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Static and dynamic displacements in $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($R = \text{Y}$, Ho; $\delta = 0.05, 0.5$): A neutron-diffraction study on single crystals

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Mean-square displacements in superconducting $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($R = \text{Y}$, Ho) were studied as function of temperature by neutron diffraction on single crystals. From a comparison of the results with the pure dynamical displacements calculated from the phonon dispersion relations of $\text{YBa}_2\text{Cu}_3\text{O}_7$ we estimate the static contributions to the displacements. In particular we find static contributions to the displacements parallel to the (a,b) plane of the chain and the apical oxygen atoms. There is no evidence of an anomalous displacement of the apical oxygen in the c direction, in contrast to extended x-ray-absorption fine-structure studies suggesting a double-well potential. We also report on a structural anomaly near T_c, which is observed in the intensity of specific Bragg reflections.

I. INTRODUCTION

Since the discovery of the cuprate high-T_c superconductors (HTSC) the structural aspects of these materials were very intensively studied.[1] The most important part of these investigations concentrated on the averaged structure obtained by x-ray- and neutron-diffraction measurements. Neutron powder diffraction proved especially powerful in determining the structure of all types of HTSC's shortly after their discovery. The influence of the oxygen doping on the structure of Y-Ba-Cu-O has been studied in detail.[2,3] This doping leads to a strong reduction of the plane Cu apical oxygen bond lengths, which was shown to scale with the superconducting T_c. Also in systems with different substitutions, the change in T_c could be shown to be accompanied by a change in the structure.[1]

The real structure of the HTSC compounds, including twinning, defects, and grain boundaries, has been studied by electron microscopy combined with electron diffraction. These studies revealed a large variety of effects.[4] A relation between the oxygen ordering into full and empty chains, and the superconducting T_c could be established.[5] This is now understood as the consequence of a varying charge transfer.[6]

Additional techniques, especially extended x-ray-absorption fine-structure (EXAFS) and high-resolution neutron diffraction combined with a pair-distribution-function analysis, have been used in order to investigate the local structure in almost all types of HTSC's. These measurements give strong indications of a difference between the local structure within a region of tenths of Å dimension and the mean structure averaged over several hundreds of Å.[7-10] Mustre de Leon *et al.* claimed to find evidence that the apical oxygen experiences a double-well potential along the c direction in Y-Ba-Cu-O.[7] The two minima are nearly equally populated and separated by ~ 0.13 Å parallel to the c axis. Egami and co-workers report local structural deviations based on powder neutron-diffraction measurements on several HTSC compounds.[8-10] They discuss various buckling schemes of the CuO_2 planes.

A point of great interest is still the structural behavior of the HTSC compounds near to the superconducting T_c. In a powder neutron-diffraction experiment, Kwei *et al.* found no change in any of the structural parameters of Y-Ba-Cu-O.[11] Also in La-Sr-Cu-O detailed powder neutron-diffraction studies could not reveal an anomaly

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at T_c.[12] Meingast *et al.*, however, showed that superconductivity in Y-Ba-Cu-O leads to a change in the temperature dependence of the orthorhombic distortion.[13] Below T_c, the orthorhombic distortion increases less on cooling than above. In La-Sr-Cu-O an anomaly has been observed in the thermal-expansion coefficients (parallel and perpendicular to the planes) and also in the superstructure reflections characterizing the structural phase transition from the tetragonal to the orthorhombic phase.[14] One could conclude that, in La-Sr-Cu-O, superconductivity freezes in the orthorhombic deformation.

Several groups reported changes of the local structure at T_c. From EXAFS measurements Mustre de Leon *et al.* claimed for Y-Ba-Cu-O that the separation of the observed double-well potential decreases by 0.02 Å at T_c.[7] Some other groups report controversial structural anomalies for the same compound based on similar EXAFS studies.[15,16] By neutron powder-diffraction measurements combined with a pair-distribution-function analysis, hints for anomalies in the local structure could be established in almost all types of HTSC.[8–10] However, an understanding of the real effect in the structure is still lacking. Ion channeling measurements on Y-Ba-Cu-O and Er-Ba-Cu-O revealed an anomalous diminuation of the Cu and/or O vibration amplitudes at T_c.[17–19] As no comparable effects have been seen in the corresponding neutron-diffraction experiments,[18] the vibration anomalies have been attributed to a local effect.

In this work we present the results of a neutron-diffraction study on a series of well characterized single crystals of $R\mathrm{Ba_2Cu_3O_{7-\delta}}$. We focus especially on the behavior of the static and dynamic displacements. The detailed knowledge of the lattice dynamics allows a quantitative analysis and interpretation of the anisotropic mean-square displacements. In spite of the fact that we measure the mean averaged structure, the displacement parameters can give clear restrictions concerning possible local deformations. We report further a subtle enhancement of a Bragg reflection intensity near T_c, which indicates an anomaly in the averaged structure.

II. EXPERIMENTAL

Crystals of R-Ba-Cu-O were prepared by the flux technique at two laboratories with R_2O_3, $BaCO_3$, and CuO as starting materials. The preparation differed only in the thermal treatment and in the procedure to adjust the oxygen contents.[20] The Ho-Ba-Cu-O crystals (CE-Saclay) have been completely surrounded by the flux after the growing process, and after extraction from the flux they exhibit an irregular shape. For the preparation of the Y-Ba-Cu-O crystals (Universität Karlsruhe) the flux was decanted before cooling beyond the BaO-CuO eutectic temperature (910 °C). This method results in thin regular plates with surfaces parallel to the (a,b) plane. Crystals obtained with the latter technique were less than 1 mm thick in c direction. These crystals proved to be almost stoichiometric, whereas the crystals prepared by the first technique showed always significant Cu deficiencies. The superconducting T_c together with other characteristical properties of the examined crystals are given in Table I.

