V2Cu3Ga8, Mo2Cu3Ga8 and W2Cu3Ga8—New compounds with a novel order variant of a bcc packing and motifs of self-similarity

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Abstract

Single crystals of the new compounds $TM_2Cu_3Ga_8$ (TM = V, Mo, W) were synthesised from the elements. Structure determinations of the isotypic compounds ($cI104$, space group $I\bar{4}3d$, $Z = 8$; $Mo_2Cu_3Ga_8$: $a = 11.9171(10)$ Å, 613 refl., 23 param., $R_1(F) = 0.022$, $wR_2(F^2) = 0.047$; $W_2Cu_3Ga_8$: 11.9248(8) Å, 346 refl., 23 param., $R_1(F) = 0.048$, $wR_2(F^2) = 0.086$; $V_2Cu_3Ga_8$: 11.7861(14) Å, 374 refl., 24 param., $R_1(F) = 0.033$, $wR_2(F^2) = 0.081$) showed a new cubic structure type which can be classified as an ordered defect variant of a bcc packing with $a' = 4a$: $[(TM)_2(Cu)_3(\square)_3][Ga_8]$. The coordination polyhedra of the transition metals consist of Ga_8-cubes with 3 sides capped by Cu leading to coordination number 11. The arrangement of the $TMGa_8Cu_3$-polyhedra is in a way they form itself a 3-fold capped cube. All compositions were confirmed by EDX measurements.
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1. Introduction

The number of intermetallic compounds is tremendous large [1] and their structure chemistry [2] covers a wide range from simple structures like alloys of the bcc of fcc-type to very complex structures, for example Cd_3Cu_4 ($cF1124$ [3]), $(Ga,Zn)_{43}Mg_{26}$ ($oC1104$ [4], Pt_5Zn_{21} ($cF416$ [5] and quasicrystals ([6]).

Nevertheless there are intermetallic systems where binary compounds are unknown or poorly characterised. Examples for this are binary systems where the melting points of the metals are very different and the reactivity of the high melting metal is not sufficient. In those cases it is difficult to decide whether binary phases are not formed because of the inertness or they just do not exist. Examples are the binary systems Mo/Zn, W/Zn or W/Ga.

In order to enable the reaction of the high melting metal even at lower temperatures we used mixtures of low melting metals to enlarge the temperature range where the system is liquid. Furthermore, the use of a metal flux is a well-established technique for the single crystal growth of new intermetallics [7]. We have shown for systems like Mo/Sn/Zn [8] and Mo/Ga/Zn [9], that the reaction of a metal with high melting point (Mo, W, …) with an excess of mixtures of metals with low melting points leads to new binary and ternary compounds like the first binary W/Ga-compounds (W_8Ga_{41}, W_6Ga_{31} [10–12]. Frequently their crystal structures are distinguished by a special kind of complexity with self-similarity. For example $Mo_7Sn_{12}Zn_{40}$ [8] ($cF944$, space group $Fm\bar{3}c$, $a = 25.4$ Å) contains $MoSn_2Zn_{10}$ icosahedra which are arranged itself as an icosahedron around a central $MoZn_{12}$ icosahedron forming a "supericosahedron".

In the course of our studies on Ga-containing intermetallics we extended the use of additional metals to copper and investigated the systems TM/Cu/Ga with TM = V, Mo and W. We synthesised and characterised the first ternary compounds $TM_2Cu_3Ga_8$. The crystal structure

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determinations of single crystals showed for the isotypic compounds a new structure type ($cI104$, $I\bar{4}3d$) which can be described as an ordered defect variant of the bcc packing.

2. Experimental

2.1. Synthesis and characterisation

2.1.1. $Mo_2Cu_3Ga_8$

Single crystals of $Mo_2Cu_3Ga_8$ were synthesised from the elements in evacuated and sealed quartz ampoules. The elements were mixed (ratio Mo:Ga:Cu about 1:6:2, total mass 500 mg), heated up to 800 °C (60 K/h), held for 12 h, cooled with 6 K/h to 500 °C, held for 8 h and then cooled to RT with 12 K/h. Single crystals were isolated by dissolution of the regulus in dil. HCl. Under these conditions $Mo_2Cu_3Ga_8$ was found as the only product. The ratio Cu:Ga can be varied without formation of by-products except platelets of Cu. The best quality of the crystals was yielded with an excess of Ga (ratio 1:10:1). Nearly single phase samples of poor crystal quality result from a stoichiometric ratio. Observed (Cu-$K_{\alpha1}$, Philips PW 1049/10) and calculated X-ray powders patterns were in very good agreement. Small amounts of Mo and/or Cu were observed as the only by-products.

The crystals of $Mo_2Cu_3Ga_8$ are dissolved by conc. HCl. DTA investigations (Netsch STA 419) revealed a melting point at 800 °C.

2.1.2. $W_2Cu_3Ga_8$

$W_2Cu_3Ga_8$ was synthesised from the elements. W, Ga and Cu (total mass: ca. 1 g) were mixed in a ratio 1:8:3, filled in an evacuated quartz tube, heated up to 1000 °C (60 K/h), held for 54 h, cooled to 500 °C with 6 K/h, held for 120 h and then cooled to RT with 18 K/h. The regulus was dissolved in dil. HCl. The residue contained as a minor share small rhombic dodecahedra with metallic lustre which were characterised as $W_2Cu_3Ga_8$. The X-ray powder diffractogram (Cu-$K_{\alpha1}$, Philips PW 1049/10) of selected single crystals was in good agreement with the values calculated for $W_2Cu_3Ga_8$ from the single crystal data. The major fraction of the residue were small single crystals of rhombohedral W_8Ga_{41} [10,12]. It was not possible to obtain $W_2Cu_3Ga_8$ as a single phase by direct synthesis.

