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Crystal Structure of Ga₅Mg₂*

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The crystal structure of a new compound in the Ga-Mg system near 70 at. % Ga has been determined by single-crystal X-ray diffraction techniques. The composition established is Ga₃Mg₂. The unit cell is body-centered tetragonal, and contains four Ga₃Mg₂ units. Lattice constants are $a=8.62_7$, $c=7.11_1$ Å; the calculated density is 4.98 g.cm⁻³. The space group as deduced from the structure analysis is I4/mmm. The Ga atoms are arranged in sheets of puckered, six-membered rings, these sheets being interconnected by Ga-Ga bonds to form a three-dimensional framework. The Mg atoms (x, x, 0; x=0.2996) are situated in rather open cavities within this framework, and have ten Ga atoms as nearest neighbors. Both of the two types of gallium atoms have four Ga and four Mg atoms as nearest neighbors. The Ga neighbors of Ga(1) (0, x, z; x=0.2982, z=0.1810) are at the corners of an irregular tetrahedron. The Ga and Mg neighbors of Ga(2) (0, 0, z; z=0.2883) form a square antiprism. Ga-Ga distances within the sheets are 2.651 and 2.683 Å; the Ga-Ga distance between sheets is 2.574 Å. Ga-Mg distances are 2.871, 2.887, and 2.974 Å.

Introduction

An investigation by Haucke (1938) of the Ga-Mg system disclosed the existence of four intermediate compounds: Ga₂Mg₅, GaMg₂, GaMg and Ga₂Mg. In the course of studies on Ga₂Mg (Smith, Mucker, Johnson & Wood, 1969), thermal analyses and powder X-ray diffraction photographs indicated still another compound richer in Ga. We have been able to isolate single crystals of this phase and to show by means of a structure determination that the stoichiometry is Ga₅Mg₂.

Experimental

As previously reported (Smith et al. 1969), preparations at 69,70 and 75 at.% Ga had first indicated the presence of Ga_5Mg_2 (71.4 at.% Ga). Cooling curves at these compositions indicated weak exothermic reactions at $150 \pm 5^{\circ}$ C; upon heating, endothermic reactions were observed at 208 ± 3 °Č. This difference in behavior is believed to be caused by supercooling or superheating effects. Supercooling was, in fact, encountered in the liquidus determinations; in general, however, our liquidus data confirm the work of Hume-Rothery & Raynor (1938). Crystals for the present work came from a preparation at 87 at. % Ga. At this composition, the liquidus is below the peritectic temperature, and the primary crystals are accordingly Ga₅Mg₂ rather than Ga₂Mg. Details of the preparation are as follows: pieces of the metals, both of 99.99% purity, were sealed in a tantalum tube and the tube was heated in a differential thermal analysis furnace assembly. The assembly was agitated above the liquidus point ($\sim 187^{\circ}$ C) to homogenize the sample. Upon slow cooling, wellformed primary crystals of Ga₅Mg₂ were easily separated mechanically from the gallium matrix. Because of its sensitivity to air, the material was handled in an argon-atmosphere drybox, and samples for X-ray examination were sealed in thin-walled glass capillaries.

Oscillation and Weissenberg photographs showed the crystals to be body-centered tetragonal. The diffraction symmetry was 4/mmm, and there were no systematic absences other than the body-centering condition, hkl missing for h+k+l= odd. Possible space groups are (*International Tables for X-ray Crystallography*, 1952): I4/mmm, I4mm, I422, $I\bar{4}m2$ or $I\bar{4}2m$. Of these, only I4/mmm is centrosymmetric. Lattice constants obtained from measurements on a singlecrystal orienter with Mo K α radiation are: $a=8.62_7$, $c=7.11_1$ Å (with an estimated accuracy of about 0.3%). The calculated density for four units of Ga₅Mg₂ per unit cell is 4.98 g.cm⁻³.

Intensity measurements were carried out on a General Electric XRD-5 diffractometer equipped with a single-crystal orienter, scintillation counter, and pulseheight discrimination circuitry. The stationary crystalstationary counter technique (Furnas, 1957) was used in conjunction with Zr-filtered Mo $K\alpha$ radiation. The crystal specimen was a parallelepiped, $0.10 \times 0.12 \times 0.14$ mm. In all, 122 reflections were recorded up to a 2θ cutoff of 45°. Four 00l reflections at $\chi = 90^{\circ}$ showed an intensity variation with φ of about $\pm 6\%$ (the linear absorption coefficient for Mo $K\alpha$ radiation is 265 cm^{-1}). These measurements were used to obtain φ -dependent absorption corrections which were applied to all reflections. The corrected intensities were reduced to relative |F|'s through the application of Lorentz-polarization factors.

