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Anomalous variation of the c lattice parameter of a sample of $YBa_2Cu_3O_{7-\delta}$ through the superconducting transition

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Using a powder diffractometer with a continuous flow arrangement, the lattice parameters of a sample of $YBa_2Cu_3O_{7-\delta}$ (with δ estimated to be between 0.10 and 0.15) were determined from 300 K down to 80 K with a temperature regulation of 0.1 K. The diffractogram showed a single phase with the orthorhombic structure. Measurements from 100–80 K were performed at close temperature intervals and showed an anomalous change in c in a narrow temperature range around T_c. This anomaly correlates with the anomaly in the nuclear quadrupole resonance frequency, positron annihilation lifetimes, and sound velocity observed by some workers. A smaller decrease in c was observed around 240 K as the sample was cooled, which again correlates with anomalies observed in sound velocity and attenuation and differential scanning calorimetry. The present observations differ from the recently published results of Horn *et al.*

Since the discovery of superconductivity around 90 K by Wu *et al.*[1] in a multiphase sample of Y-Ba-Cu-O, the superconducting phase has been identified as a distorted oxygen-deficient perovskite with the composition $YBa_2Cu_3O_{7-\delta}$. This has an orthorhombic structure. The lattice parameters have been measured by several workers[2–8] in different temperature ranges using both x-ray and neutron diffraction. However, the parameter δ has not been specifically indicated in some of these reports though the samples were superconducting around 90 K.

Anomalous behavior has been observed in the sound velocity through the transition.[9–13] A sharp anomaly in the nuclear quadrupole resonance (NQR) frequencies of the planar- and linear-chain copper atoms in a sample of $YBa_2Cu_3O_{7-\delta}$ as one passes through the transition temperature was observed by Riesemeier *et al.*[14] A similar sharp anomaly in positron-annihilation lifetimes in $YBa_2Cu_3O_{7-\delta}$ was observed by Ming-Kang Teng *et al.*[15] In all of these cases, it was suggested that the anomalies could be related to some structural distortions. However, other measurements on pellets with a different microstructure but prepared in the same way, or pellets of materials prepared by different workers, sometimes failed to show any such anomalies.

To resolve whether any structural distortions take place as the sample is cooled through the transition temperature, a direct determination of the lattice parameters through the transition by x-ray diffraction was undertaken. The results of this study are not in agreement with the recently published results of Horn *et al.*[5] using high-resolution x-ray diffractometry.

The sample of $YBa_2Cu_3O_{7-\delta}$ was prepared by high-temperature solid-state reaction. A stoichiometric mixture of high-purity powders (99.99%) were ground in acetone and heated in a platinum crucible in air at 950 °C for 24 h. After repeating this operation twice, the mixture was reground, pelletized in a tungsten carbide steel die at a pressure of 4 tons/cm^2 and heated in air at 900 °C for 24 h. Oxygen treatment of the pellet was done in a tubular furnace with gas flow at 900 °C for 24 h, then at 600 °C for 24 h and furnace cooled to room temperature in flowing oxygen. The x-ray diffractogram taken at room temperature showed the material to be single phase with an orthorhombic unit cell.

The oxygen deficiency δ was determined by iodimetry and found to be between 0.1 and 0.15. Diamagnetic susceptibility measurements indicated a transition temperature of 91 K. Samples prepared under identical conditions were found by resistivity studies to be superconducting around 90–91 K.

The low-temperature x-ray diffractograms were recorded on a Russian YPC-50 NM powder diffractometer to which a continuous flow attachment was built.[16] The temperature of the sample can be controlled between 300 and 80 K to within 0.1 K for a long time. The radiation used was Cu $K\alpha$ with a nickel filter. The diffractograms were recorded in the range of 2θ from 10° to 125° with a scanning speed of $\frac{1}{4}$ degrees per minute.

The experiment was performed as follows. In every run, the diffractogram of the sample at room temperature was taken in the 2θ range of 32°–34° to check if the peaks (013) and [(110), (103)] occurred at the same positions. This ensured that there was no inadvertent change in the zero setting of the angular scale. The flow of liquid nitrogen was then started and the sample was cooled to the required temperature, which could be maintained constant to 0.1 K over several hours. After the temperature

reached the desired value and remained steady for half an hour, the diffractogram was recorded in the range of 2θ from 10° to 125°. The whole operation took approximately 8 h for each temperature.

