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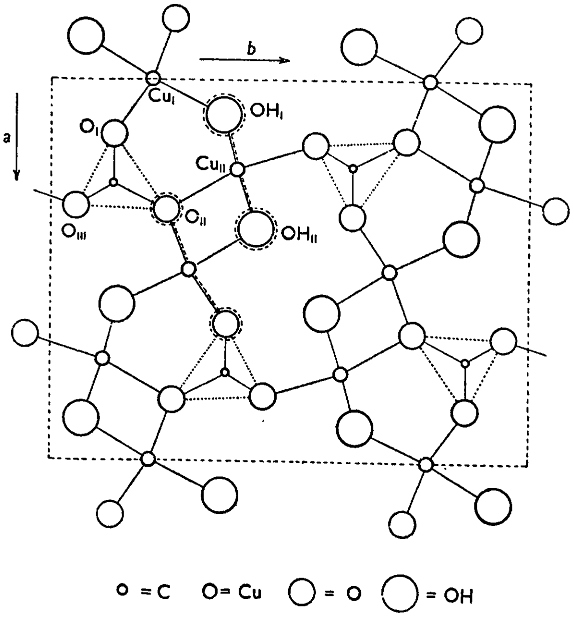

Fig. 2. Projection of the structure of malachite on (001). The broken lines from Cu atoms represent bonds to O or OH in adjacent unit cells (broken circles).

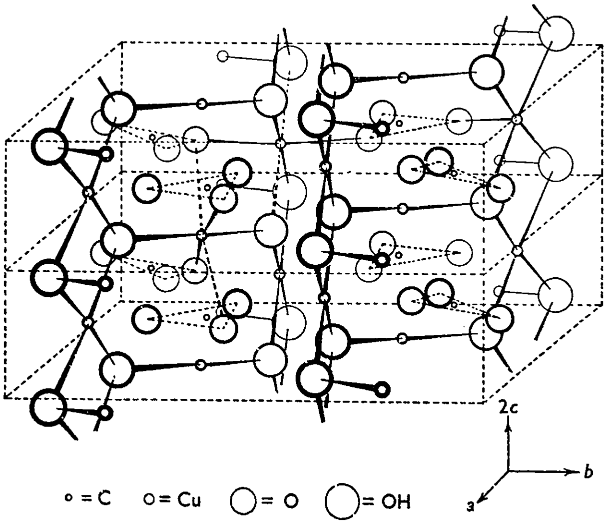

Fig. 3. The crystal structure of malachite (two unit cells).

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The Crystal Structure of Bandylite, $CuCl_2.CuB_2O_4.4H_2O$

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The crystal structure of bandylite is tetragonal C_{4h}^3–$P4/n$ with one molecule of $CuCl_2.CuB_2O_4.4H_2O$ in a cell of dimensions $a = 6{\cdot}19$ and $c = 5{\cdot}61$ A. The copper atoms are surrounded in a square planar configuration by four hydroxyl groups at a distance of 1·98 A. and two chlorine atoms on a line at right angles to this plane at 2·80 A. These distorted octahedra about copper are joined together into layers by boron atoms that are surrounded tetrahedrally by four hydroxyl groups at a distance of 1·42 A.

Introduction

The nature of the co-ordination of copper in cupric compounds has been the subject of a number of crystal-structure investigations. The type of bonding that occurs is not yet completely understood (Wells, 1947), and more interatomic distance data, of sufficient accuracy to allow deductions as to bond type, are needed. The possibility for studying the bonding of the copper (II) atom as well as the co-ordination of boron makes bandylite a crystal of some interest from a structural point of view.

The cupric atom usually occurs in sixfold co-ordination with four close neighbors in a square planar arrangement and with two more neighbors at a somewhat longer distance on a line at right angles to this plane. Boron commonly has a triangular, threefold co-ordination with oxygen but a fourfold co-ordination occurs in danburite (Dunbar & Machatschki, 1930), BPO_4 and $BAsO_4$ (Schulze, 1934), and in certain borosilicate glasses (Huggins, 1940).

