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Ion-channeling anomalies at the superconducting transition temperature in single-crystal $YBa_2Cu_3O_{7-y}$

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The temperature dependence of the Rutherford backscattering in the ⟨001⟩ axial channeling mode for each constituent atom of single-crystal $YBa_2Cu_3O_{7-y}$ has been carried out to study a change in the structural properties at the superconducting transition. Anomalies of channeling behavior observed across the superconducting transition temperature suggest a structural instability or a change in the lattice. The anomalies of channeling for Y and Ba atoms suggest the phonon softening, while those for Cu and O atoms are not explained in terms of only the phonon softening, but probably indicate complicated lattice dynamics of Cu and O atoms.

The greatest interest in the recently discovered high-temperature superconductors is whether they represent a class of materials in which a new pairing mechanism produces superconductivity. It is therefore important to identify any unconventional behavior in comparison with ordinary superconducting behavior. It is generally accepted that at superconducting transition temperatures T_c's, the lattices and their properties are essentially unchanged, while some of the properties of the conduction electrons are changed significantly. However, in high-T_c superconductors, much anomalous behavior associated with the lattice properties have been reported by several researchers. For example, the elastic anomalies that cannot be explained within a BCS model have been observed at and below T_c of $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$ (Refs. 1–3) and the c axis of $YBa_2Cu_3O_{7-y}$ exhibits an anomalous change in a narrow temperature range near T_c.[4] These results suggest that the superconducting transition in high-T_c superconductors drives or is driven by a change in the lattice properties.

It is known that the axial ion-channeling mode in Rutherford backscattering spectroscopy (RBS) is highly sensitive to lattice vibrations and small lattice displacements from regular lattice sites. From the normalized minimum yield in the axial channeling χ_{min}, rms amplitude of the lattice vibration and displacement of atoms can be derived. Therefore, the channeling technique is very useful for studying phase transitions, (such as Jahn-Teller[5] and charge-density-wave phase transitions[6,7]), which are accompanied by a structural change.

In the present paper we report the first measurement of χ_{min} of ⟨001⟩-aligned channeling for each constituent atom of $YBa_2Cu_3O_{7-y}$ for temperatures down to 50 K through the superconducting transition. The temperature dependence of the χ_{min} was found to be conventional in the normal state but very anomalous in the vicinity of T_c. It is argued below that the anomalous change in χ_{min} near T_c is probably due to the anomalous vibration or displacement of the lattice.

$YBa_2Cu_3O_{7-y}$ single crystals were grown by the flux method.[8] Two single crystals with typical dimensions of $2\times2\times0.1$ mm^3 were used for the ion-channeling measurement. Their T_c's were determined to be 90 and 91 K from resistivity measurements.

A standard experimental arrangement for ion backscattering was used with a Van de Graaff-type ion accelerator. The 1.00-MeV He^+ and D^+ ions were used as probe beams. The diameter and the divergence of the ion beam were 1.0 mm and 0.03°, respectively. The sample was set at a position where a beam direction was aligned with a channel axis of the sample by a three-axis goniometer and the sample was cooled down slowly with cryorefrigeration. It was confirmed at several points that the incident direction of ions paralleled the crystal axis. The temperature of the sample was measured by a Si-diode

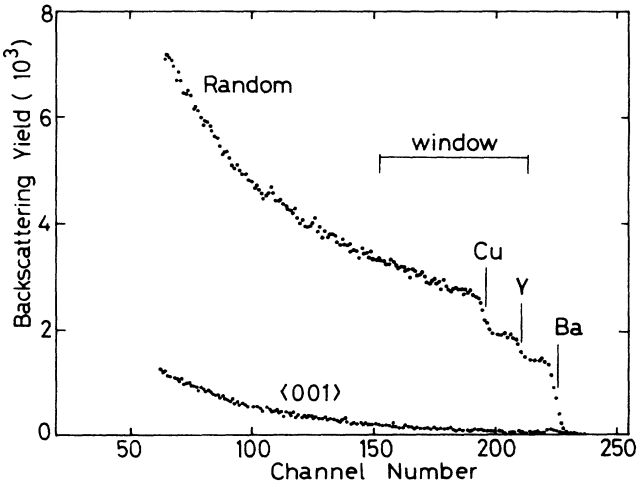

FIG. 1. ⟨001⟩-aligned and random RBS energy spectra of single-crystal $YBa_2Cu_3O_{7-y}$ taken at room temperature with 1.00-MeV He^+ ions.