The first run of experiments was performed on a sintered pellet. The diffractograms were recorded at 298 K and at a few temperatures in the range of 100–80 K. The lattice parameters were obtained by Cohen's[17] least-squares method using all the reflections in the range of 2θ up to a maximum of 120°. At all temperatures, it was found that all the peaks observed could be indexed on an orthorhombic unit cell and no unidentified peaks could be seen. This showed that the sample continued to be in a single phase with an orthorhombic unit cell. However, the c-lattice parameter showed an anomalous behavior near T_c. This could arise because the pellet had intergranular stresses which could be expected to change due to repeated thermal cycling. To insure that the observed results were not due to loss of oxygen or an increase in the oxygen deficiency, the material was reground and reheated in oxygen for 24 h as before. The sintered pellet so obtained was crushed and the powder loosely put in the sample holder and lightly pressed to have a smooth surface. If intergranular stresses were responsible for the observed anomalous behavior in the pellet, then the results with the powder could be expected to be very different. The second run of experiments was taken in close temperature intervals over 100–80 K and at wider temperature intervals from 100 K to room temperature.

Table I gives the values of the lattice parameters determined on the powder at a few representative temperatures. The accuracy in the lattice parameter values a and b was certainly better than 0.01 Å and in the c lattice parameter value was better than 0.03 Å. Also given in Table I are the values from neutron diffraction[7] at 300, 120, and 75 K. Figures 1(a)–1(c) show the temperature variation of c [Figs. 1(a) and 1(b)], and the unit-cell volume in the range of 100–80 K both for the pellet and the powder.

TABLE I. Lattice parameters of $YBa_2Cu_3O_{7-\delta}$

		Lattice Parameters (Å)			
δ	T (K)	a	b	c	Ref.
NS[a]	300	3.8206	3.8851	11.6757	
	120	3.8141	3.8812	11.6395	7
	75	3.8131	3.8806	11.6329	
0.10	272	3.846	3.883	11.661	
to	219	3.833	3.879	11.528	
0.15	125.8	3.854	3.907	11.567	
	101.8	3.824	3.884	11.588	
	96.5	3.828	3.892	11.592	Present
	93.9	3.831	3.889	11.582	work
	91.1	3.831	3.889	11.454	
	89.9	3.806	3.867	11.870	
	88.2	3.833	3.902	11.726	
	87.0	3.844	3.889	11.616	
	85.3	3.837	3.909	11.494	

[a]NS: Not specified.

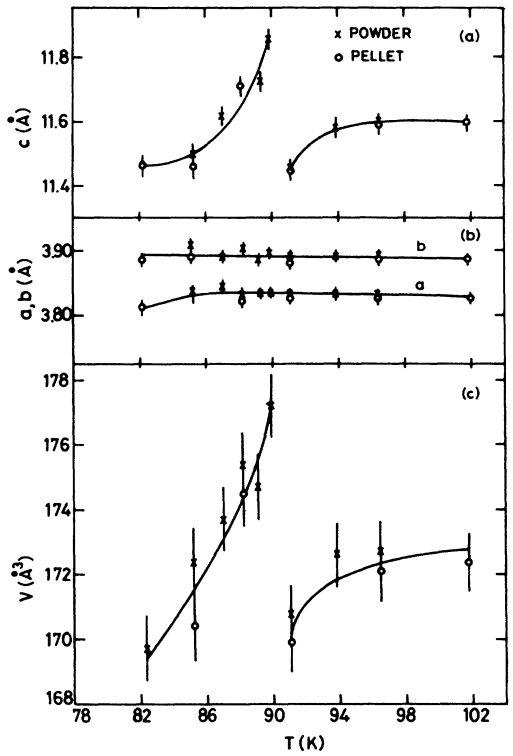

FIG. 1. Temperature variation of lattice parameters [(a), (b), and (c)] and unit-cell volume (V) in $YBa_2Cu_3O_{7-\delta}$. (a) variation of (c); (b) variation of (a) and (b); (c) variation of unit-cell volume.

One sees that the two sets of values do not differ, in general, by more than the errors in lattice parameter determination mentioned above.

The orthorhombic distortion in the present sample at room temperature appears to be smaller than for the samples of most of the other workers. It should once again be emphasized that the sample was a single-phase material with an orthorhombic structure and the x-ray diffractogram did not show any evidence for a mixture of orthorhombic and tetragonal phases. The difference in the orthorhombic distortion does not seem to have any appreciable effect on T_c, since our samples had a T_c of 91 K, the same as most of the other samples. The difference in the orthorhombic distortion might be due to details of oxygen-annealing treatment for the different samples.

