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The effect of hydrostatic pressure on the ambient temperature structure of CuO

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Abstract. Room temperature, time-of-flight, powder neutron diffraction measurements on cupric oxide, CuO, at ambient and 22(1) kbar hydrostatic pressure have provided the pressure dependence of the monoclinic lattice parameters and the single positional parameter, namely the y parameter of oxygen. The percentage changes in the cell parameters are $\Delta a/a = 0.68(4)$, $\Delta b/b = -2.02(2)$, $\Delta c/c = -0.38(2)$, $\Delta\beta/\beta = 1.02(2)$, so the volume of the cell v changes by $\Delta v/v = -2.02(4)\%$. The value of y is altered by $-0.0185(14)$. The effect of these changes is to reduce the distortion of the square-planar Cu^{2+} coordination by equalizing the bond lengths to the two oxygen pairs and making the O–Cu–O angle closer to 90° . Although there is a sizeable reduction in the bond length to the apical, next-nearest oxygen pair, this distance remains greater than the shortest O–O bond. These observations are related to previous ambient temperature studies of the pressure dependence of the Raman spectra and of the lattice parameters by synchrotron radiation, which did not determine the y parameter.

1. Introduction

The continuing interest in the role of nominally divalent copper coordinated by oxygen in the formation of high- T_c superconductors has led to a number of studies of cupric oxide CuO itself. Pure CuO provides an opportunity to study the magnetic properties of Cu^{2+} square-planar coordinated by oxygen in a relatively simple system: a complete understanding of the magnetic properties of CuO may indicate whether magnetic mechanisms actually play any role in the hole pairing in the high-temperature superconductors. An incommensurate magnetic structure forms below the Néel point at 230 K, but gives way to a commensurate structure below 217 K [1, 2]. The spin correlations above the Néel point [3, 4] and the spin wave dispersion relations have also been studied [4, 5]. In addition to these magnetic studies, the crystal structure itself and its dynamics have also been the subject of a number of investigations. The original structure, determined by Tunnell in 1933 [6], was refined by single-crystal x-ray methods in 1970 [7]. The unit cell is monoclinic, space group $C2/c$ with $Z = 4$. The Cu^{2+} ions are at centres of inversion symmetry in a single fourfold site $4c$ ($\frac{1}{4}, \frac{1}{4}, 0$) and the oxygen ions occupy a fourfold set $4e$ ($0, y, \frac{1}{4}$). The structural parameters are listed in table 1.

Following the discovery of the high- T_c superconductors, the pressure dependence of the structure and its dynamics became of interest. The behaviour of the cell dimensions has recently been reported up to a pressure of 80 kbar from a synchrotron source, single-crystal study [8]. These data were not, however, suitable for determining the pressure

Table 1. Crystallographic parameters of CuO.

Method Sample Pressure Container	X-ray Single Ambient None	V can Ambient	Neutron Powder	
			McWhan cell	
			Ambient	22(1) kbar
Parameter				
<i>a</i> (Å)	4.6837(5)	4.6840(3)	4.6863(13)	4.7162(17)
<i>b</i> (Å)	3.4226(5)	3.4273(1)	3.4276(4)	3.3582(4)
<i>c</i> (Å)	5.1288(6)	5.1316(3)	5.1333(11)	5.1126(11)
β (deg)	99.54(1)	99.512(3)	99.519(9)	100.533(8)
<i>v</i> (Å ³)	81.08(2)	81.247(8)	81.32(3)	79.61(3)
Oxygen <i>y</i>	0.4184(13)	0.4194(5)	0.4207(11)	0.4022(8)

dependence of the oxygen *y* parameter and, hence, of defining the pressure-induced changes to the ionic coordinations. Some insight into the likely behaviour of *y* has been provided by the pressure dependence of the Raman modes measured up to 350 kbar [9]. A two-parameter force constant model, dependent on the Cu–O distance in the square-planar Cu²⁺ coordination and next-shortest bond length (O–O), could not fit the shifts in frequency of the three Raman modes under the assumption that *y* remained constant with increasing pressure. A good fit could, however, be obtained with this simple model dependence if *y* decreased with increasing pressure such that $\Delta y/\Delta P = -0.25(5) \times 10^{-3} \text{ kbar}^{-1}$. We now report ambient temperature neutron powder diffraction measurements at ambient and 22(1) kbar pressure which have allowed us to determine the actual change in *y* and derive the corresponding structural changes.

