for channeling, with corrections based upon the Monte Carlo computer simulation of Barrett [11], are shown as points with error bars in Figs. 4(a) and 4(b) both for nonsuperconducting and superconducting YBCO crystals, respectively. The average values of respective atomic numbers and lattice spacing are used in this calculation. The calculated values of the thermal vibration amplitude (u) based on the Debye model for respective cases are also shown by triangles and squares. The normal trend of the decrease in u as a function of decreasing temperature is clearly seen in the case of the nonsuperconducting sample [Fig. 4(a)]. A similar trend for Y-Ba rows in the superconducting specimen has also been obtained. However, the u values obtained from the combined Y-Ba-Cu signals in the superconducting case differ considerably from the calculated ones throughout the temperature range, an effect clearly associated with the Cu-O rows. The magnitude of this observed difference is made clear by subtracting the calculated value of the normal thermal vibration amplitude at each temperature from the observed experimental values [Fig. 4(c)]. In this calculation a Debye temperature of 390 K was assumed well within experimentally determined values.

The absence of any variation in the u values [Fig. 4(b)] within the experimental errors, in the superconducting state of the sample, indicates the existence of a temperature-independent small amplitude <3.5 pm in the available wide temperature range (33 to 80 K). This behavior is quite complex, and we have two plausible approaches to interpret the data. In the first approach, we can compare u with the zero point vibration, and, in the second, we can subtract from u the normal thermal behavior and then analyze the difference. Using the relation $\langle u^2 \rangle = 3\hbar\omega_D^2 / 8\pi\rho v^3$ (where $\hbar\omega_D = k_B\theta_D$, k_B is Boltzmann's constant, θ_D is the Debye temperature, v is the velocity of sound, and ρ is the mass density), the zero-point vibration in the superconducting YBCO is obtained as 3.2 pm which is close to the measured 3.5 pm between 30 and 80 K. The longitudinal velocity of sound in YBCO along (110) in the plane (a,b) has been estimated to be 7×10^5 cm/sec by Saint-Paul *et al.* [12] and is used in the above calculation. It thus appears that the material in the superconducting state is more ordered, and a small constant amplitude of lattice vibration may persist. In resonant neutron absorption experiments in $Bi_2Sr_2CaCu_2O_8$ material, the average kinetic energy $\langle E \rangle$ of Cu in the a-b plane has not shown any variation below the superconducting transition [13], a result supporting this highly controversial conclusion.

In the alternate approach, as seen in Fig. 4(c), the difference in u values (experimental and calculated ones) shows a small increase in the temperature range 80 to 33 K, which could be an indication of phonon softening, as has been seen for a specific phonon (340 cm^{-1}) in Raman measurements [1] and also by inelastic neutron scattering [3(b)].

The large variations in u as a function of temperature [Fig. 4(b)] can be interpreted in terms of static and/or

dynamic distortion effects. As mentioned above, the channeling technique is very sensitive to small displacement ($\sim$0.01 Å) of atoms from their regular lattice sites, however, it cannot distinguish between static and dynamic displacement. The large variations in u [Figs. 4(b) and 4(c)], if associated with only thermal behavior, should be seen in specific heat [6] and Raman measurements [1]. The absence of such large variations in these measurements indicates the existence of uncorrelated structural static and dynamic displacements which cannot be detected in specific heat or Raman studies. Static changes in structure at T_c, indicating a reduction of the orthorhombicity of the $YBa_2Cu_3O_7$ system, are seen in dilatation experiments [2]. The sudden change in the u value between 100 and 80 K [Figs. 4(b) and 4(c)], indicating a dynamic or static displacement (1–1.5 pm) of Cu atoms in the *a-b* plane, appears to be related to this distortion, which seems to diminish across T_c, i.e., reducing the orthorhombicity of the system, making these rows very smooth. This is also supported from the study of the effect of uniaxial stress on T_c of this system. The pressure derivative dT_c/dp_i $(i = a, b, c)$ is comparatively large and opposite in sign for compression in the *a-b* plane [14]. However, these structural changes are an order of magnitude smaller than the ones seen in the present experiment which can be understood if the distortion is an incoherent dynamic one across T_c. Such a dynamic change may be possible if we consider the charge redistribution between the Cu-O chains and planes, as has been discussed by Khomskii and Kusmartsev [15]. These authors have suggested that there is possibly a charge transfer from Cu-O chains to Cu-O planes. This charge redistribution may cause structural fluctuations of a local nature in the region of T_c. In the neutron inelastic scattering experiments [3(a)], a shift of the apical O(4) in the $\langle 110 \rangle$ direction in the *a-b* plane in a random fashion has been suggested. If this is true, this shift of the apical O(4) of the O(4)-Cu(2)-O(2,3) pyramid can create a $\langle 110 \rangle$ buckling motion and an instability in the structure which may stabilize as the superconducting state is reached. Schweiss *et al.* [8(a)] have found, from the analysis of their neutron diffraction data, anisotropic static and dynamic displacement of atoms in YBCO crystals as a function of temperature. They have discussed the displacement of oxygen atoms located in planes and chains. Local structural distortions have also been seen in extended x-ray absorption fine-structure studies [16].

In Fig. 4(b), the u value is seen to decrease faster than expected from normal thermal behavior between 300 and 220 K, followed by practically no change up to 180 K, indicating that structural changes start at room temperature. A large displacement of chain oxygen perpendicular to the chains at room temperature is seen in Ref. [8(a)], which may cause structural instability. The origin of the anomaly around 200 K is not clear. It appears to be related to structural instability. In dilatation experiments [2] the expansion coefficient along the c axis has shown a change near 180 K. It appears that the structure tends to stabilize near 200 K, but, on further lowering of the temperature, the instability starts again and an ordered state is reached below T_c.

In conclusion, the channeling data have provided direct evidence of static and dynamic distortions associated with [001] Cu-O rows spread over a wide temperature range (300–33 K) in $YBa_2Cu_3O_{6.98}$. The lattice disorder seems to be more at 300 K, and, as the temperature is lowered, the solid changes to more ordered states with transitions around 180 K and across $T_c = 92.5$ K. Below T_c no measurable change in u is observed, and the material seems to be in a highly ordered state.

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