on the c axis as the X-ray data indicate; instead they zig-zag almost perpendicularly to the c_0 axis and at room temperature already form zig-zag chains. Since the vibrations of the vanadium atoms are isotropic in the basal plane, their zig-zag does not have any preferential direction in this plane. At the ~250 K transition the dynamical distortion of the vanadium sublattice becomes static and the distortion takes place only in one well defined direction.

This anisotropy drives the distortion of the other two sublattices in order to have local charge balance in the structure and the crystal symmetry becomes orthorhombic. This model of a transition from a dynamical to a static distortion is based on the assumption that the space group of the orthorhombic structure is either $Cmc2_1$ or $C222_1$, for which the vanadium positions are $(0yz)$ with $y \simeq 0$, $z \simeq 0$ and $(x00)$ with $x \simeq 0$, respectively, and consequently the centrosymmetric $Cmcm$ space group can be eliminated.

The large thermal vibrations of the vanadium atoms in the hexagonal phase could also be explained by a static distortion of the vanadium sublattice in the hexagonal matrix of the other two sublattices. The distortion would not have a long-range order and the classical X-ray structure determination would yield a hexagonal arrangement for the vanadium sublattice

with large thermal vibrations. However, the low R factor (1·1%) seems to indicate that the structure as determined from X-ray single-crystal data is not an average structure and thus the disordered static model can be rejected.

References

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

FRIEDEL, G. (1964). *Leçons de Cristallographie.* Paris: Blanchard.

GARDNER, R. A., VLASSE, M. & WOLD, A. (1969). *Acta Cryst.* **B25**, 781–787.

MASSENET, O., BUDER, R., SINCE, J. J., SCHLENKER, C., MERCIER, J., KELBER, J. & STUCKY, D. G. (1978). *Mater. Res. Bull.* **13**, 187–195.

MASSENET, O., SINCE, J. J., MERCIER, J., AVIGNON, M., BUDER, R., NGUYEN, V. D. & KELBER, J. (1979). *J. Phys. Chem. Solids*, **40**, 573–577.

SAYETAT, F., CHENAVAS, J., GHEDIRA, M. & MAREZIO, M. (1981). In the press.

TAKANO, M., KOSUGI, H., NAKANISHI, N., SHIMADA, M., WADA, T. & KOIZUMI, M. (1977). *J. Phys. Soc. Jpn*, **43**, 1101–1102.

The Structure of Synthetic Andersonite, Na₂Ca[UO₂(CO₃)₃].xH₂O (x ≈ 5·6)

By Alessandro Coda,* Antonio Della Giusta† and Vittorio Tazzoli

Centro di Studio per la Cristallografia Strutturale del Consiglio Nazionale delle Ricerche, Istituto di Mineralogia dell'Università, Via Bassi 4, 27100 Pavia, Italy

Abstract

Na₂Ca[UO₂(CO₃)₃].xH₂O ($x \simeq 5\cdot6$), $M_r = 644$, is trigonal, $R\bar{3}m$, $a = 17\cdot902$ (4), $c = 23\cdot734$ (4) Å, $Z = 18$, $D_m = 2\cdot8$, $D_c = 2\cdot86$ Mg m⁻³, $F(000) = 5400$, $T = 295$ K. It is found as the mineral andersonite. The structure was solved by use of a synthetic sample, and refined anisotropically to $R_w = 4\cdot9\%$ by full-matrix least-squares methods based on 794 independent counter reflections. The coordination polyhedron of U is a hexagonal bipyramid with two apical O atoms much closer to U than the others [1·81 (2) and 1·78 (2) Å, angle 180 (1)°], and six equatorial O atoms belonging to three bidentate CO₃²⁻ anions. Two independent Na atoms and one Ca have coordination numbers 6, 6 and 7 respectively. Only five water molecules in the formula were found in the final Fourier map; the possible statistical distribution of the remainder in a structure channel is discussed.

Introduction

Andersonite is a rare uranyl carbonate (tricarbonatodioxouranate) found in the Hillside mine, Yavapai

---

* Permanent address: Istituto di Cristallografia dell'Università, Viale Taramelli 16, 27100 Pavia, Italy.

† Permanent address: Istituto di Mineralogia dell'Università, Palazzo delle Scienze, Corso Europa, 16132 Genova, Italy.

