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Mo_8Ga_{41}, Another Example of Ten-Coordination of the Transition Element

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Mo_8Ga_{41} is rhombohedral, space group $R\bar{3}$, with $a_{hex}=14{\cdot}04$ (1), $c_{hex}=15{\cdot}05$ (1) Å, $Z=1$, $D_x=6{\cdot}95$ g cm^{-3}. R for 1000 reflexions is 0·09. The structure is isotypic with V_8Ga_{41} and bears a strong resemblance to Mo_6Ga_{31}. The Mo atoms are tenfold coordinated by Ga, most of the Mo–Ga distances being very short. No Mo–Mo contacts exist and no Ga–Ga pairing is observed. The structure may be derived by stacking [$MoGa_{10}$] polyhedra and centred Ga cuboctahedra. This arrangement results in layers of Ga atoms and rumpled chains of alternating Mo and Ga atoms.

Introduction

The Mo–Ga phase diagram has recently been examined in detail (Bornand, Siemens & Oden, 1973). Five intermediate phases are known to exist: Mo_3Ga, two phases between MoGa and $MoGa_2$ and two $MoGa_{\sim 5}$ phases. Except for Mo_3Ga they all crystallize in complex crystal structures. So far, only Mo_6Ga_{31} (Yvon, 1974) has been elucidated, which has a new type of structure with interesting structural features: [$MoGa_{10}$] polyhedra, Ga atoms forming extended sheets, partial occupancies of certain Ga sites and probably occupational disorder of the atomic sites which centre the Ga cuboctahedra. It was therefore interesting to examine the second Ga-rich phase $MoGa_{\sim 5}$ which forms only from samples with very high Ga contents.

Experimental

Samples containing single crystals of the new phase were prepared by heating the components (Ga and Mo powder) to 800 °C for several hours and cooling the sample slowly to room temperature. The crystals have a metallic appearance and show well developed faces but are irregular in shape. The presence of a regular triangular face facilitated the orientation and space-group determination: $R\bar{3}$ or $R3$, the only extinction being $-h+k+l=3n$ for hexagonal indices.

Crystal data

Mo_8Ga_{41}, F.W. 3626, $a=9{\cdot}533$ (9) Å, $\alpha=94°50'$ (2), space group: $R\bar{3}$ (No. 148), $V=856$ Å^3, $Z=1$, $\mu=370$ cm^{-1}, $D_x=6{\cdot}95$ g cm^{-3}, D_m not measurable, λ(Mo $K\alpha$) = 0·7107 Å, $F(000)=1607$.

1100 independent reflexions were measured on a computer-controlled diffractometer (Philips PW 1100, continuous ω–2θ scans, graphite-monochromatized Mo $K\alpha$ radiation). The lattice parameters measured on the single crystal did not differ from those derived from powder photographs (Guinier camera). Correction for absorption was made by approximation to a spherical crystal with $R=0{\cdot}008$ cm.

Structure determination and refinement

The crystal structure is an interesting example where model building and *a priori* knowledge of the transition-metal environment leads to a correct structure proposal. In fact, the $\{hki0\}$ precession photograph of this compound resembles to a large extent the $\{102\}$ zone of monoclinic Mo_6Ga_{31}. If one assumes Mo to be again tenfold coordinated by Ga and extends these polyhedra in different directions similarly to Mo_6Ga_{31}, one obtains a model belonging to space group $R\bar{3}$. This structure corresponds to the ideal composition Mo_8Ga_{41}. Refinement by full-matrix least-squares calculations (Busing *et al.*, 1971) confirmed the structure, which is identical with that derived for V_8Ga_{41} (Girgis, Petter & Pupp, 1974). The weighting scheme used was $w=1/\sigma^2$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). (Anomalous dispersion for Ga: $\Delta f'=0{\cdot}2$, $\Delta f''=1{\cdot}7$, and for Mo: $f'=-1{\cdot}7$, $f''=0{\cdot}9$.) The final $R=\sum|\Delta F|/\sum|F_o|$ is 9% for 1000 reflexions with $|F|>\sigma(|F|)$. There are no indications of deviations to the non-centrosymmetric space group $R3$. The atomic coordinates are listed in

