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ANOMALOUS ION-CHANNELING BEHAVIOR ACROSS THE SUPERCONDUCTING TRANSITION IN HIGH-T_c MATERIALS*

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Axial channeling scans with minimum RBS yields of ≤2% were obtained for 1.5 MeV $^4$He ions incident along the c-axis in YBa$_2$Cu$_3$O$_{7.8}$ and ErBa$_2$Cu$_3$O$_{7.8}$ single crystals. Large variations in the FWHM of the (001) channeling dip were observed for temperatures between 30 and 300K. An abrupt, ~8% increase was measured as the temperature was lowered through the superconducting transition ($T_c$); the relative increase across $T_c$ in the width of the axial dip was even larger for angles of incidence less than the critical angle. A simple analytical procedure for polyatomic materials yields isotropic, average thermal vibrational amplitudes that agree well with considerably less precise neutron powder diffraction results on sintered samples.

The individual contribution to the angular channeling dip from the row of Er and Ba atoms parallel to the c-axis can be isolated in the RBS scans of the Er compound. This separation reveals normal (Debye-type) behavior for atoms in the Er-Ba row, demonstrating that the anomalous changes are due solely to atomic displacements in the Cu-O row. The large magnitude (~30% in Debye temperature) of the change found for the Cu-O row at $T_c$ suggests that the atomic displacements in this row become highly correlated in the superconducting state. New measurements using x-ray and resonance backscattering yields are presented which considerably improve the experimental statistics, and which also permit more direct identification of the contributions from the individual atomic species to the observed channeling phenomena. These new results confirm that Cu and O are responsible for the observed anomalous temperature dependence. Finally, x-ray studies using specimens with different O stoichiometries reveal that the anomalous change in the FWHM shifts in temperature in direct proportion to the change in $T_c$.

INTRODUCTION

There is considerable interest in determining the degree to which electron-phonon interactions contribute to the superconducting pairing mechanism in the class of high-$T_c$ materials denoted by (RE)Ba$_2$Cu$_3$O$_{7-\delta}$. Such a determination is complicated by the fact that only relatively small (~1x1x0.05 mm$^3$) high-quality single crystals of these materials are available.

Ion-channeling$^{1-3}$ provides a direct probe of lattice vibrational amplitudes, and is fully compatible with the restrictive geometry of the available high-quality crystals. Ion channeling in small single crystals of YBa$_2$Cu$_3$O$_{7-\delta}$ was first reported by Stoeffel et al.$^4$. Although these authors noted the importance of lower temperature studies, their measurements were confined to room temperature, perhaps because of increased damage to the specimen from the incident ion beam at lower analysis temperatures.$^5$

By substantially reducing the ion dose required to obtain statistically significant information, we have successfully extended the channeling studies of high-$T_c$ materials to cryogenic temperatures. In this paper, we briefly summarize the results from our recent ion-channeling and Rutherford backscattering (RBS) studies of YBa$_2$Cu$_3$O$_{7-\delta}$ and ErBa$_2$Cu$_3$O$_{7-\delta}$, which revealed a large anomaly across the superconducting transition in the apparent vibrational amplitudes perpendicular to the c-axis of the Cu and O atoms. We then present new x-ray and resonance backscattering results obtained at higher incident He energy. These new results offer considerably improved experimental statistics, and permit more direct identification of the contributions from individual atomic species to the observed channeling phenomena. The new results confirm that Cu and O are responsible for the observed anomalous behavior. Finally, x-ray studies are presented which demonstrate that the anomalous jump in the FWHM shifts directly with stoichiometry-induced changes in $T_c$, indicating an intrinsic correlation between the anomalous behavior and the superconducting transition.
RESULTS AND DISCUSSION

