American Mineralogist
Vol. 57, pp. 318–324 (1972)

American Crystallographic Association

Summer Meeting, Ames, Iowa, August 18, 1971
Session on Mineralogical Crystallography: Abstracts

THE CRYSTAL STRUCTURE OF α Ni_7S_6

M. E. Fleet, *Department of Geology*

University of Western Ontario, London, Ontario, Canada

α Ni_7S_6 is orthorhombic with $a = 3.274$, $b = 16.157$, and $c = 11.359$ Å, space group *Bmmb*. The crystal structure has been determined on a synthetic single crystal by the application of a direct method of phase determination. The unit cell content is 22.5 Ni, 19.3 S; both S and Ni atoms are disordered within their respective sites. The S sites are arranged in alternate planes, with $x = 0$ and 1/2, which form a zig-zag arrangement extending in the b direction with a plane of symmetry at $y = 1/4$ and $y = 3/4$. There are three non-equivalent S sites per unit cell, two in 8(f) positions and one in 4(c). There are five non-equivalent Ni sites, four five-fold coordinated (pyramidal) with S, of which three are in 8(f) and one in 4(c), and one tetrahedrally coordinated with S in 8(f). The Ni is distributed to give occupancies of approximately 0.94 to the 4(c) site and to one of the pyramidal 8(f) sites, and occupancies of approximately 0.47 to the remaining three sites. The positional and anisotropic thermal parameters and site occupancies have been refined to an R of 0.116. The refined occupancies are similar to the above ideal values. Each Ni site is related to at least one neighboring Ni site by a bond distance similar to that of metallic Ni (2.492 Å) and, as such, the pyramidal and tetrahedral sites have similarities with the Ni site in millerite (NiS) and heazlewoodite (Ni_3S_2) respectively. Clearly, metallic Ni-Ni bonding has been significant in stabilizing all three of these structures.

STRUCTURAL INVESTIGATIONS OF THE Cu-Fe-S MINERAL, TALNAKHITE

S. R. Hall, E. J. Gabe[1], L. J. Cabri, M. G. Townsend, and J. Horwood, *Mineral Sciences Division, Dept. of Energy, Mines, and Resources, Ottawa, Canada.*

Talnakhite is one of several recently studied minerals with distinct crystal structures and metal-rich compositions close to that of chalcopyrite 4($CuFeS_2$). It was first identified[2] as $CuFeS_{1.8}$ with a cubic unit cell of 5.28 Å, and considered to be iso-structural with high-temperature chalcopyrite. However, subsequent work[3] showed talnakhite to have $a \sim 10.6$ Å. In this study the cell has $I\bar{4}3m$ symmetry and $a = 10.593(3)$ Å. Electron probe analyses[4] give a composition which is consistent with the stoichiometry $Cu_{18}Fe_{16}S_{32}$. An X-ray analysis, using single crystal diffractometer data, shows that the structure of talnakhite is "equivalent" to that of synthetic β phase[5]. The structure is also similar to that of chalcopyrite,

[1] Present address: Division of Chemistry, National Research Council, Ottawa.
[2] Bud'ko, I. A., and E. A. Kulagov (1963) *Dokl. Akad. Nauk.* **169**, 428.
[3] Cabri, L. J. (1967) *Econ. Geol.* **62**, 910.
[4] Cabri, L. J., and D. C. Harris (1971) *Econ. Geol.* **66**, in press.
[5] Hiller, J. E., and K. Probsthain (1956) *Z. Kristallogr.* **108**, 108.

but contains additional metals atoms with an unusual second-neighbour octahedral metal-coordination (2.72 Å). Despite the low R value of 0.05, the X-ray analysis gives no conclusive information about the ordering or ionization of the Cu and Fe atoms. Mössbauer studies indicate that talnakhite is essentially antiferromagnetic similar to chalcopyrite, but with significant differences.

