Structure of the 100 K Superconductor $Ba_2YCu_3O_7$ between $(5 \div 300)$ K by Neutron Powder Diffraction.

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Abstact. – Recently Siegrist *et al.* proposed a structure for a high-T_c superconductor $Ba_2YCu_3O_{(9-\delta)}$ based on an orthorhombic ($a = a_p$, $b = a_p$, $c = 3a_p$) perovskitelike model containing Ba and Y cations ordered over the A-sites of the ABO_3 structure. This ordering is responsible for the tripling of the c-axis. Half of the oxygen vacancies (at $z = 1/2$) are ordered, while the other half (at $z = 0$) are disordered over two sites. Using profile refinement of high-resolution neutron powder data at six different temperatures between 5 K and 300 K, we have refined the structure of a pure and well-characterised powder sample with onset of superconductivity at 100 K. At all temperatures we confirmed the previous model except that in our structure, all oxygen vacancies are ordered. Two-thirds of the copper cations have a pyramidal coordination and one-third has a square coordination. In our structure all squares are parallel to the (b, c)-plane, while in the one reported by Siegrist *et al.* the squares are disorderedly parallel to either the (a, c)- or (b, c)-plane. The difference between the two models is probably due to the fact that the single crystal used in the earlier work was highly twinned. Empirical calculations of the copper valences show that the Cu^{+++} cations are almost equally distributed over the two sites. No structural change has been detected at the transition.

Early this year Wu *et al.* [1] reported that a barium, yttrium, copper ternary oxide becomes superconducting at about 90 K with onsets several Kelvin higher. The formula ($Ba_2YCu_3O_{9-\delta}$), the crystal symmetry, the lattice parameters and the average structural

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arrangement (oxygen-deficient perovskitelike) have been proposed almost simultaneously by three groups [2-4]. Subsequently, Siegrist *et al.* [5] carried out a structural determination from single-crystal X-ray data. They confirmed the previous results and established the type of ordering between the Ba and Y cations and the location of the oxygen vacancies. The Ba and Y cations are ordered in a Ba-Y-Ba-Ba–sequence along the the c-axis. All the oxygen atoms at the same z-level as the Y atoms, together with half of those forming the equatorial squares of the octahedra surrounding the Cu atoms at $z = 0$, are missing. Such an arrangement of oxygen vacancies produces important changes in the cation coordination. The yttrium and 2/3 of the copper cations are surrounded, respectively, by rhombic prisms and apically elongated pyramids. The coordination polyhedra around the barium and 1/3 of the copper cations are more complicated because these cations are surrounded by those oxygen sites which have 0.5 occupancy factors. The authors suggest that the empty oxygen sites are ordered in such a way that the copper coordination is always a square. These squares are disordered, parallel to either the (a, c)- or (b, c)-plane. The barium coordination number is 10.

We report here a different oxygen vacancy ordering for the structure of $Ba_2YCu_3O_7$ between 5 K and 300 K, as determined by high-resolution neutron powder diffraction.

The sample was prepared from a mixture of $BaCO_3$, Y_2O_3, and CuO powders, in stoichiometric proportion according to the formula $Ba_2YCu_3O_7$. The powders were ground together to a grain size less than 10 μm and heated to 950 °C for 12 hours in air. The product was then quenched in air, reground, then heated and cooled under oxygen according to the following program: heated from ambient to 950 °C at the rate of 500° per hour, maintained at 950 °C for 10 hours and then cooled to ambient temperature at the rate of 200° per hour. The final pure black product was reground to a grain size less than 20 μm.