Three angular channeling scans across the c-axis of YBa2Cu307.8 acquired using 1.5 MeV 4He are shown in Fig. 1. Experimental details can be found in Refs. 6 and 7. A magnetic shielding measurement on this same crystal produced a very sharp (~1° wide) superconducting transition centered at 92.2 K. The acceptance gate for the RBS scans was located from just below the Cu leading edge to somewhat above that of O. The low minimum value (≤2%) observed for the Y-Ba-Cu RBS yield over a depth interval extending approximately 700 nm below the surface demonstrates the very high-quality of the single crystal specimen. These scans were taken first below Tc at a temperature of 81K, then above at 100K, then again below Tc, at 85K. The excellent reproducibility of the 81 and 85K scans demonstrates that beam-induced damage effects remained below the detection limit between these runs. An approximately 8% increase in the FWHM of the angular scans in Fig. 1 is seen as the sample temperature is lowered through the superconducting transition. Although it is difficult to see when plotted on the scale used for Fig. 1, the relative increase across Tc in the width of the angular scan is even larger near the bottom of the dip, i.e. for incident angles less than the critical angle.

Angular scans of similar quality were measured at several temperatures between 50 and 300K. Average thermal vibration amplitudes perpendicular to the c-axis were extracted from the FWHM of these scans using a prescription for polyatomic materials that includes Barrett's correction for thermal vibrations to the continuum model. There are four different atomic rows parallel to the c-axis in YBa2Cu307.8: one row is an alternating sequence of one Y and two Ba atoms; a second consists of one Cu atom and a Cu atom pair, separated by single O atoms; two additional rows consist entirely of O atoms, each with different interatomic spacings. The analysis neglects any contribution from the two [001] O rows because of their very weak channeling effect (low atomic number and large interatomic distances), and employs weighted averages of the atomic numbers and interatomic distances of the stronger Y-Ba and Cu-O rows. The average vibrational amplitudes, u1, perpendicular to the c-axis that were extracted in this manner are plotted as a function of measurement temperature in Fig. 2 (solid circles). The observed variation in u1 exhibits
a faster than normal stiffening of the YBa$_2$Cu$_3$O$_{7-\delta}$ lattice between room temperature and 120K, corresponding to an increase in Debye temperature of $\sim$100K. The additional 17% decrease in $u_1$ that occurs across $T_C$ suggests a further $\sim$140K abrupt increase in Debye temperature.

A comparison of our ion-channeling results for $u_1$ in YBa$_2$Cu$_3$O$_{7-\delta}$ with those obtained from a neutron diffraction study by F. Rotella et al. is included in Fig. 2. The small ($\sim$0.001 nm) shift required to overlap the amplitudes near the superconducting transition is well within the absolute experimental uncertainty of both techniques. Neutron diffraction data of similar quality by Francois et al. were interpreted as showing anomalous behavior in $u_1$ at $T_C$. However, the poor statistics characteristic of the neutron results render this interpretation moot. The much clearer evidence provided by the channeling data for a vibrational anomaly can be attributed to two factors. First, the channeling technique probes the vibrational amplitudes directly, while they represent only one of more than 30 parameters which are extracted simultaneously from the neutron data. Second, the channeling technique exploits the small but high-quality single-crystals, while the diffraction technique requires several grams of material and therefore employs less homogeneous, sintered specimens.

A second set of experiments was performed using ErBa$_2$Cu$_3$O$_{7-\delta}$ single crystals. Replacing Y by Er has essentially no effect on the superconducting properties; the crystals with Er exhibited a sharp ($\sim$1° width) superconducting transition centered at 92.8K in magnetic shielding measurements. As will be seen shortly, the average thermal vibrational properties of the two compounds also are practically identical. However, the substitution of Er (higher atomic number) for Y increases the RBS yield from the rare-earth element, and (higher atomic mass) concomitantly shifts the rare-earth signal to higher energy. The combination of higher yield and upward energy shift allows statistically significant counts to be acquired in a second, higher-energy gate that accepts counts only from ions backscattered from Er or Ba atoms. The additional gate makes it possible to isolate the contribution from the Er-Ba row to the observed channeling effects.

The values of $u_1$ extracted in this manner for the Er-Ba (open symbols) and for the combined Er-Ba and Cu-O rows (closed symbols) are plotted as a function of temperature in Fig. 3.
The high reproducibility of the data is evident in the sets of measurements taken just above, and just below, $T_c$. A smooth monotonic decrease with temperature is found for the $u_1$ values calculated for the Er-Ba row, and no anomaly is seen across $T_c$. In fact, the average thermal vibration amplitude for the Er-Ba row follows quite closely a simple Debye dependence, with a calculated Debye temperature of $450 \pm 25$ K. Clearly, the anomalous drop across $T_c$ occurs only for the atoms in the Cu-O row.

