Direct Evidence of Anomalous Cu-O Vibrational Modes near T_c in $ErBa_2Cu_3O_{7-\delta}$

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Ion channeling along the c axis in $ErBa_2Cu_3O_{7-\delta}$ reveals a normal (Debye-type) temperature dependence for thermal vibrations of the Er and Ba atoms between 40 and 300 K. In contrast, a substantially stronger than normal temperature dependence is found for the Cu-O atom vibrations, and a large, anomalous change (-30%) is seen at the superconducting transition. The large magnitude of the vibrational changes found for the Cu-O rows across T_c suggests that the atoms in these rows become strongly coupled in the superconducting state.

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A variety of techniques have been applied to investigate the behavior of ceramic oxide superconductors across the superconducting transition temperature, T_c. Anomalies in the structure,[1] elastic constants,[2,3] Debye temperature,[2,4] and orthorhombic distortion[5,6] have been reported. Nevertheless, the role played by phonons in the superconducting transition remains unknown.

Ion channeling provides a direct probe of lattice vibrations. When a beam of ions is incident along a major crystallographic direction, the particles are steered between the atomic rows and planes of the target by a series of correlated small-angle collisions. This channeling effect produces a dramatic reduction in the yield of small-impact-parameter collision events such as Rutherford backscattering (RBS). The critical angle of incidence below which channeling occurs can be related directly to the thermal vibrational amplitudes of the lattice atoms.[7] In our earlier study[4] of $YBa_2Cu_3O_{7-\delta}$, anomalous changes measured in ion channeling across T_c were reported. A continuum model employing corrections based upon the Monte Carlo computer simulations of Barrett[8] was used to obtain the average thermal vibration amplitude (u_1) of all four of the constituent elements (Y, Ba, Cu, and O) as a function of temperature. The u_1 values extracted from the ion-channeling results using the model are in good agreement with independent determinations by neutron diffraction,[6] although the evidence for the anomalous vibrational behavior was much clearer in the channeling study. Details of this comparison will be published elsewhere.[9] The greater sensitivity of the channeling technique in this instance can be attributed to two factors. First, ion channeling probes the lattice vibrations directly, while their amplitudes comprise only a subset of several fitting parameters that must be extracted simultaneously from the neutron-diffraction data. Second, the channeling studies were performed on high-quality single crystals, while the substantially larger specimen volume required for the diffraction studies necessitated the use of sintered specimens.

It is clearly of interest to characterize the vibrational behavior of the individual atomic species of the superconducting material. In this Letter, we report the results obtained from a study of ion channeling along the [001] direction (c axis) in $ErBa_2Cu_3O_{7-\delta}$. Replacing Y by Er has essentially no effect on the superconducting properties. Both materials exhibit a sharp ($\sim 1.5°$ in width) superconducting transition, beginning at 92.2 and 92.8 K for the Y and Er compounds, respectively. As discussed below, the *average* thermal vibrational properties of the two materials determined by channeling also are almost identical. However, substituting Er for Y (higher atomic number) increases the RBS yield, and (higher atomic mass) concomitantly shifts the rare-earth signal to higher energies. The greater yield and upward energy shift substantially improve the measurement statistics, making it possible to separate the individual channeling contributions from the Er-Ba and Cu-O rows parallel to the c axis before any beam-induced changes become significant.

Single crystals of $ErBa_2Cu_3O_{7-\delta}$ were grown by a nonstoichiometric melting technique. Mirrorlike crystals in the shape of thin flakes with ~ 1–2 mm^2 areas perpendicular to the [001] direction were annealed in flowing oxygen at 500 °C for 72 h. Magnetic shielding measurements on annealed crystals showed a sharp superconducting transition beginning at 92.8 K. The crystals were mounted on a double-axis goniometer having an angular resolution of 0.01°. Coupling was provided to a closed-cycle refrigeration unit capable of stabilizing the temperature to $\pm 3°$ between 40 and 300 K. Angular RBS channeling scans were made with a well-collimated (divergence $< 0.05°$) beam of 1.5-MeV ^{4}He ions, at a scattering angle of 150°. Scans were taken alternately at temperatures above and below T_c to ensure that any observed changes were not induced by the incident beam.

