Acta Cryst. (1961). **14**, 948

Gadolinium and Dysprosium Intermetallic Phases. II. Laves Phases and Other Structure Types

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)

Unit-cell dimensions and interatomic distances are given for the following phases: $MgCu_2$ type: GdX_2 and DyX_2 where X = Pt, Mn, Fe, Co, Ni and Al; CsCl type: GdX and DyX where X = Ag, Cu, In, Tl and Al; $AuCu_3$ type: $GdIn_3$, $DyIn_3$, $DyTl_3$, $DyPt_3$; $MoSi_2$ type: $GdAg_2$, $DyAg_2$, $GdAu_2$, $DyAu_2$; $CuTi_3$ type: Dy_3In; $CaZn_5$ type: $GdNi_5$, $DyNi_5$, $GdCo_5$, $DyCo_5$; AlB_2 type: $GdGa_2$, $DyGa_2$; $SnNi_3$ type: $GdAl_3$.

Introduction

The rare-earth metals provide an opportunity to test the effect of atomic size in the structures of intermetallic phases. Reasonable quantities of gadolinium and dysprosium metals are now available, so that a fairly extensive investigation of their alloying behavior is possible. As a result the binary alloy systems of gadolinium and dysprosium with twenty-one metallic elements have been studied. For purposes of reporting, the elements have been divided into four groups: group *A*: Ti, V, Cr, Zr, Nb, Mo, Ta, W; group *B*: Mn, Fe, Co, Ni; group *C*: Cu, Ag, Au, Pt; group *D*: Al, Ga, In, Tl, Ge. The readily identified intermetallic phases are reported in this paper. Additional phases have been found, but their structures are yet to be confirmed.

Experimental methods

Alloys were first prepared from pure metals (analyses, Table 1) with stoichiometries corresponding to alloys previously reported in the analogous systems with La, Ce, Pr, or Nd. In addition, alloys were prepared with stoichiometries intermediate between these single phase regions and any other single phase region subsequently recognized.

Table 1. *Alloy materials*

Metal		% Metal	Metal	% Metal
Gadolinium	R107	99·8+	Cobalt	99·4
Gadolinium	**Subl.	98·2	Nickel	99·5
Gadolinium	*R160	99·14	Copper	99·9+
Dysprosium	R159	99·9+	Silver	99·9+
Titanium		99·5	Gold	99·99
Chromium		99·95	Germanium	99·9999999
Zirconium		99·0+	Platinum	98·5 to 99·0
Niobium		99·4	Gallium	99·99
Molybdenum		99·966	Aluminum	99·9+
Tantalum		99·8	Indium	99·0+
Tungsten		99·9	Thallium	99·95
Manganese		99·9+	Iron	99·8
Vanadium		99·5+		

The alloy specimens, 10 to 15 g. in size, were melted under half an atmosphere of argon in a small electric arc furnace consisting of a removable water-cooled hearth and tungsten electrode with power supplied by a 400 amp. d.c. welder. Each specimen was remelted repeatedly to improve homogeneity. If the final weight differed significantly from the initial weight of the alloying metals, a chemical analysis was performed

Table 2. $MgCu_2$ *structure type*(1)

Interatomic distances: Gd has 12*M* at (*D*), 4Gd at (*E*)
M has 6*M* at (*F*), 6Gd at (*D*)