2.1.3. $V_2Cu_3Ga_8$

For the synthesis of $V_2Cu_3Ga_8$ single crystals the elements were mixed in a ratio V:Ga:Cu as 1:20:8 (total mass: ca. 1 g), sealed in an evacuated quartz tube, heated up to 1000 °C (60 K/h), held for 240 h, cooled to 400 °C with 4 K/h and to room temperature with 16 K/h. Single crystals were isolated by dissolving the regulus in dil. HCl. $V_2Cu_3Ga_8$ is formed as light grey cubes (Fig. 1) together with varying portions of $CuGa_2$ [13,14] (intergrown tetragonal platelets and cuboids), V_2Ga_5 (Mn$_2$Hg$_5$ type, tP14, P4/mbm) [15] (large dark grey tetragonal cuboids and
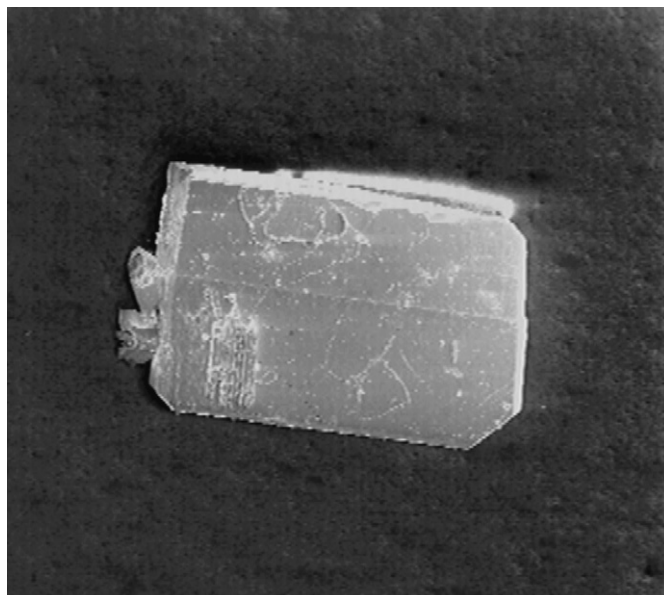

Fig. 1. SEM picture of a single crystal of $V_2Cu_3Ga_8$.
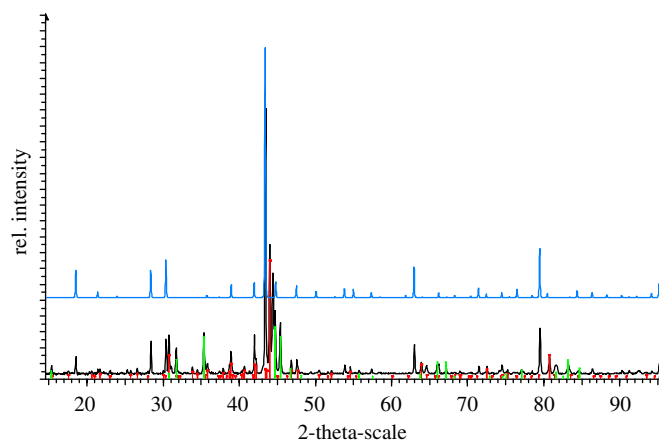

Fig. 2. Calculated (top) and observed (bottom) X-ray diffraction pattern of $V_2Cu_3Ga_8$, additional reflections (marked) are from $CuGa_2$ and $V_{11}Cu_9Ga_{46}$.

columns) and $V_{11}Cu_9Ga_{46}$ [11] (copper coloured rhombic dodecahedra). $V_2Cu_3Ga_8$ crystallises from syntheses with ratios between 1:15:6 and 1:20:8. Usually V_2Ga_5 is the domination reaction product, but at a ratio 1:20:8 $V_2Cu_3Ga_8$ is the main product, $CuGa_2$ and $V_{11}Cu_9Ga_{46}$ are only by-products. Fig. 2 shows the X-ray diffraction pattern (Cu-$K_{\alpha1}$, STOE, StadiP) of the residue.

2.1.4. EDX investigations

The compositions were confirmed by EDX measurements (Zeiss DSM 940, Link analytical Microprobe QX 2000 with energy dispersive detector) on single crystals. For this single crystals were embedded in Ag-containing epoxy resin and polished to obtain a clear and flat surface. For each compound several crystals were measured. The following results were obtained: $Mo_2Cu_3Ga_8$: 15.3% Mo,

22.8% Cu, 61.9% Ga; $W_2Cu_3Ga_8$: 15.0% W, 23.3% Cu, 61.7% Ga; $V_2Cu_3Ga_8$: 16.2% V, 22.0% Cu, 61.8% Ga. The uncertainty of these values is about ± 1%. Calculated values for $TM_2Cu_3Ga_8$ are: 15.38% TM, 23.08% Cu, 61.54% Ga.

2.2. Structure solution and refinement

2.2.1. $Mo_2Cu_3Ga_8$

A well-developed single crystal with the shape of a rhombic dodecahedron was mounted on a capillary and measured on a four circle diffractometer (Nonius CAD4, Mo-K_α-radiation, graphite monochromator). The indexing routine led to a cubic bodycentred unit cell. The refinement of 25 high angle reflection resulted in a lattice constant of 11.9171(10) Å. The measurement of $\frac{1}{4}$ of the Ewald-sphere up to $2\theta = 70°$ yielded in 3980 intensities and the Laue class $m\bar{3}m$. The reflection conditions $0kl$ with $k + l = 2n$, hhl with $2h + l = 4n$ and $00l$ with $l = 4n$ led to $I\bar{4}3d$ as the unique space group. The structure solution by Direct Methods (SHELXL [16]) with a data set of 613 independent reflections (436 with $I > 2\sigma(I)$) was started in space group $I\bar{4}3d$ and led to the four metal positions. The labelling of the metal atoms was derived from the electron densities and confirmed by a refinement of the site occupation factors. Because the deviations from full occupations are small an ordered and stoichiometric structure can be assumed. Investigations by EDX measurements of single crystals confirmed the composition $Mo_2Cu_3Ga_8$ (see experimental). Final R-factors were $R_1(F) = 0.0220$ and $wR_2(F^2) = 0.0469$.

