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Structure du germanate d'hafnium.

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D'une étude antérieure de quelques orthogermanates (Bertaut & Durif, 1954; Durif, 1956) il ressortait que les orthogermanates de formule $GeO_4M (M = Zr, Th, Ce^{IV}$ et U) appartiennent au type scheelite alors que les silicates correspondants existants (SiO_4U, SiO_4Zr et SiO_4Th) appartiennent au type zircon ou au type monazite. Une seule exception était à signaler, celle du germanate de thorium qui possède une forme haute température du type zircon. Ces composés pouvant être considérés comme la combinaison d'une molécule de GeO_2 ou de SiO_2 avec une molécule d'un oxyde du type CaF_2 il était intéressant d'étudier les possibilités d'existence d'un éventuel germanate d'hafnium et du silicate correspondant.

Tableau 1. *Dépouillement d'un diagramme de* GeO_4Hf

hkl	I_o	d_o	d_c
101	18	4,39 Å	4,40 Å
112	100	2,86	2,87
103			2,84
004	19	2,61	2,62
200	22	2,42	2,42
211	9	2,12	2,12
114	2	2,08	2,08
105	5	1,923	1,926
213	7	1,839	1,842
204	33	1,778	1,780
220	15	1,712	1,714
301	2	1,595	1,597
116	19	1,555	1,557
215	3	1,506	1,507
312	27	1,469	1,471
303			1,467
224	13	1,434	1,434
107			1,432
321	2	1,334	1,333
008	3	1,309	1,311
323	< 1	1,254	1,255
217	1	1,231	1,233
400	5	1,211	1,212
411	2	1,168	1,168
316	22	1,152	1,152
109	3	1,132	1,133
332	7	1,116	1,116
413			1,114
404	7	1,100	1,100
307			1,099
420	6	1,084	1,084
228	7	1,041	1,041
415	3	1,026	1,026
424	19	1,002	1,001
327			1,001
501	2	0,965	0,965
336	8	0,957	0,956

I_o = hauteur du pic au-dessus du fond continu.

Nous avons calciné à 1050 °C. pendant 48 heures un mélange équimoléculaire d'oxyde de germanium et d'oxyde d'hafnium. L'étude des diagrammes Debye–Scherrer du produit obtenu montre que la réaction a été totale (aucun excès des constituants de départ n'est observé sur les diagrammes) et que le composé obtenu est, comme les orthogermanates déjà cités, isomorphe de la scheelite. Ses caractéristiques cristallines sont les suivantes:

$$a = 4,849,\ c = 10,50_1\ \text{Å},\ U_x = 246,4\ \text{Å}^3,\ D_x = 8,444\ \text{g.cm.}^{-3}$$

avec 4 unités GeO_4Hf par maille conduisant à la répartition atomique suivante dans le groupe d'espace C_{4h}^6–$I4_1a$

4 Ge en 4(*a*)
4 Hf en 4(*b*)
16 O en 16(*f*)

Aucune détermination des paramètres de position des oxygènes n'a été tentée. Des considérations purement stériques permettent néanmoins d'affirmer qu'ils sont très voisins de ceux observés pour les autres germanates du type scheelite.

Le Tableau 1 donne le dépouillement d'un diffractogramme de GeO_4Hf effectué à la radiation du cobalt.

La préparation du silicate d'hafnium est plus délicate: après 72 heures de calcination à 1300 °C. d'un mélange $SiO_2 + HfO_2$ on observe encore très visiblement les constituants de départ. Ce n'est qu'après une centaine d'heures de chauffage que la réaction est totale et que l'on se trouve en présence d'une phase unique de type zircon, avec:

$$a = 6,58_1,\ c = 5,96_7\ \text{Å}\ (D_{4h}^{19}\text{–}I4/amd)\ .$$

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A new crystalline form of lauric acid.