	a (Å)	σ(*a*) (Å)	Vol. (Å³)	*D* (Å)	*E* (Å)	*F* (Å)
$GdPt_2$	7·6349	0·0008	445·05	3·165	3·306	2·699
(2)	7·637	0·001				
(3)	7·577	—				
$GdMn_2$	7·732	0·001	462·2	3·205	3·348	2·733
(4)	7·751	—				
(5)	7·724	0·005				
$GdFe_2$	7·389	0·003	403·4	3·063	3·200	2·612
(4)	7·445	—				
(5)	7·39	0·01				
$GdCo_2$	7·258	0·003	382·3	3·009	3·143	2·566
(5)	7·255	0·005				
$GdNi_2$	7·2056	0·0009	374·12	2·987	3·120	2·547
(5)	7·202	0·005				
$GdAl_2$	7·9020	0·0005	493·41	3·276	3·422	2·793
(5)	7·900	0·005				
$DyPt_2$	7·5966	0·0007	438·39	3·149	3·289	2·685
$DyMn_2$	7·5731	0·0008	434·33	3·139	3·279	2·677
(5)	7·564	0·005				
$DyFe_2$	7·321	0·001	392·4	3·035	3·170	2·588
(5)	7·325	0·01				
$DyCo_2$	7·190	0·004	371·7	2·980	3·113	2·542
(5)	7·187	0·005				
$DyNi_2$	7·142	0·004	364·3	2·961	3·093	2·525
(5)	7·155	0·005				
$DyAl_2$	7·835	0·001	481·0	3·248	3·393	2·770
(5)	7·840	0·005				

(1) *Strukturbericht*, **1**, 490 (1931).
(2) Compton & Matthias (1959).
(3) Dwight (1961).
(4) Endter & Klemm (1944).
(5) Wernick & Geller (1960).

using either standard wet chemical procedures or flame spectrophotometry.

X-ray diffraction powder photographs were made of the alloy specimens in either the 'as-melted' or annealed condition. Filings were annealed in vycor capillaries 'gettered' with zirconium wire. The X-ray photographs were made with a 57·3 mm. radius Debye–Scherrer camera with Fe $K\alpha$ radiation. Metallographic examination was carried out on the macro specimens to determine the homogeneity and to identify the phases present. Microhardness measurements (Eberbach) were also used to help identify the phases present in the microstructures.

Table 3. CsCl *structure type*(1)

Interatomic distances: Gd has 8*M* at (*D*), 6 Gd at (*a*)
M has 8 Gd at (*D*), 6*M* at (*a*)

	a (Å)	$\sigma(a)$ (Å)	Vol. (Å^3)	*D* (Å)
GdAg	3·6476	0·0008	48·53	3·157
GdCu	3·503	0·001	43·0	3·034
GdIn	3·830	0·001	56·18	3·317
GdTl	3·7797	0·0009	54·00	3·274
GdAl(2)	3·7208	0·0002	51·51	3·222
DyAg	3·608	0·001	46·97	3·125
DyCu	3·461	0·001	41·46	2·997
DyIn	3·7866	0·0009	54·29	3·281
DyTl	3·743	0·002	52·44	3·242
DyAl(2)	3·6826	0·0004	49·94	3·190

(1) *Strukturbericht*, **1** 74 (1931).
(2) Not the major constituent of powder photograph and not all other lines of the pattern identified.

Table 4. AuCu$_3$ *structure type*(1), (2)

Interatomic distances: Each atom is surrounded by 12 others at (*D*). The number and type of neighbors depends on the degree of ordering

	a (Å)	$\sigma(a)$ (Å)	Vol. (Å^3)	*D* (Å)
GdIn$_3$	4·6103	0·0002	97·99	3·260
GdTl$_3$	4·696	0·001	103·6	3·321
DyIn$_3$	4·5762	0·0009	95·83	3·236
DyTl$_3$	4·6720	0·0009	101·98	3·304
DyPt$_3$	4·072	0·001	67·52	2·879

(1) *Strukturbericht*, **1**, 486 (1931).
(2) Due to the relative values of the scattering factors, the existence of ordering could not be detected.

The diffraction patterns of the alloys of Gd and Dy with the metals of group *A* showed lines only of the metals and none corresponding to intermediate phases. The back-reflection regions of these X-ray diagrams were compared visually with similar regions of diagrams of the pure metals prepared with the same camera. Significant changes in the line positions occurred only for Gd in the Gd–Zr system and for Dy in the Dy–Zr system. The lines due to the rare-earth metal shifted in a direction indicating a smaller cell dimensions. Since the size of the Zr atom is smaller than that of the rare-earth metals, it appears that solubility is very small in the rare-earth metals except for Zr, and that the rare-earth metals do not dissolve appreciably in the group *A* metals. However, since extended annealing treatments and precision cell dimension determinations have not yet been performed, definite solubility limits cannot be given.