The measurements were performed on the four-circle diffractometer P110/5C2 at the reactor Orphée, CE-Saclay, using neutrons with 0.83 Å wavelength. The data collection was carried out in the ω-scan technique. We measured typically a half sphere of Bragg reflections up to $\sin(\Theta)/\lambda=0.77$ Å^{-1}. For each crystal the scan range had to be individually adjusted in order to achieve a complete integration over the typical multipeak structure observed in the orthorhombic twinned crystals.[21] The twinning leads to a splitting of $(h00)/(0h0)$ reflections into four spots and of $(hh0)$ reflections into three spots. In an ω scan with the c axis vertical to the diffraction plane the different contributions are separated by the angle $\Delta\omega$, which is related to the orthorhombic distortion by $\Delta\omega=\pi/2-2\arctan(b/a)$. The highest peak splitting was observed in the YBCO-6.96 and YBCO-6.98 crystals with $\Delta\omega=0.95°$ corresponding to an orthorhombic strain of $\epsilon=2(b-a)/(b+a)=0.017$. An enhanced scan width together with the c axis vertical assures the complete integration; however, it leads in some cases to contaminations of the background by neighboring Bragg reflections. A detailed description of the technique to measure and analyze the structure of these twinning crystals is given in Ref. 22. During the data collection the scan range was further varied automatically as a function of Θ in order to account for the Θ-dependent instrumental resolution.

The intensities of equivalent reflections were averaged in the orthorhombic space group *Pmmm*. Typically 1200

TABLE I. Several characterizing properties of the crystals examined in this work. Lattice constants were determined by a least-squares refinement of unsplitted reflections, which leads to the average tetragonal values. The orthorhombic strain $(b-a)/0.5(b+a)$ was deduced from the splitting of the reflections in the (a,b) plane due to the twinning.

	$\mathrm{YBa_2Cu_3O_{6.98}}$ Sample 1	$\mathrm{YBa_2Cu_3O_{6.96}}$ Sample 2	$\mathrm{YBa_2CU_3O_{6.52}}$ Sample 2	$\mathrm{HoBa_2Cu_{2.94}O_{6.94}}$	$\mathrm{HoBa_2Cu_{2.94}O_{6.48}}$
Volume [mm^3]	10	23	23	10	6.6
T_c midpoint [K]	89.8	90.75	52.8	77	20
T_c onset [K]	90.4	90.95	53.8	85	32
RT:					
c [Å]	11.696	11.680	11.742	11.682	11.724
$(a+b)/2$ [Å]	3.853	3.852	3.852	3.858	3.855
$(b-a)/0.5(a+b)$	0.017	0.017	0.010	0.009	0.005

reflections were measured in the different data collections leading to about 400 independent observations. The internal R value of the averaging procedures are lower than 2% in all data sets proving the complete integration of the profiles in spite of their multipeak structure.

The analysis of the multipeak structure of the Bragg reflections shows no contributions corresponding to pseudotetragonal parts of the crystals. This is due to the higher quality of these crystals; the first available crystals of Y-Ba-Cu-O showed always such pseudotetragonal contributions. Crystal defects seem to disturb the orthorhombic symmetry locally leading to a smaller size of the orthorhombic domains and, therefore, to the pseudotetragonality. These first crystals showed furthermore only broadened superconducting transitions. The superposition of the scattering contributions from different domains in the crystals examined here is completely incoherent. We described therefore the measured intensities corresponding to an addition of the squares of the structure factors:

$$F^2_{\substack{\mathrm{obs}\\hkl}} = \alpha F^2_{hkl} + (1-\alpha) F^2_{\bar{h}kl} , \tag{1}$$

where α is the volume part of one of the two different domain orientations. For the refinement we used the Prometheus program package in a version adapted for data sets obtained on twinned crystals.[23] Numerical absorption (lower than 2%, $\mu = 0.04\ \mathrm{cm}^{-1}$) and extinction corrections [up to 15% for the (200) reflection; Becker Coppens model for secondary extinction of type I] were applied. The refinement of the occupancies allowed to determine the oxygen concentrations of the crystals with a precision of about 1%.

The twinning leads to rather strong correlations which have to be taken into consideration by introducing several constraints. It is not possible to distinguish between the $U11$ and $U22$ mean-square displacement for Y, Ba, Cu, and O1 (for the notations see Fig. 1). We had to restrict these parameters to be identical, which seems not to be in disagreement with the surrounding coordination of these sites. Furthermore, it was necessary to fix the thermal parameters of the O2 site to those of the O3 site. Besides these correlations the twinning causes no additional complications, as it can be seen in the satisfying R values of the refinements, Table II.

III. RESULTS AND DISCUSSION

A. Displacements in YBCO-6.98

The structural parameters of the Y-Ba-Cu-O crystals with oxygen concentrations 6.98 (crystal 1) and 6.52 (crystal 2) are given in Table II for different temperatures. The notations are chosen corresponding to Fig. 1, which shows the structure of orthorhombic Y-Ba-Cu-O. We show also the structural results at room temperature obtained with crystal 2 before deoxygenation. Its oxygen content was 6.96. The structural parameters agree very well with the results obtained on crystal 1. The reproducibility of the structural parameters demonstrate the reliability of the results. In Fig. 2 we plot the temperature dependences of the anisotropic mean-square displacements for YBCO-6.98. Generally, the displacements of the atoms forming the $\mathrm{CuO_2}$ plane together with Y and Ba (displayed on the right) are lower than those of the atoms forming the chains and also lower than those of the apical oxygen O1 (displayed on the left in Fig. 2).

