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Structural anomalies in the oxygen sublattice of $YBa_2Cu_3O_7$ and $EuBa_2Cu_3O_7$ at T_c

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Temperature-dependent ion-channeling experiments with He ions were performed on Y-Ba-Cu-O single crystals and *c*-axis or *a*-axis oriented Y(Eu)-Ba-Cu-O thin films. Angular yield curves (scans) were measured above and below T_c in the different sublattices. For both, [001] and [100] crystal directions anomalous changes in the scans with respect to their halfwidths $\Psi_{1/2}$ and minimum yield values $X_{\min}$ were observed in the oxygen sublattice by cooling below T_c. In [001] direction also $\Psi_{1/2}$ in the scan from Cu revealed an anomalous increase at T_c. No special effect was observed in the Y(Eu)-Ba sublattice. The observations are discussed in terms of structural distortions above T_c which are removed upon cooling into the superconducting state. The values of the displacement amplitudes were determined in Monte Carlo simulation calculation fitting the experimental data. The main effects are displacements of the apical oxygen atoms of 3.5 pm and of 1.5 pm in the remaining oxygen sublattice.

Several experimental observations have been reported indicating structural anomalies in the high-T_c superconductors which are obviously linked to the transition from the normal into the superconducting state. Sharma, Rehn, and Baldo[1] observed in channeling experiments a rather abrupt change in the width of the angular yield curve in Y-Ba-Cu-O at T_c which they attributed to a decrease of the Cu vibration amplitude of about 1 pm. From additional results of neutron-scattering measurements Sharma *et al.*[2] concluded that the channeling anomaly is not due to an overall reduction of the average Cu vibration amplitude but probably arises from a correlated sequence of Cu and apex oxygen atom O(4) displacements forming in the superconducting state. Recent neutron diffraction experiments revealed an anomalous intensity increase below T_c of a high-indexed diffraction line which was tentatively attributed to a decrease of the O(4) vibration amplitude in *b*-axis direction.[3] Dilatation experiments showed an anomalous behavior of the thermal-expansion coefficients at T_c in the *a*- and *b*-axis directions reducing the orthorhombicity of the structure.[4] Anomalies in the axial and equatorial Cu—O bonds at T_c, which are related to the behavior of the apex oxygen, have also been observed in Y-Ba-Cu-O in extended x-ray-absorption fine-structure measurements.[5] These results indicate already that the apex oxygen atoms may play an important role in the observed anomalies. In addition, from the theoretical point of view it is claimed that the position of the energy level of O(4) essentially governs the magnitude of T_c.[6] Moreover, the importance of the presumably anharmonic coupling of the pyramidal apex oxygen motion along the *c* axis and its consequences on the isotope effect have been discussed in detail by Müller,[7] where also the related experimental and theoretical literature is reviewed. Displacements of the apex oxygen in the *c* direction can well be observed by ion channeling along the [100] direction in *a*-axis oriented thin films.

In order to get direct experimental information on possible temperature-dependent anomalies in the oxygen sublattice of the "1:2:3" structure we used He ion channeling and applied the $^{16}O(\alpha,\alpha)^{16}O$ resonant scattering at 3.05 MeV for oxygen detection. The experiments have been performed on Y-Ba-Cu-O single crystals and Y-Ba-Cu-O or Eu-Ba-Cu-O *c*-axis and *a*-axis oriented thin films. High growth quality *a*-axis films were prepared in a template procedure.[8] The angular yield curves for oxygen were obtained by measuring the resonance yield as a function of the tilt angle between the incident ion beam and the crystal direction normalized to the yield for random incidence applying background correction.[9] Angular yield curves were also taken in energy regions corresponding to scattering from the metal atoms sublattices. In thin films with thicknesses around 100 nm the signals from Cu could be completely separated from those of Y, Eu, or Ba. The angular yield curves for the different sublattices are characterized by the critical angle $\Psi_{1/2}$ which is the half-width at half-maximum of the scan curve, and the minimum yield value $X_{\min}$ which is the normalized yield for perfect alignment. Both parameters are correlated with the displacement amplitudes of the atoms with a sensitivity of about 0.1 pm. For channeling along the [001] direction (*c* axis) the ions are guided along the string potentials of mixed rows of Ba_2Y and $Cu(1)Cu(2)O(4)_3$, and two weak oxygen rows $O(1)O(2)_3$ and $O(2)_2$. In this direction a mutual influence of one kind of atoms on the scan curve of another kind is possible. A higher sensitivity for displacements of the apical oxygen atoms is expected for [100] axial channeling (*a* axis), because in this direction O(4) atoms form separate rows and no mutual effects by displacements, e.g., of Cu atoms will occur. The channeling measure-

ments have been performed with He-ion energies of 2 and 3.06 MeV at various temperatures above and below T_c. In order to keep radiation damage by the analyzing beam as low as possible a large area annular detector with a solid angle of 0.37 sterad was used in the experiments. This allowed a reduction of the accumulated charge per scan to 200 nC, and the total fluence in an experiment for the measurements above and below T_c corresponded to a damage level of about 3×10^{-4} displacements per atom (dpa). At dpa values more than 1 order of magnitude above this level no structural changes due to radiation damage were observed in channeling measurements. Monte Carlo simulation calculations have been performed to reproduce the experimental channeling data applying appropriate displacement models.

