

Then

θ^0 ,	Δa , A	$\Delta a / a$, %
19	$3 \cdot 10^{-4}$	0.006
40	$1 \cdot 10^{-4}$	0.002
59	$4 \cdot 10^{-5}$	—
76	$7 \cdot 10^{-6}$	—

Thus, although the displacement of the lines is very insignificant, in isolated concrete cases $\Delta a / a$ may be larger than the errors of precision measurements of lattice parameters. In principle, a given line displacement may be used for determining the dimensions of mosaic blocks.

We shall mention another important effect to which the existence of the additional phase gives rise.

By integration of formula (6) according to Φ , the integral reflection may be calculated; but the integrals in (6) are not expressed by elementary functions and we shall, therefore, confine ourselves here to a qualitative analysis.

It can readily be seen (Fig. 2) that the displacement of the intensity maximum does not result in the restora-

tion of its magnitude to that which it ought to have had if the additional phase difference had not been taken into account. This discrepancy increases with increase in the size of the block. The broadening of the lines follows automatically from this.

A more exact analysis may be made by graphical construction of the line contour, or by replacement of $\sin(\alpha x - \beta x^2)$ and $\cos(\alpha x - \beta x^2)$ by approximate integrands.

Conclusions

1. The finite size of blocks results in a displacement and broadening of the x-ray lines.
2. To eliminate the influence of the additional phase difference, a camera with large R should be used.

LITERATURE CITED

1. M. M. Umanskii, V. V. Zubenko, and Z. K. Zolina, *Kristallografiya* **5**, 1, 51-55 (1960) [*Soviet Physics-Crystallography*, Vol. 5, p. 43].
2. I. N. Bronshtein and K. A. Semendyaev, *Guide to Mathematics* [in Russian] p. 139, 4th Ed. (1954).

* * *

CRYSTAL STRUCTURE OF HOPEITE, $Zn_3(PO_4)_2 \cdot 4H_2O$

Kh. S. Mamedov, R. Gamidov, and N. V. Belov

Institute of Crystallography, Academy of Sciences, USSR,
 Institute of Chemistry, Academy of Sciences, Azerb. SSR,
 Translated from *Kristallografiya*, Vol. 6, No. 1, pp. 114-117,
 July-August, 1961

Original article submitted November 10, 1960

Hopeite, a rhombic modification of zinc phosphate tetrahydrate [1, 2], is characterized by the following structure parameters:

$$a = 10.64, b = 18.36, c = 5.04 \text{ \AA}^*$$

The unit cell contains (in accordance with the specific gravity 3.04) four units of the compound $Zn_3(PO_4)_2 \cdot 4H_2O$ with the symmetry space group

$$D_{2h}^{16} = Pnma$$

(more probable than $Pn2_1a$). The above-mentioned parameters and the symmetry group of hopeite are obtained from developments of layer lines (Weissenberg patterns) of rotation of the crystal about the short axis c .

On the development of the zero layer line, in addition to the regular extinctions determined by the symmetry group $Pnma$, it was noted that there was considerable weakening of all the reflections with odd-numbered h 's, indicating the presence of a pseudoperiod amounting to half the true period.

On the basis of geometry of the unit cell (including in it also the distribution of the elements of symmetry) and also the mutual arrangement of the peaks on the Patterson xy projection and the intensity ratios of these peaks, and also by making use of very simple crystal-chemistry considerations, it has been possible to construct a model of the structure which does not conflict with the experimental data.

Making use of the Pauling polyhedra, in particular the Zn octahedra and P tetrahedra, we show in Fig. 1 a projection of an idealized structure of hopeite on (001), and in Fig. 2, the (010) projection. The principal constructional detail of the structure must be considered to be a group of three Zn octahedra joined together by

* The analysis was made on hopeite specimens synthesized in accordance with [1] by R. Gamidov in the Institute of Chemistry, Academy of Sciences, Azerb. SSR.

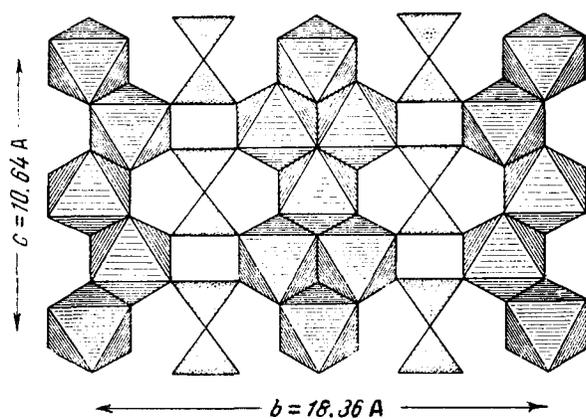


Fig. 1. xy projection of the structure of hopeite in Pauling polyhedra - Zn octahedra and P tetrahedra.