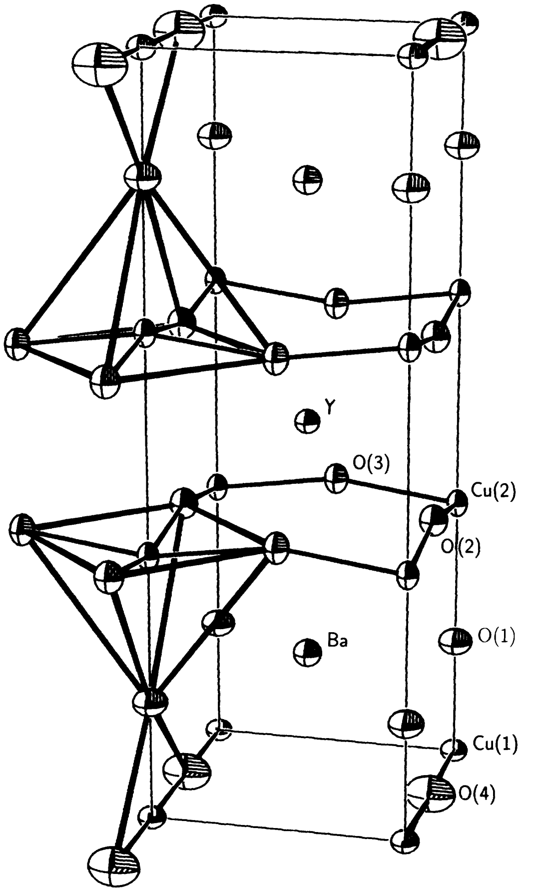

FIG. 1. Ortep plot of the structure of YBCO-6.98 at room temperature; the ellipsoids correspond to 90% occupation probability.

The temperature dependence of the displacements at Cu2 and O2/3 is more pronounced parallel to the c direction than perpendicular to it. This is the consequence of the two-dimensional structure of the $\mathrm{CuO_2}$ planes. The atoms are strongly bound by the Cu-O bonds parallel to the planes and only weakly perpendicular to it. Furthermore, there is a pronounced anisotropy for O2 with $U11 > U22$ corresponding to the movement perpendicular and parallel to the surrounding bonds. The movement perpendicular to the Cu-O2 bond corresponds to a rotation of the $\mathrm{CuO_5}$ pyramid around the c axis. The comparable rotation is quite soft in $\mathrm{Nd_2CuO_4}$ (Ref. 24) (where it corresponds to the rotation of the $\mathrm{CuO_4}$ square) and in La-Sr-Cu-O (Refs. 25 and 26) (where it corresponds to the rotation of the $\mathrm{CuO_6}$ octahedron around the c axis); however, in Y-Ba-Cu-O this rotation is hardened probably due to the influence of the Y site. The apical oxygen O1 shows very anisotropic displacements

TABLE II. The results of the structural refinements for the Y-Ba-Cu-O crystals at different temperatures. For the atom notations see Fig. 1. Mean-square displacements are in Å^2. Numbers in parentheses are statistical standard deviations of the last digit(s).

	$YBa_2Cu_3O_{6.98}$			$YBa_2Cu_3O_{6.96}$	$YBa_2Cu_3O_{6.52}$				
	Sample 1			Sample 2	Sample 2				
	296 K	90 K	45 K	296 K	296 K	170 K	60 K	53 K	45 K
Y $u_{11}=u_{22}$	0.0053 (2)	0.0032 (4)	0.0027 (4)	0.0047 (1)	0.0045 (1)	0.0031 (1)	0.0021 (1)	0.0021 (1)	0.0017 (1)
u_{33}	0.0051 (3)	0.0016 (5)	0.0009 (5)	0.0055 (1)	0.0059 (2)	0.0046 (2)	0.0034 (2)	0.0031 (2)	0.0031 (2)
Ba Z	0.183 86 (7)	0.183 67 (12)	0.183 69 (12)	0.184 20 (6)	0.189 16 (4)	0.189 21 (6)	0.189 18 (5)	0.189 23 (5)	0.189 22 (6)
$u_{11}=u_{22}$	0.0070 (2)	0.0046 (4)	0.0036 (4)	0.0070 (1)	0.0078 (1)	0.0055 (2)	0.0039 (2)	0.0037 (2)	0.0036 (1)
u_{33}	0.0070 (3)	0.0024 (5)	0.0021 (5)	0.0071 (2)	0.0080 (2)	0.0056 (2)	0.0036 (2)	0.0033 (2)	0.0033 (2)
Cu1 occ	1.008 (6)	1.002 (8)	1.011 (9)	1.010 (4)	1.003 (3)	1.002 (3)	1.005 (4)	1.004 (4)	1.003 (4)
$u_{11}=u_{22}$	0.0067 (3)	0.0037 (5)	0.0032 (5)	0.0071 (2)	0.0087 (1)	0.0057 (2)	0.0034 (2)	0.0035 (2)	0.0033 (2)
u_{33}	0.0046 (3)	0.0015 (6)	0.0018 (6)	0.0046 (2)	0.0065 (2)	0.0045 (2)	0.0031 (2)	0.0025 (2)	0.0026 (2)
Cu2 Z	0.355 01 (5)	0.354 66 (7)	0.354 64 (8)	0.355 13 (4)	0.357 54 (3)	0.357 39 (4)	0.357 16 (3)	0.357 12 (3)	0.357 13 (3)
$u_{11}=u_{22}$	0.0038 (1)	0.0020 (3)	0.0016 (2)	0.0035 (1)	0.0033 (1)	0.0022 (1)	0.0013 (1)	0.0015 (1)	0.0012 (1)
u_{33}	0.0070 (2)	0.0029 (4)	0.0020 (3)	0.0072 (1)	0.0083 (1)	0.0058 (1)	0.0039 (1)	0.0032 (1)	0.0034 (1)
O1 occ	1.003 (5)	1.002 (7)	1.004 (7)	1.001 (4)	0.995 (3)	0.995 (4)	0.992 (4)	0.994 (4)	0.995 (4)
Z	0.158 67 (6)	0.159 18 (10)	0.159 19 (10)	0.158 63 (5)	0.156 02 (4)	0.156 32 (5)	0.156 56 (5)	0.156 58 (5)	0.156 55 (5)
$u_{11}=u_{22}$	0.0106 (3)	0.0070 (4)	0.0063 (4)	0.0109 (2)	0.0123 (1)	0.089 (1)	0.070 (1)	0.0071 (1)	0.0067 (1)
u_{33}	0.0066 (3)	0.0041 (5)	0.0031 (5)	0.0070 (2)	0.0100 (2)	0.0080 (2)	0.0064 (2)	0.0057 (2)	0.0061 (2)
O2 Z	0.378 25 (4)	0.378 18 (7)	0.378 08 (7)	0.378 31 (3)	0.378 53 (2)	0.378 41 (3)	0.378 31 (3)	0.378 34 (3)	0.378 32 (3)
u_{11}	0.0069 (2)	0.0046 (4)	0.0040 (4)	0.0066 (1)	0.0064 (1)	0.0046 (1)	0.0035 (2)	0.0037 (2)	0.0033 (2)
u_{22}	0.0051 (2)	0.0037 (4)	0.0037 (4)	0.0046 (1)	0.0041 (1)	0.0031 (1)	0.0026 (2)	0.0027 (2)	0.0025 (2)
u_{33}	0.0089 (2)	0.0045 (3)	0.0036 (3)	0.0091 (2)	0.0096 (1)	0.0068 (1)	0.0052 (1)	0.0046 (1)	0.0048 (2)
O4 occ	0.986 (10)	0.977 (13)	0.971 (14)	0.964 (10)	0.517 (10)	0.523 (13)	0.524 (12)	0.514 (12)	0.527 (12)
u_{11}	0.0227 (9)	0.0116 (15)	0.0111 (15)	0.0221 (7)	0.0274 (9)	0.0181 (12)	0.0113 (10)	0.0109 (11)	0.0109 (10)
u_{22}	0.0073 (7)	0.0055 (14)	0.0041 (13)	0.0073 (6)	0.0083 (7)	0.0064 (10)	0.0050 (9)	0.0046 (10)	0.0044 (9)
u_{33}	0.0132 (7)	0.0047 (11)	0.0036 (11)	0.0130 (6)	0.0136 (7)	0.0104 (9)	0.0072 (8)	0.0069 (8)	0.0073 (9)
R_ω (%)	2.59	3.39	3.58	2.32	2.00	2.28	2.30	2.33	2.27
R (%)	2.32	3.65	3.61	1.98	1.65	2.20	2.09	2.09	2.07

