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Ion-channeling investigation of thermal vibrational amplitudes across the superconducting transition in $YBa_2Cu_3O_{7-\delta}$

R. P. Sharma, L. E. Rehn, P. M. Baldo, and J. Z. Liu
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
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Ion-channeling measurements reveal that the thermal vibrational amplitude, u_1, decreases markedly from 0.008 to 0.0056 nm as the temperature of orthorhombic single crystals of $YBa_2Cu_3O_{7-\delta}$ is lowered from 300 to 220 K. The rate of this decrease slows at lower temperatures, with u_1 reaching a value of 0.0042 nm at 100 K. Further cooling of the sample across the superconducting transition region (to 85 K) produces an abrupt, additional decrease in u_1 to 0.0035 nm. This abrupt lattice stiffening corresponds to an ~140 K increase in Debye temperature across the superconducting transition.

Since the discovery of superconductivity at high temperatures in the Y-Ba-Cu-O system,[1] particular attention has focussed on the role of phonons in producing high superconducting transition temperatures. In the tripled perovskite structure[2,3] (Fig. 1) of $YBa_2Cu_3O_{7-\delta}$ recent x-ray diffraction studies using single crystals have shown that the orthorhombic distortion in the a-b plane changes smoothly[4] through the superconducting transition T_c, although an earlier investigation on polycrystalline material indicated otherwise.[5] Additional suggestions of anomalies near T_c have been extracted from recent neutron-powder-diffraction data,[6] but their apparent magnitude was less than the experimental uncertainty. Ultrasonic measurements in polycrystalline samples revealed[7] a sharp rise in longitudinal acoustic resonant frequency across T_c, while another study[8] has shown smoother behavior, but with a greater rate of increase in sound velocity with temperature immediately below T_c. It thus seems probable that anomalies in structural deformation and/or phonon contributions do occur near T_c. However, the nonavailability of large-size single crystals of $YBa_2Cu_3O_{7-\delta}$ have precluded an unambiguous interpretation of the results.

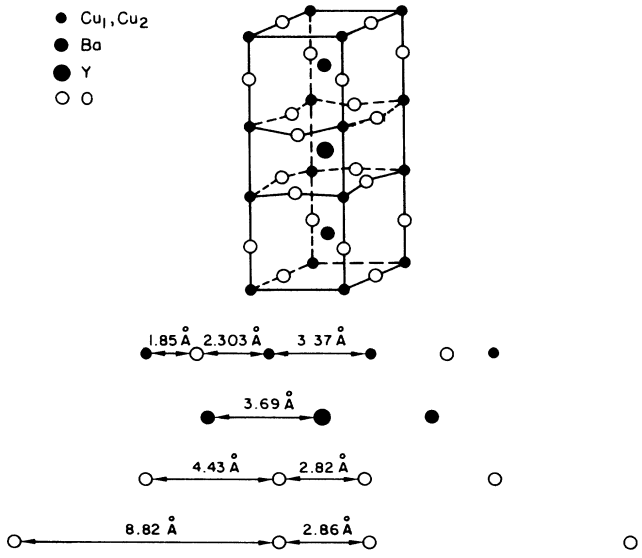

FIG. 1. The crystal structure of the orthorhombic phase of $YBa_2Cu_3O_{7-\delta}$. The Ba-Y, Cu-O, and O-O rows of atoms along the [001] direction are shown separately. Small filled circles indicate Cu atoms, medium filled circles indicate Ba atoms, and large filled circles indicate Y atoms. The oxygen atoms are shown by open circles.

Ion channeling provides an alternative technique to study lattice vibrations.[9,10] Most importantly, this technique is compatible with the small size of currently available single crystals. When a beam of energetic ions is incident along a major crystallographic direction, the particles are steered between atomic rows or planes by a series of correlated small-angle collisions. This channeling is accompanied by a dramatic reduction in the yield from small-impact-parameter collisions such as Rutherford backscattering. The critical angle of incidence below which channeling occurs is determined by the ion energy, the atomic numbers of the projectile and target, and the spacing and thermal vibrational amplitudes of the lattice atoms. Recently, Stoffel, Morris, Bonner, and Wilkens[11] have demonstrated ion channeling in small single crystals of $YBa_2Cu_3O_{7-\delta}$. Although these authors noted the importance of performing a temperature-dependent study, their experiments were limited to room temperature. In this Communication, we report accurate measurements of ion channeling along the c axis of high-quality $YBa_2Cu_3O_{7-\delta}$ single crystals as a function of temperature between 80–300 K. The results reveal a pronounced stiffening of the lattice as it is cooled below room temperature, and a relatively abrupt, ~15–20% additional decrease in the average one-dimensional thermal vibrational amplitude of the lattice atoms as the temperature is lowered through T_c.