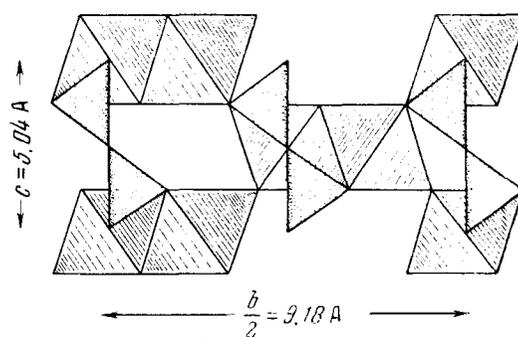


Fig. 2. Hopeite, xz projection.

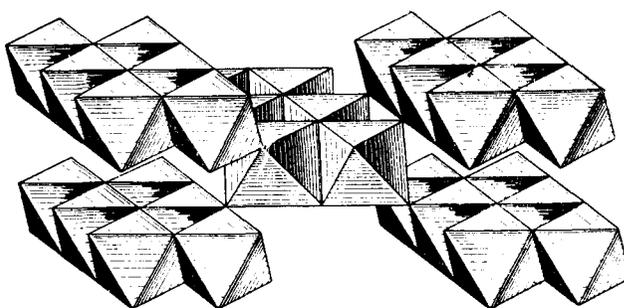


Fig. 3. Diaspore-goethite structure in Pauling octahedra.

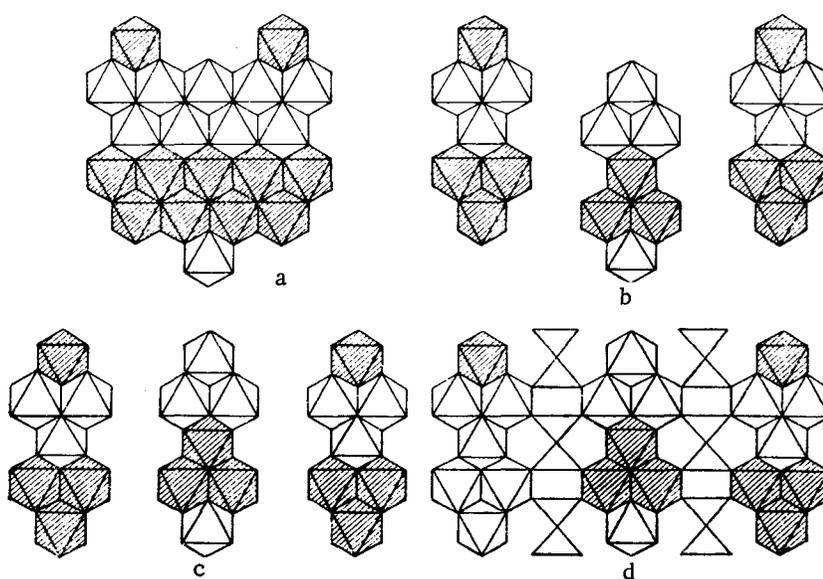
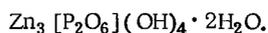


Fig. 4. Structure of hopeite as derived from the diaspore-goethite structure. a) Initial diaspore-goethite structure, b) separation of details of hopeite structure from it, c) rearrangement in the hopeite pattern, d) final result.

common sides. These groups of three octahedra represent portions of the diasporite (AlOOH) - goethite (FeOOH) structure, which is known to be a two-layer closest packing of octahedra alternating with bands of the same width (two octahedra), but void [3]. Below the void octahedra of one array are the occupied octahedra of another array, and vice versa (Figs. 3 and 4a). In the band of the initial diasporite structure on transition to hopeite, out of every 2×3 octahedra, the above-mentioned group of three is left, and in fact along the [010] plane there is an alternation of void groups of three with occupied groups of three (Fig. 4d). In the direction of the close-packing axis itself, void groups of three alternate with occupied groups of three as before, and together they produce a wall with a general direction parallel to (010). In pattern, the wall (Fig. 5) is reminiscent of wooden lattice-work gates. Arranged in the voids between these (010) lattices and making use of the wider intervals between the single Zn octahedra, are metaphosphate chains $[P_2O_6] = P_{1+1}O_6$, copying almost completely in their geometry $[Si_{1+1}O_6]_\infty$ chains. The somewhat diminished period along the (001) chain axis, that is to say, $c = 5.04$ A, compared with 5.20 A (in pyroxenes), is due to the smaller dimensions of the PO_4 tetrahedron compared with SiO_4 ($P-O \approx 1.55$ A, $Si-O \approx 1.63$ A).

