EFFECT OF HIGH PRESSURE ON THE CRYSTAL STRUCTURES OF LANTHANIDE TRIALUMINIDES

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Summary

The effect of high pressure on the crystal structures of $LnAl_3$ (Ln = Lanthanide) compounds has been determined by exposing $LnAl_3$ compounds or stoichiometric mixtures of the elements, to high-pressure and high-temperature conditions in a tetrahedral-anvil apparatus. In accordance with considerations of relative compressibilities, the application of high pressure tends to make the lower-atomic-weight lanthanides behave more like those of higher atomic weight. Thus, high-pressure-induced polymorphic changes were in the direction of structures with increased cubic character. Polymorphs or compounds first reported in this paper are $BaPb_3$-type $GdAl_3$, $HoAl_3$-type $TbAl_3$ and Cu_3Au-type $LuAl_3$. The first two are hexagonal with lattice parameters $a = 6.231$, $c = 21.173$ Å, and $a = 6.095$, $c = 35.96$ Å, respectively. The third compound is cubic, with lattice parameter a = 4.186 Å.

Introduction

Previous works published on the synthesis of the lanthanide trialuminides have shown that these compounds crystallize with a number of different crystal structures. The actual crystal structure assumed by a given $LnAl_3$ (Ln = Lanthanide) compound varies (a) with the atomic number of the lanthanide element involved, and (b) with the intensity and duration of the heat treatment used to prepare the compound. Prototype compounds representing the different structures of interest here are listed in Table 1. Van Vucht and Buschow [1] have shown that the $BaPb_3$-, $TiNi_3$- and $HoAl_3$-type structures are transition structures between a purely hexagonal Ni_3Sn-type structure and a purely cubic Cu_3Au-type structure. The per cent hexagonal (or cubic) character of these transition structures is determined by the order of stacking of the AB_3 layers of atoms which make up each crystal. The relationship among these structures has been described in detail by van Vucht and Buschow [1].

Two ideas have been advanced to explain the reason for the observed changes in crystal-structure types for the $LnAl_3$ compounds. One, proposed by van Vucht et al. [1 - 6], suggests that the variation in size of the lanthanide elements is the cause of the observed changes. According to their theory,

TABLE 1

Crystal structure types

Structure type	Crystal lattice	Space group	Hexagonal character (%)	Cubic character (%)
Ni_3Sn	hexagonal	$P6_3/mmc$	100	0
$BaPb_3$	rhombohedral	$R\bar{3}m$	67	33
$TiNi_3$	hexagonal	$P6_3/mmc$	50	50
$HoAl_3$	rhombohedral	$R\bar{3}m$	40	60
Cu_3Au	cubic	$Pm3m$	0	100

thermodynamic considerations involving the size of the lanthanide element dictate the type of AB_3 layer stacking which will be most stable under the particular synthesis conditions. The other, proposed by Gschneidner and/or Pearson [7 - 10], attributes the cause of the same changes to a variation in the contribution of $4f$ electrons to the bonding in these compounds. According to their theory, differences in the amount of $4f$ bonding dictate which structure will be thermodynamically stable.

It has been suggested [6] that a knowledge of the effect of pressure on the crystal structures of the $LnA1_3$ compounds would reveal which factor is predominant in influencing the crystal structure, i.e., the size effect or the $4f$ bonding. According to the $4f$ bonding theory, increased pressure tends to increase the participation of $4f$ bonding and would therefore favor more cubic stacking [7]. On the other hand, proponents of the size-effect theory argue that the structures with more hexagonal stacking will tend to have a smaller volume [5] and that increased pressure will therefore favor the more hexagonal stacking [6].

The research reported in this paper was designed to establish which type of stacking is favored under high-pressure conditions. To accomplish this, $LnA1_3$ compounds (or stoichiometric mixtures of the elements) were subjected to high-pressure, high-temperature conditions and then analyzed by X-ray diffraction to determine the resulting type of crystal structure.

Experimental

High-pressure experiments were carried out in a tetrahedral-anvil press designed by Hall [11, 12]. Samples were enclosed in boron nitride and heated by passing an electric current through a surrounding graphite sleeve. In each experiment the pressure was first raised to the desired level and heat was applied for an appropriate period. The sample was then quenched by turning off the electric current (rate of temperature decrease $\sim 300°C/s$), and finally the pressure was released. Full details of the experimental procedure have been published elsewhere [13].

