



A STUDY OF THE CU-O CHAINS IN THE HIGH  $T_c$  SUPERCONDUCTOR  $YBa_2Cu_3O_7$  BY HIGH RESOLUTION NEUTRON POWDER DIFFRACTION

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The structure of orthorhombic  $YBa_2Cu_3O_7$  was refined in the temperature interval 5-320K, to an accuracy higher by a factor of about two compared to previous refinements. No major structural change is observed at the onset of superconductivity but the lattice dimensions and some of the structural parameters show small anomalies near 90K and 240K. All vibrational amplitudes are normal except for those of the O4 atoms across the Cu-O chain, which are large. Good agreement with the data is obtained by assuming that the O4 atoms are located on potential minima away by at least 0.08Å from the chain axis at all temperatures. Annealing near 240K to look for a possible order-disorder transition revealed no structural changes.

### Introduction

Recent work on oxygen deficient  $YBa_2Cu_3O_7$  suggests [1] that its superconducting transition temperature,  $T_c$ , may be increased by annealing near 240K. This indicates the possibility of subtle changes in its crystal structure such as, for example, an order-disorder transition or a lattice distortion. Anomalies near 240K were also found for the specific heat [2,3], thermal expansion [4] and elasticity [5].

Low temperature neutron diffraction work [6-9] on the structure of orthorhombic  $YBa_2Cu_3O_7$  shows that it is well ordered down to 5K. Exceptions are the oxygen atoms O4 on the so-called "linear Cu-O chains" of which some are missing, and of which the displacement amplitudes (in particular those perpendicular to the chain axis) are anomalously large compared to those of the other oxygen atoms in the structure. Large and anisotropic displacement amplitudes for these atoms have also been found from single crystal diffraction work at 298K [10,11] and 20K

[11]. Above room temperature these displacements become even larger and are apparently the precursor of a high temperature phase transition to an oxygen deficient conducting phase, with finally complete loss of the O4 chain atoms from the structure near 1000K to yield semi-conducting  $YBa_2Cu_3O_6$  [12-14]. Below room temperature the displacement amplitudes parallel to the Cu-O chain axis decrease but those perpendicular to the chain axis remain large even at 5K. No structural anomaly near 240K has been found from neutron powder diffraction measurements so far. High-resolution X-ray measurements [15], however, showed anomalous behaviour of the lattice at 90K, i.e. at, or near,  $T_c$ .

In our original structural work [6,7] we looked very carefully for evidence of further lowering of the symmetry with temperature. However, because the domain size is small ( $\approx 800\text{Å}$  along  $c$  [16]), the highest resolution of the best neutron and synchrotron powder diffractometers cannot be obtained in practice. A further

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subtle splitting of diffraction lines might then possibly be missed, as for example, was the orthorhombic splitting for  $\text{La}_2\text{CuO}_4$  in the first experiments [17]. Furthermore, if the domain size (coherence length) for additional ordering is small ( $<100\text{\AA}$ ), or if ordering occurs only in one or two dimensions, the resulting superlattice peaks, whose intensity will in any case be very small, will also be broad, and difficult to observe above the background. Finally, ordering may be sample dependent, and in particular may depend on annealing the sample at low temperature. Since it is now possible to produce very pure, single phase, stoichiometric and well ordered  $\text{YBa}_2\text{Cu}_3\text{O}_7$  we decided to repeat the structural measurements using the new high resolution neutron powder diffractometer D2B at ILL Grenoble [18].

#### Experimental

Two independent samples with slightly different oxygen contents were prepared, one in Grenoble and the other in Geneva. The Grenoble sample had the composition  $\text{YBa}_2\text{Cu}_3\text{O}_{6.86}$  (as determined from the diffraction measurements described below) and was prepared as a black powder by a sintering method described previously [6]. It was transferred in a desiccator to a cryostat with a helium atmosphere and cooled from room temperature to 239K over a period of 24 hours. It was held at 239K for 24 hours and then cooled to 5K over a further period of 24 hours. The (uniform) rate of cooling was precisely controlled. Measurements were made on D2B with a wavelength of  $1.59\text{\AA}$  at increasing temperature back up to 300K. The sample was then "quenched" from 300K to 5K within 15 minutes, and the structural measurements repeated. No superlattice peaks were ever observed, and only two tiny peaks of less than 1% of the main reflexions could not be indexed on the known orthorhombic cell. These impurity peaks did not change with temperature. To improve resolution of the structure in real space, the wavelength was then reduced to  $1.05\text{\AA}$ , and the measurements carefully repeated at 5 temperatures between 5K and 300K. Since the resolution of the diffraction pattern was limited by sample domain size broadening, the high intensity (lower resolution) configuration of D2B [18] was used. Reducing the wavelength from the  $1.91\text{\AA}$  used by Capponi et al.[6] increases the number of reflexions by a factor of 6, producing much more reliable values for structural parameters such as vibrational amplitudes.

The Geneva sample had the composition  $\text{YBa}_2\text{Cu}_3\text{O}_{6.91}$  (see below) and was prepared by citrate pyrolysis [19] as 12 black sintered ceramic cylinders of 0.5 g each. Details of preparation and physical measurements to characterize this sample will be published elsewhere [20]. Its superconductive transition temperature was 95K. Specific heat measurements on that sample showed no anomaly at 240K [21]. The material was kept in a desiccator, and was not crushed for the diffraction measurements which were performed under the same experimental conditions as described above. The two tiny peaks observed in the Grenoble sample were absent, and no extra peaks were observed at any temperature. Complete data sets up to  $2\theta=145^\circ$  were obtained at 16 different temperatures, results obtained under

the same experimental conditions. A typical diffraction pattern for this sample (that at 5K) is represented in Fig1.

