Acta Cryst. (1961). **14**, 946

Gadolinium and Dysprosium Intermetallic Phases. I. The Crystal Structures of DyGa and GdPt and Their Related Compounds

By N. C. Baenziger and J. L. Moriarty, Jr.

Department of Chemistry, University of Iowa, Iowa City, Iowa, U.S.A.

(*Received* 17 *June* 1960 *and in revised form* 21 *November* 1960)

The intermetallic phases DyGa, DyGe, GdGa and GdGe are isostructural with the CrB structure type. The phases GdPt, DyPt, GdNi and DyNi have structures which are only slight distortions of the FeB structure type. The structures were determined by a combination of single crystal and powder methods.

Introduction

During an investigation of forty-two binary systems involving gadolinium and dysprosium, the intermediate phases DyGa and GdPt and several isotypes were found. The solution of their crystal structures was achieved with the aid of single crystal methods as well as powder methods.

Experimental

The alloys were prepared by arc-melting stoichiometric proportions of the component metals on a water-cooled copper hearth under an argon gas atmosphere. The purities of the metals used were: gadolinium and dysprosium, 99·8+%; gallium, 99·99%, platinum 98·5 to 99·0%. Fragments of the crushed alloys of DyGa (30·0 wt.% Ga) and GdPt (58·6 wt.% Pt) were examined by X-ray methods using a Buerger precession camera with Mo $K\alpha$ radiation. Upon repeated trials fragments were found which consisted of only a few crystals. The largest crystal was then aligned to obtain the diffraction data. Intensities for both structures were estimated by visual comparison with a series of spots of known relative intensity. The data from both compounds were from 'poor' single crystals relative to those used in standard single crystal work. Absorption corrections could not be made in the usual fashion because the crystal fragments were so irregular. The absorption effects appeared to vary uniformly across the precession film, in some cases parallel to the horizontal axis, in other orientations, perpendicular to the horizontal axis. A convenient way to achieve partial compensation for this effect was used in the last stages of the structure refinement by replacing the isotropic temperature factor by $\exp-(h^2\mathrm{A}+k^2\mathrm{B}+l^2\mathrm{C})$, where A, B and C are constants. The values of these constants, as determined by the least-squares method, have no validity as temperature factors (some were even negative). However, the use of this exponential factor reduced the discrepancy factor, R, from 0·24 to 0·14 for DyGa and from 0·25 to 0·20 for GdPt. The parameters changed less than 0·001 units after the introduction of the factor in the calculations.

DyGa

The unit cell dimensions of orthorhombic DyGa and its isotypes are given in Table 1. Precession photographs of $(h0l)$ through $(h3l)$, $(hk0)$, and $(hk1)$ were used in determining the structure of DyGa. The systematic absences were characteristic of space groups $Cmcm$, $Cmc2_1$ and $C2cm$. The calculated density with four formula units per unit cell is 8·04 g.cm.$^{-3}$ for DyGa.

Table 1. *Unit-cell dimensions of* DyGa, GdPt *and their isotypes*

CrB Type structures

	a (Å)	$\sigma(a)$ (Å)	b (Å)	$\sigma(b)$ (Å)	c (Å)	$\sigma(c)$ (Å)	Vol. (Å^3)
DyGa	4·300	0·004	4·067	0·001	10·89	0·02	190·4
GdGa	4·341	0·008	4·066	0·003	11·02	0·02	194·5
DyGe	4·112	0·002	3·924	0·006	10·81	0·02	174·4
GdGe	4·175	0·002	3·960	0·003	10·61	0·01	175·4

FeB Type structures

	a (Å)	$\sigma(a)$ (Å)	b (Å)	$\sigma(b)$ (Å)	c (Å)	$\sigma(c)$ (Å)	Vol. (Å^3)
GdPt	5·574	0·005	4·458	0·003	7·164	0·003	178·0
DyPt	5·466	0·011	4·453	0·013	7·118	0·009	173·3
GdNi	5·428	0·002	4·353	0·002	6·931	0·002	163·8
DyNi	5·353	0·004	4·319	0·002	6·895	0·002	159·4

Interatomic distances

For DyGa

Dy has 4Ga at 3·04, 1Ga at 3·11, 2Ga at 3.16, 2Dy at 3·66, 4Dy at 3·86 Å.

Ga has 2Ga at 2·58, 4Dy at 3.04, 1Dy at 3·11, 2Dy at 3·16 Å.

For GdPt

Gd has 1Pt at 2·93, 4Pt at 2·98, 1Pt at 3·02, 1Pt at 3·03, 4Gd at 3·69, 2Gd at 3·75, 2Gd at 3·82 Å.

Pt has 2Pt at 2·86, 1Gd at 2·93, 4Gd at 2·98, 1Gd at 3·02, 1Gd at 3·03 Å.

