

## The crystal structure of $V_2Ga_5$

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With 3 figures

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### Auszug

Die Metallverbindung  $V_2Ga_5$  ist isotyp mit  $Mn_2Hg_5$ . Raumgruppe ist  $D_{4h}^5-P4/mbm$ ;  $a = 8,968 \text{ \AA}$ ,  $c = 2,693 \text{ \AA}$ ,  $Z = 2$ . Die Struktur wurde durch Betrachtungen über Kugelpackungen gefunden und auf Grund der  $(hk0)$ -Interferenzen verfeinert. Die  $z$ -Koordinaten ergaben sich durch semi-quantitative Vergleiche der beobachteten und berechneten Intensitäten der höheren Schichtlinien. Die Ga-Atome besetzen eine 8- und eine 2-zählige Lage mit  $z = 0$  und acht nächsten Nachbarn, die V-Atome eine 4-zählige Lage mit  $z = 1/2$  und zwölf nächsten Nachbarn.

### Abstract

The intermetallic compound  $V_2Ga_5$  is isotypic with  $Mn_2Hg_5$ , with space group  $D_{4h}^5-P4/mbm$ . The lattice is tetragonal:  $a = 8.968 \text{ \AA}$ ,  $c = 2.693 \text{ \AA}$ , with two formula units in the unit cell. The structure was solved by using packing considerations, and refinement of atomic positions using  $hk0$  data. The  $z$  coordinates were checked by semi-quantitative comparison of observed and calculated intensities for the upper levels. Gallium occupies 8- and 2-fold positions at  $z = 0$  with ten nearest neighbors, and vanadium a 4-fold position at  $z = 1/2$  with 12 nearest neighbors.

### Introduction

The vanadium-gallium system is of interest because  $V_3Ga$  is a high magnetic-field superconductor. During a study of the phase relations in the V—Ga system<sup>1</sup> an attempt was made by F. TRUMBORE to form  $V_3Ga$  from the liquid state by slowly cooling a vanadium solution

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<sup>1</sup> H. J. LEVINSTEIN and J. H. WERNICK, to be published.

rich in gallium from 1000°C. Needle-shaped crystals formed which did not appear to be  $V_3Ga$ . From x-ray fluorescence evidence a tentative formula of  $VGa_2$  was assigned to this alloy. However, during preliminary x-ray diffraction experiments it was decided that  $(VGa_2)_x$  could not be reconciled with the observed density and the volume of the unit cell. There was reason to believe that this alloy was somewhat richer in Ga, which agreed with the formula  $V_2Ga_5$ , reported by VAN VUCHT and coworkers<sup>2</sup>.

### Experimental

Weissenberg photographs using  $CuK\alpha$  radiation were taken of the  $hk0$  level. Also survey photographs of  $h0l$ ,  $h1l$ ,  $h2l$ ,  $h3l$  and  $h4l$  were taken with the precession camera, using  $MoK\alpha$  radiation. The lattice is tetragonal, with unit-cell dimensions  $a = 8.968 \text{ \AA}$ ,  $c = 2.693 \text{ \AA}$ . The most probable space group is  $D_{4h}^5-P4/mbm$  with two formula units per unit cell. On the basis of this the calculated density is  $6.907 \text{ g/cm}^3$ , compared to an observed density of about  $6.5 \text{ g/cm}^3$  by the method of Archimedes. The bulk material used in the density determination was quite porous, and the actual density is expected to be somewhat higher than measured. The density of  $V_2Ga_5$  is higher than either that of Ga ( $5.904 \text{ g/cm}^3$ ) or of V ( $5.96 \text{ g/cm}^3$ ) which indicates more efficient packing of the atoms in the intermetallic compound.

In view of the fact that  $c = 2.693 \text{ \AA}$ , no significant overlap can occur in the electron-density projection down this axis. Therefore, careful intensity measurements were made for the  $hk0$  zone only. The intensities were estimated visually by comparison with a photographic scale of known intensities.