County, Arizona; the formula was given as $Na_2Ca[UO_2(CO_3)_3].6H_2O$ by Axelrod, Grimaldi, Milton & Murata (1951). The crystal chemistry of uranyl carbonates (Čejka, 1965) is interesting as they seem to play a role in U geochemical migration and in U fixation in limestones. An unrefined crystal structure determination of synthetic andersonite, based on precession data of poor quality, was presented several years ago (Coda, 1963); one of the six water molecules was missing in the Fourier map; hence an accurate water-content determination and a new crystal structure analysis, with data of better quality, was planned.

Experimental

No natural crystals suitable for single-crystal X-ray determination were available. By addition of a solution of uranyl nitrate to a solution of potassium carbonate and then, at neutrality, of a solution of sodium and calcium nitrates, synthetic andersonite is easily obtained when left to stand; its powder diffraction profile and that of the mineral are identical. The growth of crystals for X-ray diffraction is difficult; the best results were obtained by slow ionic diffusion from the solution, through pure water, against an ethanol layer. The crystals are yellow-green, fluorescent, pseudocubic rhombohedra, each with a small pinacoid normal to the threefold axis.

A manual GEC diffractometer with a scintillation counter was used. Accurate lattice constants were determined with Ni-filtered Cu $K\alpha$ radiation (θ values of nine reciprocal-lattice central rows were measured and their d's were extrapolated to $\theta = 90°$; the constants were calculated by least squares). The measurement of the intensities was carried out with the $\omega-2\theta$ technique (Table 1). Two standard reflections were monitored every 3 h, with no variations about the means exceeding 1·5%. The standard deviations of the intensities were based on counting statistics; the more

asymmetric the backgrounds, the less reliable were considered the measurements. (Table 1).

The intensities were corrected in the usual way; the crystal was approximated to a sphere with the same volume as the rhombohedron (radius 0·065 mm); transmission factors were applied (range 1–1·2). No extinction effects were detected.

Structure determination and refinement

The structure was solved by inspection of a three-dimensional Fourier synthesis phased with the U coordinates of Coda (1963).

The final weighted R_w factor was 0·049 after three cycles of weighted anisotropic least-squares refinement with a modified Busing, Martin & Levy (1962) ORFLS program. Scattering factors for neutral atoms (analytical approximation) were used; an anomalous-dispersion correction for Mo $K\alpha$ radiation was applied to U, Ca and Na (International Tables for X-ray Crystallography, 1974). The refinement of the secondary-extinction coefficient yielded a negligible negative figure, of the same order as its standard deviation; therefore no correction was applied in the final refinement.

The anisotropic thermal parameters are rather inaccurate, because of the U dominance; this is reflected in the imaginary components of C(2) and O(4). Nevertheless, anisotropic refinement was applied, in order to obtain a cleaner final ΔF Fourier map. However, no particular meaning can be ascribed to the individual anisotropic parameters, with the exception of U. The final coordinates and equivalent isotropic

Table 1. *Crystal and diffraction data for* $Na_2Ca[UO_2-(CO_3)_3].5.6H_2O$

Space group: $R\bar{3}m$, from reciprocal-lattice symmetry and morphological considerations; confirmed by the structure analysis
Crystal: rhombohedron, edge 0·105 mm
Radiation: Mo $K\alpha$, Zr-filtered, $\lambda = 0.7107$ Å
$\mu = 13.8$ mm^{-1}, $\mu R = 0.90$ (see text)
Scan speed: 2° min^{-1}
Scan angular range: $1.2° \leq \Delta\omega \leq 2°$, according to the peak intensity
Total background counting time: equal to the scan measuring time; stationary counter–stationary crystal
θ range: 2–20°
Maximum (sin $\theta)/\lambda$: 0·481 Å^{-1}
Number of independent measured reflections: 794
$\sigma(I) = [I + (B_1 + B_2)B_1/B_2]^{1/2}$; B_1 and B_2 are the two backgrounds at the integration extremes, with $B_1 \geq B_2$

Table 2. *Atomic coordinates*

In this and all subsequent tables estimated standard deviations are shown in parentheses. M is the multiplicity and S the point symmetry. The figures given in the last column (B_H in Å^2) represent the equivalent isotropic thermal parameters (Hamilton, 1959).

