and criticisms have been greatly appreciated; to Dr. Paul F. Kerr for photographing and interpreting the x-ray diffraction pattern; and to Dr. George C. Branner for permission to publish this article.

CRYSTALLOGRAPHIC DATA ON MELLITE

Tom. F. W. Barth and C. J. Ksanda, *Geophysical Laboratory.*

I

Mellite is one of the few organic minerals. Its formula is $Al_2C_{12}O_{12} \cdot 18H_2O$, which corresponds to a hydrous salt of the hexacarboxylic mellitic acid, and is thus far the only representative of the benzene ring in the mineral kingdom. It occurs in coal seams in middle Europe and Russia; the tetragonal crystal form is frequently nicely displayed by very simple face combinations. In Goldschmidt's "Atlas der Kristallformen" only the following forms are listed: (001), (010), (110), (011), and (111). The crystals are semi-transparent with a honey-yellow color, from which the mineral takes its German name, Honigstein. As far as the authors are aware no recent investigation of this mineral is on record. Des Cloizeaux in his "Manuel de Minéralogie" (vol. **2,** p. 70) gives a good description of it, but in more recent textbooks very little space is devoted to it.

Through the courtesy of Professor F. Bernauer, Technische Hochschule, Berlin-Charlottenburg, several beautiful, small crystals from Artern in Thuringia were sent to us for x-ray investigation.

II

Rotation photographs with the crystal rotating about the a-axis and the c-axis were obtained by using Fe-K_α-radiation. From these photographs it was found that the primitive translations along these directions were:

$$a_0 = 22.0\,\text{Å}$$
$$c_0 = 23.3\,\text{Å}$$
$$a_0/c_0 = 1.055$$

Since the crystallographic axial ratio a'/c' is given as 0.7463, this means that the crystallographic a-axis should be rotated 45° in order to correspond with the internal symmetry of the crystal, the crystallographic axial ratio being obtained by dividing the true axial ratio by $\sqrt{2}$.

In the unit cell, which is nearly a cube, there must be 16 molecules of the formula $Al_6C_{12}O_{12} \cdot 18H_2O$; the calculated density of the crystal then becomes, $D = 1.65$. Direct determinations on three crystals from Artern gave: 1.574, 1.636, 1.642 (according to Kenngott).

To check the size of the unit cell a Laue photograph was taken with the beam of incidence slightly inclined to the direction of the *c*-axis (tungsten target, 60 k.v. tension). The Laue diagram produced in this way is reproduced in Fig. 1. It contains more than

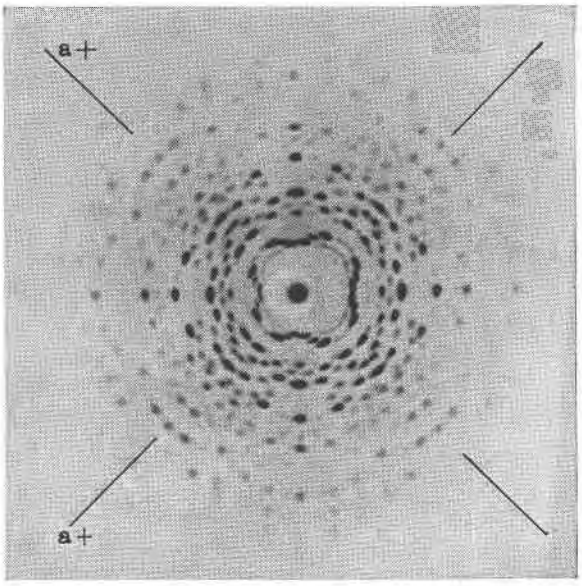

FIG. 1. LAUE PHOTOGRAPH OF MELLITE.

500 spots all of which have been indexed. It should not be necessary, however, to tabulate all of them here, for a few critical spots suffice to prove the correctness of the proposed unit cell. It is seen that the spots closest to the primary beam on the left-hand side of the photograph are much weaker than the corresponding spots on the right-hand side. Since the structure factor is the same for any two planes belonging to the same form, the weakening on the left-hand side is due solely to the fact that these planes reflect *x*-rays, the wave lengths of which lie close to the low wave-length limit.