Morphology and optical properties

A morphological, optical, and X-ray investigation of a sample of bandylite has been described by Palache & Foshag (1938). On the basis of goniometric measurements they report the crystal class as tetragonal, holohedral. Observation of extinctions on X-ray photographs then led them to propose the space group D_{4h}^7–$P4/nmm$. They also found bandylite to be optically uniaxial and negative with strong pleochrism. The refractive indices reported were $\omega = 1{\cdot}691$ and $\epsilon = 1{\cdot}641$.

The crystals used in the present investigation were kindly loaned by the United States National Museum. They are intimately associated with atacamite and are light blue to green in color. The (001) cleavage is perfect and the crystals are soft and easily deformed.

Unit cell and space group

Zero-, first-, and second-level Weissenberg photographs were taken about the *a* and *c* axes. Cu $K\alpha$ and Mo $K\alpha$ radiations were used for the zero-level and Cu $K\alpha$ radiation for the first- and second-level photographs. The tetragonal unit cell was found to have

$$a = 6{\cdot}19 \quad \text{and} \quad c = 5{\cdot}61 \text{ A}.$$

With one molecule of $CuCl_2 . CuB_2O_4 . 4H_2O$ per unit cell the calculated density is 2·67 g.cm.$^{-3}$, in good agreement with 2·8 g.cm.$^{-3}$, the density observed by a sink-and-float method using mixtures of tetrabromoethane and benzene.

An examination of a zero-level Weissenberg photograph taken about *c* showed C_4 symmetry only, and not C_{4l} as one would expect for the tetragonal holohedral class (D_{4h} Laue symmetry). In order to verify this contradiction with D_{4h} symmetry, *c*-axis Weissenberg photographs were prepared from crystals of various sizes and shapes using both Cu $K\alpha$ and Mo $K\alpha$ radiations. In all cases the gross intensity features were in agreement and definitely excluded any mirror lines on the photograph, and hence also excluded D_{4h} Laue symmetry. From these, and Weissenberg photographs taken about the *a* axis, the Laue symmetry C_{4h} was established. The only systematic extinctions were for $(hk0)$ reflections with $h+k$ odd. This indicates that the space group is C_{4h}^3–$P4/n$.

Preliminary structure determination

The intensities were estimated with the aid of a standard scale prepared by exposing a strip of photographic film to a strong reflection from the crystal as the crystal and film went back and forth through the reflecting position with the Weissenberg motion. The number of passes through the reflection was taken to be proportional to the intensity. This method gave a standard scale with spots having the same shape as the spots whose intensities were to be measured. The intensity range over which reflections were recorded was increased by using three superimposed films. When Mo $K\alpha$ radiation was used the films were interleaved with brass foil 0·001 in. thick.

The intensities were corrected for Lorentz and polarization factors with Lu's chart (1943). The photographs used to determine the parameters were taken with Mo $K\alpha$ radiation, and the crystals were under 0·15 mm. in their largest dimension. The absorption of the crystals for Mo $K\alpha$ radiation was so small that the absorption corrections were well within the limits of errors in the intensity estimations and hence were neglected.

In the space group C_{4h}^3–$P4/n$ the two- and fourfold positions are consistent with the Laue symmetry D_{4h}, and in order to get the lower symmetry, C_{4h}, that is actually observed the eightfold positions must be occupied. The only atoms occurring eight times in the unit cell are oxygen and hydrogen, and therefore the oxygen atoms must occupy these positions.* The eightfold positions involve *x*, *y* and *z* parameters.

The copper, chlorine and boron atoms must go into the twofold positions which involve, at most, a *z* parameter. A trial structure was proposed, with copper and chlorine atoms in 2(*c*), boron in 2(*a*) and oxygen in 8(*g*) positions, which gave good agreement between observed and calculated intensities. This model consisted of copper atoms surrounded by four oxygen atoms in a square planar arrangement and two chlorine atoms on a line at right angles to this plane. These distorted octahedra about copper are linked together by boron atoms which are surrounded by four oxygen atoms in a nearly tetrahedral configuration. All the oxygen atoms are equivalent, and it seems reasonable from valence considerations to distribute the hydrogen atoms so that each oxygen is joined to a hydrogen atom. This arrangement of the hydrogen atoms satisfies the electrostatic valency rule (Pauling, 1944, p. 384) if one charge of the copper atom is considered to belong to the chlorine atoms and the other to the four surrounding OH groups. From now on the eightfold positions will be considered to be occupied by OH groups.