CRYSTAL CHEMISTRY OF A NEW SULFOSALT MINERAL, NUFFIELDITE ($Pb_{10}Bi_{10}Cu_4S_{28}$)[1]

I. Kohatsu and B. J. Wuensch, *Department of Metallurgy and Materials Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.*

Nuffieldite is a new sulfosalt mineral discovered near Alice Arm, British Columbia. Kingston (1968)[2] proposed $Pb_{10}Bi_{10}Cu_4S_{27}$ as the ideal composition on the basis of application of several analytical techniques to a very limited amount of material. The present structural analysis was performed on crystals kindly provided by Dr. Kingston. Nuffieldite is orthorhombic, space group $Pbnm$ or $Pbn2_1$, with $a = 14.387(7)$, $b = 21.011(15)$, $c = 4.046(6)$Å. The composition was assumed to be $(Pb,Bi)_5CuS_7$, with $Z = 4$, to conform to the equipoint multiplicities available in the possible space groups. Intensities were collected photographically with an equi-inclination Weissenberg camera employing the multiple film technique, and measured with an automatic photoscanner. The crystal employed was a flat needle of 0.018 mm diameter, giving $\mu r_{max} = 2.56$ for CuKα. The heavy atoms were located by the symbolic addition procedure. Fourier maps based on signs determined from the heavy atom positions revealed Cu and seven S atoms. The asymmetric unit contains 13 atoms all located in position $4(c)m$. Least-squares refinement was also attempted for the acentric space group. Negligible shifts from the symmetry plane at $z = \frac{1}{4}$ occurred, and refinement did not proceed beyond the results of the centric model in spite of the increase in the number of adjustable parameters. The structure contains stibnite-like chains parallel to c with an associated Cu in a tetrahedral site. These units are identical to those which form the structure of aikinite, $PbCuBiS_3$. In nuffieldite, however, the aikinite-like units are separated by an intervening zig-zag layer of PbS-like structure along (010).

[1] Research supported by the National Science Foundation and an I.B.M. Fellowship.

[2] Kingston, P. W. (1968) *Can. Mineral.* 9, 440.

CRYSTALLOGRAPHY OF SINNERITE ($Cu_6As_4S_9$)[1]

E. Makovicky and B. J. Skinner, *Yale University, New Haven, Connecticut.*

Synthetic sinnerite crystals were prepared from Cu, As, and S in evacuated silica glass tubes at 450°C. Similarly to their natural counterparts (Marumo and Nowacki, 1964)[2] they are intricately twinned simulating rhombohedral holohedry in X-ray patterns. The structure is based on a pronounced sphalerite substructure. Weissenberg photographs of the twins revealed that sinnerite is triclinic, space group $P\bar{1}$, with $a = 9.06$, $b = 9.83$, $c = 9.08$Å, $\alpha = 90°00'$, $\beta =$

[1] Research supported by NSF grants GA 4142 and GA 27523.

[2] Marumo, F., and W. Nowacki (1964) *Schweiz. Mineral. Petrogr. Mitt.* 44, 439.

109°30′, $\gamma = 107°48'$. Every twin contains 6 individuals mutually related by three primary and one derived twin law. Twinning restores the sphalerite sublattice and for two of the laws, parts of the triclinic lattice. Untwinned reflections gave directly a difference Patterson and, after minimalization, difference Fourier maps. Copper atoms do not deviate appreciably from the tetrahedral positions of the ideal sphalerite-type structure. Arsenic atoms coordinated by sulphur atoms form a network extending parallel to (010).

CHARGE REFINEMENT OF A LIGHT-ATOM MINERAL STRUCTURE: KERNITE[1]

W. F. Cooper, F. K. Larsen, and P. Coppens, *Chemistry Department, State University of New York at Buffalo, Buffalo, New York 14214.*

Because of their low temperature factors mineral structures are suitable for a valence shell refinement by the Extended *L*-shell method[2]. The mineral kernite is of especial interest because it contains boron atoms in both tetrahedral and trigonal positions and bridging as well as hydroxylic oxygen atoms.[3] The positional parameters as determined by Giese[3] were used as input in the refinement of 3604 symmetry-independent reflections, which were measured on an automated Picker diffractometer. The conventional least squares refinement resulted in $R(F^2) = 4.7\%$ and $R_w(F^2) = 3.5\%$, while the valence shell refinement with optimized Slater type orbital (STO) scattering factors led to a final $R(F^2) = 3.6\%$ and $R_w(F^2) = 2.5\%$ for 212 parameters and 2492 non-zero reflections. It is found that all boron atoms are positive, but the charges on the trigonally coordinated atoms are somewhat larger (+0.66(.02), +0.56(.02)), than those on the tetrahedral borons (+0.46(.02), +0.51(.02)). Both sodium atoms are positive by 0.3–0.4 electrons, while negative charges are found on all oxygen atoms, without much distinction as to bonding environment.