The results of 2-MeV, He^+ channeling measurements in [001] direction on three single crystals and one *c*-axis oriented thin film are summarized in Fig. 1. Here the increase of the critical angle $\Delta\Psi_{1/2}$ by cooling below T_c (temperature difference of the measurements was about 30 K) is displayed for the different metal atom sublattices. No special effect and values close to those expected for a pure Debye behavior in the applied temperature range were observed in the Y-Ba sublattice, while an anomalous increase occurred in the total Y-Ba-Cu or in the separately measured Cu sublattice in the thin film. The latter effect is therefore ascribed solely to the Cu sublattice. The average increase of 6% is close to the value of 7% reported by Sharma *et al.*[10] The scattering of the data in Fig. 1, which was even more pronounced in our 3.06-MeV measurements (average increase in $\Psi_{1/2}$ of 5% in the Cu sublattice) probably is due mainly to the dependence of the anomaly on the tilt plane in the scan measurements. An influence of the tilt plane on the changes of $\Psi_{1/2}$ by atomic displacements has also been demonstrated in Monte Carlo simulation calculations. In addition, it cannot be excluded that a different quality of the samples under investigation may influence or in some cases even prevent the appearance of the anomaly.

As an example of the measurements in the oxygen sublattice in [001] direction we show angular scans of a single crystal ($T_c=91$ K) performed at temperatures of 95 and 70 K in Fig. 2. $\Delta\Psi_{1/2}$ in this example corresponds to a change of about 8%. The average absolute increase out of five measurements yields a value of 0.025° which is significantly above a change of 0.010° estimated for a pure temperature effect by thermal vibrations in the larger temperature range of 100 to 30 K. Additional measurements of the changes in the minimum yield value $\Delta X_{\min}$ (unity: percent points, pp) which could be performed with higher statistical accuracy as compared to the scan measurements, also yielded an anomalous decrease by cooling below T_c. The average observed decrease by 3 ± 1 pp is well above the value of 1 pp expected from the pure influence of the thermal vibration amplitude. These measurements in [001] direction already clearly indicate a strong anomaly in the oxygen sublattice of Y-Ba-Cu-O.

As mentioned above anomalous displacements especially of the apical oxygen atoms should be detected with higher sensitivity in [100] channeling measurements, where O(4) atoms form separate rows. We therefore have performed experiments on *a*-axis oriented Y-Ba-Cu-O and Eu-Ba-Cu-O thin films having different T_c values. According to Ref. 11 the size of the anomaly, however, should not depend on the magnitude of T_c. The results of minimum yield measurements performed with good statistical accuracy above and below T_c are summarized in Fig. 3. A clear change for all samples is observed when cooling below T_c. The average decrease out of seven measurements is 4 ± 1 pp. Again the observed values are well above a number of about 1 pp calculated for the normal temperature dependence in the applied temperature range thus clearly supporting the observation in [001] direction. In addition, also angular scans have been measured. Examples for the different sublattices in an Eu-Ba-Cu-O film ($T_c=60$ K) measured at temperatures of 70 and 50 K are displayed in Fig. 4. It is interesting to note that in this case of [100] channeling the change in the critical angle of Cu and Eu-Ba is very similar and the numerical value ($\Delta\Psi_{1/2}^{Cu}\approx\Delta\Psi_{1/2}^{Eu\text{-}Ba}\approx0.025°$) is close to 0.02° expected for the normal temperature effects in the investigated range. Similar observations were made in three other films indicating that the *real* anomaly

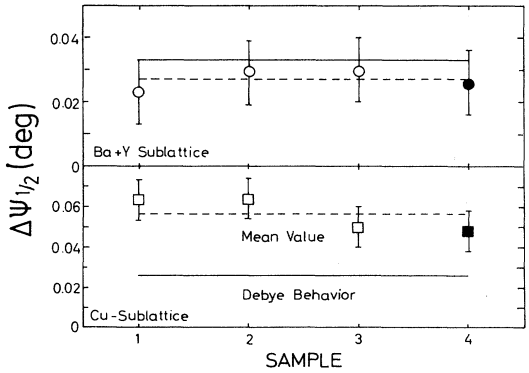

FIG. 1. Increase of the widths of [001] axial channeling scans $\Delta\Psi_{1/2}$ in different Y-Ba-Cu-O single crystals and a thin film (full symbol) by cooling below T_c measured with 2-MeV He ions in the metallic sublattices. The expected normal temperature dependence is indicated by a full line.

