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A Refinement of the Crystal Structure of Copper(II) Oxide with a Discussion of Some Exceptional E.s.d.'s

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The crystal structure of copper(II) oxide has been refined from single-crystal diffractometer data. It is found that the coordination of oxygen around copper is more properly described as a plane four coordination rather than a 4+2 distorted octahedral one. The copper atom shows anisotropy of thermal vibration, the largest component of vibration being approximately perpendicular to the plane formed by the coordinated oxygen atoms. An anomaly in the magnitudes of the $\sigma(U_{ij})$'s of the copper is explained. This anomaly is found to be connected with the fact that there are weak contributions from the copper atom to reflexions which according to the space group should contain only oxygen contributions. In connexion with the extinction correction a modification is pointed out which should be made in Zachariasen's formula when the crystal is of 'arbitrary shape'.

Introduction

In connexion with studies of oxidation products of copper based β-brass (Norrby, Kierkegaard & Magnéli, 1963; Norrby, Johansson, Kierkegaard & Magnéli, 1964; Norrby, Nygren, Lindberg, Kierkegaard & Magnéli, 1966) it became desirable to undertake a redetermination of the previously investigated crystal structure of CuO (Tunell, Posniak & Ksanda, 1935). Furthermore, a need for accurate Cu(II)–O distances of various compounds became acute when studying spinels containing copper and other transition metals (Åsbrink, 1965). In the course of this investigation, which included the use of an automatic single crystal X-ray diffractometer, some interesting problems of methodological character arose. The physical interpretation of the least-squares refined parameters and the significance of their estimated standard deviations also presented problems. Thus the emphasis of this study was laid not only on the structural features of CuO, but also on more general aspects of the methods used.

Experimental

Single crystals of CuO were obtained by a flux method. Powdered commercial analytical grade copper(II) oxide was mixed in equimolar proportions with sodium carbonate and melted in a platinum crucible, heated in a conventional resistance furnace. The melt was kept at 900 °C for 20 hours and then cooled to 500 °C at a rate of 1·5 °C.min^{-1}. The solidified material was then air quenched and the sodium carbonate dissolved in hot water. The residue consisted of small, needle-shaped, dark, highly reflecting crystals of CuO. Out of this material a prismatic single crystal with a parallelogram-shaped base was selected. The dimensions of the crystal were 0·057 × 0·013 × 0·010 mm, the long edge being parallel to the *c* axis.

A fine crystalline powder sample of CuO was obtained in a hydrothermal (600 °C, 1800 b) recrystallization of the starting material. The unit-cell dimensions were determined from a Guinier photograph of this powder taken with Cu $K\alpha_1$ radiation and KCl as an internal standard at 20 °C, see Table 1.

The single-crystal X-ray diffraction intensities were measured with a General Electric Datex automatic four circle diffractometer, the crystal being rotated around the c^* axis. The operation program was written in ALGOL (Norrestam, 1966) for the computer FACIT EDB. (This program has now been modified for a CD 3600 computer.)

The width of the scan interval in the 2θ–θ scan technique used was calculated according to the formula

$$\Delta 2\theta = a + b\,\mathrm{tg}\theta \text{ (in degrees)} \qquad (1)$$

The constants were assigned the values $a = 2{\cdot}24$, $b = 1{\cdot}78$ after a careful study of the widths of the peaks of some selected reflexions evenly distributed in the 2θ range to be investigated. The take off angle used was 2·5°. With the 2θ scan speed chosen, 1° min^{-1}, a back and forth scan over each reflexion was performed. The background intensities were measured for 100 sec at each end of the scan interval. Mo K radiation was used, and the $K\beta$ radiation was reduced by a Nb filter placed on the detector side. Nb was chosen rather than Zr because the latter element gives such a diminutive plateau for background measurement at low 2θ angles. A scintillation counter of NaI(Tl) type was used in conjunction with a pulse height analyser set to receive 97% of the radiation. Knowing from preliminary Weissenberg investigations that the lattice was C centred, reflexions were registered within two octants ($k, l \geq 0$) of the reciprocal lattice sphere out to $2\theta = 100°$, giving a total number of 522 observations. Of these 39 were of the type $h0l$ with l odd, all of which had a net intensity which did not deviate significantly from zero. Thus the presence of a **c** glide mirror plane was ascertained.

To increase the accuracy of the data a number of the remaining 483 reflexions were remeasured: first the 56 weakest at a 2θ scan speed of $\frac{1}{4}$° min^{-1} and 400 sec background measurement time; then 10 reflexions of intermediate intensity at $\frac{1}{2}$° min^{-1} and 200 sec background; finally some of the stronger reflexions under the original conditions, because of inconsistent differences between their two background intensities, probably caused by occasional disturbances.

Data reduction and least-squares refinement

The diffractometer output data were treated by a program by Coppens, Leiserowitz & Rabinovich (1965), modified for CD 3600 by Olofsson & Elfström, University of Uppsala, Sweden, effecting Lorentz, polarization and absorption corrections. This program was further modified by Brandt & Åsbrink at this Institute for the preparatory calculations for extinction correction. The linear absorption coefficient for CuO with Mo $K\alpha$ radiation was calculated to 269 cm^{-1} by use of Table 3.2.2A of *International Tables for X-ray Crystallography* (1962*a*). The transmission factors varied between 0·67 and 0·79 for the reflexions $00l_0$ and 200 respectively. Reflexions with large relative errors, $\sigma(I)/I \geq 0{\cdot}6$ were excluded. The number of reflexions was reduced further by introducing the arithmetic mean of F_{obs} for crystallographically equivalent reflexions.