**Structure refinement:** At first the refinements were made with the same ILL version of the Rietveld program used for earlier work [6]. The background was estimated and subtracted manually. Then the Wiles and Young [22] version of the program was used with automatic background

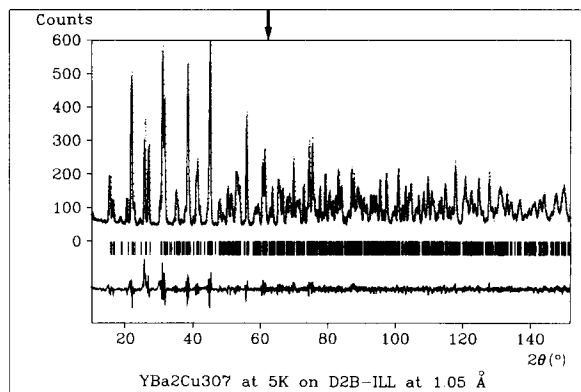


Fig.1: Observed, calculated and difference neutron powder diffraction patterns of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.91}$  (Geneva sample) at 5K. The arrow shows the limit of the earlier neutron data[6]

refinement. Since there were no significant differences between the results obtained with the two programs, for consistency all results reported here were obtained with the latter program. Except for the oxygen atom O4 on the Cu-O chain, the structure model used was that refined previously [6-9,23]: space group Pmmm ( $N^{\circ}47$  [24]), Ba in  $2t$  ( $1/2, 1/2, \pm z$ ;  $z=0.185$ ), Y in  $1h$  ( $1/2, 1/2, 1/2$ ), Cu1 in  $1a$  ( $0, 0, 0$ ), Cu2 in  $2q$  ( $0, 0, \pm z$ ;  $z=0.355$ ); O1 (called O4 in ref. 23) in  $2q$  ( $0, 0, \pm z$ ;  $z=0.159$ ); O2 in  $2s$  ( $1/2, 0, \pm z$ ;  $z=0.377$ ); O3 in  $2r$  ( $0, 1/2, \pm z$ ;  $z=0.378$ ). As to the O4 chain atom (called O1 in ref. 23), two models were tested. One (unsplit-atom model) assumed the O4 site to be located on the Cu-O chain axis, i.e. at the one-fold position  $1e$  ( $0, 1/2, 0$ ; point symmetry mmm), with nearly full occupancy and anisotropic temperature factor. The other (split-atom model) assumed this site to be displaced along  $[100]$  perpendicular to the Cu-O chain axis, i.e. at the two-fold position  $2k$  ( $\pm x, 1/2, 0$ ;  $x=0.020$ ; point symmetry  $2mm$ ), with nearly half occupancy and isotropic temperature factor. The latter model was recently refined on neutron diffraction data of relatively low resolution ( $\sin\theta/\lambda=0.45\text{\AA}^{-1}$  [25]). Preliminary refinements of both models on our data with variable occupancy factors showed that the occupancy factors of O4 did not vary significantly as a function of temperature. Thus they were fixed in the final refinements at the average refined values 0.86(1) and 0.91(1) (0.430(5) and 0.455(5) for the split-atom refinements) corresponding to the compositions  $\text{YBa}_2\text{Cu}_3\text{O}_{6.86}$ (1) (Grenoble) and  $\text{YBa}_2\text{Cu}_3\text{O}_{6.91}$ (1) (Geneva), respectively. In view of the low estimated stan-

standard deviations for the refined occupancy factors and the accurately known neutron scattering lengths (better than 1% for oxygen) the difference in oxygen content between the more reduced Grenoble sample and the less reduced Geneva sample can be taken with confidence. Refinements of the occupancy factors for the so-called O5 sites (those at 1/2, 0, 0) showed that they were not significantly occupied at any temperature and the occupancies were therefore set to zero for the final refinements. The number of param-

eters refined was 29 (30 for the unsplit-atom refinement) of which 6 for the background function (for a description see [22]).

### Results and discussion

The structural parameters and agreement indices for  $YBa_2Cu_3O_{6.86}$  and  $YBa_2Cu_3O_{6.91}$  as obtained from the split-atom refinement are summarized in Table 1a and 1b. The refinements with unsplit O4 atoms had about the same  $R_f$  values and did not yield parameters which differed sig-

Table 1a: Structural parameters and refinement indices for  $YBa_2Cu_3O_{6.91}$  (Geneva sample)