The tetrahedral-anvil press was calibrated for sample pressure in the following manner. The lanthanide- aluminum sample, boron nitride tube and graphite sleeve were replaced by a cylinder of AgCl which contained a wire or sliver of Bi, Yb or Ba. Otherwise the parts of the high-pressure cell were the same as those used in the synthesis experiments. Each of the metals mentioned above exhibits a change in crystal structure at a well-established pressure. This structural change was detected by monitoring the electrical resistance of the metal as the pressure on the cell was increased. Since no attempt was made in these calibration runs to establish equilibrium in the cell, the pressure transition points for Bi, Yb, and Ba reported by Jeffery et al. [14] (and corrected for Decker's improved NaCl equation of state [15] for upstroke only, were used. The transitions occurred at the following applied oil pressures: Bi (27.0 kbar), 1800 psi; Yb (39.1 kbar), 3200 psi; and Ba (56.1 kbar), 5850 psi. A calibration curve was prepared from these data, and the pressures of the synthesis runs were determined from the applied oil pressure by reference to this curve.

The authors recognize that the actual pressure attained during a synthesis experiment is only roughly approximated by the calibration procedure described above. This is so for the following reasons: (1) interpolation and extrapolation procedures involved in preparing a calibration curve covering a 65 kbar range, from three experimental points only is bound to introduce some error; this error will be greatest in the range 0 - 27 kbar, where pressure cell characteristics of the tetrahedral press cause irregularities in the applied pressure /sample-pressure relationship [16], and in the range 56 - 65 kbar, where a non-linear extrapolation is required; (2) the pressure calibrations were made at room temperature, whereas the synthesis experiments were made at high temperatures (400 - 1700°C). Heating of the sample and the pressure cell causes expansion and localized-pressure increases. Above about 600°C, the pyrophyllite $(Al_2O_3 \cdot 4SiO_2 \cdot H_2O)$ pressure cell undergoes chemical and structural transformations resulting in volume decreases with attendant localized pressure decrease. These effects tend to cancel one another, but the quantitative relationship is currently unknown.

It should be clear that the pressures reported here are not necessarily those attained under the temperature conditions of the experiments. They are reported primarily as operational data, to allow these experiments to be repeated elsewhere and to give a rough idea of, the actual pressures involved. The tetrahedral-anvil press was calibrated for sample temperature in the following manner. The lanthanide-aluminum sample, boron nitride tube and graphite sleeve were replaced by a cylinder of boron nitride which contained the junction of a Pt/Pt-10% Rh thermocouple at its center. The thermocouple wires emerged from the cell through opposite edges of the tetrahedron. Temperatures were determined as a function of power input (watts) at applied oil pressures of 3000, 5000 and 7000 psi. At each pressure,

temperatures were determined at 50 watt intervals up to 1500 - 1600°C maximum temperature (about 500 watts at 7000 psi). It was found that a given power input gave lower sample temperatures as pressure was increased. By plotting power input *vs.* a reduced temperature, T/T_0, where T = measured temperature for some power input and pressure, and T_0 = measured temperature for 250 W at the same pressure, a single curve is obtained which may be used to determine the temperature from power input at any pressure [17]. Corrections for pressure effect on the thermocouple were not made.

There was a temperature variation from run to run of about ±35°C (total spread) at the lower temperatures (around 300°C) which increased gradually to about ±60°C (total spread) at the higher temperatures (around 1600°C). During the calibration experiments, a given power input was maintained only long enough for the e.m.f., measured by the potentiometer, to stabilize to a constant value. During the synthesis experiments, power input was maintained for minutes, hours or, on occasion, even for days. Uncertainty in our reported temperatures must therefore be set at least as high as the experimentally-determined variation from run to run noted above.

The elements Al, Sc, Y, Sm, Tm and Lu were each obtained in ingot form and reduced to powder by filing. The filings which passed a 100-mesh sieve were used. Before filing, the stated purity of each element except Sm and Al was 99.9%; the purities of the Sm and Al were unknown. All experiments involving Sc, Y, Sm, Tm and Lu were made using stoichiometric mixtures of the powdered elements. Since these lanthanides were handled in air, there was probably some oxide formation. The amount formed (if any) was never sufficient to cause an observable X-ray spectrum.

The following compounds were kindly supplied by J.H.N. van Vucht and K. H. J. Buschow of the Philips Research Laboratories, Eindhoven, The Netherlands: $GdAl_3$ (Ni_3Sn-type), $TbAl3$ ($BaPb_3$-type), $DyAl_3$ ($TiNi_3$-type), $HoAl_3$ (mixture of $HoAl_3$- and Cu_3Au-types) and $ErAl_3$ (Cu_3Au-type). These compounds were crushed with a mortar and pestle and the resulting powder used without further preparation.