According to Tunell *et al.* (1935) CuO crystallizes in the monoclinic space group $C2/c$ (No. 15) with four CuO units in the unit cell. Assuming these data with pertinent positional parameters, a full-matrix least-squares refinement was started, minimizing $\Sigma w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2$ with unit weights. The least-squares program used was *UCLALS* 1 (Ganzel, Sparks & Trueblood, 1966) modified for the computer UNIVAC 1107 by

Table 1. *Crystallographic data for* CuO *and least-squares refined parameters, with e.s.d.'s*

Space group: $C2/c$ (No. 15)
Unit-cell dimensions:
$a = 4{\cdot}6837 \pm 5$, $b = 3{\cdot}4226 \pm 5$, $c = 5{\cdot}1288 \pm 6$ Å
$\beta = 99{\cdot}54 \pm 1°$, $V = 81{\cdot}08 \pm 2$ Å^3, $Z = 4$, $D_x = 6{\cdot}515 \pm 2$ g.cm^{-3}
4 Cu in 4(c): $(\frac{1}{4}, \frac{1}{4}, 0; \frac{3}{4}, \frac{3}{4}, 0; \frac{1}{4}, \frac{3}{4}, \frac{1}{2}; \frac{3}{4}, \frac{1}{4}, \frac{1}{2})$
4 O in 4(e): $(0, y, \frac{1}{4}; \frac{1}{2}, \frac{1}{2}+y, \frac{1}{4}; 0, \bar{y}, \frac{3}{4}; \frac{1}{2}, \frac{1}{2}-y, \frac{3}{4})$
with $y = 0{\cdot}4184 \pm 13$.

Components of the mean square vibration tensor (Å^2)

The U_{ij} values given are defined by the temperature factor $\exp\{-2\pi^2(U_{11}a^{*2}h^2 + 2U_{12}a^*b^*hk + \ldots)\}$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	
Cu	573 ± 16	786 ± 17	454 ± 15	209 ± 38	134 ± 11	84 ± 36	($\times 10^{-5}$)
O	68 ± 11	111 ± 13	56 ± 10	0	30 ± 9	0	($\times 10^{-4}$)

R.m.s. components of thermal displacement (Å) along principal axes of the ellipsoid of vibration

	$R(1)$	$R(2)$	$R(3)$
Cu	0·065 ± 2	0·067 ± 5	0·096 ± 4
O	0·061 ± 15	0·089 ± 10	0·105 ± 6

R.m.s. radial thermal displacement (Å)

Cu	0·0134 ± 1
O	0·151 ± 5

Rømming, University of Oslo, Norway. In the course of this investigation it became necessary to change to a CD 3600 computer. The LS program used on this computer is called *LALS*, which is in principle the program *UCLALS* 1 modified and adopted for CD 3600 by Liminga, Lundgren & Brändén, University of Uppsala, Sweden.

It was known from the study by Tunell *et al.* (1935) that copper in CuO is surrounded by four close coplanar and two distant oxygen atoms, the latter two completing a highly distorted octahedron. Since the atomic arrangement around the copper atom is so anisotropic it was reasonable to expect an anisotropic thermal vibration. Therefore anisotropic thermal parameters were applied for copper and oxygen. Atomic scattering factors for Cu^+ and O^- were derived from Table 3.3.1 A of *International Tables for X-ray Crystallography* (1962*b*). f_{Cu^+} was dispersion corrected (the real part) according to Cromer (1965).

With the assumptions made the convergence was very good, all shifts being $<10^{-6}$ after five cycles of refinement. It was observed, however, that $|F_{\rm obs}|$ was less than $|F_{\rm calc}|$ for the strongest 10% of the reflexions and this was interpreted as being a result of extinction. The formula for the correction for this effect has been given by Zachariasen (1963, 1965) as:

$$|F_{\rm corr}| \simeq |F_{\rm obs}| \left(1 + \frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2} \cdot \frac{\partial[A^*(2\theta)]}{\partial\mu} \cdot \left(\frac{\partial[A^*(0)]}{\partial\mu}\right)^{-1} \cdot C \, . \, I_{\rm obs}\right) . \qquad (2)$$

Note: the normalizing factor $\left(\frac{\partial[A^*(0)]}{\partial\mu}\right)^{-1}$ is to be included as in the formula above only for crystals of spherical or cylindrical shape. It was thus not included in the present investigation.

$|F_{\rm corr}|$ was estimated in the way reported by Åsbrink & Werner (1966). The constant C in (2) was determined to $0{\cdot}00186 \pm 14$, on an absolute scale. (When comparing C values in different investigations one must of course account for the eventual use of the normalizing factor mentioned above.)

The refinement including only the 90% 'extinction free' reflexions ended in an R value equal to 3·8%, R being defined as $\Sigma||F_{\rm obs}| - |F_{\rm calc}||/\Sigma|F_{\rm obs}|$.

After the extinction correction five cycles of refinement with all the reflexions included resulted in a lower R value equal to 3·2% but scarcely any significant changes in the parameter values.

The earlier trend of $|F_{\rm obs}| < |F_{\rm calc}|$ for the strongest reflexions disappeared. The degree of overdetermination in this refinement was about twenty-twofold, the number of observations, m, being 267 and the number of parameters refined, n, being 12. The thermal parameters are given as the components of the mean-square vibration tensor **U** and also as the root mean-square (r.m.s.) components of thermal displacement along principal axes of the ellipsoid of vibration; see Table 1. The r.m.s. values were obtained by the program *ORFFE* (Busing, Martin & Levy, 1966) adapted for CD 3600 by the Uppsala group mentioned earlier. All estimated standard deviations given are single σ values that include the effect of the e.s.d.'s of the unit-cell dimensions. A list of final $F_{\rm obs}$ and $F_{\rm calc}$ is given in Table 2. A discussion of the structure follows in the last paragraph.