This arrangement of the atoms (Fig. 1) gives a structure consisting of directly superimposed layers of the composition $CuOHH_3BO_3$. These layers are held together by chlorine atoms which lie half-way between copper atoms in adjacent layers.

If this structure is projected on to the *a b* plane, the copper and chlorine atoms are directly superimposed and the OH groups and boron atoms are well resolved. Moreover, the electron density of the Cu + Cl atoms is so great that the signs of all the observed $(hk0)$ reflections are determined by the Cu + Cl contribution.

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* The hydrogen atoms themselves do not contribute enough to the scattering to cause a lowering of symmetry of the magnitude observed. Later in the investigation chemical considerations lead to placing OH groups in these eightfold positions.

In order to establish approximate x and y parameters for the OH groups an electron-density projection was carried out on to the $a\,b$ plane with ($hk0$) data obtained from Mo $K\alpha$ Weissenberg photographs and signs determined from the Cu + Cl contribution (Fig. 2). As would be expected, there are large diffraction effects from the very high Cu + Cl peak. There is a large negative area surrounding the main peak and there are a number of fairly high spurious peaks. However, the OH groups and boron atoms stand out clearly and it is possible to fix rough x and y parameters for the OH groups. These parameters are expected to differ from the true ones because of the diffraction effects inherent in the Fourier projection.

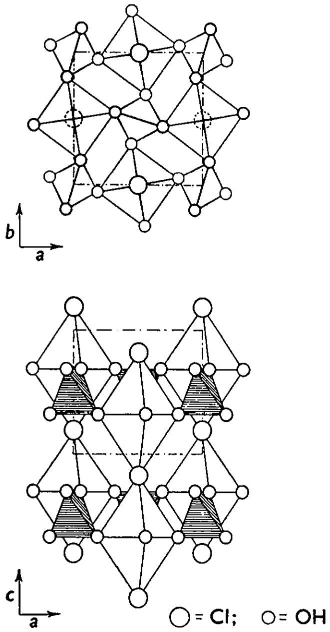

Fig. 1. The co-ordination polyhedra in bandylite. The copper atoms are at the centers of the distorted octahedra and the boron atoms are at the centers of the tetrahedra. The broken line indicates the unit cell outline and the $a\,c$ projection shows how the chlorine atoms serve to bind adjacent layers together.

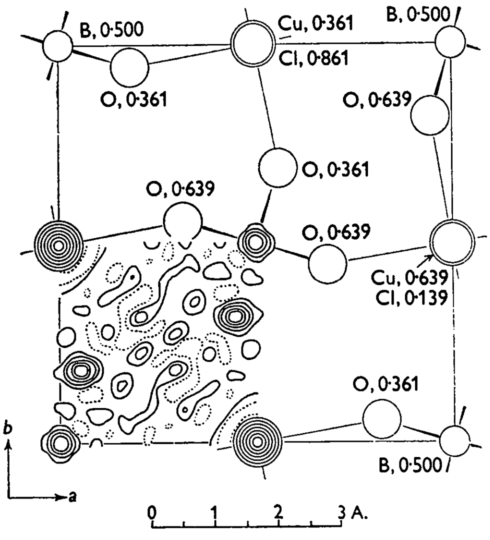

Fig. 2. Electron-density projection on to the $a\,b$ plane. The zero-electron contour is dotted and the contour lines are at intervals of 2 e.A.$^{-2}$ except around the Cu + Cl peaks where the interval is 8 e.A.$^{-2}$. The numbers are the z parameters of the atoms.

The approximate z parameters were determined for Cu, Cl and OH by a trial-and-error procedure with ($0kl$) data from Mo $K\alpha$ Weissenberg photographs. In order for satisfactory agreement to be obtained in this zone a temperature factor appeared to be necessary. Since the need for a temperature factor did not arise with the ($hk0$) reflections this behaviour indicates either an anisotropy in thermal motion or a one-dimensional disorder. Various schemes were tried to account for this anisotropic factor. Vibrations in the z direction of the copper, chlorine and hydroxyl groups separately and in various combinations were tried. Good agreement could be obtained only for a general vibration, or disorder, of all the atoms in the z direction. This was taken into account by multiplying the calculated structure factors by e^{-Bl^2/c^2}.