Single crystals of $YBa_2Cu_3O_{7-\delta}$ were grown by a partially nonstoichiometric melting method similar to the one reported by Kaiser *et al.*[12] These mirrorlike crystals, in the form of thin flakes 1–2 mm^2 in area, were annealed in flowing oxygen at ~430 °C for 48 h. A magnetic shielding measurement on the annealed crystals showed a very sharp superconducting transition at T_c=92 K, with a

transition width of ~1 K. The ion-channeling measurements were carried out using a small (0.5×0.5 mm), well-collimated (divergence $<0.05°$) beam of 1.5 MeV He^+ ions. The single crystals of $YBa_2Cu_3O_{7-\delta}$ were mounted with the help of thermally conducting epoxy on a precision double-axis goniometer having an angular resolution of 0.01°. The target holder could be cooled to 80 K using flowing liquid nitrogen, and the temperature could be varied in small steps up to room temperature by adjusting the nitrogen flow. The backscattered α particles were detected by a Si surface-barrier detector [full width at half maximum (FWHM) of 16 keV] placed at an angle of 138° with respect to the incident beam. The vacuum in the chamber was maintained at $<4\times10^{-6}$ Pa. A [001] single crystal of $YBa_2Cu_3O_{7-\delta}$ was first oriented parallel to the incident beam direction using a laser, and angular scans about the [001] direction were made at several different temperatures. The energy window for the Rutherford backscattering yield was set to accept counts from immediately below the Cu edge in the spectrum to just above the O edge. Because the single crystals of $YBa_2Cu_3O_{7-\delta}$ are susceptible to radiation damage,[13] the target-detector geometry was arranged so that only 3 nC of beam were required to provide statistically sufficient backscattered counts at a given angular setting. Radiation damage effects were first noticed as a slight increase in the minimum yield following a dose of ~500 nC. A complete set of measurements was repeated three times, and a fresh crystal was mounted each time the accumulated dose had reached 500 nC. Furthermore, the channeling scans were taken alternately at temperatures below and above T_c, to ensure that any observed changes were not induced by the incident ions.

Examples of the observed channeling dips as a function of specimen tilt angle are shown in Fig. 2. When the [001] axis is aligned with the incident beam direction, the α particle backscattering yield is reduced to only 2–3% of the random yield, indicating a very high-quality single crystal. The FWHM of the channeling dips at different temperatures are plotted as a function of specimen temperature in Fig. 3. The FWHM increases by ~25% as the temperature of the sample is lowered from room temperature to 100 K. An important point to note is that this increase is significantly faster than the normal pattern of decreasing thermal vibrational amplitude with decreasing temperature. Finally, a relatively abrupt additional increase of about 8% in the FWHM occurs as the specimen temperature is lowered further from 100 to 85 K (Fig. 3). The high reproducibility of the data is evidenced by the small scatter seen in the several measurements taken just above, and again just below, T_c. A standard deviation of $<2\%$ (corresponding to approximately the size of the data symbols) was found for the determination of the FWHM.