Now that we know the abrupt change observed at $T_c$ is due solely to the Cu-O row, the necessary change in the Cu and O vibrational amplitudes must be even larger than the 17% extracted from the combined signal in the YBa$_2$Cu$_3$O$_{7-\delta}$ results given above. To obtain a better estimate, we again neglect the two weak O-O rows, and assume that the measured scattering from the Er-Ba and Cu-O rows represents the average of the two rows. We then subtract, point-by-point, the normalized Er-Ba axial scan from twice the normalized combined scan, to obtain a first-order estimate of the [001] angular scan for the Cu-O row. The result of this subtraction procedure is displayed graphically in Fig. 4 for scans taken just above (100 K) and just below (80 K) $T_c$. Within the stated assumptions, this subtraction and subsequent analysis yields an estimated change in $u_1$ of the Cu and O vibration amplitudes from 0.0043 to 0.0055 nm, i.e. an almost 30% increase in amplitude, and hence essentially of $\Theta_D$ (380 to 500 K), across $T_c$.

In order to obtain more direct information concerning the behavior of the atoms in the Cu-O row, we have recently extended our channeling studies of high-$T_c$ materials to higher incident He energies. Higher energies offer two advantages: (1) resonance ($\alpha,\alpha$) reactions strongly enhance the backscattering yield for O, and (2) the cross section for Cu K$_\alpha$ x-ray production increases (by almost two orders of magnitude when going from 1.5 to 6.5 MeV He). It should be noted that although the cross section for L-shell x-ray production is typically greater than that for the K-shell, the significantly larger orbits of L-shell electrons make L x-ray measurements relatively insensitive to thermal vibrational amplitudes. It was therefore necessary to use the K-shell x-rays, despite their substantially lower cross sections.
A recent overview\textsuperscript{14} is available which describes the increased backscattering yield from O for He energies $\geq 2\text{MeV}$, and emphasizes factors relevant to ion-beam analysis of the high-$T_c$ materials. To obtain the best statistics regarding O, an incident He energy near $7.5 \text{ MeV}$ appears best. Unfortunately, the maximum He energy available from our accelerator is $\sim 6.6 \text{ MeV}$. At this energy, the O atoms generate approximately 40-50% of the backscattering signal acquired using a gate of appropriate width located below the O leading edge.

Angular backscattering scans obtained for an YBa$_2$Cu$_3$O$_{7-\delta}$ single crystal at temperatures of 80 and 100K using 6.55 MeV $^4$He are shown in Figs. 5a (Y-Ba-Cu gate located above the O leading edge) and 5b (Y-Ba-Cu-O gate located below the O leading edge). Again, we see an approximately 9% increase in the FWHM of the combined Y,Ba and Cu yield as the specimen becomes superconducting. Before comparing the scans in Figs. 2 and 5a too closely, however, it is important to note some differences to be expected at the higher He energy. First, in the continuum approximation, the FWHM is expected to be inversely proportional to the square root of the incident particle energy. The actual decrease in FWHM between Figs. 2 and 5a is about 10% larger than this. The additional 10% decrease is attributed to the fact that the acceptance gate in Fig. 5a (Y-Ba-Cu) corresponds to a depth interval centered at $\sim 5 \mu m$, compared to the significantly shallower 700nm layer for Fig. 2. Similarly, since the minimum yield is expected to vary only weakly with incident energy,\textsuperscript{15} the increase in minimum yield from $<2$ to 4-5% between Figs. 2 and 5a is also attributed to the substantially greater depth interval probed at the higher energy.

Approximately 40% of the counts in Fig. 5b are due to O atoms, where we find a correspondingly narrower FWHM and a higher minimum yield than in Fig. 5a. It should be noted that the O counts, because the acceptance gate lies just below the O surface step, are coming from a shallower depth ($\leq 1 \mu m$) than are the Y, Ba and Cu counts in the same gate. Despite the difference in analyzed depths, the relative increase in the FWHM across $T_c$ is much larger in Fig. 5b than in 5a, confirming that the O atoms are also playing a major role in the observed anomaly.