Refinement of parameters

Since the Fourier projection on the $a\,b$ plane does suffer from diffraction effects which may appreciably alter the OH positions, a least-squares treatment (Hughes, 1941) was carried out on the ($hk0$) data. A comparison of the parameters derived from the Fourier projection and the least-squares treatment gave the following results:*

	Fourier	Least squares
x	0·318	0·316
y	0·552	0·554

The z parameters for the OH, Cu and Cl atoms were refined by a least-squares treatment on the ($0kl$) zone. In this treatment an expression for an anisotropic temperature factor was used and two assumptions were made. These were that the OH groups lie in the same plane as the copper atoms, which they surround, and that the chlorine atoms lie half-way between copper atoms in adjacent layers. These constraints seem to be reasonable and also give good agreement between observed and calculated structure factors. The least-squares treatment on the ($0kl$) zone gives the following z parameters: $z_{Cu} = 0{\cdot}639$, $z_{OH} = 0{\cdot}639$, $z_{Cl} = 0{\cdot}139$.

The complete set of parameters is:

Cu	$x=0$	B	$x=0$
	$y=0{\cdot}500$		$y=0$
	$z=0{\cdot}639$		$z=0{\cdot}500$
Cl	$x=0$	OH	$x=0{\cdot}316$
	$y=0{\cdot}500$		$y=0{\cdot}554$
	$z=0{\cdot}139$		$z=0{\cdot}639$

The temperature factor is e^{-Bl^2/c^2}, where $B = 0{\cdot}305$ A.^{2}

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* Parameters are referred to the origin in the *Internationale Tabellen* which is not at a center of symmetry. The $a\,b$ projection however is centrosymmetric about this origin.

Table 1. *Calculated and observed values of the* 0*kl* *structure factors*

0*kl*	$F_{\text{calc.}}$	$\lvert F_{\text{obs.}} \rvert$	0*kl*	$F_{\text{calc.}}$	$\lvert F_{\text{obs.}} \rvert$	0*kl*	$F_{\text{calc.}}$	$\lvert F_{\text{obs.}} \rvert$
001	−64	54	031	36	46	061	14	18
002	−16	26	032	−74	72	062	4	<6
003	40	48	033	16	20	063	−10	8
004	−60	58	034	18	24	064	30	30
005	8	<10	035	−20	20	065	− 1	<8
006	24	26	036	32	30	066	−14	8
007	−18	18	037	− 2	<8	067	8	<8
008	20	20	038	−14	12	071	4	<8
011	−30	32	040	58	68	072	−30	32
012	76	60	041	−14	26	073	2	<10
013	−12	24	042	− 4	<6	074	8	<8
014	−16	20	043	10	14	075	− 4	<8
015	14	14	044	−32	38	076	16	18
016	−28	32	045	2	<8	080	20	24
017	2	<8	046	14	10	081	1	<8
018	12	8	047	− 8	<8	082	0	<4
020	−80	72	048	14	10	083	− 6	<8
021	20	26	051	− 1	<8	084	−12	<10
022	6	<4	052	30	36	085	− 2	<8
023	−12	14	053	− 1	<6	091	− 4	<8
024	36	42	054	− 8	<6	092	26	20
025	− 2	<6	055	1	<10	093	− 2	<8
026	−16	14	056	−16	22	0,10,0	−28	26
027	8	<8	057	0	<8			
028	−14	12	060	−48	48			