The a.c. susceptibility of this sample as a function of temperature was measured with a mutual inductance bridge operating at 113 Hz (fig. 1). The a.c. field generated by the primary coil was 0.02 Oe peak to peak. For each temperature the sample was displaced from one to the other of the two secondary pick-up coils, thus eliminating parasitic contributions. Both the real part (X') and the imaginary part (X'') of the susceptibility were measured and expressed in the same units. Note that even at the transition, X'' is small, which usually
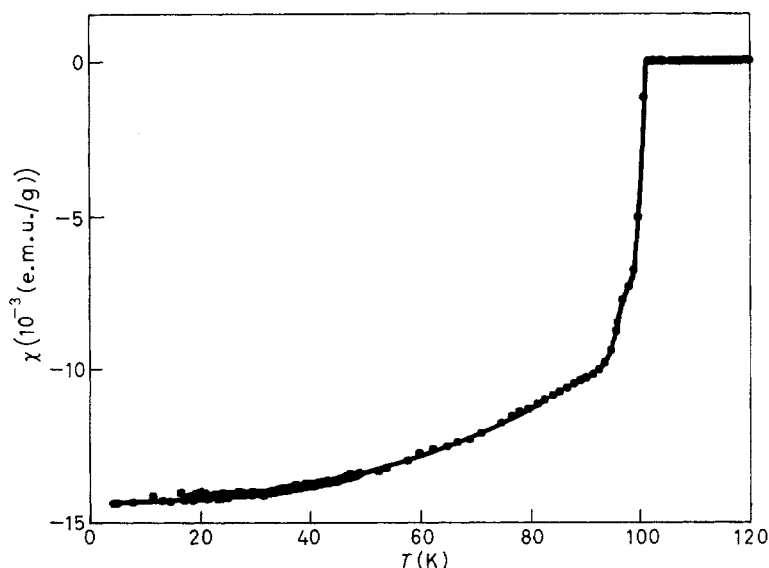

Fig. 1. – a.c. susceptibility *vs.* temperature for $Ba_2YCu_3O_7$.

indicates a small Meissner effect. This small variation might be due to the fine grain size.

Powder X-ray photographs showed that all the observed reflections could be indexed with the orthorhombic cell given by Siegrist *et al.* [5]. Although our samples contained small single crystals (largest dimension $\sim 300\,\mu m$), we decided to use powder diffraction techniques because the crystals appeared highly twinned. A qualitative analysis showed that the twinning is due to the pseudo-tetragonal symmetry of the orthorhombic $(a \approx b)$ lattice of $Ba_2YCu_3O_7$.

Neutron diffraction diagrams were collected at 5, 30, 75, 120, 200, and 300 K with a neutron wavelength of 1.909 Å on the high-resolution diffractometer D1A at the ILL [6]. The 30 K and 200 K runs were for 12 hours, and the others for 3 hours. Figure 2 shows the observed and calculated profiles for the 200 K data.
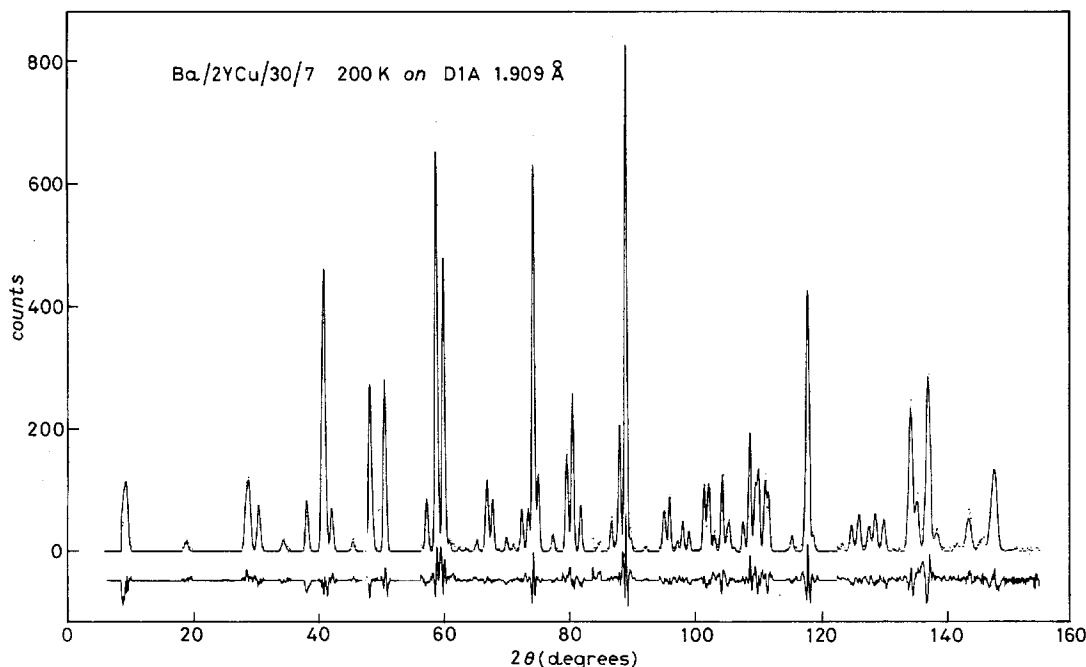