	5K	40K	70K	85K	95K	110K	130K	150K
a	3.8091(1)	3.8093(1)	3.8097(1)	3.8097(1)	3.8099(1)	3.8102(1)	3.8109(1)	3.8115(1)
b	3.8788(1)	3.8787(1)	3.8788(1)	3.8788(1)	3.8789(1)	3.8791(1)	3.8793(1)	3.8795(1)
c	11.6369(3)	11.6376(3)	11.6397(3)	11.6409(3)	11.6425(3)	11.6445(3)	11.6477(3)	11.6512(3)
v	171.93(1)	171.95(1)	172.00(1)	172.02(1)	172.05(1)	172.11(1)	172.19(1)	172.28(1)
Ba								
z	0.1845(2)	0.1841(2)	0.1841(2)	0.1841(2)	0.1846(2)	0.1842(2)	0.1841(2)	0.1842(2)
B	0.25(2)	0.25(2)	0.32(2)	0.26(2)	0.30(2)	0.35(2)	0.37(2)	0.39(2)
Y								
B	0.25(2)	0.22(2)	0.26(2)	0.28(2)	0.31(2)	0.30(2)	0.28(2)	0.34(2)
Cu1								
B	0.28(2)	0.28(2)	0.28(2)	0.30(2)	0.32(2)	0.31(2)	0.31(2)	0.35(2)
Cu2								
z	0.3552(1)	0.3548(1)	0.3550(1)	0.3551(1)	0.3551(1)	0.3550(1)	0.3549(1)	0.3553(1)
B	0.18(1)	0.23(1)	0.23(1)	0.22(1)	0.25(1)	0.26(1)	0.29(1)	0.30(1)
O1								
z	0.1595(1)	0.1595(1)	0.1594(1)	0.1594(1)	0.1595(1)	0.1593(1)	0.1589(1)	0.1591(1)
B	0.42(2)	0.44(2)	0.43(2)	0.51(2)	0.50(2)	0.48(2)	0.50(2)	0.53(2)
O2								
z	0.3779(1)	0.3781(1)	0.3781(1)	0.3781(1)	0.3782(1)	0.3781(1)	0.3779(1)	0.3783(1)
B	0.37(2)	0.35(2)	0.38(2)	0.40(2)	0.38(2)	0.39(2)	0.41(2)	0.42(2)
O3								
z	0.3772(1)	0.3774(1)	0.3775(1)	0.3774(2)	0.3773(2)	0.3775(2)	0.3776(2)	0.3774(2)
B	0.32(2)	0.35(2)	0.36(2)	0.36(2)	0.37(2)	0.38(2)	0.39(2)	0.43(2)
O4								
x	0.0219(19)	0.0228(17)	0.0223(18)	0.0225(19)	0.0209(21)	0.0254(16)	0.0249(17)	0.0271(16)
B	0.35(4)	0.24(4)	0.30(4)	0.35(4)	0.39(4)	0.36(4)	0.38(4)	0.38(4)
O4*								
B11	0.94(9)	0.91(8)	0.92(9)	0.99(9)	0.95(9)	1.17(10)	1.14(10)	1.37(11)
B22	0.25(7)	0.18(6)	0.18(6)	0.31(7)	0.32(7)	0.15(7)	0.12(7)	0.30(7)
B33	0.45(8)	0.29(7)	0.43(8)	0.39(8)	0.45(8)	0.57(8)	0.68(9)	0.43(8)
$R_f$	2.07	2.32	2.47	2.31	2.22	2.49	2.59	2.38
$R_f$	2.07	2.33	2.46	2.31	2.22	2.48	2.62	2.39
$R_p$	5.98	5.78	5.86	5.99	5.85	5.88	5.91	5.91
$R_i$	3.73	3.89	4.03	4.13	3.99	4.21	4.25	4.14
$R_{wp}$	7.67	7.43	7.51	7.65	7.53	7.58	7.66	7.61
$R_{exp}$	6.00	5.80	5.80	5.95	5.94	5.81	5.81	5.93
	170K	190K	210K	230K	240K	250K	270K	320K
a	3.8121(1)	3.8128(1)	3.8136(1)	3.8143(1)	3.8148(1)	3.8151(1)	3.8158(1)	3.8177(1)
b	3.8798(1)	3.8802(1)	3.8806(1)	3.8812(1)	3.8815(1)	3.8817(1)	3.8822(1)	3.8836(1)
c	11.6542(3)	11.6580(3)	11.6620(3)	11.6662(3)	11.6681(3)	11.6699(3)	11.6737(3)	11.6827(3)
v	172.37(1)	172.47(1)	172.59(1)	172.71(1)	172.77(1)	172.82(1)	172.93(1)	173.21(1)
Ba								
z	0.1843(2)	0.1842(2)	0.1842(2)	0.1841(2)	0.1848(2)	0.1843(2)	0.1847(2)	0.1844(2)
B	0.43(2)	0.48(2)	0.48(2)	0.51(2)	0.51(2)	0.53(2)	0.59(2)	0.64(2)
Y								
B	0.33(2)	0.32(2)	0.41(2)	0.38(2)	0.38(2)	0.42(2)	0.45(2)	0.49(2)
Cu1								
B	0.37(2)	0.39(2)	0.42(2)	0.44(2)	0.40(2)	0.46(2)	0.46(2)	0.51(2)
Cu2								
z	0.3552(1)	0.3551(1)	0.3552(1)	0.3552(1)	0.3551(1)	0.3551(1)	0.3552(1)	0.3552(1)
B	0.32(1)	0.36(1)	0.37(1)	0.40(1)	0.38(2)	0.42(2)	0.45(2)	0.52(2)
O1								
z	0.1591(1)	0.1591(1)	0.1591(1)	0.1590(1)	0.1588(2)	0.1590(2)	0.1588(2)	0.1588(2)
B	0.56(2)	0.57(2)	0.62(2)	0.64(2)	0.67(2)	0.66(2)	0.68(2)	0.75(2)
O2								
z	0.3779(1)	0.3781(1)	0.3778(1)	0.3780(1)	0.3784(2)	0.3781(2)	0.3778(2)	0.3779(2)
B	0.43(2)	0.45(2)	0.49(2)	0.52(2)	0.56(3)	0.53(2)	0.56(2)	0.62(2)
O3								
z	0.3778(2)	0.3777(2)	0.3781(2)	0.3778(2)	0.3777(2)	0.3780(2)	0.3778(2)	0.3780(2)
B	0.44(2)	0.47(2)	0.48(2)	0.53(2)	0.47(2)	0.52(2)	0.55(2)	0.64(2)
O4								
x	0.0278(15)	0.0307(13)	0.0321(13)	0.0313(14)	0.0307(17)	0.0336(13)	0.0342(14)	0.0356(13)
B	0.38(4)	0.34(4)	0.38(4)	0.48(5)	0.59(6)	0.43(5)	0.62(5)	0.50(5)
O4*								
B11	1.39(10)	1.66(11)	1.83(12)	1.82(12)	1.86(14)	2.05(13)	2.25(14)	2.40(14)
B22	0.12(7)	0.16(7)	0.15(7)	0.21(7)	0.30(8)	0.13(7)	0.29(8)	0.17(7)
B33	0.64(9)	0.48(8)	0.59(9)	0.77(9)	0.88(11)	0.73(9)	0.98(10)	0.78(10)
$R_f$	2.76	2.79	2.82	3.04	2.74	2.95	3.20	3.41
$R_f$	2.76	2.79	2.83	3.06	2.75	2.98	3.21	3.43
$R_p$	5.82	5.80	5.74	5.73	6.29	5.75	5.59	5.74
$R_i$	4.55	4.46	4.63	4.78	4.67	4.94	4.91	5.18
$R_{wp}$	7.51	7.44	7.36	7.31	8.10	7.43	7.21	7.31
$R_{exp}$	5.81	5.81	5.82	5.81	6.81	5.81	5.82	5.83

