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CuO: x-ray single-crystal structure determination at 196 K and room temperature

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Abstract. An x-ray single-crystal determination of the CuO structure has been made at 196 K, i.e. below the Néel temperature 230 K, and, as a check, the crystal structure at room temperature was also determined. The correct space group for the structure at both temperatures was found to be Cc . Earlier results of magnetic and neutron diffraction measurements can be explained as antiferromagnetic coupling between copper atoms via oxygen (superexchange) in chains running in the $[1\ 0\ -1]$ direction. The structural results show changes with temperature in Cu–O distances in these chains: in each $-Cu-O-Cu-$ group the longer distance is increased and the shorter decreased when passing from 196 K to room temperature. This implies a weaker antiferromagnetic coupling at room temperature. The refinement of CuO-structure at room temperature reported earlier by Åsbrink and Norrby (1970) showed the symmetry to be $C2/c$. An attempt to refine CuO in the space group Cc with the old data was not successful. The different results obtained with different crystals are tentatively explained from published observations regarding valence fluctuations in CuO and non-stoichiometry caused by cation vacancies.

1. Introduction

Numerous studies on high-temperature superconductors of the type Re–Ba/Sr–Cu–O have focused attention on the role of copper–oxygen planes in determining the physical properties of these compounds. In the light of recently published reports, the interaction between Cu and O ions is relevant to all cupric-oxide-based HTSCs, thus, the structure and properties of CuO are currently of considerable interest.

The CuO phase was characterised by magnetic susceptibility (χ) measurements (O’Keeffe and Stone 1962, Roden *et al* 1989). The temperature dependence of χ was found not to fulfil the Curie–Weiss law since, besides the slight kink at about 230 K (T_N), the magnetic susceptibility continued to rise above the Néel temperature, reaching a flat maximum at about 540 K. Almost constant magnetisation was observed below 130 K. In connection with the specific heat measurements (Jin-Heng Hu and Johnston 1953), showing a weak anomaly at 225 K, the above results were interpreted as antiferromagnetic ordering in copper oxide. Neutron powder diffraction and neutron inelastic scattering studies (Brockhouse 1954, Yang *et al* 1988) confirmed antiferromagnetic long-range ordering in CuO. Single-crystal neutron diffraction measurements (Forsyth *et al* 1988) revealed a magnetic structure with twice the a and

c parameters of the chemical unit cell. A recent magnetic experiment on a powder sample by Brese *et al* (1990) did not confirm any singularity at the proposed T_N . Studies at high pressure using x-ray powder diffraction (Åsbrink *et al* 1991) and x-ray single-crystal diffraction (Åsbrink *et al* 1990) gave indication of a possible phase transition at about 85 Kbar. Taking into consideration these results we deemed it valuable to determine the structure of CuO monocystal at 196 K (LT) and, for comparison, at room temperature (RT), in order to correlate it with the phase transition at 230 K and with the magnetic structure. We also relate these results to the earlier structure description at room temperature by Åsbrink and Norrby (1970, hereafter referred to as ÅN).

2. Experiment

2.1. Crystal growth

The crystal used was obtained from a salt flux. As the copper oxide source was used anhydrous CuSO_4 (Merck, p.a.) which disintegrates into CuO and SO_3 at a temperature below 600 °C. As a flux was used a mixture of 39 weight % KF, obtained by drying $\text{KF}\cdot 2\text{H}_2\text{O}$ (Mallinckrodt Analytical Reagents) at 200 °C, and 61 weight % KCl (Merck, p.a.). According to Plato (1907), this mixture is a eutectic composition in the system KF–KCl, melting at 605 °C. In an alumina crucible 0.13 mol flux and 0.013 mol CuSO_4 were mixed and heated, at first for 3 h at 200 °C; then the temperature was increased by 200 °C/h to 880 °C, where it was kept for 8 hours and finally it was decreased by 25 °C/h down to 600 °C, followed by cooling in air to room temperature. The product obtained consisted of grey–black platelets. X-ray investigations of several such plates showed all of them to be more or less twinned. However, the crystal used for the intensity collection was in practice a single crystal: judging from intensities, the degree of twinning was not higher than 0.5%.