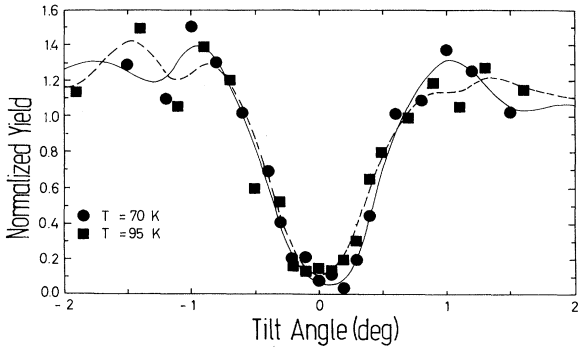

FIG. 2. [001] axial channeling scans in the oxygen sublattice of a Y-Ba-Cu-O single crystal ($T_c=91$ K) measured above and below T_c with 3.06-MeV He ions. The lines are spline fits through the data points which serve as guides to the eye.

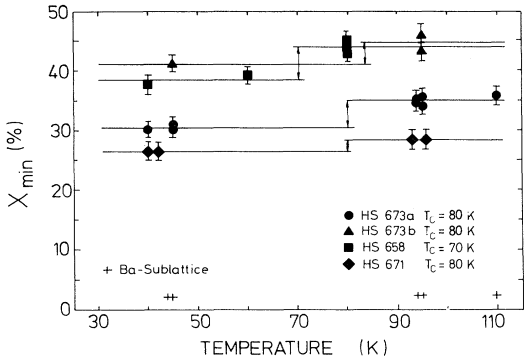

FIG. 3. Minimum yield values X_{min} in the oxygen sublattice for [100] axial channeling in different *a*-axis oriented thin films at various temperatures above and below T_c. Measurements in the Ba sublattice, which reflect the normal temperature effect, are included for comparison. The straight lines are drawn as a guide to the eye.

in the Cu sublattice must be small. In contrast, a clear anomalous change of 0.04° is seen in Fig. 4 for the oxygen sublattice. The normal temperature dependence of the oxygen vibration amplitude would be within the accuracy of our goniometer which is in the range of 0.005°. The average value of $\Delta\Psi_{1/2}$ for oxygen out of 6 measurements on different films was 0.035°±0.02°. The large error estimated for these scan measurements arises from the poor

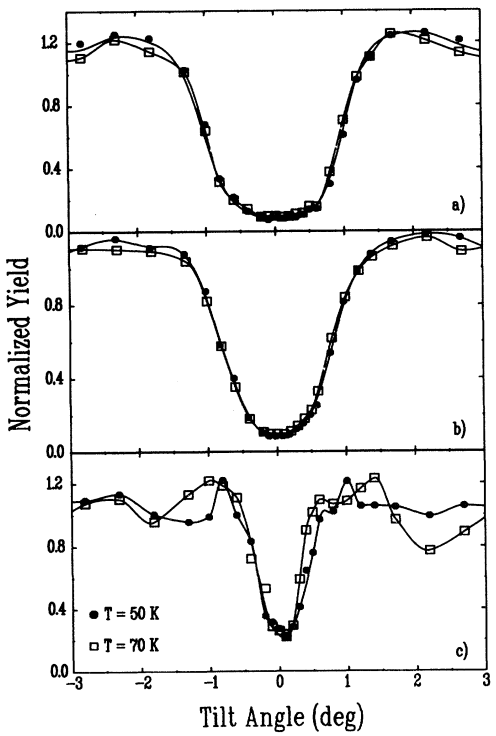

FIG. 4. [100] axial channeling scans for an *a*-axis oriented Eu-Ba-Cu-O thin film measured in the different sublattices: (a) Eu-Ba, (b) Cu, and (c) O below (50 K) and above (70 K) T_c (65 K). The lines are spline fits through the data points which serve as guides to the eye.

statistics which, however, could not be improved to keep the damage level below a critical value.

The channeling process in Y-Ba-Cu-O and the influence of possible structural distortions on $\Psi_{1/2}$ and X_{min} were simulated by Monte Carlo computer calculations. To this end the $YBa_2Cu_3O_7$ crystal structure was stored in an atomic layer-by-layer format in the [001] and [100] crystal directions. The trajectories of 3×10^4 He ions homogeneously distributed over a unit cell area with incident energies of 2 or 3.06 MeV were calculated applying a binary collision model. Temperature-dependent vibration amplitudes were used from neutron-diffraction data[2] and from phonon-model calculations based on phonon-dispersion measurements performed in our laboratory.[12] The values were averaged for the same atomic species on different lattice sites, e.g., Cu(1), Cu(2) and O(1), O(2), O(3), and O(4), respectively. The total amplitudes (static or dynamic) were assumed to be isotropically distributed. As a simple model for the explanation of the experimental observations we assumed small static distortions in the Cu-O sublattice above T_c which are removed below T_c. The values of the atomic displacements were adjusted to reproduce the observed anomalous changes of $\Psi_{1/2}$ and X_{min}.