Table 1b: Structural parameters and refinement indices for  $YBa_2Cu_3O_{6.86}$  (Grenoble sample)

	5K	80K	110K	200K	300K
a	3.8103(1)	3.8108(1)	3.8114(1)	3.8142(1)	3.8180(1)
b	3.8789(1)	3.8789(1)	3.8792(1)	3.8807(1)	3.8835(1)
c	11.6287(3)	11.6328(3)	11.6373(3)	11.6527(3)	11.6726(3)
V	171.87(1)	171.95(1)	172.06(1)	172.48(1)	173.07(1)
Ba					
z	0.1849(1)	0.1851(1)	0.1851(2)	0.1853(2)	0.1857(2)
B	0.27(2)	0.32(2)	0.36(2)	0.49(2)	0.65(2)
Y					
B	0.29(2)	0.33(2)	0.34(2)	0.42(2)	0.54(2)
Cu1					
B	0.36(2)	0.38(2)	0.42(2)	0.49(2)	0.59(2)
Cu2					
z	0.3555(1)	0.3555(1)	0.3556(1)	0.3559(1)	0.3560(1)
B	0.22(1)	0.25(1)	0.26(1)	0.37(2)	0.50(2)
O1					
z	0.1597(1)	0.1598(1)	0.1596(1)	0.1596(2)	0.1592(2)
B	0.51(2)	0.53(2)	0.55(2)	0.67(2)	0.80(2)
O2					
z	0.3781(1)	0.3781(1)	0.3780(1)	0.3781(2)	0.3782(2)
B	0.37(2)	0.38(2)	0.41(2)	0.52(2)	0.65(3)
O3					
z	0.3771(2)	0.3773(2)	0.3774(2)	0.3775(2)	0.3777(2)
B	0.37(2)	0.40(2)	0.41(2)	0.52(2)	0.62(3)
O4					
x	0.0265(15)	0.0279(15)	0.0286(15)	0.0343(14)	0.0377(14)
B	0.22(4)	0.24(4)	0.29(4)	0.38(5)	0.58(6)
O4*					
B <sub>11</sub>	1.18(10)	1.32(10)	1.42(11)	2.22(14)	2.92(18)
B <sub>22</sub>	0.18(7)	0.18(7)	0.18(7)	0.31(8)	0.40(9)
B <sub>33</sub>	0.21(8)	0.24(8)	0.35(9)	0.33(9)	0.59(11)
R <sub>f</sub> *	2.57	2.62	2.65	3.12	3.48
R <sub>f</sub>	2.57	2.62	2.64	3.14	3.50
R <sub>i</sub>	4.80	4.93	5.03	5.62	6.21
R <sub>p</sub>	5.41	5.37	5.51	5.37	5.22
R <sub>wp</sub>	7.68	7.66	7.85	7.75	7.53
R <sub>exp</sub>	2.68	2.68	3.11	2.78	2.79

\*Refinement with unsplit atom model (O4 in site (0, 1/2, 0)) and anisotropic  $B_{ii}$ (O4) temperature factors.  
 Lattice parameters in Å and volume in Å<sup>3</sup>  
 Form of temperature factors(Å<sup>2</sup>):  
 isotropic:  $\exp(-B\sin^2\theta/\lambda^2)$   
 anisotropic:  $\exp(-(h^2a^2B_{11}+k^2b^2B_{22}+l^2c^2B_{33}))$   
 for a definition of the various R values see [22]

nificantly from those of the split-atom refinements. Exceptions are the thermal displacement amplitudes of the atom on the Cu-O chain axis, O4 (for values see Table 1) which, for the linear chain model were anomalously large. Except for the occupancy factors of O4 and the lattice parameters, the structure parameters for both compositions agree within 3 e.s.d.'s, and they are consistent with those reported in previous work [6-9,23,25]. Their precision, however, is higher by a factor of 2, on the average. This can be attributed to the inclusion of high-order reflexions in the present structure refinements, and to the quality of the samples.

**Lattice dimensions:** The axial lengths are determined to an accuracy of 1/4000, apart from any constant scale error in the neutron wavelength, which was calibrated to 1.0499Å by normalising the cell volume to that found for a sample of similar composition by precise X-ray measurements [15]. The error resulting from a lack of external calibration of the oxygen content is small and does not affect the following conclusions. The two samples have about the same cell volume, V, and b-parameter, but their orthorhombic splitting parameter (b-a)/(b+a) differs. That of the Grenoble material is systematically smaller than that of the Geneva material as expected from its lower oxygen content. The temperature dependence of the lattice parameters are reported in Figs 2a-d. Their change can be summarized as follows. As the tem-

perature is decreased the lattice contracts mainly along the c direction, i.e. perpendicular to the structural slabs built up by the quasi two-dimensional network of Cu-O bonds (see Fig 2 of ref.7). The contraction within these slabs is stronger along the a direction (i.e. perpendicular to the Cu-O chains) than along the b direction (i.e. parallel to these chains). Small anomalies for a, b, c and V at 90K are apparent from the graphs. They are magnified in the graph of (b-a)/(b+a) shown in Fig 2e. This parameter increases with decreasing temperature and shows a cusp around 90K, in agreement with previous X-ray measurements [15]. Its rate of increase below 90K is much smaller. There also appears to be an anomaly near 240K. This needs further confirmation.

