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The Crystal Structure of Copper Bromide Telluride

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The crystal structure of CuBrTe has been determined. The compound is tetragonal with unit cell dimensions $a = 16.417$ Å, $c = 4.711$ Å, $Z = 16$, and space group $I4_1/amd$. Three-dimensional counterdiffraction intensity data (Mo$K\alpha$) were refined with full-matrix least-squares to a conventional unweighted R of 0.066. The structure consists of infinite tellurium spirals with bromine tetrahedra interspersed. Two basic types of disordered copper atoms were found. One type is at the center of the bromine tetrahedra and has several possible locations for each atom. The other type of copper lies on two possible sites in a distorted tetrahedral environment with tellurium and two bromine atoms as nearest neighbors.

Introduction

Several chalcogenide halides of copper, gold, mercury, and bismuth have been synthesized and characterized by Rabenau et al. (*1*). Complete crystallographic structure determinations have been carried out for AuBrSe (*2*), $AuBrTe_2$, and $AuITe_2$ (*3*). The copper compounds form the series CuXTe (X = Cl, Br, I). These compounds were reported to be all of the same symmetry, belonging to the space group $I4_1/amd$ (*4*). Since these substances appear to be isostructural, a structure determination for one member of the series would, in essence, determine the structures of all three. The crystal structure of CuBrTe has been determined.

Experimental

Single crystals of CuBrTe have been synthesized in this laboratory by chemical transport (*5*). The crystals were produced by reaction of CuBr and tellurium in a sealed Vycor tube. The tube was heated in a temperature gradient of 420° to 200°, with the reactants at the high temperature end and the crystals growing at the lower temperature end. The crystals are black and prismatic-c shaped. The identity was confirmed by comparison of the X-ray powder diffraction data (*4*).

The crystal used for intensity data collection was 0.035 × 0.047 × 0.112 mm, mounted and rotated about the c-axis—the long crystal dimension. Rotation and Weissenberg photographs taken with nickel-filtered copper radiation ($\lambda = 1.54178$ Å) confirmed previously reported symmetry and unit cell constants (*4*). The observed systematic absences also confirmed the space group given by Rabenau.

Intensity measurements were made at room temperature with a Buerger Weissenberg diffractometer using zirconium-filtered molybdenum radiation ($\lambda = 0.7169$ Å). The diffraction maxima were counted with an ω scan, background readings being taken on both sides of the peak. All diffractometer angles were set manually. Reflections were measured to an upper limit of $2\theta = 47.0°$; there were no experimentally observable reflections beyond this point. Check reflections were counted periodically to monitor instrument drift during data collection; no

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TABLE I

CRYSTAL DATA

Tetragonal	$\mu(\text{Mo}K\alpha) = 291.22\ \text{cm}^{-1}$
$a = 16.42\ (4)$ Å	Observation conditions
$c = 4.71\ (4)$ Å	hkl: $h + k + l = 2n$
$v = 1269.697$ Å^3	$hk0$: h, $(k) = 2n$
$D_m = 5.62\ \text{g}\cdot\text{cm}^{-3}$[a]	$0kl$: $k + l = 2n$
$D_c = 5.67\ \text{g}\cdot\text{cm}^{-3}$	hhl: $(l = 2n)$; $2h + l = 4n$
$Z = 16$	Space group $I4_1/amd$ (141)

[a] Taken from Ref. (*4*).

drift was observed. The crystal data are summarized in Table I.

Structure Determination and Refinement

Two hundred and ninety-four unique nonextinct reflections were scanned; 162 of these whose net intensity was greater than (total background)$^{1/2}$ were considered to be observed. The remaining 132 were treated as unobserved but allowable reflections. The data were corrected for background, Lorentz, and polarization effects. An absorption correction was made using 512 points of integration. The transmission coefficients, T, in the expression $I_{\text{corr}} = I_{\text{obsd}}/T$ ranged from 0.37 to 0.39, a very narrow range. The correction was done with two independent programs, both yielding identical results. Both absorption correction programs were checked by the method suggested by Cahen and Ibers (*6*). The scattering factors used were those of Hanson et al. (*7*).