2.2. Data collection and refinement

A single crystal of irregular prismatic shape was selected by checking its quality with Weissenberg photographs. Unit cell dimensions were obtained from least-squares refinement of 19 Θ values ($8 < \Theta < 21^\circ$) on a Stoe 4-circle diffractometer with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The same specimen, cooled in a stream of nitrogen, with the temperature maintained at 193(1) K, was used for intensity data collection from the low-temperature phase (LTP). Experimental conditions for data collection are listed in table 1. Three intensity standards were monitored every 240 min. The intensity data were corrected for Lorentz, polarization and absorption effects, with transmission factors calculated by numerical integration, using a program by Norrestam (1990). Initial atomic coordinates were taken from the earlier paper (ÅN). The refinement was performed with the full-matrix SHELX76 program (Sheldrick 1976). An isotropic secondary extinction parameter κ was included in the structure factor calculation: $F_c = F(1 - \kappa F^2 / \sin \Theta)$ and was found to be significant (table 1). Atomic scattering factors for Cu^+ and O^- were taken from *International Tables for X-ray Crystallography* (1974) and anomalous dispersion corrections from Cromer and Liberman (1970). Calculations were carried out on a Vax 11/750 computer. The drawing has been prepared using the ORTEP76 program (Johnson 1976).

Table 1. Experimental conditions for the data collection and the structure refinement

	RT	LT			
Unit cell dimensions:					
$a(\text{\AA})$	4.6927(4)	4.6893(4)			
b	3.4283(4)	3.4268(4)			
c	5.1370(6)	5.1321(7)			
$\beta(^{\circ})$	99.546(9)	99.653(7)			
Unit cell volume, $V(\text{\AA}^3)$	81.50	81.30			
Formula units/unit cell, Z		4			
Intensity data collection:					
$(\sin \Theta/\lambda)_{\max} (\text{\AA}^{-1})$	1.079	1.077			
Range of h, k and l indices		-10 to 10,	-7 to 7 and	-11 to 11	
Standard reflections (hkl)		-4 0 0,	0 2 0,	0 0 4	
Number of measured reflections	1648	1596			
Number of observed refl. ($I_{\text{net}} > 0$)	1501	1492			
Number of unique reflections	417	417			
Internal agreement, R_{int}	0.043	0.042			
Absorption correction:					
Linear absorption coef., μ	249.7	250.3			
Transmission factor range	0.355 to 0.538	0.353 to 0.530			
Structure refinement:					
Minimization of		$w \sum (F_o - F_c)^2$			
Weighting scheme		$[\sigma^2(F) + 0.00053 F_o ^2]^{-1}$	$[\sigma^2(F) + 0.00050 F ^2]^{-1}$		
Final R factors		Cc	$C2/c$	Cc	$C2/c$
$R = \sum (F_o - F_c) / \sum F_o $	0.0416	0.0560	0.0404	0.0588	
$R_w = \sum w^{1/2} (F_o - F_c) / \sum w^{1/2} (F_o)$	0.0347	0.0431	0.0358	0.0451	
$R_G = [\sum w (F_o - F_c)^2 / \sum w (F_o)^2]^{1/2}$	0.0375	0.0471	0.0379	0.0505	
Number of refined parameters	18	13	18	13	
κ -in isotropic secondary extinction coefficient	0.059(2)	0.063(2)	0.059(2)	0.060(2)	
Residual $\Delta\rho_{\min}$ and $\Delta\rho_{\max}$, ($e/\text{\AA}^3$)	-1.7 and 1.3				

3. Results

3.1. Structure determination at LT

There are two possible space groups fulfilling the extinction rules for the CuO single-crystal data at LT: $C2/c$ and Cc . All the unique reflections were used in structure calculations in both symmetry cases, lowering significantly the estimated standard deviations (ESD) for all atomic parameters compared to the case with omitted 'less significant intensities' ($I > 3\sigma(I_o)$). Unfortunately, it is not common practice to use these so called 'less significant intensities' in structure refinements, and in this way valuable experimental information is lost causing less accurate results than possible—even if the R factors, defined in table 1, are improved in this way (cf Arnberg *et al* 1979). The centrosymmetric model with 13 free parameters based on the initial structure (\AA N) yielded a conventional reliability factor (on F), $R = 0.059$ and $R_w = 0.045$, leaving unchanged the essential features of the structure.

The non-centrosymmetric model, described by 18 parameters in the Cc space group, converged to $R = 0.040$ and $R_w = 0.036$ (table 1). The results are summarized in table 2, where the positional and thermal parameters are listed. The related Cu as well as O-atom positions for centro- and non-centrosymmetric models differ

Table 2. Positional parameters in CuO. For comparison, parameters resulting from the centrosymmetric description are shown in parentheses. These latter ones however, are rejected by the Hamilton test (see text).

