The crystal-structure and optical properties of matlockite (PbFCl).

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It has recently been shown by W. Nieuwenkamp (1) that matlockite is identical in chemical composition and crystal-structure with artificial lead fluochloride PbFCl. His conclusion is based upon powder photographs of the two substances and a fluorine determination of a specimen of matlockite from Matlock, Derbyshire. The present work was undertaken primarily to check Nieuwenkamp's interesting results. Access to an exceptionally fine suite of matlockite specimens in the British Museum collection made possible single crystal X-ray measurements, accurate optical determinations, and a new chemical analysis.

The first description of matlockite was given by R. P. Greg (2) who recognized a new mineral distinct from phosgenite on specimens of decomposed galena from ‘one of the air-shafts of an old level near Cromford’ (3), about a mile and a half south of Matlock, Derbyshire. Greg attributed the discovery to Mr. Bryce M. Wright of Liverpool, a mineral dealer who was also successful in collecting a few good specimens of the new mineral from old heaps of the mine at Cromford. The British Museum collection includes some of Wright's original material, and also part of the specimen which Greg passed on to Dr. Robert Angus Smith for chemical analysis. Other specimens acquired at later dates (including two from the Arkwright and Rutland mines,[1] respectively) all come from the Matlock district.

[1] Probably identical with the Rutland Cave mine, Derbyshire, a well-known locality for aurichalcite.

Four chief types of matlockite can be recognized:

(1) Single crystals mostly square, tabular, transparent and colourless or yellow to pale amber, varying in size up to an inch square and nearly a quarter of an inch thick.

(2) Flat aggregates of platy crystals in sub-parallel growth rarely quite colourless and generally translucent to opaque.

(3) Hemispherical, rosette-like aggregates of platy crystals resembling similar crystallizations of baryte and reaching three-quarters of an inch in diameter.

(4) Stumpy, double pyramidal crystals with small prism faces generally revealing composite growth on the pyramid faces. These measure about one half inch across and are less common than the other three types.

Matlockite occurs in cavities of galena and compact baryte ('cawk'), both sometimes altered, and is often associated with phosgenite, anglesite, cerussite, blende, and colourless fluorite.

The specimen chosen for complete study including chemical analysis consisted of tabular fragments previously broken from a platy aggregate (2 × 1 × 1/8 inch) showing good basal cleavage. The cleavage fragments picked out for chemical analysis were carefully examined for any enclosures of fluorite but none could be observed.[1] Mr. Hey also failed to detect even a trace of calcium. It is certain, therefore, that the fluorine content found by chemical analysis is proper to matlockite and no part of it can be attributed to admixed fluorite. Mr. Hey's analysis and density determinations are given in table 1. The fluorine was determined by precipitation as lead fluochloride. Table 1 also shows the results of the only other two recorded chemical analyses performed on matlockite, one by R. A. Smith on Greg's original material (2) and the second by C. Rammelsberg (4) on material sent to him by W. G. Lettsom from Cromford. Comparing all three analyses with the theoretical figures for lead fluochloride, PbFCl, and lead oxychloride Pb_2OCl_2, it is obvious that the chemical distinction of these two compounds can scarcely be based on the small differences in lead and chlorine content but only on the detection and estimation of a few per cent. of fluorine. It is not surprising, therefore, that the earlier analysts completely overlooked this component and failed to arrive at the true composition of matlockite.

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[1] Mr. Arthur Russell tells me that he possesses crystals of matlockite enclosing small colourless cubes of fluorite.

