

# Isotypy in aktashite $\text{Cu}_6\text{Hg}_3\text{As}_4\text{S}_{12}$ and nowackiite $\text{Cu}_6\text{Zn}_3\text{As}_4\text{S}_{12}$ \*

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In 1966 Marumo determined the structure of nowackiite, one of five new minerals (imhofite, sinnerite, wallisite, and rathite-IV) from the Legenbach deposit (Binntal, Switzerland).<sup>1,2</sup> The structure of nowackiite is conveniently represented as a defect sphalerite structure in which some of the S positions on the triad axes remain unoccupied. Four As atoms coordinate the empty places; such As is a vertex of a trigonal pyramid with a base made up of three S atoms; and the (Cu, Zn) positions have complete tetrahedral coordination. The Cu and Zn atoms cannot be distinguished by x-ray diffraction; in nowackiite they may be arranged in an ordered fashion. The structure was determined by interpreting a three-dimensional Patterson synthesis constructed exclusively from superlattice reflections. This method of interpreting a Patterson synthesis was first developed and successfully used in the case of nowackiite.

An analysis with the microprobe gave the formula  $\text{Cu}_6\text{Zn}_3\text{As}_4\text{S}_{12-13}$ ; the application of the rule of Grimm and Sommerfeld (requiring that in tetrahedral structures the quotient of the division of the sum of the valence electrons by the number of atoms, including unoccupied positions, shall be equal to four), together with a detailed analysis

of the structure, led to the more exact formula  $\text{Cu}_6\text{Zn}_3\text{As}_4\text{S}_{12}$ . It may be assumed that  $\alpha$ -trechmamsite and nowackiite are identical.<sup>3</sup>

Aktashite was discovered in 1968 by V. S. Gruzdev in the Gal-Khai deposit (Yakutiya), and shortly afterward found by V. I. Vasil'ev in Ak-Tash deposit. A description of this mineral was given in Refs. 4 and 5, and the structure was determined by Belov et al.<sup>6</sup> Chemical analysis led to the formula  $\text{Cu}_6\text{Hg}_3\text{As}_4\text{S}_{12}$ , which as a result of structural determination was changed to  $\text{Cu}_6\text{Hg}_3\text{As}_4\text{S}_{12}$ . The correctness of this emendation was confirmed by the rule of Grimm and Sommerfeld. The presence of heavy Hg atoms permitted the structure to be determined with the aid of Patterson methods alone. The structural parameters of nowackiite and aktashite are given below; Table II lists the atomic coordinates and  $B_{\text{iso}}$  values. The isotypy of these two compounds is obvious; the atomic coordinates are very similar. Owing to the presence of large Hg atoms the unit cell of aktashite is naturally larger, and we can speak with confidence only of "similarity" of the two structures.<sup>6</sup> The isomorphism of Cu and Hg in tetrahedral gaps is also observed in the structures of sulfo salts, e.g., in schwazite  $(\text{Cu}_6^{3+}(\text{Cu}, \text{Hg})_6^{4+}(\text{SbS}_3)_4\text{S})$ , Ref. 7], where the Hg atoms replace Cu atoms in general tetrahedral coordination.

TABLE I. Comparison Between Structural Parameters of Nowackiite and Aktashite

Nowackiite	Aktashite
$\text{Cu}_6\text{Zn}_3\text{As}_4\text{S}_{12}$	$\text{Cu}_6\text{Hg}_3\text{As}_4\text{S}_{12}$
$a_h = 13.44 \pm 0.015 \text{ \AA}$	$a_h = 13.730(3) \text{ \AA}$
$c_h = 9.17 = 0.01$	$c_h = 9.329(1)$
$C_3^2 = R3$	$C_3^2 = R3$
Z=3 in hexagonal unit cell	Z=3 in hexagonal unit cell
$\rho_c = 4.38 \text{ g/cm}^3$	$\rho_c = 5.72 \text{ g/cm}^3$