Determination of structure

Thermal analyses and powder patterns indicated that the composition of the new phase was in the general

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vicinity of 70 at. % Ga. An assumption of 20 Ga and 8 Mg atoms within the unit cell was consistent with those observations. Moreover, the density calculated for such a composition fitted nicely on the nearly straight line which relates density and composition for intermediate compounds in this system.

Solution of the Patterson function was successfully obtained in terms of the centrosymmetric space group 14/mmm. This space group provides 32-fold general positions and various 16-, 8-, 4-, and 2-fold special positions. Sixteen Ga atoms in a 16(n), 0, x, z position (with x=0.30, z=0.175) and four Ga atoms in a 4(e), 0,0, z position (with z = 0.325) accounted for the twelve largest (non-origin) peaks in the Patterson map. A structure factor calculation based on these atoms gave an Rindex of 0.32. An electron-density synthesis which followed displayed an 8-fold Mg atom in an 8(h), x, x, 0position with x = 0.30. Inclusion of this atom-type and least-squares refinement of the structural parameters lowered the R index to 0.118 when unit weights were employed, and to 0.072 when a more appropriate weighting scheme was employed (see below).

Final refinement was made following the application of an extinction correction of the form $F_o(\text{corrected}) =$ $F_o(1+\beta I_o)$, where I_o is the raw intensity and β is the extinction parameter. A value for β of $1 \cdot 1 \times 10^{-5}$ gave the lowest R index and was not further refined. Three cycles of least-squares refinement using the full-matrix program of Gantzel, Sparks & Trueblood (ACA Program No. 317, unpublished) reduced the value of $R = \Sigma (K|F_o| - |F_c|) / \Sigma K|F_o|$ to 0.038 (all reflections). The quantity minimized was $\sum w(|F_o| - (1/K)|F_c|)^2$ where K is the scale factor relating $|F_o|$ and $|F_c|$ and the w's are given by the following weighting scheme: $w = F^{1/4}, F_o < A; w = A^{5/4}F_o^{-1}, F_o > A$. When the structure factors were placed on an absolute scale, A = 61. Atomic scattering factors for neutral Ga and Mg were those listed in International Tables for X-ray Crystallography (1962); real and imaginary anomalous dispersion corrections, although rather small in the present case, were those of Cromer (1965). Changes in parameter values

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in the last cycle were <0.01 times the standard deviations. A difference synthesis prepared from the final parameters showed no excursions from zero of more than 0.6 e.Å⁻³. The isotropic temperature parameters obtained in the refinement are rather uniform, and thus there is no evidence of partial occupancy or substitutional disorder. Details of the refinement in *I4/mmm* being entirely satisfactory, no further consideration was given to the other space-group alternatives.

Final parameters are given in Table 1. Table 2 lists observed and calculated structure factors.

Discussion of structure

The structure is illustrated in Figs.1 and 2, the latter being a stereoscopic view of the contents of an entire unit cell. A notable feature is the presence of an extended framework of Ga atoms. Centered across levels of $Z = \frac{1}{4}$ and $Z = \frac{3}{4}$ are sheets containing puckered, cyclohexane-like rings of Ga atoms. These sheets are related to one another by mirror planes at Z=0 and $\frac{1}{2}$, and are connected by Ga(1)-Ga(1) bonds parallel to the Z axis. Both kinds of Ga atoms have four Ga and four Mg atoms as nearest neighbors. The Ga neighbors of the sixteenfold atom, Ga(1), are at the corners of a nonregular tetrahedron (bond angles range from 82·1° to 121.6°). The Ga neighbors of the fourfold atom, Ga(2), are at the corners of a square, and together with four Mg neighbors form a square antiprism around Ga(2). Mg atoms at Z=0 and $\frac{1}{2}$ are in cavities between adjacent sheets of Ga atoms, and are displaced from lines joining the centers of the six-membered rings. It may be remarked that somewhat distorted and puckered hexagonal layers are also found in metallic Ga (Sharma & Donohue, 1962). Connexity within and between sheets is, however, different so that the coordination number of each Ga atom is instead seven.