2. Experimental details

The crystal structure of CuO at 22(1) kbar has been determined from time-of-flight neutron powder patterns obtained using the POLARIS diffractometer [10] at ISIS, Rutherford Appleton Laboratory. The sample material was obtained by crushing crystals grown by Mrs B M Wanklyn at the Clarendon Laboratory, Oxford University, by the flux method in a platinum crucible [11]. The starting materials for the flux were MoO₃, V₂O₃ and K₂CO₃ in the molar ratios 68 CuO + 14 MoO₃ + 9 V₂O₃ + 9 K₂CO₃. This source and preparative method also provided the single-crystal samples used in the magnetic structure [1, 2] and spin correlation studies [3]. Ambient pressure patterns were collected by the detector bank at $2\theta = 90^\circ$ from an $\approx 700 \text{ mm}^3$ sample contained in a cylindrical, thin-walled vanadium can and from one of $\approx 70 \text{ mm}^3$ inside a pressure cell of the McWhan type [12]. Approximately hydrostatic conditions were maintained by including 'Fluorinert' pressure-transmitting fluid inside the sample can. The high-pressure pattern was obtained after the cell had been loaded to 10 tons and then clamped. No standard was included since the synchrotron measurements [8] provide a check on the pressure calibration of the cell. Figure 1 illustrates the pressure cell patterns obtained at ambient and 10-ton load. The small peak at $\approx 2.1 \text{ \AA}$ is the strongest (113) alumina peak from the sleeve inside the pressure cell and demonstrates the effectiveness of the fixed diffraction geometry of a pulsed neutron source.

