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Equiatomic compounds of Y and the lanthanide elements with Ga. By A.E. DWIGHT, J.W. DOWNEY and R.A. CONNER, JR., *Argonne National Laboratory, Argonne, Illinois, U.S.A.*

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The CrB-type (B_f) structure has been identified in thirteen equiatomic AGa compounds in which the A component is Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, or Lu. Unit-cell constants are presented for all the compounds as well as the calculated and observed d spacings and intensities for NdGa.

Introduction

The CrB-type structure has been reported in ScGa, YGa (Schob & Parthé, 1965), LaGa, CeGa (Hohnke & Parthé, 1965), PrGa (Iandelli, 1960), GdGa, DyGa (Baenziger & Moriarty, 1961) and TbGa (Cable, Koehler & Wollan, 1964). The present work was carried out to determine whether all of the lanthanide-Ga equiatomic compounds were isostructural, and to obtain accurate unit-cell constants.

Experimental

The alloys were prepared by arc melting on a water-cooled copper hearth under an argon-helium atmosphere. Ga of 99.99% purity and Y and the lanthanide elements of 99.0% purity were used. Since the weight losses on melting were less than 1% of the initial weight, the final compositions were assumed to be identical with the intended compositions. The buttons were homogenized in evacuated capsules

at temperatures ranging from 600 to 1100°C. Powdered samples for X-ray diffraction studies were obtained by crushing the buttons and, since the alloys were brittle, a stress-relief anneal was not necessary.

Debye-Scherrer diffraction patterns were taken on powdered samples with filtered Cr $K\alpha$ radiation and a 114.6 mm diameter camera. The powdered samples of CeGa and LaGa were sealed in evacuated capillaries to retard oxidation, while the remaining alloy samples were glued to a quartz filament. The patterns were indexed by means of the Battelle Indexing Charts (Bell & Austin, no date) and the unit cell was found to be orthorhombic with extinctions typical of the CrB-type structure. The space group is $Cmcm$, no. 63, with both the rare earth and Ga atom in 4(c) positions, $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) + 0, y, \frac{1}{2}; 0, \bar{y}, \frac{1}{2}$. The alloys EuGa and YbGa were prepared with difficulty owing to loss of Eu and Yb. The diffraction patterns were not solved but were not of the CrB-type.

Table 1. *The lattice constants of gallium compounds with the CrB-type structure*

Compound	a_0 (Å)	b_0 (Å)	c_0 (Å)	V/M (Å ³)
ScGa ⁽¹⁾	4.022 ± 0.004*	10.204 ± 0.008	3.895 ± 0.004	
YGa ⁽⁶⁾	4.2963 ± 0.009	10.8760 ± 0.0023	4.0738 ± 0.009	47.59
YGa ⁽¹⁾	4.320 ± 0.004	10.86 ± 0.01	4.073 ± 0.004	
LaGa ⁽⁶⁾	4.5226 ± 0.006	11.5876 ± 0.0017	4.2559 ± 0.0006	55.76
LaGa ⁽²⁾	4.50 ± 0.01	11.39 ± 0.03	4.23	
CeGa ⁽⁶⁾	4.4651 ± 0.0003	11.4248 ± 0.0007	4.2153 ± 0.0002	53.76
CeGa ⁽²⁾	4.47 ± 0.01	11.34 ± 0.03	4.21 ± 0.01	
PrGa ⁽⁶⁾	4.4410 ± 0.0001	11.3370 ± 0.0003	4.1992 ± 0.0001	52.85
PrGa ⁽³⁾	4.452	11.331	4.195	
NdGa ⁽⁶⁾	4.4164 ± 0.0002	11.2758 ± 0.0006	4.1835 ± 0.0002	52.08
SmGa ⁽⁶⁾	4.3806 ± 0.0001	11.1219 ± 0.0003	4.1471 ± 0.0001	50.51
GdGa ⁽⁶⁾	4.3372 ± 0.0003	11.0316 ± 0.0008	4.1106 ± 0.0003	49.17
GdGa ⁽⁴⁾	4.341 ± 0.008	11.02 ± 0.02	4.066 ± 0.003	
TbGa ⁽⁶⁾	4.3114 ± 0.0002	10.9394 ± 0.0005	4.0851 ± 0.0002	48.17
TbGa ⁽⁵⁾	4.33	10.90	4.06	
DyGa ⁽⁶⁾	4.2913 ± 0.0011	10.8740 ± 0.0029	4.0672 ± 0.0011	47.45
DyGa ⁽⁴⁾	4.300 ± 0.004	10.89 ± 0.02	4.067 ± 0.001	
HoGa ⁽⁶⁾	4.2740 ± 0.0007	10.8008 ± 0.0019	4.0501 ± 0.0007	46.74
ErGa ⁽⁶⁾	4.2523 ± 0.0009	10.7443 ± 0.0023	4.0329 ± 0.0009	46.06
TmGa ⁽⁶⁾	4.2371 ± 0.0007	10.6822 ± 0.0018	4.0218 ± 0.0007	45.51
LuGa ⁽⁶⁾	4.2090 ± 0.0005	10.5817 ± 0.0013	4.0001 ± 0.0005	44.54