Table 2. *Calculated and observed values of the* *hk*0 *structure factors*

*hk*0	$F_{\text{calc.}}$	$\lvert F_{\text{obs.}} \rvert$	*hk*0	$F_{\text{calc.}}$	$\lvert F_{\text{obs.}} \rvert$	*hk*0	$F_{\text{calc.}}$	$\lvert F_{\text{obs.}} \rvert$
110	−50	46	440	46	56	790	16	16
130	50	60	460	−28	32	800	20	22
150	−18	28	480	28	26	820	−34	32
170	36	40	4,10,0	−36	34	840	36	34
190	−32	26	4,12,0	24	<16	860	−28	22
1,11,0	24	<16	510	−46	52	880	36	32
200	−80	66	530	34	40	910	−38	42
220	44	52	550	−36	40	930	28	24
240	−68	60	570	44	40	950	−34	26
260	56	56	590	−24	18	970	22	18
280	−36	36	5,11,0	24	<16	10,0,0	−28	26
2,10,0	38	26	600	−48	58	10,2,0	34	24
2,12,0	−22	16	620	50	56	10,4,0	−24	14
310	86	66	640	−56	54	10,6,0	16	18
330	−62	58	660	30	28	11,1,0	16	16
350	32	44	680	−30	24	11,3,0	−16	<14
370	−38	40	6,10,0	24	<16	11,5,0	26	18
390	18	14	710	44	42	12,0,0	24	16
3,11,0	−14	<16	730	−18	26	12,2,0	−34	20
400	58	56	750	24	26	12,4,0	26	18
420	−32	42	770	−24	14			

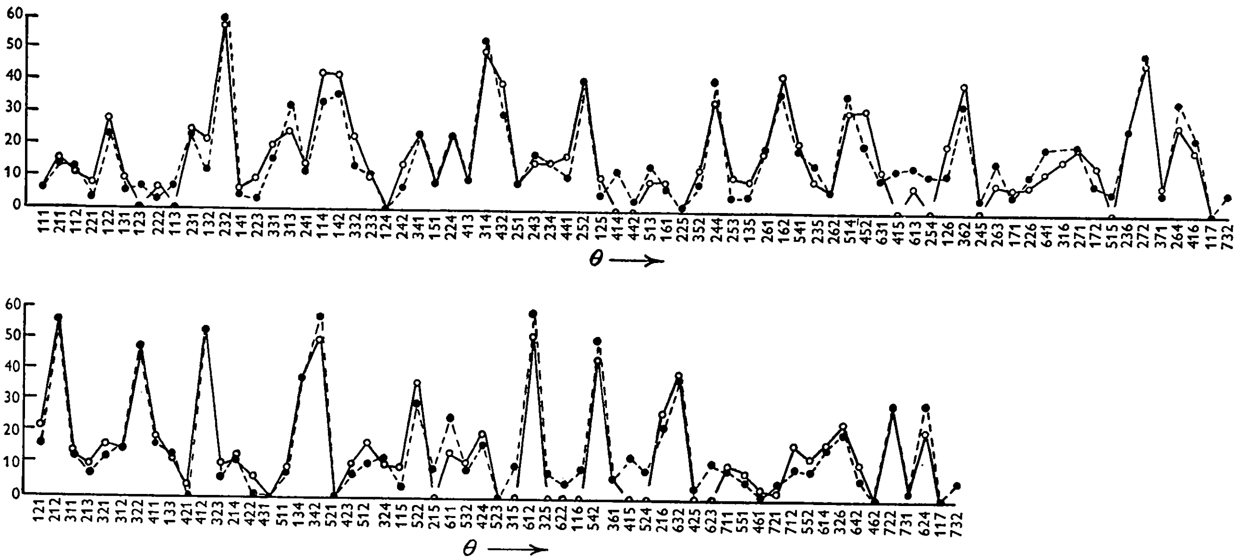

Fig. 3. Plots of $F_{\text{calc.}}$ (broken line) and $F_{\text{obs.}}$ (full line) as a function of increasing θ for all reflections in the range of the Weissenberg photographs that are not recorded in Tables 1 and 2.

Calculated and observed structure factors for the (0*kl*) and (*hk*0) reflections are tabulated in Tables 1 and 2. The origin of co-ordinates has been shifted to the center of symmetry, so that the phase angle would reduce to a plus or minus sign. The observed reflections were obtained from zero-level Weissenberg photographs taken about the *a* and *c* axes with Mo *Kα* radiation. The atomic scattering curves for Cu, Cl, B, O and H were taken from the *Internationale Tabellen*. As a further test of the proposed structure the reflections, not corrected for absorption, on first- and second-level Weissenberg photographs taken about the *a* and *c* axes with Cu *Kα* radiation, were used to derive observed structure factors which are compared with those calculated from the parameters. The agreement is shown by the graphs in Fig. 3.

