

Low-Temperature Structures of CuO and AgO and Their Relationships to Those of MgO and PdO

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The CuO structure has been refined from time-of-flight neutron diffraction data collected at 11 K. Crystal data: $C2/c$, $a = 4.6833(2)$ Å, $b = 3.4208(1)$ Å, $c = 5.1294(2)$ Å, $\beta = 99.567(1)^\circ$, $V = 81.031(7)$ Å³. The Cu–O distances are 1.951(1) and 1.961(1) Å (each $2\times$) with corresponding O–Cu–O angles of $84.315(7)^\circ$ and $95.685(7)^\circ$. Data for a mixture of AgO and Ag₂SO₄ were collected at 9 K. Crystal data for AgO: $P2_1/c$, $a = 5.8517(3)$ Å, $b = 3.4674(2)$ Å, $c = 5.4838(3)$ Å, $\beta = 107.663(3)^\circ$, $V = 106.02(1)$ Å³. The formula for AgO is better written as Ag(I)Ag(III)O₂. The Ag(III) atoms are 4-coordinated: Ag–O = 2.008(3) (2x) and 2.036(3) (2x), and the Ag(I) atoms are 2-coordinated by O: Ag–O = 2.147(3) (2x). A comparison of the CuO, AgO, PdO, and MgO structures is presented. © 1990 Academic Press, Inc.

Introduction

The structure and properties of copper oxides are currently of considerable interest. CuO and AgO are known to have closely related structures of different symmetries at room temperature, but AgO is diamagnetic and CuO is reported to have somewhat unusual antiferromagnetism. A weak specific heat anomaly in CuO at about 230 K is not reflected in any singularity in the magnetic properties. For these reasons, we considered it valuable to refine the low-temperature structures from available powder neutron diffraction data.

The structure of CuO has been known at room temperature for considerable time (1),

and accurate details have been worked out by Åsbrink and Norrby (2). The structure is essentially a monoclinic distortion of the tetragonal PdO structure (3) which contains mutually perpendicular strings of edge-sharing MO₄ rectangles running along a and b . Magnetic susceptibility measurements (4) on CuO show that its susceptibility has a small constant positive value at low temperatures (<120 K) thereafter smoothly increasing to a broad maximum at 500–600 K. Calorimetric measurements (5) show a broad but weak anomaly in the heat capacity at 230 K which has been interpreted (6) as an antiferromagnetic Néel point but the integrated peak corresponds to a ΔS of only about $0.3 \text{ JK}^{-1} \text{ mol}^{-1}$. This behavior is in contrast to other antiferromagnetic transition metal monoxides such as MnO, FeO,

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CoO, and NiO, for which the temperatures of the specific heat anomaly and susceptibility maximum closely coincide (7).

AgO was originally thought to be isostructural with CuO, since both have similar monoclinic cells (8, 9). The structure of AgO (which is better written as Ag(I)Ag(II)O_2) was subsequently shown (10) to have lower symmetry ($P2_1/c$ instead of $C2/c$) and was proposed to be Ag(I)Ag(III)O_2 . This proposal is supported by a recent room-temperature X-ray structure refinement (11) and the observed diamagnetism (12). It was also observed (10) that the AgO structure is metrically close to cubic so that a simple relationship is metrically close to cubic so that a simple relationship to the rocksalt structure of MgO (and other transition metal monoxides) should exist.

We report here the low-temperature structures of AgO and CuO and compare them with the room temperature structures. We show how the structures of PdO, CuO, AgO, and MgO (which all have different symmetries) are related by simple topological transformations. We also report new magnetic data for CuO which confirm the absence of any singularities at the proposed Néel temperature.

Experimental

CuO

The sample of CuO used for the neutron studies was purchased from Mattheson, Coleman, and Bell (>99.9%). The CuO for the magnetic studies was purchased from Baker (99.9%) and annealed in oxygen overnight at 500°C to eliminate the possibility of any hydrated oxide. The magnetic measurements were made on a SQUID constructed by the SHE corporation. Powder neutron diffraction data were collected on the Neutron Powder Diffractometer (NPD) at the Manuel Lujan, Jr. Neutron Scattering facility at Los Alamos National Laboratory.