Aspects of the structural refinement

Comments on rejected reflexions

All reflexions rejected because of large relative errors in the intensities were of the type $k+l=2n+1$. With copper in 4(*c*) and oxygen in 4(*e*) (see Table 1) these reflexions are made up predominantly from contributions (see below) from the oxygen atoms and should hence be rather weak. The average structure factor for the rejected reflexions was calculated and found to be

Table 2. *Observed and calculated structure factors*

H	K	L	FO	FC
-2	0	0	68.2	-70.2
-2	0	2	100.2	-101.3
-2	0	4	51.5	-50.7
-2	0	6	48.8	-49.0
-2	0	8	25.2	-24.6
-2	0	10	25.9	-25.9
-4	0	0	66.5	68.1
-4	0	2	47.9	47.4
-4	0	6	28.5	29.9
-4	0	8	33.4	32.7
-4	0	10	16.8	17.1
-6	0	0	31.0	-30.4
-6	0	4	27.6	-27.7
-6	0	6	33.6	-33.4
-6	0	8	18.8	-18.8
-8	0	0	28.0	27.9
-8	0	2	21.5	20.4
-8	0	4	28.1	28.0
-8	0	6	17.8	17.5
-8	0	8	17.6	22.5
-10	0	2	22.2	-20.4
-1	1	0	21.5	-20.7
-1	1	1	84.3	83.1
-1	1	2	16.8	16.2
-1	1	3	79.1	80.0
-1	1	4	9.1	-9.3
-1	1	6	7.0	5.5
-1	1	9	23.3	22.6
-3	1	0	12.1	-12.1
-3	1	1	73.4	-75.5
-3	1	2	9.9	9.5
-3	1	3	54.4	-54.5
-3	1	7	30.9	-29.8
-3	1	9	25.7	-26.4
-5	1	0	5.3	-4.9
-5	1	4	5.5	-4.9
-5	1	5	32.0	31.9
-5	1	7	29.6	30.2
-5	1	9	21.4	20.0
-7	1	1	28.9	-31.4
-7	1	3	26.6	-26.0
-7	1	4	6.5	-5.0
-7	1	5	27.7	-28.2
-7	1	7	20.4	-20.3
-9	1	1	17.5	18.3
-9	1	3	23.5	21.9
-9	1	5	16.9	17.4
0	2	0	67.5	-69.9
0	2	1	17.4	12.8
0	2	2	75.6	-75.3
0	2	3	8.8	-8.0
0	2	4	46.9	-46.8
0	2	5	7.8	6.6
0	2	6	38.6	-38.9
0	2	8	23.8	-23.8
0	2	10	23.5	-21.3
-2	2	0	72.3	73.2
-2	2	1	11.0	11.3
-2	2	2	56.2	57.1
-2	2	3	7.0	-7.6
-2	2	4	53.5	53.4
-2	2	5	6.2	5.9
-2	2	6	33.3	33.0
-2	2	8	28.8	28.9
-2	2	10	16.5	18.4
-4	2	0	42.8	-43.2
-4	2	1	4.0	4.7
-4	2	2	49.2	-50.2
-4	2	4	36.5	-36.4
-4	2	6	33.4	-34.3
-4	2	8	23.0	-22.3
-4	2	10	20.1	-21.3
-6	2	0	32.4	34.0
-6	2	1	7.5	6.3
-6	2	2	28.5	29.2
-6	2	4	32.7	32.1
-6	2	6	21.3	23.1
-6	2	8	24.5	23.3
-8	2	0	19.0	-19.9
-8	2	2	24.5	-24.4
-8	2	4	21.6	-19.7
-8	2	6	22.8	-21.7
-1	3	1	61.2	-61.9
-1	3	3	37.4	-38.7
-1	3	5	42.2	-41.0
-1	3	7	23.8	-22.4
-1	3	9	24.8	-24.1
-3	3	1	36.6	37.2
-3	3	3	46.2	46.2
-3	3	5	26.4	27.4
-3	3	7	30.5	30.2
-3	3	9	16.3	16.8
-5	3	1	38.3	-37.5
-5	3	3	24.3	-25.9
-5	3	5	32.5	-31.7
-5	3	7	18.2	-18.7
-5	3	9	21.4	-22.1
-7	3	1	20.6	19.5
-7	3	3	26.9	27.0
-7	3	5	17.7	17.6
-7	3	7	23.2	22.3
-9	3	1	22.0	-19.9
-9	3	3	15.7	-14.7
0	4	0	36.1	36.5
0	4	1	6.2	4.8
0	4	2	38.6	39.3
0	4	3	6.8	-5.3
0	4	4	28.0	28.7
0	4	6	25.8	26.6
0	4	8	17.3	18.2
-2	4	0	38.9	-38.6
-2	4	2	31.6	-32.4
-2	4	4	33.6	-32.5
-2	4	6	22.5	-23.0
-2	4	8	20.6	-21.5
-4	4	0	26.5	27.2
-4	4	1	6.6	6.3
-4	4	2	31.9	31.2
-4	4	4	25.2	24.4
-4	4	6	23.8	24.4
-4	4	8	17.4	17.4
-6	4	0	24.9	-24.1
-6	4	2	18.9	-21.0
-6	4	3	5.7	-5.5
-6	4	4	23.7	-23.2
-6	4	6	17.3	-17.7
-8	4	0	15.2	15.7
-8	4	2	20.2	18.7
-8	4	4	16.8	15.6
-1	5	1	25.4	25.2
-1	5	3	29.4	27.4
-1	5	5	19.3	20.1
-1	5	7	18.7	19.9
-3	5	1	27.4	-26.8
-3	5	3	21.6	-21.5
-3	5	5	21.5	-22.7
-3	5	7	15.8	-16.3
-5	5	1	19.6	18.9
-5	5	3	21.9	21.8
-5	5	5	15.7	16.8
-7	5	1	13.6	-17.9
-7	5	3	15.0	-15.0
0	6	0	24.6	-23.6
0	6	2	16.5	-17.0
0	6	4	21.3	-20.8
0	6	6	14.6	-13.5
-2	6	0	18.6	16.8
-2	6	2	22.8	22.2
-2	6	4	14.3	15.2
-2	6	6	18.4	18.7
-4	6	0	20.1	-20.1
-4	6	2	14.7	-14.8
-4	6	4	19.7	-19.0
-1	7	1	14.4	-14.3
-1	7	3	17.9	-15.4
-3	7	1	14.5	15.2
0	0	2	75.9	72.0
0	0	4	77.2	75.5
0	0	6	35.4	35.4
0	0	8	33.4	33.8
0	0	10	18.0	17.7
2	0	2	89.9	-89.7
2	0	4	43.5	-44.3
2	0	6	41.7	-41.6
2	0	8	21.7	-21.5
2	0	10	20.8	-22.2
4	0	2	43.4	41.6
4	0	4	43.1	43.4
4	0	6	23.8	23.5
4	0	8	23.8	24.3
6	0	2	37.5	-36.8
6	0	4	27.0	-22.1
6	0	6	22.8	-24.2
8	0	2	18.0	18.1
8	0	4	21.2	21.5
1	1	1	103.6	-101.6
1	1	2	15.5	15.1
1	1	3	62.7	-62.2
1	1	4	7.4	-7.4
1	1	5	51.0	-49.8
1	1	7	30.3	-29.2
1	1	9	25.7	-24.9
3	1	1	58.8	59.1
3	1	2	8.2	7.3
3	1	3	54.7	54.3
3	1	5	33.7	33.6
3	1	7	27.4	28.5
3	1	9	18.9	18.3
5	1	1	44.7	-44.5
5	1	3	29.9	-31.6
5	1	5	28.7	-28.8
5	1	7	19.1	-19.3
7	1	1	28.3	24.9
7	1	3	24.9	25.3
7	1	5	16.1	18.1
9	1	1	19.7	-20.2
9	1	3	16.4	-15.4
0	2	1	12.9	12.8
0	2	3	8.0	-8.0
0	2	5	7.2	6.6
0	2	8	23.1	-23.8
0	2	10	22.6	-21.3
2	2	1	8.7	7.9
2	2	2	53.2	52.8
2	2	3	8.5	-8.5
2	2	4	47.1	46.8
2	2	6	29.2	28.8
2	2	8	26.5	25.1
4	2	1	6.2	8.0
4	2	2	45.5	-44.3
4	2	4	30.4	-29.9
4	2	6	27.5	-27.1
4	2	8	18.3	-17.8
6	2	2	26.0	25.9
6	2	4	25.1	25.5
6	2	6	16.7	17.7
8	2	2	22.1	-21.5
8	2	4	15.1	-15.9
1	3	1	44.3	44.0
1	3	3	50.8	50.4
1	3	5	27.9	28.2
1	3	7	30.1	29.2
1	3	9	15.9	16.3
3	3	1	47.6	-48.5
3	3	3	29.4	-30.1
3	3	5	33.5	-32.2
3	3	7	15.5	-18.4
5	3	1	25.9	25.9
5	3	3	31.7	30.6
5	3	5	16.7	18.5
5	3	7	17.6	20.3
7	3	1	25.0	-25.5
7	3	3	16.1	-16.6
7	3	5	19.9	-19.2
0	4	0	35.9	36.5
0	4	2	40.0	39.3
0	4	4	28.0	28.7
0	4	6	26.4	26.6
0	4	7	4.9	-4.3
0	4	8	17.7	18.2
2	4	1	6.5	6.4
2	4	2	30.7	-30.9
2	4	4	26.2	-29.8
2	4	6	21.5	-20.9
2	4	8	18.4	-19.2
4	4	2	28.2	28.7
4	4	4	21.7	21.4
4	4	6	19.9	20.3
6	4	2	18.5	-19.2
6	4	4	19.8	-19.3
1	5	1	26.6	-29.4
1	5	3	24.0	-22.6
1	5	5	21.2	-22.8
1	5	7	19.5	-16.1
3	5	3	22.4	23.6
3	5	5	18.7	17.3
5	5	1	21.3	-21.5
5	5	3	16.4	-16.6
5	5	5	15.5	-16.9
0	6	6	17.3	-13.5
2	6	2	22.1	21.6
7	5	1	14.2	14.5
0	6	2	19.6	-17.0
0	6	4	20.4	-20.8
2	6	4	18.7	14.5
1	7	1	18.0	16.0
1	7	3	10.9	13.4

