

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 Ga₅Mg₂. The unit cell is body-centered tetragonal, and contains four Ga₅Mg₂ 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 Ga₅Mg₂ (71.4 at.% Ga). Cooling curves at these compositions indicated weak exothermic reactions at $150 \pm 5^\circ\text{C}$; upon heating, endothermic reactions were observed at $208 \pm 3^\circ\text{C}$. 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 ($\sim 187^\circ\text{C}$) to homogenize the sample. Upon slow cooling, well-formed 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 $h+k+l=\text{odd}$. Possible space groups are (*International Tables for X-ray Crystallography*, 1952): *I4/mmm*, *I4mm*, *I422*, *I4m2* or *I42m*. Of these, only *I4/mmm* is centrosymmetric. Lattice constants obtained from measurements on a single-crystal 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 pulse-height discrimination circuitry. The stationary crystal-stationary counter technique (Furnas, 1957) was used in conjunction with Zr-filtered Mo *K* α 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 00*l* reflections at $\chi=90^\circ$ showed an intensity variation with φ of about $\pm 6\%$ (the linear absorption coefficient for Mo *K* α 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 $|F|^2$'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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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 Ga_5Mg_2 . 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 Ga_5Mg_2 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 Ga_5Mg_2 phase than do the Mg–Mg interactions. A similar behavior was noted in Ga_2Mg (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. Its 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.

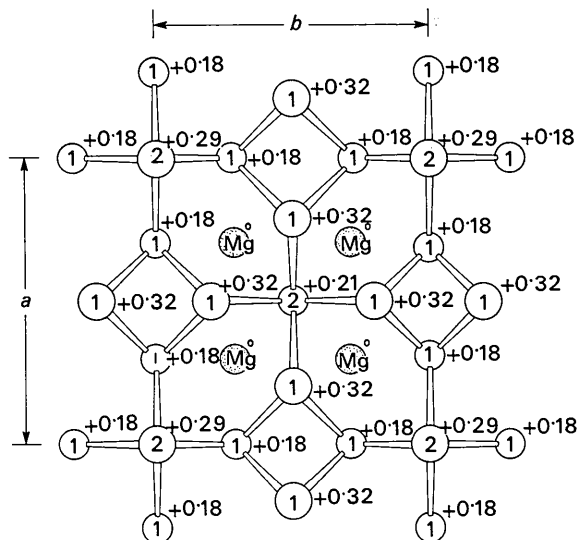


Fig. 1. Portion of Ga_5Mg_2 structure for $0 \leq Z \leq \frac{1}{2}$. Numerals within open circles identify type of Ga atom. Elevations along Z are also indicated. The remainder of the structure is generated by a body-centering condition and/or mirroring across $Z = \frac{1}{2}$ level.

Table 3. *Interatomic distances in Ga_5Mg_2 ; angles around Ga(1) are also given*

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

Atom 1	Atom 2	Distance Å	E.s.d. Å	Atom 1	Atom 2	Distance Å	E.s.d. Å	
Ga(1)	Ga(1)	2.574	0.003	Ga(2)	4Ga(1)	2.683	0.002	
	2Ga(1)	2.651	0.002		4Mg	2.871	0.006	
	Ga(2)	2.683	0.002		Mg	2Ga(2)	2.871	0.006
	2Mg	2.887	0.005			4Ga(1)	2.887	0.005
2Mg	2.974	0.002	4Ga(1)	2.974		0.002		
$\angle \text{Ga(1)-Ga(1)-Ga(1)}$				$82.1 \pm 0.1^\circ$				
$\angle \text{Ga(1)-Ga(1)-Ga(2)}$				$121.6 \pm 0.1 (2 \times)$				

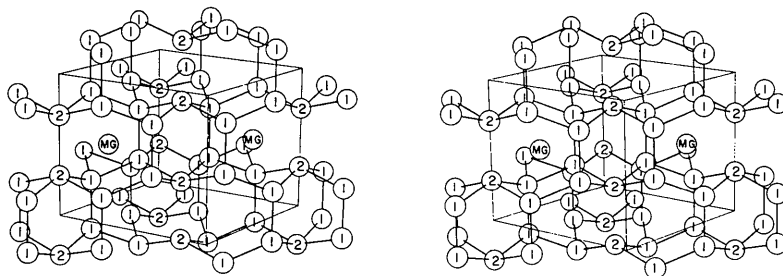


Fig. 2. Stereoscopic view of the structure. The unit cell is outlined; the c axis is vertical, while the a and b axes are directed to the left and right, respectively. For simplicity, only two of the eightfold Mg atoms are shown.

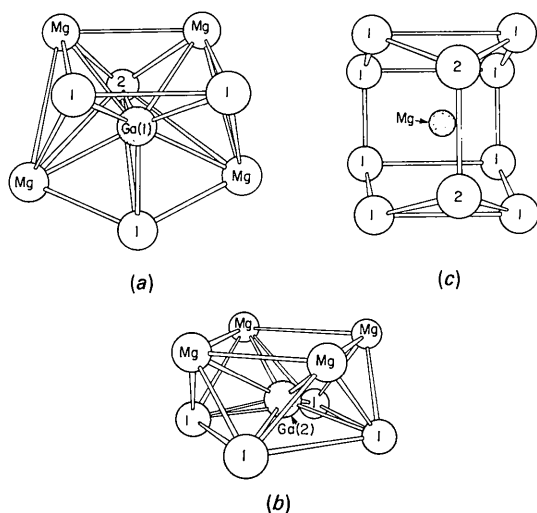


Fig. 3. Ball-and-stick drawings of the coordination polyhedra for (a) Ga(1), (b) Ga(2), and (c) Mg. The site symmetries for these atoms are $4mm$, m and mm , respectively. In all cases, the c axis is vertical. Numerals indicate the type of Ga atoms. The central atom is stippled.

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 $Zr_4Co_4Ge_7$ (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 $a = 13.228 \pm 0.004$, $c = 5.229 \pm 0.003$ Å and $c/a = 0.3952 \pm 0.0002$. The structure was refined by the least-squares method, giving a final R value of 0.092 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 $CuAl_2$ -type family.

Introduction

In their study of the ternary system titanium–nickel–silicon, 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-