**Atomic parameters:** As can be seen on Table 1 the displacement from the chain of the split atom O4 assumes non-zero values at all temperatures, and its temperature factor, B(O4), is comparable to those of the other oxygen atoms in the structure. For comparison the values for the anisotropic temperature factors  $B_{ii}$ (O4\*) as obtained from refinements with unsplit O4\* atoms are included in the Table. As expected they are very large, in particular those perpendicular to the chain axis,  $B_{11}$ . The temperature dependence of all refined atomic parameters is represented in Fig 3 (positional coordinates) and Fig 4 (temperature factors). For the positional coordinates the most striking variations occur with

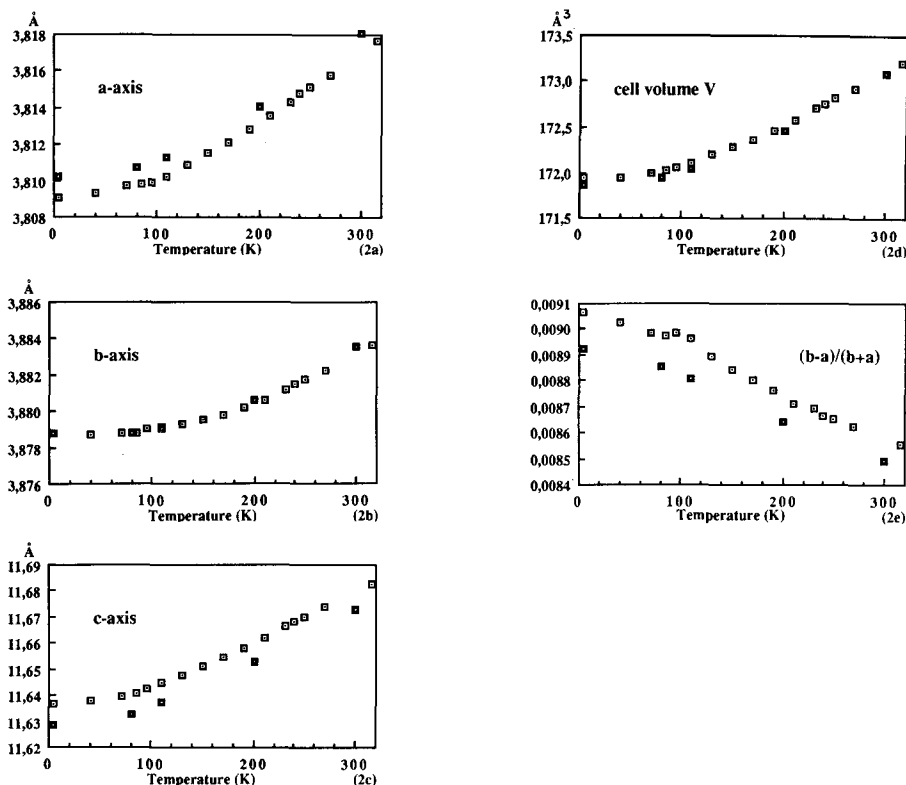


Fig.2: Cell parameters a, b, c, V, and orthorhombic lattice distortion parameter (b-a)/(b+a) as a function of temperature. Open squares:  $YBa_2Cu_3O_{6.91}$ ; filled squares:  $YBa_2Cu_3O_{6.86}$ .

the displacement parameter  $x(O4)$ . It decreases strongly down to about 90K, extrapolates to a non-zero value, and varies only little below 90K. There may also be an anomaly near 240K. Whether or not  $x(O4)$  undergoes discontinuous changes at these temperatures cannot be determined from the accuracy of the data. However the results clearly suggest that the Cu-0 chains are not linear. A structural drawing representing a possibly disordered zig-zag Cu-O chain is shown in Fig 5.

The z coordinates of most other atoms do not change much with temperature or sample preparation. At low temperature the values for O1 tend to increase while those for Ba, Cu2 and O3 tend to decrease. For the more reduced sample the Ba and Cu2 atoms move to slightly higher z values. This trend is consistent with previous reports [12] showing that z(Ba) increases from 0.184 to 0.191 on reducing  $YBa_2Cu_3O_7$  to  $YBa_2Cu_3O_6$ , while z(Cu2) increases from 0.355 to 0.363. The O1 and O2-O3 planes remain at the same z-level on oxidation. Whether or not some of the z coordinates show anomalies near 90K or 240K cannot be decided from the accuracy of the data.

The isotropic temperature factors, B, increase normally with temperature from their usual zero point values, becoming proportional to T at high temperature. Anomalies may occur at 90K and 240K but they are clearly at the limit of detectability of the data.

**Bond lengths and bond angles:** Except for the bonds involving the displaced O4 atom the values calculated from the present data are consistent with, but about twice as precise as those reported previously. At 95K, the bond and contact distances for the displaced O4 atoms are [Cu1-O4]=1.9412(3)Å, [Ba-O4]=2.851(5), 2.963(5)Å and [O1-O4]=2.6863(8)Å, compared to the values 1.9395(1)Å, 2.895(2)Å and 2.6851(8)Å, respectively, as calculated from a structure model which assumes no O4 displacements (i.e. linear Cu-0 chains). Similarly, the O4-Cu1-O4 bond angles of the Cu-0 zig-zag chains at 95K are 175.3(3)°, compared to 180° for a model which assumes linear Cu1-O4 chains. The differences between the bond lengths of the two samples are consistent with previously observed trends. The Ba-O2 and Ba-O3 distances, for example, in the more reduced sample are shorter and approach the value of the two (symmetry equivalent) bonds as observed in tetragonal  $YBa_2Cu_3O_6$  ([Ba-O2]=2.948(3)Å at 750°C) [12].