smaller by a factor of about 3 than the average of the remaining reflexions of this type. This result is obviously consistent with the structural model adopted.

Comments on weighting schemes

Besides refining with unit weights attempts were also made with a few other weighting schemes. Although weights based on counter statistics ought to be the best and most natural choice, they have often been found not to work well, see Abrahams & Reddy (1965). This probably depends on systematic errors such as thermal diffuse scattering, multiple diffraction, and inaccurate absorption and extinction corrections dependent on errors in the mathematical description of the crystal and on inaccurate linear absorption coefficients, *i.e.* errors which at present cannot be easily corrected for. In this investigation too such weights were found to be unsatisfactory when analysing weighted squares of residuals as functions of F_{obs} and $\sin\theta$ respectively. Similarly, the weighting schemes proposed by Hughes (1941) and Cruickshank (1965) respectively were found not to work well in this case. The least unsatisfactory analyses were obtained with unit weights and they are given in Table 3. This relative success with unit weights might be partially explained by the fact that the weakest reflexions had been remeasured at a lower scan speed, as mentioned previously. With such weight analyses, thermal parameters and e.s.d.'s should be interpreted with caution. It should, however, be pointed out that the rather large variations in the weight analyses also depend on the low number of reflexions in each of the intervals of F_{obs} and $\sin\theta$ used.

Table 3. *Weight analyses after last cycle of final least-squares refinement*

The upper part of the Table contains normalized weighted squares of residuals averaged over intervals in F_{obs} with equal number of reflexions. In the lower part the averages are taken over approximately equal volumes of the reciprocal lattice sphere.