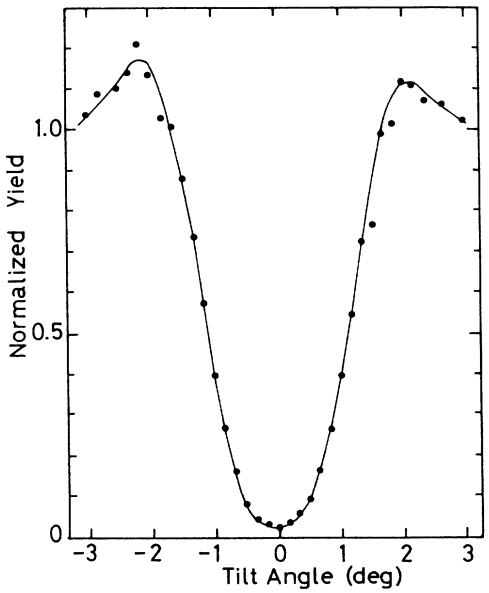

FIG. 2. RBS yields as a function of tilt angle. The RBS yield is measured within the energy window marked in Fig. 1 and normalized to the random yield.

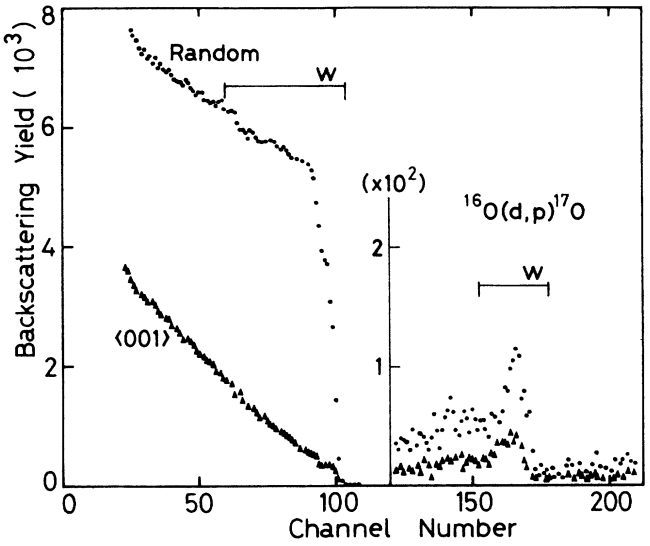

FIG. 3. Typical spectra for RBS and high-energy protons taken by 1.00-MeV D^+ ion beam at room temperature. *W*'s indicate energy windows.

thermometer attached to the bottom of the sample and was controlled within ± 0.1 K with the aid of an additional small heater on the sample holder. In the actual experiment, we paid special attention to the ion fluence in order to minimize the radiation damage of the sample.[6,9] The total ion fluence for one sample was restricted within ~ 400 nC/1.0 mm ϕ.

The results of ion channeling for two single crystals were substantially the same. Figure 1 shows typical RBS energy spectra at room temperature obtained by using the He^+ ions. For RBS and nuclear-reaction (see Fig. 3) experiments, a Si-surface-barrier (annular type) detector was used. (The active area, the scattering angle, and the distance between a sample and the detector are 50 mm^2, 174°, and 35 mm, respectively.) In this figure, one spectrum is the channeling one along the ⟨001⟩ axis, and the other is the random spectrum ($\sim 5°$ off the channeling axis). The magnitude of the RBS yield along the ⟨001⟩ direction is extremely smaller than that of the random direction. Moreover, the normalized RBS yields obtained within the energy window marked in Fig. 1 are shown as a function of the tilt angle in Fig. 2. From these measurements, the normalized minimum yields along the ⟨001⟩ directions are determined to be of the order of 0.03, which is in good agreement with the results of the ion channeling in $YBa_2Cu_3O_{7-y}$ reported already.[9,10] These facts indicate that the samples used in the present work are very high-quality single crystals.

Furthermore, to obtain the clearly distinguished information on each element of $YBa_2Cu_3O_{7-y}$, we used particle-induced x-ray emission (PIXE) and nuclear-reaction methods with 1.00-MeV D^+ ions. For PIXE experiments, a Si (Li) solid-state detector was used. (The active area, the scattering angle, and the distance between a sample and the detector are 30 mm^2, 150°, and 25 mm, respectively.) Figure 3 shows the ⟨001⟩-aligned energy spectrum and the random one for RBS and high-energy protons. Here, the high-energy protons were produced by the nuclear reactions. The information of the O atoms was determined by the nuclear reaction. Figure 4 shows the ⟨001⟩-aligned and the random characteristic x-ray spectrum for Y, Ba, and Cu atoms obtained by the PIXE method.