Table 1. *Atomic and thermal parameters*

Atomic fractional coordinates ($\times 10^4$), occupancy factors and their least-squares values ($\times 10^2$), as well as thermal parameters, with respective standard deviations in parentheses.

	x/a	y/b	z/c	Occupancy	B(Å^2)
Ga(1)	0	0	0	1 102 (1)	1·1 (1)
Ga(2)	0	0	5000	1 102 (1)	2·4 (2)
Ga(3)	5000	0	5000	1 103 (1)	1·2 (1)
Ga(4)	1071 (2)	2378 (2)	39 (3)	1 100 (1)	1·1 (1)
Ga(5)	1148 (3)	1254 (3)	1636 (3)	1 100 (1)	1·2 (1)
Ga(6)	3068 (2)	3182 (2)	2673 (3)	1 102 (1)	1·3 (1)
Ga(7)	23 (2)	1859 (2)	2852 (3)	1 100 (1)	1·1 (1)
Ga(8)	1667 (3)	1507 (3)	3904 (3)	1 100 (1)	1·4 (1)
Ga(9)	1829 (3)	3136 (3)	4934 (3)	1 100 (–)	1·4 (1)
Mo(1)	0	0	3018 (2)	<1 96 (1)	0·7 (1)
Mo(2)	2903 (2)	3057 (2)	975 (3)	<1 95 (1)	0·4 (1)

Table 1 and a stereo drawing of the crystal structure is given in Fig. 1 (Johnson, 1965).*

Structural results and discussion

Composition

The crystal structure of Mo_8Ga_{41} is interesting for several reasons. One is the rather odd composition, being almost the same as for Mo_6Ga_{31}. However, contrary to the composition corresponding to these ideal-structure formulae, the overall Ga content of the Mo_8Ga_{41} phase turned out to be slightly higher than that in Mo_6Ga_{31} as determined by microprobe analysis (Table 2)† and confirmed by refinement of the occupancy factors (Table 1). It turned out that Mo_8Ga_{41} has defects on Mo sites, in contrast to Mo_6Ga_{31}, for which certain Ga sites were found to be only partially occupied. Both phases may have a domain of existence which could be related to the presence of atomic sites with mixed occupation. Crystal structures containing such sites are known to exist for certain transition-metal aluminides, *e.g.* $FeAl_2$ (Corby & Black, 1973), Co_5Al_{13} (Hudd & Taylor, 1962) or VAl_{10} (Ray & Smith, 1957).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30608 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† This analysis has been carried out by M. J. Bertrand, Département de Minéralogie, Université de Genève.