with the shortest axis of the thermal ellipsoid being parallel to the c direction and hence parallel to the bonds to the two Cu sites. These bonds seem to fix the apical oxygen quite effectively like the Cu-O bonds in the CuO_2 plane. However the O1 displacements parallel to the plane are rather large. Together with the large values for U33 of O2 this indicates a slight instability against tilting of the whole CuO_5 pyramid around an axis lying in the (a,b) plane in analogy to what happens in the La-Cu-O system.[27]

The thermal parameters of the atoms forming the chains again reflect their bond coordination. Parallel to the chain direction, and hence parallel to the Cu-O bonds the displacement of O4 is comparable to the corresponding parameters in the CuO_2 plane. However, perpendicular to the chains we observe extremely large values at room temperature and a strong temperature dependence.

The temperature dependence of the chain oxygen $U11$ parameter and that of the apical oxygen $U11=U22$ parameter indicate some static contributions. To estimate these static displacements we compare in Fig. 3 our results to those of a lattice dynamics calculation. For Y-Ba-Cu-O with an oxygen concentration near to that of the YBCO-6.98 crystal a great number of phonon-dispersion curves have been measured in the main symmetry directions at room temperature. This allowed researchers to develop a quantitative lattice-dynamics model.[28] With this model we calculated the anisotropic thermal parameters as a function of temperature. This method supposes that there are no temperature dependencies of any phonon energies and more generally that there are no anharmonic effects.

The largest difference between the measured and the calculated mean-square displacements is found in the $U11$ value of the chain oxygen, Fig. 3. As the observed curve is just shifted against the calculated one by a constant amount, the difference strongly suggests a static displacement. In additional refinements we fixed the $U11$ parameter to the calculated values and allowed a displacement of the equilibrium position from (0,0.5,0) to $(x,0.5,0)$. At all temperatures this split model results in a constant x value corresponding to 0.074(10) Å. However, we observe no reduction of the reliability factors. The fact that we never observe a similarly enlarged $U11$ value at the Cu1 site suggests that the obtained static displacement of the chain oxygen is caused by a real zig-zag mode, as it was first proposed in the powder neutron-diffraction work of Francois *et al.*[29] Furthermore, our value of 0.074 Å agrees well with their result of 0.08 Å, but not with the larger displacement of 0.15 Å, reported by Wong-Ng *et al.*[30] Some further differences between the measured and the calculated mean-square displacements are observed for Ba and the chain Cu, see Fig. 3. Also these deviations seem to be caused by the zig-zag arrangement of the chains. In particular the Ba atom seems to be shifted parallel to the (a,b) plane.

