Absence of discontinuities in ion-channeling parameters for $YBa_2Cu_3O_{7-\delta}$ thin films

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We have measured the ion-channeling minimum yield (χ_{min}) and angular width ($\Psi_{1/2}$) for Y, Ba, Cu, and O in 2000 Å (001)-oriented films of $YBa_2Cu_3O_{7-\delta}$ on MgO. The measurements mapped out a 30 K region around the critical temperature (T_c) in 1–2 K steps, and T_c was determined *in situ*. A $^{16}O(\alpha,\alpha)^{16}O$ resonance was used to study the O motions. χ_{min} increases and $\Psi_{1/2}$ decreases with increasing temperature for all elements, as expected for a smooth increase in vibration amplitude. We see no anomalous jumps in either parameter, which differs from previous reports on $YBa_2Cu_3O_{7-\delta}$ bulk single crystals. [S0163-1829(97)50802-2]

Since the discovery of high-temperature superconductors a variety of measurements have been performed to determine the structural parameters of these materials, and there have been many contradictory reports. Neutron-diffraction studies[1–3] on $YBa_2Cu_3O_{7-\delta}$ (YBCO) show no anomalies in the refined structural parameters, but Schweiss *et al.*[3] found a weak increase in a high-index diffraction line which could be simulated by a decrease of the vibration amplitude of the apical oxygen along the *b* direction below the critical temperature (T_c). Raman spectroscopy[4,5] and inelastic neutron-scattering studies[6,7] found anomalous softening of phonon modes corresponding to motion of oxygen along the *c* axis. The orthorhombic splitting (*b-a*) in YBCO measured by x-ray diffraction was found to increase anomalously near T_c in powder samples,[8] to have no anomaly in another measurement on twinned single crystals,[9] and to have a small anomalous increase in untwinned single crystals.[10] Capacitance dilatation experiments on untwinned YBCO crystals also showed an anomaly in (*b-a*), but here the anomaly consisted of a decrease in (*b-a*) near and below T_c.[11] Mustre de Leon *et al.* claimed to see a double-well potential for the apical oxygen parallel to the *c* axis,[12] but this has not been seen in several other experiments.[1,3] Finally, several recent ion channeling experiments suggest the existence of anomalies in the displacements of Cu and O atoms in YBCO and $ErBa_2Cu_3O_{7-\delta}$ (Refs. 13–15) near T_c, but results from different groups seem to be in direct contradiction. While Sharma *et al.*[13] and Remmel *et al.*[15] interpret their results in terms of an anomalous increase in Cu and O displacements as the temperature is increased through T_c, the experiments of Haga *et al.*[14] indicate an anomalous decrease in displacements at the superconducting phase transition. Furthermore, neutron resonance absorption spectroscopy measurements showed an anomalous decrease in the momentum of the Cu atoms in the *a-b* plane of $Bi_2Sr_2CaCu_2O_8$,[16] but there was no evidence for such anomalies in YBCO.[17] We have therefore used high quality crystalline *c*-oriented thin films for a more detailed investigation of this controversy. While there is a slight compromise in the crystalline quality of thin films

in comparison with bulk single crystals, there are also distinct advantages to the use of thin crystals in channeling measurements, as we describe below. Furthermore, we have focused our measurements on the region around T_c to investigate in greater detail the anomalies reported by other groups. Thus we have mapped out a 30 K region around T_c, measuring the ion-channeling minimum yield (χ_{min}) in 1–2 K steps and the angular width ($2\Psi_{1/2}$) of the channeling dip at three temperatures above and three temperatures below T_c. Our experiments differ from previous works in the much higher temperature resolution (± 1–2 K).

In ion-channeling experiments positive ions impinge on a crystal near a low index direction, and a detector, placed at a large angle ($>90°$) with the incident beam direction, monitors the backscattered particles. The channeled yield is obtained with the ion beam aligned along a low index direction to give the maximum channeling effect (a dip), while the random yield is obtained with the beam misaligned to extinguish the effect due to any plane or axis. χ_{min} for a particular crystal direction is the ratio of these yields. $2\Psi_{1/2}$ is the full width at half maximum of the channeling yield dip obtained from a complete angular scan through the crystallographic direction. For an increase in the static or dynamic atomic displacement amplitude perpendicular to the incoming beam direction, χ_{min} increases while $\Psi_{1/2}$ decreases.[18]