TABLE 1. *Chemical analyses and densities of matlockite from Cromford, Derbyshire.*

	1.	2.	3.	4.	5.
Pb ...	79·55	82·35	82·16	79·24	82·73
F ...	7·11	[3·56]	[4·46]	7·21	—
O ...	—	—	—	—	3·13
Cl ...	13·44	14·08	13·38	13·55	14·14
Total ...	100·10	100·00	100·00	100·00	100·00
Density	7·05	7·21	5·3947	—	—

1. Analyst, M. H. Hey, 1934. B.M. 54607.
2. Analyst, R. A. Smith (2), 1851.
3. Analyst, C. Rammelsberg (4), 1852; density figure much too low.
4. Theoretical figures for matlockite, PbFCl.
5. Theoretical figures for lead oxychloride, Pb_2OCl_2.

The figures in square brackets obtained by subtracting the sum of the lead and chlorine percentages from 100 were assumed by Greg and Rammelsberg to represent the oxygen content. They are now rightly included as fluorine.

Crystallography.—The specimen of matlockite chosen for chemical analysis carried several minute plates suitable for X-ray and goniometric study. The following faces were observed (001), (110), (100), (101), and (111). The predominant forms on all platy crystals so far examined are (001) and (110); the (100) faces are always much smaller than (110). The basal plane is often imperfect and sometimes possesses a wavy surface probably due to vicinal growths. The cleavage face (001), however, yields good light-reflections. The angles (110) : (111) and (100) : (101) were measured on several crystals and the mean axial ratio found to be $a:c = 1:1·763$, a value in close agreement with the ratio 1 : 1·7627 deduced from Greg's measurements.

X-ray examination.—Rotation photographs of one of the measured crystals were then taken about the [001], [100], and [110] axes. Layer-line measurements gave approximate unit-cell dimensions, and high order equatorial diffractions yielded the more accurate values a 4·09, c 7·21 Å. The ratio c/a is identical with the axial ratio obtained by goniometry. Assuming the unit cell contains 2PbFCl the calculated density of matlockite is 7·16 approximately the mean of Greg's and Hey's observed values. These cell dimensions are identical with those obtained by Nieuwenkamp and Bijvoet (5) from a powder photograph of artificial PbFCl (d 7·05). At this stage therefore powder photographs of artificial PbFCl and matlockite (B.M. 54607) were taken. They also were found to be identical with each other. The identity of matlockite and artificial PbFCl is therefore well established.

It is necessary, however, still to test whether the conclusions of Nieuwenkamp and Bijvoet as to the space-group and crystal-structure of PbFCl are supported by X-ray photographs of single crystals of matlockite. A Laue photograph of a minute crystal along the [001] axis shows a tetragonal axis of symmetry and planes of symmetry parallel to [100] and [110]. This limits the permissible space-groups for the mineral to the D_{2d}, C_{4v}, D_4, and D_{4h} classes. Rotation photographs were then completely indexed. The diffractions (100), (210), (300), (320), (410), (430), and (500) are all definitely absent even after long exposures; thus $(hk0)$ is halved for $(h+k)$ odd; no other systematic halvings could be observed. The space-group is therefore limited unequivocally to D_{4h}^7.

The unit cell of matlockite contains two lead, two chlorine, and two fluorine atoms. Of these the lead atoms with the highest atomic number will contribute most to X-ray diffractions. They will necessarily occupy one of the three twofold positions possible in the space-group D_{4h}^7. These positions are (*a*) $\frac{1}{2}00$, $0\frac{1}{2}0$; (*b*) $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$; and (*c*) $00u$, $\frac{1}{2}\frac{1}{2}\bar{u}$; and are simply derived from the alternative coordinates given in the tables of Niggli and Wyckoff. In the latter setting the alternating fourfold axes pass through the corners and centre of the unit cell, whereas in the setting adopted here and by Nieuwenkamp the simple fourfold axes occupy these positions in accordance with Astbury's figure of the symmetry elements of the space-group. The lead atoms cannot occupy positions *a* and *b*, for in both cases they would contribute nothing to the intensities of diffractions from planes of the type (hkl) when $(h+k)$ is odd. From table 2 it will be seen that many such planes, e.g. (211), give strong diffractions. Successive orders of (001) should also be strong, whereas the four, sixth, and eighth are weak. If, however, the lead atoms be placed in positions $00u$, $\frac{1}{2}\frac{1}{2}\bar{u}$, with $u =$ about 0·2, then the correct sequence of intensities from the basal plane can be accounted for. If next the chlorine atoms be placed either in *a* or *b* positions, $(hk0)$ diffractions for $(h+k)$ odd should be weaker than those for $(h+k)$ even. Moreover, Nieuwenkamp and Bijvoet (6) have tested this possibility for the isomorphous compound PbFBr where the larger scattering power of the bromine atom would produce marked differences in the two types of diffraction. No such differences exist. A study of the structures of the analogous compounds BiOCl, BiOBr, and BiOI by the present writer[1] has also shown that the halogen atoms do not