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The normal chain monocarboxylic acids with even number of carbon atoms are known to exist in three crystalline forms which have been called *A*, *B* and *C* by Piper *et al.* (1926), and respectively γ, β and α by Thiband & Dupré La Tour (1930). The different forms can be distinguished from each other by the value of the long spacing which, for a given acid, is greatest for the γ-form and smallest for the α-form. Lomer (1955) has described the spontaneous but slow transformation, in the solid state, of α-lauric and α-myristic acid to the γ-form and determined

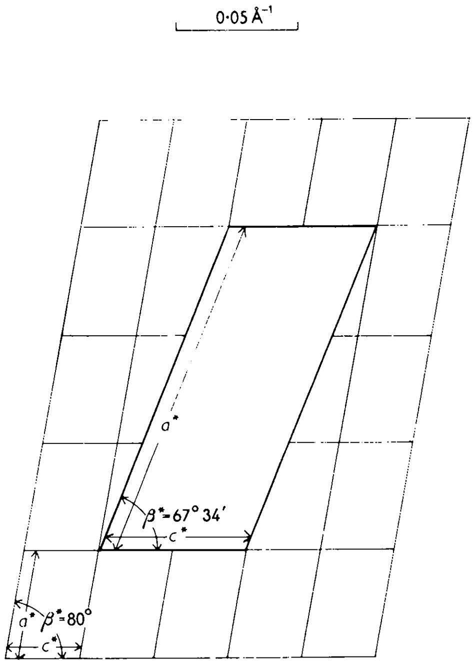

Fig. 1. The a^*c^* face of the reciprocal cell of the new form of lauric acid superimposed on the a^*c^* plane of the reciprocal lattice of the γ-form.

the unit-cell dimensions of the latter form from powder photographs. For lauric acid the dimensions were

$$a = 22{\cdot}1,\ b = 5{\cdot}24,\ c = 32{\cdot}0\ \text{Å};$$
$$\beta = 99°\ 58',\ \alpha = \gamma = 90°.$$

It was recently decided to try to check these figures by single-crystal methods.

A small quantity of γ-lauric acid was dissolved in ether and the solution allowed to evaporate slowly to dryness. The resulting material consisted of a tangle of fibres together with a few small plates. Three of these plates were selected for single-crystal examination: the remaining material was ground and a powder photograph of it taken. This photograph was identical with that used in the determination of the cell dimensions of the γ-form. Weissenberg and oscillation photographs were taken of each of the three single crystals and the unit cell was found to be triclinic with

$$a = 7{\cdot}45,\ b = 5{\cdot}40,\ c = 17{\cdot}5\ \text{Å};$$
$$\alpha = 96°\ 53',\ \beta = 113°\ 8',\ \gamma = 81°\ 7'.$$

This cell is thus different from that of the powdered fibres and does not account for all the lines on the powder photograph. There is, however, a simple relationship between the two cells which is illustrated in Fig. 1, in which the a^*c^* face of the single crystal reciprocal cell is shown superimposed on the a^*c^* plane of the reciprocal lattice of the powdered fibres. The perpendicular separations of the a^*c^* planes in the two reciprocal lattices do not differ by more than three percent.

The value of the long spacing ($1/c^*$) in the single crystal is 16·0 Å which is just half of that of the γ-form. It is of course possible that the spacing is really twice as long as reported, but no trace of weak spots to support this supposition could be found. The cell dimensions of the β form of stearic acid have been reported by von Sydow (1955) as

$$a = 5{\cdot}591,\ b = 7{\cdot}404,\ c = 49{\cdot}38\ \text{Å};\ \beta = 117°\ 22',$$

and the space group as $P2_1/a$. The short dimensions of this cell are not unlike those given above for the lauric acid plates but the space group is different and even if the long spacing of the lauric acid plates were doubled it would not agree with the value to be expected for the β-form of lauric acid.

Thus, although the unit-cell dimensions now reported bear some resemblance to those of both the β and γ-forms, they do not agree closely with either: they are quite different from those of the α-form and so it appears that a fourth crystalline form of lauric acid must be added to those previously known.

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The structure of crystalline uranium.

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It was proposed by Cash (1935) that the use of powder data in structure determinations of substances available only in powder form could be developed into a more powerful technique if photographs were made with as many different consecutive $K\alpha$ wavelengths as possible, so that as much of the diffraction pattern as possible could be observed in the high-resolution back-reflection region of the camera. The present work was undertaken in 1936 by one of us (A. H. C.) to test this notion. As uranium was then available only as a powder, it seemed a suitable and interesting test substance. But before these

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* Deceased, 19 August 1936. Mr Cash performed all of the experimental work reported here and had measured all the films before his untimely death.

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