substituted by Sn atoms, while in another V*a*–Sn–Ga (V*a* = Ta, Nb, V) system compound, Nb_5Sn_2Ga, the 8(*h*) sites are all substituted by Sn atoms (Ukei *et al.*, 1989). The common point of the structures of these two compounds is that the 4(*a*) sites, at the centers of the Archimedean antiprisms, are always occupied by Ga atoms. This fact indicates that Ga atoms have a strong tendency to be coordinated by V*a* atoms to form a kind of polyhedron which characterizes the structure.

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Structure of V_2Sn_2Ga

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Abstract. Gallium ditin divanadium, $M_r = 408{\cdot}98$, orthorhombic, *Acam*, $a = 6{\cdot}7191$ (7), $b = 18{\cdot}798$ (2), $c = 5{\cdot}603$ (1) Å, $V = 707{\cdot}7$ Å^3, $Z = 8$, $D_x = 7{\cdot}68$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 27{\cdot}0$ mm^{-1}, $F(000) = 1416$, room temperature, final $R = 0{\cdot}044$, $wR = 0{\cdot}054$ for 794 unique reflections with $|F_o| > 3\sigma(F_o)$. The crystal structure of the title compound is a new type. It consists of two kinds of bands of linked GaV_5 pentagons and Sn-atom clusters which alternate along the *b* axis.

Introduction. V–Sn–Ga is a member of V*a*–Sn–Ga (V*a* = Ta, Nb, V) ternary systems, which have been the subject of our interest because most of the binary compounds composed of V*a*, Sn and Ga elements exhibit superconductivity, and also because the three-component diagrams of V*a*–Sn–Ga systems are not known. Research on the Ta–Sn–Ga system has been carried out by Ye, Horiuchi, Shishido, Ukei & Fukuda (1990) and on another member, Nb–Sn–Ga, by Ukei, Shishido & Fukuda (1989). In this work, we focused our concern on the V–Sn–Ga system and succeeded in synthesizing single crystals of V_2Sn_2Ga for the first time in the same way as that applied in the compounds of the Ta–Sn–Ga and Nb–Sn–Ga systems. Details of crystal growth and physical properties will be presented elsewhere. Here, we describe the structure determination of the title compound.

Experimental. Single crystals were synthesized by the self-component flux method (Shishido, Ye, Toyota, Ukei, Sasaki, Horiuchi & Fukuda, 1989). The crystal used for the single-crystal X-ray diffraction study was about $0{\cdot}12 \times 0{\cdot}06 \times 0{\cdot}21$ mm in size. Intensity data were collected on a Rigaku AFC-5 four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. The lattice parameters were refined from 25 reflections with $25 < 2\theta < 35°$. A total of 3212 reflections in the range $2 < 2\theta < 70°$ ($-10 \le h \le 10$, $-30 \le k \le 30$, $0 \le l \le 9$) were collected under the following conditions: ω–2θ-scan mode, scan width $\Delta\omega = (1{\cdot}1 + 0{\cdot}4\tan\theta)°$, scan speed (2θ) 4° min^{-1}. Two standard reflections, measured at an interval of 100 reflections, showed no significant fluctuation in intensity. Reflection data were corrected for Lorentz–polarization effects and an empirical absorption correction was applied. The minimum and maximum transmission factors were 0·26 and 0·51, respectively. After the above corrections, the intensities of symmetrically equivalent reflections were averaged to give 794 unique reflections with $|F_o| > 3\sigma(F_o)$.

The structure was solved with the aid of Patterson and Fourier syntheses. Full-matrix least-squares refinement of variable atomic coordinates with anisotropic temperature factors and an isotropic extinction coefficient, minimizing $\sum w(\Delta F)^2$ with $w = 1/\sigma^2(F_o)$, converged to $R = 0{\cdot}044$, $wR = 0{\cdot}054$ for

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Table 1. *Atomic parameters for* V_2Sn_2Ga