[1] Unpublished.

occupy either the *a* or *b* positions. The observed intensities can be explained if the Cl atoms be placed at *c* with $u = 0{\cdot}65$. Whereas both the lead and chlorine atoms can be placed with certainty, the positions suggested for fluorine cannot be determined from the diffraction intensities. The length of the diagonal of the base of the unit cell is a little more than twice the diameter of a fluorine ion; this supports their proposed location at *a*. Moreover, the lead and fluorine atoms of the cubic form of lead fluoride PbF_2 occupy the same relative positions. The structure of matlockite is therefore defined by the atomic positions:

Pb ... ... $00u$, $\frac{1}{2}\frac{1}{2}\bar{u}$; $u = 0{\cdot}208$.
Cl ... ... $00v$, $\frac{1}{2}\frac{1}{2}\bar{v}$; $v = 0{\cdot}65$.
F ... ... $\frac{1}{2}00$, $0\frac{1}{2}0$.

and except for a slight increase in the parameter of the lead atoms is in agreement with Nieuwenkamp and Bijvoet's proposed structure for artificial lead fluochloride, PbFCl.

TABLE 2. *Observed intensities and calculated structure-factors for rotation photographs of a single crystal of matlockite.* (B.M. 54607.)

Diffracting plane.	$\frac{\sin\theta}{\lambda}$.	Observed Intensity.	Structure-factor S'.
(001)	0·069	m	24·2
(002)	0·139	vs	−59·6
(003)	0·208	mw	−29·3
(004)	0·278	w	27·4
(005)	0·347	s	58
(006)	0·417	vvw	10
(007)	0·486	m	−49·5
(008)	0·555	vw	−17·5
(009)	0·625	ms	29·0
(100)	0·122	absent	0
(110)	0·173	vs	75·3
(200)	0·244	s	80·4
(210)	0·274	absent	0
(220)	0·346	s	68·7
(300)	0·366	absent	0
(310)	0·387	s	57·4
(320)	0·441	absent	0
(330)	0·519	m	49·4
(400)	0·488	m	56·6
(410)	0·504	absent	0
(420)	0·547	s	53·1
(430)	0·613	absent	0
(500)	0·612	absent	0
(510)	0·624	vs	45·1
(211)	0·278	s	40·4
(212)	0·303	s	50·6
(213)	0·340	m	−46·2
(214)	0·386	m	−56·3
(221)	0·353	vvw	6·4
(222)	0·373	m	−48·9
(223)	0·404	vw	−14·9
(224)	0·443	nil	13·3
(301)	0·374	mw	35·9
(302)	0·392	mw	44·5
(303)	0·422	w	−41·2
(304)	0·460	w	−51·8

Cu − Kα radiation with nickel filter was used, $\lambda = 1{\cdot}539$ Å.
s = strong, m = medium, w = weak, vw = very weak.
The S' values are calculated from the following expressions:—
For $h+k$ even and both h and k even:—$S' = \mathrm{Pb}\cos 2\pi ul + \mathrm{Cl}\cos 2\pi vl + \mathrm{F}$.
For $h+k$ even and both h and k odd:—$S' = \mathrm{Pb}\cos 2\pi ul + \mathrm{Cl}\cos 2\pi vl - \mathrm{F}$.
For $h+k$ odd:—$S' = \mathrm{Pb}\sin 2\pi ul + \mathrm{Cl}\sin 2\pi vl$.