Table 6. AlB$_2$ *structure type* (*hexagonal*) (1)

Interatomic distances: Gd has 12 Ga at (*D*)
Ga has 3 Ga at (*E*), 6 Gd at (*D*)

	a (Å)	$\sigma(a)$ (Å)	*c* (Å)	$\sigma(c)$ (Å)	Vol. (Å^3)	*D* (Å)	*E* (Å)
GdGa$_2$	4·221	0·001	4·141	0·002	63·89	3·197	2·437
DyGa$_2$	4·2011	0·0003	4·0655	0·0005	62·14	3·165	2·426

(1) *Strukturbericht*, **3**, 28 (1937).

Table 7. SnNi$_3$ *structure type* (*hexagonal*) (1)

Interatomic distances: Gd has 6 Al at 3·154, 6 Al at 2·929
Al has 2 Ge at 3·154, 2 Gd at 2·929
4 Al at 3·154, 4 Al at 2·929

GdAl$_3$ $a = 6{\cdot}308 \pm 0{\cdot}003$ Å, $c = 4{\cdot}589 \pm 0{\cdot}009$ Å, Vol. = 158·1 Å^3

(1) *Strukturbericht*, **5**, 7 (1940).

The unit-cell dimensions of the intermetallic phases found in groups *B*, *C* and *D* are presented in Tables 2 through 9. The unit cell dimensions were calculated from back-reflection data by a least-squares fitting of $\sin^2\theta_o = \sin^2\theta_c + K\varphi\sin\varphi$, where φ is $=\pi/2-\theta$, and *K* is a constant. For each structure type, intensity calculations were made for a representative compound

Table 5. CaZn$_5$ *structure type* (*hexagonal*) (1)

Interatomic distances: Gd has 6M_{I} at (*D*), 12M_{I}I at (*E*)
M_{I} has 3 Gd at (*D*), 6M_{II} at (*F*)
M_{II} has 4 Gd at (*E*), 4M_{I} at (*F*), 4M_{II} at (*G*)

	a (Å)	$\sigma(a)$ (Å)	*c* (Å)	$\sigma(c)$ (Å)	Vol. (Å^3)	*D* (Å)	*E* (Å)	*F* (Å)	*G* (Å)
GdNi$_5$	4·9129	0·0008	3·9640	0·0005	82·86	2·836	3·156	2·437	2·456
(2)	4·899	0·005	3·973	0·005					
(3)	4·910	—	3·988	—					
DyNi$_5$	4·8756	0·0002	3·9673	0·0001	81·67	2·815	3·143	2·432	2·438
(2)	4·869	0·005	3·969	0·005					
GdCo$_5$	4·978	0·005	3·973	0·002	85·26	2·874	3·185	2·452	2·489
(2)	4·974	0·005	3·973	0·005					
(4)	4·984	—	3·967	—					
DyCo$_5$	4·933	0·002	3·989	0·001	84·07	2·848	3·172	2·451	2·466
(2)	4·926	0·005	3·988	0·005					

(1) *Structure Reports*, **11**, 59. (2) Wernick & Geller (1959). (3) Endter & Klemm (1944). (4) Dwight (1961).