In the tripled perovskite structure of $ErBa_2Cu_3O_{7-\delta}$, Er and Ba occupy the body-centered-cubic sites, while Cu atoms are located at the cube corners. Hence four different atomic rows exist parallel to the c axis:[4] one row (1) is an alternating sequence of one Er and two Ba atoms; a second row (2) consists of subunits of one Cu

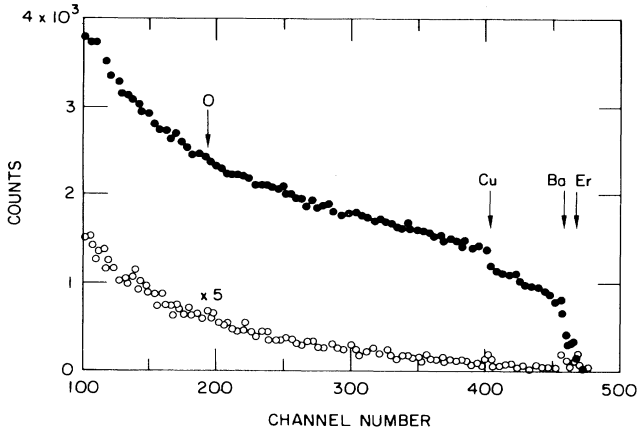

FIG. 1. Aligned (c axis) and random RBS spectra of $ErBa_2Cu_3O_{7-\delta}$ taken with 1.5-MeV $^4He^+$ at a scattering angle of 150°C.

atom and a Cu atom pair, each subunit separated by a single O atom; two additional rows (3 and 4) contain only O atoms, each with a different interatomic spacing. As discussed in Ref. 4, the latter two are not strong channeling rows because the interatomic spacings are relatively large and the atomic number of O is low. An angular channeling scan across the [001] axis therefore collects information predominantly, and simultaneously, from the Er-Ba and Cu-O rows.

Information concerning the two individual rows is separated as follows. An RBS spectrum taken with the beam incident along a nonchanneling direction and one taken with the beam aligned along the [001] axis are shown in Fig. 1. Note that the aligned yield remains between 1.5% and 4% of the random yield over the entire analyzed depth (~700 nm). The clearly separated Cu, Ba, and Er edges, denoted in this figure by the arrows at channel numbers 398, 452, and 461, respectively, represent the highest-energy particles backscattered from that particular element. The O edge is located in channel number 193. Because the O RBS signal is too low to yield statistically meaningful data, no attempt was made to monitor the O portion of the RBS spectrum. Information about the Er-Ba rows is obtained by setting a gate to accept only those RBS counts between channels 405 and 464, i.e., only particles that have backscattered from either Er or Ba atoms. A second gate, between channels 225 and 384, accepts RBS counts from all three elements, and therefore collects the integrated information from both types of rows.

Examples of the channeling dips observed in the RBS yield as a function of specimen tilt angle at temperatures of 80 and 100 K are shown in Fig. 2 for the combined Er-Ba-Cu and for the Er-Ba gates. The large reduction in counts, to $\lesssim 2\%$ of the random yield when the [001] axis of the specimen is aligned with the incident beam direction, again demonstrates a very high-quality, single-

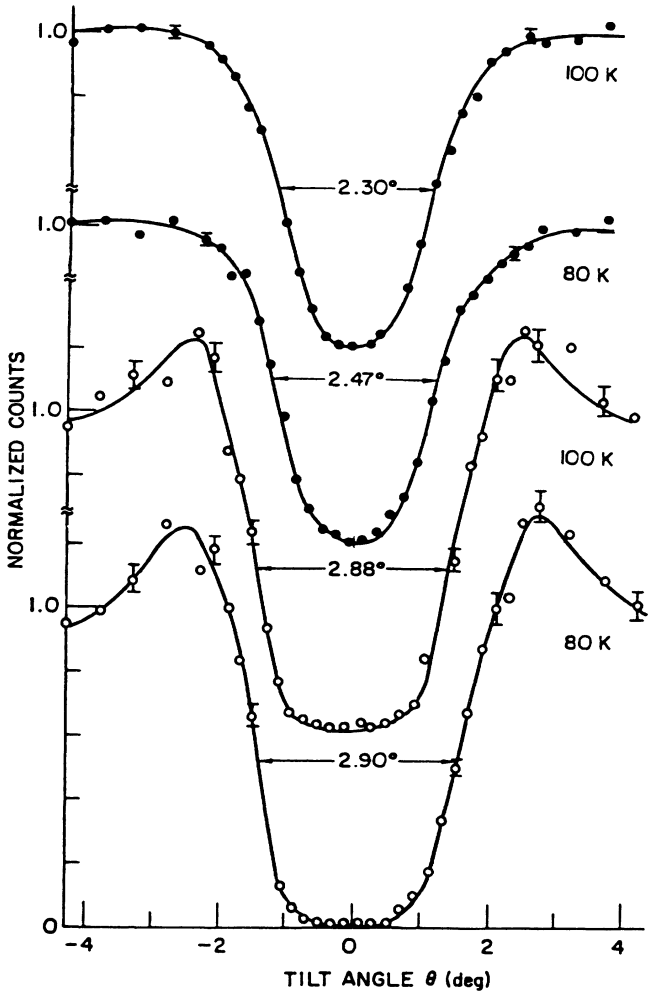

FIG. 2. [001] axial channeling scans obtained with the combined Er-Ba-Cu (closed symbols) and with the Er-Ba (open symbols) gates at 80 and 100 K.

crystal specimen. The substantially greater width of the Er-Ba axial scans is a direct consequence of the high atomic numbers of Er and Ba; the lower minimum yield and more clearly defined compensating shoulders are due primarily to the smaller energy range of the Er-Ba gate, which makes the measurement more surface sensitive.