2.2.2. $W_2Cu_3Ga_8$

A rhombic dodecahedron isolated from the W/Cu/Ga-melt was mounted on a capillary and measured on a four circle diffractometer (Nonius CAD4, Mo-K_α-radiation, graphite monochromator). The indexing routine led to a cubic bodycentred unit cell. The refinement of 25 high angle reflection resulted in a lattice constant of 11.9242(8) Å. The measurement of $\frac{1}{8}$ of the Ewald-sphere up to $2\theta = 70°$ gave 1960 intensities. Because of unit cell dimensions and symmetry a compound isotypic to $Mo_2Cu_3Ga_8$ was assumed and the refinement started with the known structure model. The refinement with 346 independent reflections (251 with $I > 2\sigma(I)$) converged without problems at R-factors of $R_1(F) = 0.0483$ and $wR_2(F^2) = 0.0863$. The refinements of the site occupation factors were consistent with an ordered and stoichiometric compound.

2.2.3. $V_2Cu_3Ga_8$

A cube like single crystal was isolated from the melt, mounted on a glass capillary and measured on a STOE IPDS single crystal diffractometer (Mo-K_α-radiation, graphite monochromator). The indexing routine showed a bodycentred cubic unit cell with $a = 11.7861(14)$ Å. The

measurement of a full Ewald-sphere up to $2\theta = 60°$ gave 14,094 intensities. Unit cell dimensions and symmetry suggested a structure of the $Mo_2Cu_3Ga_8$ type. The refinement with 374 independent reflections (302 with $I > 2\sigma(I)$) and 24 variables resulted in R-factors of $R_1(F) = 0.0334$ and $wR_2(F^2) = 0.0813$. In contrast to $Mo_2Cu_3Ga_8$ and $W_2Cu_3Ga_8$ the position of Cu showed a significant deficit (occupation 88.0(8)%) which was considered in the refinement.

Data of the refinements of $Mo_2Cu_3Ga_8$, $W_2Cu_3Ga_8$ and $V_2Cu_3Ga_8$ are listed in Table 1. Coordinates and thermal displacement parameters are given in Table 2. Selected distances are shown in Table 3. Further details on the structure refinements (complete list of distances and angles, F_o/F_c-list) may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) (fax: +49)724-808-666: e-mail: crysdata@fiz-karlsruhe.de) on quoting the registry numbers CSD-416813 ($Mo_2Cu_3Ga_8$), 416814 ($W_2Cu_3Ga_8$) and 416815 ($V_2Cu_3Ga_8$).

3. Results and discussion

3.1. Structure description

The crystal structure of $Mo_2Cu_3Ga_8$ (Fig. 3) represents a new structure type. The easiest description makes use of its close relation to the bcc packing or the CsCl type, respectively. The two independent Ga atoms built up a nearly undistorted cubic primitive array. Mo occupies $\frac{1}{4}$ of the cubic voids in a way as it is observed in the PtHg$_4$ type [18] (Fig. 4) which is also found for other Ga-rich compounds like CrGa$_4$ [10,19], MnGa$_4$ [10,20] and ReGa$_4$ [21]. In ReGa$_4$ Re forms ReGa$_8$ cubes which are connected by common corners in all directions. The Cu atoms occupy $\frac{1}{2}$ of the free cubic voids (i.e. in total 3/8 of all). Thus the structure of $Mo_2Cu_3Ga_8$ can be classified as an ordered defect variant of a bcc packing with a 64-fold super structure and $a' = 4a$: $[(TM)_2(Cu)_3(\square)_3][Ga_8]$.

The coordination polyhedra (Fig. 5) of the four independent metal atoms can directly be derived from the CsCl-type. Mo has a cubic surrounding of 8 Ga atoms. With respect to the MoGa$_8$ cubes the Cu atoms cap three neighboured sides of the cube leading to an 11-fold coordination of Mo. The MoGa$_8$ cubes are nearly regular with Mo–Ga distances between 2.564(1) and 2.603(1) Å. The Mo–Cu distances of 2.773(1) Å are slightly longer (7%). For a regular bcc structure a difference of 15.5% is expected. Fig. 5 shows that the Ga1–Ga2 vertices which belong to the capped sides are expanded (Ga1–Ga2: 2.733(1) to 3.240(1) Å). The Cu atoms have also a cubic coordination of Ga-atoms (2.632(1)–2.660(1) Å). Additionally two opposite sides are capped by Mo. Despite the smaller atomic radius of Cu ($r_{Cu} = 1.28$ Å [22]) the Cu–Ga distances are longer than the Mo-Ga distances ($r_{Mo} = 1.40$ Å [22]). Both of the Ga atoms

Table 1

Crystallographic data and refinement for $TM_2Cu_3Ga_8$ (TM = V, Mo, W)