Fig. 2. – Observed (points) and calculated (line) neutron powder pattern for $Ba_2YCu_3O_7$ at 200 K, with the difference marked below.

All reflections were accounted for by a single $Ba_2YCu_3O_7$ phase, with the exception of three extremely small peaks which were found to be absent when examined and the same temperature on the very high-resolution diffractometer D2B with a different cryostat. Our sample is then apparently quite pure. In particular, we searched at all temperatures for any evidence of line broadening, splitting, or additional reflections, which might indicate a superstructure.

Profile refinement was based on the model of Siegrist *et al.* [5], using the program of Rietveld [7, 8]. The space group is *Pmmm*, $Z = 1$ with Ba at $2t\,(1/2\,1/2\,z)$, Y at $1h\,(1/2\,1/2\,1/2)$, Cu1 at $1a\,(0\,0\,0)$, Cu2 at $2q\,(0\,0\,z)$, O1 at $2q\,(0\,0\,z)$, O2 at $2s\,(1/2\,0\,z)$, O3 at $2r\,(0\,1/2\,z)$, O4 at $1e\,(0\,1/2\,0)$ and O5 at $1b\,(1/2\,0\,0)$. Beyers *et al.* [4] on the basis of convergent beam electron diffraction data, found evidence for the absence of the mirror plane perpendicular to our [0 1 0] axis and proposed the noncentric space group *Pm2m*. The atomic positions are the same, except that displacements along [0 1 0] are permitted.

Since the objective was to determine the oxygen vacancy ordering, the O4 and O5 oxygen occupancies were allowed to vary together with the atomic coordinates, temperature factors and profile parameters. Rapid convergence was obtained, with the O4 occupancy converging to 1.0 and the O5 occupancy to 0.0 to within 3 standard deviations at each temperature. For the final refinement, O5 was removed completely from the structure.

The introduction of the alternative acentric space group, $Pm2m$, did not produce any improvement in the refinement. If the structure does not contain the centre of symmetry, the acentricity must be very small. This can also be deduced from the normal values obtained for the thermal factors.

TABLE I. – *Lattice dimensions a, b, c (Å) and atomic coordinate and temperature factor parameters B (Å^2) for $Ba_2YCU_3O_7$. Then $B = 8\pi^2 \langle u^2 \rangle$, where $\langle u^2 \rangle$ is the mean square atomic displacement in Å^2, and B_{11} its componenent along the axis x.*