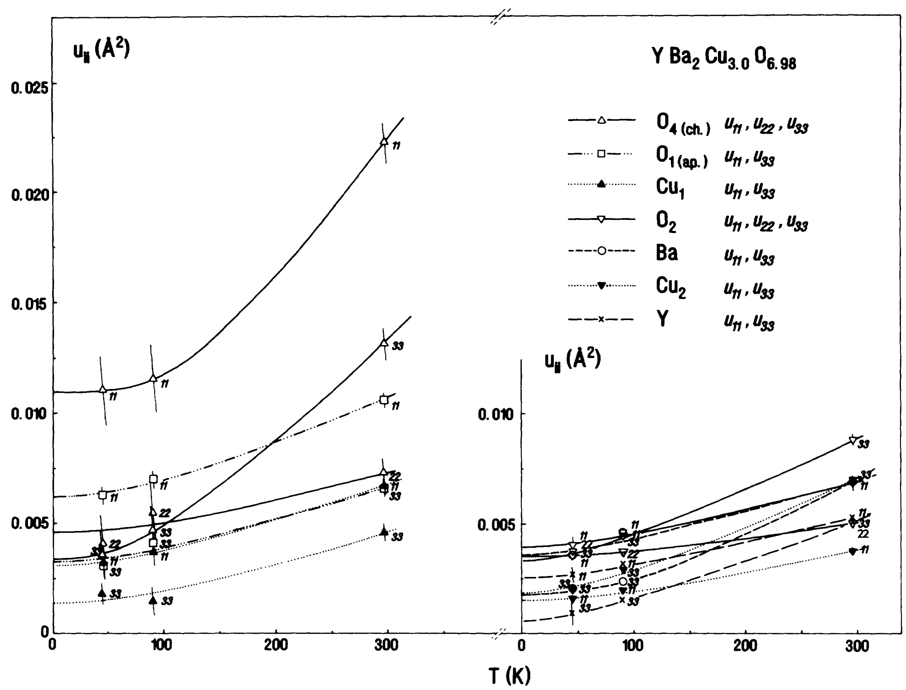

FIG. 2. The mean-square displacements of YBCO-6.98 as function of temperature; the lines are guides to the eye.

An anharmonic double-well potential of the apical oxygen has been widely discussed as a possible mechanism for superconductivity in HTSC.[30,31] Indeed, Mustre de Leon *et al.* reported an anomalous behavior of the apical oxygen based on EXAFS studies.[7] They propose that the apical oxygen feels a double-well potential whose minima are separated by 0.13 Å along the *c* direction. This double well has given rise to several speculations since then.[32] However, our measured mean-square displacement of the apical oxygen in the *c* direction agrees perfectly with the calculations. Especially, we find no evidence for any additional contributions. The proposed separation into two minima would lead to an additional static contribution to $U33$ of 0.0042 Å^2. The entire value of the mean-square displacement in this direction would amount to more than twice the observed value, which differs by six standard deviations from our result. Therefore, the proposed two-well potential can be excluded. In the (a,b) plane, however, the apical oxygen shows clear additional contributions which cannot be explained in the dynamical harmonic model. It might be possible that the anomalies observed in the EXAFS spectra are not due to an anomalous behavior of the apical oxygen parallel to the *c* direction but parallel to the (a,b) plane.

For Y and the atoms forming the CuO$_2$ plane we find a satisfying agreement between the measured thermal parameters and the calculations. The corresponding phonons seem to be quite well described by the harmonic model.

B. The effects of deoxygenation

After deoxygenation the crystal had an oxygen content of 6.52. It showed diffuse intensity at the position of the

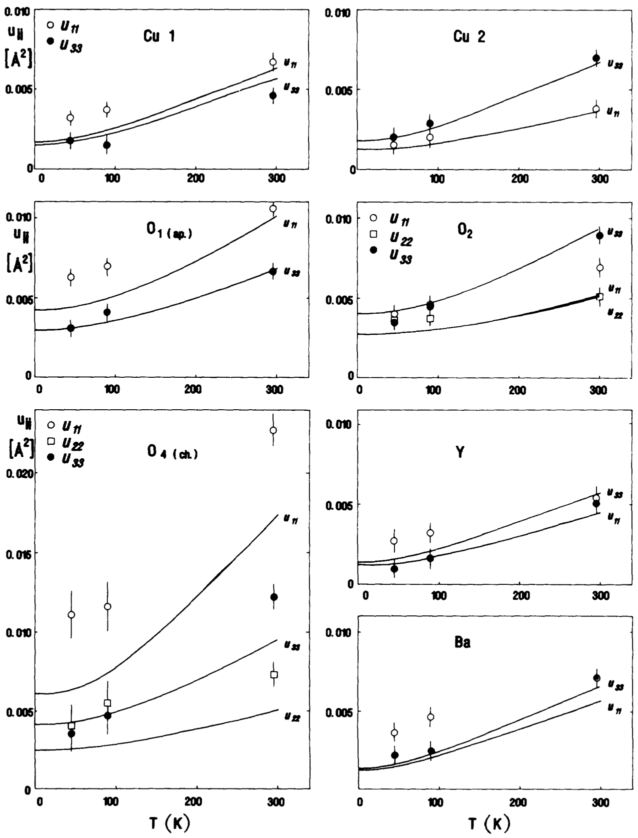

FIG. 3. The measured mean-square displacements of YBCO-6.98 as function of temperature compared with the pure dynamical displacements obtained by a lattice-dynamics model. The solid lines correspond to the calculations.

superstructure reflections which are characteristic for the ortho II phase.[4] The ortho II phase is characterized by an alternation of full and empty chains which gives rise to a doubling of the *a* axis, leading to superstructure reflections along the *a* direction. In Fig. 4 we show an intensity map in the neighborhood of the diffuse (2.5 0 0) reflection.

We performed ω scans at $(h00)$ for $2.26 < h < 2.74$. The diffuse intensity is only weakly modulated in the a^* direction with a maximum at (2.5 0 0). The increase of intensity at (2.26 0 0) is caused by the strong Bragg peak (200). The weak modulation along the a^* direction corresponds to a small correlation of the chain ordering along the *a* direction, i.e., perpendicular to the chains themselves. However, note that in spite of the reduced correlation length the superconducting transition is quite sharp and T_c quite high in respect to the oxygen concentration. Similar results have been reported by Zeiske *et al.*[33]

The refinement of an orthorhombic I model, with the small cell, can describe only the average structure of this compound. In Fig. 5 we show the temperature dependences of the thermal parameters in YBCO-6.52. The deoxygenation has almost no effect on the thermal parameters of the atoms forming the CuO_2 planes. Therefore, the phonons associated with these atoms should show only slight energy shifts.