Cu K$_\alpha$ x-rays generated in the YBa$_2$Cu$_3$O$_{7-\delta}$ single crystal were also acquired during the same angular scans used to obtain the data shown in Fig 5. The cross section\textsuperscript{16} for Cu K$_\alpha$ x-ray
production drops by about 90% in going from 6.55 to 3 MeV, which corresponds to a depth about 10 \mu m below the surface. Also, the 8 keV x-rays are attenuated by 90% over the same interval of 10 \mu m.\textsuperscript{17} Hence the acquired Cu K\textsubscript{\alpha} signal corresponds to an analyzed depth of many microns.

The x-ray data for three successive scans, one below, a second above, and finally a third below T\textsubscript{c}, are displayed in Fig. 6. Again the reproducibility of successive scans is excellent, demonstrating that beam-induced damage is not significant. Even with the very large depth, the minimum yield in Fig. 6 is <10%, showing the excellent crystal quality. The FWHM of the Cu x-ray scans are within a few per cent of those obtained using the combined Cu-Y-Ba RBS signals (Fig. 5.a). This similarity is of little fundamental significance, and simply indicates that the somewhat larger channeling strength of the Y-Ba row is compensated for by the greater depth of analysis for the x-ray results. Most importantly, however, the Cu signal is isolated in the x-ray scans in Fig. 6. The large change (> 8%) in the FWHM across T\textsubscript{c} therefore confirms that the Cu atoms play an important role in the observed anomaly.

Additional Cu K\textsubscript{\alpha} x-ray scans were taken on an ErBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\delta} single crystal that had been carefully annealed to produce an O stoichiometry of O\textsubscript{6.6} (\delta = 0.4). Magnetic shielding measurements on this crystal again showed a sharp superconducting transition, but now centered at the lower temperature of 54K. Angular scans taken of this crystal at temperatures of 42, 63, 80 and 100K with 6.0 MeV \textsuperscript{4}He are shown in Fig. 7. Clearly the anomalous increase in the FWHM has shifted from ~90K to between 42 and 63K, paralleling the shift of T\textsubscript{c}. In another sample that had been annealed to produce an O stoichiometry of O\textsubscript{6}, as expected no evidence for a superconducting transition was found down to a temperature of 4K, and no anomalous jump in the FWHM was seen down to the lowest measurement temperature of 40K. These results indicate an intrinsic correlation between the observed anomaly and the superconducting transition.

**SUMMARY AND CONCLUSIONS**

Our ion-channeling studies on high-quality single crystals of YrBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\delta} and ErBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\delta} reveal substantial changes with temperature in the FWHM of [001] axial scans,
including an anomalous jump across $T_c$. Experiments on specimens prepared with different O stoichiometries, and thus different $T_c$'s, indicate an intrinsic correlation between the observed anomaly and the superconducting transition. The anomalous change is due solely to atoms on the [001] Cu-O rows. A simple analytical prescription for polyatomic materials yields average thermal vibration amplitudes that agree well with less precise values obtained from neutron diffraction studies of sintered material. This same analysis implies that an almost 30% change in Debye temperature occurs for the Cu and O atoms across $T_c$.

Although the channeling evidence for an anomaly in the displacements of the Cu and O atoms at $T_c$ is overwhelming, the implication of a large change in Debye properties at the superconducting transition clearly conflicts with previously reported changes, \(^{12,18-22}\) which are much smaller, only on the order of one part in $10^4$ or less. An alternative explanation for the anomalous jump in the FWHM across $T_c$ is that the vibrations of the Cu and O atoms become strongly correlated in the superconducting state. Physically, the consequences of such correlations on channeling scans is easy to understand. Lattice vibrations decrease the FWHM because displaced atoms penetrate into the channeled-ion trajectory, causing dechanneling. The effect of correlated displacements is to physically shadow some of the penetrating atoms, thereby increasing the FWHM of an angular scan. Monte Carlo computer simulations by Barrett and Jackson\(^{23}\) have shown that introducing correlations obtained from neutron elastic scattering measurements increases the FWHM for 2-MeV He in Mo by 3%. Strong correlations can be expected to produce even larger effects. For example, Oen\(^{24}\) has stated that nearest neighbor scattering alone can change the FWHM by 10%, which is just the magnitude found in the present studies. Oen further comments that the effect of correlations will be largest near the bottom of the angular dip, which again conforms to the present findings. For these reasons, we believe that the observed anomaly at $T_c$ indicates that the displacements perpendicular to the c-axis of the atoms in the [001] Cu-O rows become strongly correlated in the superconducting state.