All X-ray work was carried out on a G.E. XRD-5 powder-diffraction unit. Nickel-filtered copper radiation [λ ($K\alpha$) = 1.54178 Å and λ ($K\alpha_1$) = 1.54051 Å] was used with a 143.2 mm Debye-Scherrer camera. Powdered samples were mounted in a glass capillary that was rotated during exposure. The Nelson-Riley method [18] was used to correct for absorption. A silicon (a = 5.4305 Å) or diamond (a = 3.5670 Å) internal standard was used with the non-cubic substances. The lattice parameters of the non-cubic substances were determined by a least-squares refinement [19], after the absorption correction had been applied. Powder intensities were calculated by use of the computer program POWDER [20]. Atomic positions used for the $BaPb_3$- and $HoAl_3$-type structures were those reported by Bailey [30] and by van Vucht and Buschow [1], respectively. Observed powder intensities were estimated visually from the films without reference to a calibration, strip.

Results

Crystallographic data for $LnAl_3$ compounds are given in Table 2. Our data on Ni_3Sn-type $GdAl_3$, $BaPb_3$-type $TbAl_3$, $TiNi_3$-type $DyAl_3$ and Cu_3Au-type $ErAl_3$ were taken from X-ray spectra of the untreated compounds supplied by van Vucht and Buschow. The remainder of the crystallographic data were obtained from compounds that had been subjected to, or synthesized at, high pressures and temperatures. X-ray data for compounds or polymorphs previously unreported, and for $ScAl_3$, are given in Tables 3 - 6. A discussion of each system investigated is as follows:

Se + 3Al

Synthesis at 62 kbar and 970°C for 64 min resulted in the formation of Cu_3Au-type $ScAl_3$. The lattice parameter compares favorably with the value previously published [31].

Y + 3Al

Synthesis at pressures as low as 15 kbar and as high as 64 kbar, with temperatures of 700 - 800°C, resulted only in the formation of $BaPb_3$-type YAl_3. This result seems somewhat surprising in view of our results for $TbAl_3$. At pressures as low as 33 kbar, $TbAl_3$ changes from the $BaPb_3$-type to the $HoAl_3$-type structure (see section on $TbAl_3$ for further details). Since Y is generally considered to be only slightly larger than Tb, it seems reasonable to expect that YAl_3 would crystallize in the $HoAl_3$-type or the $TiNi_3$-type structure at pressures as high as 64 kbar. However, synthesis attempts under the most extreme

conditions (64 kbar and 800°C for 315 min) failed to produce either of these structures. When higher temperatures were used (970°C and above), the principal product was YAl_2.

Sm + 3Al

      Synthesis at 64 kbar and 890°C for 113 min resulted in the formation of Ni_3Sn-type $SmAl_3$. Temperatures of 970°C and above produced mainly $SmAl_2$.

GdAl₃ (Ni₃Sn-type)

      Treatment at 41 kbar and 970°C for 5 min produced a partial conversion to the $BaPb_3$-type structure. At the same temperature but with a pressure of 45 kbar, the transformation to the $BaPb_3$-type structure was complete in 5 min. Treatments at higher pressures (max. 64 kbar) did not result in any further transformation. At temperatures of 1240°C and above, the principal product was $GdAl_2$.

TbAl₃ (BaPb₃-type)

      Treatment at 29 kbar and 970°C for 5 min did not cause any change, but with the same temperature, at 33 kbar for 5 min, partial conversion to the $HoAl_3$-type structure resulted. This was somewhat surprising since the expected order of transformation was $BaPb_3$-type (67% hexagonal stacking)