The FWHM of the channeling dips are plotted as a function of measurement temperature in Fig. 3. The high reproducibility of the data can be seen in the sets of measurements taken just below (80 K) and just above (100 K) T_c; a standard deviation of $\leq 3\%$ was determined for these measurements. A relatively smooth, monotonic decrease in the FWHM for the Er-Ba rows (open symbols) is seen with increasing temperature. In contrast, the FWHM obtained using the integrated signal from all three elements (closed symbols) shows a significantly stronger dependence on temperature, and an abrupt drop of ~7% in the FWHM is evident between

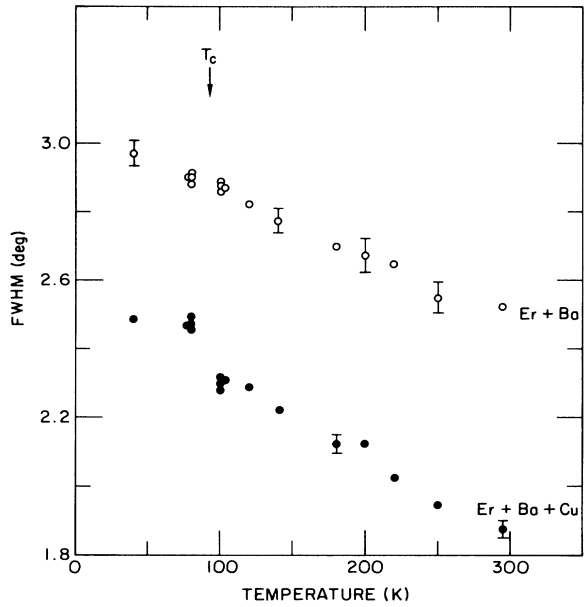

FIG. 3. FWHM of axial scans for the Er-Ba-Cu (closed symbols) and for the Er-Ba (open symbols) gates.

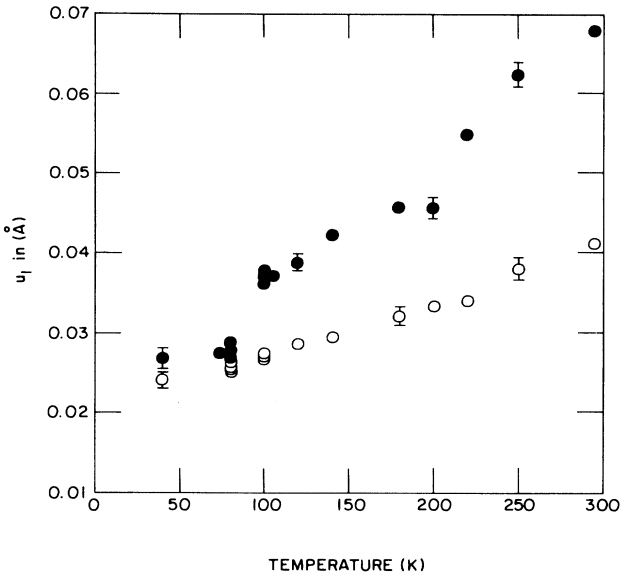

FIG. 4. u_1 extracted from the data in Fig. 3 as described in text: combined Er-Ba-Cu results (closed symbols); Er-Ba only (open symbols).

80 and 100 K. The anomalous drop is only slightly smaller than the decrease (8%) reported[4] for $YBa_2Cu_3O_{7-\delta}$. In that previous report, the drop at T_c was interpreted as resulting from an abrupt increase in the average thermal vibrational amplitudes of all four elements (Y, Ba, Cu, and O). From the separation present in the Fig. 2 data, however, it is clear that *the anomalous drop across T_c arises solely from the Cu-O rows.*

We first analyze the temperature dependence of the FWHM as was done previously,[4] i.e., assuming that the average rms thermal vibration amplitude, u_1, of each element is the same in two orthogonal directions perpendicular to the c axis. For this assumption, the half-angle of the channeling dip, $\psi_{1/2}$, is related to u_1 by[8]

$$\psi_{1/2}=0.8F_{RS}(\xi)\Psi_1, \quad (1)$$

where Ψ_1, the Lindhard[10] characteristic angle for channeling in a static lattice, is given by $[2Z_1Z_2e^2/Ed]^{1/2}$. E is the energy of the incident particle, d is the lattice spacing along the channeling direction, Z_1 and Z_2 are the atomic numbers of the projectile and target atoms, respectively, e is the electron charge, and F_{RS} is proportional to the square root of the continuum Moliere potential. Values of F_{RS} vs ξ are given by Appleton and Foti.[11] The normalized distance of closest approach is $\xi=1.2u_1/a$, where a is the Thomas-Fermi screening distance.