Compound	$V_2Cu_3Ga_8$	$Mo_2Cu_3Ga_8$	$W_2Cu_3Ga_8$
Temperature	293(2)K	293(2)K	293(2)K
Crystal shape	Cube like polyhedron	Rhombic dodecahedron	Rhombic dodecahedron
Size	$0.2 \times 0.2 \times 0.2\,mm^3$	$0.1 \times 0.1 \times 0.1\,mm^3$	$0.1 \times 0.1 \times 0.1\,mm^3$
Crystal system	Cubic	Cubic	Cubic
Space group	$I\bar{4}3d$ (Nr. 220)	$I\bar{4}3d$ (Nr. 220)	$I\bar{4}3d$ (Nr. 220)
Unit cell	$a = 11.7861(14)\,Å$	$a = 11.9171(10)\,Å$	$a = 11.9242(8)\,Å$
	$V = 1637.2(4)\,Å^3$	$V = 1692.4(3)\,Å^3$	$V = 1695.5(3)\,Å^3$
	$Z = 8$	$Z = 8$	$Z = 8$
$d_{calc.}$	$6.899\,g/cm^3$	$7.381\,g/cm^3$	$8.745\,g/cm^3$
Radiation	$MoK\alpha$, $\lambda = 0.71073\,Å$	$MoK\alpha$; $\lambda = 0.71073\,Å$	$MoK\alpha$; $\lambda = 0.71073\,Å$
Data collection	STOE IPDS II,	Nonius – CAD4	Nonius – CAD4
	$0° \leqslant \omega \leqslant 180°$;	$\omega/2\theta$-scan	$\omega/2\theta$-scan
	$\psi = 0°$, 111°; $\Delta\omega = 2$	$0.37 + 0.41 \tan\theta$	$0.70° + 0.35 \tan\theta$
Measure time	300 s	45 s	60 s
Theta range	$3° < 2\theta < 60°$	$3° < 2\theta < 70°$	$3° < 2\theta < 70°$
	$-16 \leqslant h \leqslant 16$	$-19 \leqslant h \leqslant 19$	$0 \leqslant h \leqslant 19$
	$-16 \leqslant k \leqslant 16$	$0 \leqslant k \leqslant 19$	$0 \leqslant k \leqslant 19$
	$-16 \leqslant l \leqslant 16$	$0 \leqslant l \leqslant 19$	$0 \leqslant l \leqslant 19$
μ	$35.54\,mm^{-1}$	$35.14\,mm^{-1}$	$59.24\,mm^{-1}$
Absorption correction	STOE, XSHAPE [17]	empirical, Ψ-scan	empirical, Ψ-scan
$R_{int.}/R_{sigma}$	0.122/0.027	0.123/0.059	0.228/0.101
Refinement	SHELXL [16]	SHELXL [16]	SHELXL [16]
$N(hkl)$ meas.; unique	14094, 374	3980, 613	1960, 346
$N'(hkl)$ ($I > 2\sigma(I)$)	302	436	251
Parameters refined	24	23	23
R-values	$R_1(F) = 0.0334$, $wR_2(F^2) = 0.0813$	$R_1(F) = 0.0220$, $wR_2(F^2) = 0.0468$	$R_1(F) = 0.0483$, $wR_2(F^2) = 0.0863$
All data	$R_1 = 0.0463$	$R_1 = 0.0496$	$R_1 = 0.0932$
Weighting scheme	0.0424/11.28	0.0110/0.0	0.0161/0.0
Extinction correction	0.00041(4)	0.0010(1)	0.00024(5)
Refinement as twin (inversion)	0.80(11)	0.97(2)	0.39(12)
Goodness of fit	1.093	1.018	1.121
Residual electron density (max., min., sigma)	$+0.71/-1.05/0.25\,e^-/Å^3$	$+1.01/-1.58/0.32\,e^-/Å^3$	$+3.86/-4.56/0.87e^-/Å^3$

Table 2

Atomic coordinates, isotropic displacement parameters (in ($Å^2$)) and site occupation factors (in (%)) for $TM_2Cu_3Ga_8$ (TM = V, Mo, W), e.s.d.'s in parentheses

Compound	Atom	Site/symmetry	X	y	z	$U_{eq.}$	Sof[a]
$V_2Cu_3Ga_8$							
	V	16c/.3.	0.98843(11)	0.98843(11)	0.98843(11)	0.0040(5)	100(1)
	Cu	24d/2..	0.00505(13)	0.0	0.75	0.0053(5)	88.0(8)
	Ga1	48e/1	0.12614(7)	0.11698(15)	0.38025(7)	0.0091(4)	99(1)
	Ga2	16c/.3.	0.11359(12)	0.11359(12)	0.11359(12)	0.0082(5)	101(1)
$Mo_2Cu_3Ga_8$							
	Mo	16c	0.98183(3)	0.98183(3)	0.98183(3)	0.0023(1)	102.5(5)
	Cu	24d	-0.0121(1)	0.0	0.75	0.0085(2)	97.3(5)
	Ga1	48e	0.11521(5)	0.12115(7)	0.37916(4)	0.0069(1)	100.4(9)
	Ga2	16c	0.10767(7)	0.10767(7)	0.10767(7)	0.0059(2)	99.9(6)
$W_2Cu_3Ga_8$							
	W	16c	0.98057(6)	0.98057(6)	0.98057(6)	0.0051(3)	97.9(9)
	Cu	24d	-0.0159(4)	0.0	0.75	0.0108(7)	96.4(14)
	Ga1	48e	0.1139(3)	0.1198(5)	0.3785(4)	0.0110(5)	105(2)
	Ga2	16c	0.1067(3)	0.1067(3)	0.1067(3)	0.0067(9)	107(2)

[a]In order to check for mixed occupations and/or vacancies site occupation factors were treated by turns as free variables at the end of the refinement.

have similar 11-fold surroundings which are built up by a Ga_6 octahedron because of the underlying cubic primitive lattice of the Ga atoms. Five of the eight sides are capped by two Mo and three Cu atoms. The distances to the 6 Ga atoms of the octahedra are not equal but reflect the distortion of the Ga_8 cubes.

Table 3
Selected distances (in (Å)) in $TM_2Cu_3Ga_8$ (TM = V, Mo, W), e. s. d.'s in parentheses