		5 K	30 K	75 K	120 K	200 K	300 K
	a	3.8128 (1)	3.8124 (2)	3.8131 (1)	3.8141 (1)	3.8164 (2)	3.8206 (1)
	b	3.8806 (2)	3.8807 (2)	3.8806 (2)	3.8812 (2)	3.8824 (2)	3.8851 (1)
	c	11.6303 (5)	11.6303 (5)	11.6329 (5)	11.6395 (5)	11.6546 (5)	11.6757 (4)
Ba	z	0.1826 (5)	0.1830 (3)	0.1827 (5)	0.1827 (5)	0.1841 (3)	0.1841 (4)
	B	0.14 (10)	0.41 (7)	0.20 (11)	0.32 (10)	0.83 (7)	0.59 (10)
Y	B	0.61 (11)	0.71 (7)	0.58 (11)	0.54 (10)	0.66 (6)	0.58 (10)
Cu1	B	0.01 (11)	0.39 (7)	0.09 (11)	0.02 (11)	0.38 (7)	0.38 (11)
Cu2	z	0.3542 (3)	0.3543 (2)	0.3547 (3)	0.3545 (3)	0.3547 (2)	0.3549 (3)
	B	0.37 (3)	0.46 (5)	0.47 (8)	0.37 (8)	0.48 (5)	0.51 (7)
O1	z	0.1595 (4)	0.1592 (3)	0.1590 (5)	0.1588 (4)	0.1587 (3)	0.1581 (4)
	B	0.37 (14)	0.72 (8)	0.70 (13)	0.58 (13)	0.79 (8)	0.93 (12)
O2	z	0.3773 (4)	0.3764 (3)	0.3771 (5)	0.3775 (4)	0.3768 (3)	0.3779 (4)
	B	0.0 (1)	0.27 (6)	0.0 (1)	0.0 (1)	0.26 (6)	0.11 (9)
O3	z	0.3769 (5)	0.3773 (4)	0.3773 (5)	0.3770 (5)	0.3776 (3)	0.3777 (5)
	B	0.43 (11)	0.54 (7)	0.37 (11)	0.25 (10)	0.61 (6)	0.31 (9)
O4	B_{11}	1.7 (4)	1.6 (3)	1.4 (4)	2.0 (4)	2.5 (3)	3.2 (5)
	B_{22}	1.3 (4)	1.5 (3)	1.0 (4)	0.9 (4)	1.5 (3)	0.6 (4)
	B_{33}	2.4 (6)	3.1 (4)	2.1 (6)	2.3	3.9 (4)	3.5 (6)
R_n		7.12	7.47	8.01	8.06	6.94	7.15
R_p		13.14	12.85	14.42	14.19	12.60	14.17
R_e		9.34	5.63	10.32	10.39	5.75	10.84

Table I lists the final positional and thermal parameters, together with the cell constants. R_n is the R-factor for integrated intensities, R_p the profile R-factor, and R_e the profile R-factor expected from statistics. The plot of the difference between the observed and calculated profiles in fig. 2 is typical of the very satisfactory fits obtained at all temperatures with this same structure.

The atomic coordinates have been obtained with much higher precision than is possible with the very small twinned crystals available from this material for X-ray diffraction.

With rising temperature, the thermal B-factors for all atoms increase normally, except for O4 where the vibrational amplitude perpendicular to the Cu1-O4 bond, already important at low temperature, increases still further. This was the only atom for which it was found necessary to take account of anisotropic vibration. The precision with which thermal parameters are determined is not high, as evidenced by the larger standard deviations obtained for these parameters, but the relative magnitudes appear significant.