TABLE 2

Crystallographic data

Compound	Structure type	Unit-cell dimensions (Å)		Volume per formula unit ($Å^3$)	Ref.
		a	*c*		
$LaAl_3$	Ni_3Sn	6.662	4.609	88.58	1
$CeAl_3$	Ni_3Sn	6.545	4.609	85.49	1
$PrAl_3$	Ni_3Sn	6.504	4.604	84.33	1
$NdAl_3$	Ni_3Sn	6.472	4.606	83.54	1, 21
$SmAl_3$	Ni_3Sn	6.383(2)*	4.598(1)	81.12(7)	this work
		6.380	4.597	81.02	1, 2, 22
$GdAl_3$	Ni_3Sn	6.333(2)	4.599(1)	79.87(7)	this work
		6.320	4.592	79.42	1, 2, 21
		6.308	4.589	79.07	23
		6.331	4.600	79.84	24
	$BaPb_3$	6.231(2)	21.173(6)	79.10(7)	this work
$TbAl_3$	$BaPb_3$	6.175(2)	21.170(7)	77.68(8)	this work
		6.175	21.180	77.71	1, 2
		6.176	21.165	77.68	24
	$HoAl_3$	6.095(3)	35.96(2)	77.13(12)	this work
$DyAl_3$	$TiNi_3$	6.091(2)	9.533(3)	76.57(7)	this work
		6.082	9.531	76.33	415
		6.097	9.534	76.73	25
	$HoAl_3$	6.074(2)	35.87(1)	76.41(7)	this work

TABLE 2 (*continued*)

Crystallographic data

Compound	Structure type	Unit-cell dimensions (Å)		Volume per formula unit (Å^3)	Ref
		a	*c*		
		6.065	35.86	76.16	5
		6.080	35.940	76.71	1
	Cu$_3$Au	4.236(1)		76.01	this work
		4.249		76.71	5
HoAl$_3$	TiNi$_3$	6.06	9.53	75.77	5
	HoAl$_3$	6.067(2)	35.83(1)	76.14(7)	this work
		6.049	35.73	75.48	5
		6.052	35.900	75.98	1
	Cu$_3$Au	4.230(1)		75.69(5)	this work
		4.231		75.74	5
		4.22		75.15	4
		4.248		76.66	26
ErAl$_3$	HoAl$_3$	6.026	35.62	74.68	5
		6.025	35.675	74.77	4
	Cu$_3$Au	4.214(1)		74.83(5)	this work
		4.211		74.67	5
		4.215		74.88	27
		4.212		74.72	26
TmAl$_3$	Cu$_3$Au	4.203(1)		74.25(5)	this work
		4.200		74.09	28
YbAl$_3$	Cu$_3$Au	4.202		74.19	1
LuAl$_3$	Cu$_3$Au	4.186(1)		73.35(5)	this work
YAl$_3$	Ni$_3$Sn	6.28	4.58	78.21	2, 29
		6.276	4.582	78.15	30
	BaPb$_3$	6.197(2)	21.136(8)	78.10(8)	this work
		6.194	21.138	78.04	1, 2
		6.19	21.3	78.53	29
		6.204	21.184	78.46	30
ScAl$_3$	Cu$_3$Au	4.103(1)		69.07(5)	this work
		4.10		68.92	31

*Number in ( ) represents the standard deviation in the last significant figure.

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to TiNi$_3$-type (50% hexagonal stacking) to HoAl$_3$-type (40% hexagonal stacking) (see ref. 1 for a detailed discussion of these structures and their relationships).

TABLE 3

X-ray data for BaPb$_3$-type GdAl$_3$

hkl	d (Å) cal.	obs.	Intensity obs.	cal.	hkl	d (Å) cal.	obs.	Intensity obs.	cal.
1 0 1	5.229	5.258	w	42	3 1 5	1.411	1.411	m	15
1 0 4	3.779	3.775	m	100	0 2 13	1.394	1.395	m	12
0 1 5	3.331	3.333	m	90	4 0 1	1.347	--	--	4
1 1 0	3.116	3.122	vs*	90	2 0 14	1.319	1.320	m	15
0 2 1	2.676	2.677	mw	39	4 0 4	1.307	1.309	w	10
2 0 2	2.615	2.612	w	12	2 2 9	1.299	1.299	s	30
0 2 4	2.404	2,406	vs	89	0 4 5	1.285	1.286	m	11
0 1 8	2.376	2.379	vw	2	2 1 13	1.273	1.273	vw	5
0 0 9	2.353	2.355	m	42	1 3 10	1.222	--	--	3
2 0 5	2.275	2.276	vs	87	1 2 14	1,215	1.214	w	8
2 1 1	2.000	2.031	mw	18	3 2 4	1.205	1.203	w	8
0 2 7	2.014	--	--	6	2 3 5	1.188	1.188	mw	9
1 2 2	2.003	2.002	w	6	4 1 0	1.178	1.177	m	10
1 0 10	1.971	1.973	w	7	0 0 18	1.176			4
2 1 4	1.903	1.900	mw	23	4 0 10	1.138	1.138	vw	3
2 0 8	1.900			9	1 3 13	1.102	1.101	mw	4
1 1 9	1.877	1.877	m	42	1 1 18	1.101			7
1 2 5	1.838	1.836	mw	26	3 1 14	1.064	1.065	mw	8
3 0 0	1.799	1.799	mw	17	4 1 9	1.053	1.053	m	7
2 1 7	1.691	--	--	5	1 4 9	1.053			7
0 2 10	1.666	1.666	mw	12	4 0 13	1.039	1.039	mw	4
1 2 8	1.616	1.614	w	5	3 3 0	1.039			4
1 0 13	1.559	1.558	s	6	0 2 19	1.030	--	--	3
2 2 0	1.558			30	2 4 1	1.019	1. 018	w	3
1 3 1	1.493	--	--	3	0 4 14	1.007	--	--	6
3 1 2	1.482	--	--	2	2 4 4	1.001	1.001	w	9
2 1 10	1.469	1.470	mw	9	4 2 5	0.991	0.991	mw	10
0 1 14	1.456	1.456	mw	9	3 2 13	.986	--	--	4
1 3 4	1.440	1.441	mw	14	3 0 18	.985	--	--	3
3 0 9	1.429	1.427	mw	8	0 3 18	.985	--	--	3
0 3 9	1.429			8	2 1 19	.978	--	--	4