In agreement with the model, the rational formula for hopeite will be



On the basis of the cell contents and the model structure cited, it could be expected that the eight H_2O particles would be arranged in two fours in mirror planes, and the 16 OH groups in two eights in common positions along the apexes of the Zn octahedra not connected to P tetrahedra. This, however, would be contradicted by the arrangement of H_2O at the junction of three Zn octahedra, whereas the now generally accepted tetrahedral model of water (Bernal-Fowler) permits only two cation neighbors. The location of hydroxyl groups at these points of junction would, however, result in an excellent balance of the valence forces according to Pauling's second rule ($1 = 3 \times 2/6$). Likewise, the arrangement in the general positions, at the O apexes, at which two Zn octahedra meet, by equal (statistical distribution) rights of eight OH and eight H_2O results in the establishment between

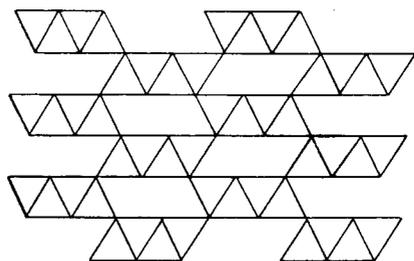


Fig. 5. Latticework layers (of a thickness of one layer) of Zn octahedra in hopeite.

Atoms	x	y	z
(4) Zn_1	0	$1/4$	0
(8) Zn_2	$1/4$	$1/6$	$1/2$
(8) P	0.104	0	$1/4$
(4) O_1	0	0	0^*
(4) O_2	0	0	$1/2^*$
(8) O_3	0.160	0.071	$1/4$
(8) O_4	0.340	0.071	$3/4$
(4) $O_5(OH)$	0.160	$1/4$	$1/4^{**}$
(4) $O_6(OH)$	0.340	$1/4$	$3/4^{**}$
(8) $O_7(OH, H_2O)$	0.084	$1/6$	$3/4^{***}$
(8) $O_8(OH, H_2O)$	0.414	$1/6$	$1/4^{***}$

* These O atoms are each common to two P tetrahedra in the metaphosphate chain $[PO_3]_{00}$. In the hopeite cell, (all) the inversion centers coincide with them, at one of them the origin of the coordinates is also situated.

** These OH groups in mirror planes are each common to three Zn octahedra.

*** Eight OH and eight H_2O statistically distributed in $2 \times 8 = 16$ positions.

them of a hydrogen bond and again in a satisfactory valence balance ($1/2 \div 2/3 = 2 \times 2/6$). A certain excess of positive forces compensates their deficiency at the O atoms (common to Zn and P), where we have $2 > 5/4 + 1/3 = 17/12$. The undoubted partial hydrogen bonding of the H_2O molecules (along the other edges of the Zn octahedra) also with these O materially corrects the last inequality.

The fairly approximate coordinates of all the atoms resulting from the model are given in the Table in respect of the origin, the center of symmetry, which in this structure (Fig. 1) is situated at the O atom, common to two PO_4 tetrahedra in the metaphosphate chain. The coordinates given are satisfactorily confirmed by an electron density projection on xy.

We have refrained from giving the interatomic distances before the coordinates have been defined more exactly on the basis of our continued work on hopeite, which ought not to affect the model itself.

The idealized hopeite model provides a good explanation of the pseudoperiod $b/2$. The structural pattern is repeated according to this period, but not identically (Fig. 1).

Of the chemical analogs of hopeite only ludlamite, $Fe_3 [PO_4]_2 \cdot 4H_2O$, has been studied [4]. From the considerable closeness of the structural parameters a related structural pattern was also to be expected for ludlamite, but this was not confirmed, evidently due to the considerable crystal-chemical difference of the cations Zn^{2+} and Fe^{2+} . Nevertheless, the octahedral coordination of the two cations in these chemical analogs renders probable a ludlamite modification of hopeite, and vice versa.

In conclusion we shall compare the structural parameters of hopeite and diasporite, since according to

what has been said the structure of the former is a derivative of the "fundamental" structure of diaspore.