### Structure determination

The space group  $P4/mbm$  has a mirror plane at  $z = 0$  and at  $z = 1/2$ , and all atoms must lie on them since the  $c$  axis is so short. The alternation of intensities on the  $h0l$  (and upper-level) photograph, with  $h00$  resembling  $h02$ ,  $h04$ , etc., but not  $h01$ , which itself resembled  $h03$ , etc., showed that some atoms lie at  $z = 0$  and some at  $z = 1/2$ .

<sup>2</sup> J. H. N. VAN VUCHT, H. A. C. M. BRUNING and H. C. DONKERSLOOT, New compounds related to the superconductors  $V_3Ga$  and  $Nb_3Sn$ . *Physics Letters* **7** (1963) 297.

From packing considerations, the best trial structure appeared to be:

2 Ga in (*d*)  $0, \frac{1}{2}, 0; \frac{1}{2}, 0, 0$ , site symmetry  $mmm$

8 Ga in (*i*)  $x, y, 0$  etc., site symmetry  $m$

4 V in (*h*)  $x, \frac{1}{2} + x, \frac{1}{2}$  etc., site symmetry  $mm$

A quick confirmation of the  $z$  coordinates was given by a calculation of the relative intensities of the 001, 002 and 003 reflections.

After correcting the 56 observed  $hk0$  reflections for Lorentz, polarization and absorption effects, a Patterson synthesis was computed. The positions of the gallium atoms were indicated unambiguously in this projection, whereas an approximate position for the vanadium atoms was indicated. A derivative-sharpened Patterson<sup>3</sup> (with a fraction of the normal sharpened Patterson added) was calculated in an attempt to resolve the V-Ga peaks better, but no significant improvement was noticed.

Wilson statistics for the determination of the scale factor and over-all temperature factor gave a value for  $B$  of about zero.

A least-squares refinement of the trial structure, using the Busing-Martin-Levy least-squares program<sup>4</sup>, with five variables (the three positional parameters plus the scale factor and over-all temperature factor) and unit weights, refined  $R$  from 38.3% to 15.9% in three cycles. At this point the three crystallographically independent atoms were given individual temperature factors (seven variables), which reduced  $R$  to 15.3% in three cycles. All three temperature factors were slightly negative, ranging from  $-0.53$  to  $-0.14$ .

A second, independent estimate of the intensities was made in the hope that this might reduce the errors responsible for the negative temperature factors.  $R$  was reduced to 14.4% in three cycles but the temperature factors were still around  $-0.5$ . Individual weights were given to all reflections at this point. As expected, the atomic positions remained virtually unchanged, while the scale factor and the temperature factor changed.  $R$  went from 14.4 to 14.9%, and weighted  $R$  from 15.6 to 22.0%. These last three cycles of refinement were accepted as final mainly because the temperature factors were now

<sup>3</sup> R. A. JACOBSON, J. A. WUNDERLICH and W. N. LIPSCOMB, The crystal and molecular structure of cellobiose. *Acta Crystallogr.* **14** (1961) 598–607.

<sup>4</sup> W. R. BUSING, K. O. MARTIN and H. A. LEVY, A Fortran crystallographic least-squares program. ORNL-TM-305 (1962).

Table 1. *Fractional coordinates and isotropic temperature factors*

	$x$	$\sigma_x$	$y$	$\sigma_y$	$z$	$\sigma_z$	$\beta$	$\sigma_\beta$
Ga(8-fold)	.29368	.00063	.56030	.00054	.00000	—	-.22	.28
Ga(2-fold)	.50000	—	.00000	—	.00000	—	-.06	.33
V(4-fold)	.31970	.00095	.81970	—	.50000	—	-.17	.35

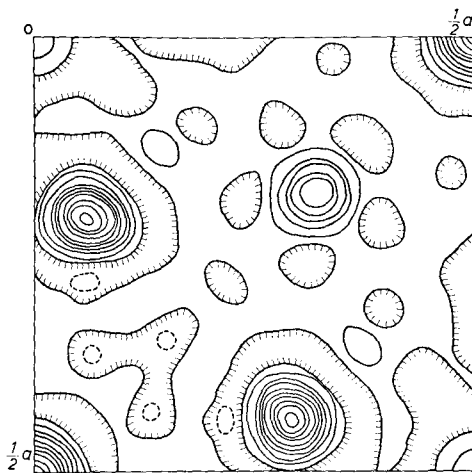


Fig. 1. Electron-density projection along  $c$ . Contours have been drawn at 10 electrons/ $\text{\AA}^2$ , starting at zero; negative contours have been drawn with dashed lines