The temperature dependence of the bond lengths are represented in Fig 6. Except for [Ba-O4] and [Cu2-O1] the bonds expand only slightly with temperature. The relatively strong expansion of [Cu2-O1] reflects the relatively strong thermal expansion of the lattice along c. It is presumably related to the bonding situation within the square-pyramidal Cu2 coordination sphere which is characterized by four short

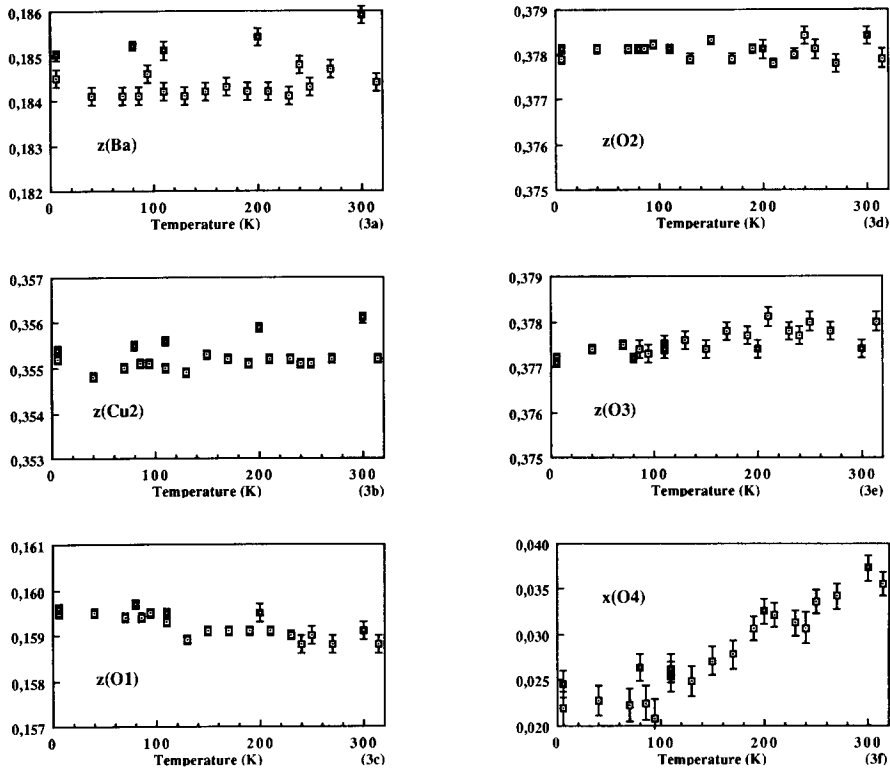


Fig.3: Fractional atomic coordinates as a function of temperature. Same symbols as Fig.2.

(i.e. strong) bonds within the base ( $[\text{Cu2-O3}]=1.9566(3)\text{\AA}$  at 95K) and one long (i.e. weak) bond toward the apex ( $[\text{Cu2-O1}]=2.277(2)\text{\AA}$  at 95K). The relatively strong expansion of  $[\text{Ba-O4}]$  is presumably related to the displacements of O4. As with the thermal parameters, anomalies near 90K and 240K are possible but cannot be detected with certainty from the present graphs.

#### Conclusion

The present study of the high temperature superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_7$  reveals structural anomalies near  $T_c$ , and also perhaps near 240K. It shows that a structure model which assumes linear Cu1-O4 chains leads to unusually large vibration amplitudes of O4 across the chain. An alternative model, which satisfies the new high resolution data at least as well with one less parameter, requires that the O4 atoms are disordered between two potential minima at about  $0.1\text{\AA}$

to either side of the chain at all temperature. This is not the kind of oxygen disorder observed previously at high temperature, with apparent occupation of the O5 positions within the channels running along  $[100]$ . Whether the positional disorder within the Cu-O zig-zag chains is static or dynamic cannot be decided from these quasi elastic data. In case of dynamic disorder the structure is likely to become ordered at low temperature, which would perhaps explain the anomalies near 240K and 90K. Evidence for a structural phase transition at the superconducting transition temperature was very recently reported from another neutron powder diffraction experiment [26].

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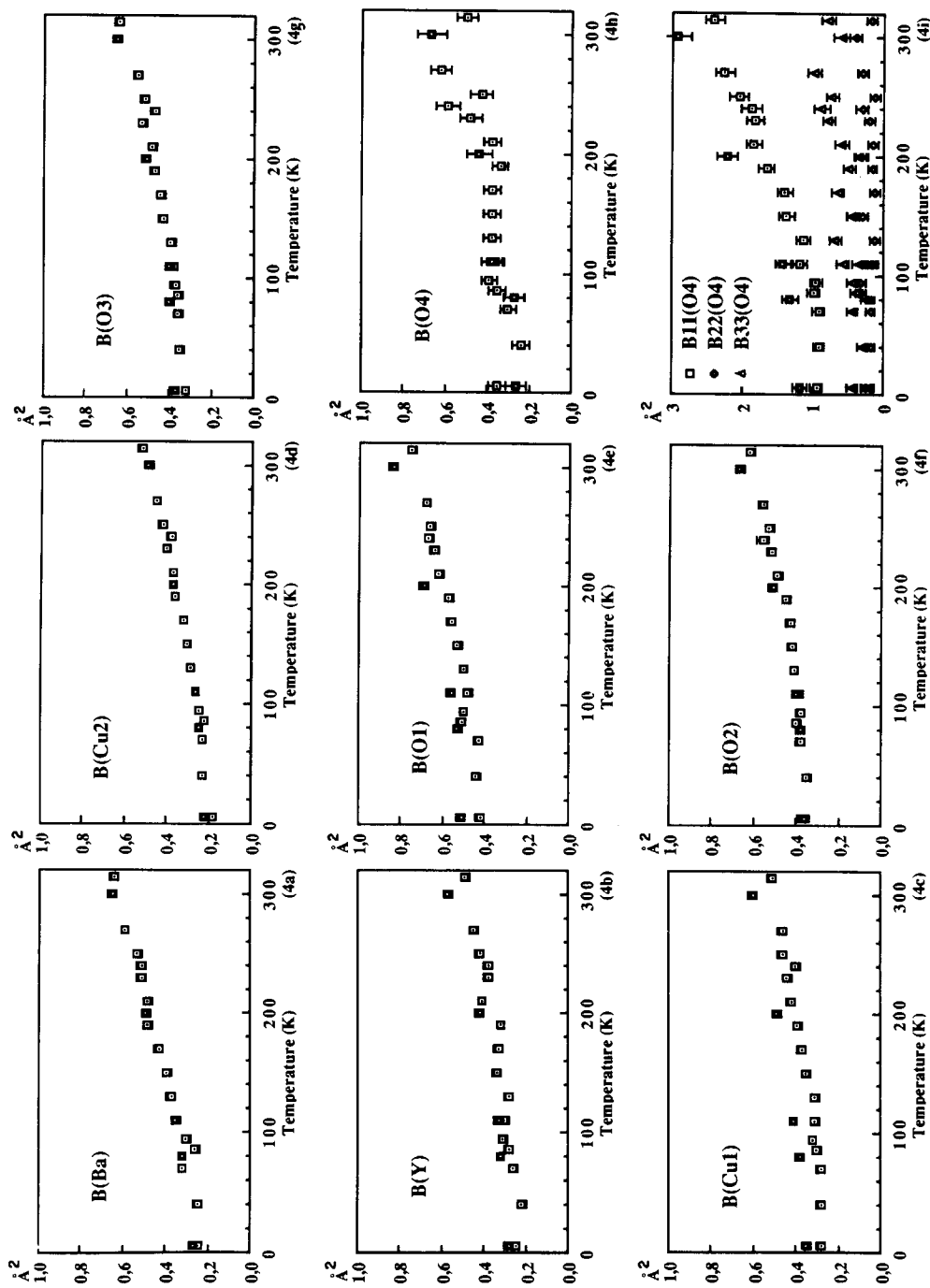