The least-squares scale factor is quite sensitive to the choice of scattering factor in the refinement. An experimental determination of the scale factor is therefore being attempted to obtain additional information on the charge distribution. Bonding effects are further being studied by the calculation of difference maps with the calculated structure factors based on parameters from a high order refinement.

[1] Research supported by the National Science Foundation.

[2] Coppens, P., D. Pautler, and J. F. Griffin (1971) *J.A.C.S.* 93, 1051.

[3] Giese, R. F. (1966) *Science* 154, 1453.

THE CRYSTAL STRUCTURES OF THREE ION-EXCHANGED FORMS OF FAUJASITE

J. J. Pluth and Verner Schomaker, *University of Washington, Seattle, Washington 98195.*

Two crystals of faujasite (the mineral) were ion-exchanged with aqueous solutions—one KCl, the other $BaCl_2$—then heated to about 400°C under vacuum in capillaries, sealed off, and studied at room temperature on a diffractometer with Nb-filtered MoKα radiation. For the Ba^{2+}-exchanged crystal the process was repeated, but with CsCl as the exchange solute. The structures were refined on F^2 with anisotropic temperature factors to final conventional R values ranging

from 0.103 to 0.117 and average estimated standard deviations for the T(Si,Al)—O bond lengths of the order of 0.002 Å.

For the K^+-exchanged crystal the non-framework electron density was assigned to K^+ ions (8.6, 13.0, and 31.6 per unit cell in sites I, I′, and II); for the Ba^{2+} crystal to Ba^{2+} (7.0, 4.7, and 11.4 in I, I′, and II) and unexchanged Na^+ (3.7 in II); and for the Cs^+ crystal to Cs^+ (4.9, 19.5, 2.7, and 4.2 in I′, II, II′, and III) and unexchanged Ba^{2+} and Na^+ (3.4 and 5.1, respectively, in I and II). These assignments were based on the magnitudes of the electron density, the indicated cation-to-oxygen bond lengths, the known cation site preferences, and, in the Ba^{2+} and Cs^+ cases, a subsequent electron-microprobe analysis of the crystal.

The metal-to-oxygen bond lengths are approximately equal to the appropriate ionic-radius sums. The three structures show significant differences in framework distortion.

RELATION BETWEEN T—O—T ANGLE AND STABILITY OF $LiAlSi_2O_6$-III (γ-SPODUMENE) AND OTHER HIGH-QUARTZ SOLID SOLUTIONS

C. T. Li, *Owens-Illinois Technical Center, Toledo, Ohio,* and P. J. Shlichta, *University of Southern California, Los Angeles, California.*

$LiAlSi_2O_6$-III (γ-spodumene), a stuffed high-quartz solid solution, transforms at elevated temperatures into $LiAlSi_2O_6$-II (β-spodumene), a stuffed keatite solid solution. During the transformation, the average T—O—T bond angle (where T = Si or Al in random distribution) is reduced from 151.8° to 149.4° (Li, 1968[1]; Li and Peacor, 1968[2]). In contrast, high-quartz solid solutions with a lower silica content, such as $Li_2O \cdot Al_2O_3 \cdot 3SiO_2$, have a lower T—O—T angle and are stable (Li, 1970[3]). This suggests that the high T—O—T angle is a source of strain energy in these structures and that their structural parameters and transformational stability can be explained in terms of the minimization of the T—O—T angle. A geometric analysis of these structures indicates that the observed values of c/a and x (the oxygen-atom parameter) for both $LiAlSi_2O_6$-III and $Li_2O \cdot Al_2O_3 \cdot 3SiO_2$ do indeed correspond to a minimization of the T—O—T angle provided that (a) the T—O and Li—O distances are regarded as optimal invariants and (b) the minimum O—O distance is at least 2.60 Å. This interpretation also indicates that high-quartz solid solutions are stable, at least at elevated temperatures and pressures, throughout the compositional range of the quartz-eucryptite phase diagram; moreover, an order-disorder transition is predicted for β-eucryptite.