There are several advantages to the use of high quality crystalline thin films as opposed to the thick bulk samples used in several previous reports.[13,14] The right combination of film thickness, beam energy, and detector angle allows for separation of the backscattered signals from Y, Ba, and Cu (see Fig. 1), thus enabling determination of χ_{min} and $\Psi_{1/2}$ for each element individually. This is not possible with bulk single crystal YBCO, since the signals from the different elements overlap. In our films the signal from O falls on top of the larger substrate signal, making analysis of the O yield difficult, but we took advantage of a $^{16}O(\alpha,\alpha)^{16}O$ resonance[19] to increase the O yield. An additional advantage of using thin films is that the superconducting phase transition can easily be monitored by resistance measurements.
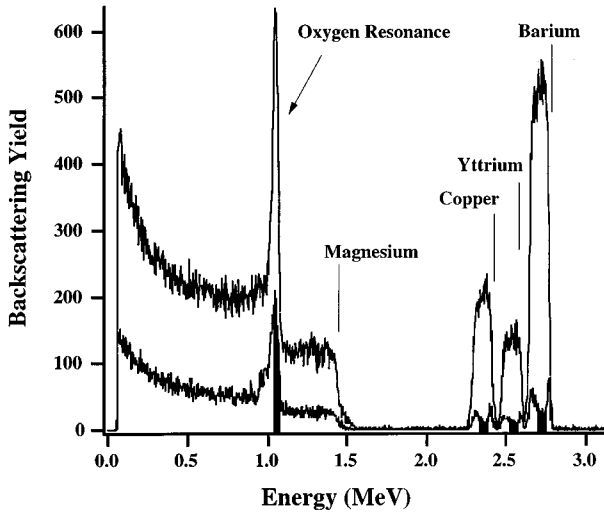

FIG. 1. Typical random and $\langle 001 \rangle$ aligned spectra of 3.1 MeV $^4\mathrm{He}^{2+}$ ions backscattered from a 2000 Å YBCO film on MgO. Backscattering yields were integrated in the shaded regions indicated in the figure.

This allows for beam damage calibration before the experiment, as well as accurate determination of T_c during the experiment, both of which are new aspects of our measurements.

We used 2000 Å high quality, c-axis-oriented YBCO films that were grown on (001) MgO by 90° off-axis sputtering.[20] The growth procedure has been described in detail elsewhere.[21] The films typically have $T_c \sim 84-89$ K and transition width $\Delta T < 1$ K, and they give ion-channeling $\chi_{\min}$ of about 3% immediately behind the Ba surface peak, as can be seen from channeled and random spectra in Fig. 1. The channeled yield increases near the interface with the substrate as a consequence of the film growth procedure.

Beam damage to our sample was minimized by using a 150 mm^2 annular surface barrier detector placed only 2 cm from the sample and a 2 mm aperture attached to the back of the detector (which insured beam collimation to <0.05°). A special electron suppression grid was placed between the sample and detector for accurate beam normalization. To avoid subtle errors in normalization we made sure that the collection time for different points did not deviate by more than 2%.

The sample alignment was monitored with a laser during the experiment. The sample moved slightly when the goniometer was cooled, so at each temperature of the $\chi_{\min}$ measurement we checked the laser reflection off the sample surface and adjusted the goniometer if necessary. This procedure insured alignment to within 0.004°.

By using a beam energy of 3.1 MeV, which is slightly higher than the 3.045 MeV $^{16}\mathrm{O}(\alpha,\alpha)^{16}\mathrm{O}$ resonance energy, we could excite the 40 keV wide resonance for oxygen atoms in the middle region of the film. It was important to keep the beam energy constant and avoid ice buildup on the surface in order to probe the same depth region at each temperature.

Prior to the channeling measurements, we evaluated the effects of ion-beam damage on the superconducting phase transition of our films. The crystals were irradiated with 3.1

MeV $^4\mathrm{He}^{2+}$ along a random direction and resistivity versus temperature near $T=89$ K was determined. A two point probe was sufficient for the resistance measurement, since exact values of the resistivity were not needed. A beam dose of 13 μC/mm^2 changed T_c and ΔT by less than 0.3 K, while an accumulated dose of 107μC/mm^2 increased the width by ~ 1.5 K and lowered T_c by ~ 1 K. The damage created in the crystal under channeling conditions is smaller by a factor of $1/\chi_{\min}$ (1/20 to 1/10 in our case). For the $\chi_{\min}$ measurements we could therefore use 1 μC per datapoint, thus enabling a relative uncertainty in $\Delta \chi_{\min}/\chi_{\min}$ of less than 2.5% for all elements, and still use less than 10 μC/mm^2 for a data set of 22 points. The six datapoints of the $\Psi_{1/2}$ measurement added less than another 7μC/mm^2 to the total accumulated charge for the irradiated spot. We can compare this dose to that used in the experiments of Sharma $et\ al.$ They used 400 nC before changing irradiated spot. With a beam spot size of $(0.5\ \mathrm{mm})^2$ and a beam energy of 1.5 MeV, this scales to a dose of 6.8 μC/mm^2 at our beam energy of 3.1 MeV (scattering cross section $\propto 1/E^2$), which is a factor of 2.5 smaller than ours. However, while Sharma $et\ al.$ were performing angular scans, most of our beam was incident under channeling conditions, in which the scattering probability, and thereby the damage, is greatly reduced. Our total dose per sample spot was therefore comparable to that of previous measurements on bulk samples. An additional advantage of thin films is the fact that most of the damage is created in the substrate and not in the film itself. In the previous bulk measurements, the integration region extended farther into the sample where damage due to channeling and increased nuclear stopping power is more prevalent. We therefore did not change samples or irradiated region on the sample for a complete data set of $\chi_{\min}$ and $\Psi_{1/2}$, as was done in previous work.[13]