Nearest neighbor Ga–Ga distances in Ga₅Mg₂ (Table 3) show a somewhat smaller range of values ($2\cdot571-2\cdot683$ Å) than found in Ga₂Mg($2\cdot556-2\cdot835$ Å) or in metallic gallium ($2\cdot484-2\cdot788$ Å). The shortest dis-

Table 1. Final parameters for Ga₅Mg₂

E.s.d.'s in parentheses.

	number	104 x	104 y	104 z	В
Ga(1)	16(<i>n</i>)	0	2982 (2)	1810 (2)	$1.2 \pm 0.1 \text{ Å}^2$
Ga(2)	4(e)	0	0	2883 (4)	1.3 ± 0.1
Mg	8(<i>h</i>)	2996 (6)	2996 (6)	0	1.5 ± 0.1

Table 2. Absolute values of observed and calculated structure factors for Ga_5Mg_2

HKL	Fil	FC	нкс	FC	FC	HKL	FU	FC	HKL	FO	۶C	нкι	FO	FC	HKL	FD	FC	HKL	FU	FC	HKL	FD	FC	HKL	FD	FC
200	45	42	530	4	2	4 1 1	12	11	402	95	98	442	58	58	323	10	11	114	32	32	105	3	,	206	11	9
4 0 0	161	174	730	124	125	611	12	11	6 O Z	72	73	642	43	42	5 2 3	147	149	3 1 4	10	8	305	82	78	406	59	57
600	120	126	440	88	89	811	23	24	8 O Z	43	40	842	12	10	723	7	4	514	34	35	505	38	40	116	31	30
800	29	25	640	64	64	321	33	33	112	0	2	5 5 2	61	64	433	47	46	714	6	5	705	54	53	316	19	14
1 1 0	8	7	840	4	1	521	45	44	312	75	75	752	25	25	633	31	31	224	56	56	215	84	83	516	48	47
310	89	88	550	64	68	721	20	18	512	36	36	662	33	32	833	6	4	424	16	17	415	26	25	226	69	65
510	51	54	750	3	5	431	35	34	712	47	48	103	43	41	543	46	47	624	16	15	615	24	24	426	25	25
710	53	56	660	47	46	631	24	24	222	80	78	303	91	91	743	32	33	334	16	15	325	39	41	336	72	69
910	5	7	101	9	7	831	13	14	422	17	18	503	4	2	653	44	44	534	3	3	525	84	84	446	27	23
220	96	92	301	86	88	541	31	31	622	10	9	703	60	61	004	23	24	734	9	9	435	31	29	107	12	15
420	5	5	501	34	35	741	22	23	822	35	35	213	129	128	204.	- 4	2	444	9	11	635	22	19	307	20	23
620	11	11	701	51	54	651	28	27	332	100	98	413	18	18	404	11	11	644	10	10	545	48	48	217	29	30
820	41	42	901	4	1	002	150	145	532	39	37	613	21	20	604	10	9	554	41	42	006	114	111	327	9	12
330	201	198	211	55	52	202	81	82	732	65	65	813	60	61												

tance, 2.571 Å, is between Ga(1) atoms in different sheets. Thus, gallium-gallium bonding within the sheets is weaker than bonding between sheets. As Sharma & Donohue (1962) point out, this same phenomenon occurs in metallic gallium; a comparison of distances shows the effect to be more pronounced in the element than in Ga₅Mg₂. There is one slightly longer distance of 3.010 ± 0.006 Å which occurs between Ga(2) atoms along the Z axis. While this may correspond to a weak bond, we have not in the following discussion considered these atoms as neighbors of one another.

The individual Ga-Mg distances are 2.871, 2.887, and 2.974 Å. By way of comparison, the metallic radii of Ga and Mg are 1.41 and 1.60 Å, respectively (values from the compilation of Teatum, Gschneidner & Waber, 1959). Thus, the observed Ga-Mg distances are all shorter than the sum of atomic radii. The shortest Mg-Mg distance in Ga₅Mg₂ is 3.46 ± 0.01 Å, some 0.26 Å longer than twice the metallic radius of Mg. It thus appears that the Ga-Ga and Ga-Mg interactions contribute substantially more to the stability of the Ga₅Mg₂ phase than do the Mg-Mg interactions. A similar behavior was noted in Ga₂Mg (Smith, Mucker, Johnson & Wood, 1969).