The anisotropy of O4 cannot be taken as evidence for the space group proposed by Beyers *et al.* [4]. In fact the minor axis of the thermal ellipsoid for O4 is along the [0 1 0] axis.
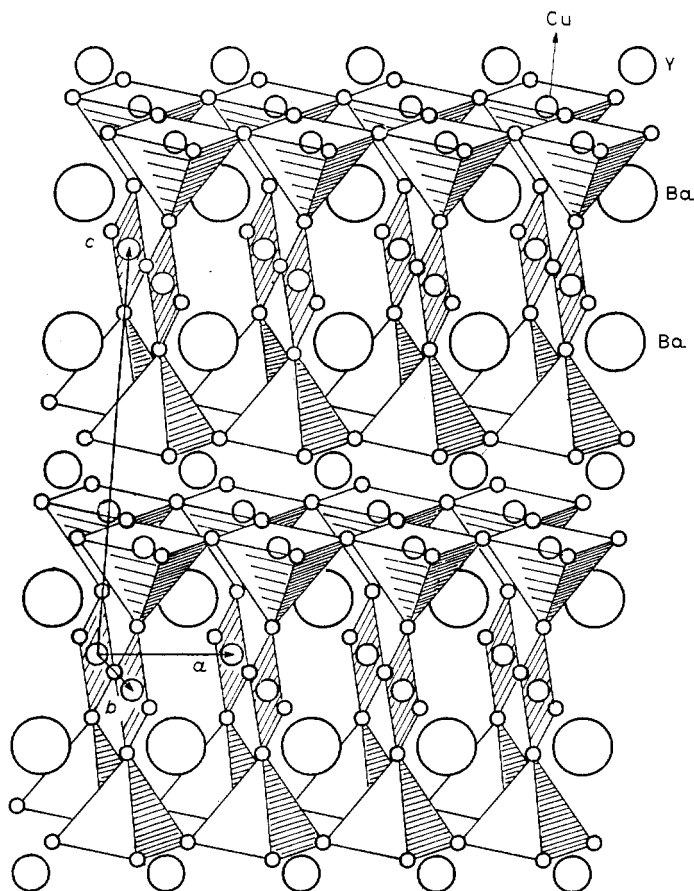

Fig. 3. – Structure of $Ba_2YCu_3O_7$ showing the CuO_5 pyramids and CuO_4 squares. The cations are not drawn to scale.

Figure 3 shows the perovskite structure ABO_3 in which the Ba and Y cations are ordered in the A-position along the *c*-axis (vertical), tripling it. The copper atoms, occupying the B-positions, are no longer at the centres of oxygen octahedra because the plane of oxygen atoms at $z = 1/2$ has been removed. This implies that if the conductivity mechanism is due to the overlapping of the Cu 3*d* and O 2*p* orbitals, then this material is a two-dimensional conductor. We have found as well, that in the $z = 0$ plane, every second line of oxygen atoms parallel to [0 1 0] has also been removed. This corresponds to a complete absence of O5 and a complete occupancy of O4. The coordination of the copper atoms at $z = 0$ consists then of oxygen squares all aligned within the (b, c)-plane. This oxygen vacancy ordering is different from that proposed by Siegrist *et al.* [5], where the oxygen vacancies in the $z = 0$ plane are disordered over the two sites O4 and O5. In their model, the oxygen coordination for the copper cations is also square, but these squares are parallel either to the (a, c)- or to the (b, c)-plane in a disordered fashion.

The barium and yttrium cations are surrounded by ten and eight oxygen atoms, respectively. The average barium and yttrium oxygen distances are given in table II. They compare well with the corresponding distances in other oxide compounds. For all the bonds, the standard deviations are small, and are reflected by similar small variations in the values obtained for the six independent measurements.