The Fourier program used was based on the electron density expressions given in the International Tables. These equations do not include equivalence relationships between reflections within the same octant of reciprocal space for systems of higher than orthorhombic symmetry. Therefore, care was taken to generate a complete octant of planes data (i.e., generate $F_{\text{obsd}}\ khl$ from $F_{\text{obsd}}\ hkl$) before generating Patterson, Fourier, or difference maps. The electron density expressions and the coordinates for the general and special position sets used in this determination are those of the second origin given for space group $I4_1/amd$ with the origin at the center of symmetry (*8*).

The tellurium atoms were located from a three-dimensional Patterson function. Three cycles of block diagonal refinement using isotropic temperature factors gave $R = 0.489$ ($R = \sum |\Delta F|/\sum |F_o|$). The bromine atoms were located from a Fourier map calculated with the data as phased from the tellurium refinement. Five cycles of block diagonal refinement

TABLE II

ATOM LOCATIONS AND OCCUPANCY FACTORS

Atom	Positions set	Occupancy factor
Te	16*f*	1.0
Br	16*h*	1.0
Cu(1)	32*i*	0.25
Cu(2)	8*e*	0.25
Cu(3)	8*e*	0.25
Cu(4)	16*h*	0.25

TABLE III

FINAL POSITIONAL AND THERMAL PARAMETERS[a,b] FOR CuBrTe

Positional and Isotropic Thermal Parameters

Atom	x	y	z	B
Te	0.1429(2)	0.0	0.0	—
Br	0.0	0.1158(4)	0.6201(16)	—
Cu(1)	0.3591(18)	0.6218(18)	0.8714(105)	1.58
Cu(2)	0.0	0.25	0.2815(130)	4.38
Cu(3)	0.0	0.25	0.8403(207)	2.90
Cu(4)	0.0	0.3200(41)	0.1217(154)	8.58

Anisotropic Thermal Parameters ($\times 10^4$ Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te	185(19)	240(19)	313(23)	0.0	0.0	8(10)
Br	187(25)	300(35)	405(41)	0.0	0.0	−29(16)

[a] The anisotropic thermal parameter is defined as: $f = f_0\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*))$.

[b] Estimated standard deviations are given in parentheses; x, y, and z are fractional coordinates.