	M	S	x	y	z	B_H
U	18	m	0·22372 (4)	−0·22372	0·01171 (5)	1·76 (4)
Ca	18	m	0·5442 (2)	−0·5442	0·0566 (3)	1·9 (2)
Na(1)	18	m	0·1842 (4)	−0·1842	0·1622 (5)	2·9 (4)
Na(2)	18	m	0·1271 (5)	−0·1271	0·8912 (5)	3·6 (4)
O(1)	18	m	0·2621 (7)	−0·2621	0·8471 (8)	2·3 (1)
O(2)	36	1	0·5061 (9)	0·3134 (9)	0·0708 (6)	2·6 (7)
O(3)	36	1	0·2706 (9)	0·3857 (9)	0·0859 (5)	2·3 (6)
O(4)	36	1	0·3664 (9)	0·4594 (9)	0·0193 (6)	2·6 (7)
O(5)	36	1	0·4067 (9)	0·4133 (9)	0·0948 (6)	2·5 (7)
O(6)	18	m	0·2746 (7)	−0·2746	0·0489 (8)	3·3 (7)
O(7)	18	m	0·1735 (7)	−0·1735	0·9757 (8)	2·8 (7)
$H_2O(1)$	18	m	0·5605 (7)	−0·5605	0·1622 (7)	2·3 (6)
$H_2O(2)$	18	m	0·4093 (6)	−0·4093	0·1379 (7)	2·2 (6)
$H_2O(3)$	18	m	0·403 (1)	0	0·5000	2·8 (7)
$H_2O(4)$	36	1	0·183 (1)	0·192 (1)	0·0593 (6)	4·9 (9)
C(1)	18	m	0·255 (1)	−0·255	0·901 (2)	4·0 (1)
C(2)	36	1	0·349 (1)	0·421 (1)	0·066 (1)	2·0 (1)

temperature factors (Hamilton, 1959) are given in Table 2.*

The water content

In the final well phased F_{obs} or ΔF Fourier maps there appears no trace of one of the six water molecules in the formula $Na_2Ca[UO_2(CO_3)_3].6H_2O$ proposed by Axelrod et al. (1951). Therefore, a re-determination of the water content of andersonite by chemical and/or thermal-analysis methods seemed advisable. Combined TH–DTG–DTA data collection (respectively, thermal weight change, rate of weight change and rate of enthalpy change), and a simultaneous determination of CO_2 leaving the heated sample by means of a continuous-titrating device, were performed by Paulik (1966) at the Institute of General Chemistry in Budapest by using his Derivatograph. They are in very good agreement with Čejka's (1969) independent determinations, discussed in a paper on thermal decomposition of tricarbonatodioxouranates. Further important results were obtained by Urbanec & Čejka (1979).

Čejka (1980) points out that in the preceding communication the calculations must be corrected by replacing Na_2CaUO_5 for Na_2CaUO_4, and summarizes all the previous investigations as follows: several decomposition processes exist and are overlapping, and therefore it is not easy to draw definitive conclusions about the reaction scheme; however, correlation of results obtained with different methods shows that the water content in synthetic andersonite ranges from 5·4 to 5·8 molecules, and never reaches $6H_2O$; thus the average content may be settled as $5·6H_2O$.

Description of the structure

The molecular dimensions are reported in Table 3; an ORTEP plot of the structure, showing the Na(1), Na(2) and Ca coordination polyhedra, with their connections, is given in Fig. 1.

The characteristic anionic unit is the already known $UO_2(CO_3)_3^{4-}$ (Mazzi & Rinaldi, 1961; Cromer & Harper, 1955; Graziani, Bombieri & Forsellini, 1972): the U coordination number is 8; U is surrounded by a hexagonal-bipyramidal polyhedron, with two apical O atoms having U—O distances much shorter than the six equatorial ones; the equatorial coordination is formed by three bidentate CO_3^{2-} anions: only in rutherfordine

* Lists of structure factors, anisotropic thermal parameters and details of the analysis of the thermal ellipsoids have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35907 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Interatomic distances (Å) and angles (°)

The single and double primes before groups of atoms mean that the distance or angle involved occurs once or twice respectively, by symmetry in the same coordination polyhedron; otherwise the prime on an atom denotes equivalence by symmetry to the atom without a prime.