[1] Li, C. T. (1968) *Z. Kristallogr.* **127**, 327–348.
[2] Li, C. T., and D. R. Peacor (1968) *Z. Kristallogr.* **126**, 46–65.
[3] Li, C. T. (1970) *Z. Kristallogr.* **132**, 118–128.

THE CRYSTAL STRUCTURES OF URANOPHANE AND BETA-URANOPHANE

Deane K. Smith and Frances V. Stohl, *The Pennsylvania State University, University Park, Pennsylvania 16802.*

The composition $[Ca(H_3O)_2](UO_2)_2(SiO_4)_2 \cdot 3H_2O$ exists in two polymorphic forms, uranophane and beta-uranophane. The crystal structure of uranophane was

[1] Smith, D. K., Jr., J. W. Gruner, and W. N. Lipscomb (1957) *Amer. Mineral.* **42**, 594.

reported by Smith, Gruner, and Lipscomb (1957).[1] This structure has been further refined using a full three-dimensional-data set collected on a Picker FACS-1 diffractometer. In addition the beta-uranophane structure has been solved using three-dimensional data.

Uranophane is monoclinic; $a = 15.85$, $b = 6.97$, $c = 6.64$ Å, $\beta = 97.6°$ with $Z = 2$, and the space group is $P2_1$. Beta-uranophane is also monoclinic with $a = 13.90$, $b = 15.39$, $c = 6.61$ Å, $\beta = 91.4°$, and $Z = 4$. Its space group is $P2_1/a$. Both minerals usually form fibrous aggregates with the fiber direction parallel to the b axis in uranophane and the a axis in beta-uranophane.

In both structures the prominent structural unit consists of chains of edge-sharing $(UO_2)O_5$ polyhedra and SiO_4 tetrahedra. These chains lie parallel to the fiber axis and are cross-linked to other chains by corner sharing to form layers parallel to (100). The Ca ions, hydronium ions, and water molecules lie between these layers. The two structures differ only in the manner in which the layers are stacked.

STRUCTURAL CHARACTERIZATION OF SUBCALCIC ALUMINAN AUGITES[1]

HIROSHI TAKEDA, *NASA Manned Spacecraft Center, Houston, Texas 77058.*

To investigate the nature of the immiscibility gap and the cooling rate of volcanic pyroxenes, the crystal structures of two pairs of coexisting aluminan pyroxenes with Fe/(Fe + Mg) roughly $\frac{1}{3}$, have been refined by least-squares. Preliminary results have been reported on an aluminan augite-pigeonite pair from Apollo rock 12052 (Brett *et al.*, 1971; Takeda and Reid, 1971) and an aluminan bronzite from Taka-sima, Japan (Takeda, 1971). This paper deals with an aluminan augite coexisting with this bronzite supplied by the late Prof. H. Kuno (HK56051801). As to composition this augite $(Al_{.12}Fe^{3+}_{.08}Ti_{.03}Fe^{2+}_{.18}Mg_{.79}Ca_{.75}Na_{.05})(Si_{1.73}Al_{.27})O_6$ is intermediate between diopside and the 12052 augite. The crystal data are: a 9.707, b 8.858, c 5.274Å, β 106.52°, $C2/c$, $Z = 4$. The structure has been refined to a final R value of 0.043 for 821 observable reflections measured by a Picker FACS1 system with MoKα radiation using a graphite monochromator. The mean (Si, Al)-O(non-bridging) distance is 1.615Å, and the mean M1(Mg69%)-O distance is 2.057Å. The trends of the structural changes from subcalcic augite to diopside can best be traced by the mean distances given below. An O2-M2-O2 angle of 157.7° compares with 162.8° for 12052 augite, which approaches the value of the 12052 pigeonite (171.2°) and that of the Taka-sima bronzite (170.8°). The directions of elongation of apparent anisotropic thermal ellipsoids are consistent with the above trends. The structure of subcalcic augite characterized by the M2 cation coordinating close to oxygen atoms in an M1-octahedral chain (O1, O2) seems to be an unstable configuration. It may be considered a new type of metastable structure quenched from high temperature. No change of symmetry of the cell appears on quenching. This may explain the immiscibility gap that exists between the coexisting phases.