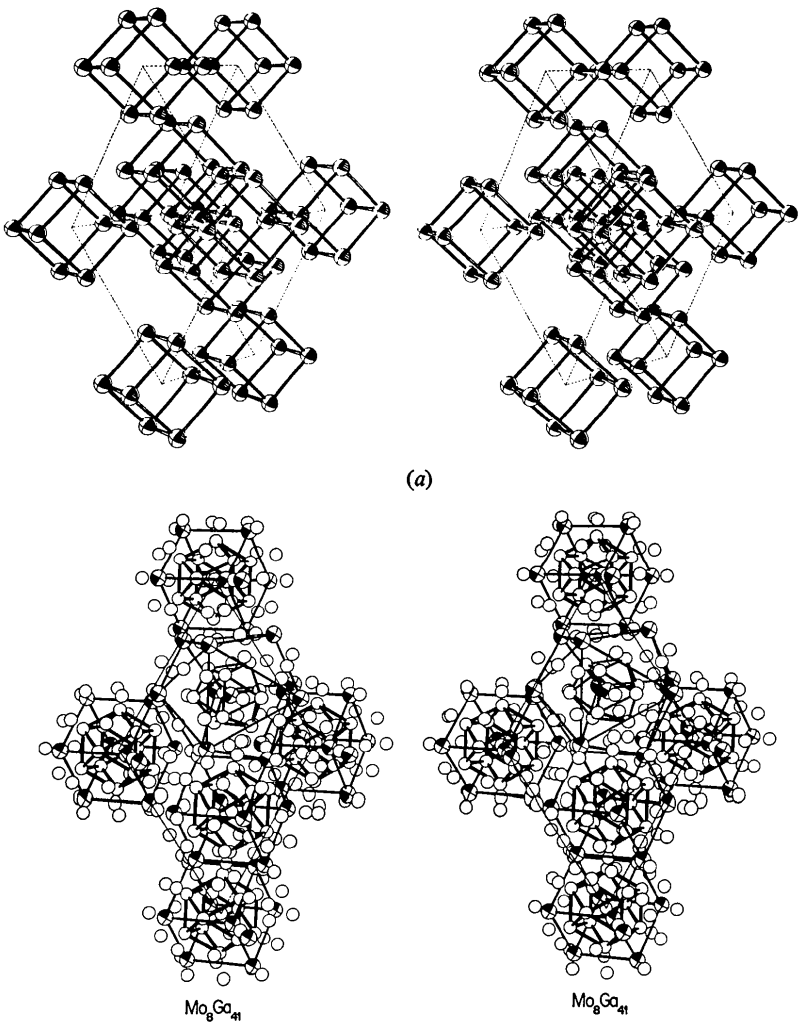

Fig. 1. Stereoscopic pair of Mo_8Ga_{41}, $R\bar{3}$, hexagonal unit cell, viewed along **c**. (*a*) Mo atoms only are shown. (*b*) Structural elements common to Mo_6Ga_{31} and Mo_6Ga_{41} are outlined.

Table 2. *Compositions of the two* $MoGa_5$ *phases*

Phase	Ideal composition	Actual composition (microprobe analysis)
Mo_6Ga_{31}	$MoGa_{5\cdot167}$	$MoGa_{5\cdot1\pm0\cdot1}$
Mo_8Ga_{41}	$MoGa_{5\cdot125}$	$MoGa_{5\cdot3\pm0\cdot1}$

Comparison of V_8Ga_{41} *and* Mo_8Ga_{41}

In view of the great structural variety among Al- and Ga-rich transition-metal compounds, it was almost surprising to find that Mo_8Ga_{41} and V_8Ga_{41} are isostructural. There are, however, two minor differences worth mentioning. In V_8Ga_{41}, all atomic sites have full occupancy: the structural formula corresponds therefore to its actual composition. This is not the case for Mo_8Ga_{41}, which was found to be slightly richer in Ga because of defects on Mo sites. The other structural difference concerns the positional parameter of the transition-metal sites V(1) and Mo(1) [$z_{V(1)}=0\cdot3140$ *versus* $z_{Mo(1)}=0\cdot3018$] giving rise to slightly different shapes of the [$MoGa_{10}$] polyhedra (Table 3).

Description of the structure and comparison with Mo_6Ga_{31}

The crystal structure of Mo_8Ga_{41} can be described in the following way: as in Mo_6Ga_{31}, the most striking features are ten-coordinated Mo atoms and layers of Ga atoms. These layers are orthogonal, consist of squares of Ga atoms and enclose an almost regular cube of Mo atoms. The Mo atoms of this cube surround a cuboctahedron of Ga atoms, which is centred by one Ga atom, Ga(1). One can consider this cube as a building block and derive the crystal structure of Mo_8Ga_{41} by arranging these blocks on a rhombohedral lattice [Fig. 1; see also Fig. 4 of Girgis, Petter & Pupp (1974)]. It is interesting to find the same building block in monoclinic Mo_6Ga_{31}. However, in this crystal structure two cubes are fused together and join faces. This new building block contains two Ga cuboctahedra and is also surrounded by orthogonal sheets of Ga atoms (Fig. 2).

