Sn(2^v) bridges to form the two-dimensional zigzag $(Sn_4)_\infty$ atom band.

The structure of V_2Sn_2Ga described above is quite different from those of two other *Va*–Sn–Ga (*Va* = Ta, Nb, V) ternary compounds, Ta_5SnGa_2 (Ye, Horiuchi, Shishido, Ukei & Fukuda, 1990) and Nb_5Sn_2Ga (Ukei *et al.*, 1989). This can explain their different physical properties. One of the common points among the structures of *Va*—Sn—Ga compounds is the coordination of *Va* atoms which form characteristic 'columns' or 'bands' such as $(Ga_2Ta_8)_\infty$, $(Ga_2Nb_8)_\infty$ and $(GaV_2)_\infty$ in the structures. Sn atoms always play a role of filling those columns or bands.

For convenience of description, we have described the structure as if the specimen used for the structure analysis were V_2Sn_2Ga. In fact, scanning electron microscopic energy-dispersive spectroscopic analysis of the specimen showed the chemical composition to be $V_{1{\cdot}67}Sn_{1{\cdot}67}Ga$ and this result has been previously reported as a chemical formula of $V_5Sn_5Ga_3$ (Ye, Horiuchi, Shishido, Toyota, Ukei, Sasaki & Fukuda, 1990). This compound is considered to be one where 4% V and Sn of V_2Sn_2Ga are substituted by Ga atoms. Therefore, the compound is essentially V_2Sn_2Ga.

We thank Professor M. Tokonami for his encouragement, and also Professor K. Hiraga and Dr K. Ukei for valuable discussions.

References

FINGER, L. W. (1969). *Carnegie Inst. Washington Yearb.* **67**, 216–217.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

SHISHIDO, T., YE, J., TOYOTA, N., UKEI, K., SASAKI, T., HORIUCHI, H. & FUKUDA, T. (1989). *Jpn. J. Appl. Phys.* **28**, 1519–1520.

UKEI, K., SHISHIDO, T. & FUKUDA, T. (1989). *Acta Cryst.* C**45**, 349–350.

YE, J., HORIUCHI, H., SHISHIDO, T., TOYOTA, N., UKEI, K., SASAKI, T. & FUKUDA, T. (1990). *J. Cryst. Growth*, **99**, 969–974.

YE, J., HORIUCHI, H., SHISHIDO, T., UKEI, K. & FUKUDA, T. (1990). *Acta Cryst.* C**46**, 1193–1195.

Acta Cryst. (1990). C**46**, 1197–1199

Structure of Gadolinium Monosilicide

BY D. A. NAGAKI AND A. SIMON*

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, *D*-7000 *Stuttgart* 80,
Federal Republic of Germany

(*Received* 1 *August* 1989; *accepted* 16 *October* 1989)

Abstract. Single crystals of GdSi grown in an iodide flux. M_r = 185·34, orthorhombic, *Pnma*, a = 7·973 (3), b = 3·858 (2), c = 5·753 (2) Å, V = 177·0 (1) Å^3, Z = 4, D_x = 6·95 g cm^{-3}, λ = 0·71069 Å, μ = 38·6 mm^{-1}, $F(000)$ = 311·9, T = 295 K, R = 0·0295, wR = 0·0292 for 279 independent reflections with $F_o > 3\sigma(F_o)$. The compound has FeB-type structure. The Gd—Gd interatomic distances range from 3·643 (1) to 4·281 (1) Å. The Si atom has seven Gd neighbors forming a capped trigonal prism at distances 2·985 (2) to 3·158 (2) Å and two Si neighbors, both at a distance of 2·490 (3) Å. The Si—Si—Si angle is 101·6 (2)°.