From the unit cell dimensions, space group, and the number of formula units per unit cell it appeared that DyGa might be isostructural with an analogous compound, ThAl, reported by Braun & Van Vucht (1955). The atom positions described by these authors can also be represented in space group *Cmcm*. The least-squares refinement was therefore carried out using the atom parameters reported for ThAl as the starting parameters. The lowest overall discrepancy factor obtained, $R = 0\cdot135$ excludes all absent reflections. Including the absent reflections in the final refinement stage yields an R factor of 0·147.

GdPt

The unit cell dimensions of GdPt and its isotypes are given in Table 1. Precession photographs of GdPt for the indices (0*kl*) through (2*kl*) and (*hk*0) through (*hk*2) were used in the structure determination. Systematic absences corresponded to space groups *Pnma* and *Pn*2₁*a*. The calculated density with four formula units per unit cell is 11·91 g.cm.$^{-3}$ for GdPt.

Trial atom parameters for gadolinium ($x = 0\cdot180$, $z = 0\cdot125$) and platinum ($x = 0\cdot040$, $z = 0\cdot610$) based on the parameters listed by Pearson (1958) for FeB and USi (space group *Pnma*) did not refine below an overall R value of 0·4. Patterson projections onto the (001) and (100) planes confirmed that $x_{Gd} - x_{Pt} = 0\cdot14$ and also that z parameters of 0·15 and 0·65 would be as satisfactory as 0·10 and 0·60. The refinement of the structure based on the new z parameters led to an overall R value of 0·20, omitting the absent reflections. A discrepancy factor, $R = 0\cdot22$, was obtained when all absent reflections were included in the final refinement stage.

Standard errors in atomic positions have not been given for either the DyGa or GdPt structures as they would be doubtful in significance due to the large absorption errors present in the data. From the way in which the parameters changed during refinement, however, an estimate of ±0·001 parameters units would appear to be reasonable. In the case of the DyGa structure the parameter values also appear to be in reasonable agreement with the values reported for PrGe.

Discussion

A search of the literature revealed that DyGa (and ThAl) not only was isostructural with CrB, but, furthermore, was isostructural with PrGe (reported to have the CaSi type structure). Upon changing the origin of the CaSi type structures and converting the parameters, the close relation of all the structures can be seen from the values in Table 2. A comparison of the parameter values of the GdPt structure is also given with the FeB isotypes in Table 3.

In the borides, the boron atoms occur in a zig-zag arrangement with the chain angle reported as about 117°. A much smaller angle, 102·9° was observed in the DyGa structure. The difference in chain angle is probably not significant, however, since the high chain angles are found in all the cases where the atoms involved have a much smaller scattering factor relative to the other atoms present. Consequently, their positions may not be determined as accurately.

Table 2. DyGa *related compounds*(1)

	y_{Me}	y_X	Chain angle
DyGa(2)	0·140	0·426	102·9°
GdGa(2)	—	—	—
DyGe(2)	—	—	—
GdGe(2)	—	—	—
PrGe	0·141	0·426	102·6
CaGe	0·146	0·424	100·7
CaSn	0·143	0·416	96·6
CaSi	0·14	0·43	105
ThCo	0·136	0·416	91·2
ThAl	0·147	0·443	116
ζ-CrB(3)	0·146	0·440	115
(4)	0·143	0·43	106·7
NiB	0·146	0·440	118·5
VB	—	—	—
γ-TaB	0·146	0·440	116
γ-NbB	0·146	0·440	117
WB	—	—	—
β-MoB	—	—	—

(1) Crystallographic data from compilation by Pearson (1958) unless otherwise noted.
(2) Present work.
(3) Kiessling (1949).
(4) Frueh (1951).

Table 3. GdPt *related compounds*(1)

	Atom parameters				
	x_M	z_M	x_X	z_X	Chain angle
GdPt(2)	0·185	0·144	0·040	0·653	102·5°
DyPt(2)	—	—	—	—	—
GdNi(2)	—	—	—	—	—
DyNi(2)	—	—	—	—	—
ThSi	0·18	0·13	0·03	0·61	113·6
USi	0·180	0·125	0·028	0·611	112
PuSi	—	—	—	—	—
ZrSi	0·178	0·125	0·032	0·611	112·7
TiB	0·177	0·123	0·029	0·603	113·4
ζ-MnB	0·180	0·125	0·031	0·614	110
CoB	0·180	0·125	0·037	0·625	110
FeB	0·180	0·125	0·031	0·620	112

(1) Crystallographic data from compilation by Pearson (1958) unless otherwise noted.
(2) Present work.

The authors wish to thank the Lunex Company, Pleasant Valley, Iowa, for supplying the rare-earth metals used in this study. The project was supported by Grant G6225 of the National Science Foundation. Computations were made with the aid of NSF Grant G6085.

References

Braun, P. B. & Van Vucht, J. H. N. (1955). *Acta Cryst.* **8**, 246.

Frueh, A. J. (1951). *Acta Cryst.* **4**, 66.

Kiessling, R. (1949). *Acta Chem. Scand.* **7**, 595.

Kiessling, R. (1950). *Acta Chem. Scand.* **4**, 209.

Pearson, W. B. (1958). *A Handbook of Lattice Spacings and Structures of Metals and Alloys.* London: Pergamon Press.