(1) Schob & Parthé (1965).

(2) Hohnke & Parthé (1965).

(3) Iandelli (1960).

(4) Baenziger & Moriarty (1961).

(5) Cable, Koehler & Wollan (1964).

(6) Present work.

* The error limits reflect the precision with which the d spacings could be read. It is recognized that small variations in composition will cause variations in unit-cell constants larger than the error limits.

Unit-cell constants of the CrB-type compounds were determined with a least-squares program (Mueller, Heaton & Miller, 1960). A program by Mueller, Meyer & Simonsen (1962) was used to calculate d_c for comparison with d_o . Intensity calculations were made for the compound NdGa by means of the relation $I \sim (F)^2$ (Lp factor) (multiplicity), to determine the atomic positional parameters. F^2 values were calculated with the program by Busing, Martin & Levy (1962).

Results and discussion

The unit-cell constants and the volumes of the compounds are given in Table 1 and are plotted against atomic number in Fig. 1. The data for the compound YGa are located on the plot by placing the volume per formula weight (V/M) for this compound on the V/M curve for the lanthanide compound where it lies between Dy and Tb. It has been noted in other studies (Dwight, Downey & Conner, 1967) that Tb is the lanthanide which most nearly resembles Y in alloying behavior. Approximate unit-cell constants, obtained from three high angle lines, have been published earlier (Dwight, Conner & Downey, 1965) for seven of these compounds. The unit cell constants given in Table 1 were obtained by a least-squares method, and are to be preferred over the earlier values.

The calculated and observed d spacings and intensities of NdGa are listed in Table 2. Intensity calculations were made to obtain an approximate set of atomic positional parameters, y_{Nd} and y_{Ga} . The intensities were calculated for five sets of parameters, and the intensities that agree best with the observed intensities are given in Table 2. The atomic positional parameters for NdGa are estimated to be $y_{Nd} = 0.142 \pm 0.004$, $y_{Ga} = 0.426 \pm 0.004$. These may be compared with the values given by Schob & Parthé (1965) for the compound YGa, $y_Y = 0.138$ and $y_{Ga} = 0.417$.