The values of u_1 extracted in this manner from the FWHM data using average Z_2 values of 60 and 20.6 and corresponding d values of 0.369 and 0.251 nm for the Er-Ba and Cu-O rows, respectively, are plotted as a function of temperature in Fig. 4. The estimated standard deviation is $\lesssim 3\%$ for the combined data (closed symbols), while it is $\sim 4\%$ for the Er-Ba data because of the somewhat smaller total number of counts. The effect of the two different depth intervals over which the Er-Ba and the combined data are collected is not taken into account since, as shown in Fig. 1, the depth dependence of channeling is small over this range ($\lesssim 700$ nm). The combined data are strikingly similar to those published earlier for the Y compound. Both materials show the anomalous increase of $\sim 25\%$ in u_1 between 80 and 100 K, and a further increase of $\sim 80\%$ between 100 and 300 K. As expected from the FWHM data (Fig. 3), the Er-Ba data exhibit a much weaker temperature dependence between 40 and 300 K, and show no anomaly across T_c.

The observed u_1 values can be used to estimate the lattice Debye temperature Θ_D by fitting with the expression[11]

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

Here $x=\Theta_D/T$, $\phi(x)$ is the Debye function which is tabulated by Appleton and Foti,[11] and M_2 is the atomic weight in atomic mass units. The variation of u_1 for the Er-Ba rows (Fig. 4) yields a normal pattern of increasing thermal vibration amplitude with increasing temperature. That is, Eq. (2) yields a Debye temperature of 450 ± 25 K for the Er-Ba rows at all measurement temperatures. For the two rows combined, the results are again strikingly similar to what was reported previously for $YBa_2Cu_3O_{7-\delta}$. The calculated Θ_D drops abruptly from 640 to 420 K across T_c, and then decreases still

further until at room temperature a Θ_D of 340 K is calculated. However, now that we know the change observed in the FWHM is due solely to the Cu-O rows, the necessary change in the Cu and O parameters is, of course, even larger than indicated by the above analysis. A first-order estimate of this change can be obtained as follows. First, as above, we neglect the O-O rows and note that the channeling potentials for the two strong rows are not very different. We then subtract, point by point, the normalized Er-Ba axial scan from twice the normalized combined scan to obtain $\psi_{1/2}^{\text{Cu-O}}$. Within the stated assumptions, this analysis yields a change in u_1 of the Cu and O atoms from 0.0043 to 0.0055 nm between 80 and 100 K, i.e., an almost 30% increase in amplitude for the Cu-O vibrations, and hence essentially in Θ_D (380 to 500 K), across T_c.

Clearly, while the above estimates based upon a single vibrational amplitude yield good agreement with neutron-diffraction results, as well as a simple Debye-type temperature dependence for the Er and Ba atoms, a 30% increase in vibrational amplitude for the Cu and O atoms across T_c is very large in comparison to previously reported anomalies of Debye properties across T_c, which are on the order of one part in 10^4. An alternative explanation for the large changes in channeling observed across T_c is that the displacements of the Cu and O atoms become strongly correlated in the superconducting state. Physically, the effect of such correlations on the observed channeling dips is easy to understand.[12] Lattice vibrations decrease in the FWHM of the angular scan because displaced atoms penetrate into the channeled-ion trajectory, causing dechanneling. The effect of correlated displacements is to physically shadow the penetrating lattice atoms, thereby increasing the FWHM of an angular scan. Monte Carlo computer simulations by Barrett and Jackson[12] have shown that introducing correlations obtained from neutron elastic scattering can decrease the axial width for 2-MeV He in Mo by 3%. Strong correlations can be expected to produce even larger effects. Unfortunately, such modeling requires the development of sophisticated computer codes, and results are not currently available for a multicomponent target such as $ErBa_2Cu_3O_{7-\delta}$. Nevertheless, the idea that vibrational correlations can produce the magnitude of changes observed in the present channeling studies is well established. Hence the anomalous temperature dependence found here for axial channeling scans across the Cu-O rows suggests that the atoms in the Cu-O rows become strongly coupled upon cooling through T_c.

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