TABLE IV

Observed and Calculated Structure Factors for CuBrTe

K	FO	FC
H= 2, L= 0		
2	3018	-2892
H= 4, L= 0		
2	1317	-1237
4	7679	-7832
H= 6, L= 0		
0	3505	-3271
4	3220	3177
6	2127	1873
H= 8, L= 0		
0	9746	10247
4	1640	-1721
6	2685	-2649
8	6430	6450
H= 10, L= 0		
0	4425	-3877
2	2466	-2427
4	1383	-1285
8	2641	-2791
10	2506	-2416
H= 12, L= 0		
0	2075	1882
4	3222	-3345
10	1628	1717
12	1558	-1434
H= 14, L= 0		
0	3202	3218
4	2480	2641
6	1181	1190
8	2847	2854
12	1329	1275
H= 16, L= 0		
0	3471	3321
4	1935	-2140
6	2143	-2322
8	2185	2041
H= 18, L= 0		
0	2419	-2292
2	1023	-982
8	1542	-1682
10	1221	-1169
H= 20, L= 0		
0	1985	2169
2	1107	1043
H= 1, L= 1		
3	918	744
H= 2, L= 1		
1	874	-852
H= 3, L= 1		
0	4750	-4732
2	2376	-2348
H= 4, L= 1		
1	5403	5281
3	3737	3652
H= 5, L= 1		
0	1897	-1877
H= 6, L= 1		
1	2305	-2050
3	1313	-1211
H= 7, L= 1		
0	2244	2082
2	1219	1041
4	6143	6135
6	1999	2064
H= 8, L= 1		
3	3779	3746
5	1758	-1703
7	1574	-1599
H= 9, L= 1		
0	1470	-1497
2	1177	-1257
4	1179	1144
H= 10, L= 1		
3	1472	-1333
9	1119	1275
H= 11, L= 1		
0	3024	-3065
2	1231	-1212
4	2386	-2451
8	2687	-2601
H= 12, L= 1		
1	2779	2892
3	2115	2149
7	3380	-3552
H= 13, L= 1		
4	1865	1995
H= 14, L= 1		
1	1227	-1238
7	1247	1462
H= 15, L= 1		
4	2679	2737
H= 16, L= 1		
3	1859	1859
7	1185	-1277
H= 17, L= 1		
0	1746	-1931
H= 1, L= 2		
1	1726	-1797
H= 2, L= 2		
0	2288	2367
H= 3, L= 2		
3	4319	-4223
H= 4, L= 2		
0	5113	-4974
2	3294	-3151
H= 5, L= 2		
3	3298	-3182
5	2514	2303
H= 6, L= 2		
0	4371	4195
2	2085	2113
4	852	-719
H= 7, L= 2		
1	1241	-1172
7	992	910
H= 8, L= 2		
2	918	1001
4	3138	3092
6	2655	2576
H= 9, L= 2		
3	1083	-889
H= 10, L= 2		
2	1428	-1407
4	3591	-3533
6	2919	-2763
H= 11, L= 2		
3	2981	-3032
5	2398	2243
11	2328	-2279
H= 12, L= 2		
0	2319	-1960
2	972	-836
4	1091	1104
10	1596	-1523
H= 13, L= 2		
3	1353	-1088
7	1103	708
H= 14, L= 2		
0	3040	3043
2	1813	1877
8	1931	2081
10	1993	2196
H= 16, L= 2		
0	1285	-1502
4	1011	635
8	1416	-891
10	1205	-1039
H= 17, L= 2		
3	998	-922
H= 18, L= 2		
4	1684	-1880
6	1428	-1514
H= 19, L= 2		
3	1323	-1339
H= 1, L= 3		
0	1329	1967
H= 2, L= 3		
1	2071	2364
H= 3, L= 3		
0	1369	-1279
2	2434	-2462
H= 4, L= 3		
3	890	-1260
H= 6, L= 3		
1	1418	1384
3	2598	2415
5	1002	-810
H= 7, L= 3		
0	2348	2233
2	3230	3058
6	1951	2105
H= 8, L= 3		
1	1626	-1493
3	1177	-875
7	1548	1747
H= 9, L= 3		
4	1393	-1493
H= 10, L= 3		
1	2061	2120
3	1652	1795
7	2667	-2603
9	974	380
H= 11, L= 3		
2	1991	-1872
6	1951	-1795
10	1113	-1413
H= 12, L= 3		
9	1045	813
H= 13, L= 3		
0	1353	1381
2	1111	921
8	1351	1133
10	1061	831
H= 14, L= 3		
3	1446	1520
7	1000	-1095
11	1482	1192
H= 15, L= 3		
0	1023	995
2	1474	1334
8	1315	744
10	1085	1279
H= 17, L= 3		
2	1107	-839
6	1045	-1003
H= 18, L= 3		
1	1331	1241
3	1159	948
H= 2, L= 4		
0	1955	-2702
H= 4, L= 4		
2	1676	-1777
4	1786	-1757
H= 6, L= 4		
0	1965	-1924
2	776	735
4	3046	2835
6	2055	2098
H= 8, L= 4		
2	1704	1570
6	980	1021
H= 10, L= 4		
0	2506	-2257
2	1650	-1701
H= 12, L= 4		
0	876	947
H= 14, L= 4		
0	1301	-1188
4	2017	2138
6	1899	1934

with tellurium and bromine using isotropic temperature factors reduced R to 0.220.

No one set of positions in this space group is consistent with the locations of copper atoms as indicated from Fourier and difference maps based on the phases calculated after location of tellurium and bromine. It is proposed that the copper atoms lie on four sets of positions, each partially occupied. Table II lists these atom locations and the corresponding occupancy factors which resulted from further block diagonal refinement, $R = 0.073$. The copper atoms have been assigned numbers in parentheses to distinguish the four sets of special positions.

Three cycles of full-matrix least-squares refinement using the 162 observed reflections, anisotropic temperature factors for tellurium and bromine, and isotropic temperature factors for all four types of copper converged on the parameters given in Table III, giving

TABLE V

Bond Distances and Angles in CuBrTe

Te–Te[a]	2.751(3) Å
Te–Te[b]	4.69(7)
Te–Br	3.511(5)
Br–Br[c]	3.933(8)
Br–Br[d]	3.969(9)
Te–Cu(32*i*)[e]	3.574(44)
Br–Cu(32*i*)	2.593(35)
Br–Cu($8e_1$)[f]	2.315(20)
Br–Cu($8e_2$)	2.434(42)
Br–Cu(16*h*)	2.587(72)
Cu(32*i*)–Cu($8e_1$)	3.158(32)
Cu(32*i*)–Cu($8e_2$)	3.827(68)
Cu(32*i*)–Cu(16*h*)	4.329(75)
Cu($8e_1$)–Cu($8e_2$)	1.752(115)
Cu($8e_1$)–Cu(16*h*)	3.285(92)
Cu($8e_2$)–Cu(16*h*)	1.755(102)
Te–Te–Te	100.2°
Br–Br–Br	68.3

[a] In the tellurium spiral.