Details of the data collection and struc-

TABLE I
NEUTRON DIFFRACTION DATA COLLECTION
AND ANALYSIS

Diffractometer	NPD, Manuel Lujan, Jr. Neutron Scattering Center, +153 and +90 banks
Scattering lengths (b in 10^{-15} m)	Cu 7.72 Ag 5.97 O 5.81
Refinement	Rietveld technique (17); program GSAS (18)
Background	Fourier series 9-term for $\text{AgO/Ag}_2\text{SO}_4$ 12-term for CuO
Absorption Function minimized	Empirical formula (19, 20) $\sum w_i (I_0 - I_i)^2$
Peak shape	Convolution of two back-to-back exponentials with a Gaussian (21)

ture refinement are given in Table I. The initial structural model was obtained from the recent room-temperature, single-crystal refinement (2). Our refinement proceeded smoothly to a final reduced χ^2 of 2.16 with the conventional $R_{\text{wp}} = 0.097$ and $R_p = 0.070$. The final profile fit is shown in Fig. 1. The final coordinates are given in Table II, and anisotropic thermal parameters are given in Table III. These are compared to the room-temperature, single-crystal study. The Cu–O bond lengths are 1.951(1) Å and 1.961(1) Å (each $2\times$), and the supplementary O–Cu–O angles are 84.315(7)° and 95.685(7)°. Structure amplitudes are deposited in Table IV.¹

¹ See NAPS document No. 04795 for 112 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P. O. Box 3513, Grand Central Station, New York, NY 10163. Remit in Advance \$4.00 for microfiche copy or for photocopy, \$7.75 up to 20 pages plus \$0.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling, for the first 20 pages, and \$1.00 for additional 10 pages of material, \$1.50 for postage of any microfiche orders.

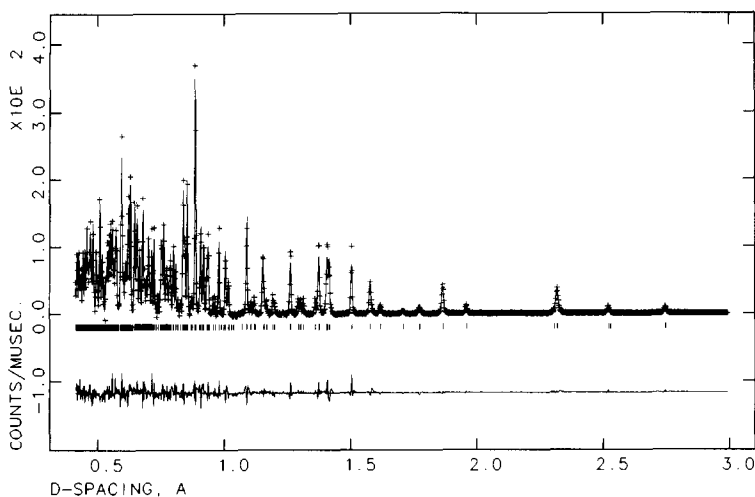


FIG. 1. Neutron diffraction profile fit for CuO (+ 148° detector bank). The data points are shown as '+' marks and the solid line is the calculated profile. The difference curve at the bottom is on the same scale. The background has been subtracted from the plot.

No extra reflections (that might arise from a magnetic superstructure or from reduction in symmetry to $P2_1/c$) or split peaks were detected. A published abstract of a talk (5) refers to the observation of a weak line at $1/2\ 0\ -1/2$ (corresponding to a cell doubled in the a and c directions) ascribed to magnetic ordering but this line ($d = 5.78\ \text{\AA}$) falls outside the range of our measurements which were limited to $0.5 < d < 4.0\ \text{\AA}$. In

the time-of-flight instrument used, data for higher d spacings were not collected as successive pulses would then overlap.

