An X-ray study on the crystal-structure of gümbelite.

(With Plate II.)

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Introduction.

DANA[1] classifies gümbelite in the kaolin division under pyrophyllite, and expresses the view that it may be an impure pyrophyllite. The present study, however, has shown that the unit cell of gümbelite is very similar to that of muscovite. Also the chemical analysis reveals a closer similarity to muscovite, particularly to a variety called hydromuscovite.

There are available no published X-ray data on gümbelite. Also from the mineralogical and chemical standpoint gümbelite is not an extensively studied mineral. Dana records two chemical analyses, both of which are unsatisfactory. A more up-to-date description and analysis of gümbelite, found at Shunga, Zaonezhye peninsula, Lake Onega, Karelia, Russia, has been reported by Timofeev.[2] This gümbelite occurs in veins in carboniferous slate. Sheets of fine, flexible fibres of about 1 cm. long are packed with the fibre axis perpendicular to the walls. According to Timofeev, fibres of 0·003 to 0·005 mm. in diameter can be separated.

Description of the X-ray photographs.

When a small bundle of gümbelite from Karelia is placed with its axis perpendicular to the X-ray beam, and a rotation photograph taken, a fibre diagram is obtained which differs from a powder photograph in that: (i) on the equator there are half a dozen short, sharp reflections, like those found on single-crystal photographs (these are later called the even orders of $00l$ reflections, with a spacing $d_{001} = 20{\cdot}0$Å.); (ii) not all the Debye lines are complete circles, but some of them vanish somewhat above the first layer-line, others above the second layer-line, (pl. II, figs. 1 and 2); (iii) none of the Debye lines is of uniform blackening: more intense portions (subsequently called bulges) are either at the equator, or at heights corresponding to one or another of the layer-lines of about 5·2Å. identity period along the fibre direction.

Oscillation photographs of thin bundles of gümbelite exhibit spotty Debye arcs, showing that the fibres are not good single crystals, and also that they are not packed completely at random.

The appearance of the X-ray pattern of gümbelite can be explained if the crystallites of the specimen are imagined to lie with the (001) plane parallel to

[1] Dana, Descriptive mineralogy, 6th edition, New York, 1892.

[2] V. M. Timofeev, Trav. Soc. Nat. Leningrad, 1925, vol. 55, part 1, pp. 95–101. A description in English of the occurrence in the shungite deposit is given, with a map, in the XVII International Geological Congress guide-book 'The Northern Excursion, The Karelian ASSR', 1937, p. 55. See also V. M. Timofeev, The petrography of Karelia, 1935 [M.A. 7–197.]

the fibre direction (cf. the shortness of the $00l$ spots). The a (5·2Å.) and b (9·0Å.) axes, however, can make any angle with the fibre direction in their plane. A certain preferred orientation would account for the bulges on the layer-lines. A reciprocal lattice model of such a specimen will be obtained by rotating the reciprocal lattice (of a perfect crystal) about the c^* axis, which is the normal of the (001) plane, i.e. a system of circles with their centres on, and their planes perpendicular to, the c^* axis. A rotation photograph, corresponding to such a model, should exhibit Debye arcs, if the axis of rotation is in the plane of the circles. As the radius of the reciprocal circles depends on the indices h and k, then also the maximum height any Debye arc can attain is determined by the same indices. Thus, the length of the arcs can give additional information for indexing.

Indexing.

The identity period along the fibre direction is approximately 5·2Å., as measured from the layer-lines. The spots on layer-lines of gümbelite are too indistinct for reliable measurement, thus only $4\sin^2\theta$ values of those reflections the arcs of which cross the equator are available. As for a more accurate determination of the length of the axes a and b, experience has shown that though in silicates the lengths of two axes vary from 8·9 to 9·2Å., and from 5·14 to 5·3Å. respectively, the axial ratio remains constant within a fraction of one per cent. The square of

TABLE I. $4\sin^2\theta = \rho^2$ values for gümbelite from Nordhalben and from Karelia. The indices hkl are for a monoclinic unit cell with [110] along the fibre direction. a 5·21, b 9·02, c 20·12 Å, β 96·0°. A dot (·) in the column of estimated intensities (Int.) indicates a line with a bulge on the equator. B = a broad line. $\Delta\rho^2 = \rho^2_{obs.} - \rho^2_{calc.}$ Cu K_α radiation.