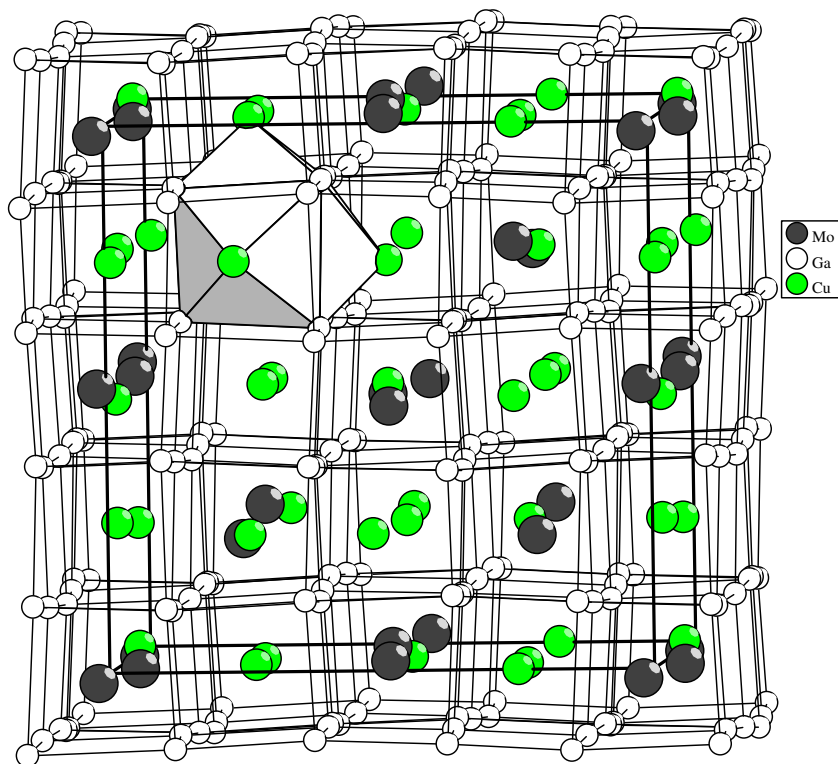| $V_2Cu_3Ga_8$				$Mo_2Cu_3Ga_8$				$W_2Cu_3Ga_8$			
V	Ga2	2.549(3)		Mo	Ga2	2.563(1)		W	Ga2	2.559(7)	
	Ga2	2.555(3)			Ga2	2.597(1)			Ga2	2.604(7)	
	Ga1	2.564(1)	3x		Ga1	2.599(1)	3x		Ga1	2.604(4)	3x
	Ga1	2.568(1)	3x		Ga1	2.603(1)	3x		Ga1	2.607(4)	3x
	Cu	2.820(1)	3x		Cu	2.772(1)	3x		Cu	2.760(1)	3x
Cu	Ga1	2.549(2)	2x	Cu	Ga1	2.568(1)	2x	Cu	Ga1	2.538(6)	2x
	Ga1	2.562(2)	2x		Ga1	2.599(1)	2x		Ga1	2.635(6)	2x
	Ga1	2.616(1)	2x		Ga2	2.633(1)	2x		Ga2	2.617(3)	2x
	Ga2	2.675(2)	2x		Ga1	2.660(1)	2x		Ga1	2.688(4)	2x
	V	2.820(1)	2x		Mo	2.772(1)	2x		W	2.760(1)	2x
	Cu	2.827(3)			Cu	3.267(2)			Cu	3.263(8)	
Ga1	Cu	2.549(2)		Ga1	Cu	2.568(1)		Ga1	Cu	2.538(6)	
	Cu	2.562(2)			Mo	2.599(1)			W	2.604(4)	
	V	2.564(1)			Cu	2.599(1)			Cu	2.635(1)	
	V	2.568(1)			Mo	2.603(1)			W	2.607(4)	
	Cu	2.616(1)			Cu	2.660(1)			Cu	2.688(4)	
	Ga2	2.723(1)			Ga2	2.733(1)			Ga2	2.707(4)	
	Ga1	2.878(2)	2x		Ga1	2.914(1)	2x		Ga1	2.919(6)	2x
	Ga1	3.058(2)	2x		Ga1	3.053(1)	2x		Ga1	3.081(6)	2x
	Ga2	3.147(3)			Ga2	3.240(1)			Ga2	3.248(4)	
Ga2	V	2.549(3)		Ga2	Mo	2.563(1)		Ga2	W	2.559(7)	
	V	2.555(3)			Mo	2.597(1)			W	2.604(7)	
	Cu	2.675(1)	3x		Cu	2.633(1)	3x		Cu	2.617(3)	3x
	Ga1	2.723(1)	3x		Ga1	2.733(1)	3x		Ga1	2.707(4)	3x
	Ga1	3.147(3)	3x		Ga1	3.240(1)	3x		Ga1	3.248(4)	3x

Fig. 3. Crystal structure of $Mo_2Cu_3Ga_8$; thin lines between Ga-atoms emphasise the cubic primitive packing, the shaded polyhedron represents the 8 + 3 coordination $MoGa_8Cu_3$ (see text).
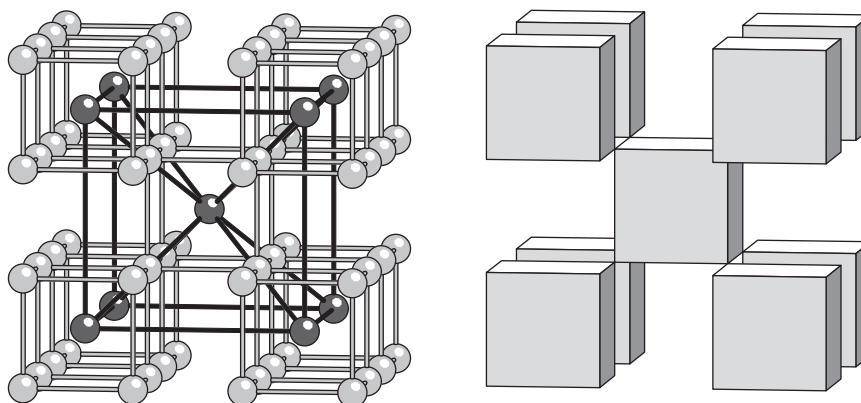
Fig. 4. Crystal structure of ReGa$_4$ (PtHg$_4$-type); left side as an atom model, right side as a polyhedra model with ReGa$_8$ cubes arranges as bodycentred cubes.
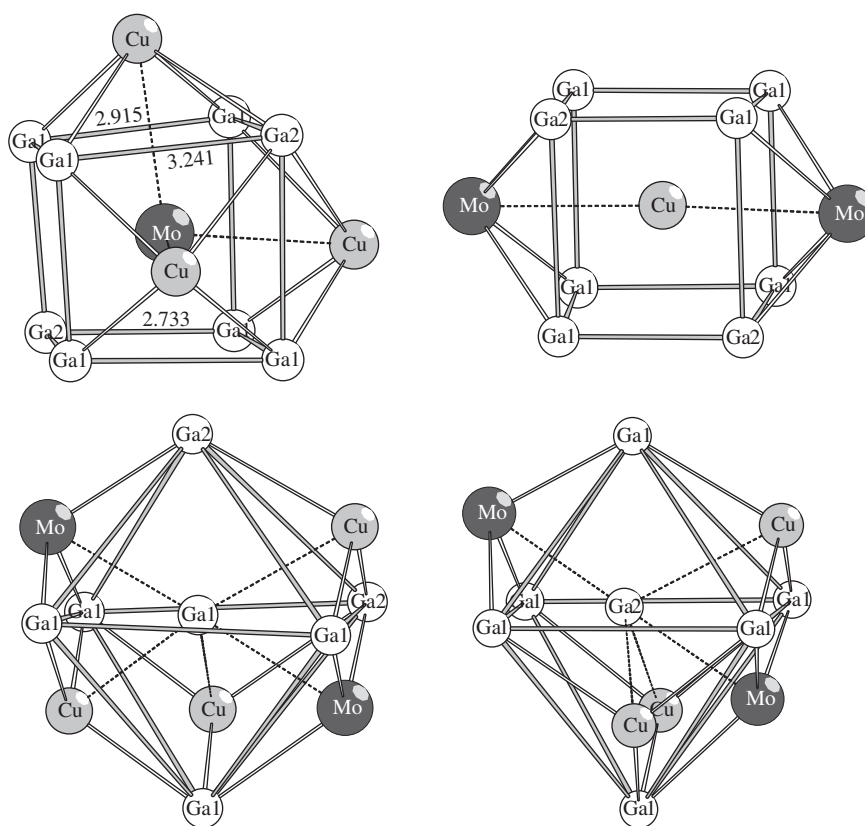