F_{obs}	$w\Delta^2$	Number of reflexions
0·0–10·9	0·72	26
10·9–16·5	0·83	27
16·5–18·7	1·79	27
18·7–21·2	1·54	26
21·2–23·0	0·86	27
23·0–25·8	0·64	27
25·8–28·7	1·19	26
28·7–33·6	0·78	27
33·6–47·6	0·34	27
47·6–103·6	1·32	27
$\sin\theta$		
0·00–0·36	0·93	41
0·36–0·45	0·53	31
0·45–0·52	0·54	29
0·52–0·57	1·73	22
0·57–0·61	0·48	25
0·61–0·65	0·79	30
0·65–0·68	0·70	18
0·68–0·71	1·04	28
0·71–0·74	1·29	23
0·74–0·77	2·57	20

Anomalous e.s.d.'s

The estimated standard deviations of the components U_{12} and U_{23} of the vibration tensor for the copper atom are 2–3 times larger than the corresponding values for the remaining components as seen from Table 1. This rather surprising fact can be explained in the following way. As the correlation between each U_{ij} and the other parameters refined is rather insignificant, the e.s.d.'s may to a good approximation be given as

$$\sigma^2(U_{ij}) \simeq \frac{1}{\sum\limits_{h,k,l} w\left(\dfrac{\partial|F_c|}{\partial U_{ij}}\right)^2} \cdot \frac{\sum\limits_{h,k,l} w\Delta^2}{m-n} \,. \tag{3}$$

It might thus be sufficient to investigate the magnitude of the sum $\Sigma w\left(\dfrac{\partial|F_c|}{\partial U_{ij}}\right)^2$ for the different vibration tensor components U_{ij}, which are defined in Table 1, in order to compare the various $\sigma(U_{ij})$'s. According to Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) relations of the following type hold:

$$v\,\frac{\partial|F_c|}{\partial U_{\text{Cu},12}} = -\sum_s 4\pi^2(h_s a^* k_s b^*)G_{\text{Cu},s} \,. \tag{4}$$

Here v is the sign of $\cos\alpha$, α being the phase angle for the reflexion in point. The summation over s is here over all the symmetry-equivalent Cu positions in the unit cell. (h_s,k_s,l_s) are a set of equivalent indices as defined by Cruickshank. As the space group of CuO is centrosymmetric, $G_{\text{Cu},s}$ is the contribution to F_c of a Cu atom at one equivalent position. With this definition of $G_{\text{Cu},s}$ and the symmetry operations for position 4(*c*) given in Table 1, equation (4) may be written

$$\begin{aligned} v\,\frac{\partial|F_c|}{\partial U_{\text{Cu},12}} &= -\,8\pi^2 f_{\text{Cu}}(ha^*kb^*)[\exp\{-2\pi^2(h^2a^{*2}U_{\text{Cu},11} \\ &+k^2b^{*2}U_{\text{Cu},22}+l^2c^{*2}U_{\text{Cu},33}+2ha^*kb^*U_{\text{Cu},12} \\ &+2ha^*lc^*U_{\text{Cu},13}+2kb^*lc^*U_{\text{Cu},23})\}\cos 2\pi(hx+ky+lz) \\ &-\exp\{-2\pi^2(h^2a^{*2}U_{\text{Cu}\,11}+k^2b^{*2}U_{\text{Cu},22}+l^2c^{*2}U_{\text{Cu},33} \\ &-2ha^*kb^*U_{\text{Cu},12}+2ha^*lc^*U_{\text{Cu},13} \\ &-2kb^*lc^*U_{\text{Cu},23})\}\cos 2\pi(-hx+ky+l(z+\tfrac{1}{2})] \,. \end{aligned} \tag{5}$$

With the substitutions exp′ for the first and exp″ for the second exponential in equation (5) and noting that $x=y=\frac{1}{4}$, $z=0$ for copper one obtains

$$\begin{aligned} v\,\frac{\partial|F_c|}{\partial U_{\text{Cu},12}} &= -8\pi^2 f_{\text{Cu}}(ha^*kb^*)\,[\exp' . \cos\frac{\pi}{2}(h+k) \\ &\quad -\exp'' . \cos\frac{\pi}{2}(-h+k+2l)] \,. \end{aligned} \tag{6}$$

In equation (6) the value of exp′ is usually only slightly different from that of exp″. Furthermore $h+k=2n$, $-h+k+2l=2m$, n and m being integers, *i.e.* each of the cosine factors may take either the value $+1$ or -1. It is evident that when they take the same value, $\left(\dfrac{\partial|F_c|}{\partial U_{\text{Cu},12}}\right)^2 = \left(\dfrac{\partial|F_c|}{\partial U_{\text{Cu},12}}\right)^2 v^2$ will be very small, and when they take opposite values, $\left(\frac{\partial|F_c|}{\partial U_{\mathrm{Cu},12}}\right)^2$ may be large. Now the cosines will have the same values when $k+l=2p$, p being an integer. Thus, for reflexions with $k+l$ *even, i.e.* for reflexions with contributions from both Cu and O, the quantity $\left(\frac{\partial|F_c|}{\partial U_{\mathrm{Cu},12}}\right)^2$ is usually very small. For reflexions with $k+l$ *odd* on the other hand, *i.e.* the so called oxygen reflexions, the value of $\left(\frac{\partial|F_c|}{\partial U_{\mathrm{Cu},12}}\right)^2$ may be rather large. However, only about 10% of all the reflexions are of the last type, *i.e.* the sum $\sum_{h,k,l} w \left(\frac{\partial|F_c|}{\partial U_{\mathrm{Cu},12}}\right)^2$ will be small and $\sigma^2(U_{\mathrm{Cu},12})$

$$\propto \frac{1}{\sum_{h,k,l} w \left(\frac{\partial|F_c|}{\partial U_{\mathrm{Cu},12}}\right)^2}$$ will be big.

