

Superconducting Cuprates and Related Oxides. IV. Temperature – Unit Cell Parameter Relationships of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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The compound $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is a rare-earth cuprate with the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -type structure and with transition to superconductivity near 90 K. The transition from the normal conducting to the superconducting state is not related to a structural phase transition, where the structure is described in two different space groups above and below the transition temperature. However, it is possible that some physical properties apart from the conductivity are different from each other above and below the transition temperature. In this work, the thermal expansion of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was investigated in the temperature range from 40 to 300 K using synchrotron X-ray powder diffraction and neutron powder diffraction.

The compound was made by solid-state reactions of stoichiometric mixtures of BaCO_3 (Merck p.a.), Ho_2O_3 (Fluka p.a.) and CuO (Merck p.a.) as described previously.¹ The purity of the reaction product was investigated from X-ray powder patterns measured on a Stoe diffractometer with a curved position-sensitive detector that covers a 2θ range of 40° . With two positions of the detector a range of approximately 80° in 2θ was measured. The sample investigated showed no signs of impurities.

The superconductivity of the sample was investigated qualitatively by the flux exclusion method with a small permanent magnet and a disc of the compound suspended by a thin thread and cooled to liquid-nitrogen temperature. The transition temperature of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was measured on a Faraday balance to be 90 K.

The neutron diffraction powder patterns of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were measured in the temperature range 40–150 K with the neutron powder diffractometer at Risø.² The neutron wavelength of 2.3262 \AA was determined from a least-squares refinement of a powder pattern of a standard sample of Al_2O_3 with $a = 5.12984 \text{ \AA}$, $\alpha = 55.28^\circ$. The

powder was housed in a 15 mm diameter aluminium container. The patterns were measured in the 2θ range 7.00 – 111.666° in steps of 0.05289° in 2θ .

A profile refinement by the Rietveld method³ was used to calculate the atomic positions in the structure and to determine the unit-cell parameters. Starting parameters for these calculations were taken from the structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.⁴ The least-squares program EDINP⁵ was used with scattering lengths taken from Ref. 6. However, it appeared that the aluminium container was contributing considerably to the neutron powder diffraction diagram, and the program DBW3.2S⁷ was then used instead of EDINP.⁵ The DBW3.2S program can refine up to eight different structures at the same time, and in this case $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and Al were regarded as the two phases present. The refinements of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ showed that the variation of the unit cell parameters vs. temperature is greatest for the c -axis. This is displayed in Fig. 1.

For a further investigation of the thermal expansion, synchrotron X-ray powder patterns of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were measured at the powder diffractometer at the B2 beam line at HASYLAB⁸ and at Station 8.3 at Daresbury.⁹ The wavelength used at HASYLAB was 1.5407 \AA , determined by a least-squares fit of five lines of a silicon standard (SRM 640b from NIST) with $a = 5.4305 \text{ \AA}$. The powdered sample of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was a flat plate supported on a single crystal of silicon cut parallel to the (711) plane that gives no scattering contribution to the diffraction pattern. The sample was glued to the support by a thin film of vacuum grease (Baysilon-Paste from Bayer). Only selected parts of the diffraction pattern were measured in steps of 0.01° in 2θ , and these sections of the pattern were used in a least-squares refinement of the structure, using the program EDINP⁵ and scattering contributions for neutral atoms taken from Ref. 10. The models arrived at for the neutron diffraction data were used as starting values. The refinements were also made with the program DBW3.2S,⁷ and

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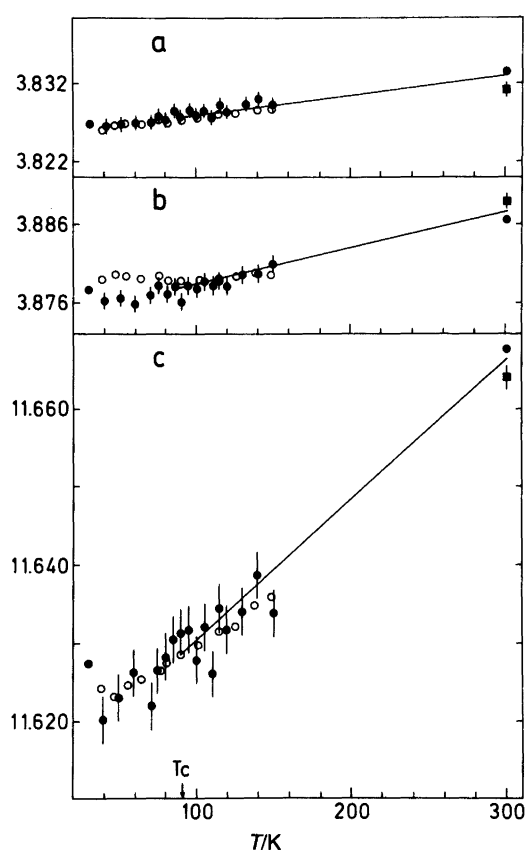


Fig. 1. Unit-cell parameters in Å of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ vs. temperature. The symbols represent the following data: open circles, neutron diffraction data; filled circles with error bars, X-ray diffraction data HASYLAB; filled circles without error bars, X-ray diffraction data Daresbury; filled squares with error bars, data from Ref. 1. The size of the symbols and the error bars indicates the standard deviations. A line is drawn from the points at T_c to 300 K to guide the eye.

Fig. 1 shows the values of the unit-cell parameters for these data.

Two powder patterns of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were measured at Daresbury at 30 and 300 K, respectively, with a wavelength of 1.5045 Å. The sample was a flat plate, and the diffraction patterns were measured in steps of 0.01° in 2θ in the 2θ interval $4.0\text{--}130.0^\circ$. In the least-squares profile refinement of the structure the program DBW3.2S⁷ was used again. The values of the unit-cell parameters determined in the refinements are also displayed in Fig. 1.

Several investigations have reported the temperature – unit cell parameter relationships of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.^{11–15} The results of these investigations show that the c -axis has a larger thermal expansion coefficient than the a - and b -axes. They also show the thermal expansion coefficient of the b -axis exhibits a jump at T_c which is not seen in the case of the a -axis.¹⁵ The orthorhombicity $2(b+a)/(b-a)$ thus shows an anomaly at T_c owing to the smaller thermal expansion of the b -axis below than above T_c .

The present investigation of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ shows similar results. The thermal expansion of the c -axis is larger

than that of the b -axis, which again is slightly larger than that of the a -axis above T_c . Below T_c the thermal expansion of the b -axis is possibly smaller than that above T_c . In this temperature range the values of the b -axis determined from the three measurements show a spread of 0.003 Å. The values from the neutron diffraction powder patterns and from the synchrotron X-ray powder pattern, measured at Daresbury, have smaller standard deviations and are thus regarded as more reliable than the values determined from the synchrotron X-ray powder data measured at HASYLAB. However, these data included only sections of the powder patterns, while the pattern from Daresbury and the neutron diffraction powder patterns were full patterns measured in the abovementioned 2θ ranges.

The investigation thus shows that the onset of superconductivity only results in a minor change in the thermal expansion coefficient of the lattice. No drastic changes in the intensities and positions of the Bragg reflections were observed in patterns recorded above and below T_c , which indicate that no phase transition involving space-group changes take place at the transition from the normal to the superconducting state.

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