AgO

The sample of AgO was prepared by reacting aqueous AgNO_3 with $\text{K}_2\text{S}_2\text{O}_8$ at 90°C in dim light, using known methods (8, 9). Details of the data collection and analysis are the same as those for CuO.

The presence of Ag_2SO_4 in our neutron diffraction pattern indicates incomplete washing of the product (note that Ag_2SO_4 is

TABLE II
POSITIONAL PARAMETERS^a FOR CuO AT 11 K

Atom	Site	x	y	z	$100 U_{\text{eqv}}^b$
Cu	4c	1/4	1/4	0	0.27 [0.59]
O	4e	0	0.4179(2) [0.418(1)]	1/4	0.34 [0.75]

^a Space group $C2/c$. This study: $a = 4.6833(2)\ \text{\AA}$, $b = 3.4208(1)\ \text{\AA}$, $c = 5.1294(2)\ \text{\AA}$, $\beta = 99.567(1)^\circ$; Single-crystal study (2) at room temperature in brackets: $a = 4.6837(5)\ \text{\AA}$, $b = 3.4226(5)\ \text{\AA}$, $c = 5.1288(6)\ \text{\AA}$, $\beta = 99.54(1)^\circ$.

^b U_{eqv} is defined as 1/3 the trace of the matrix of anisotropic coefficients.

TABLE III
ANISOTROPIC THERMAL PARAMETERS FOR
CuO AT 11 K^a

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	17(2) 57(2)	42(2) 79(2)	27(2) 45(2)	11(2) 21(4)	12(1) 13(1)	2(2) 8(4)
O	36(3) 68(11)	56(3) 111(13)	17(3) 56(10)	0 0	16(2) 30(9)	0 0

^a All values to be multiplied by $10^{-4}\ \text{\AA}^2$. The lower numbers are those determined from the room-temperature study (2).

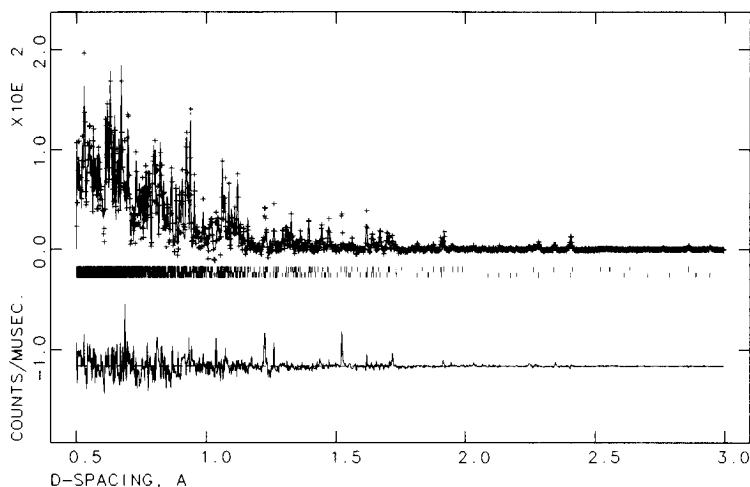


FIG. 2. Neutron diffraction profile fit for the AgO/Ag₂SO₄ mixture (+ 148° detector bank). The upper tic marks are those denoting the Ag₂SO₄ phase.

only slightly soluble in cold water). Although the Ag₂SO₄ could not be completely modeled, we believe our structure of AgO to be largely unaffected. The neutron diffraction profile fit is shown in Fig. 2, and the imperfect Ag₂SO₄ structural model used in the multiphase refinement is given in Table VI. (An X-ray study of pure Ag₂SO₄ was made, and neither the reported structure of Ag₂SO₄ (13) nor that of Cu₂SO₄ (14) satisfactorily modeled the data.) The final statistical residuals are $R_{wp} = 0.050$, $R_p = 0.033$, and

reduced $\chi^2 = 2.00$. Coordinates are given in Table V and compared to those derived from the single-crystal, room-temperature X-ray study. The Ag(III)–O bond lengths are 2.008(3) and 2.036(3) Å (each 2×), and the Ag(I)–O bond lengths are 2.147(3) and 2.693(3) (each 2×). The supplementary O–Ag(III)–O angles are 88.55(6)° and 91.45(6)°.