TABLE II – *Bond lengths* (Å) *for* $Ba_2YCu_3O_7$

		5 K	30 K	75 K	120 K	200 K	300 K
Ba	-O1 × 4	2.733 (1)	2.734 (1)	2.734 (1)	2.735 (1)	2.738 (1)	2.741 (1)
	-O2 × 2	2.982 (6)	2.971 (4)	2.979 (6)	2.984 (6)	2.969 (4)	2.982 (5)
	-O3 × 2	2.957 (6)	2.957 (4)	2.960 (6)	2.958 (6)	2.954 (4)	2.959 (6)
	-O4 × 2	2.854 (4)	2.857 (3)	2.855 (4)	2.856 (4)	2.871 (3)	2.876 (4)
	-mean	2.852 (95)	2.851 (93)	2.852 (95)	2.854 (95)	2.854 (93)	2.860 (95)
Y	-O2 × 4	2.409 (3)	2.415 (2)	2.411 (3)	2.408 (3)	2.414 (2)	2.409 (3)
	-O3 × 4	2.384 (4)	2.381 (2)	2.382 (4)	2.385 (3)	2.382 (2)	2.385 (3)
	-mean	2.396 (12)	2.398 (17)	2.396 (14)	2.396 (12)	2.398 (16)	2.397 (12)
Cu1	-O1 × 2	1.855 (5)	1.851 (4)	1.850 (5)	1.848 (5)	1.849 (3)	1.846 (5)
	-O4 × 2	1.940 (0)	1.940 (0)	1.940 (0)	1.941 (0)	1.941 (0)	1.942 (0)
	-mean	1.898 (42)	1.896 (45)	1.895 (45)	1.894 (46)	1.895 (46)	1.894 (48)
	-Z	2.426 (22)	2.446 (18)	2.451 (22)	2.458 (22)	2.450 (13)	2.462 (22)
Cu2	-O1 × 1	2.264 (6)	2.269 (4)	2.276 (7)	2.278 (6)	2.284 (4)	2.298 (6)
	-O2 × 2	1.925 (1)	1.923 (1)	1.924 (1)	1.926 (1)	1.926 (1)	1.929 (1)
	-O3 × 2	1.958 (1)	1.959 (1)	1.958 (1)	1.958 (1)	1.959 (1)	1.961 (1)
	-mean	2.006	2.007	2.008	2.009	2.011	2.015
	-Z	2.273 (10)	2.275 (9)	2.271 (10)	2.264 (10)	2.257 (8)	2.233 (9)
Cu	-mean Z	2.322	2.332	2.331	2.331	2.321	2.309

The two crystallographically independent copper cations are surrounded by 4 and 4+1 oxygen atoms, respectively. The Cu1 cation is at the center of a rhombuslike square, the rhombicity being about 4%. The Cu2 cation is also at the center of a rhombuslike square, however, with a fifth oxygen neighbour at about 2.27 Å, its coordination polyhedron is an apically elongated rhombic pyramid.

It should be noted that the copper coordination polyhedron network in $Ba_2YCu_3O_7$ is completely different from that found in high-T_c superconducting $La_{1.85}Sr_{0.15}CuO_4$ [9]. In the latter compound the copper cations are surrounded by 4+2 oxygen atoms forming apically elongated octahedra. At room temperature, in the tetragonal phase, the equatorial square is perfect by symmetry, and the four Cu-O distances are equal (1.890 Å). This value is very close to the average Cu1-O distance found at room temperature for $Ba_2YCu_3O_8$. However, in the latter case the coordination number for the Cu1 cation is definitely 4, whereas in the former there are two oxygen neighbours at 2.412 Å. The rhombic square around the Cu2 cations is somewhat larger, as the Cu2-O distance, averaged over the square, is 1.945 Å at room temperature. The fifth oxygen atom at the pyramid apex is at 2.298 Å.

It is possible from well-determined interatomic distances to deduce the cation valences. These have been calculated by using the Zachariasen [10] formula which relates bond distances D_{ij} to bond strengths s_{ij}. Then the cation valence Z_i is obtained by summing the bond strengths over the anion neighbours

$$Z_i = \sum_j s_{ij} = \sum_j \exp\left[(D1 - D_{ij})/(A.D1)\right].$$

Zachariasen did not give the constants $D1$ and A for the Cu-O bond. We chose for $D1$ (the distance corresponding to unit strength) the value 1.74 Å, which for $A = 0.178$, gives 2.33 valence units for the average copper valence in $Ba_2YCu_3O_7$. The calculated values are given in table II. It is clear that above and below the transition the Cu^{+++} cations are distributed between the two sites almost equally. For example, at 200 K, 46% and 54% of the Cu^{+++} cations are distributed over the sites Cu1 and Cu2, respectively. At 30 K, below the transition, the distribution does not change. If the superconductivity mechanism is based on the presence of Cu^{+++}, then both sites must be taken into account.

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