For $U_{\mathrm{Cu},23}$ the following relation can be derived:

$$v\frac{\partial|F_c|}{\partial U_{\mathrm{Cu},23}} = -8\pi^2 f_{\mathrm{Cu}}(kb^*lc^*)\,[\exp'.\cos\frac{\pi}{2}(h+k) - \exp''.\cos\frac{\pi}{2}(-h+k+2l)]\,. \tag{7}$$

The same arguments as used above lead to the conclusion that

$$\sigma^2(U_{\mathrm{Cu},23}) \propto \frac{1}{\sum w \left(\frac{\partial|F_c|}{\partial U_{\mathrm{Cu},23}}\right)^2}$$

should be big and of the same magnitude as $\sigma^2(U_{\mathrm{Cu},12})$.

$U_{\mathrm{Cu},13}$ on the other hand differs from the other two cross components as is shown below:

$$v\frac{\partial|F_c|}{\partial U_{\mathrm{Cu},13}} = -8\pi^2 f_{\mathrm{Cu}}(ha^*lc^*)\,[\exp'.\cos\frac{\pi}{2}(h+k) + \exp''.\cos\frac{\pi}{2}(-h+k+2l)]\,. \tag{8}$$

Here the two terms within the squared brackets cooperate when $k+l=2n$, *i.e.* for the group of strong reflexions and counteract only for the few and weak 'oxygen reflexions'. Thus $\sum w\left(\frac{\partial|F_c|}{\partial U_{\mathrm{Cu},13}}\right)^2$ must become considerably larger than the other two sums mentioned above and $\sigma^2(U_{\mathrm{Cu},13})$ considerably smaller than $\sigma^2(U_{\mathrm{Cu},12})$ and $\sigma^2(U_{\mathrm{Cu},23})$.

The corresponding derivative of $|F_c|$ with respect to the component $U_{\mathrm{Cu},11}$ is

$$v\frac{\partial|F_c|}{\partial U_{\mathrm{Cu},11}} = -4\pi^2 f_{\mathrm{Cu}}(ha^*)^2\,[\exp'.\cos\frac{\pi}{2}(h+k) + \exp''.\cos\frac{\pi}{2}(-h+k+2l)]\,. \tag{9}$$

Analogous expressions hold for the derivatives of $|F_c|$

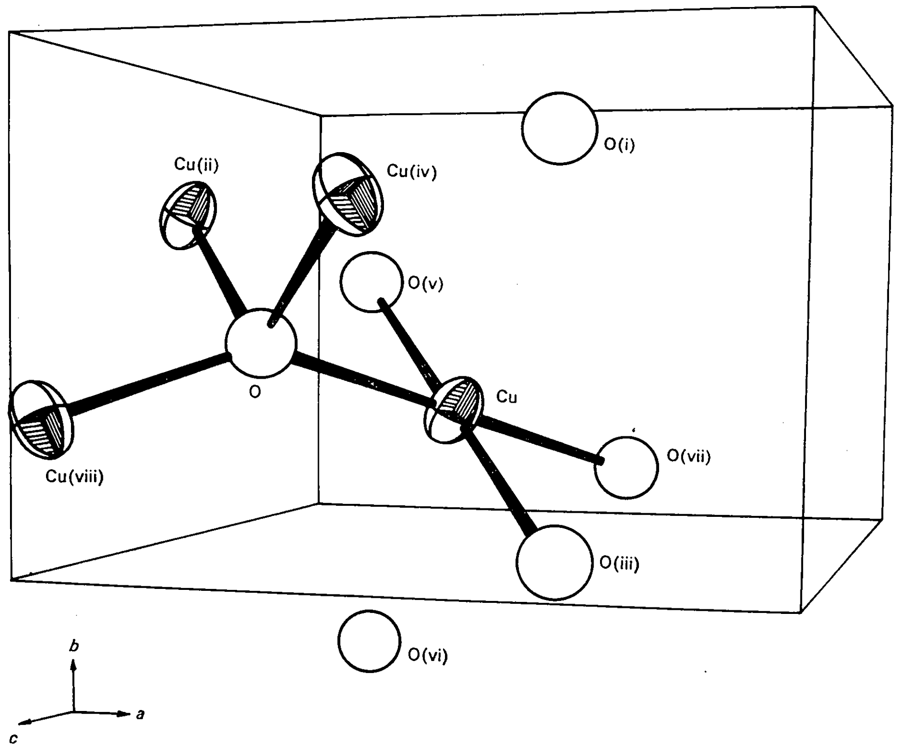

Fig. 1. A perspective view showing the distorted tetrahedral coordination of anisotropic copper atoms around an isotropic oxygen atom and the plane coordination of four oxygen atoms around a copper atom. The two distant oxygen atoms completing the very distorted octahedron around the copper atom are also drawn as are the contours of the unit cell.

with respect to $U_{\mathrm{Cu},22}$ and $U_{\mathrm{Cu},33}$. Relations (8) and (9) are identical with respect to the contents of the square brackets.

It could be expected that the values of $\sigma(U_{\mathrm{Cu},12})$ and $\sigma(U_{\mathrm{Cu},23})$ should be particularly sensitive to the weighting procedure applied, *i.e.* especially to the weights used for the weak reflexions. This was also found to be the case. However, with all the different weighting procedures tried the σ-values of these components remained exceptionally high.

Copper contribution to the 'oxygen reflexions'

A consequence of the anisotropy of the Cu atoms is that they will contribute also to the structure factors of the 'oxygen reflexions', *i.e.* the reflexions with $k+l=2n+1$. For these reflexions the Cu contribution should be zero according to the special reflexion condition given in *International Tables for X-ray Crystallography* (1952). It must thus be realized that this condition is derived for isotropic atoms. The expression for the Cu contribution, A_{Cu}, to the structure factor $F_c(hkl)$, $k+l=2n+1$, is

$$\begin{aligned} A_{\mathrm{Cu}} = \sum_s A_{\mathrm{Cu},s} &= 2f_{\mathrm{Cu}}[\exp' . \cos \frac{\pi}{2}(h+k) \\ &+ \exp'' . \cos \frac{\pi}{2}(-h+k+2l)] \\ &= 2f_{\mathrm{Cu}}(-1)^{\frac{1}{2}(h+k)}[\exp' - \exp''] \,, \end{aligned} \tag{10}$$

exp′ and exp″ being defined above. The reason for A_{Cu} being different from zero is thus that exp′ ≠ exp″, *i.e.* that $U_{\mathrm{Cu},12}$ and/or $U_{\mathrm{Cu},23}$ are different from zero.