As can be seen from Fig. 1, ions incident along the

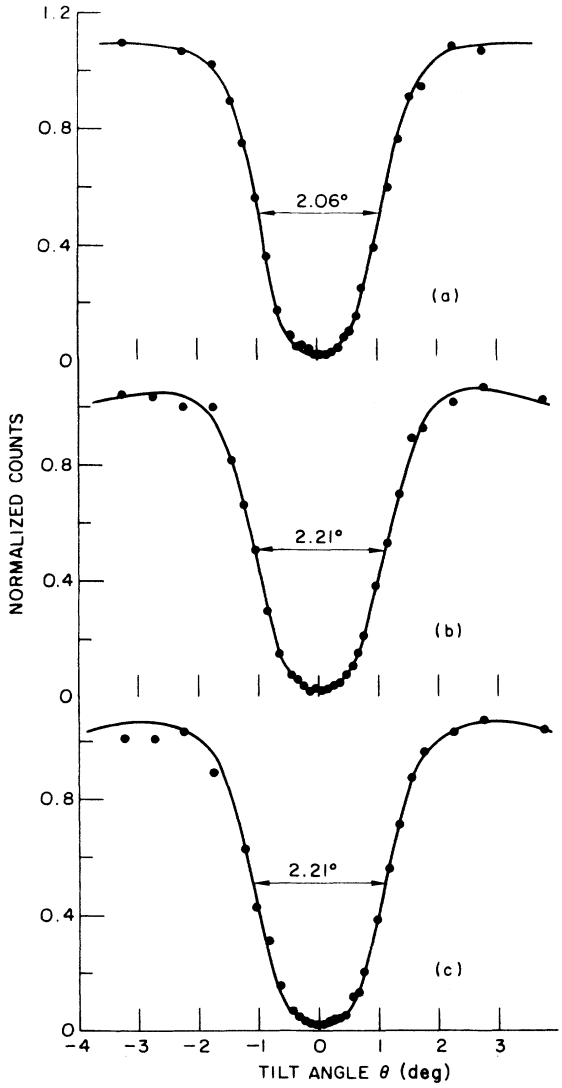

FIG. 2. The [001] axial dips at (a) 100 K, (b) 85 K, and (c) 81 K; the scans were taken first at 81 K, followed by 100 K, and then 85 K.

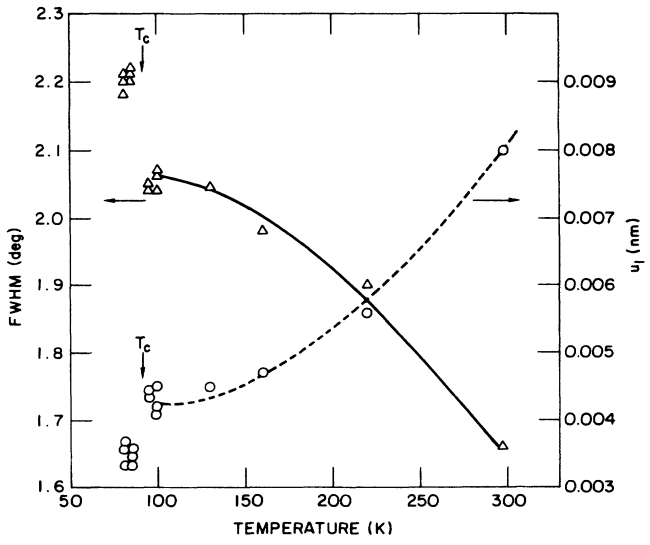

FIG. 3. Plot of FWHM of the angular scans as a function of temperature. The open circles along the dashed line show the variation of u_1 with temperature. Note the initial rapid decrease of u_1 with decreasing temperature, and the abrupt change across T_c.

[001] direction are traveling parallel to the four Cu-O rows, the Y-Ba row, and the four O-O rows that define each unit cell. Analysis of channeling phenomena in such a polyatomic crystal is complex, since each row contains different atomic species and different interatomic spacings. This situation, which has been discussed previously in detail by Gemmel,[14] is generally treated by first characterizing each type of row as weak or strong, according to its ability to deflect ions incident at small angles. Incident ions can be expected to remain channeled with respect to strong rows, while being essentially not channeled by weak rows. In the present case, the strong rows are clearly those of Y-Ba and Cu-O, while the O-O rows are weak. Taking into account the different atomic concentrations, we next analyze the present channeling results using arithmetic averages for the atomic numbers and lattice spacings along the two strong rows.

In the continuum approximation for high-energy ions, Lindhard[15] has shown that the critical angle, ψ_1, for channeling in a static lattice is given by

$$\psi_1 = \left[\frac{2Z_1 Z_2 e^2}{Ed} \right]^{1/2} . \quad (1)$$

Here E is the energy of the incident particle, d is the spacing between the atoms along the channeling direction, Z_1 and Z_2 are the atomic numbers of the projectile and the target atoms, respectively, and e is the electron charge. Based on the computer simulation studies of ion trajectories by Barrett,[16] the FWHM of the channeling dip with thermal vibrations ψ is given by

$$\psi = 1.6[V_{\mathrm{RS}}(1.2u_1)/E]^{1/2} . \quad (2)$$

In this expression, u_1 is the one-dimensional rms thermal vibrational amplitude, V_{RS} is the continuum potential for a static atomic row, computed employing Moliere's approximation to the Thomas-Fermi potential. This angle in degrees can be expressed as

$$\psi = 1.6 F_{\mathrm{RS}}(\xi)\psi_1, \quad \xi = \frac{1.2u_1}{a} , \quad (3)$$

where a is the Thomas-Fermi screening distance. A graph of the function $F_{\mathrm{RS}}(\xi)$ vs ξ has been given by Appleton and Foti.[17]