Introduction. New ternary halide silicides, Gd_4I_5Si and Gd_3I_3Si, can be prepared by reaction of GdI_3, Gd and Si (Nagaki, Simon & Borrmann, 1989). The products were normally multiphasic and vigorously decomposed by water. Black malleable needles were found in the residue which were stable in air and showed no visible reactivity with H_2O over a period of hours. The crystals were identified as GdSi *via* Guinier films followed by a single-crystal investigation. We report on this investigation for two reasons. First, the structure is not known in detail. Second, iodide fluxes could serve as a valuable tool to grow crystals of binary rare-earth metal silicides at low temperature.

Experimental. Black ribbon-like crystals of GdSi were obtained by heating a mixture of Gd, GdI_3 and Si (mole ratio 7:5:3) in sealed Ta ampoules at 1273 K for 14 d, by-products besides Gd_4I_5Si were unreacted Gd and GdI_3 and GdOI. Single-crystal data were measured from a suitable single crystal which had the dimensions 0·40 × 0·10 × 0·02 mm and was mounted in a 0·3 mm glass capillary. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated

---

* To whom all correspondence should be addressed.

0108-2701/90/071197-03$03.00

Table 1. *Atomic coordinates* (× 10⁴) *and anisotropic displacement parameters* (Å² × 10⁴) *for* GdSi [*Pnma*, a = 7·974 (2), b = 3·859 (2), c = 5·752 (2) Å]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Gd(1)	1791 (1)	2500	3857 (1)	23 (5)	69 (5)	64 (5)	0	−4 (1)	0
Si(1)	5371 (4)	2500	6269 (4)	62 (14)	79 (14)	79 (14)	0	15 (8)	0

The anisotropic displacement exponent takes the form: $-2\pi^2(h^2a^2U_{11} + \ldots + 2hkabU_{12})$.

Mo $K\alpha$ radiation; cell parameters from 25 reflections (21·0 < 2θ < 33·0°); systematic absences consistent with *Pnma*; total of 1180 reflections measured with $4{\cdot}0 \leq 2\theta \leq 60{\cdot}0°$ in the range $-11 \leq h \leq 11$, $0 \leq k \leq 5$, $0 \leq l \leq 8$; no significant variation in intensity of one standard reflection; ω scan with a width of 1·20° + 0·35tanθ, detector aperture width 2·20 mm + 1·05tanθ; 279 unique reflections with $F_o > 3\sigma(F_o)$; linear absorption coefficient 38·6 mm^{-1}, empirical absorption correction applied on the basis of ψ scans of 8 reflections, $\Delta\psi$ = 10°, min., max. transmission coefficient 0·19, 0·38. The structure was refined on F by the full-matrix least-squares method to R = 0·0295, wR = 0·0292. $w = 1/[\sigma^2(F) + 0{\cdot}001F^2]$, GOF = 1·34; maximal final shift/e.s.d. ≤ 0·004; residual electron density 2 e Å^{-3}. All calculations were performed on a MicroVAX II using the *SHELXTL-Plus* package (Sheldrick, 1988); atomic scattering factors taken from *SHELXTL-Plus*.

Table 2. *Bond lengths* (Å)

Gd—Gd:	1—1*c*, 1—1*d*, 1*a*—1*e*, 1*a*—1*f*, 1*b*—1*f*, 1*c*—1*d*	3·643 (1)
	1*c*—1*f*, 1*d*—1*f*	3·689 (1)
	1*a*—1*b*, 1*c*—1*d*	3·858 (1)
	1—1*e*, 1*a*—1*c*, 1*b*—1*d*	4·281 (1)
Si—Gd:	1—1*a*, 1—1*b*	2·975 (3)
	1—1*c*, 1—1*d*	2·985 (2)
	1—1*f*	3·024 (2)
	1—1*e*	3·158 (2)
	1—1	3·174 (3)
Si—Si:	1—1*a*, 1—1*b*	2·490 (3)