Figure 5 shows the temperature dependence of $\chi_{min}(T)$ measured by the D^+ ion beam, where χ_{min} is defined within the energy window marked in Fig. 3. This result was obtained for one sample, and the result for another sample was also substantially the same. Here, we may note that χ_{min}'s obtained by D^+ ions are larger than the

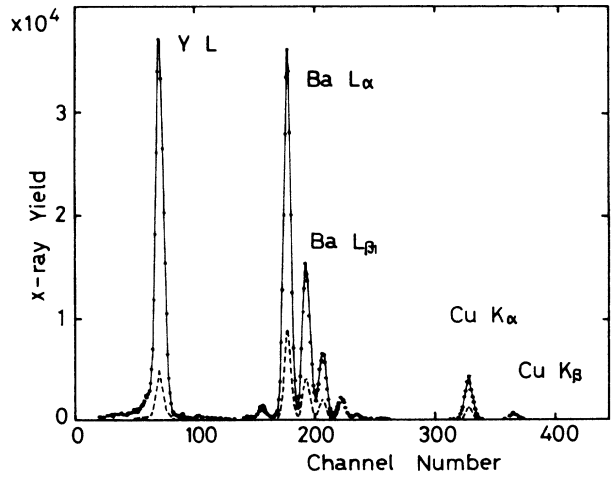

FIG. 4. ⟨001⟩-aligned and random PIXE spectra for Y, Ba, and Cu obtained at room temperature with 1.00-MeV D^+ ions. The dashed line indicates the ⟨001⟩-aligned spectrum.

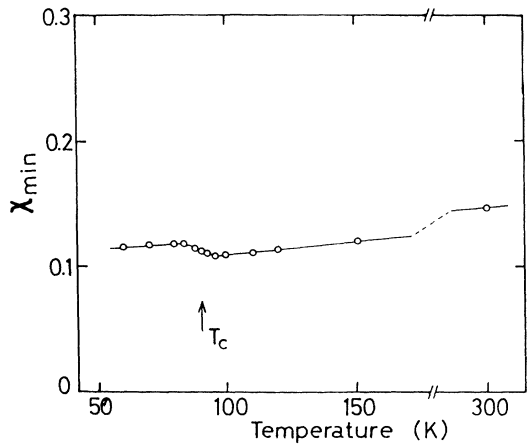

FIG. 5. Normalized minimum yield χ_{min} of RBS taken with D^+ ions as a function of temperature. T_c indicates the superconducting temperature determined by resistivity measurement. The data points were taken with descending temperature.

value determined by He^+ ions as shown in Figs. 1 and 2. The disagreement is mainly due to the difference of the effective width of energy windows defined in each experiment. In other words, the region measured by D^+ ions is much wider than the one observed by He^+ ions with the same energy, and the extrapolated χ_{min} value at the surface is similar to the one obtained by He^+ ions. Thus, the disagreement is not essential. The χ_{min} decreases monotonically with decreasing temperature, which is similar to the typical temperature dependence of χ_{min} of a conventional solid. However, at near T_c the χ_{min} increases rapidly and then decreases gradually as temperature decreases. Thus, the abrupt increase in χ_{min} is observed across T_c.

According to Barrett's equation,[11] χ_{min} for a monatomic lattice is given by the atomic density of the sample and the rms amplitude square of the lattice vibration of the atoms in the plane normal to the channeling axis. In the case of crystals that consist of many different atoms, the expression for χ_{min} is much more complicated but Barrett's equation can still be used as a guiding principle for searching the fundamental process. It is widely accepted that unless any structural transition occurs, χ_{min} is proportional to the rms amplitude square of the lattice vibration. Therefore, it can be concluded that the decrease in χ_{min} with decreasing temperature in the normal state of $YBa_2Cu_3O_{7-y}$ is due to the decrease in the rms amplitude of the thermal vibration; a stiffening of the lattice is observed while the increase in χ_{min} observed near T_c cannot be interpreted in terms of such a thermal vibration of atoms.