Space group	Atom	<i>x</i>	<i>y</i>	<i>z</i>
LT:				
<i>Cc</i>	Cu	0.25	0.2468(2)	0
<i>C2/c</i>	Cu	[0.25]	[0.25]	[0]
<i>Cc</i>	O	-0.0115(14)	0.4171(8)	0.2537(19)
<i>C2/c</i>	O	[0]	[0.4149(8)]	[0.25]
RT:				
<i>Cc</i>	Cu	0.25	0.2467(3)	0
<i>C2/c</i>	Cu	[0.25]	[0.25]	[0]
<i>Cc</i>	O	-0.0104(14)	0.4177(8)	0.2602(14)
<i>C2/c</i>	O	[0]	[0.4163(7)]	[0.25]

Thermal parameters $U_{ij}/10^{-4} \text{ \AA}^2$ in CuO. The U_{ij} are defined by temperature factor:

$$\exp[-2\pi^2(U_{11}a^2h^2 + 2U_{12}a^*b^*hl + \dots)].$$

Space group	Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
LT:							
<i>Cc</i>	Cu	55(1)	75(1)	41(1)	5(1)	18(1)	15(1)
<i>C2/c</i>	Cu	[54(1)]	[76(1)]	[42(1)]	[4(1)]	[20(1)]	[5(1)]
<i>Cc</i>	O	55(6)	113(7)	43(5)	-5(11)	21(4)	-5(10)
<i>C2/c</i>	O	[64(6)]	[76(7)]	[46(6)]	[0]	[20(5)]	[0]
RT:							
<i>Cc</i>	Cu	66(1)	87(1)	58(1)	0(1)	22(1)	18(1)
<i>C2/c</i>	Cu	[66(1)]	[89(1)]	[58(1)]	[4(1)]	[23(1)]	[13(1)]
<i>Cc</i>	O	62(6)	119(7)	54(6)	-5(11)	31(4)	-20(10)
<i>C2/c</i>	O	[68(1)]	[88(6)]	[64(6)]	[0]	[25(4)]	[0]

significantly. Taking into account the difference in numbers of refined parameters in both models, the results have been subjected to the Hamilton significance test (Hamilton 1965). It is based on the R -factor ratio $\mathcal{R} = R_1/R_0$, where R_0 and R_1 are respectively the generalized weighted R factors, defined in table 1 as R_G , for a structure resulting from an unrestricted least-squares refinement (here in the space group *Cc*) and a refinement with restraints on some of the parameters (in the space group *C2/c*). This test allows to decide whether addition of parameters gives a significant improvement of the agreement between observed and calculated structure factors. Using the notation from Hamilton's paper we have:

Space group	No of parameters	R_G
<i>Cc</i>	18	0.0379
<i>C2/c</i>	13	0.0505

and $\mathcal{R} = [R_G(C2/c)/R_G(Cc)] = 1.332$. The refinement with 417 independent observations in the space group *Cc* was taken as the unrestricted case. Restriction to the *C2/c* is a linear hypothesis of dimension $18 - 13 = 5$. The interpolated value of \mathcal{R} at the 0.005 significance level is:

$$\mathcal{R}(LT)_{5,399,0.005} = 1.023$$

where the second index indicates the number of degrees of freedom for the unrestricted refinement ($417 - 18 = 399$). Thus, at a high level of confidence we can reject the centrosymmetric description of the low-temperature CuO single-crystal structure (table 2).

3.2. Structure determination at RT

Similar estimations were made with the room-temperature data set. It appeared that this structure too can be described in the Cc as well as in the $C2/c$ space group. Once again, the Hamilton test suggested the choice of a non-centrosymmetric model, since:

$$R(\text{RT}) = [R_G(C2/c)/R_G(Cc)] = 0.0471/0.0375 = 1.256.$$

This result seems inconsistent with the earlier $\dot{A}N$ description of the structure at room temperature. Therefore, using the old data set of 267 intensity data, where so-called insignificant reflections were excluded, we recalculated the model in non-centrosymmetric space group Cc . Despite a slightly lower resulting R factor = 0.0328, in comparison to 0.0330 in the space group $C2/c$, the oxygen atom exhibited non-positive definite thermal parameters. Thus we may confirm that the previous CuO crystal, from 1970, was correctly described as centrosymmetric. In the light of studies on the valence fluctuation effect in the Cu-O bond, by using x-ray photoelectron spectroscopy (Parmigiani and Samoggia 1988), it becomes evident that in the copper oxide there can be observed simultaneously both $\text{Cu}^{2+}\text{-O}^{2-}$ and $\text{Cu}^{1+}\text{-O}^{1-}$ states. The CuO crystal, then, may be treated as containing a homogeneous mixture of these two valency states, or as consisting of numerous narrow structure domains, with the lower local symmetry. In this case, the centrosymmetric space group corresponds to the time-averaged, or site-averaged non-equivalent Cu and O ions. It is then also possible to think that, in the present crystal, the number of domains with a unique type of valence state is predominant.