	Diopside[2]	Taka-sima	Kakanui[2]	12052
Ca(+Na) in M2	1.0	0.80	0.71	0.61
M2-O1, O2(Å)	2.357	2.315	2.297	2.253
M2-O3(Å)	2.639	2.649	2.662	2.717

[1] Support of an NRC-NASA Associateship is gratefully acknowledged.

[2] Data by Clark *et al.*, 1969.

CRYSTALLOGRAPHY OF LUNAR PYROXENES

C. T. Prewitt and G. E. Brown, *Department of Earth and Space Sciences, State University of New York, Stony Brook, New York 11790.*

Lunar clinopyroxenes are of two types, pigeonite ($P2_1/c$) and augite ($C2/c$) and occur in intimate intergrowths as a result of exsolution and epitaxy during cooling. We have examined these crystals at temperatures from ambient to above 1000°C, using single-crystal heaters designed for the precession camera and four-circle diffractometer. Measurements at high temperatures are complicated by cation diffusion within and between the intergrown pyroxenes, by changes in the domain structure of pigeonite, and by a compositionally dependent phase transition in pigeonite. However, information concerning the thermal histories of lunar and terrestrial pyroxenes has been obtained from refinements of Fe/Mg distributions between octahedral sites and from measurements of diffuseness of the primitive [$(h + k)$ odd] reflections of pigeonite. Previous results for pigeonite crystals appear as follows:

degree of cation ordering	$(h + k)$ odd reflections	pigeonite example
low	sharp	lunar rock 12021
low	diffuse	lunar rocks 12052 and 10003
high	sharp	—
high	diffuse	Isle of Mull, Scotland

In order to aid our understanding of these observations, we have measured single-crystal diffraction data for the Mull pigeonite at room temperature and at 900°C (25 degrees above the transition temperature). Preliminary refinement of the high-temperature structure in space group $C2/c$ resulted in an unweighted R index of 0.053 for observed reflections. Of major interest in the room-temperature structure are the cation ordering ($K_D = 0.036$)* and the large apparent anisotropy of the thermal motion parallel to the c axis. In the high-temperature structure, the M cations are more disordered ($K_D = 0.104$), the M—O distances are significantly larger (~2%), and isotropic temperature factors are about three times larger than in the room-temperature structure.

* $K_D = X_{Mg}^{M2}(1 - X_{Mg}^{M1})/X_{Mg}^{M1}(1 - X_{Mg}^{M2})$.

THE CRYSTAL STRUCTURE OF A BABINGTONITE[1]

T. Araki, *University of Chicago, Chicago, Illinois 60637* and T. Zoltai, *University of Minnesota, Minneapolis, Minnesota 55455*

The crystal structure of a babingtonite, $Ca_2(Fe, Mn, Mg)^{2+}Fe^{3+}HSi_5O_{15}$, $a = 7.509$, $b = 11.697$, $c = 6.719$, $\alpha = 91.43°$, $\beta = 93.89°$, $\gamma = 104.26°$, $Z = 2$, $P\bar{1}$, was determined by solving the three-dimensional Patterson synthesis. The initial coordinates of all the atoms found on M_2 maps were located in subsequent Fourier syntheses. Four cycles of least-squares refinement with isotropic temperature factors led to an R value of 6.1% on 3265 reflections, which were collected on a Hilger Watts automated four-circle diffractometer using Zr-filtered MoKα radiation.