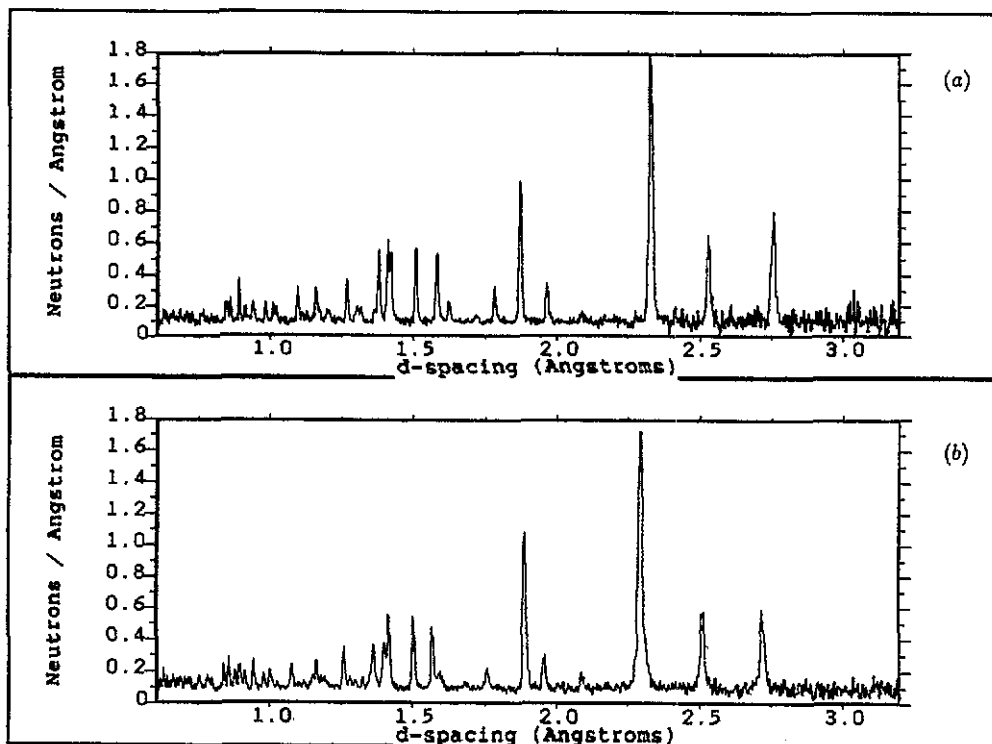


Figure 1. Neutron time-of-flight powder diffraction patterns of CuO at ambient temperature in a McWhan cell: (a) at ambient pressure, (b) under a load of 10 tons (22(1) kbar). The data have already been corrected for the wavelength dependence of the incident flux.

Data from the pressure cell runs were first corrected for the wavelength dependence of the pressure cell transmission measured by main-beam monitor detectors placed before and after the cell. Time-of-flight Rietveld refinements were then made on the cell data between 3000 and 16000 μs (corresponding to an approximate d -spacing range of $\approx 0.6 \text{ \AA}$ to $\approx 3.3 \text{ \AA}$) using the program TF14LS [13] which is based upon the Cambridge Crystallographic Subroutine Library. The isotropic temperature factors obtained from the sample outside the pressure cell were used in the analysis of the cell patterns, which were understandably of lower quality due to the smaller specimen volume and a higher background. The profile fit obtained in the refinement of the high-pressure pattern is illustrated in figure 2. Table 1 lists the parameters obtained from the three refinements and the values found in the single-crystal x-ray study [7]. It can be seen that there is good agreement between the three ambient pressure measurements, which gives us added confidence in our high-pressure parameters. A fit of the two largest fractional cell parameter changes, $\Delta b/b$ and $\Delta \beta/\beta$, to the synchrotron results [8] indicates that the pressure on our sample was 22(1) kbar, in good agreement with previous experiments with the pressure cell in which calibrants had been included. It should be noted, however, that there is considerable disagreement between our values for $\Delta a/a$ and $\Delta c/c$ and those derived from a quadratic fit to the synchrotron data in the range from ambient to 80 kbar. Our results show that the fractional change in these lattice constants is greater than had previously been quoted. Increasing the hydrostatic pressure to 22(1) kbar produces a