$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	Wyckoff notation	Occupancy	x	y	z	B_{eq} (Å^2)
V(1)	8 (*f*)	1·0	0·4684 (2)	0·07569 (8)	$\frac{1}{2}$	0·69
V(2)	8 (*e*)	1·0	$\frac{3}{4}$	0·15949 (8)	$\frac{1}{4}$	0·64
Ga	8 (*e*)	1·0	$\frac{3}{4}$	0·01814 (5)	$\frac{1}{4}$	0·82
Sn(1)	8 (*f*)	1·0	0·42472 (9)	0·11137 (3)	0	0·74
Sn(2)	8 (*f*)	1·0	0·42048 (9)	0·22207 (3)	$\frac{1}{2}$	0·71

Table 2. *Interatomic distances* (Å) *and angles* (°)

Ga—V(1)	2·591 (1)	Ga—V(1^{ii})	2·591 (1)
Ga—V(1^{i})	2·688 (2)	Ga—V(1^{iv})	2·688 (2)
Ga—V(2)	2·657 (2)	Ga—V(2^{ii})	3·861 (1)
Ga—Ga(ii)	2·8015 (9)	Ga—Ga(iv)	3·4281 (4)
Ga—Sn(1)	3·1322 (8)	Ga—Sn(1^{i})	3·044 (1)
V(1)—V(1^{i})	2·877 (2)	V(1)—V(1^{ii})	4·057 (2)
V(1)—V(2)	2·833 (2)	V(1)—Sn(1)	2·8955 (9)
V(1)—Sn(1^{ii})	2·725 (2)	V(1)—Sn(2)	2·771 (2)
V(2)—V(2^{ii})	2·8015 (9)	V(2)—Sn(1)	2·7490 (7)
V(2)—Sn(2)	2·8720 (8)	V(2)—Sn(2^{iii})	2·869 (1)
Sn(1)—Sn(1^{ii})	3·6553 (9)	Sn(1)—Sn(2)	3·4899 (9)
Sn(1)—Sn(2^{ii})	3·1161 (9)	Sn(1)—Sn(2^{v})	3·2993 (9)
Sn(2)—Sn(1^{ii})	3·1161 (9)	Sn(2)—Sn(2^{ii})	3·6189 (9)
Sn(2)—Sn(2^{iii})	3·5199 (9)	Sn(2)—Sn(2^{v})	3·1769 (9)

V(1)—Ga—V(1^{i})	66·02 (4)	V(1^{i})—Ga—V(1^{iv})	97·99 (5)
V(1)—Ga—V(2)	65·32 (5)	V(2)—Ga—V(2^{ii})	46·51 (4)
V(1)—V(2)—Ga	56·21 (5)	V(1)—V(2)—Sn(1)	62·48 (3)
V(1)—V(2)—Sn(2)	58·11 (4)	Sn(1)—V(2)—Sn(2)	76·73 (2)
Sn(2)—V(2)—Sn(2^{v})	67·20 (3)	Sn(2^{iii})—V(2)—Sn(2^{v})	78·21 (4)
Sn(1)—V(1)—Sn(2)	76·00 (4)	Sn(1)—V(1)—Sn(1^{ii})	81·07 (4)
Sn(1^{ii})—V(1)—Sn(2)	69·08 (5)		

Symmetry code: none x, y, z; (i) $-x, -y, -z$; (ii) $\frac{1}{2}-x, y, \frac{1}{2}+z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (iv) $\frac{1}{2}+x, 1-y, \frac{1}{2}-z$; (v) $1-x, \frac{1}{2}-y, \frac{1}{2}-z$.

794 unique reflections. $(\Delta/\sigma)_{max} = 0{\cdot}21$. Maximum and minimum electron density in final difference Fourier map were ± 3 e Å^{-3}. Isotropic secondary-extinction coefficient g_{iso} was refined to $0{\cdot}10\,(2) \times 10^{-8}$. Neutral atomic scattering factors with correction for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed with the use of the least-squares program *RFINE*2 (Finger, 1969) on a HITAC M680H computer of the University of Tokyo.

Discussion. Table 1 gives the final atomic coordinates and Table 2 the interatomic distances and selected angles.* The projection of the structure along the *c* axis is illustrated in Fig. 1.

The structure is basically composed of two kinds of atom bands which spread two-dimensionally perpendicular to the *b* axis. One of them consists of $(GaV_2)_\infty$ clusters while the other consists only of Sn atoms. These two bands alternate along the *b* axis.