We also give data for the closest analog of diaspore, goethite.

	a	b	c	
Hopeite $Zn_3[P_2O_6](OH)_4 \cdot 2H_2O$	10.64	18.36	5.04 A	} $Z = 4$ } $D_{2h}^{16} = Pnma$
Diaspore $AlOOH$	9.04	2.84	4.43	
Goethite $FeOOH$	10.0	3.06	4.64	

The c/a ratio in the three structures is 4.73, 4.70, and 4.64. The resemblance, especially to goethite (large cations Zn^{2+} and Fe^{2+}), is fairly considerable. In accordance with the model, the parameter b in the case of hopeite ought to be six times larger than in the case of goethite, which in fact emerges with considerable, and therefore accidental, accuracy.

The model of the structure excludes cleavage perpendicular to the metaphosphate chains, i.e., along (001) ("vague" according to [1]) and permits medium cleavages along (100) and (010) (cf. [1] and [2]). The parallel (010) layers of heavy Zn atoms determine the well-

pronounced negative character of hopeite with N_p direction along [010].

LITERATURE CITED

1. E. Dana, Descriptive Mineralogy [Russian translation] (2nd Edition, Moscow, 1954).
2. A. G. Betekhtin, Course in Mineralogy [in Russian] (Moscow, 1950).
3. N. V. Belov, "Outlines of structural mineralogy," VIII. Mineralog. sb. L'vovsk. geol. o-va pri un-te 11, 3-21 (1957).
4. T. Ito, X-ray Studies on Polymorphism, Tokyo (1950).

* * *

CRYSTAL STRUCTURES OF HAFNIUM-BERYLLIUM COMPOUNDS

(Preliminary communication)

P. I. Kripyakevich, M. A. Tytkina, and E. M. Savitskii

I. Franko L'vov State University

A. A. Baikov Institute of Metallurgy, Academy of Sciences, USSR,

Translated from Kristallografiya, Vol. 6, No. 1, pp. 117-118,

July-August, 1961

Original article submitted May 3, 1960

The hafnium-beryllium system has hitherto not been investigated [1]. We prepared alloys containing 0.0025, 0.005, 0.013, 0.025, 0.10, 0.56, 1.24, 2.44, 7.74, 10.50, 16.80, 20.90, 33.73, and 51.64 atom-% (0.05, 0.1, 0.25, 0.5, 2.0, 10.0, 20.0, 33.0, 62.5, 70.0, 80.0, 84.0, 91.0, and 95.5 wt-%) of hafnium (in the charge) by melting Hf and Be in an argon atmosphere in a high-frequency furnace (for high beryllium contents) or an electric-arc furnace (for high hafnium contents), and studied them by the methods of x-ray structural analysis (Debye photographs and Preston photographs taken in Cr-K radiation) and microstructure. For some of the alloys, the melting point, hardness, and microhardness of the structural constituents were also determined. The microhardness ($H\mu$) was determined using the PMT-3 instrument with a load of 100 g to an accuracy ± 30 kg/mm².

The investigation showed that three compounds exist in the system:

1) $HfBe_2$, structural type AlB_2 , space group $C6/mmm - D_{6h}^1$, $a = 3.783 \pm 0.002$, $c = 3.163 \pm 0.001$ A, $c/a = 0.836$, $H\mu = 980$ kg/mm²; 2) $HfBe_5$, type $CaZn_5$,

space group $C6/mmm - D_{6h}^1$, $a = 4.534 \pm 0.010$, $c = 3.471 \pm 0.010$ A, $c/a = 0.765$, $H\mu = 1340$ kg/mm²; 3) Hf_2Be_{17} , type U_2Zn_{17} , space group $C\bar{6}m2 - D_{3h}^1$, $a = 7.499 \pm 0.002$, $c = 21.905 \pm 0.006$ A, $c/a = 2.921$, $H\mu = 1085$ kg/mm²; 4) $HfBe_{13}$, type $NaZn_{13}$, space group $Fm\bar{3}c - O_h^f$, $a = 10.005 \pm 0.002$ A, $H\mu = 1200$ kg/mm².

Thus, the Hf-Be system in the crystal-chemical respect resembles the Zr-Be system, in which there are also four compounds isostructural with the compounds found by us or with related structures [2-4].

LITERATURE CITED

1. M. Hansen and K. Anderko, Constitution of binary alloys, (1958).
2. N. C. Baenziger and R. E. Rundle, Acta crystallogr. 2, 258 (1949).
3. J. W. Nielsen and N. C. Baenziger, Acta crystallogr. 7, 132 (1954).
4. A. Zalkin, R. G. Bedford, and D. E. Sands, Acta crystallogr. 12, 700 (1959).