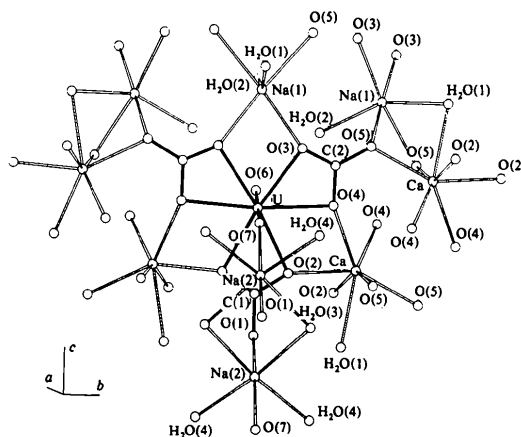|			
'U—O(6)	1·81 (2)	"O(2)—U—O(4)	65·6 (4)
'U—O(7)	1·78 (2)	"O(3)—U—O(4)	53·8 (4)
"U—O(2)	2·41 (1)	'O(2)—U—O(2')	53·2 (7)
"U—O(3)	2·44 (1)	'O(3)—U—O(3')	69·6 (7)
"U—O(4)	2·46 (1)	'O(6)—U—O(7)	179·6 (9)
'C(1)—O(1)	1·29 (4)	"O(1)—C(1)—O(2)	122 (2)
"C(1)—O(2)	1·27 (2)	'O(2)—C(1)—O(2')	116 (3)
'C(2)—O(3)	1·31 (2)	'O(3)—C(2)—O(4)	119 (2)
'C(2)—O(4)	1·26 (2)	'O(3)—C(2)—O(5)	119 (2)
'C(2)—O(5)	1·29 (2)	'O(4)—C(2)—O(5)	122 (2)
"Na(1)—O(3)	2·30 (2)	'Na(2)—O(1)	2·43 (2)
"Na(1)—O(5)	2·46 (2)	'Na(2)—O(7)	2·47 (2)
'Na(1)—H₂O(1)	2·43 (2)	"Na(2)—H₂O(3)	2·53 (2)
'Na(1)—H₂O(2)	2·40 (2)	"Na(2)—H₂O(4)	2·43 (2)
"Ca—O(2)	2·31 (1)	"Ca—O(4)	2·38 (1)
"Ca—O(5)	2·36 (1)	'Ca—H₂O(1)	2·55 (2)

Fig. 1. ORTEP plot (Johnson, 1965) of the crystal structure of andersonite, showing the U, Na(1), Na(2) and Ca coordination polyhedra. The projection plane forms an angle of 17° with the O(6)—U—O(7) axis.

(Cromer & Harper, 1955) is the same kind of coordination obtained with two bidentate and two unidentate CO_3^{2-} groups. The UO_2^{2+} ion, always linear, is known in a great number of uranyl chelate complexes (Cattalini, Croatto, Degetto & Tondello, 1971), with U—O distances ranging between 1·6 and 1·8 Å.

In andersonite the O(6)—U—O(7) angle in UO_2^{2+} is 180 (1)°, and the linearity is not due to symmetry constraints. The apical U—O distances are similar: U—O(6) = 1·81 (2) and U—O(7) = 1·78 (2) Å. The distances of O(6) and O(7) from the least-squares plane of the U and equatorial O atoms (Table 4) are 1·77 (2) and 1·81 (2) Å respectively; the angle between this plane and the linear UO_2^{2+} is 87·5 (1)°.

Table 4. *Distances (Å) from the best plane involving the U and equatorial atoms*

Primes are as in Table 3. The least-squares U–equatorial-atom plane has been calculated by interpolation of U, "O(2), "O(3), "O(4).

'U	−0·03 (1)	'C(1)	−0·33 (3)	'O(6)	1·77 (2)
"O(2)	−0·09 (2)	'O(1)	−0·71 (2)	'O(7)	−1·81 (2)
"O(3)	−0·11 (2)	"C(2)	0·17 (3)		
"O(4)	0·21 (2)	"O(5)	0·37 (2)		

In andersonite the $UO_2(CO_3)_3^{4-}$ ion is cut by a mirror plane, passing through the atoms of the uranyl ion. The equatorial U—O distances are in the range 2·41–2·46 (1) Å. The U–equatorial O atoms ensemble is only approximately planar (Table 4); moreover, the distances of the $UO_2(CO_3)_3^{4-}$ non-U-bound atoms from the best plane show rather tilted CO_3^{2-} anions, in opposite directions; the two equivalent ones are less tilted than the third.