Fig. 5. Coordination polyhedra in Mo$_2$Cu$_3$Ga$_8$, Mo dark grey, Cu light grey, Ga white; bonds to capping atoms are drawn as dotted lines.

Mo$_2$Cu$_3$Ga$_8$ shows a close relationship to Ni$_3$Ga$_4$ [23] (see group–subgroup relation). The structure of Ni$_3$Ga$_4$ is a defect variant of the CsCl type with $\frac{1}{4}$ unoccupied cubic voids. In Mo$_2$Cu$_3$Ga$_8$ these voids are occupied by Mo, $\frac{1}{2}$ of the Ni sites is replaced by Cu while the other Ni positions remain free.

Furthermore, there are similarities to γ-brass and related structures which are observed for many intermetallics, for example Cu$_9$Ga$_4$ [24]. γ-brass can be described as a 27-fold super structure of a bcc packing ($a' = 3a$). In the regular γ-brass structure (cI52, $I\bar{4}3m$) 52 of the 54 positions of the

bcc packing are occupied. The size of the voids is reduced by a significant distortion of the lattice and the $8+6$ coordination. Therefore the four different sites have coordination numbers of 11 (site 24g), 12 (two sites 8c) and 13 (site 12e). In Mo$_2$Cu$_3$Ga$_8$ 104 of 128 sites are occupied and the deviations from the bcc packing are much smaller. In sum a less dense arrangement results for Mo$_2$Cu$_3$Ga$_8$ because a higher amount of the cubic voids remains empty. This may be explained by the tendency in Mo$_2$Cu$_3$Ga$_8$ to keep up the $8+3$ coordination of the Mo atoms. In this way the ReGa$_4$ type can be seen as the most

extreme example where a structure with $\frac{3}{4}$ of empty voids is "stable" against distortion.

3.2. Motif of self-similarity

The structure of $Mo_2Cu_3Ga_8$ shows small but significant deviations from the topology of a bcc packing (or CsCl type, respectively). Because the Mo atoms form a bcc packing for its own with a "pseudo-lattice constant" of $a/2$ the typical $8+6$ pattern is expected with a difference of about 15% between the eight shorter and the six longer distances. For $Mo_2Cu_3Ga_8$ with $a = 11.917\,\text{Å}$ Mo–Mo distances of $\sqrt{3}\cdots a/4 = 5.16\,\text{Å}$ (8x) and $a/2 = 5.96\,\text{Å}$ (6x) can be calculated. While the 8 short distances are very close to these values (5.160–5.196 Å) there are large deviations for the six longer distances with values of 5.543 Å (3x) and 6.405 Å (3x), i. e. the $8+6$ pattern is split to a $8+3+3$ pattern. The short distances of 5.543 Å occur in the direction where the cubes are capped by Cu (two times the Mo–Cu distance). This means the coordination polyhedron of Mo ($MoGa_8Cu_3$) is surrounded by 11 other $MoGa_8Cu_3$ polyhedra as a 3-fold capped cube and CN 14 of the bcc packing ($8+6$) is reduced to CN 11 ($8+3$). Fig. 6 shows the coordination of the $MoGa_8Cu_3$ polyhedron by the $8+3$ Mo atoms and the Mo-polyhedra.

This continues the row of intermetallic structures with motifs of self similarity in a way that the arrangement of the coordination polyhedra mirrors the polyhedron itself. In the structure of $Mo_2Cu_3Ga_8$ 3-fold capped cubes are arranged as 3-fold capped cubes. Further examples for polyhedra with higher symmetry are $ReGa_4$ with body-centred cubes of bodycentred cubes (Fig. 4), $Mo_7Sn_{12}Zn_{40}$ with icosahedra of icosahedra [8], $MoZn_6$ with cuboctahedra of cuboctahedra [9–11] and $MoZn_{6-x}Ga_x$ ($x = 1.5$) with anticuboctahedra of anticuboctahedra [9–11].