In a study of lanthanide-germanium equiatomic compounds, Tharp, Smith & Johnson (1965) reported the presence of the CrB-type structure in NdGe through ErGe, and

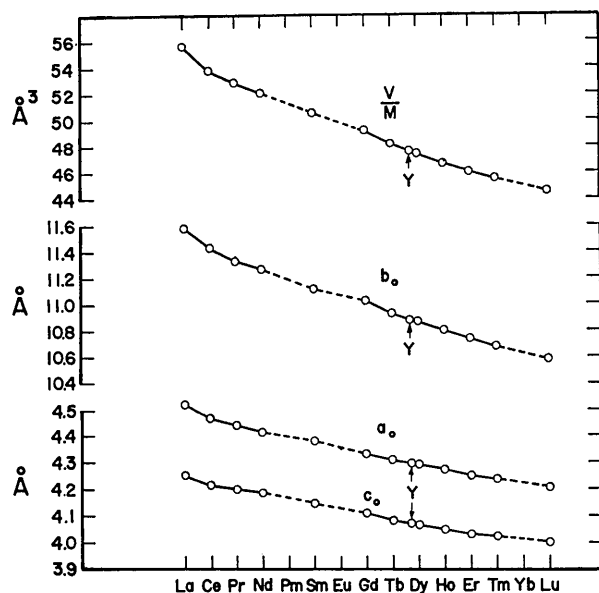


Fig. 1. Unit-cell constants and volume per formula weight of the CrB-type YGa and lanthanide-Ga compounds vs. atomic number.

Table 2. Calculated and observed d spacings and intensities for NdGa

Wavelength of radiation Cr $K\alpha_1 = 2.28962 \text{ \AA}$

hkl	d_c	d_o	I_c	I_o
020	5.638	5.610	1	<i>vw</i>
110	4.112	4.078	4	<i>vw</i>
021	3.360	3.348	24	<i>m</i>
111	2.933	2.923	100	<i>vs</i>
130	2.862	2.855	43	<i>s</i>
040	2.819	2.813	24	<i>ms</i>
131	2.362	2.358	43	<i>s</i>
041	2.338	2.335	19	<i>m</i>
200	2.208	2.205	23	<i>m</i>
002	2.092	2.090	19	<i>m</i>
220	2.056	—	0	—
150	2.008	—	0	—
022	1.961	1.957	1	<i>vvw</i>
060	1.879	—	0	—
112	1.864	—	0	—
221	1.845	1.844	9	<i>m</i>
151	1.811	1.810	9	<i>m</i>
240	1.738	1.736	11	<i>m</i>
061	1.714	1.713	9	<i>m</i>
132	1.689	1.687	18	<i>ms</i>
042	1.680	1.677	11	<i>m</i>
241	1.605	1.602	13	<i>ms</i>
202	1.519	1.518	17	<i>ms</i>
170	1.513	1.513	17	<i>ms</i>
222	1.466	—	0	—
310	1.460	—	0	—
152	1.449	—	0	—
260	1.431	—	0	—
171	1.423	—	0	—
080	1.409	—	0	—
062	1.398	—	0	—
311	1.378	1.378	16	<i>m</i>
330	1.371	1.371	8	<i>w</i>
261	1.354	1.354	15	<i>ms</i>
023	1.354		3	
242	1.337		18	
081	1.336	1.336	9	<i>s</i>
113	1.326	1.319	17	<i>m</i>
331	1.306	1.3025	15	<i>m</i>
133	1.2536	1.2533	17	<i>m</i>
043	1.2499	1.2506	8	<i>w</i>
350	1.2327	—	0	—
172	1.2261	1.2260	51	<i>s</i>
190	1.2053	—	0	—
312	1.1971	—	0	—
280	1.1881	1.1878	1	<i>vvw</i>
351	1.1825	1.1825	14	<i>w</i>
262	1.1812	—	0	—
082	1.1689	—	2	—
191	1.1582	1.1582	20	<i>w</i>
223	1.1541	1.1541	27	<i>w</i>

a tetragonal structure from GdGe through LuGe. Hohnke & Parthé (1965) found a change in crystal structure in lanthanide silicon equiatomic alloys, with the FeB-type in LaSi through ErSi and the CrB-type in EuSi through LuSi. In both series there are alloys in which polymorphism exists. The lanthanide-Ga compounds in the present investigation showed no evidence of a polymorphic transformation. It is evident that the factors which favor the CrB-type structure over the FeB-type are stronger with Ga than with Ge or Si.