Furthermore, the effect of radiation damage on the $\chi_{\min}$ of our films was evaluated in the following way. Each experiment was divided into two runs. The first run began at the lowest temperature and $\chi_{\min}$ was measured at 11 points of increasing temperature. The second run started at a high temperature and $\chi_{\min}$ was measured at 11 points of decreasing temperature. Finding the same value for $\chi_{\min}$ at the beginning and end of the two runs, we could rule out any changes in $\chi_{\min}$ due to crystal damage.

Figure 2 shows the results of the $\chi_{\min}$ measurements. It is clear from the plot that there are no anomalous jumps in $\chi_{\min}$ for Y, Ba, Cu or O in the vicinity of T_c. The step shown in Fig. 2 represents the anomalous jump in $\chi_{\min}$ reported in Ref. 14 but to our knowledge never reproduced. $\Psi_{1/2}$ was measured on the same sample spot after the $\chi_{\min}$ experiment. Angular scans were performed at three temperatures below and three temperatures above T_c. Each scan consisted of 24 points, and each point required a 0.1 μC of beam dose. The tilt plane was at 10° with the (100) plane. A random spectrum to normalize the data was obtained as the last step (azimuthal angle was continuously rotated during acquisition to avoid artifacts from any plane or axis). Our $2\Psi_{1/2}$ data are shown in Fig. 3 along with the step as reported by Sharma $et\ al.$[13] between 85 and 100 K. We see no jumps of this size in the width of the rocking curve at or near T_c, only a gradual change indicating a smooth increase in vibration amplitude. Figure 4 shows typical rocking curves for all ele-
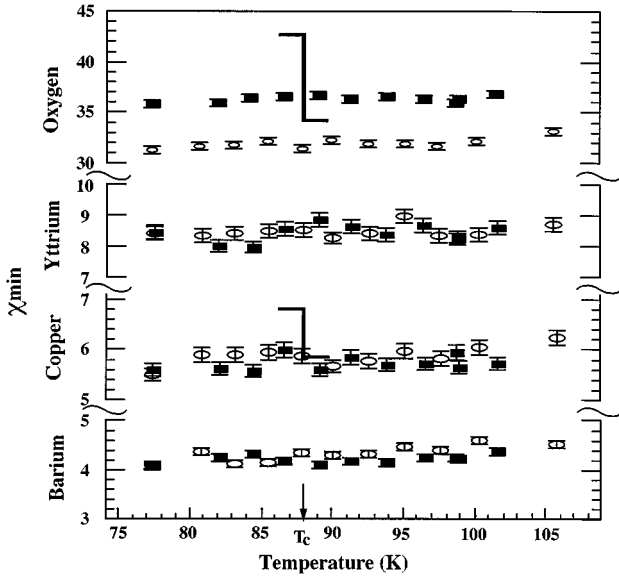
FIG. 2. χ_{min} versus temperature for O, Y, Cu, and Ba in YBCO. The O yield from the two runs are different because the runs were performed on different days and so the beam energy was slightly different. The errors are evaluated from counting statistics. The steps indicated on the oxygen and copper data are taken from Ref. 14.

ments. The curves are smooth and symmetric, indicating a scan straight through the axis without the influence of any plane.