Figure 1(a) shows a very sharp and *pronounced* anomaly in the lattice parameter c through the transition. c increases abruptly at the transition temperature through about 0.4 Å and then recovers its original value as the temperature is reduced below T_c. No such large pronounced anomaly is seen in the lattice parameters a and b. Figure 2 shows the prominent x-ray diffraction peaks at 298, 91.1, 89.9, and 85.3 K. One sees clearly a shift of the peaks to a larger value of 2θ as the temperature is reduced from 298 to 91.1 K, and again from 89.9 to 85.3 K. However, at 89.9 K, the peaks occur at smaller 2θ values than at 91.1 K, clearly arising from an anomalous increase in the lattice parameter c. One should also note in Fig. 2, that at 89.9 K, the relative intensities of the peaks (103)

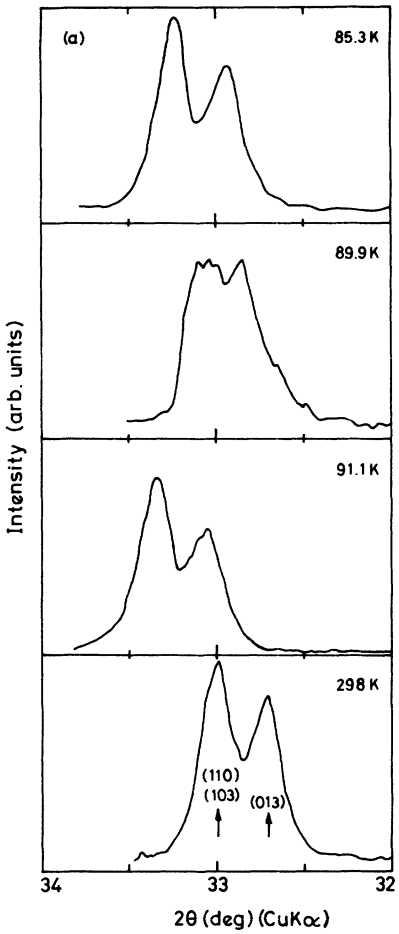

FIG. 2. Shifts in (103), (110), and (013) x-ray Bragg peaks in $YBa_2Cu_3O_{7-\delta}$ before and after superconducting transition at selective temperatures.

and [(110), (013)] have become nearly equal and the widths of the peaks have increased to give a broad, nearly unresolved peak. However, both at higher and lower temperatures than 89.9 K, the peaks are well resolved and the peak (013) has a lower intensity than the outer peak. It was also observed that at 89.9 K the peak [(116), (123)] had broadened considerably. But the peak was sharper both at higher and lower temperatures.

Since the results on the pellet and the loosely filled powder are in agreement in exhibiting the anomaly, the anomaly cannot be attributed to changing intergranular stress effects. Impurity phases are not seen and even if present, cannot account for the anomalous shifts in the peaks characteristic of the 1:2:3 phase.

No thermal hysteresis was seen since each run took about 8 h and the sample was allowed to warm up to room temperature between successive runs.

Horn *et al.*[5] have not observed such an anomalous behavior in c though a careful perusal of their graph depicting the variation of c as a function of temperature shows a deviation from the smooth graph around T_c. They observed a very small anomaly in their orthorhombic distortion a-b. However, the present accuracy of 0.01 Å in the determination of the parameters a and b does not allow us to draw any definite conclusion about the existence of such an anomaly from our data.

Several experiments on sound velocity indicate an anomalous behavior near T_c. In particular, Ewert *et al.*[12] measured the longitudinal and transverse sound velocities in a pellet of $YBa_2Cu_3O_{7-\delta}$ which had a density 75% of the theoretical value. Srinivasan *et al.*[13] measured the longitudinal sound velocity on a pellet about 1 cm in thickness prepared in our institute using the same procedure that was used in preparing the pellet for x-ray diffraction in the present study. Both these observers found that the sound velocity showed an abrupt rise as the sample was cooled through the transition and hysteresis was observed on performing the experiments while cooling and warming the sample. Srinivasan *et al.*[13] speculated that this anomaly may be related to a softening of the acoustic mode propagating along the c axis as a precursor to the transition as T_c is approached and a hardening of the acoustic mode after the superconducting transition when the structure reverts to a stable one. Ewert *et al.*[12] as well as Ramachandran, Ramdass, and Srinivasan[18] noted that in denser samples with a finer grain size, the anomalous behavior of sound velocity disappears. This could be due to a more random distribution of grain orientations leading to a smoothening out of the anomaly.