We may now give a physical explanation to the anomaly discussed in the former section: the information about the vibration components $U_{\mathrm{Cu},12}$ and $U_{\mathrm{Cu},23}$ is evidently spread out not only over the reflexions with $k+l=2n$, which is the case for the other copper vibration components, but also over the reflexions with $k+l=2n+1$. As most of the latter are too weak to be observed, the corresponding part of the information is lost and $U_{\mathrm{Cu},12}$ and $U_{\mathrm{Cu},23}$ are obtained with a lower accuracy than the other comparable components.

The Cu contributions to the reflexions *hkl* with $k+l=2n+1$ were obtained in a structure factor calcu-

Table 4. *Interatomic distances and angles, with e.s.d.'s*

The upper part of the Table refers to the almost rectangular parallelogram of oxygen atoms around a central copper atom and to the two distant oxygen atoms. The lower part refers to the distorted tetrahedron of copper atoms around an oxygen atom.

The code of symmetry-related positions is as follows (see Fig. 1):

(None)	x	y	z				
i	$x+\frac{1}{2}$	$y+\frac{1}{2}$	z	v	x	$-y+1$	$(z+\frac{1}{2})-1$
ii	$(x+\frac{1}{2})-1$	$y+\frac{1}{2}$	z	vi	x	$-y$	$(z+\frac{1}{2})-1$
iii	$x+\frac{1}{2}$	$(y+\frac{1}{2})-1$	z	vii	$x+\frac{1}{2}$	$\frac{1}{2}-y$	$(z+\frac{1}{2})-1$
iv	x	$-y+1$	$z+\frac{1}{2}$	viii	$(x+\frac{1}{2})-1$	$\frac{1}{2}-y$	$z+\frac{1}{2}$

From atom	Vertex atom	to atom	Distance	Angle
Cu	—	O O(vii)	1·9608 ± 13 Å	—
Cu	—	O(iii) O(v)	1·9509 ± 26	—
Cu	—	O(i) O(vi)	2·7840 ± 37	—
O	—	O(iii)	2·9005 ± 3	—
O	—	O(v)	2·6246 ± 19	—
O	Cu	O(iii)	—	95·72 ± 4°
O	O(iii)	O(vii)	—	90·29 ± 12
O	Cu	O(vi)	—	106·95 ± 11
O(iii)	Cu	O(vi)	—	89·17 ± 6
O	—	Cu Cu(viii)	1·9608 ± 13	—
O	—	Cu(ii) Cu(iv)	1·9509 ± 26	—
Cu	—	Cu(ii)	2·9005 ± 3	—
Cu(iv)	—	Cu(viii)		
Cu	—	Cu(iv)	3·0830 ± 4	—
Cu(ii)	—	Cu(viii)		
Cu	—	Cu(viii)	3·1734 ± 4	—
Cu(ii)	—	Cu(iv)	3·7484 ± 4	—
Cu	O	Cu(ii)	—	95·72 ± 4
Cu(iv)	O	Cu(viii)		
Cu	O	Cu(iv)	—	104·03 ± 5
Cu(ii)	O	Cu(viii)		
Cu	O	Cu(viii)	—	108·85 ± 21
Cu(ii)	O	Cu(iv)	—	145·82 ± 25

lation in which only the Cu atoms were included. The result showed that the Cu contributions to these reflexions were minute, the largest absolute value being 3·0, and the largest relative value being 40% of the total F_c value.

In a paper by Britton & Dunitz (1965) on the crystal structure of silver cyanate, a similar effect, *viz.* Ag contribution to 'light atom reflexions' caused by the anisotropy of the Ag atoms, was reported. Because of the higher atomic number and the higher anisotropy of Ag compared with Cu in this investigation, the Ag contribution in many cases even dominated the F_c values for the 'light atom reflexions' in that investigation. However, Britton & Dunitz did not discuss any anomalous e.s.d.'s.

Discussion

Coordination and crystal structure

It was shown above that the least-squares refinement converged very well when assuming space group, cell content and atomic positions according to Tunell *et al.* (1935). Only one positional parameter was refined and the value obtained is equal within a few of our e.s.d.'s to that given by those authors. Thus, the description of the coordination given in their work is still adequate. The copper atom is coordinated to four coplanar oxygen atoms situated at the corners of an almost rectangular parallelogram. The oxygen atom is coordinated to four copper atoms situated at the corners of a distorted tetrahedron. Interatomic distances and angles are given in Table 4. See also Fig. 1. The sum of the covalent atomic radii (see Slater, 1964) is 1·95 Å in excellent agreement with the data tabulated here. Transition metal oxides are mostly described as being more ionic than covalent. With a difference of 1·8 between the Pauling electronegativities for oxygen and copper a conventional 'per cent ionic character' of about 40% could be estimated (see Wells, 1962*a*). With the considerations above taken into account, the bonding in CuO could be regarded as mainly covalent.

In the sin θ/λ region utilized in this work the scattering factor curves for Cu^0, Cu^+, and Cu^{2+} coincide almost completely, as well as those for O^0, O^-, and O^{2-}. Therefore the scattering factors of Cu^+ and O^- were selected, as already mentioned, this being a reasonable compromise.

The shortest intermetallic distance found is 2·90 Å. This is 0·2 Å longer than the sum of two 'Slater-radii' for Cu. It is therefore evident that there is no metal–metal bonding in this compound.