Table 2 shows the general agreement of observed intensities and calculated structure factors for a large number of diffractions. Fig. 1 gives, diagrammatically, successive sections of the structure across the *c* [001] axis and shows that the structure is of the layer type. This conclusion is fully supported by the good *c* cleavage. The cleavage flakes, however, are extremely brittle and this probably explains Greg's statement that matlockite 'cleaves, but not readily, parallel to P'. Rammelsberg notes more accurately that the mineral has 'only one, though very complete cleavage'. It is reasonable to expect that in a simple layer structure of this type there will be a high negative birefringence because the light vibrations should travel more slowly across a layer than in a direction perpendicular to it.

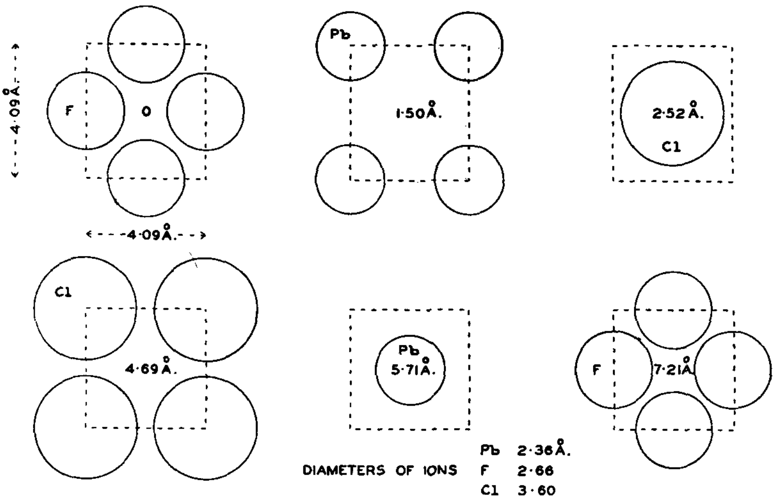

FIG. 1. Sections of the crystal-structure of matlockite at successive levels in the unit cell at the heights indicated along the *c*[001] axis.

Optical data.—Larsen (7) has determined the approximate refractive indices of matlockite from Cromford but gives no details of his method. His values are ω 2·15 ϵ 2·04. He also describes the mineral as 'perceptibly uniaxial negative' and lists it as both biaxial and uniaxial. It was found possible to grind and polish a prism from a cleavage plate selected from similar material used for chemical analysis and X-ray work. The plate chosen is 2·5 mm. thick, quite transparent, and gives a perfect uniaxial interference-figure with negative sign. The prism angle is 37° 17′ and the refracting faces enclose angles of 89° 31′ and 91° 43′ with the (001) cleavage. The correction to be applied to the values of ε has been calculated and is less than 0·0002. The refractive indices can be measured accurately only to the third place of decimals so that the correction for the slightly mis-cut prism faces is negligible.

Table 3 shows that the refractivity, birefringence, and dispersion of matlockite are all high. Larsen's value for ω is in good agreement, but his value for ω − ε appears to be too low. The only other optical measurement recorded for matlockite from Cromford, Derbyshire appears in Greg's original paper, where Prof. W. H. Miller stated 'A slice parallel to the plane *c*, 0·0204 inch thick, being placed in the polarizing instrument having the planes of polarization of the polarizer and analyser at right angles to each other, the angular radius of the first blue ring in air was found to be 22° 81′.' Assuming the values of ω and ε for λ 4861 given in table 3 the calculated angular radius of the first light ring is 23°. Miller's measurement therefore constituted the first proof of the high birefringence of matlockite.