The basic unit of the $(GaV_2)_\infty$ band is the GaV_5 pentagon which is formed by five V atoms at the apices of the pentagon and one Ga atom at the center. The Ga—V distances inside the pentagon range from 2·591 to 2·688 Å and are remarkably shorter than the others (average 3·120 Å), indicating relatively strong interactions between Ga and V atoms. These GaV_5 pentagons connect to each other in a zigzag manner by sharing edges to form the two-dimensionally spread $(GaV_2)_\infty$ band. In the Sn region, the distance Sn(1)—Sn(2^{ii}) [also Sn(2)—Sn(1^{ii})] is shorter than the other Sn—Sn distances. Thus, these four Sn atoms make a deformed Sn_4 tetrahedron and this may be regarded as the geometrical basic unit of the band. Each tetrahedron is linked to two neighbors by sharing edges to form an $(Sn_4)_\infty$ column running along the *c* axis. These columns are connected to each other *via* Sn(2)—

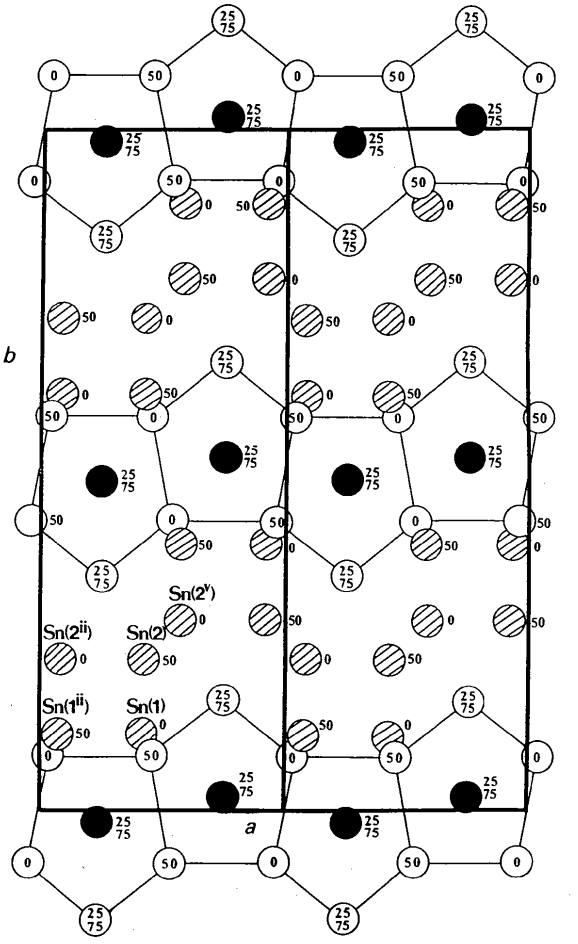

Fig. 1. Projection of the crystal structure of V_2Sn_2Ga along the *c* axis (two unit cells). Atom key: open circles V, filled circles Ga, shaded circles Sn. Numbers correspond to *z* parameters.

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52687 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$Sn(2^v)$ 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 V*a*–Sn–Ga (V*a* = 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 V*a*—Sn—Ga compounds is the coordination of V*a* 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 $V_{1.67}Sn_{1.67}Ga$ 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.

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Structure of Gadolinium Monosilicide

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Abstract. Single crystals of GdSi grown in an iodide flux. $M_r = 185{\cdot}34$, orthorhombic, *Pnma*, $a = 7{\cdot}973\ (3)$, $b = 3{\cdot}858\ (2)$, $c = 5{\cdot}753\ (2)$ Å, $V = 177{\cdot}0\ (1)$ Å^3, $Z = 4$, $D_x = 6{\cdot}95$ g cm^{-3}, $\lambda = 0{\cdot}71069$ Å, $\mu = 38{\cdot}6$ mm^{-1}, $F(000) = 311{\cdot}9$, $T = 295$ K, $R = 0{\cdot}0295$, $wR = 0{\cdot}0292$ 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 $0{\cdot}40 \times 0{\cdot}10 \times 0{\cdot}02$ mm and was mounted in a 0·3 mm glass capillary. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated

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