[b] Between tellurium spirals.

[c] Within a tetrahedron.

[d] Between tetrahedra.

[e] Type 1 copper (32*i*); type 2 copper (8*e*, 16*h*).

[f] Subscripts distinguish the two 8*e* copper positions.

an $R = 0.066$. No oscillation in the values of the positional and thermal parameters was observed. The observed and calculated structure factors are given in Table IV. A difference map generated after refinement to $R = 0.066$ did not indicate any alternative assignment of atoms; the peaks observed were very small compared to those used for previous assignments and were randomly distributed.

Inclusion of anomalous dispersion corrections for the scattering factors of tellurium and bromine had no observable effect on the agreement. Attempts at refinement with all the reflections, including those called unobserved, or with anisotropic temperature factors for the copper atoms, were fruitless. Both block diagonal and full-matrix least-squares refinements failed to converge on positional or thermal parameters under these conditions.

Important interatomic distances and angles are summarized in Table V.

Discussion

The tellurium atoms in CuBrTe are arranged in the same manner as in tellurium metal (*9*), forming infinite spirals in the *c* direction. The Te–Te distance in tellurium metal is 2.86 Å as compared to 2.75 Å in CuBrTe. The tellurium spirals are alternately right- and left-handed and are related by mirror planes parallel to the *c*-axis (Fig. 1). The spirals in tellurium metal are all of the same handedness.

The bromine atoms form tetrahedra. These tetrahedra are dispersed between the tellurium spirals. The tetrahedra centered at $y = \frac{1}{4}$ are rotated 90° to those centered at $y = \frac{3}{4}$ (Figs. 1 and 2).

There are two basic types of positions found for the copper atoms, resulting from partial occupation of general and special sets of positions. One type of position occupied by copper is that resulting from the coordinates determined for the set 32*i* with occupation factor 0.25, Cu(1) in Tables II and III. These positions are located between the tellurium spirals and the bromine tetrahedra in a distorted tetrahedral environment with two bromine and two tellurium atoms as nearest neighbors. There are 32 possible positions for this type of copper atom. The coordinates determined place these 32 positions in 16 "pairs" such as the one shown in Fig. 3. This assignment accounts for 8 copper atoms. In a

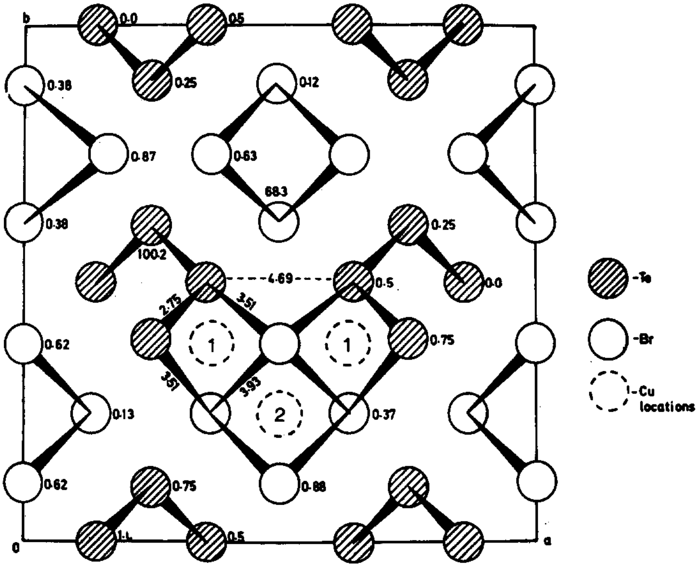

FIG. 1. CuBrTe viewed down the *c*-axis showing the arrangement of the Te and Br atoms and the location of type 1 and type 2 copper positions.