For the apical oxygen and the chain atoms the comparison with YBCO-6.98 reveals some remarkable differences. The displacements of the apical oxygen in the *c* direction, which are in perfect agreement with the calculations for YBCO-6.98, show a static contribution of 0.05 Å for the composition 6.52. The natural explanation of this effect is given by the alternation of full and empty chains. The apical oxygen shifts from $z/c = 0.159$ for full chains (YBCO-7.0) to $z/c = 0.153$ for empty chains (YBCO-6.0). The distance between these two positions amounts just to 0.07 Å. In the ortho II phase one half of the apical oxygen is situated near to a full chain and the other half near to an empty chain, and hence on positions corresponding to YBCO-7.0 or to YBCO-6.0 in a single minimum potential. However, again there is no evidence for a double-well potential. A similar static displacement along the *c* direction observed for the plane Cu ($\sim$0.04 Å) seems also to be produced by the ortho II arrangement.

Also the $U33$ parameter of the Ba atom shows a static displacement. Again, there is a strong variation of the *z* parameter from YBCO-7.0 ($z/c = 0.184$) to YBCO-6.0 ($z/c = 0.195$), which affects the Ba distribution in the case of reduced CuO chains. At the Ba site one further obtains anisotropic thermal parameters parallel to the

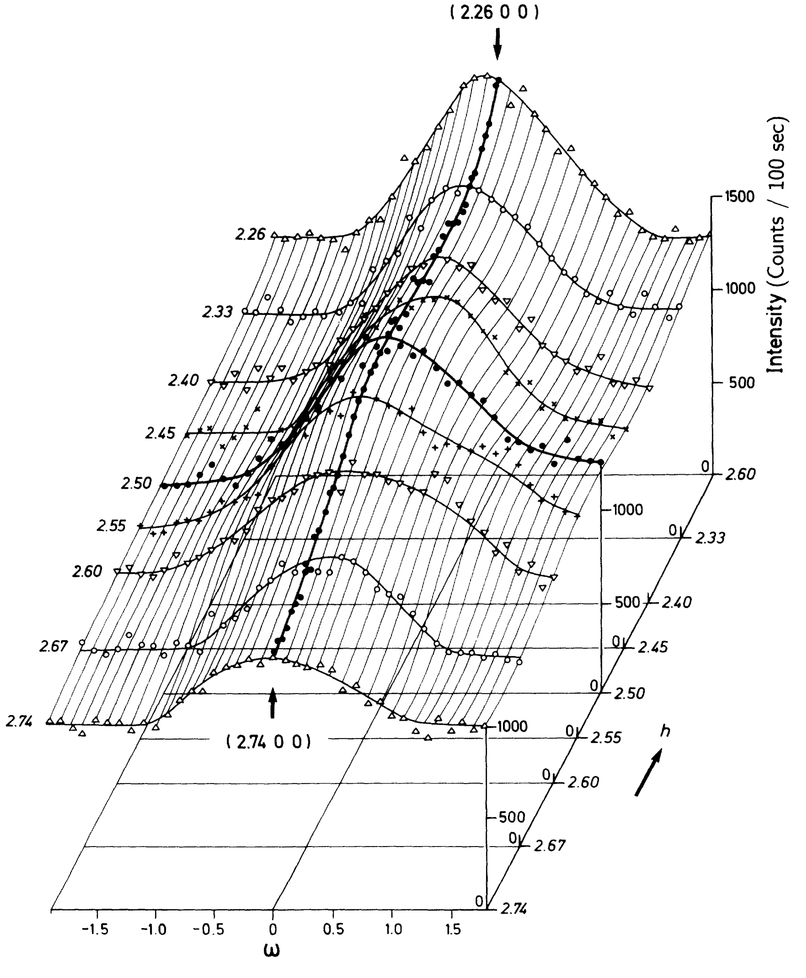

FIG. 4. Intensity map of diffuse scattering near the superstructure reflection of the ortho II phase (2.5 0 0) for the YBCO-6.52 crystal.

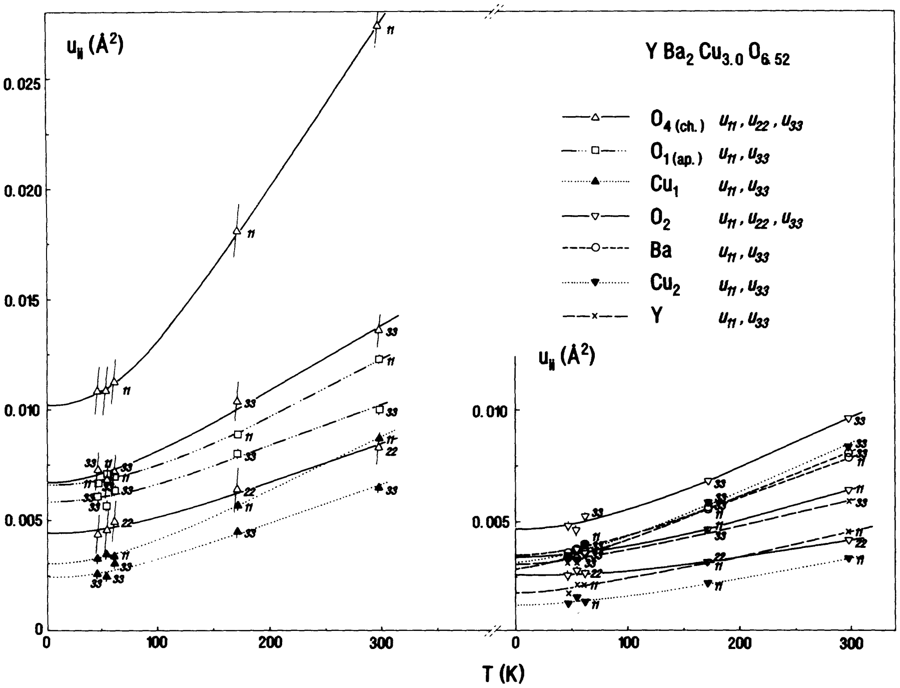

FIG. 5. The mean-square displacements of YBCO-6.52 as function of temperature; the lines are guides to the eye.

planes $U11 > U22$ at all temperatures when relaxing the tetragonal constraint. It suggests a static displacement of the Ba site towards the occupied CuO chains. Such Ba displacements have been reported by Zeiske *et al.*[33] and by Burlet *et al.*[34] based on studies of the superstructure reflections. Burlet *et al.*[34] found, in addition, displacements in the c direction for the apical oxygen and the plane Cu which agree well with our results.