When looking at the arrangement of the six nearest oxygen atoms to a copper atom, it is seen that two distant oxygen atoms complete a highly distorted

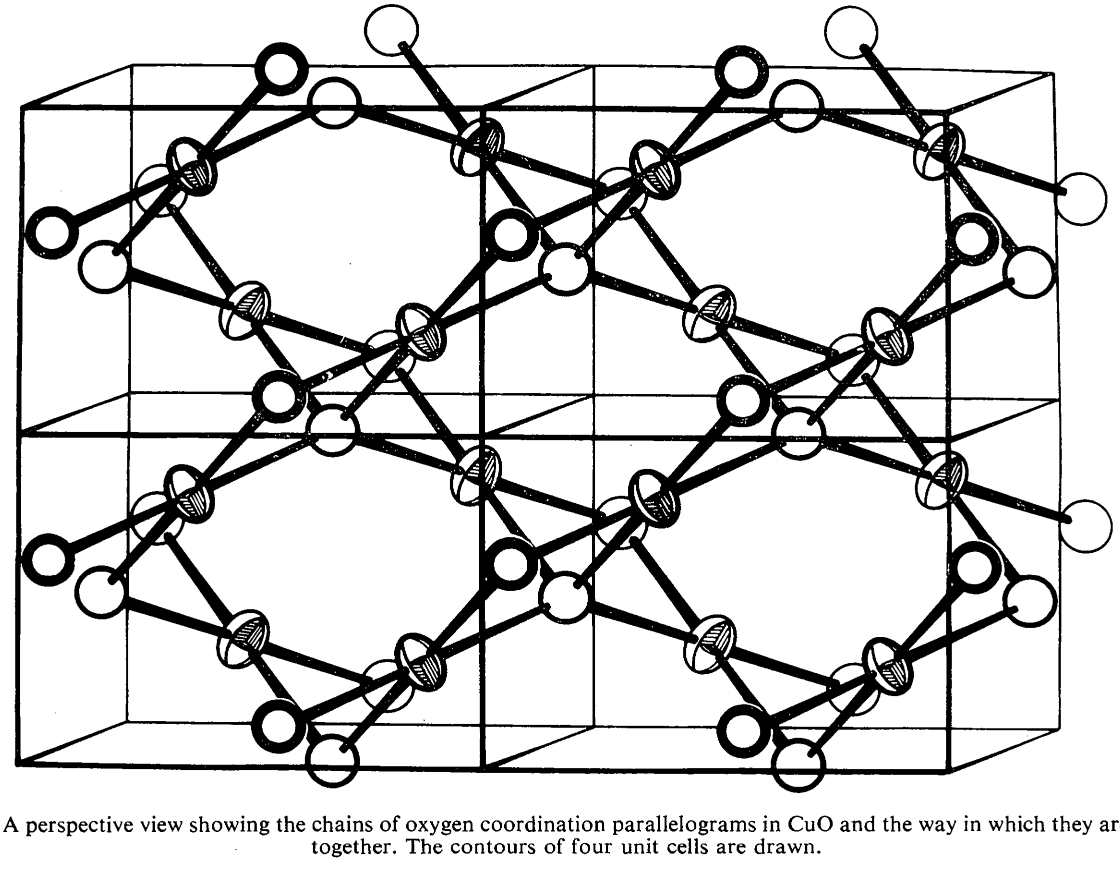

Fig. 2. A perspective view showing the chains of oxygen coordination parallelograms in CuO and the way in which they are linked together. The contours of four unit cells are drawn.

octahedron, see Table 4 and Fig. 1. The coordination of copper observed for example in CuF_2 and $CuCl_2$ (*e.g.* Wells, 1962*b*) is commonly referred to as 4+2. This distortion from a regular octahedral coordination is generally explained as a consequence of the Jahn–Teller effect. In CuO, however, the deviation from such coordination is considerable. The elongation of the interatomic distance is 0·82 Å or about 42%; in CuF_2 it is only 0·34 Å or about 18%, and in $CuCl_2$, 0·65 Å or about 28%. Furthermore the elongation does not take place purely along a fourfold axis of the octahedron, but is tilted 17° from that direction.

The crystal structure could be described in the following way. The building elements are the oxygen coordination parallelograms, which form chains by sharing edges. Such chains traverse the structure in the [110] and $[\bar{1}10]$ directions, the two types of chains alternating in the [001] direction. Each type of chain is stacked in the [010] direction with a separation between the chains of about 2·7 Å. At this distance no bonding should occur. Each individual chain in a group of stacked chains of [110] type is linked to each chain in the two adjacent groups of $[\bar{1}10]$ type by corner sharing. Fig. 2 demonstrates the crystal structure thus described. The Figures are drawn with aid of the program *ORTEP* (Johnson, 1966).

Character of the thermal vibration

A simple Student's type of test on the differences between the r.m.s. values of the copper atom given in Table 1 shows that $R(3)$ is significantly longer than $R(1)$ and $R(2)$, while the latter two are not mutually different. Thus the thermal motion of the copper atom can be pictured as an ellipsoid of revolution. The r.m.s. components are so oriented, see Fig. 1, that the largest component of vibration, $R(3)$, is normal to the plane formed by the copper atom and its four bonded oxygen atoms.

A similar test on the r.m.s. values of the oxygen atom yields that a distinct anisotropy has not been shown for this atom. Inevitably, the structural parameters of an element as light as oxygen will always be determined with lower precision than those of copper. Apart from this it will be seen, however, that the atomic arrangement around the oxygen atom is much more isotropic than that for the copper atom, which should force the thermal vibration of the oxygen atom to be more isotropic.

A least-squares refinement with anisotropic thermal parameters for copper and an isotropic parameter for oxygen was then carried out. In this way only nine parameters were refined. No significant changes were observed, however, and the R value increased only by 0·1% units. Since the type of thermal parameter for oxygen in this case seems to be immaterial, all results and discussions given above refer to the least-squares refinement with anisotropic thermal parameters for both kinds of atoms as described in the previous paragraph.

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