The structure is composed of two five-member single chains, which are parallel to each other and stretch along [110] in the unit cell. Cation polyhedra form a sequence by sharing edges and corners between the silicate chains. One of the Fe octahedra is occupied by bivalent Fe partly replaced by Mn and Mg with

[1] Supported by NSF.

average cation-oxygen distance of 2.169 Å, the other by trivalent Fe with average cation-oxygen distance of 2.048 Å. Of the two types of Ca cations, one is surrounded by six oxygens at distances 2.29 through 2.71 and two additional oxygens at 3.07 Å, the other by eight oxygens with distances of 2.35 through 2.88 Å.

The structure of babingtonite, arrangement of the silicate chains and cation polyhedra, is similar to rhodonite ($a = 7.682$, $b = 11.818$, $c = 6.707$ Å, $\alpha = 92.355°$, $\beta = 93.948°$, $\gamma = 105.655°$, $Z = 10$ (Mn, Ca)SiO_3, $P\bar{1}$).

THE ORIGIN OF PLAGIOCLASE SATELLITES

K. Toman, *Wright State University, Dayton, Ohio* and A. J. Frueh, *University of Connecticut, Storrs, Connecticut.*

According to our calculations $\langle J \rangle$, the intensity-average ratios (intensity averages corrected for the influence of atomic scattering factors) of "difference" reflections in a crystal with superstructure depend on the square of $|B_H|$, the length of the reciprocal vector, as $\langle J \rangle = \alpha + \beta |B_H|^2 - \gamma |B_H|^4$, where α involves electron-density differences and β and γ atomic position differences among quasi equivalent atoms in different subcells.

This theory was applied to our measurement of "e" and "f" satellite intensity on a plagioclase with 55% anorthite. The results show that the largest contribution to satellite intensity comes from differences in positions of atoms in different subcells, but that there is a high probability of ordering of Ca and Na ions. Our results are compared with Korekawa-Jagodzinski's and Megaw's models of plagioclase.

CRYSTAL STRUCTURE OF A LUNAR PLAGIOCLASE OF COMPOSITION An84[1]

Daniel E. Appleman, *U. S. Geological Survey, Washington, D. C. 20242*

A crystal-structure refinement has been carried out on a plagioclase-feldspar single crystal from Apollo 12 lunar igneous rock 12038. The crystal is triclinic, $P\bar{1}$; $a = 8.180(3)$, $b = 12.874(3)$, $c = 14.196(3)$Å, $\alpha = 93.45(2)$, $\beta = 116.06(2)$, $\gamma = 90.63(2)°$; approximate cell contents $8[(Ca_{0.834}Na_{0.161}Mg_{0.021}Fe_{0.011}K_{0.004})\ (Al_{1.784}Si_{2.176}Fe_{0.016}Ti_{0.003})\ O_8]$. Reflections with $(h + k)$ even, l even (a reflections) are strong and sharp; b reflections [$(h + k)$ odd, l odd] are moderately strong and slightly diffuse; c reflections [$(h + k)$ even, l odd] are extremely weak and very diffuse, making almost continuous streaks parallel to b^*; d reflections [$(h + k)$ odd, l even] are not observable. Several "split b" or "e"-type satellite reflections are present. Refinement was carried out by Fourier and least-squares methods using 4164 measured X-ray diffraction maxima of types a and b; type c reflections are too weak to measure. The resulting structure is very similar, even in detail, to that found by Fleet, Chandrasekhar and Megaw (*Acta Cryst.* 21, 1966, p. 782) for a terrestrial bytownite of composition An80. The general ordering scheme for Al/Si appears to be the same, and the Ca/Na distribution is consistent with that tentatively proposed for bytownite. The degree of order is apparently somewhat less than the maximum permitted by the composition and space group. The observed diffraction effects are consistent with the hypothesis that the crystal consists of a mosaic of small, anorthite-like domains with identical structures, but displaced by the translation $(a + b + c)/2$, thus causing the extreme diffuseness or absence of reflections with $(h + k + l)$ odd.

[1] Publication authorized by the Director, U. S. Geological Survey. Work carried out in cooperation with the National Aeronautics and Space Administration.