C. Structural analysis on Ho-Ba-Cu-O

Most of the effects seen in Y-Ba-Cu-O are observed for Ho-Ba-Cu-O compounds in a similar way. Before entering into details we want to point out some general differences between our Y-Ba-Cu-O and Ho-Ba-Cu-O crystals. The temperature dependences of the mean-square displacements are displaced in Figs. 6 and 7 for

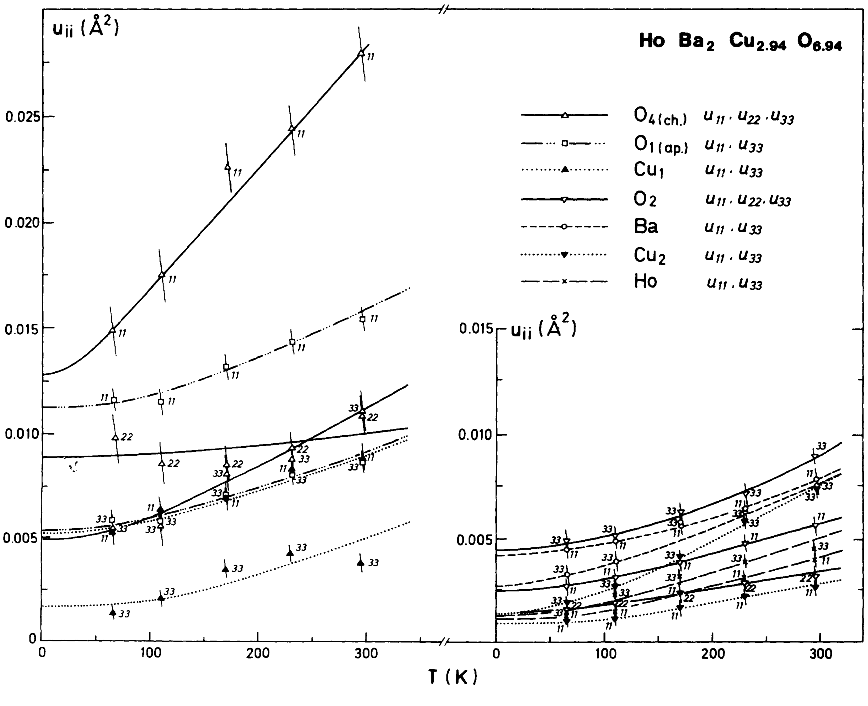

FIG. 6. The mean-square displacements of $\text{HoBa}_2\text{Cu}_{2.94}\text{O}_{6.94}$ as function of temperature; the lines are guides to the eye.

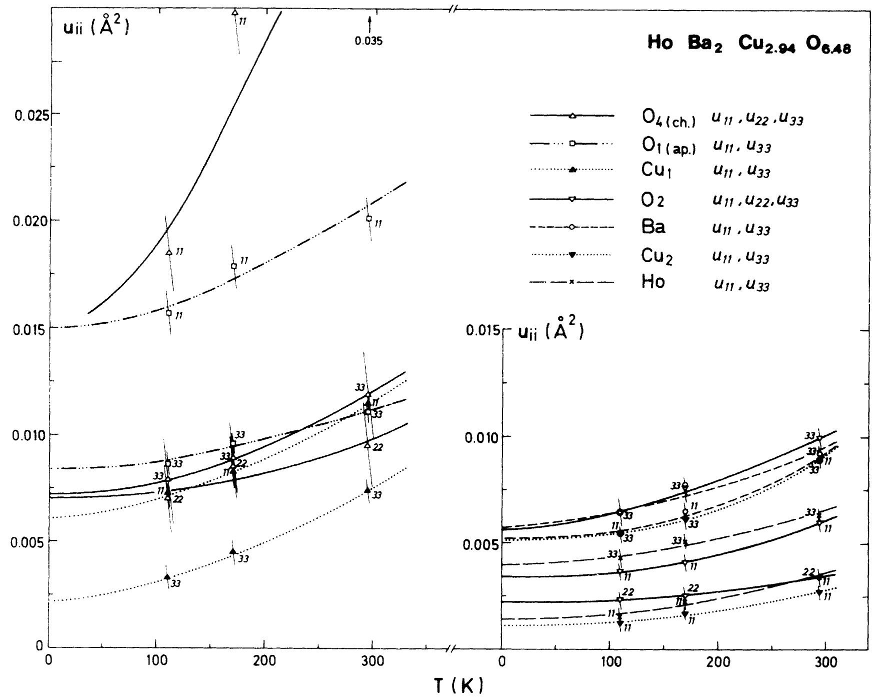

FIG. 7. The mean-square displacements of $HoBa_2Cu_{2.94}O_{6.48}$ as function of temperature; the lines are guides to the eye.

Ho-Ba-Cu-O with two compositions. For both compositions there are bigger static displacements for the atoms surrounding the chain Cu compared to the Y-Ba-Cu-O crystals. This effect is even more pronounced in the (a,b) plane as compared to the c direction. The explanation seems to be a quite drastic deficiency of 6% on the Cu1 site. These vacancies produce severe distortions and affect the thermal parameters of the surrounding atoms. However, the Cu vacancies are not caused by the Ho substitution; they exist also in Y-Ba-Cu-O crystals grown in a similar fashion.[21,35] We find a diffuse intensity with a shape almost similar to that of YBCO-6.52, shown in Fig. 4. In spite of the Cu vacancies the ortho II structure seems to be realized in a similar way.