Table 8. $MoSi_2$ *structure type* (*tetragonal*) (1)

Interatomic distances: Gd has 2*M* at (*D*), 8*M* at (*E*)
M has 1 Gd at (*D*), 1*M* at (*D*), 4 Gd at (*E*), 4*M* at (*E*)

	a (Å)	σ(*a*) (Å)	*c* (Å)	σ(*c*) (Å)	Vol. (Å³)	*D* (Å)	*E* (Å)
$GdAg_2$	3·728	0·001	9·296	0·006	129·2	3·099	3·057
$DyAg_2$	3·6957	0·0002	9·213	0·001	125·8	3·071	3·031
$GdAu_2$	3·7320	0·0006	9·014	0·003	125·5	3·004	3·036
$DyAu_2$	3·6940	0·0006	8·956	0·003	122·2	2·985	3·009

(1) *Strukturbericht*, **1**, 741 (1931).

Table 9. $CuTi_3$ *structure type* (*tetragonal*) (1), (2)

Dy_3In $a = 4·602 \pm 0·004$ Å, $c = 4·945 \pm 0·004$ Å, Vol. = 104·7 Å³

(1) Pearson, (1958), p. 618.

(2) Due to the relative values of the scattering factors, the existence of ordering could not be detected.

in order to verify the choice of the structure. Powder diagrams of alloys intermediate to the single phase regions gave evidence that if any homogeneity ranges exist, they must be quite narrow.

The authors are indebted to Dr J. R. Doyle for preparing the computer programs for the LGP-30 for the evaluation of the cell dimensions. The rare-earth metals were furnished through the courtesy of the Lunex Company, Pleasant Valley, Iowa; American Metal Climax, Inc. donated the germanium, and the Climax Molybdenum Company furnished the molybdenum. The research was supported by a National Science Foundation Grant G6225. The computations were made possible by another NSF Grant, G6085.

References

Compton, V. B. & Matthias, B. T. (1959). *Acta Cryst.* **12**, 651.

Dwight, A. E. (1961). *Trans. Amer. Soc. Met.* **53**, 477.

Endter, F. & Klemm, W. (1944). *Z. anorg. Chem.* **252**, 377.

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

Wernick, J. H. & Geller, S. (1959). *Acta Cryst.* **12**, 662.

Wernick, J. H. & Geller, S. (1960). *Trans. Amer. Inst. Min. Met. Engrs.* **218**, 866.

Acta Cryst. (1961). **14**, 950

The Hydrogen Positions in Portlandite, $Ca(OH)_2$, as Indicated by the Electron Distribution

By Howard E. Petch

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England,
and Department of Metallurgy and Metallurgical Engineering, McMaster University, Hamilton, Ontario, Canada

(*Received* 28 *September* 1960)

X-ray diffraction and Fourier synthesis techniques have been used to determine the electron distribution in a crystal of portlandite with sufficient accuracy to establish the hydrogen positions. The atoms have been found to occupy the following positions:

$$\begin{array}{ll} \text{Ca} & (0, 0, 0) \\ \text{O} & \pm(\frac{1}{3}, \frac{2}{3}, u) \\ \text{H} & \pm(\frac{1}{3}, \frac{2}{3}, v) \end{array}$$

with $u = 0·2330 \pm 0·0004$ and $v = 0·395 \pm 0·008$. Independent anisotropic temperature factors were introduced for the calcium and oxygen ions. Also, in the final stages of refinement, systematic differences between the observed and calculated structure factors became apparent and their causes were traced to the Hartree scattering curves for Ca^{++} and O^{--} which were first used in the determination of the calculated structure factors. Semi-empirical scattering curves were derived and their use leads to an excellent agreement between the observed and calculated structure factors. After this work was completed new theoretical values for the scattering factors Ca^{++} and O^{-} became available and these have been compared with the derived semi-empirical values.

Introduction

Portlandite, $Ca(OH)_2$, and brucite, $Mg(OH)_2$, are isomorphous and their structures have been known for many years. They possess a simple layer structure in which each cation is at the centre of an octahedron which is defined by hydroxyl ions, one at each corner. These octahedra may be thought of as joined together in sheets perpendicular to the three-fold axis of the trigonal crystal by having hydroxyl ions in common. The sheets are stacked vertically one above the other. The brucite structure was determined by Aminoff (1919). Megaw (1933) obtained accurate values for the