Mathias *et al.*[19] have found softening of the torsional modulus of $YBa_2Cu_3O_{7-\delta}$ at the superconducting transition. The change is 3–4 orders of magnitude larger than for a typical superconductor. It is not clear if this anomaly could be correlated with the present observations on the lattice parameter c.

Riesemeier *et al.*[14] observed that the two NQR frequencies due to planar copper atoms and linear-chain copper atoms both showed a sudden decrease in value of T_c. Once the transition was crossed, there was a recovery of the frequencies to their original value as the temperature was lowered further. The abrupt increase in c at T_c followed by the recovery of c to its original value observed in the present study is consistent with the observations of Riesemeier *et al.*

Ming-Kang Teng *et al.*[15] have shown that in positron annihilation the zero time t_0, the average lifetime (τ_M), the free annihilation time (τ_i), as well as the long lifetime component (τ_2) as a function of temperature, show a sharp peak between 90.5 and 92.5 K with a width of 1 K. The annihilation probability of the long-life component (I_2) and the trapping rate of positrons versus temperature exhibit a dip in the transition temperature region. Both these anomalies can arise due to an *abrupt decrease* in the electron density at positron sites as the transition temperature is approached. A more interesting observation is that all the above parameters reach their normal values (i.e., values above T_c) after passing the superconducting transition. From Fig. 1(c) we see that the volume of the unit cell increases anomalously at the transition and recovers its original value as the sample is cooled below T_c.

Figure 3 shows the variation of the lattice parameters and the cell volume in the range of 300–91.1 K. One again sees a sharp drop in the c parameter around 240 K. The results of longitudinal sound velocity in 65% dense pellet of Srinivasan *et al.*[13] are shown in Fig. 4. A steep

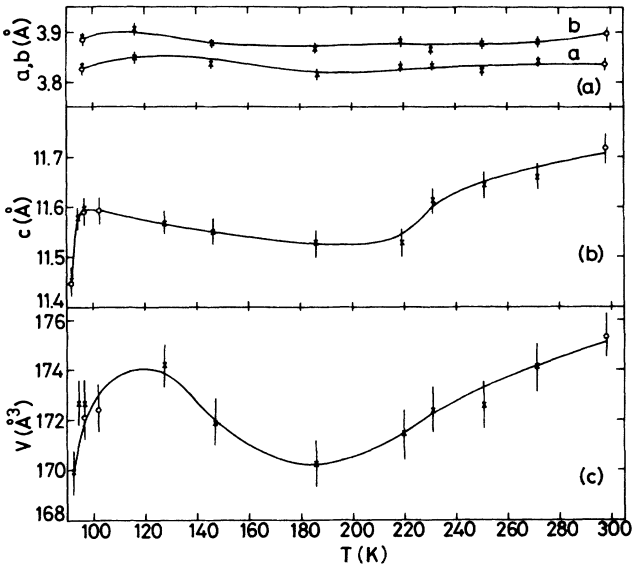

FIG. 3. Temperature variation of lattice parameters [(a), (b), and (c)] and unit-cell volume (V) in the range of 91–300 K. (a) variation of (a) and (b); (b) variation of (c); (c) variation of unit-cell volume.