3.3. Group–subgroup relations

The relation of the structure of $Mo_2Cu_3Ga_8$ to Ni_3Ga_4, $ReGa_4$, CsCl and the bcc packing (W-type) can also be described with a group–subgroup relation [25,26] shown in Fig. 7. The first step (klassengleich, order 2) is the trivial transition from W type to CsCl type (loss of I-centering). The second step to $ReGa_4$ (klassengleich, order 4) from $Pm\bar{3}m$ to $Im\bar{3}m$ doubles the lattice constant. While the Ga atoms on site 8c still form a perfect cubic primitive packing the Cs site is split into two positions with multiplicities 2 and 6. The site 2a is occupied by Re and site 6b remains free. So $ReGa_4$ is a defect variant of CsCl with $\frac{3}{4}$ vacancies: $[Re,(\delta)_3]Ga_4$ (or a filled variant of α-Po type). The third step reduces the symmetry from $Im\bar{3}m$ to $Pm\bar{3}n$ (klassengleich, order 2). The site symmetries are lowered, but the structure still contains only special positions without free variables and should be regarded as a virtual structure which is necessary to explain the next step. The transition to space group $Ia\bar{3}d$ is again klassengleich of order 4 with $a' = 2a$. The sites 2a and 6b transform to sites 16a and 48f, respectively. The 8e site is split into two sites, 16b and 48g. In the structure of Ni_3Ga_4 the sites 16a and 48f are occupied by Ga where the value of the free variable x is very close to 0. The second sublattice (with reference to the CsCl structure) is only partially filled, the site 16b remains free while Ni occupies the 48g site, so in total $\frac{1}{4}$ of the cubic voids are empty. Site 48g, too, has one free variable that allows a movement in direction of the face diagonal. The last transition to space group $I\bar{4}3d$ is translationengleich and leads to the $Mo_2Cu_3Ga_8$ structure. The sites 16a and 16b both transform to 16c with one free parameter (x, x, x). Site 48g transforms to a general site 48e without symmetry while 48f splits into two sites 24e. In $Mo_2Cu_3Ga_8$ Ga is on sites 16c and 48e, Mo on 16c and Cu on one of the 24e sites, the second remains free. The two sublattices of the 24e sites are connected by a centre of inversion. Because only one of the 24e sites is occupied by Cu it results an acentric structure. The primitive cubic lattice of the Ga atoms is split in a ratio 1:3 (or 2:6), the positions of the second primitive cubic sublattice form a 2:3:3 pattern.

In sum the deviations of $Mo_2Cu_3Ga_8$ from a bcc packing are very small. With regard to the "ideal" positions (Mo: 0,

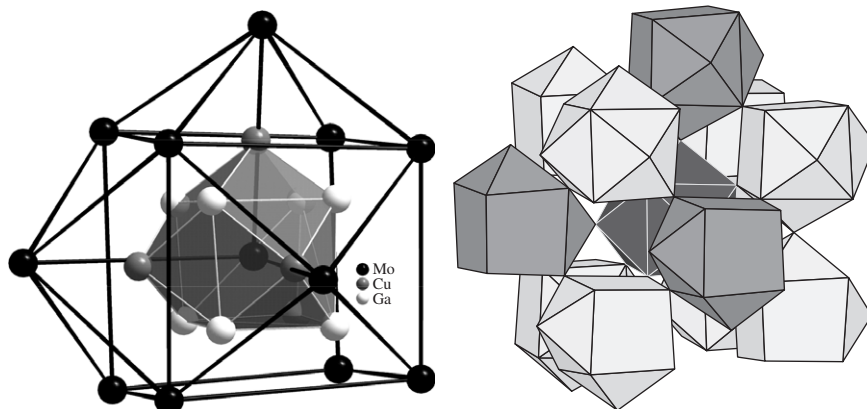Fig. 6. Coordination of the $MoGa_8Cu_3$ polyhedron by the $8+3$ Mo atoms (left) and the Mo-polyhedra (right).
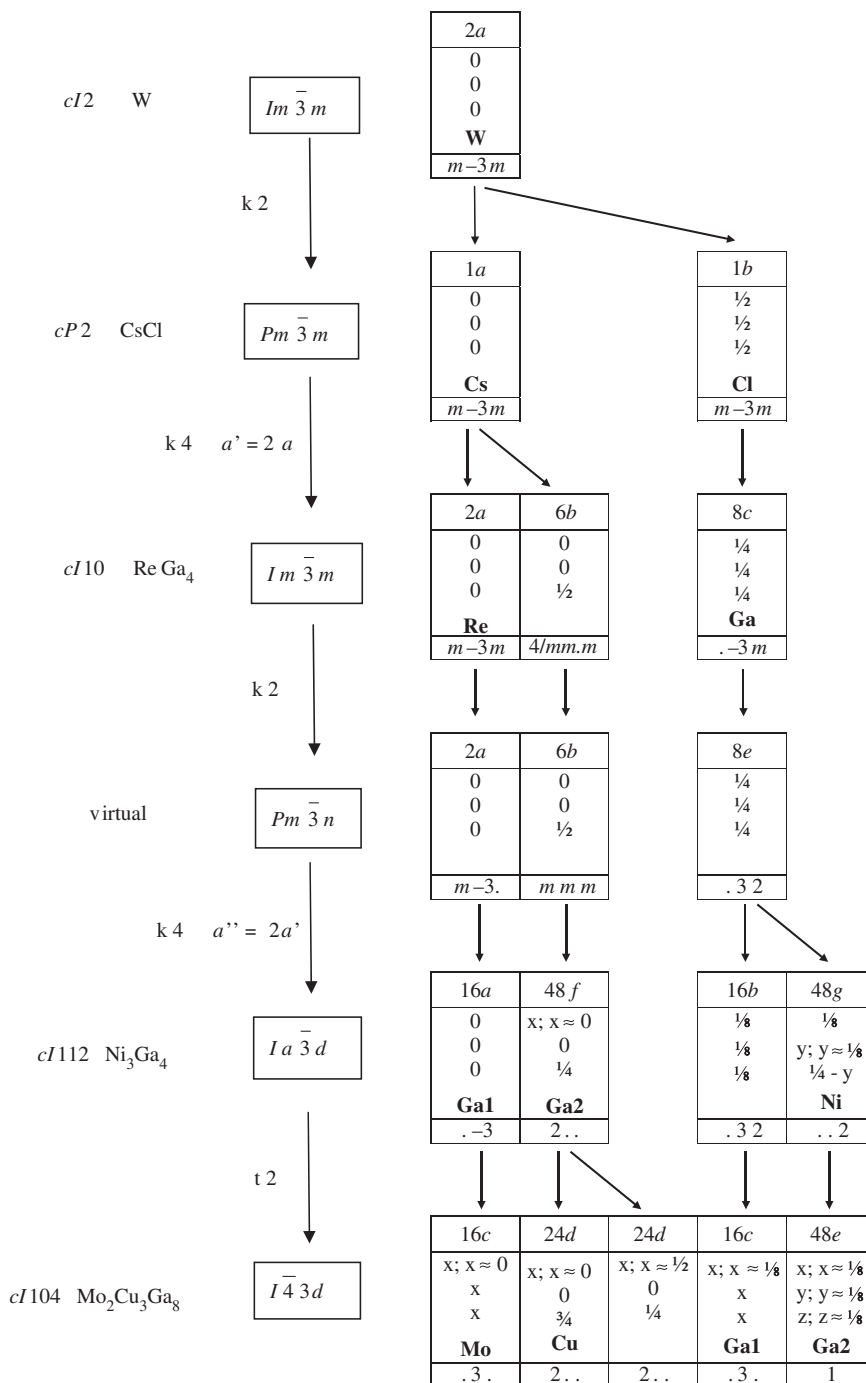
cI2   W $Im\bar{3}m$