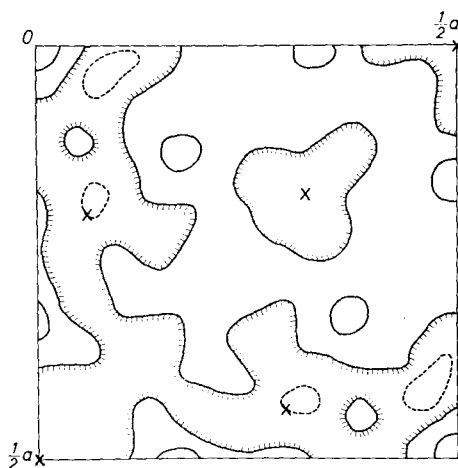


Fig. 2. Fourier difference synthesis of the projection along  $c$ . Contours start at zero and have been drawn at intervals of  $5e/\text{\AA}^2$ . Negative regions are indicated by dashed lines. Atomic positions are given by crosses

less than a standard deviation away from zero. Table 1 gives the final values of the parameters and their standard deviations. Fig. 1 shows the final electron-density map and Fig. 2 the final difference synthesis.

The question of the  $z$  coordinates was originally solved by packing considerations. Even though it has been observed that not all atoms have the same  $z$  coordinate, there are still three combinations possible. If we keep the 8-fold Ga arbitrarily at  $z = 0$ , then either of the remaining Ga and V can be at  $z = 1/2$ , or both. A semi-quantitative

Table 2. *Interatomic distances\**

1-10	2.689 ± .006 Å (Ga-Ga)	9-11	2.654 ± .010 Å (Ga-V)
1-7	2.959 ± .010 Å (Ga-Ga)	4-11	2.739 ± .006 Å (Ga-V)
1-11	2.698 ± .009 Å (Ga-V)	4-3	3.855 ± .011 Å (Ga-Ga)
1-4	2.726 ± .008 Å (Ga-Ga)		

$c = 2.693 \text{ \AA}$

\* See Fig. 3 for numbering system.

Table 3. *Angles between interatomic vectors\**

4-1-11	60° 39'	9-11-9'	60° 59'
7-1-11	56° 43'	4-11-4'	58° 53'
11-4-1	59° 10'	1-11-1'	59° 53'
9-4-11	58° 32'	11-1-1'	60° 4'
4-9-11	61° 42'	11-4-4'	60° 33'
7-11-1	66° 32'	11-9-9'	59° 31'
4-11-1	60° 11'	4-9-5	66° 48'
9-11-4	59° 47'	9-4-5	56° 36'

The standard deviations of the above angles are less than 30'. Atoms translated by  $c$  have been primed.

\* See Fig. 3 for numbering system.