Nordhalben $\rho^2_{obs.}$	Karelia $\rho^2_{obs.}$	Int.	Karelia hkl	$\Delta\rho^2 \times 10^4$
0·0233	0·0240	8·	002	+3
0·0935	0·0945	8·	004	−2
0·1173	0·1173	7·	110 $11\bar{1}$	0 −9
0·1274	0·1280	1·	111	+1
0·1552	0·1560	5·	$11\bar{3}$	−1
0·1742	—	(1)	023 ? 113 ?	
0·1912	0·1924	5·	$11\bar{4}$	−3
0·2093	0·2126	10·	006	−4
0·2279	0·2312	5·	114	+1
0·2506	—	(1)	$11\bar{5}$? 025 ?	
0·2866	0·2882	4·	115	−9
0·2981	0·3017	4·	$11\bar{6}$	+3
0·3540	0·3545	5	116 200 $20\bar{2}$	−45 +47 −28
0·3723	0·3791	5·	008	+14
0·4002	0·4057	3B	202 $20\bar{4}$	+100 −34
0·4665	0·4666	3·	220 $22\bar{1}$	−22 +15
0·4917	0·4892	3·	221 $22\bar{3}$ 204	+49 −41 +33
0·5503	0·5565	3B	223	+56
0·5814	0·5922	9·	0 0 10	+5
—	0·7742	1·	$22\bar{8}$	+35
0·8197	0·8250	3	$24\bar{2}$ 310 227	+33 +22 −9
0·8809	0·8747	3	$24\bar{4}$ 312 $31\bar{4}$	+12 −6 +48
0·9366	0·9342	3	228	+99
1·0469	1·0457	6·	$33\bar{1}$ $33\bar{2}$	−6 −40
—	1·0703	1	331 $33\bar{3}$	−48 +54
1·1419	1·1604	5·	0 0 14	+8

The reflections at ρ^2 0·1742 and 0·2506 are those which may necessitate the adoption of a triclinic unit cell for gümbelite from Nordhalben, see the section *Conclusions*.

the axial ratio is about 2·9 for chain structures (amphiboles and pyroxenes), and 3·0 for sheet structures. Because the axial lengths of gümbelite are so nearly equal to the corresponding axes of muscovite, and for other considerations which follow, the ratio $(b/a)^2 = 3{\cdot}00$ is accepted for gümbelite. This means that the spacing d_{020} is very nearly equal to d_{110}. The lengths of the a and b axes will be calculated in this way, in agreement with the position of reflections of the type $\{hhl\}$. For the third axis, d_{001}(20·00Å.) is accurately measurable (cf. table I).

Chemical composition.

Table II shows the chemical composition of two gümbelites, found in the same localities as the specimens now investigated, though they are not from the same samples. Timofeev (loc. cit.) states that in pure samples gümbelite is quite white, but it is often tinted yellow or greenish by iron oxides. He concludes that iron and lime are supplied from outside, as well as 0·24 % of the water, which do not take part in composition. Eliminating the uncombined water, FeO, and CaO,

TABLE II. Chemical composition of gümbelite: I from Shunga, Karelia (Timofeev, loc. cit.), and II from Nordhalben, Bavaria (Kobell, quoted from Dana).

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O+.	H_2O-.	insol.	Total.
I.	49·54	0·87	29·51	—	0·70	4·14	0·25	0·35	8·21	6·56	0·24	—	100·37
II.	50·52	—	31·04	3·00	—	1·88	—	—	3·18	7·00	—	1·46	98·08

and recasting the analysis in atomic proportions on the basis of O_{48} (which is the number of oxygen atoms in muscovite-like structures), table III is obtained. From table III the similarity of gümbelite from Karelia to muscovite, particularly to hydromuscovite variety 'A', of Brammall, Leech, and Bannister,[1] is obvious when the metal atoms are grouped according to structurally equivalent positions.

TABLE III. Comparison of the chemical composition of gümbelite from Karelia, and that of hydromuscovite 'variety A' (Brammall et al., loc. cit.) in atomic proportions based on O_{48}.

	Gümbelite.		Hydromuscovite.		Muscovite (ideal).	
Si	12·77	16·00	12·00	16·00	12	16
Ti	0·17		—		—	
Al	3·06		4·00		4	
Al	5·91	7·50	7·06	7·52	8	8
Mg	1·59		0·20		—	
Fe	—		0·22		—	
Ca	—		0·04		—	
K	2·70	2·88	2·66	2·88	4	4
Na	0·18		0·22		—	
(OH)+	11·28	48·00	10·88	48·00	8	48
O	36·72		37·12		40	

The density of gümbelite.