A possibility exists that static atom displacements, rather than dynamic thermal displacements, are responsible for the observed anomaly. Since the velocity of MeV He ions is $\sim10^9$ cm/s,
while thermal displacement velocities are only on the order of $10^5$ cm/s, the channeled ions
experience in reality a static lattice with the atoms displaced only slightly from their equilibrium
positions. In principle therefore, even though the observed effects are clearly induced by
temperature changes, there is no way to distinguish between static and dynamic thermal
displacements using channeling of MeV ions. Egami and co-workers\textsuperscript{25} have proposed that
microdomains of small static displacements are important to the high transition temperature (105K)
of Tl$_2$Ba$_2$CaCu$_2$O$_8$, and more recently\textsuperscript{26} have suggested that similar static displacements may
occur in the superconducting state in YrBa$_2$Cu$_3$O$_{7.8}$. For static or dynamic displacements our
results, which clearly show wider axial scans in the superconducting state, imply smaller, and/or
more strongly correlated displacements, below $T_C$. 
References


FIGURE CAPTIONS

Fig. 1. [001] axial scans of YBa$_2$Cu$_3$O$_{7.8}$ acquired with 1.5 MeV $^4$He using RBS counts from Y, Ba and Cu. The first scan was taken at 81K, the second at 100K and the third at 85K. $T_c$ for this crystal is 92K.

Fig. 2. The average thermal vibration amplitude, $u_1$, plotted as a function of temperature. The values (solid circles) were extracted as described in the text from the FWHM of scans such as shown in Fig.1. Note the strong decrease between 300 and 100K, and the abrupt additional drop of $\sim$17% across $T_c$. Results (open triangles) from the neutron diffraction study of F. Rotella et al.$^{11}$ on sintered specimens of YBa$_2$Cu$_3$O$_{7.8}$ are also shown.

Fig. 3. Vibrational amplitudes in ErBa$_2$Cu$_3$O$_{7.8}$ as a function of measurement temperature (Cu-O and Er-Ba rows combined-solid circles; Er-Ba row only- open circles). Normal Debye behavior (solid line) is found for the Er-Ba vibrations. A significantly stronger than Debye dependence on temperature is found for the Cu-O row. The anomaly across $T_c$ occurs only for the Cu-O vibrations.

Fig. 4. Results of subtraction procedure used to obtain a first-order estimate of the axial scan from the [001] Cu-O row in ErBa$_2$Cu$_3$O$_{7.8}$. This estimate yields an almost 30% increase in the Cu-O vibrational amplitude across $T_c$.

Fig. 5. [001] axial scans of YBa$_2$Cu$_3$O$_{7.8}$ acquired above and below $T_c$ with 6.55 MeV $^4$He using RBS counts from (a) Y, Ba and Cu, and (b) Y, Ba, Cu and O.

Fig. 6. Cu K$_\alpha$ axial scans acquired simultaneously with the RBS information shown in Fig. 5.

Fig. 7. [001] axial scans taken for Cu K$_\alpha$ x-rays using an ErBa$_2$Cu$_3$O$_{7.8}$ single crystal that had been annealed to lower the O content to O$_{6.6}$, and hence drop the superconducting transition to 54K. Note that the shift of the anomalous jump in the FWHM directly parallels the shift in $T_c$. 
Fig. 2

- CHANNELING DATA
- NEUTRON DIFFRACTION
- ARGONNE DATA

Temperature (K)

ψ in Å
Fig. 3
Fig. 4

Normalized RBS counts (2x ErBaCu-ErBa)

Tilt angle $\theta$ (degrees)