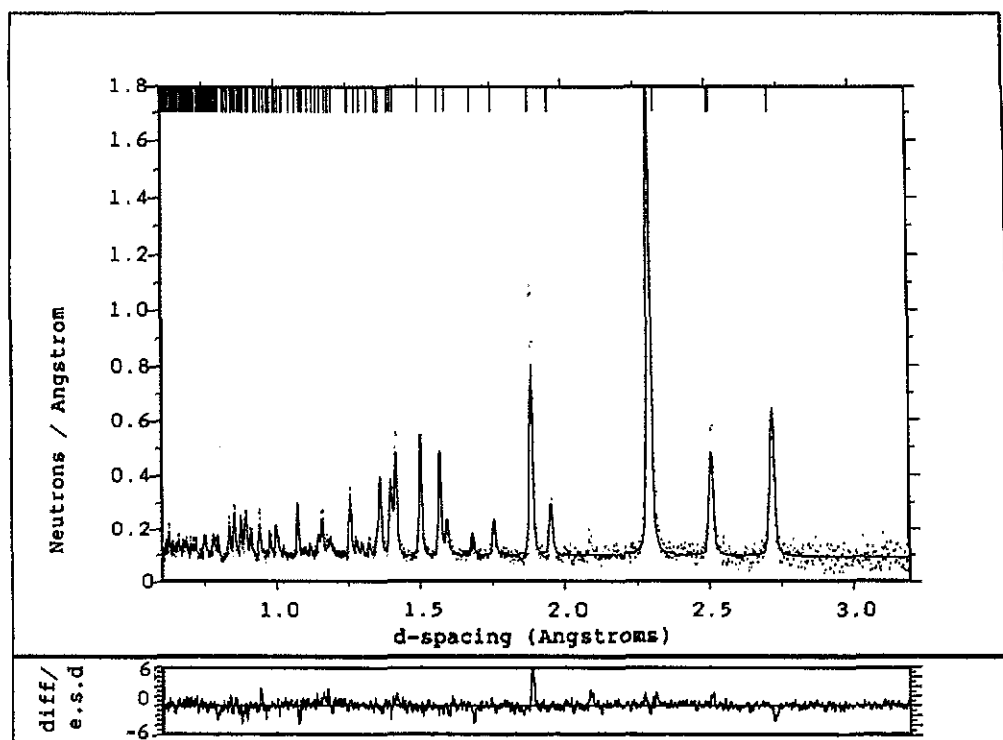


Figure 2. Profile fit to the neutron powder pattern from CuO in a McWhan cell at 22(1) kbar.

change in the oxygen y parameter of $-0.0185(14)$ and percentage changes in the cell parameters of $\Delta a/a = 0.68(4)$, $\Delta b/b = -2.02(2)$, $\Delta c/c = -0.38(2)$ and $\Delta\beta/\beta = 1.02(2)$, and so the volume of the cell v changes by $\Delta v/v = -2.02(4)\%$.

3. Discussion

A decrease of the oxygen y positional parameter with increased pressure has already been inferred by Reimann and Syassen [9], who pointed out that a constant y would lead to the two Cu–O distances defining the square plane diverging further from equality as pressure was applied. However, the actual rate of decrease in y that we find is $-0.79(6) \times 10^{-3} \text{ kbar}^{-1}$ over the pressure interval from ambient to 22 kbar, some three times greater than the value of $-0.25(5) \times 10^{-3} \text{ kbar}^{-1}$ that they deduced from their simple model for the pressure dependence of the Raman frequencies in the pressure range from ambient to 80 kbar. As a consequence, the longer of the two Cu–O distances actually decreases faster than does the shorter distance, whereas their postulated y dependence leads to an almost constant value for the longer of these two distances. Table 2 shows that, at a pressure of 22 kbar, the distances are effectively equal and the angle O–Cu–O has become closer to 90° , changing from $84.3(1)^\circ$ at ambient pressure to $84.7(1)^\circ$. Although the largest change in Cu^{2+} coordination is a reduction in the distance to the apical oxygen atoms from $2.788(1)$ to $2.696(3) \text{ \AA}$, this distance remains greater than the shortest O–O separation. The structural implications of parameter changes

Table 2. Bond distances and angles about the Cu²⁺ ion in CuO at ambient and 22(1) kbar pressure. The closest O–O separation is also given.

Oxygen		Cu–O distance (Å)		
Number	Position	Ambient pressure		22(1) kbar Neutron
		X-ray	Neutron	
1	(0, y, $\frac{1}{2}$)	1.961(2)	1.962(1)	1.959(1)
2	($\frac{1}{2}$, $\frac{1}{2}-y$, $-\frac{1}{2}$)			
3	($\frac{1}{2}$, $y-\frac{1}{2}$, $\frac{1}{2}$)	1.951(2)	1.950(1)	1.959(1)
4	(0, $1-y$, $-\frac{1}{2}$)			
5	($\frac{1}{2}$, $\frac{1}{2}+y$, $\frac{1}{2}$)	2.784(4)	2.790(1)	2.696(3)
6	(0, $-y$, $-\frac{1}{2}$)			
Angles (deg)				
(O(5) is an apical oxygen)				
O(1)–Cu–O(4)		84.3(1)	84.3(1)	84.7(1)
O(1)–Cu–O(5)		73.1(2)	72.9(1)	75.1(1)
O(4)–Cu–O(5)		89.2(2)	89.2(2)	89.1(1)
O–O distance (Å)		2.625(2)	2.625(1)	2.639(1)

induced by hydrostatic pressure is therefore to make the square-planar Cu²⁺ coordination more regular.

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