Our Cu $2\Psi_{1/2}$ data show a smooth increase between 79 and 98 K with a slope of $0.0022(5)°/K$. For comparison, Sharma *et al.*[13] report a step in the combined Y-Ba-Cu $2\Psi_{1/2}$ of $0.15°$ between 85 and 100 K for a beam energy of 1.5 MeV, which scales to a slope of $0.0070°/K$ at 3.1 MeV ($\Psi_{1/2} \sim 1/E$), or ~ 3 times larger than our slope. Our data therefore neither support the interpretation of a step, nor the large change in $\Psi_{1/2}$ between 85 and 100 K measured by Sharma *et al.* However in this experiment it was not possible to distinguish the contributions from the different elements. The step in $2\Psi_{1/2}$ was later contributed to atoms in the Cu-O row in an experiment on $ErBa_2Cu_3O_{7-\delta}$. They found that the change in the Er-Ba yield is small and the corresponding change in the Er-Ba-Cu yield was large, leading to the conclusion that the anomalous step is due to the Cu atoms. Our experiments enable an individual determination for all the elements in YBCO and give a different picture. Our measured slopes in $2\Psi_{1/2}$, $0.0023(15)°/K$ for Y, $0.0035(4)°/K$ for Ba, and $0.0038(10)°/K$ for O, are all larger than for Cu.

The reason for this discrepancy may possibly stem from the different depths sampled in the two experiments. In the bulk single crystal experiments data are obtained from deeper in the crystal. It is possible that enhanced sensitivity to atomic motions is obtained as a result of accumulated dechanneling effects. Were this the case, a simple analysis of the anomaly in terms of $\Psi_{1/2}$ or χ_{min} would be unreliable and yield a large overestimate of the vibrational amplitude jump.

Remmel *et al.*[15] measure an average change in $2\Psi_{1/2}$ for Cu in one YBCO film and Y-Ba-Cu in three single YBCO crystals of about $0.112°$ over a 30 K region (using 2 MeV He^+). If one does not assume a step (as was done) between these two temperature points, but rather a slope, their experi-
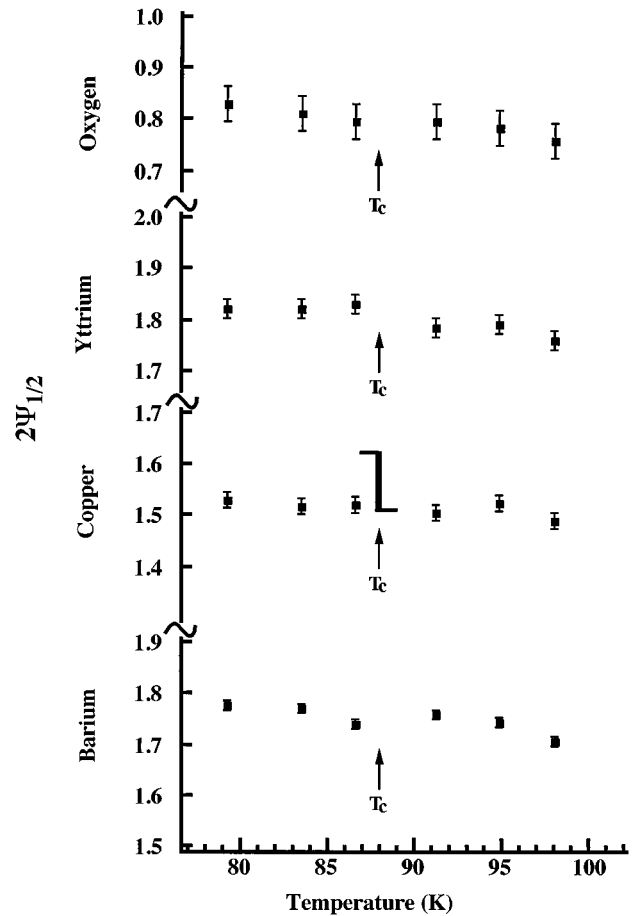

FIG. 3. $2\Psi_{1/2}$ versus temperature for Cu, Ba, O, and Y in YBCO. The errors are evaluated from counting statistics. The step indicated on the copper data is taken from Ref. 13.

ment gives a slope of $0.0037°/K$, which scales to $0.0030°/K$ at 3.1 MeV and is only 1.3 times our value. Our data are therefore consistent with theirs, but due to the much finer temperature resolution of our experiment we rule out a discontinous step change in our films. Comparing the Y-Ba data, we find that our measured value for the slope of $\Psi_{1/2}$ is about twice their value.

The oxygen measurement may be more interesting since they conclude from calculation and experiment that most of the suggested anomaly in the Cu and O parameters may be due to anomalous displacements of oxygen. They measure a change in $2\Psi_{1/2}$ of $0.050°$ for oxygen over a 25 K region. Again comparing the slope from their measurement, $0.002°/K$, to ours, we find that ours is twice as large. In the complementary measurement of χ_{min}, we find an oxygen slope of $0.03(1)/K$ which is considerably smaller than the $0.1/K$ estimated from data in Ref. 15. A more recent experiment by another group[22] does not confirm such a large change of the oxygen displacement amplitude at T_c.