Another way of describing the crystal structures of Mo_6Ga_{31} and Mo_8Ga_{41} is to consider the [$MoGa_{10}$] polyhedra as building blocks. A new and much larger structural element may then be found, which is common to both crystal structures. It can be derived by arranging the [$MoGa_{10}$] polyhedra on the vertices of another tenfold polyhedron which is identical in shape to the small $MoGa_{10}$ polyhedron [Figs. 1(*b*) and 2(*b*)]. The $MoGa_{10}$ subunits within this large polyhedron share apices only. In other words, each Ga atom belongs to 2 small [$MoGa_{10}$] polyhedron and is found at the midpoint between 2 Mo atoms. This peculiar arrangement results in rumpled chains of

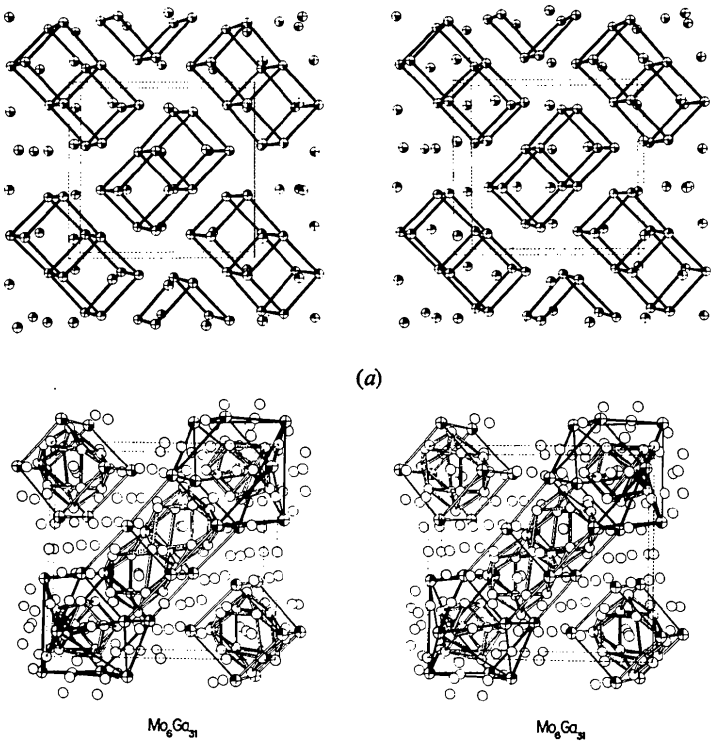

Fig. 2. Stereoscopic pair of Mo_6Ga_{31}, $P2_1/c$. (*a*) Mo atoms only are shown. (*b*) Structural elements common to Mo_8Ga_{41} and Mo_6Ga_{31} are outlined.

Table 3. *Interatomic distances* (Å)

Only distances less than 3·5 Å are listed.