TABLE 3. *Refractive indices of matlockite for various wave-lengths.*
(B.M. 54607.)

Line.	Wave-length.	ω.	ε.	ω − ε.	Probable limits of error in (ω − ε).
Li_α	6708 Å.	2·124	1·991	0·133	± 0·002
H_α(C)	6563	2·127	1·994	0·133	0·002
—	6330	2·133	1·998	0·135	0·001
—	6180	2·136	2·000	0·136	0·001
—	5920	2·143	2·006	0·137	0·001
Na	5893	2·145	2·006	0·139	0·001
—	5640	2·152	2·012	0·140	0·001
—	5530	2·156	2·014	0·142	0·001
Tl_α	5350	2·164	2·021	0·143	0·001
—	5270	2·166	2·022	0·144	0·002
—	5180	2·172	2·026	0·146	0·002
H_β(F)	4861	2·191	2·039	0·152	0·002
—	4800	2·195	2·042	0·154	0·003
—	4480	2·219	2·057	0·162	0·003
H_γ(G′)	4340	2·23	2·07	0·16	0·005
—	4250	2·24	2·07	0·17	0·005

Dispersive power, $P = (n_F - n_C) / (n_{Na} - 1)$:—
$P_\omega = 0{\cdot}056$, $P_\epsilon = 0{\cdot}045$.

A large number of cleavage plates of varying thicknesses were then examined in convergent light, and Larsen's suggestion that biaxial figures can be observed with this mineral was confirmed. The same plate showed uniaxial and biaxial figures which sometimes changed their character when the plate was viewed from the opposite direction. The irregularity of the effect precluded macroscopic twinning as an explanation. The biaxial character of a tetragonal substance can, however, be due to: (1) True orthorhombic symmetry with mimetic twinning; (2) strain; or (3) sub-parallel growth. The first possibility is rendered improbable by the coincidence of all high-order (*hkl*) and (*khl*) spots on the X-ray rotation photographs. It would be possible to distinguish a difference of 0·001 Å between the *a* and *b* dimensions of matlockite if it were pseudo-tetragonal.

If the biaxial nature is due to strain then it might be possible by annealing biaxial matlockite to restore the uniaxial character. Having determined the melting-point of matlockite as 490° ± 10° C., some biaxial fragments were very slowly heated to 450° C. kept there for an hour and then slowly cooled down to air-temperature. This procedure follows closely the operation of annealing glass. Most of the thicker plates of matlockite shattered violently at temperatures well below 200° C. All the thin plates left at the end of the experiment gave uniaxial pictures. A few uniaxial plates about 1 mm. thick were then carefully heated to about 400° C. and cooled rapidly on an iron plate or in water. Those plates which were not shattered by the process retained perfect uniaxial figures. It is unlikely, therefore, that the biaxial character of some plates is due to strain. I had observed that many of the plates giving definite biaxial figures were not bounded by parallel (001) faces but appeared to be sub-parallel growths. Two uniaxial cleavage flakes were then mounted on a glass wedge and examined in convergent polarized light. The interference-figure obtained gave a small value of 2E. These tests make it probable therefore that the biaxial character of matlockite is anomalous and depends on the angle of tilt between single crystal layers.