Table 4. *Observed and calculated  $hk0$  structure factors*

$h k 0$	$ F_o $	$F_c$	$h k 0$	$ F_o $	$F_c$	$h k 0$	$ F_o $	$F_c$	$h k 0$	$ F_o $	$F_c$
2 0 0	11.2	-4.20	10 1 0	4.9	-4.98	5 3 0	31.2	25.14	5 5 0	46.5	-52.54
4 0 0	38.9	38.74	11 1 0	25.1	-24.51	6 3 0	43.2	-47.47	6 5 0	22.7	-19.89
6 0 0	26.6	18.02	2 2 0	25.0	-21.80	7 3 0	10.6	-9.17	7 5 0	32.6	-30.44
8 0 0	47.6	-53.24	3 2 0	33.7	36.40	8 3 0	26.2	21.71	8 5 0	27.0	25.83
10 0 0	24.4	21.65	4 2 0	36.7	36.11	9 3 0	5.6	1.62	9 5 0	31.8	-32.73
1 1 0	13.4	-6.64	5 2 0	5.0	2.71	10 3 0	-	-2.39	10 5 0	21.8	-20.43
2 1 0	7.2	-1.13	6 2 0	31.5	26.97	11 3 0	15.0	11.50	6 6 0	34.4	26.06
3 1 0	35.8	-36.47	7 2 0	23.2	16.45	4 4 0	25.6	21.68	7 6 0	15.6	14.62
4 1 0	66.8	81.95	8 2 0	38.0	39.78	5 4 0	26.2	-24.50	8 6 0	6.3	7.19
5 1 0	4.8	4.19	9 2 0	4.9	1.91	6 4 0	5.6	3.36	9 6 0	1.6	2.88
6 1 0	5.8	2.95	10 2 0	40.8	44.73	7 4 0	41.2	-45.33	7 7 0	32.2	31.89
7 1 0	49.8	-54.09	11 2 0	28.9	-28.80	8 4 0	6.8	2.93	8 7 0	4.8	4.97
8 1 0	5.2	6.51	3 3 0	54.6	-74.77	9 4 0	39.9	39.36	9 7 0	4.9	-3.56
9 1 0	3.3	0.72	4 3 0	3.7	-1.45	10 4 0	5.1	3.08	8 8 0	42.8	53.07

comparison of the calculated and observed structure factors of  $h0l$  and upper levels for the three possibilities showed that the assumed  $z$  coordinates (all Ga at  $z = 0$ , V at  $z = 1/2$ ) were indeed correct.

Tables 2 and 3 give interatomic distances and angles. Observed and calculated structure factors are listed in Table 4.

### Discussion

It is interesting that all interatomic distances range between 2.654 and 2.959 Å, regardless of whether these are Ga—Ga or Ga—V distances (this disregards the 3.855 Å distance, which is not considered to be between nearest neighbors). Also, all the angles between interatomic

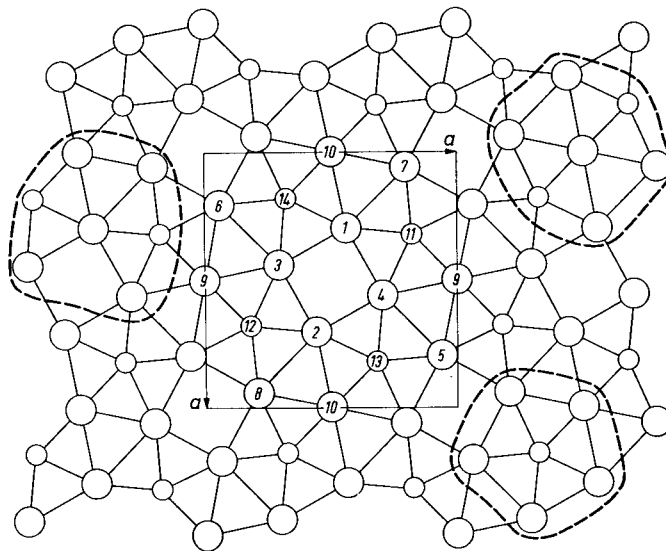


Fig. 3. Diagram of the projection along  $c$ , showing nearest-neighbor configurations for the three crystallographically independent atoms. Gallium is represented by large circles, vanadium by small ones. Since Ga is at  $z = 0$  and V at  $z = 1/2$ , and the atoms have neighbors a distance  $c$  away, V has 12 nearest neighbors and Ga has ten in both cases. The numbering system corresponds to that used in Tables 2 and 3

vectors are about  $60^\circ$  as seen in Table 3, except when they are required to be  $90^\circ$  by space-group symmetry. Any three close neighbors lie, therefore, in triangles which are approximately equilateral, an arrangement which is typical of close-packing configurations.

The shortest Ga—Ga distance is 2.689 Å, considerably longer than the shortest Ga—Ga distance of 2.484 Å observed<sup>5,6</sup> in orthorhombic Ga. Other distances in the latter structure are 2.691, 2.730, 2.788 and 3.753 Å.