Fig.4: Temperature factors . Same symbols as Fig.2.

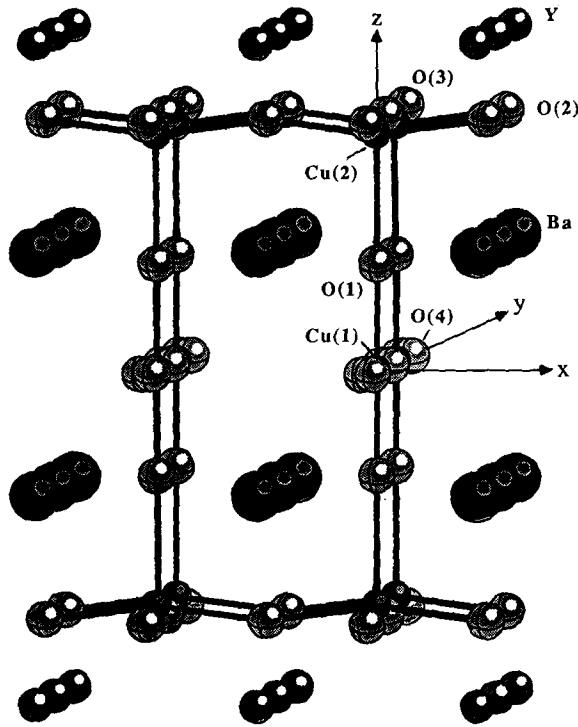


Fig.5: Partial structure of orthorhombic  $YBa_2Cu_3O_7$  showing disordered  $Cu_1-O_4$  chains with split-atom position  $O_4$ .