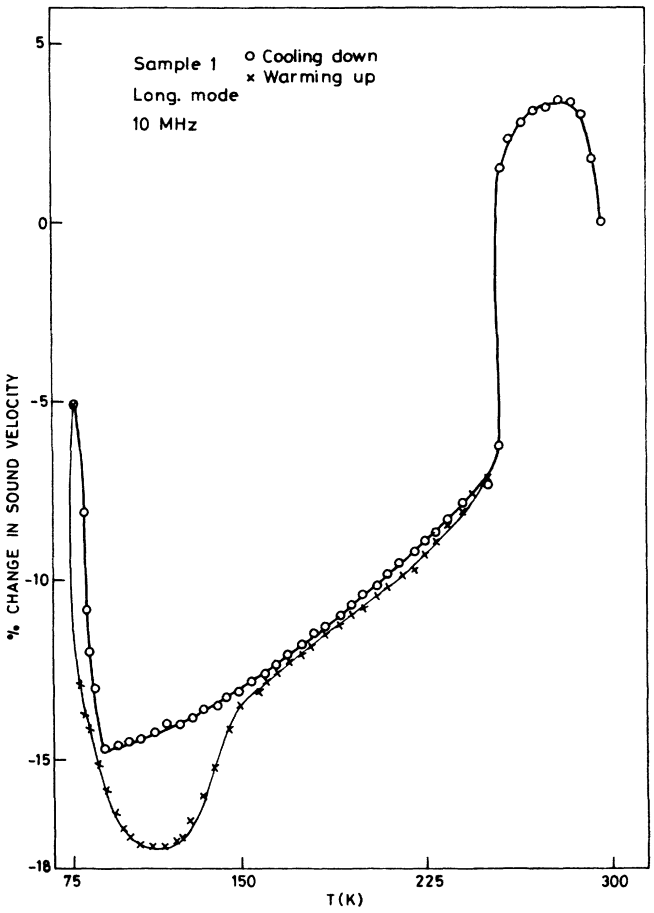

FIG. 4. Temperature variation of longitudinal sound velocity in $YBa_2Cu_3O_{7-\delta}$.

drop in sound velocity is seen around 250 K and the variation of the sound velocity with temperature is similar to the variation of c in Fig. 3(a). He Yusheng *et al.*[10] observed anomalies in ultrasonic attenuation and differential scanning calorimetry (DSC) at 250 and 160 K. They speculated on a possible structural distortion at these temperatures. These speculations appear to be borne out by present results.

In summary, an anomalous change in c has been observed in a sample of $YBa_2Cu_3O_{7-\delta}$ both at T_c and around 240 K. δ was between 0.1 and 0.15. The variation in c observed here is consistent with anomalies in NQR frequencies by Riesemeier *et al.*[14] and in positron annihilation by Ming-Kang Teng *et al.*[15] and in sound velocity by Srinivasan *et al.*[13] However, other workers have not observed these anomalies. There is, therefore, reason to believe that details of annealing treatment may be the cause for the contradictory results. It is necessary to make detailed studies on samples prepared under differing annealing treatments to understand under what conditions such anomalies appear. Such structural distortions may have a role in the superconducting properties.

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[1]M. K. Wu *et al.*, Phys. Rev. Lett. **58**, 908 (1987).
[2]T. Siegrist *et al.*, Phys. Rev. B **35**, 7137 (1987).
[3]Ivan K. Schuller *et al.*, Solid State Commun. **63**, 385 (1987).
[4]A. C. Momin *et al.*, Solid State Commun. **64**, 329 (1987).
[5]P. M. Horn *et al.*, Phys. Rev. Lett. **59**, 2772 (1987).
[6]W. I. F. David *et al.*, Nature **327**, 28 (1979).
[7]J. J. Capponi *et al.*, Europhys. Lett. **3**, 130 (1987).
[8]M. Francois *et al.*, Solid State Commun. **63**, 1149 (1987).
[9]D. P. Almond, E. Lambson, G. A. Saunders, and Wang Hong, J. Phys. F **17**, L221 (1987).
[10]He Yusheng *et al.*, J. Phys. F **17**, L244 (1987).
[11]V. Muller *et al.*, in *Proceedings of the Eighteenth International Conference on Low Temperature Physics* [Jpn. J. Appl. Phys. **26**, Suppl. 26-3, 993 (1987)].
[12]S. Ewert *et al.*, Solid State Commun. **64**, 1153 (1987).
[13]R. Srinivasan, V. Ramachandran, A. T. Seshadri, and G. Ananda Ramdass, Pramana **29**, L603 (1987).
[14]H. Riesemeier *et al.*, Solid State Commun. **64**, 309 (1987).
[15]Ming-Kang Teng *et al.*, Phys. Lett. A **124**, 363 (1987).
[16]R. Srinivasan and K. S. Girirajan, Pramana **19**, 203 (1982).
[17]H. P. Klug and L. E. Alexander, *X-ray Diffraction Procedures* (Wiley, New York, 1974), pp. 597–604.
[18]V. Ramachandran, G. Ananda Ramdass, and R. Srinivasan, in Proceedings of the International Conference on High-Temperature Superconductors and Materials and Mechanisms of Superconductivity, Interlaken, 1988 [Physica C (to be published)].
[19]H. Mathias *et al.*, Phys. Rev. B **36**, 2411 (1987).