Table 1 gives the indices of these 12 planes with calculated wave lenths and observed intensities of the reflected x-ray beams. It is evident that the minimum wave length must be about $\lambda_{min} = 0.25$Å, which corresponds to the tension applied, 60 k.v., thus corroborating the correctness of the proposed cell.

TABLE 1.

CRITICAL SPOTS ON THE LAUE DIAGRAM PROVING THE CORRECTNESS OF THE PROPOSED UNIT CELL.
(60 k.v. W—target)

Left-hand side			Right-hand side		
Indices	λ calc.	Int. obs.	Indices	λ calc.	Int. obs.
931	0.39	10	$\bar{9}31$	0.50	10
951	0.32	2	$\bar{9}51$	0.43	6
971	0.26	3	$\bar{9}71$	0.35	10
791	0.25	3	$\bar{7}91$	0.35	10
591	0.28	2	$\bar{5}91$	0.40	6
391	0.36	10	$\bar{3}91$	0.46	10

III

The symmetry class and space group of mellite can be deduced from the nature of the x-ray diffraction patterns. Since the Laue diagram shows holohedral tetragonal symmetry, the classes C_4, S_4, and C_{4h} are excluded; and V_d and C_{4v} are made highly improbable by the external face development and the pyroelectrical properties.[1] The remaining possible point groups are D_{4h}, the bipyramidal class, and D_4, the trapezohedral class.

There are 30 different space groups in these classes and a discrimination between them can only be made by the application of space-group criteria, *i.e.*, special extinctions in the x-ray diffraction pattern. An analysis of the Laue photograph shows that all types of planes occur in all orders. The fundamental lattice is therefore the simple tetragonal lattice, Γ_t, the correct space group is either D_{4h}^1, D_{4h}^7, or any one of the first 8 in D_4, but a further distinction cannot be made from the Laue diagram, because the presence or absence of odd order reflections from (100) and (001) are critical. An x-ray goniometer photograph (Weissenberg picture)

[1] Cf. W. G. Hankel, *Abh. kgl. sächs. Ges. Wiss.*, (math.-phys. Kl.), **12**, 552, 1882.

was therefore obtained with the crystal oscillating about the c-axis, Mo-K_α-radiation. A complete record of this film will not be given: the data of interest in this connection are compiled in Table 2, from which it is seen that 100 is present in the 3d and 5th orders, consequently D_{4h}^1—P4/m m m—is the only possible space group in the bipyramidal class.

TABLE 2.

OBSERVED X-RAY REFLECTIONS FROM THE SECOND ORDER TETRAGONAL PRISM
(Mo-K_α-radiation)

Intensities	Spacing	Indices	Order	a_0
1	7.3	100	3	21.9
10	5.4	100	4	21.6
4	4.36	100	5	21.8
2	2.71	100	8	21.7
4	1.83	100	12	22.0
1−	1.57	100	14	22.0
2	1.36	100	16	21.8
1−	1.22	100	18	22.0
4	1.095	100	20	21.9

Oscillation photographs on the base show very definitely that most orders of 001 are extinguished: only the 4th and 8th orders have been observed.

This observation was carefully checked by the use of soft radiation ($\lambda = 2.286$Å, Cr-K_α) and long exposure. But no trace could be seen of any basal reflections other than the 4th and the 8th orders (see Table 3). The missing reflections—all orders of 001 not divisible by 4—constitute thus the only systematic extinctions encountered in the diffraction spectrum of mellite.

TABLE 3.