The magnitude of χ_{min} depends on not only the rms amplitude of the lattice vibration but also the lattice displacements of the atoms. As a possible mechanism of the increase in χ_{min} with decreasing temperature, the structural change or the softening of the phonon that is related to the structural instability have generally been taken. In fact, it is known that in the Jahn-Teller transition[5] the gradual rise of χ_{min} revealed just above the transition temperature is due to the phonon softening and in the charge-density wave phase transition[6,7] the enormous rise in χ_{min} at the transition temperature is caused by the displacement of atoms from regular sites of the high-temperature phase.

Figure 6 shows the temperature dependence of the χ_{min} for each constituent atom of $YBa_2Cu_3O_{7-y}$ obtained by the PIXE and nuclear reaction methods with 1.00-MeV D^+ ions. In the normal state, the χ_{min}'s for all constitute atoms monotonically decrease with decreasing temperature; these features are explained in terms of the lattice stiffening. However, in the vicinity of T_c, the temperature dependence of χ_{min} for each atom is very curious, especially those for Cu and O atoms. χ_{min}'s for Y and Ba atoms exhibit the abrupt rise of χ_{min} with decreasing temperature, which is almost the same as the results of RBS shown in Fig. 5. The behavior is probably interpreted in terms of the phonon softening or the small displacement of atoms, while those for Cu and O atoms begin to reveal the increase or decrease at temperatures above T_c and large up and down changes in the χ_{min}'s are observed with decreasing temperature. These enormous changes in the χ_{min}'s of Cu and O atoms observed in a narrow temperature range are not simply explained in terms of the phonon softening or the small displacement of atoms, which indicate the complicated lattice dynamics of Cu and O atoms. Here, it should be noticed that Sharma *et al.*[9,12] also observed the abrupt change in the width of the ⟨001⟩ channeling dips at T_c. However, our interpretation does not agree with theirs. Though the origin of this discrepancy is unclear at this moment, we think that sensitivity of χ_{min} to all types of defects, disorder, etc. is better than that of the width of a channeling dip.

Anomalous behavior of Cu and/or O atoms in $YBa_2Cu_3O_{7-y}$ have been observed near T_c on other measurements also; the Debye-Waller factor for the O atoms per-

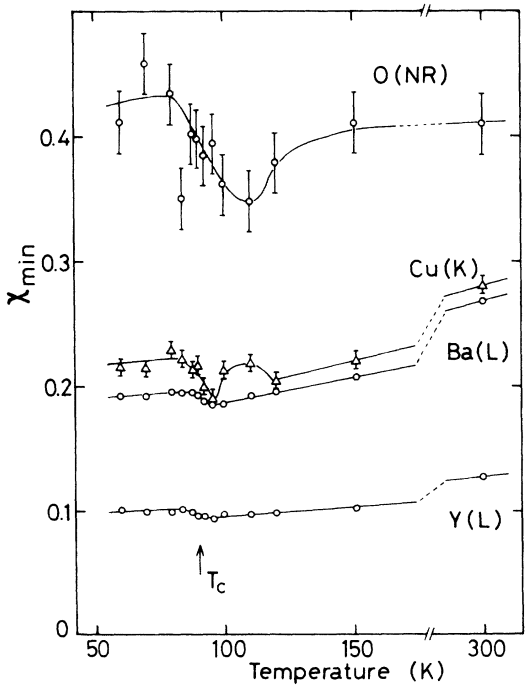

FIG. 6. χ_{min}'s for each element obtained by PIXE and nuclear-reaction methods as a function of temperature.

pendicular to the c plane obtained from the extended x-ray-absorption fine-structure method[13] and the breathing-mode vibration of O atoms around Cu atoms determined from the Raman scattering measurement.[14] Furthermore, the measurement of the neutron diffraction exhibits the discontinuous change of the Cu—O bond length perpendicular to the c plane at T_c (Ref. 15) and that there is the difference in the occupancy ratio of O atoms in the chain site between the normal and superconducting states.[16] These results, including the present one, strongly suggest that a change in the lattice dynamics of Cu and/or O atoms occurs in the vicinity of T_c.

It is known that the Cu and O atoms play an important role in the mechanism of the superconductivity in high-T_c compounds, while Y and Ba atoms mainly contribute to the crystal bonding, but do not directly relate to the superconductivity. Therefore, it is very interesting whether the structural anomalies observed in $YBa_2Cu_3O_{7-y}$ have implications for the mechanism of superconductivity. In order to make clear the correlation between the superconducting state and the anomalies of χ_{min}'s, further analysis on the temperature dependence of χ_{min}'s is in progress on single crystals of high-T_c compounds.

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