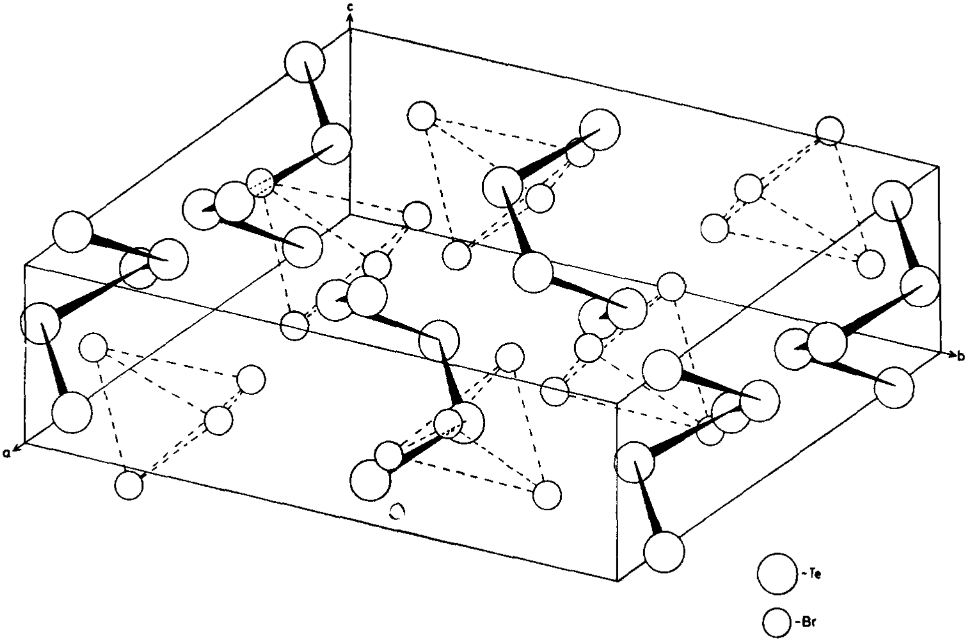

FIG. 2. Trimetric projection of unit cell showing spacial arrangement of tellurium and bromine.

given unit cell, there will be a copper atom on 8 of these 32 possible positions.

The coordinates determined for Cu(2), Cu(3), and Cu(4) (see Tables II and III) fall in the vicinity of the bromine tetrahedra (Fig. 4). For one bromine tetrahedron, Fig. 4 shows all of the possible copper locations that arise from the coordinates for the three assignments 8*e*, 8*e*, and 16*h* with occupation factors of 0.25, 0.25, and 0.25, respectively. These assignments account for the remaining eight copper atoms in the unit cell.

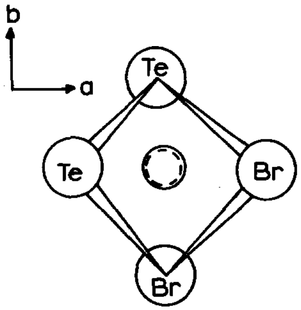

FIG. 3. Type 1 copper atom location, showing the pair of copper positions with two tellurium and two bromine atoms arranged as a distorted tetrahedron.

Since there are four bromine tetrahedra per unit cell, there must be two of this second kind of copper atom located somewhere on the eight possible locations on each tetrahedron, as shown in Fig. 4.

No specific situation analogous to the first type of copper proposed here has been encountered. The second type of disordered

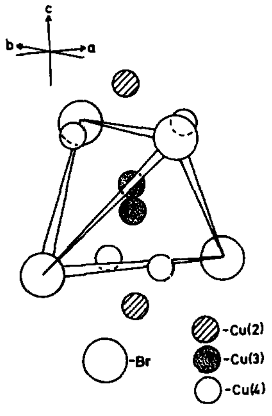

FIG. 4. Type 2 copper atom location, showing bromine tetrahedron with the possible copper positions in the center.

copper position is similar to the average structure of β-CuBr proposed by Hoshino (*10*). It was proposed for that system that copper was statistically distributed on four or five metastable positions in the bromine tetrahedron.

The overall structure of CuBrTe may be viewed as that of tellurium metal with the spirals separated by insertion of copper and bromine atoms. The distance of closest approach of the tellurium spirals here is 4.69 Å as compared to 3.74 Å in tellurium metal. The Te–Te–Te angle within the spiral is 100.2° in CuBrTe and 102° in Te metal. The various Cu–Br distances found compare very well with the known Cu(I)–Br distance of 2.49 Å.