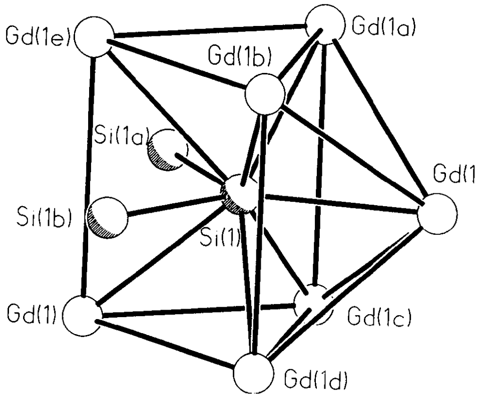

Fig. 1. Coordination polyhedron around the Si atom in GdSi. The interatomic distances are presented in Table 2. Si is 0·758 Å out of the plane formed by Gd atoms 1*a*, 1*b*, 1*c*, 1*d*.

Discussion. The FeB-type structure of GdSi had been established from photographic data (Hohnke & Parthé, 1966; Raman & Steinfink, 1967), but no positional parameters were available. The single-crystal investigation confirms the FeB-type structure. The lattice constants and atomic parameters are summarized in Table 1.* The structure consists of parallel chains of face-sharing elongated Gd_6 trigonal prisms that contain Si atoms at their centers. The coordination polyhedron is shown in Fig. 1 and significant interatomic distances are presented in Table 2. The structures of rare-earth metal monosilicides and their relation to other *AB*-type structures have been thoroughly discussed (Hohnke & Parthé, 1966; Raman & Steinfink, 1967; Raman, 1968; Parthé, 1981) as well as their derivation from an h.c.p. structure by periodic unit-cell twinning ('chemical twinning') (Andersson & Hyde, 1974; Hyde, Andersson, Baker, Plug & O'Keefe, 1979). Using the notation described by Parthé (1981), the following values were assigned to GdSi: s = 3·85 (1) Å, ω = 4·28 (1) Å, u = 3·090 Å, ω/u = 1·39, ω/s = 1·11 and α = 101·7 (2)°. The value for ω/s falls into the range 1·08–1·13 as expected for $\Delta = -1$ (Parthé, 1981).

Besides the trigonal prisms of the Gd atoms, the zigzag chains of Si atoms with short (2·49 Å) Si—Si distances are a characteristic feature of the GdSi structure. These chains are easily rationalized in terms of a simple picture of chemical bonding. From band-structure calculations for ternary iodide silicides (Nagaki, Simon & Borrmann, 1989), a description as $Gd^{3+}Si^{3-}$ is allowed at least with respect to the number of electrons available for bonding within the sublattices of Gd and Si, respectively. According to this description, strong heteropolar bonding between Gd and Si atoms occurs besides rather weak homonuclear bonding between the Si atoms. The weak homonuclear bonding can be specified somewhat more quantitatively: Taking the single-bond distance $d(1)$ = 2·35 Å from elemental Si, the Pauling bond order n (Pauling, 1973) for the chain distance

---

* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52735 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

2·49 ($2{\cdot}49 = 2{\cdot}35 - 0{\cdot}6 \log n$) corresponds to $n = 0{\cdot}58$, a value near 0·5 as expected for bonds between Si atoms from the above electronic balance.

The authors express thanks to Dr H. Borrmann for assistance with the single-crystal X-ray diffraction work.

References

Andersson, S. & Hyde, B. G. (1974). *J. Solid State Chem.* **9**, 92–101.

Hohnke, D. & Parthé, E. (1966). *Acta Cryst.* **20**, 572–582.

Hyde, B. G., Andersson, S., Baker, M., Plug, C. M. & O'Keefe, M. (1979). *Prog. Solid State Chem.* **12**, 273–327.

Nagaki, D. A., Simon, A. & Borrmann, H. (1989). *J. Less-Common Met.* In the press.

Parthé, E. (1981). *Structure and Bonding in Crystals*, Vol. II, edited by M. O'Keefe & A. Navrotsky, pp. 259–296. New York: Academic Press.

Pauling, L. (1973). *The Nature of the Chemical Bond and the Structure of Molecules and Crystals.* Ithaca, New York: Cornell Univ. Press.