Figure 3 shows the arrangement of the atoms in  $V_2Ga_5$  for several unit cells as projected down the  $c$  axis. The environments of the three crystallographically independent atoms are shown by the heavy dashed outlines. Vanadium has ten close Ga neighbors (five above, at  $z = 1$ , and five below, at  $z = 0$ ), plus two V neighbors a distance  $c$  above and below itself, for a total of 12 nearest neighbors. Both galliums, although crystallographically in different positions, have the same environment: four Ga in the same plane, two Ga  $c$  above and below, and four V at  $\pm \frac{1}{2} c$ , for a total of ten nearest neighbors.

$V_2Ga_5$  is isotypic<sup>7</sup> with<sup>8</sup>  $Mn_2Hg_5$ , and its structure bears a marked resemblance<sup>9</sup> to that of  $Pd(NH_3)_4Cl_2 \cdot H_2O$ . In the latter,  $NH_3$  occupies the site of the eightfold Ga, Cl replaces fourfold V,  $H_2O$  is in the two-

Table 5. Comparison of observed interatomic distances in  $V_2Ga_5$  and  $Mn_2Hg_5$ \*

I $V_2Ga_5$		Ratio II/I	II $Mn_2Hg_5$
$a = 8.968$ Å		1.09	$a = 9.758$ Å
$c = 2.693$		1.11	$c = 2.998$
1—10	2.689 Å	1.10	2.95 Å
1—7	2.959	1.09	3.22
1—11	2.698	1.09	2.94
1—4	2.726	1.08	2.95
9—11	2.654	1.09	2.90
4—11	2.739	1.10	3.02
11—11	2.693	1.11	3.00

\* Both have the space group  $P4/mbm$ .

<sup>5</sup> A. J. BRADLEY, The crystal structure of gallium. *Z. Kristallogr.* **91** (1935) 302—316.

<sup>6</sup> B. D. SHARMA and J. DONOHUE, A refinement of the crystal structure of gallium. *Z. Kristallogr.* **117** (1962) 293—300.

<sup>7</sup> K. SCHUBERT, H. G. MEISSNER, M. PÖTZSCHKE, W. ROSSTEUTSCHER und E. STOLZ, Einige Strukturdaten metallischer Phasen (7). *Naturwiss.* **49** (1962) 57.

<sup>8</sup> J. F. DE WET, The crystal structure of  $Mn_2Hg_5$ . *Acta Crystallogr.* **14** (1961) 733—738.

<sup>9</sup> B. N. DICKINSON, The crystal structure of tetramminopalladous chloride  $Pd(NH_3)_4Cl_2 \cdot H_2O$ . *Z. Kristallogr.* **88** (1934) 281—297.

fold Ga position, and Pd is located at the origin and the center of the unit cell, which, in the  $V_2Ga_5$  structure, are vacancies. In Table 5 a comparison of cell dimensions and interatomic distances is shown for  $V_2Ga_5$  and  $Mn_2Hg_5$ . The Ga—Ga distance in  $V_2Ga_5$  and the Hg—Hg distance in  $Mn_2Hg_5$  across the diagonal mirror plane are the longest of the observed distances. This corresponds to the distance between atoms 1 and 7 in Fig. 3. The ratio of equivalent interatomic distances as indicated in Table 5 is quite constant.

#### Acknowledgment

The authors wish to thank F. A. TRUMBORE of Bell Telephone Laboratories for preparing the crystals of  $V_2Ga_5$  used in this study. Also we are indebted to Prof. Dr. F. LAVES for calling to our attention his papers<sup>10,11</sup> on the crystal structure of gallium, which appeared prior to that of SHARMA and DONOHUE<sup>6</sup>, and that of BRADLEY<sup>5</sup>.

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<sup>10</sup> F. LAVES, Kristallstruktur des Galliums. *Naturwiss.* **20** (1932) 472.

<sup>11</sup> F. LAVES, Kristallstruktur und Morphologie des Galliums. *Z. Kristallogr.* **84** (1933) 256—298.