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Peak heights of electron density and Patterson function in the crystal. By TOSIO SAKURAI, *The Institute of Physical and Chemical Research, Rikagaku Kenkyusho, Yamatomachi Kita-adachigun, Saitama, Japan*

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Peak heights of atoms in a Fourier map and the corresponding Patterson functions are tabulated in a practically useful form, for various atoms with various temperature factors.

Peak heights of the electron density in a Fourier map and the Patterson function can be calculated by integrations of atomic form factors:

$$\begin{aligned} \rho_i(0) &= \int f_i d\tau \\ P_{ij}(0) &= \int f_i f_j d\tau, \end{aligned} \quad (1)$$

where f_i is the i th atomic form factor including the temperature factor, and $d\tau$ is a volume element in reciprocal space. The knowledge of the values of ρ_i and P_{ij} including the effect due to the temperature factors gives a useful guide for the identification of atomic species in the course of the structure analysis. Such values have not been published in any convenient tabulated form so far as the author is aware.

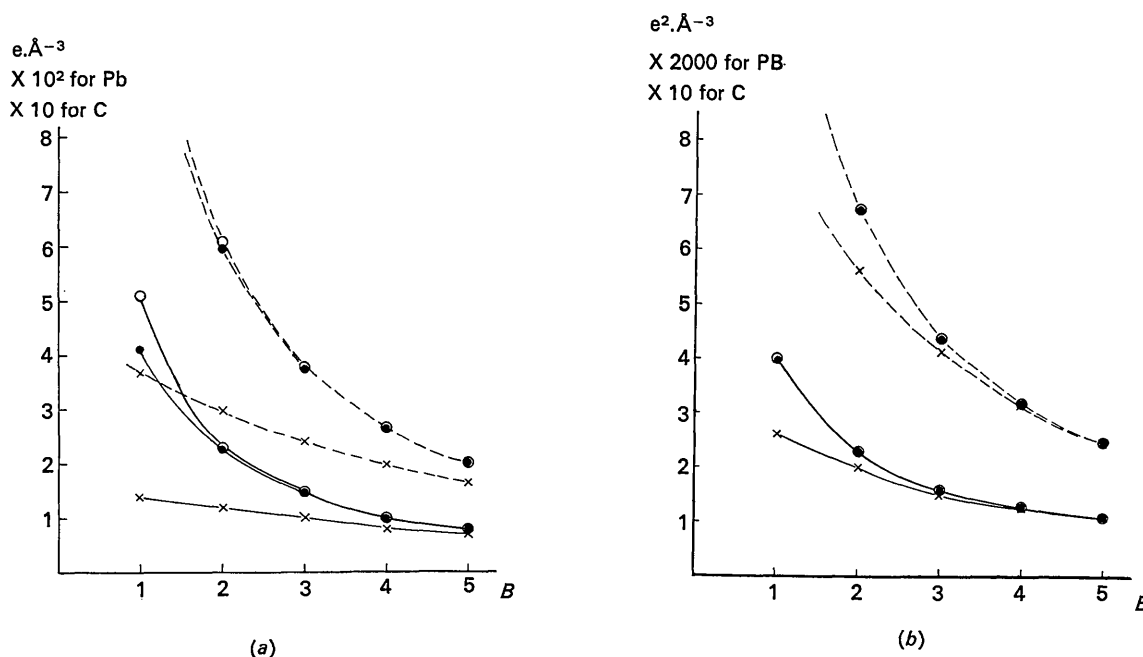


Fig. 1. Variation of peak heights with temperature factor. (a) $\rho(0)$, (b) $P_{ij}(0)$. Range of integration: open circles, infinite range; solid circles, Mo $K\alpha$ range; crosses, Cu $K\alpha$ range. Full lines, carbon; dashed lines, lead.