The magnetic susceptibility of CuO as a function of temperature is shown in Fig. 3. The almost constant magnetization below 130 K is confirmed as is the absence of any singularity at the supposed Néel tempera-

TABLE V
POSITIONAL PARAMETERS^a FOR AgO AT 9 K

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	100 <i>U</i> _{iso} ^b
Ag(1)	2a	0	0	0	0.13(5) [0.87]
Ag(3)	2d	1/2	0	1/2	0.17(5) [1.83]
O	4e	0.2949(3) [0.2959(9)]	0.3470(5) [0.345(2)]	0.2187(4) [0.2221(9)]	0.10(4) [1.26]

^a Space group $P2_1/c$. This study: $a = 5.8517(3)$ Å, $b = 3.4674(2)$ Å, $c = 5.4838(3)$ Å, $\beta = 107.663(3)^\circ$; Single-crystal study at room temperature (11) in brackets: $a = 5.859(2)$ Å, $b = 3.484(1)$ Å, $c = 5.500(1)$ Å, $\beta = 107.51(2)^\circ$.

^b U_{eqv} is given for the X-ray study and is defined as 1/3 the trace of the matrix of anisotropic coefficients.

TABLE VI
POSITIONAL PARAMETERS^a FOR Ag₂SO₄ AT 9 K

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	100 <i>U</i> _{iso}
Ag	16g	1/8	1/8	0.4437(4) [0.450]	1.0(1)
S	8a	1/8	1/8	1/8	-0.4(1)
O	32h	-0.0192(5) [0.022]	0.0571(2) [0.058]	0.2112(3) [0.208]	0.89(7)

^a Space group $Fddd$. This study: $a = 5.7960(3)$ Å, $b = 12.6670(7)$ Å, $c = 10.2238(5)$ Å; Previous study (13) in brackets: $a = 5.847$ Å, $b = 12.659$ Å, $c = 10.251$ Å.

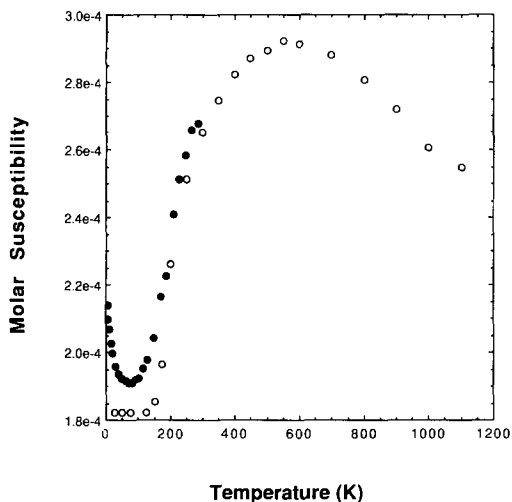


FIG. 3. Molar magnetic susceptibility of CuO as a function of temperature. The sample has been corrected for core diamagnetism (22). The open circles are data from (4), and the closed circles are those collected in this study. The data differ by 2% at 250 K.

ture of 230 K. The Curie tail at low temperatures is probably due to unpaired spins at the surface of the small particles. Preliminary EPR results show peak shifts as the sample is cooled which would support the idea of weak magnetic ordering. AgO has a diamagnetic susceptibility at room temperature of $\chi = -0.155 \times 10^{-6}$ emu/g (-19.1×10^{-6} emu/mole) (8, 15, 16).