We have recently learned that high-resolution powder diffraction (Langford and Louer 1991) revealed apparently anomalous features of CuO in comparison to other divalent metal oxides. Diffraction data coupled with the total-pattern-fitting technique showed a marked line-profile asymmetry, which varies systematically throughout the reciprocal space. The magnitude of the effect is sample dependent. No significant peak displacements due to lattice imperfections were detected, but line profile characteristics may point on non-stoichiometry due to cation vacancies. Considering those results, if comparing the unit cell volume of the old sample with that of the present one (81.08(2) and 81.50(2) \AA^3) we can conclude that our present sample contains less cation vacancies. If so, it is also not unreasonable that the symmetry of the present sample is lower than that of the old one.

3.3. Structure description

In the centrosymmetric structure ($\dot{A}N$) the copper atom was coordinated by four coplanar oxygen atoms forming an almost rectangular parallelogram, while the oxygen coordination polyhedron had four Cu atoms at the corners of a distorted tetrahedron. The CuO_4 units, by sharing opposite edges, formed two ribbons of parallelograms running in the $[1\ 1\ 0]$ and $[-1\ 1\ 0]$ directions. In the $[1\ 0\ 1]$ and $1\ 0\ -1]$ directions, two types of $-\text{Cu}-\text{O}-\text{Cu}-$ chains could be differentiated (figure 1).

Table 3. Bond distances (Å) and angles (deg) in CuO.

Distance	LT	RT
Cu-O(1)	2.781(5)	2.801(5)
Cu-O(6)	2.785(5)	2.774(5)
Cu-O	2.019(8)	2.041(7)
Cu-O(3)	1.932(7)	1.956(6)
Cu-O(5)	1.977(7)	1.958(6)
Cu-O(7)	1.907(8)	1.886(7)
Cu-Cu(2)	2.904(1)	2.906(1)
Cu-Cu(4)	3.098(1)	3.075(1)
Cu-Cu(8)	3.755(1)	3.755(1)
Cu(2)-Cu(4)	3.173(1)	3.179(1)
Cu(2)-Cu(8)	3.073(1)	3.075(1)
Cu(4)-Cu(8)	2.904(1)	2.906(1)
Bond angles		
Cu-O-Cu(2)	94.6(3)	93.3(3)
Cu-O-Cu(4)	101.5(3)	101.6(3)
Cu-O-Cu(8)	145.4(2)	145.9(2)
Cu(2)-O-Cu(4)	109.1(1)	108.6(1)
Cu(2)-O-Cu(8)	106.9(3)	106.3(3)
Cu(4)-O-Cu(8)	97.0(3)	98.2(3)
O-Cu-O(3)	94.6(3)	93.3(3)
O-Cu-O(5)	83.5(3)	82.2(3)
O-Cu-O(7)	178.5(1)	179.3(1)
O(3)-Cu-O(5)	176.7(3)	175.4(3)
O(3)-Cu-O(7)	86.4(3)	86.4(3)
O(5)-Cu-O(7)	96.7(3)	98.2(3)

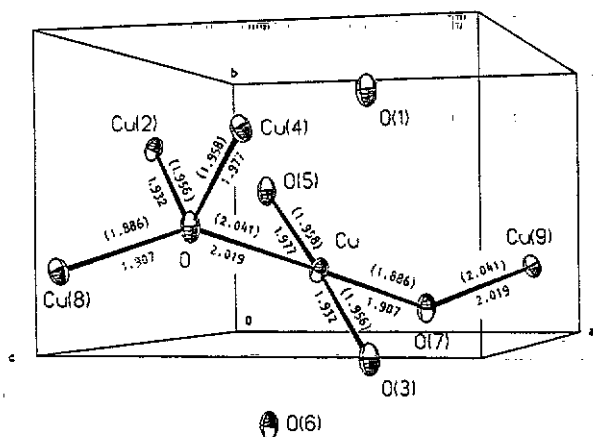


Figure 1. Perspective view of the CuO unit cell, showing coordination of Cu and O ions. Bond distances (Å) for the low-temperature and the room-temperature structures are given, the latter in parentheses.