2a
0
0
0
W
m−3m

k 2

cP2   CsCl $Pm\bar{3}m$

1a	1b
0	½
0	½
0	½
Cs	**Cl**
m−3m	m−3m

k 4   a' = 2 a

cI10   Re Ga$_4$ $Im\bar{3}m$

2a	6b	8c
0	0	¼
0	0	¼
0	½	¼
Re		**Ga**
m−3m	4/mm.m	.−3m

k 2

virtual $Pm\bar{3}n$

2a	6b	8e
0	0	¼
0	0	¼
0	½	¼
m−3.	m m m	. 3 2

k 4   a'' = 2a'

cI112   Ni$_3$Ga$_4$ $Ia\bar{3}d$

16a	48f	16b	48g
0	x; x ≈ 0	⅛	⅛
0	0	⅛	y; y ≈ ⅛
0	¼	⅛	¼ - y
Ga1	**Ga2**		**Ni**
.−3	2..	. 3 2	. . 2

t 2

cI104   Mo$_2$Cu$_3$Ga$_8$ $I\bar{4}3d$

16c	24d	24d	16c	48e
x; x ≈ 0	x; x ≈ 0	x; x ≈ ½	x; x ≈ ⅛	x; x ≈ ⅛
x	0	0	x	y; y ≈ ⅛
x	¾	¼	x	z; z ≈ ⅛
Mo	**Cu**		**Ga1**	**Ga2**
. 3 .	2 . .	2 . .	. 3 .	1

Fig. 7. Group–subgroup relation showing the connection between the bcc packing and Mo$_2$Cu$_3$Ga$_8$.

0, 0; Cu: 0, 0, ¾; Ga1: ⅛, ⅛, ⅛; Ga2: ⅛, ⅛, ⅜) there are shifts as following: Mo: 0.37, Cu: 0.14, Ga1: 0.14, Ga2: 0.36 Å.

3.4. W$_2$Cu$_3$Ga$_8$

Compared to Mo$_2$Cu$_3$Ga$_8$ the structure of W$_2$Cu$_3$Ga$_8$ shows only small differences. In agreement to the slightly larger metal radius of tungsten (r_W = 1.41 Å [22]) the lattice constant is enlarged and the W–Cu and W–Ga distances are (almost) a little bit elongated. The deviations from the ideal bcc arrangement are slightly larger. In a certain way the W–Ga distance is remarkable by itself because to our knowledge W$_2$Cu$_3$Ga$_8$ is the first ternary intermetallic phase containing tungsten and gallium.

3.5. V$_2$Cu$_3$Ga$_8$

The differences between V$_2$Cu$_3$Ga$_8$ and Mo$_2$Cu$_3$Ga$_8$ are small and are mainly a result of the different metal radii of vanadium and molybdenum. More pronounced features

are the differences between the V–Ga distances of the cube (2.55–2.57 Å) and the V–Cu distances of the capping atoms (2.82 Å) which amount to ca. 10%. The shifts from the positions of an ideal bcc packing are smaller (V: 0.24, Cu: 0.06, Ga1: 0.11, Ga2: 0.23 Å).

The deficit on the Cu site may be caused by a mixed V/Cu occupation or a real deficit on this site. A clear separation is not possible because there are reasons for both. On the one hand the radii of vanadium and copper are more similar ($r_V = 1.36$ Å; $r_{Cu} = 1.28$ Å) so a substitution is more likely. On the other hand $CrGa_4$ [10,19] and $MnGa_4$ [10,20] are known to adopt the $ReGa_4$ structure, which corresponds to a "complete" Cu deficit.

The close relation to the bcc packing according to a superstructure with $a' = 4a$ is clearly seen in Fig. 2. The strong reflection at $2\theta = 43°$ is the reflection (440). This is very similar to Cu_9Ga_4 with a γ-brass structure [24] and $CrGa_4$ where the reflections (330) and (220), respectively, are extremely strong, too.

4. Conclusions

Structures of intermetallic compounds with a small part of a high melting metal and a major part of a low melting metal seem to be characterised by the formation of complex but highly symmetric structures with motifs of self-similarity. In case of the systems $TM_2Cu_3Ga_8$ ($TM =$ V, Mo, W) the transition metals are 11-fold coordinated by a cube of 8 Ga atoms which is threefold capped by Cu atoms. The cubic structure represents a new structure type ($cI104$, $I\bar{4}3m$) and can be explained as a 64-fold superstructure of a bcc packing ($a' = 4a$). The connection between the bcc packing and this new structure type is represented by a group–subgroup relation. Shifts of the metal atoms (about 0.4 Å) result in a three-dimensional arrangement in which the $TMGa_8Cu_3$-polyhedra itself are arranged in the way of 3-fold capped cubes.

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