Coordination polyhedra (C.P.'s) for the three independent atoms are shown in Fig. 3. The C.P. for Ga(2) is a square antiprism of 4mm symmetry; Ga(2) is displaced, however, along the fourfold axis so that distances to its four Ga(1) neighbors are shorter than those to its four Mg neighbors. Ga(1) also has eight neighbors. It's C.P., however, is entirely different, having only a mirror plane as an element of symmetry. The C.P. for Mg, of *mm* symmetry, is quite unusual. It is seen to be a rather open cage of ten atoms made up of parts from two six-membered Ga rings. The failure of Mg to achieve a C.P. based (more or less) on triangular faces reflects, we judge, the propensity of Ga toward network formation.



Fig.1. Portion of Ga₅Mg₂ structure for $0 \le Z \le \frac{1}{2}$. Numerals within open circles identify type of Ga atom. Elevations along Z are also indicated. The remainder of the structure is generated by a body-centering condition and/or mirroring across $Z = \frac{1}{2}$ level.

Table 3. Interatomic distances in Ga₅Mg₂; angles around Ga(1) are also given

Distance E.s.d. Atom Atom Atom Atom Distance E.s.d. 2 Å 1 Å 1 2 Å Å 4Ga(1) 2.5740.003 0.002 Ga(1) Ga(1) Ga(2) 2.683 2Ga(1) 2.651 0.002 4Mg $2 \cdot 871$ 0.006 Ga(2) 2.6830.002 0.006 2Mg 2.887 0.002 Mg 2Ga(2) 2.871 4Ga(1) 2Mg 2.974 0.002 2.887 0.005 2.974 4Ga(1) 0.002< Ga(1) - Ga(1) - Ga(1) $111.7 \pm 0.1^{\circ} (2 \times)$ < Ga(1) - Ga(1) - Ga(1) $82 \cdot 1 \pm 0 \cdot 1^{\circ}$ < Ga(1) - Ga(1) - Ga(2) 106.5 ± 0.1 < Ga(1) - Ga(1) - Ga(2) $121.6 \pm 0.1 (2 \times)$

E.s.d.'s include only the uncertainties in positional parameters.

Fig. 2. Stereoscopic view of the structure. The unit cell is outlined; the c axis is vertical, while the a and b axes are directed to the left and right, respectively. For simplicity, only two of the eightfold Mg atoms are shown.



Fig. 3. Ball-and-stick drawings of the coordination polyhedra for (a) Ga(1), (b) Ga(2), and (c) Mg. The site symmetries for these atoms are 4mm, m and mm, respectively. In all cases, the c axis is vertical. Numerals indicate the type of Ga atoms. The central atom is stippled.

Just as gallium possesses a unique structure among the elements, it appears that Ga_5Mg_2 may also have a unique structure. A search of standard references such as Pearson's (1967) book reveals no A_5B_2 compounds isotypic with Ga_5Mg_2 . Nor does Mg, in fact, form an A_5Mg_2 phase with any of the other Group IIIA elements.

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The Crystal Structure of Zr₄Co₄Ge₇ (V-Phase)

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The crystal structure of the V-phase $Zr_4Co_4Ge_7$ has been determined by single-crystal X-ray diffraction analysis. The structure is of a new type with four formula units in a tetragonal unit cell of space group I4/mmm (D_{4h}^{17}), having the dimensions $a=13\cdot228\pm0\cdot004$, $c=5\cdot229\pm0\cdot003$ Å and $c/a=0\cdot3952\pm0\cdot0002$. The structure was refined by the least-squares method, giving a final R value of $0\cdot092$ for the 392 independent structure factors observed. It may be characterized as intermediate between the tetrahedrally close packed structures (σ -phase related structures, Laves phases) and the structures of the CuAl₂-type family.

Introduction

In their study of the ternary system titanium-nickelsilicon, Westbrook, DiCerbo & Peat (1958) reported the occurrence of a ternary phase of the composition $Ti_4Ni_4Si_7$ to which they ascribed the name 'V-phase'. Subsequently Jordan (1963) found thirteen isotypic compounds in which the large titanium atoms were replaced by zirconium, niobium or tantalum, the smaller transition metal component nickel by cobalt and iron, and germanium could substitute silicon. The phases were reported to be nearly homogeneous at the composition 4:4:7, with the possible exemption of two phases, where the exact composition has not been determined. While investigating similar ternary systems (including hafnium as the larger transition metal component) Markiv, Gladyševskij & Fedoruk (1966), Markiv, Gladyševskij, Kripjakevič & Fedoruk (1966) and Markiv (1966) independently discovered a number of isotypic phases at the approximate composition 1:1:2, having a body-centered tetragonal unit cell. This unit cell could be used to index the powder patterns of the V-