In the present LT structure, except for a slight thermal contraction of the unit cell dimensions and lower values of thermal parameters, as compared to the earlier ÅN description, the most important structural change was observed in the Cu coordination configuration (figure 1). Now, the lower crystal symmetry implies non-equivalence of the formerly equal (in $C2/c$) symmetry-related pairs of Cu–O bonds. Interatomic distances and bond angles for the LT structure are shown in table 3; they are recorded using the notation of figure 1. For comparison, the corresponding data for the RT structure are also shown. The off-centre position of the Cu ion in the coordination polyhedron is in accordance with a generally observed tendency for cations too small to completely fill the space within the coordination figure (Dunitz and Orgel 1960); thus the Cu ion is displaced towards one of the edges of the coordination parallelogram. In the present structure the relevant edge is formed between O(3) and O(7) atoms, connected with the Cu atom by the two shorter Cu–O(3) and Cu–O(7) bonds, as compared to the opposite pair of longer bonds: Cu–O and Cu–O(5). As a consequence, in both $-\text{Cu}-\text{O}-\text{Cu}-$ chains along $[1\ 0\ -1]$ and $[1\ 0\ 1]$, one can observe an alternating sequence of the long and short Cu–O distances [e.g. Cu(8)–O–Cu and Cu–O(3)–Cu(4)].

It is worthwhile to remark that in calculating bond strength, S , using a formula presented by Brown (1991), the valency sum for Cu, $\sum S$, obtained with the results from ÅN is identical to the one obtained with the present RT results, namely 1.99. It must be pointed out that these calculations included also the two very long Cu–O distances to the two remote O ligands, completing the octahedral coordination.

4. Discussion

Following neutron diffraction studies of CuO (Brockhouse 1954, Yang *et al* 1988, Forsyth *et al* 1988) long-range antiferromagnetic ordering of Cu^{2+} spins has been observed in the magnetic structure below T_N , described by a unit cell, with twice the a and c parameters of the chemical unit cell. This antiferromagnetic coupling (AFC) was defined as a superexchange interaction, involving diamagnetic O ions (Anderson 1959). To our knowledge, no detailed theory has been developed, regarding the influence of the configuration of the $\text{Me}^{2+} - \text{O}^{2-} - \text{Me}^{2+}$ unit on the strength of the superexchange coupling (SEC), although Anderson has shown that a collinear configuration must be the most favourable for SEC. The coupling has a maximum value for an angle of 180° and minimum for 90° . The strength of SEC should fall off rapidly with increasing length of one Me–O bond or the other.

It should be observed that the changes of the chemical structure connected with the magnetic phase transition, reasonable as they seem, are at the border of significance. Looking at the tetrahedral surrounding of each O atom, which is dependent on the Cu–O–Cu configuration, there is one long Cu–[O]–Cu(8) distance (3.755(1) Å) and considerably shorter other ones (2.904(3) to 3.173(1) Å) in the LT structure. The longer of the near-neighbour Cu–Cu distances, with the bond angle $145.4(2)^\circ$ between the Cu(8)–O and Cu–O bonds (1.907(8) and 2.019(8) Å, respectively), forms the $-\text{Cu}-\text{O}-\text{Cu}$ chain running parallel to $[1\ 0\ -1]$. The antiferromagnetic coupling, discussed in several papers earlier referred to, was actually assumed to run in this direction. On going from the LT to the RT structure, one can observe an elongation of the longer Cu–O bond and a shortening of the shorter Cu(8)–O distance, which could mean weakening the strength of the AF interaction between the two Cu^{2+} ions

involved. The corresponding change is not observed in another chain along $[1\ 0\ 1]$, where AFC seems to be unlikely due to geometric restrictions, since the angle $\text{Cu-O}(3)\text{-Cu}(4) = 109.1(1)^\circ$ is much closer to 90° . In this chain, at RT, the alternating, short and long Cu-O bonds sequence disappears; Cu-O(5), equivalent by symmetry to Cu(4)-O(3), and Cu-O(3) become equal within the ESDs. Relating these facts to the diffuse neutron scattering, recorded by Yang *et al* 1988 around the magnetic reflection $(\frac{1}{2}\ 0\text{-}\frac{1}{2})$ in a wide temperature range above T_N , we can say that there is no contradiction between observed changes of the Cu-O-Cu(8) unit and an assumed lower coupling strength at RT. In other words, a weak coupling between Cu^{2+} ions along $[1\ 0\text{-}1]$ direction persists even above T_N . The same conclusion emerges from the anomalous behaviour of the magnetic susceptibility, which reaches a maximum at about 540 K, far above T_N .

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