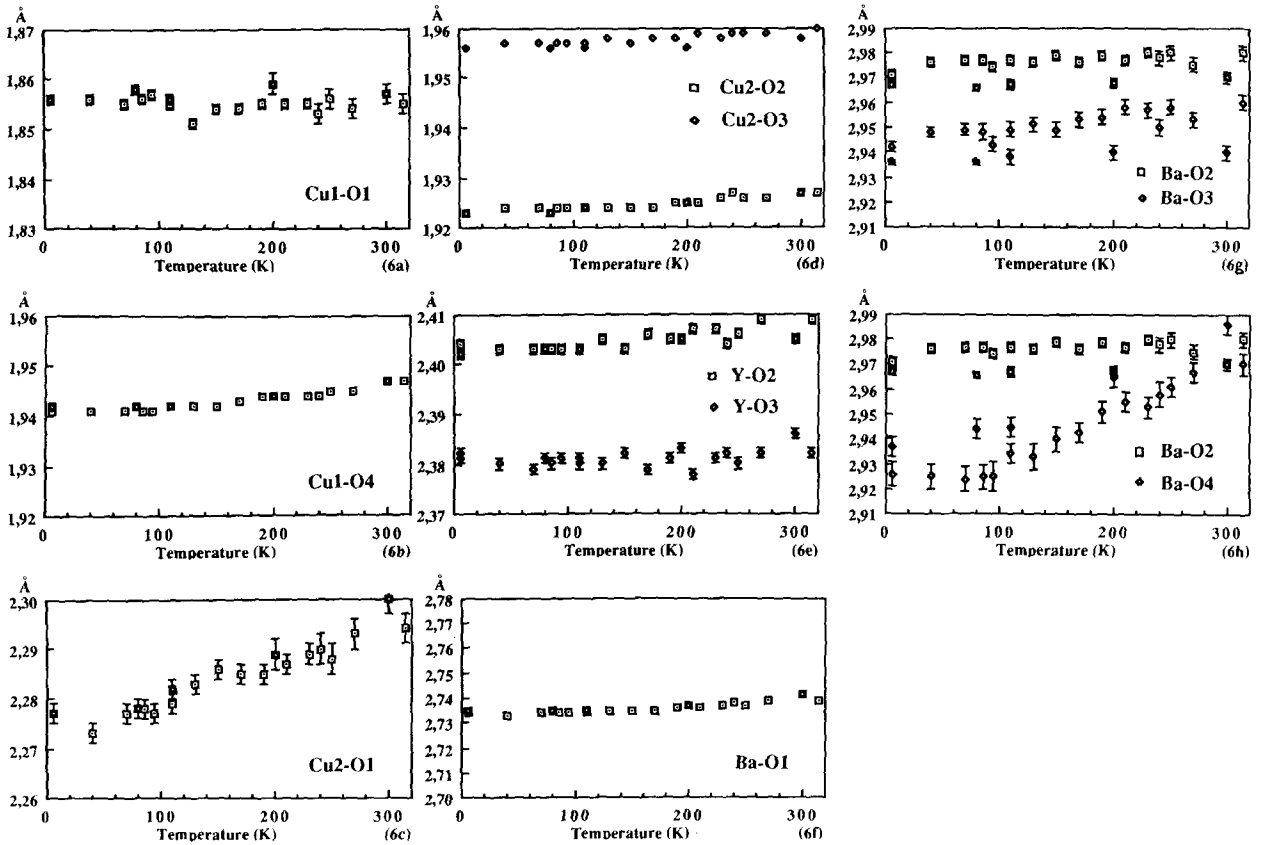


Fig.6: Bond lengths as a function of temperature. Same symbols as Fig.2.



## References

1. R. N. Bhargava, S. P. Herko and W. N. Osborne, *Phys. Rev. Lett.* **59**, 1468-1471 (1987)
2. T. Laegreid, K. Fossheim, E. Sandvold, O. Traetteberg, S. Julsrud, T. Helgesen, C.E. Gough and J.S. Abell, submitted to *Phys. Rev. B* (1987)
3. R. Calemczuk, E. Bonjour, J.Y. Henry, L. Forro, C. Ayache and M.J.G.M. Jurgens, to be published (1988)
4. R. Yaorzong, L. Liping, H. Xuelong, M. Xianglei, M. Guangyao, P. Dingkung, H. Junbao, Z. Yuheng, Submitted to *Chinese Phys. Lett.* (1987)
5. W. Yening, S. Huimin, Z. Jinsong, X. Ziran, G. Min, N. Zhongmin and Z. Zhifang, *J. Phys. C: Sol. State Phys.* **20**, L665-L668 (1987)
6. J.J. Capponi, C. Chaillout, A.W. Hewat, P. Lejay, M. Marezio, N. Nguyen, B. Raveau, J.L. Soubeyrou, J.L. Tholence and R. Tournier, *Europhysics Lett.* **3**, 1301-1307 (1987)
7. M. François, E. Walker, J.L. Jorda, P. Fischer and K. Yvon, *Sol. State Commun.* **63**, 1149-1153 (1987).
8. J.E. Greedan, A.H. O'Reilly and C.V. Stager, *Phys. Rev.* **B35**, 8770-8773 (1987)
9. F. Beech, S. Miraglia, A. Santoro and R.S. Roth, *Phys. Rev.* **B35**, 8778-8781 (1987)
10. M.F. Garbaskas, R.H. Arendt and J.S. Kasper, General Electric, report 87GRD113 (1987)
11. A. Renault, G.J. Mc Intyre, G. Collin, J.P. Pouget and R. Comes, *J. Physique* **48**, 1407-1412 (1987)
12. A.W. Hewat, J.J. Capponi, C. Chaillout, M. Marezio and E.A. Hewat, *Sol. State Commun.* **64**, 301-307 (1987)
13. J.D. Jorgensen, M.A. Beno, D.G. Hinks, L. Soderholm, K.J. Volin, R.L. Hitterman, J.D. Grace, Ivan K. Schuller, C.U. Segre, K. Zhang and M.S. Kleefisch, *Phys. Rev.* **B36**, 3608-3616 (1987)
14. P. Bordet, C. Chaillout, J.J. Capponi, J. Chénavas and M. Marezio *Nature* **327**, 687-689 (1987)
15. P.M. Horn, D.T. Keane, G.A. Held, J.L. Jordan-Sweet, D.L. Kaiser, F. Holtzberg and T.M. Rice, *Phys. Rev. Lett.* **59**, 2772-2775 (1987)
16. E.A. Hewat, M. Dupuy, A. Bourret, J.J. Capponi and M. Marezio, *Sol. State. Commun.* **64**, 517-520 (1987)
17. J.D. Jorgensen, H.-B. Schüttler, D.G. Hinks, D.W. Capone II, K. Zhang, M.B. Brodsky and D.J. Scalapino, *Phys. Rev. Lett.* **58**, 1024-1027 (1987)
18. A.W. Hewat, *Mat. Science Forum* **9**, 69 (1986)
19. D.H.A. Blank, H. Kruidhof and J. Flokstra, *J. Phys. D: Applied Phys.*, to be published.
20. A. Junod, A. Bezinge, D. Cattani, M. Decroux, D. Eckert, M. François, A. Hewat, J. Muller and K. Yvon, submitted to *Helvetica Physica Acta* (1988)
21. A. Junod, A. Bezinge and J. Muller, *Physica C*, to be published
22. D. B. Wiles and R. A. Young, *J. Appl. Cryst.* **14**, 149-151 (1981)
23. M.A. Beno, L. Soderholm, D.W. Capone II, D.G. Hinks, J.D. Jorgensen, I.K. Shuller, C.U. Segre, K. Zhang and J.D. Grace, *Appl. Phys. Lett.*, **51**, 57-59 (1987)
24. *International Tables for Crystallography Vol. A*, D. Reidel publishing company (1983)
25. Z. Jirak, F. Pollert, A. Triska and Vratislav, *Phys. Stat. Sol. (a)* **102**, K61-66 (1987)
26. W.I.F. David, P.P. Edwards, M.R. Harrison, R. Jones and C.C. Wilson, *Nature* **331**, 245-247 (1988)