Discussion

The copper atoms occur in an arrangement that is quite similar to that found in other cupric compounds (Wells, 1947, 1949). That is, copper is surrounded by four nearest neighbors in a plane and two next-nearest neighbors on a line at right angles to this plane. The nearest neighbors in bandylite are four hydroxyl groups at a distance of 1·98 A. and the next nearest are two chlorine atoms at 2·80 A. This same configuration occurs for some of the copper atoms in atacamite, $Cu_2Cl(OH)_3$ (Wells, 1949). The distances in that case are 2·02 A. for the Cu–OH bonds and 2·76 A. for the Cu–Cl bonds.

The boron atoms lie at the center of a nearly tetrahedral arrangement of hydroxyl groups. The angles made by two OH groups with the boron atom are 113° 22′ and 104° 38′. The O–O distance within a tetrahedron is 2·25 A. A somewhat similar co-ordination occurs in danburite, $CaB_2Si_2O_8$, where the B–O distances are reported to be 1·40, 1·50, 1·53 and 1·59 A. (Dunbar & Machatschki, 1930). The B–O distance in BPO_4 is 1·44 A. and in $BAsO_2$ it is 1·49 A. (Schulze, 1934). The B–O distance in bandylite, 1·42 A., is somewhat smaller than the average of these but it is longer than the bond distances for triangularly co-ordinated boron which are 1·35, 1·35 and 1·38 A. in CaB_2O_4 (Zachariasen, 1931).

The layer nature of the structure serves to explain the high negative birefringence, the good cleavage parallel to (001), and the anisotropic temperature factor, which corresponds to either a larger amplitude of vibration perpendicular to the layers than in the plane of the layers or to a disorder leading to variable interlayer spacing. The nature of the bonding within layers can be reasonably understood by assuming sp^3 hybridization for the B–OH bonds and dsp^2 hybridization for the Cu–OH bonds. The nature of the forces holding the layers together resides in the nature of the bonds between copper and chlorine. The large bond distance of 2·80 A. and the lack of excess low-energy bonding orbitals in copper when it is dsp^2 hybridized leads one to the conclusion that the Cu–Cl bond must be largely ionic in nature.

The bandylite structure can be considered as made up of giant molecules of composition $(CuOH.H_3BO_3^+)$ bonded together parallel to each other by Cl^- ions. It is reasonable to assume that the positive charge is localized around the copper atom. As far as the Cu–Cl bond forces are concerned we would expect the copper to act as a cuprous ion. The ionic radius of 0·96 A. for the cuprous ion calculated by Pauling (1944, p. 346) and the ionic radius of the chloride ion of 1·81 A. (Pauling, 1944, p. 346) add to give 2·77 A., in remarkable agreement with the value observed in bandylite (2·80 A.). Similar calculations for other long bonds with copper, on the assumption of a purely ionic bond, give surprisingly good agreement with observed distances (Table 3).

Table 3. *Bond lengths*

Bond	Calculated (A.)	Observed (A.)	Compound*
Cu–Cl	2·77	2·80	Bandylite
		2·76	$Cu_2Cl(OH)_3$
Cu–Br	2·91	3·0	$Cu_2Br(OH)_3$
Cu–OH†	2·36	2·36	$Cu_2Cl(OH)_3$
		2·3	$Cu_2Br(OH)_3$

* The bond distances in $Cu_2Cl(OH)_3$ and $Cu_2Br(OH)_3$ are taken from Wells (1949).

† The ionic radius of the OH group is taken as 1·40 A.

The close agreement of some of the above distances is quite obviously fortuitous, but the general trend when going from one copper bond to another indicates that the ionic character of the two long copper bonds probably predominates in these compounds.

It is a pleasure to thank Dr H. P. Klug for suggesting this problem and for reading the manuscript, and to express my appreciation to the United States National Museum for loaning a sample of bandylite.

Note added 7 *August* 1950. After this manuscript had been submitted for publication Prof. M. Fornaseri communicated privately to the author some results on the structure of bandylite which he had obtained independently. There is serious disagreement between us on only one point. The space group used by Fornaseri, D_{4h}^7, is based on D_{4h} Laue symmetry. Details of Fornaseri's investigation are not yet available so it is not possible to examine the evidence in support of his space group.