A complication in the interpretation of the results arises due to the complexity of the mixed atomic row channeling process in [001] (*c* axis) direction. Here an influence of oxygen displacements on the channeling behavior of Cu has been detected which, however, is not mutual. For example, a reduction of the Cu amplitude by 1 pm causes an increase of the critical angle for Cu by 7% in agreement with our observations and the analysis by Sharma *et al.*[1,10] Such Cu displacements do not influence the channeling behavior in the oxygen sublattice in the simulation calculations. In contrast, however, a reduction of the displacements in the O(4) sublattice from 10 to 6.9 pm, which reproduces the increase of the critical angle observed in the measurements of the oxygen sublattice, also covers almost half of the effect observed in the Cu sublattice. This is demonstrated in Fig. 5 where calculations of the critical angle of Cu as a function of the Cu displacements amplitude are shown with oxygen displacement values as a parameter.

The quoted decrease of the O(4) amplitude fitting the observed increase of $\Psi_{1/2}$ in the oxygen sublattice causes a decrease in X_{min} of 1 pp only, which is considerably smaller than the experimental observation of about 3 pp. This indicates that displacements of oxygen atoms on other sites have to be involved in the structural distortion. For channeling in [100] direction (*a* axis) the agreement in the X_{min} change by using the value of the O(4) amplitude decrease is better. Here a calculated value of 3 pp is moderately smaller than the observation of 4 pp. But the direction of the deviation again points to other oxygen sites involved in the distortions, possibly O(1) atoms, which also form separate rows in [100] direction. The corresponding calculated increase of the critical angle in the total oxygen sublattice is 0.03° which is well in agreement with the measured value of 0.035°. According to the results of channeling in [100] direction the changes of the Cu amplitudes must be small (<0.3 pm), i.e.,

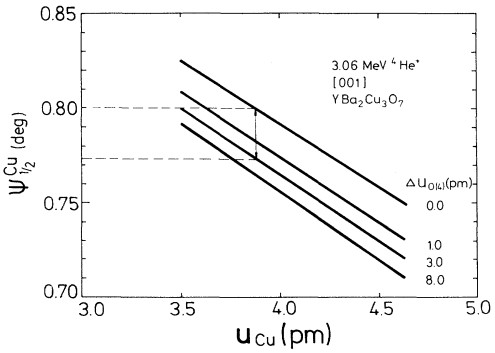

FIG. 5. Calculated critical angle $\Psi_{1/2}$ for Cu in the mixed row Cu(1)Cu(2)O(4)$_3$ in [001] direction as a function of an average total Cu vibration amplitude u with an additional displacement amplitude Δu of the O(4) atoms as a parameter. The calculations show, that about half of the experimentally observed anomalous change of $\Psi_{1/2}$ in the Cu sublattice (0.05°) can be explained by O(4) atom displacements.

would be in the range of the changes of the thermal vibration amplitude. We, however, cannot exclude an anisotropic displacement component in [100] direction, which experimentally would be detected only in channeling measurements along the [001] direction.

In conclusion, we have performed temperature-dependent channeling experiments above and below T_c in [001] and [100] directions of Y(Eu)-Ba-Cu-O single crystals and thin films. Signals in the scattering measurements have been detected from the metal sublattices and applying the 3.05-MeV $^{16}O(\alpha,\alpha)^{16}O$ resonance from oxygen atoms. The measurements revealed direct experimental evidence for anomalous effects ($\Psi_{1/2}$ and X_{min}) across T_c in the oxygen sublattice while no effect could be detected in the Y(Eu)-Ba sublattice. A comparison of results in the [001] and [100] directions for Cu suggests that displacements of this atomic species if present must be anisotropic in the [100] direction. The interpretation of the observations in the mixed rows direction is possible only by Monte Carlo simulations, which revealed an influence of O(4) atoms displacements on the channeling behavior of Cu. The remaining effect in this sublattice yields an anomalous displacement of about 0.5 pm. The main effect in the oxygen sublattice is made by O(4) atoms, but in addition other oxygen sites must be involved in the distorted structure for a best fit to the overall experimental data. Channeling measurements cannot discriminate between static and dynamic effects. In our model we assume structural distortions at temperatures above T_c which are removed by cooling into the superconducting state. The quantity of the distortions in a mixed displacement model was obtained by Monte Carlo simulation calculations with the following values: 3.1 pm for O(4) atoms, 1.5 pm for O(1) atoms, and 0.5 pm for Cu atoms.

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