TABLE II. Atomic Coordinates and Values of  $B_{\text{iso}}$  (in Angstroms)

Nowackiite				Aktashite					
Atom	x/a	y/b	z/c	$B_{\text{iso}}$	Atom	x/a	y/b	z/c	$B_{\text{iso}}$
(Cu, Zn) (1)	0.0741(3)	0.2332(3)	0.5957(3)	0.89	Cu	0.076(1)	0.2321(5)	0.0030(2)	1.02(2)
(Cu, Zn) (2)	0.3065(3)	0.2275(3)	0.5920(3)	0.72	Hg	0.310(2)	0.2263(4)	0.0031(5)	1.93(3)
(Cu, Zn) (3)	0.3495(3)	0.5539(3)	0.0058(4)	1.45	Cu	0.345(4)	0.552(3)	0.0450(6)	0.93(6)
As(1)	0.5533(2)	0.1650(2)	0.0071(2)	0.84	As	0.5610(6)	0.173(2)	0.0000(4)	0.75(3)
As(2)	0	0	0.9503(2)	0.52	As	0	0	0.9503	0.21(3)
S(1)	0.3695(4)	0.1026(4)	0.0792(5)	0.91	S	0.372(3)	0.0999(5)	0.035(2)	0.45(3)
S(2)	0.4330(4)	0.4150(4)	0.0705(5)	0.93	S	0.437(3)	0.423(3)	0.0660(5)	0.39(3)
S(3)	0.1251(4)	0.1646(4)	0.0909(6)	1.03	S	0.115(3)	0.1581(5)	0.1079(4)	0.65(2)
S(4)	0.2099(4)	0.4750(4)	0.2961(5)	0.81	S	0.203(3)	0.475(3)	0.0961(6)	0.54(4)

(z =  $\frac{1}{3}$ lit + 0.9503)

Interatomic distances (Å)

As-S = 2.24 - 2.27  
(Cu, Zn)-S = 2.27 - 2.35

As-S = 2.20 - 2.37  
Cu-S = 2.25 - 2.43  
Hg-S = 2.45 - 2.55

Ionic radii (Å)

Cu=0.96; Zn=0.74

Hg=1.10

\*To N. V. Belov — for his ninetieth birthday.

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<sup>4</sup>V. I. Vasil'ev, in: *Aspects of the Metallogenesis of Mercury* [in Russian], Nauka (1968), p. 111; in: *Ore Formations and Genesis of Endogene Deposits of the Altai-Shushenskaya Region* [in Russian], Nauka, Moscow (1968), p. 76; Author's Abstract of Dissertation for Degree of Candidate of Geological-Mineralogical Science [in Russian], Novosibirsk (1970).

<sup>5</sup>V. S. Gruzdev, N. M. Chernitsova, and N. G. Shumkova, *Dokl. Akad. Nauk SSSR* **206**, 694 (1972).

<sup>6</sup>L. N. Kaplunnik, E. A. Pobedimskaya, and N. V. Belov, *Dokl. Akad. Nauk SSSR* **251**, 96 (1980) [*Sov. Phys. Dokl.* **25**, 141 (1980)].

<sup>7</sup>R. Kalbskopf, *Tschermaks Mineral. Petrog. Mitt.* **16**, 173 (1971).

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## Neutron-diffraction refinement of the structure of carbonate-cancrinite

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From an experimental set of neutron data — 772 F (*hkl*) values, obtained from a single crystal of carbonate-cancrinite  $\text{Na}_{7.6}\text{Ca}_{0.4}[\text{Si}_6\text{Al}_6\text{O}_{24}] \cdot 1.0\text{CO}_3 \cdot 2.2\text{H}_2\text{O}$ —the positions of all the nonhydrogen atoms are determined and refined. It is shown that the  $\text{OH}_m$  ( $m = 1, 2, 3$ ) groups lie, together with the C atoms, on the  $6_3$  axis; most of them are  $\text{OH}^-$  anions.