The work of Nieuwenkamp and the present authors has now established the true chemical composition and crystal-structure of matlockite. The mineral is not, as might have been supposed on purely chemical grounds, a mixed crystal of lead fluoride PbF_2 and lead chloride $PbCl_2$. One of the dimorphous forms of PbF_2 is isomorphous with $PbCl_2$, but both are orthorhombic and possess crystal-structures intermediate in type between that of fluorite and a layer structure. Matlockite can be directly compared, however, with bismuth oxychloride (BiOCl).[1] They are isostructural and in a limited sense isomorphous. That is, PbFCl and BiOCl do not form mixed crystals but may be expected to form oriented parallel growths with each other. The crystal-structure of litharge PbO, the tetragonal form of lead oxide, is not known with absolute certainty. Its high negative birefringence and platy cleavage suggest, however, a layer structure and it is significant that the base of the unit cell of litharge has approximately the same dimensions as those of matlockite and bismuth oxychloride. The data given in table 4 show the chemical, crystallographic, structural, and optical relationships between matlockite and the above-mentioned compounds. Although no mineral with the composition Pb_2OCl_2 is known to exist, the compound has been made artificially and was one of the early substitutes for white-lead paint. R. Ruer (8) has noted that artificial Pb_2OCl_2 grows in the form of needles. Such a crystal habit does not suggest identity of artificial Pb_2OCl_2 with tabular matlockite, but this point was missed by Ruer. A powder photograph of artificial Pb_2OCl_2 prepared by M. H. Hey has been taken and found to be much more complex than the matlockite pattern. So far single needles suitable for X-ray work have not been successfully prepared. The true symmetry and crystal-structure of this artificial compound, once thought to be identical with matlockite, remain unknown.

In conclusion, it should be said that no evidence so far exists showing that fluorine has been overlooked in any other mineral hitherto regarded as an oxychloride. For instance, the mode of occurrence of mendipite and the absence of fluorine-bearing minerals in the Mendip Hills render it unlikely that mendipite contains any fluorine. To place the matter quite beyond doubt some fragments of a specimen of mendipite studied by Dr. L. J. Spencer (13) and analysed by Prof. E. D. Mountain have been tested for fluorine with a negative result. A preliminary X-ray study of this mineral shows that its crystal-structure is quite different from that of matlockite (see table 4). The rare minerals laurionite, paralaurionite, fiedlerite, and penfieldite are products of the action of sea-water upon slag-heaps of ancient workings at Laurion, Greece, and the presence of fluorine is improbable. So-called matlockite from this locality has been noted both by G. F. Herbert Smith (14) and by A. Lacroix, (15) but this could not be confirmed. The latter gave a full account of the

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[1] The crystal-structure of BiOCl, BiOBr, and BiOI shortly to be published by the author.

Table 4. *X-ray and optical data for matlockite and certain related compounds.*

Compound.	Unit-cell contents.	Unit-cell dimensions			Birefringence.	Optical Orientation.
		a.	*b.*	*c.*		
Matlockite ...	$2PbFCl$	4·09	4·09	7·21 Å.	−0·139 (Na)	optic axis ⊥ cleavage (001)
Artificial bismuth oxychloride	$2BiOCl$	3·889	3·889	7·374	negative large	optic axis ⊥ cleavage (001)
Litharge (9) ...	$2PbO$	3·99	3·99	5·01	−0·13 (Li)	optic axis ⊥ cleavage (001)
Artificial (10) lead chloride	$4PbCl_2$	4·53	7·61	9·03	0·0604	Bx_o ⊥ cleavage (001)
Artificial (11) lead fluoride, α form	$4PbF_2$	3·80	6·41	7·61	?	?
Artificial (12) lead fluoride, β form	$4PbF_2$	5·93	5·93	5·93	isotropic	——
Mendipite ...	$4(Pb_3O_2Cl_2)$	9·50	11·87	5·87	0·07	Bx_a ⊥ (100)

optics of a mineral which can hardly be reconciled with the optical properties of matlockite from Cromford, Derbyshire. Lacroix described square tablets showing four sectors in twin position each giving a negative biaxial figure with 2E 55°. A. de Schulten also studied crystals from the same material and observed in addition some uniaxial plates but no chemical tests were carried out. I am indebted to Professor Lacroix for the loan of one of the original specimens from Laurion, Greece, upon which he identified matlockite. The specimen is a small fragment of scoriaceous material carrying many crystals of laurionite, but a careful search has so far failed to reveal any mineral which answers to his description. An X-ray study of all the Laurion minerals is needed; it may prove that one of them at least is identical with one or other of the artificial lead oxychlorides.

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