X-RAY REFLECTIONS FROM THE BASE.
(Cr-K_α-radiation)

Intensity	Spacing	Indices	Order	c_0
10	5.80	001	4	23.2
10	2.93	001	8	23.4

It is generally true that it is safe to use the presence but not the absence of reflections for distinguishing between space groups. But in view of the fact that mellite has such a large unit cell with a great many atoms in the generally equivalent positions, the systematic extinctions become very significant, and it should be permissible to use the absence of certain reflections as space-group criteria.

If the absent reflections are *not* accepted as criteria, the space group D_{4h}^1 and its sub-group D_4^1 still remain as possibilities, but in all probability the space groups D_4^3 and/or D_4^7, which are the only ones requiring the characteristic extinctions encountered in mellite,[2] are the correct ones. This means that mellite must be placed in the trapezohedral class of the tetragonal system, which is interesting because thus far no other mineral has been encountered with such symmetry. The two space groups, D_4^3–$P4_12$, and D_4^7–$P4_32$, are enantiomorphic: the one is the mirror image of the other, and a distinction between them cannot be made by means of x-rays. Some crystals of mellite may be left-handed and belong to D_4^7 while others may be right-handed and belong to D_4^3. Examples of compounds exhibiting enantiomorphic symmetry, some crystals of which are left-handed while others are right-handed, are recorded in the literature.

Crystals isomorphous with the groups D_4^3 and D_4^7 should rotate the plane of polarization of light, and also exhibit characteristic etch-figures. Thus a conclusive proof of the space-group determination would be afforded if any such properties of mellite could be demonstrated. However, this is not the case: on a plate of mellite, 1 mm. thick cut normal to the c-axis, the typical anomalously biaxial interference figure, $(-)2V=8°$, was observed, but no indication of circular polarization could be detected. The etch-figures on the base (produced by means of very dilute HNO_3) are squares, the outlines of which are parallel to the traces of the second order tetragonal prism. It is thus evident that no other crystallographic properties, except the x-ray diffraction effects, indicate that mellite crystallizes with trapezohedral rather than bipyramidal symmetry.

A more detailed knowledge of the actual atomic arrangement in mellite cannot be obtained. There are 16 equivalent points in the general positions of D_{4h}^1, and since there are also 16 molecules in

[2] See, for instance, K. Herrmann, Auslöschungstabellen, *Z. Krist.*, **68**, 288, 1928.

the unit cell, it becomes highly probable that all molecules ($Al_2C_{12}O_{12} \cdot 18H_2O$) are structurally identical, and repeated 16 times within each unit according to the crystallographic symmetry of this space group, therefore the molecule itself need not have any symmetry properties, the location of each individual atom in the molecule being determined by an independent set of three parameter values, *xyz*; since there are 80 atoms within each molecule no less than $80 \times 3 = 240$ different parameter values determine the complete structure of mellite. The full formula for the unit cell is: ($Al_{32}C_{192}O_{480}H_{576}$).

An arrangement in D_4^3 or D_4^7 differs from the one in D_{4h}^1 in that it has twice as many degrees of freedom: 460 parameter values. It is therefore obviously impossible, from the diffraction effects alone, to give even the slightest suggestion as to the actual atomic arrangement within the unit of structure, and since we know so little about the configuration and general leptologic relations of the H_2O-group in hydrous compounds, it is, for the time being, impossible to solve completely the structure of mellite.

Summary

From *x*-ray data obtained from rotation, oscillation, *x*-ray goniometer, and Laue photographs the unit of structure of mellite was found to be a tetragonal prism, the dimensions of which are: $a_0 = 22.0$Å, $c_0 = 23.3$Å, $a_0/c_0 = 1.055$, comprising 16 molecules of the formula ($Al_2C_{12}O_{12} \cdot 18H_2O$); calculated density 1.65. Although the geometrical and the physical properties of mellite correspond to a holohedral crystal symmetry, very definite space-group criteria indicate that the mineral is really isomorphous with D_4^3 and/or D_4^7, two enantiomorphic groups in the trapezohedral class; mellite thus being the first known mineral exhibiting tetragonal trapezohedral symmetry. The atomic arrangement depends on at least 240 parameters.