Raman, A. (1968). *Inorg. Chem.* **7**, 973–976.

Raman, A. & Steinfink, H. (1967). *Acta Cryst.* **22**, 688–691.

Sheldrick, G. M. (1988). *SHELXTL-Plus Structure Determination Software Programs.* Nicolet Instrument Corporation, Madison, Wisconsin, USA.

Acta Cryst. (1990). C**46**, 1199–1202

Structure and Absolute Chirality of $Rb_4LiH_3(SO_4)_4$ at 293 K

By F. J. Zúñiga, J. Etxebarria, G. Madariaga and T. Breczewski*

Dpto. Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644,
Bilbao, Spain

(*Received* 1 *June* 1989; *accepted* 25 *September* 1989)

Abstract. Lithium tetrarubidium trihydrogentetrasulfate, $Rb_4LiH_3(SO_4)_4$, $M_r = 736{\cdot}1$, tetragonal, $P4_1$, $a = 7{\cdot}615\,(2)$, $c = 29{\cdot}458\,(5)$ Å, $V = 1708{\cdot}2\,(6)$ Å^3, $Z = 4$, $D_x = 2{\cdot}86$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 11{\cdot}63$ mm^{-1}, $F(000) = 1384$, $T = 293$ K, $R = 0{\cdot}042$, 4966 unique reflections. Crystals optically laevorotatory at 293 K belong to the enantiomorphic space group $P4_1$, rotatory power $\rho = -0{\cdot}28°$ mm^{-1} at $\lambda = 6330$ Å. The structure consists of tetrahedral sulfate groups arranged together with Rb atoms on layers stacked perpendicularly to the tetragonal axis.

Introduction. The title compound belongs to a new family of crystals with general formula $M_4LiH_3(XO_4)_4$ (M = K, Rb and X = S, Se), which exhibit phase transitions between 100 and 140 K.

For $Rb_4LiH_3(SO_4)_4$ crystals, the pyroelectric, dielectric, elastic and thermal properties in the temperature range 100 to 400 K have been reported (Wolejko, Piskunowicz, Breczewski & Krajewski, 1988; Wolejko, Pakulski & Tylczynski, 1988), confirming the existence of a ferroelastic phase transition at 132 K. From the behaviour of the measured physical properties, these authors have suggested that the transition is of second-order type and have assigned the symmetry change 4*mm*–*mm*2.

Mróz, Kiefte & Clouter (1988) have also reported experimental results on the behaviour of the velocity of phonons [101] and [011] through the transition, and have assigned the same sequence of point symmetry groups as above. On the basis of dielectric and heat capacity measurements, Hempel, Maack & Sorge (1989), have confirmed the second-order nature of the phase transition. However, the results obtained for the elastic-stiffness coefficients are not compatible with the previously mentioned point-group scheme. Consequently, these authors have proposed a 4–2 sequence for the point-group symmetry in this material.

On the other hand, a similar ferroelastic phase transition has also been found at 100 K in the analogous compound $Rb_4LiH_3(SeO_4)_4$ (Pietraszko & Lukaszewicz, 1988). It has been reported that the space group is $P4_1$ (or $P4_3$) at 293 K, and therefore (Aizu, 1972) the point-group sequence should be 4–2 in this case.

With the aim of clarifying the contradictory results published for the (Rb,S) compound, we have undertaken a crystallographic study. X-ray anomalous scattering together with optical-activity measurements have allowed us to determine the structure and absolute chirality of the material in the paraelastic phase. We will also present some preliminary results about the low-temperature phase.

Experimental. Crystals were grown isothermally at 310 K from an acid aqueous solution (pH < 1) of stoichiometric initial salts by using the dynamic method. Large colourless crystals, with a mor-

---

* On leave from the Institut of Physics, A. Mickiewicz University, Grunwaldzka 6, 60-70 Poznan, Poland.

0108-2701/90/071199-04$03.00