As can be seen from the diagrams, the possible type one copper locations (Cu(1)) define "pairs" of possible copper positions. The coordinates determined for the type two coppers (Cu(2), Cu(3), Cu(4)) produce possible copper locations which fall close to one another, forming groups in the bromine tetrahedra. Refinement was tried using sets of positions of smaller multiplicity with larger occupation factors in an effort to fix definitely the location of the copper atoms.

Specifically, refinement was tried with copper assigned to 16*g* with $x = 0.36$ and occupation factor (o.f.) equal to 1.0; to 16*g* with $x = 0.36$, o.f. = 0.5 (8 atoms) and the remaining 8 atoms on sets 4*a* and 4*b*; to 16*g* with $x = 0.36$, o.f. = 0.5 and the remaining 8 atoms on two sets of 8*e* (both with o.f. = 0.5); and to 16*g* with $x = 0.36$, o.f. = 0.5, two sets of 8*e* (o.f. = 0.25) and 16*h* (o.f. = 0.25). In all cases, the agreement was not as good, and the isotropic temperature factors were generally very large. The final model proposed is substantiated over the above alternatives by the Hamilton significance test (*11*) which favors the final model over all of the ones above at the 0.005 level.

After the apparent disorder of the copper atoms was detected, a very long exposure rotation photograph was taken about the *c*-axis. This photograph showed very faint rows of spots interspersed at intervals of one-third the original spacing. These reflections were far too weak to be measured on the diffractometer. The possibility of a superlattice or polytype structure in which the proposed copper locations are systematically occupied should be investigated further. The space group involved here contains a relatively high degree of symmetry and possible position combinations. The authors feel that the model being proposed is reasonable, given the available data.

From primary valence considerations, these compounds are novel, in that one would not predict bonding between the three species Cu^{1+}, Br^{1-}, and Te^0. Magnetic data reported by Rabenau (*4*) indicate that copper in CuBrTe is monovalent. A structure consisting of tellurium spirals with copper and bromine interspersed is reasonable. The "metastable" positions (type one) in which copper is found could be simply due to the fact that it is not bound strongly to tellurium and there is more than one place in which the copper atom will fit without strain.

Preliminary crystallographic information has indicated that the three compounds, CuClTe, CuBrTe, and CuITe, are isostructural. In light of the observed disorder in CuBrTe, it would be worthwhile investigating the structures of the other two compounds in order to determine if analogous situations exist.

The presence of disordered copper atoms could suggest an explanation for the semiconducting nature of these compounds.

Acknowledgment

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References

1. A. Rabenau and H. Rau, *in* "Inorganic Syntheses" (A. Wold and J. K. Ruff, Eds.), Vol. 14, pp. 160–173, McGraw-Hill, New York (1973).
2. D. Mootz, A. Rabenau, H. Wunderlich, and G. Rosenstein, *J. Solid State Chem.* **6**, 583 (1973).

3. H. M. Haendler, D. Mootz, A. Rabenau, and G. Rosenstein, *J. Solid State Chem.* **10**, 175 (1974).

4. A. Rabenau, H. Rau, and G. Rosenstein, *Z. Anorg. Allgem. Chem.* **374**, 43 (1970).

5. P. M. Carkner and H. M. Haendler, *J. Cryst. Growth*, to appear.

6. D. Cahen and J. Ibers, *J. Appl. Cryst.* **5**, 298 (1971).

7. H. P. Hanson, F. Herman, J. D. Lee, and S. Skillman, *Acta Crystallogr.* **17**, 1040 (1964).

8. N. F. M. Henry and K. Lonsdale, Eds., "International Tables for X-Ray Crystallography," Vol. 1, pp. 245, 246, Kynoch Press, Birmingham, England (1959).

9. R. W. G. Wyckoff, "Crystal Structures," 2nd ed., Vol. 1, p. 36, Interscience, New York (1963).

10. S. Hoshino, *J. Phys. Soc. Japan* **7**, 560 (1952).

11. W. C. Hamilton, *Acta Crystallogr.* **18**, 502 (1965).

12. J. A. Ibers, Northwestern Univ., Evanston, Ill. (1968 version).

13. W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn. (April 1971 version).

14. F. R. Ahmed, National Research Council Crystallographic Series, National Research Council, Ottawa, Canada.