To extract the information regarding the one-dimensional thermal vibrational amplitude, u_1, from the ψ values obtained at different temperatures, an averaging procedure is followed. First, the critical angle, ψ_1, for the Ba-Y and the Cu-O rows is calculated separately from Eq. (1) using properly weighted average values for the atomic number (Z_2) and the atomic spacing (d) for each row. We have used average Z_2 values of 50.3 and 20.6 for the Ba-Y and Cu-O rows, respectively; the corresponding d values are 0.369 and 0.273 nm. Next, the arithmetic mean of the two ψ_1 values (0.98° for Cu-O and 1.31° for Ba-Y rows) is substituted in Eq. (2), and u_1 is obtained from the experimentally determined ψ value at each temperature. These values of u_1 are also plotted in Fig. 3; the estimated error is $\lesssim 4\%$.

As seen in Fig. 3, a relatively abrupt $\sim 8\%$ increase occurs in the FWHM of the channeling dip as the temperature is lowered below the superconducting transition ($T_c = 92$ K). This increase is direct evidence that a corresponding decrease has occurred in the thermal vibrational amplitude. Neutron diffraction studies[3] have provided thermal Debye parameters, B, for the different atoms in the Y-Ba-Cu-O system at room temperature. Using an average value of $B = 4.98 \times 10^{-3}$ nm^2 from that work[3] weighted according to the atomic concentrations in the strong Ba-Y and Cu-O rows, we have also calculated the value of u_1 using the expression $B = 8\pi^2 \langle u_1^2 \rangle$ where $\langle\ \rangle$ denotes an average value. This room-temperature value of u_1, 0.0079 nm, agrees well with the present one of 0.008 nm. Proceeding a step further, the observed u_1 values were used to estimate the lattice Debye temperature by fitting to the expression[17]

$$u_1 = 12.1 \left[\left(\frac{\phi(x)}{x} + \tfrac{1}{4} \right) / M_2 \Theta_D \right]^{1/2} .$$

Here $x = \Theta_D/T$, $\phi(x)$ is the Debye function which is tabulated by Appleton *et al.*,[17] Θ_D and T are the Debye temperature and crystal temperature (in degrees Kelvin), respectively, and M_2 is the atomic weight in atomic mass units, for which we have used a weighted average mass of 51 for $YBa_2Cu_3O_{7-\delta}$. The value of the Debye temperature (Θ_D) obtained in this fashion from the room temperature data is 370 K, in excellent agreement with the value of 370 ± 5 K extracted from the volume expansion measurements of You *et al.*[4] In a similar way, Θ_D was calculated from the values of u_1 obtained at lower temperatures. At 220 K, the observed $u_1 = 0.0056$ nm indicates that Θ_D has increased to 475 K. At the sample temperature of 160 K, Θ_D becomes 510 K, then remains approximately the same as the temperature is lowered to 100 K. With a further decrease in the sample temperature to 85 K, where u_1 becomes 0.0035 nm, the calculated Debye temperature increases to 650 K. Due to the weighted average value used for the mass of this polyatomic material, the variation in Θ_D can be expected to be more reliable than the absolute value obtained at each point. The observed variation in Θ_D indicates a faster than normal stiffening of the $YBa_2Cu_3O_{7-\delta}$ lattice as the temperature is lowered from room temperature down to 220 K. The 17% additional decrease observed in the thermal vibration amplitude across the superconducting transition (Fig. 3) corresponds to an ~ 140 K change in Debye temperature. Because the continuum potential for channeling by a row falls off rapidly with distance, the effect of neighboring rows on the axial channeling potential is small at distances of the order of thermal vibrational amplitudes. Since channeling of the α particles is governed predominantly by the isolated, strong Ba-Y and Cu-O rows, this large increase in Debye temperature is apparently due to an average decrease in the thermal vibrational amplitude of the lattice atoms, rather than any structural change in the a-b plane.

In summary, the present measurements provide direct evidence of large changes with temperature in the thermal

vibrational amplitude of the lattice atoms in orthorhombic $YBa_2Cu_3O_{7-\delta}$. The rapid stiffening of the lattice observed between 297 and 220 K is consistent with a parallel increase seen in the elastic constants in this same temperature range. Finally, an additional rather abrupt stiffening occurs across the superconducting transition temperature, which corresponds to an $\sim$140 K increase in Debye temperature.

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