Ga(1)–6Ga(8)	2·779 (3)	Ga(7)–Mo(1)	2·606 (3)
2Mo(1)	2·983 (5)	Mo(2)	2·629 (4)
		Ga(6)	2·738 (5)
Ga(2)–6Ga(4)	2·897 (3)	Ga(8)	2·773 (5)
6Ga(5)	2·988 (4)	Ga(9)	2·791 (5)
		Ga(5)	2·813 (5)
Ga(3)–2Mo(1)	2·537 (2)	Ga(3)	2·871 (3)
2Ga(6)	2·784 (3)	Ga(8)	3·037 (5)
2Ga(5)	2·823 (3)	Ga(5)	2·038 (5)
2Ga(4)	2·823 (4)	Ga(4)	3·293 (4)
2Ga(7)	2·871 (3)		
		Ga(8)–Mo(1)	2·605 (4)
Ga(4)–Mo(2)	2·656 (4)	Mo(2)	2·630 (4)
Mo(2)	2·666 (4)	Ga(9)	2·676 (5)
Ga(3)	2·823 (4)	Ga(7)	2·773 (5)
Ga(2)	2·897 (3)	Ga(1)	2·779 (3)
2Ga(4)	2·899 (4)	Ga(9)	2·823 (5)
Ga(5)	2·907 (5)	Ga(6)	2·865 (5)
Ga(9)	2·916 (6)	Ga(7)	3·037 (5)
Ga(6)	2·942 (4)	Ga(4)	3·468 (4)
Ga(5)	3·036 (4)	Ga(5)	3·471 (5)
Ga(6)	3·075 (4)		
Ga(7)	3·293 (4)	Ga(9)–Mo(2)	2·629 (4)
Ga(8)	3·468 (4)	Mo(2)	2·642 (4)
		Ga(8)	2·676 (5)
Ga(5)–Mo(1)	2·681 (5)	Ga(6)	2·784 (5)
Mo(2)	2·689 (4)	Ga(7)	2·791 (5)
Ga(7)	2·813 (5)	Ga(8)	2·823 (5)
Ga(3)	2·823 (5)	Ga(6)	2·853 (4)
Ga(4)	2·907 (5)	Ga(4)	2·916 (6)
2Ga(5)	2·931 (6)	Ga(5)	2·982 (4)
Ga(9)	2·982 (6)		
Ga(2)	2·988 (4)	Mo(1)–3Ga(8)	2·605 (4)
Ga(4)	3·036 (4)	3Ga(7)	2·606 (3)
Ga(7)	3·038 (5)	3Ga(5)	2·681 (5)
Ga(6)	3·119 (5)	Ga(1)	2·983 (5)
Ga(8)	3·471 (5)	Mean	2·666*
Ga(6)–Mo(2)	2·564 (5)	Mo(2)–Ga(3)	2·537 (2)
Mo(2)	2·577 (5)	Ga(6)	2·564 (5)
Ga(7)	2·738 (5)	Ga(6)	2·577 (5)
Ga(9)	2·784 (5)	Ga(9)	2·629 (4)
Ga(3)	2·784 (3)	Ga(7)	2·629 (4)
Ga(9)	2·853 (4)	Ga(8)	2·630 (4)
Ga(8)	2·865 (5)	Ga(9)	2·642 (4)
Ga(4)	2·942 (4)	Ga(4)	2·656 (4)
Ga(4)	3·075 (4)	Ga(4)	2·666 (4)
Ga(5)	3·119 (5)	Ga(5)	2·689 (4)
		Mean	2·622*

* Sum of metallic radii: $r_{Mo}+r_{Ga}=2{\cdot}81$ Å.

alternating Mo and Ga atoms crossing the entire crystal structure. Every atom lies on such a chain except the central atom of the Ga cuboctahedron whose existence is a requirement of the three-dimensional stacking of tenfold polyhedra, and therefore represents a singularity in this crystal structure. Similar chains of alternating atoms of transition-metal (T) and B-metal (B) also occur in Mo_6Ga_{31}, $CrGa_4$ and in certain aluminides, *e.g.* VAl_{10} or V_4Al_{23}. In view of the very short interatomic distances within these chains (Table 3), they can be regarded as a framework, which is responsible for the stability of these crystal structures (Brown, 1957; Laves, 1962). They may also present an interesting feature for low-temperature physicists. In fact the short interatomic distances probably reflect strong T–B interactions that could correspond to a high local density of electronic states close to the Fermi level. Similar but linear chains of transition-element atoms are characteristic of the A15 structure type, which has been found to be particularly favourable for the existence of high superconducting transition temperatures.

The author would like to point out that the crystal structure of V_8Ga_{41} was solved before the work on Mo_8Ga_{41} was completed and thanks Drs Girgis, Petter and Pupp for communicating to him their results prior to publication. It is also a great pleasure to thank Professor E. Parthé for his helpful criticism and the many lively discussions during this work.

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