A 'molecule' of gümbelite comprising 48(O,OH,F) and a number of metal atoms corresponding to the composition (table II), weighs $1539 \times 1{\cdot}650 \times 10^{-24}$g. The volume of the unit cell of gümbelite of Karelia is 940×10^{-24}cm.^{3} (see below, p. 14), which gives a density of 2·702 g./cm.^{3}, which does not agree with the

[1] A. Brammall, J. G. C. Leech, and F. A. Bannister, Min. Mag., 1937, vol. 24, pp. 507–520.

density 2·946 g./cm.^{3} as reported by Timofeev, but which compares favourably with the density of the specimen used. Dr. Max H. Hey kindly determined (by flotation) the density of Karelian gümbelite used in the present study, and found 2·770$\pm$0·005. (The writer obtained a density somewhat less than 2·80 g./cm.^{3}) The difference of 2·5 % between the densities obtained by the macroscopic (Dr. Hey) and X-ray methods might be caused because (i) the chemical analysis and the density reported by Timofeev is not strictly applicable to the sample used in this work, or (ii) although the spacings d_{110} and d_{001} are quite accurate, the assumption that the ratio $(b/a)^2 = 3{\cdot}00$ is somewhat arbitrary. For example, a ratio of 2·9 (that of the chain structures) would decrease the volume of the unit cell by 1·2 %, and would reduce the observed discrepancy to 1·3 %.

Optical properties.

According to Timofeev, gümbelite from Karelia has straight extinction (though occasionally oblique extinction has been observed, which is explained by the free orientation, and bending of the fibres). The refractive index n_γ coincides with the length of the fibre. 2E = 68° 52′, 2V = 42° 21′, with a maximum deviation of 2° on either side. Dispersion is not observed; a direct determination of double refraction by means of compensator did not give definite results.

It can be seen that the refractive indices of gümbelite do not differ much from those of hydromuscovite, and those of muscovite (particularly when [110] is taken parallel to n_γ).

TABLE IV. Comparison of optical data.

	n_α	n_β	n_γ
Hydromuscovite 'A', Wales (Brammall et al.) ...	—	1·575	1·580
Gümbelite, Karelia (Timofeev)	1·568	1·571	1·596
Muscovite (textbooks)	1·561	1·594	1·600

The analogy between gümbelite and muscovite.

Assuming gümbelite to have a monoclinic unit cell with its [110] direction parallel to the fibre, the unit cell *a* 5·21, *b* 9·02, *c* 20·12Å., *β* 96·0°, will be in close agreement with observations (cf. table I). In comparison, the unit cell of muscovite has *a* 5·18, *b* 9·02, *c* 20·04Å., and *β* 95·5°. This similarity between the unit cells of gümbelite and muscovite is accompanied by a similarity in chemical composition and in optical properties. With this muscovite-like unit cell, orientated with the [110] direction preferably along the fibre direction, all the bulges are accounted for. Deviations in the plane of *ab* up to 30° must occur to account for the length of the arcs. It seems, however, that the deviations are smaller than 60°, as some of the bulges on the first layer-line of type $\{11l\}$ are not extended to the equator (cf. fig. 1).

A photograph of gümbelite from Nordhalben, Bamberg, Bavaria (pl. II, fig. 2) displays less marked preferred orientation. The *c* axis of this gümbelite is 1·0 % larger than for Karelian gümbelite, but the *a* and *b* axes are of the same length, within the error of measurement. Except for two weak lines reaching the equator, the patterns of the two gümbelites are similar. The $4\sin^2\theta$ values for both gümbelites are included in table I. There is a slight preference, in gümbelite from Nordhalben, for the *b*[010] direction to lie parallel to the needle axis, in a sector of semi-angle 30° in the plane of *ab*. [Gümbelite of Nordhalben is flaky rather than fibrous, and easily separated into short, irregular needles.]

The X-ray pattern of gümbelite was imitated by registering on the same film a number of rotation photographs of muscovite. For each exposure a different line in the cleavage plane between the directions [110] and [010] was set parallel to the axis of rotation. In fig. 3 the axis of rotation lies in a sector from $-6°$ to $+22°$ from the [110] direction towards [010], in steps of approximately 3°. The gaps in the arcs appear because the experiment was not continued until *b*[010] became vertical.

Conclusions.

It has been shown that the X-ray fibre diagram of gümbelite from Karelia, its unit cell, chemical composition, and optical properties are comparable with those of muscovite, particularly with those of hydromuscovite. Gümbelite from Karelia is monoclinic, a 5·21, b 9·02, c 20·12 Å., β 96·0°. The [110] direction lies predominantly parallel to the fibre direction, though deviations over 30° (but less than 60°) occur in the (001) plane. The density obtained by X-ray methods is 2·70 g./cm.^{3}, and 2·770 g./cm.^{3} by macroscopic methods.