Discussion

The CuO structure is built up of perpendicular strings of edge-sharing CuO_4 rectangles. AgO is closely related but concerted rotations of alternate O_4 rectangles result in Ag atoms being alternately in rectangular and linear coordination. Crystal chemical reasoning and the observed diamagnetism suggest that the 2-coordinated Ag is Ag(I) and the 4-coordinated Ag is low-spin Ag(III). The relationship between the two structures is illustrated in Fig. 4. Although only small displacements of O atoms are

required to go from one structure to the other, the structures of each compound change remarkably little (other than an almost uniform contraction) on going from room temperature to low temperature, suggesting that incipient soft mode behavior is unlikely. This does not of course rule out the possibility of such a mode contributing to the remarkable properties of the high-temperature copper oxide superconductors.

The relationships between these structures and those of PdO and MgO are also of interest. Figure 4 shows schematically how the mutually perpendicular paths of MO_4 groups in PdO are sheared to produce the CuO structure. If CuO had the PdO structure (with a Cu–O bond length of 1.955 Å and $c/a = 1.75$ as in PdO) the next-nearest O neighbors of Cu would be eight at 3.53 Å. The shearing operation brings two next-nearest neighbors closer so that in the real CuO structure there are Cu–O distances of 1.95, 1.96, and 2.78 Å (each $2\times$). In AgO the corresponding distances are Ag(I)–O: 2.15, 2.69, and 2.89 Å (all $2\times$) and Ag(III)–O: 2.01, 2.04, and 2.80 Å (all $2\times$). The figure also illustrates that continuing the operation on CuO will result finally in the MgO structure with six equidistant neighbors.

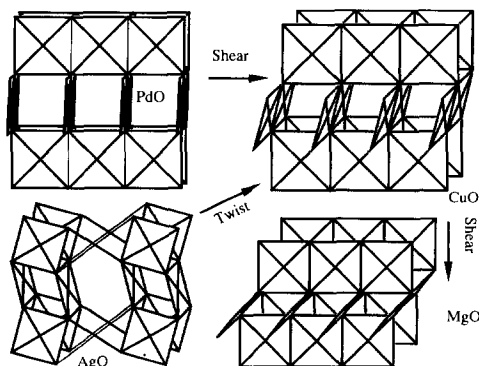


FIG. 4. Transformation of the structure of AgO to that of CuO by rotation of alternate MO_4 rectangles and further to the rocksalt structure or to the PdO structure by a shear.

TABLE VII
COORDINATES OF O ATOMS AND UNIT CELLS OF PdO, CuO, MgO, AND AgO^a

	x	y	z	a/c	b/c	β	Space group
PdO	1/4	1/4	1/4	0.806	0.806	90	$C4_2/mcm$ (PA_2/mmc)
CuO	1/4	0.334	1/4	0.913	0.667	99.56	$C2/c$
MgO	1/4	1/2	1/4	1.0	0.577	109.48	$Fm3m$
AgO	0.273	0.353	0.218	1.067	0.632	107.66	$P2_1/c$

^a Metal atoms at 0, 0, 0 and 1/2, 0, 1/2. The symmetry operations of $P2_1/c$ [$\pm(x, y, z; x, 1/2 - x, 1/2 + z)$] apply in each case. These make the metal atom positions face-centered. The origin has been shifted by 1/4, 1/4 from that in Table II for CuO.

To compare the MgO structure to that of CuO we need to consider a monoclinic cell obtained from the cubic one by the transformation (1 1/2 -1/2/0 -1/2 -1/2/-1 1/2 -1/2). Table VII shows a comparison of the four structures with a common monoclinic cell. The position of CuO intermediate between PdO and MgO is now clear.

The inverse of the above transformation matrix is (1/2 0 -1/2/1/2 -1 1/2/-1/2 -1 -1/2) and it is also revealing to apply this reverse transformation to the monoclinic cells of Table VII. The resulting cells are reported in Table VIII. The positions of the cations remain face centered (cubic for MgO). It is interesting that AgO is also very nearly cubic as was recognized by Scatturin (10), but it should be noted that the cell is not strictly a unit cell in this case as it contains three of one kind of Ag and one of the second kind of Ag. Nevertheless it shows that the structure of AgO could be converted

directly to that of MgO by a process that involved mainly small displacements of O atoms.