In the Y-Ba-Cu-O crystals we observe a hardening of the Y vibration parallel to the c axis due to the deoxygenation. The same effect is even more pronounced in the Ho-Ba-Cu-O crystals, where we find additionally a hardening of the Ho vibrations parallel to the planes. This observation agrees with results of Bornemann *et al.*,[36] who report an increase of Gd vibration frequencies by the reduction of GdBCO-7.0 to GdBCO-6.0. This effect should be related to the reduction of the charge carrier concentration in the CuO_2 planes. The reduced screening of phonons by the disappearance of charges could be an attempt to explain the frequency increase on deoxygenation.

D. Structural anomalies at T_c

In order to analyze structural anomalies near the superconducting T_c we collected complete diffraction data sets at T_c and slightly above and below for YBCO-6.52. We observed no differences in any of the structural parameters which amount to more than one error bar. We therefore confirm the results of earlier studies[11] for the ortho II phase. However, we found a weak intensity increase at the transition into the superconducting phase at the (1,2,12) reflection. We passed several times through T_c in order to measure the effect and found no evidence for a hysteresis or an influence of the cycling. Furthermore we repeated the same kind of measurement on the YBCO-6.98 crystal. The results are plotted in Fig. 8. The full lines above T_c and the broken continuations below correspond to the intensity calculated with the interpolated thermal parameters (shown in Figs. 2 and 5). The observed intensity increase of a Bragg reflection indicates an anomaly in the averaged mean structure.

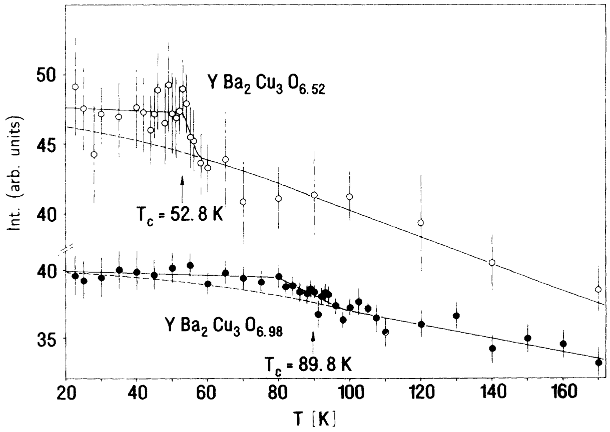

FIG. 8. The intensity of the (1 2 12) Bragg reflection as function of temperature for YBCO-6.98 and YBCO-6.52. The solid lines above T_c correspond to the intensity calculated with the interpolated structural parameters; they are continued below T_c by the broken lines. The solid lines below T_c are guides to the eye.

As already stated above, this intensity gain is not reflected by a significant change in the refined structural parameters based on the complete data sets. A possible explanation could be as follows: The (1 2 12) reflection has a pronounced orthorhombic character; this means that the ratio $F^2_{(1,2,12)}/F^2_{(2,1,12)}$ differs strongly from 1. Therefore the observed effect seems to be caused by a change of some structural parameters which are connected to the orthorhombic distortion. We can simulate the increase of the (1 2 12) intensity by changing only the anisotropic thermal parameters $U11$ and $U22$ of the apical oxygen site. A decrease of $U22$ can explain the observed intensity increase in Y-Ba-Cu-O near T_c.

In La-Sr-Cu-O Braden *et al.* showed that superconductivity leads to a freezing of the rotation of the $\mathrm{CuO_6}$ octahedra.[14] Our observation for Y-Ba-Cu-O is related to thermal-expansion measurements by Meingast *et al.*[13] They showed that on cooling through T_c the rate of increase of the orthorhombic deformation is reduced. If one assumes an anomalous tilt instability of the $\mathrm{CuO_5}$ pyramids for Y-Ba-Cu-O, as is realized in our simulation, there might be an analogous structural response on the superconductivity in these two systems. Ion channeling measurements find an anomalous diminuation of the thermal vibration of the Cu and/or O in the (a,b) plane when channeling parallel to the c direction;[17–19] these results agree with our explanation according to shifts in the $U11$, $U22$ thermal parameters of the apical oxygen.

IV. CONCLUSIONS

Detailed structural studies on $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ (R=Y, Ho, $\delta\sim0.05,0.5$) using neutron diffraction on single crystals allow us to determine the anisotropic mean-square displacements of all atoms. The comparison with a well established lattice-dynamics model makes it possible to subtract the dynamic displacements corresponding to a harmonic model. This analysis shows that the chain oxygen in YBCO-6.98 is statically displaced perpendicular to the chains by 0.074(10) Å. As there is no anomalous displacement of the chain Cu we can confirm the zig-zag arrangement proposed by Francois *et al.*[29] This arrangement may further cause some static displacements of the Ba atom in the (a,b) direction. In YBCO-6.98 we find a perfect agreement between the measured and the calculated mean-square displacements of the apical oxygen in the c direction. There is no indication for a strong anharmonic potential of the apical oxygen along this direction in contrast to reported EXAFS results. However, there seem to be anharmonic effects on this oxygen parallel to the (a,b) planes.

The YBCO-6.52 crystal of reduced oxygen content shows diffuse intensity at the position of the superstructure reflections which characterize the ortho II phase. The structural analysis reveals several static displacements which are caused by the coexistence of full and empty chains in this structure. Especially a displacement of the Ba atom along the a direction is confirmed.[33,34]

The Ho-Ba-Cu-O crystals examined in our study show a rather strong Cu deficiency in the chains, ~6%. These vacancies affect the static and dynamic displacements. In Ya-Ba-Cu-O and even more pronounced in Ho-Ba-Cu-O, the oxygenation from O-6.50 to O-6.98 leads to a strong increase of the temperature dependence of the R displacements in the c direction, and, hence, to a decrease of the corresponding vibration frequencies.

We observe a slight increase in the intensity of the (1 2 12) Bragg reflection at T_c, which indicates that the averaged mean structure is affected by the transition into the superconducting phase. The observed intensity increase can be explained by a shift in the $U22, U11$ thermal parameters from the apical oxygen site, and hence by an effect which is related to the orthorhombic distortion.

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