Each Na(1), Na(2) and Ca coordination polyhedron is crossed by a mirror plane. They exhibit coordination numbers 6, 6 and 7 respectively. The only connections between them, as shown in Fig. 1, are between Ca and Na, by sharing an $O(5)$–$O(5')$–$H_2O(1)$ face, and between two Na's by sharing an $H_2O(3)$–$H_2O(3')$ edge.

Concerning water molecules, we already know that one sixth were undetectable in Fourier maps. Table 5 shows selected distances and angles between O atoms that could be ascribed to H bonds: only those shorter than 3·01 Å are listed [the next shortest distance is $H_2O(1)$–$H_2O(4) = 3·09$ Å].

The distance $H_2O(1)$–$O(1) = 2·91$ Å is between different coordination polyhedra and very likely it is the only H bond from $H_2O(1)$. An H-bond system consistent with symmetry cannot be drawn; in particular, the $H_2O(2)$ and $O(6)$ atoms lie on mirror planes, and then only a statistical distribution of the $H_2O(2)$ H atoms can be postulated.

Discussion

The analysis of ionic strengths, although only of qualitative value, can help to provide some indications on the lack of charge balance, so that a starting hypothesis on the missing water molecules can be drawn. The calculation, sketched in Table 6, is based on Brown & Wu's (1976) coefficients. Concerning the contribution of H bonds, the appropriate ionic-strength gain or loss [based on Brown's (1976) plot *versus* H···O distance] was applied; however, no contribution was taken into account when the H bond involved two water molecules equivalent by symmetry.

Table 6 shows one 'pathological' oxygen: O(1); its low ionic strength suggests that a strong H bond – with

Table 5. *Selected distances (Å) and angles (°) between O atoms*

Only distances not longer than 3·01 Å and angles between 85 and 125° have been included. Distances marked with an asterisk are within the same coordination polyhedron.

$H_2O(1)$–O(1)	2·91 (2)	O(1)–$H_2O(1)$–O(2)	91 (2)
*$H_2O(1)$–O(2)	2·92 (2)	O(1)–$H_2O(1)$–O(5)	96 (2)
*$H_2O(1)$–O(5)	3·01 (2)	O(2)–$H_2O(1)$–O(5)	99 (2)
$H_2O(2)$–$H_2O(2')$	2·72 (2)	O(6)–$H_2O(2)$–$H_2O(2')$	122 (2)
$H_2O(2)$–O(6)	3·01 (2)	$H_2O(2)$–$H_2O(2')$–$H_2O(2'')$	97 (2)
$H_2O(3)$–O(5)	2·88 (2)	O(5)–$H_2O(3)$–O(5')	91 (2)
$H_2O(4)$–$H_2O(4')$	2·83 (3)	$H_2O(4)$–$H_2O(4')$–$H_2O(4'')$	95 (2)

Table 6. *Ionic strengths of O atoms*

Each O on the left is bound to the atoms shown in the central column (through H bonding if an O appears here). No contribution is calculated for water–water interactions.

		Ionic strength
O(1)	C(1), Na(2), $H_2O(1)$	1·62 e
O(2)	C(1), Ca, U	2·25
O(3)	C(2), Na(1), U	1·93
O(4)	C(2), Ca, U	2·21
O(5)	C(2), Na(1), Ca, $H_2O(3)$	1·94
O(6)	U, $H_2O(2)$	1·85
O(7)	Na(2), U	2·04
$H_2O(1)$	Ca, Na(1), O(1), 2H	2·25
$H_2O(2)$	Na(1), $H_2O(2)$, O(6), 2H	2·08
$H_2O(3)$	Na(2), O(5), 2H	2·00
$H_2O(4)$	$H_2O(4)$, 2H	2·00

the water molecules not found in the Fourier maps – is very likely.

The structure exhibits a wide channel along the threefold axis, and the hypothesis can be put forward that the missing water is statistically 'dispersed' in it. The δ curve in Fig. 2 shows that a point lying on the threefold axis has a distance from the nearest atom ranging between 1·7 and 3·7 Å. Each symbol on the left represents – in every interval along c – the atom nearest to a point on the threefold axis in the same interval, and the distance is given by δ; the broken line represents the minimum H bond. The ρ curve shows the final ΔF electron density along the threefold axis; a broken line indicates the average O electron density. The matching of δ and ρ information may suggest the preferred water positions, since positive ρ peaks coinciding with short δ distances can be found, in theory, only with H-bonding atoms.