Small flakes of gümbelite from Nordhalben exhibit a similar X-ray pattern, though with a less notable preferred orientation in the (001) plane. The unit cell is also monoclinic, and of the same dimensions as gümbelite from Karelia, except that the c axis is 1·0 % larger ($d_{001} = 20{\cdot}20$ Å.). In the case of gümbelite from Nordhalben, however, a triclinic unit cell may seem necessary, to bring the indices of two weak lines into a better agreement. The triclinic unit cell would have $d_{100} = 5{\cdot}18$, $d_{010} = 8{\cdot}97$, $d_{001} = 20{\cdot}20$ Å. The angle between the (010) and (001) planes is 84·85°, the angle between the (100) and (001) planes 84·26°, and the angle between the [100] and [010] directions 90°.

A complete determination of the crystal-structure of gümbelite is not claimed, but it seems that gümbelite should be classified amongst muscovites, with some substitution (in a ratio 1 to 4 approximately) of magnesium for aluminium.

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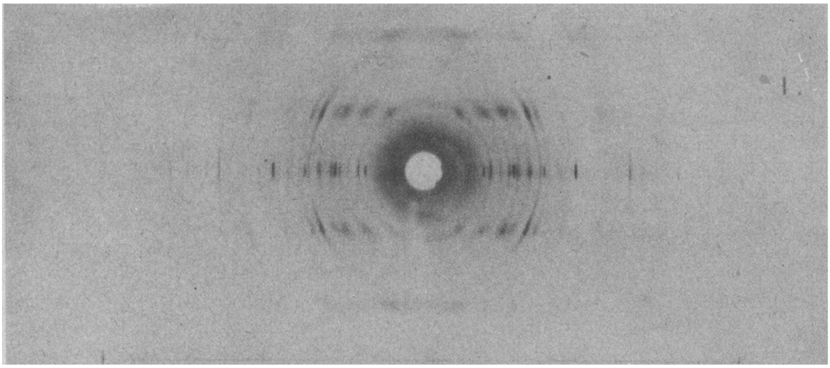
Explanation of Plate II.

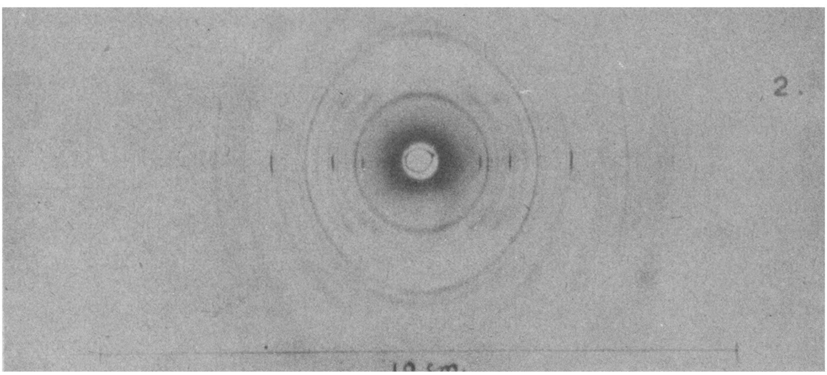
Fig. 1. Rotation photograph of gümbelite from Shunga, Karelia, Russia, about the fibre direction.

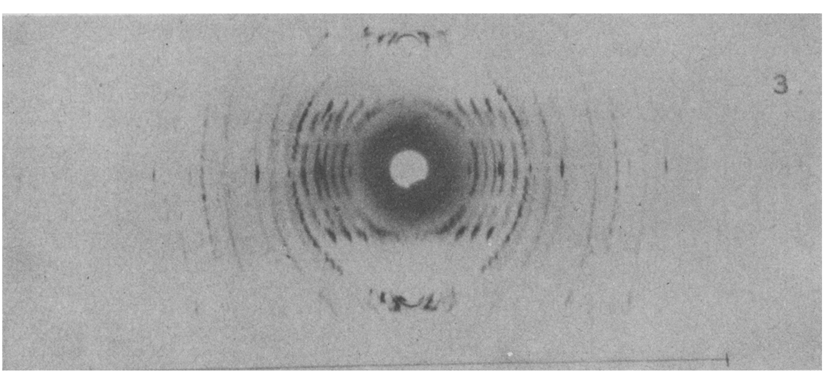
Fig. 2. Rotation photograph of gümbelite from Nordhalben, Bavaria, about the elongation of the flake. (British Museum specimen, reg. no. 44126.)

Fig. 3. Imitated pattern of gümbelite—muscovite rotated consecutively about several axes between [110] and [010] in the cleavage plane.

Figs. 1, 2, and 3 were taken in a cylindrical camera of 60·0 mm. diameter, using filtered CuK$_\alpha$ radiation. A length of 100 mm. was marked on the original photographs.







E. ARUJA: X-RAY PHOTOGRAPHS OF GÜMBELITE.