Tilt plane might have an effect on the magnitude of the changes in these parameters. Nevertheless our χ_{min} and $2\Psi_{1/2}$ data indicate that there are no abrupt steps in the vibration amplitudes or static displacements. However, it is difficult to tell whether the slope of χ_{min} or $\Psi_{1/2}$ with temperature is anomalous since neither experiment on thin films has mapped out the temperature dependence of the channeling parameters in a larger region from a temperature much
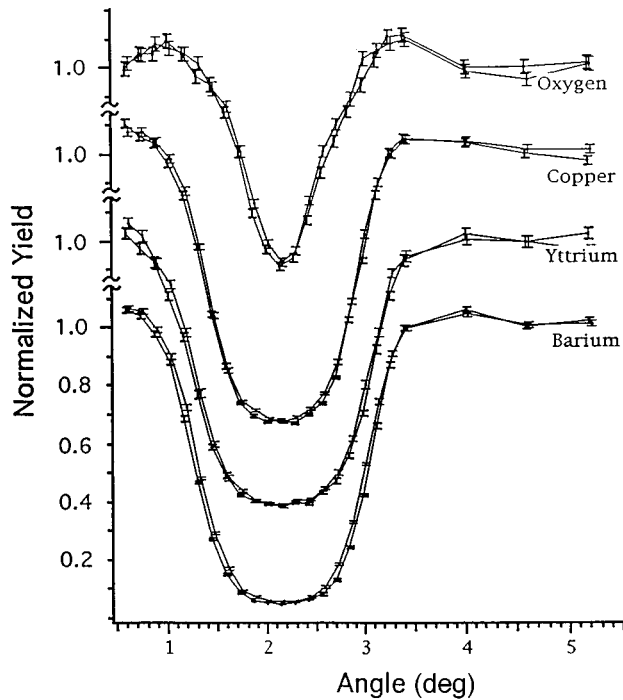
FIG. 4. Typical rocking curves for Y, Ba, Cu, and O for the highest and lowest temperatures.

below T_c up to room temperature.

In order to compare the experiments discussed above, it is important to consider the crystal quality. Bulk single crystals are inherently better than thin films since they are not strained by matching to the substrate lattice. The crystals of Sharma *et al.* have nominal χ_{min} of $\sim 2\%$, while χ_{min} over the full integration region can be higher [up to 4% (Ref. 13)]. Our films have χ_{min} 3% behind the surface peak, while χ_{min} for the integration regions used for the Y-Ba-Cu sublattices ranges from 4% to 9%. However, it is not clear if the larger intrinsic χ_{min} of the thin films could mask any anomalous effects. On the other hand, our thin films give a larger $\Psi_{1/2}$ (1.6° as compared to 1.5° after energy scaling for bulk single crystals[23]); a larger $\Psi_{1/2}$ is usually related to better crystallinity. One might speculate that thin films would be more prone to radiation damage due to the presence of strain and surface effects, but we found no evidence for radiation damage in the χ_{min} measurements. In addition, an important factor is the change in crystal quality induced by the beam during a measurement. Given the much larger integration region used in the bulk crystal experiment, the channeling parameters measured in those experiments may be more affected by induced crystal damage as discussed previously. The question remains if the anomalies observed are sample dependent, or if there is an inherent difference between films and bulk single crystals. It would therefore be advantageous to perform more measurements on YBCO films grown on other substrates and on other bulk single crystals since the crystals used by Sharma *et al.* contain Au impurity atoms that sit on Cu sites [about 1.7% of the Cu atoms are replaced by Au (Ref. 22)]. It is not clear what effect these Au atoms might have on the channeling parameters.

Our observation of no anomalous jumps due to dynamic vibrations is supported by neutron resonance absorption spectroscopy measurements on large oriented YBCO crystals. In these experiments the Doppler broadening of a neutron absorption resonance, induced by the momentum distribution of Cu atoms, was measured as a function of temperature. No anomalies were observed from 10 to 300 K for motions in the *a-b* plane.[17]

In summary we have mapped out the temperature dependence of the ion-channeling χ_{min} and $\Psi_{1/2}$ in a 30 K region around T_c to probe for any anomalies in the structural parameters of YBCO. Neither measurement shows any discontinuities near the superconducting phase transition. These experiments have been repeated several times on different samples, and none of the experiments have indicated vibrational discontinuities near T_c. From our results we therefore have no reason to expect anything but a smooth increase in atomic vibrations for YBCO thin films in this region.

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