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Note added in proof. Roden and co-workers verified the anomaly in the magnetic susceptibility at 230 K (23). Yang, Tranquada, and Shirane conducted constant-wavelength neutron diffraction experiments on CuO below its Néel temperature (24). They found several magnetic peaks which suggests a doubling of the chemical cell to accommodate antiferromagnetic ordering with spins along the [010] direction.

References

1. G. TUNNEL, E. POSNIAK, AND C. J. KSANDA, *Z. Kristallogr.* **90**, 120 (1935).
2. S. ÅSBRINK AND L.-J. NORRBY, *Acta Crystallogr.* **B26**, 8 (1970).
3. J. WASSER, H. A. LEVY, AND S. W. PETERSON, *Acta Crystallogr.* **6**, 661 (1953).
4. M. O'KEEFFE AND F. S. STONE, *J. Phys. Chem. Solids* **23**, 261 (1962).
5. J.-H. HU AND H. L. JOHNSTON, *J. Amer. Chem. Soc.* **75**, 2471 (1953).
6. B. N. BROCKHOUSE, *Phys. Rev.* **94**, 781 (1954).

TABLE VIII
ALTERNATIVE "UNIT CELLS" FOR PdO, CuO, MgO,
AND AgO

	a/c	b/c	α	β	γ
PdO	0.623	1	77.09	82.39	97.61
CuO	0.804	1	85.69	86.41	93.59
MgO	1	1	90	90	90
AgO	0.950	1	88.00	92.71	87.29

7. D. J. CRAIK (Ed.), "Magnetic Oxides, Part 1," Wiley, New York (1975).
8. J. A. McMILLAN, *Acta Crystallogr.* **7**, 640 (1954).
9. W. S. GRAFF AND H. H. STADELMAIER, *J. Electrochem. Soc.* **105**, 446 (1958).
10. V. SCATTURIN, P. BELLON, AND A. J. SALKIND, *Ric. Sci.* **30**, 1034 (1960).
11. M. JANSEN AND P. FISCHER, *J. Less-Common Met.* **137**, 123 (1988).
12. J. A. McMILLAN, *J. Inorg. Nucl. Chem.* **13**, 28 (1960).
13. B. N. MEHROTA, TH. HAHN, W. EYSEL, H. RÖPKE, AND A. ILLGUTH, *Neues Jb. Miner. Mh.*, 408 (1978).
14. H. J. BERTHOLD, J. BORN, AND R. WARTCHOW, *Z. Krist.* **183**, 309 (1989).
15. A. B. NEIDING AND I. A. K. KAZARNOVSKII, *Dokl. Akad. Nauk SSSR* **78**, 713-716 (1951).
16. W. KLEMM, *Z. Anorg. Chem.* **201**, 32 (1931).
17. H. M. RIETVELD, *J. Appl. Crystallogr.* **2**, 65 (1969).
18. A. C. LARSON AND R. B. VON DREELE, Generalized Structure Analysis System, LANSCE, MS-H805, Manuel Lujan, Jr. Neutron Scattering Center, Los Alamos, NM 87545 (1989).
19. K. D. ROUSE, M. J. COOPER, AND A. CHAKERA, *Acta Crystallogr.* **A26**, 682 (1970).
20. A. W. HEWAT, *Acta Crystallogr.* **A35**, 248 (1979).
21. R. B. VON DREELE, J. D. JORGENSEN, AND C. G. WINDSOR, *J. Appl. Crystallogr.* **15**, 581 (1982).
22. P. W. SELWOOD, "Magnetochemistry," 2nd ed., Interscience, New York (1956).
23. B. RODEN, E. BRAUN, AND A. FREIMUTH, *Solid State Commun.* **64**, 1051 (1987).
24. B. X. YANG, J. M. TRANQUADA, AND G. SHIRANE, *Phys. Rev. B* **38**, 174 (1988).