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The structure of cancrinite, one of the framework aluminosilicates, has been studied by x-ray diffraction on the natural mineral.<sup>1</sup> Natural cancrinite contains variable amounts of various cations, anion groups, and water molecules; moreover, the Si/Al ratio can vary over wide limits. In this connection it seems advisable to refine the structure of cancrinite on synthetic specimens. It is most convenient to begin this task with crystals in which Si/Al  $\approx$  1, since on this condition the Si and Al atoms in framework aluminosilicates are arranged in an orderly fashion.<sup>2</sup>

According to Kosova and Dem'yanets,<sup>3</sup> cancrinites with the stoichiometric Si/Al ratio can be obtained only in the presence of  $\text{CO}_3^{2-}$  ions or other interstitial anions ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{Cl}^-$ , etc.) in the original solution. We investigated a specimen of cancrinite containing  $\text{CO}_3^{2-}$  anions (carbonate-cancrinite). The presence of fairly large single crystals of  $\text{CO}_3$ -cancrinite, obtained in hydro-

thermal conditions, enables us to make use of neutron diffraction — a method which is sensitive to the positions of light atoms. This method also enables us to distinguish Si from Al atoms,<sup>4</sup> whereas in x-ray diffraction this problem must be solved indirectly by analyzing the Si–O and Al–O distances in the tetrahedra.

The chemical analysis results for the single crystals were as follows:

Components:	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{CaO}$	$\text{Fe}_2\text{O}_3$	$\text{K}_2\text{O}$	$\text{CO}_2$	$\text{H}_2\text{O}$
Contents in %	35.86	29.32	23.31	2.44	trace		4.67	4.03

The composition of the crystals was  $\text{Na}_{7.6}\text{Ca}_{0.4}[\text{Si}_6\text{Al}_6\text{O}_{24}] \cdot 1.0\text{CO}_3 \cdot 2.2\text{H}_2\text{O}$ . The unit-cell parameters [ $a = 12.62(1)$  Å,  $c = 5.138(2)$  Å] differ from those for natural cancrinite.<sup>1</sup> The integral intensities of the diffraction peaks were measured by  $\theta$ – $2\theta$  scanning in the automatic neutron diffrac-

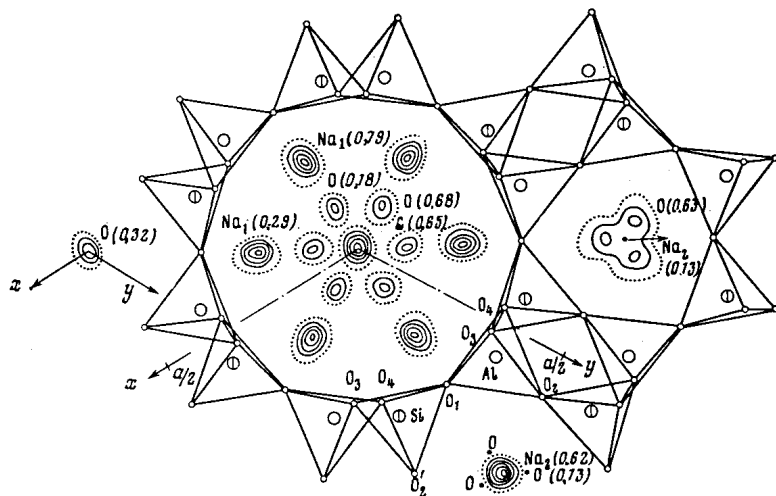


FIG. 1. Projection of difference Fourier synthesis on (0001) plane. For clarity we show channels of both types; circles mark positions of atoms for which the contributions are subtracted from  $F_{\text{exp}}$ ; dots mark zero level; curves are drawn at equal intervals of nuclear density; maxima on axis of broad channel and in narrow channel are shown separately; values of Z are indicated in parentheses.