An independent verification of the Laue symmetry found in this investigation has been received from C. Frondel (private communication). He has checked some of his own Weissenberg photographs of bandylite and reports that the intensity distribution supports the C_{4h} Laue symmetry.

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A Modification of the Cohen Procedure for Computing Precision Lattice Constants from Powder Data*

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The Cohen scheme for weighting the measurements upon the lines of powder patterns is shown to be inappropriate, and a modified weighting is proposed. Examples are given to illustrate the improvement in precision resulting from the modified method.

Cohen's method (Cohen, 1935, 1936 *a*, *b*, *c*) of analytical extrapolation, to eliminate the effect of the systematic errors inherent in all present types of precision cameras, is now firmly established as probably the most generally useful technique available for the precision determination of lattice constants.† One of its chief advantages lies in the fact that the basic analytical extrapolation can be extended to a least-squares treatment to reduce the effect of random errors in the initial data, and to estimate the precision of the calculated parameters from the criterion of external consistency (Jette & Foote, 1935).

Cohen has given formulae for this least-squares treatment. In his derivations, however, he has weighted the original measurements according to a system which the present discussion will show to be not generally appropriate. Consequently, his formulae are found to lead to lattice constants that differ somewhat from the most probable, and frequently to an underestimation of their precision, as compared with a corrected treatment. Since the estimation of the error of a precision measurement is fully as important as the measurement itself, this defect of Cohen's procedure has considerable significance, as will be illustrated by several examples, even though the changes in the calculated lattice constants themselves in general are not large.

Cohen's analytical extrapolation and least-squares treatment

To treat the systematic errors, Cohen (1935, 1936*a*) proposed modifying the Bragg relationship to

$$\frac{n\lambda}{2d}=\sin(\theta+\Delta\theta)=\cos\tfrac{1}{2}(\phi+\Delta\phi). \qquad (1)^*$$

Here ϕ is the diffraction angle which is measured experimentally, and $\Delta\phi$ is the small angle, due to the net effect of all the systematic errors, which must be added to ϕ to make their sum $\phi+\Delta\phi$ fulfill the Bragg relation. Then, by squaring, expanding the right-hand term by Taylor's theorem, and neglecting all powers of the small angle $\Delta\phi$ except the first, Cohen obtained

$$\frac{n^2\lambda^2}{4d^2}=\cos^2\tfrac{1}{2}\phi-\tfrac{1}{2}\Delta\phi\sin\phi \qquad (2)$$

as the general modified form of the Bragg relationship applicable to experimentally measured diffraction angles.

Next Cohen expressed $\Delta\phi$ in the analytical form appropriate to the camera used. For back-reflection Debye–Scherrer cameras he preferred $\Delta\phi=K_1\phi$ (correcting an earlier suggestion of $\Delta\phi=K_1\sin\phi$) as being the best approximation, and Warren (1943) has confirmed this conclusion for the range $\phi\leqslant 60°$. Similarly, for back-reflection symmetrical focusing cameras he found $\Delta\phi=K_2\phi$ for $\phi\leqslant 60°$. While the functional form of $\Delta\phi$ for the third important type of precision camera,

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* The basic elements of this modified computation were developed several years ago in an equivalent form, though one somewhat less convenient than that presented below, while the author was employed at the Magnesium Laboratories, The Dow Chemical Company, Midland, Michigan.

† A comprehensive survey and bibliography of the subjects of systematic errors in X-ray cameras and the precision measurement of lattice constants has been given by Buerger (1942, chap. 20), while contributions of more recent date have been made by Warren (1943), Thomas (1948), Ekstein & Siegel (1949), and Straumanis (1949).

* Since only back-reflection methods (where the incident X-ray beam *enters* the camera through a hole in the film) are sensitive enough to lay claim to precision and at the same time possess a geometry to which the analytical extrapolation is easily adaptable, it is convenient to write all formulae in terms of the 'back-reflection angle' ϕ (where $\phi=180°-2\theta$) rather than in terms of the usual Bragg angle θ.