In practice, some reserve is necessary, as we are searching for a statistical water molecule, *i.e.* a fraction of O electron density, in a Fourier map dominated by U. With this limitation in mind, Fig. 2 suggests $H_2O(2)$, O(1) and O(6) as the only H-bonding candidates. Instead, the $H_2O(1)$ peak corresponds to a long distance, whereas the C(1) negative peak is consistent
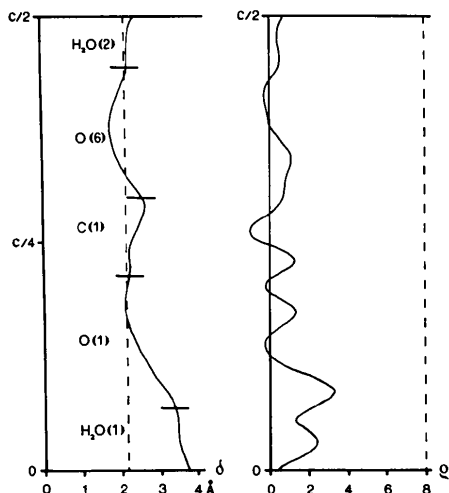
Fig. 2. Plots of: δ, minimum distances from the threefold axis (the broken line represents the minimum H bond); ρ, electron density, on a relative scale, along the same axis, in the interval $0 \leq z \leq \frac{1}{2}$ (the broken line represents the average O electron density).

with the inability of C to form H bonds. There is no evidence in disagreement with our hypothesis, and – with caution – the more likely locations of the last water molecule may be inferred.

Probably, the water distributed in the channel is important for the stability of the entire crystal building.

References

AXELROD, J. M., GRIMALDI, F. S., MILTON, C. & MURATA, K. J. (1951). Am. Mineral. 36, 1–22.

BROWN, I. D. (1976). Acta Cryst. A32, 24–31.

BROWN, I. D. & WU, K. K. (1976). Acta Cryst. B32, 1957–1959.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

CATTALINI, L., CROATTO, U., DEGETTO, S. & TONDELLO, E. (1971). Inorg. Chim. Acta. Rev. 5, 19–43.

ČEJKA, J. (1965). Sb. Vys. Šk. Chem. Technol. Praze Mineral. 7, 75–144.

ČEJKA, J. (1969). Collect. Czech. Chem. Commun. 34, 1635–1656.

ČEJKA, J. (1980). Private communication.

CODA, A. (1963). Atti Accad. Naz. Lincei Rend. Cl. Sci Fis. Mat. Nat. Sez. 8a, 34, 299–304.

CROMER, D. T. & HARPER, P. E. (1955). Acta Cryst. 8, 847–848.

GRAZIANI, R., BOMBIERI, G. & FORSELLINI, E. (1972). J. Chem. Soc. Dalton Trans. pp. 2059–2061.

HAMILTON, W. C. (1959). Acta Cryst. 12, 609–610.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–101, 149–150. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MAZZI, F. & RINALDI, F. (1961). Period. Mineral. 30, 1–20.

PAULIK, F. (1966). Private communication.

URBANEC, Z. & ČEJKA, J. (1979). Zb. Celostatnej Konf. Term. Anal. 8th (Proc. 8th All-State Conf. on Thermal Analysis, Vysoké Tatry), pp. 213–216. Bratislava: Slov. Chem. Spolocnost SAV.

Orthorhombic Gadolinium Nickel Silicide Gd₃NiSi₂ with a Filled-up Hf₃P₂ Structure Type

BY K. KLEPP AND E. PARTHÉ

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève 4, Switzerland

Abstract

Gd_3NiSi_2 is orthorhombic, space group $Pnma$, with $a = 11 \cdot 398$ (4), $b = 4 \cdot 155$ (1), $c = 11 \cdot 310$ (1) Å, $Z = 4$, $D_x = 7 \cdot 27$ Mg m^{-3}, μ(Mo $K\alpha$) $= 41 \cdot 5$ mm^{-1}, $F(000) = 992$. $R = 0 \cdot 059$ (542 F_o). The rare-earth atoms form trigonal prisms centered by Ni and Si atoms. The Gd and Si arrangement corresponds to that for Hf and P reported for Hf_3P_2. The Ni atoms occupy trigonal prismatic holes leading to the formation of infinite isotactic Si branched chains, $-Si-Ni(Si)-$, running parallel to b. The trigonal prisms are deformed in a