TABLE 3 *(continued)*

X-ray data for BaPb$_3$-type GdAl$_3$

hkl	——d (Å) ——		—Intensity—		—hkl—	——d (Å) ——		—Intensity—	
	cal.	obs.	obs.	cal.		cal.	obs.	obs.	cal.
2 3 14	.958	.960	ms*	7	2 0 23	.871	.871	w	7
5 1 4	.953			5	3 4 5	.868	--	--	5
3 3 9	.950	.951	w	8	2 4 13	.864	.865	mw	8
1 5 5	.945	--	--	6	5 2 0	.864			7
2 2 18	.939	.939	m	13	4 0 19	.859	.858	s*	3
2 4 10	.919	.918	s*	4	4 2 14	.846	.846	mw	13
0 1 23	.908	.908	w	4	6 0 9	.840			7
0 2 22	.907			3	0 6 9	.840	840	m	7
6 0 0	.899	.900	w	6	1 2 23	.839			8
1 3 19	.894	--	--	3	5 1 13	.833			5
5 1 10	.881	--	--	3	1 4 18	.832	.833	m	5
5 0 14	.879	--	--	3	4 1 18	.832			8
4 3 4	.875	--	--	4					

* Interference from Si standard

Previous reports indicate that lower temperatures favor a more hexagonal stacking [4, 5]; experiments were therefore made at a pressure of 58 kbar with different temperatures for about 4 h durations. At 510°C and below, the BaPb$_3$-type structure was retained, and at 580°C and above, there was complete transformation to the HoAl$_3$-type structure.

Finally, experiments were made at different pressures but with the same temperature (580°C) for about 4 h each. At 33 kbar and below, no change occurred, and at 45 kbar and above, conversion to the HoAl$_3$-type structure was complete. At 37 kbar and at 41 kbar there was some very slight conversion, but the X-ray spectrum of the converted material (in the presence of a strong BaPb$_3$-type spectrum) was not sufficiently clear to reveal the identity of the new structure. An additional experiment was therefore made at 39 kbar and 580- 640°C for 63 h. The result was total conversion to the HoAl$_3$-type structure.

One last experiment was then made, at 51 kbar and 520°C for 7 days. Previous experiments at this temperature for much shorter times had always resulted in no conversion. It was hoped that use of this minimum temperature for a much longer time would finally cause conversion to the TiNi$_3$-type structure. Unfortunately, these hopes were not realized; conversion was complete to the HoA1$_3$-type structure. Attempts to prepare Cu$_3$Au-type TbAl$_3$, at the highest pressures and temperatures available, were unsuccessful. At 64 kbar, conversion was always to the HoAl$_3$-type structure. At temperatures of 1240°C and above, a considerable decomposition to TbAl$_2$ was observed.

DyAl$_3$ (TiNi$_3$-type)

This phase is prepared at atmospheric pressure by annealing for 3 weeks at 800°C [4]. At all pressures of 15 kbar (the lowest pressure used in this study) and above, a 5 min treatment at 800° C converted this material to the HoAl$_3$-type structure. At 15 kbar, a 5 h treatment at 720° C resulted in complete conversion to the HoAl$_3$-type structure.

TABLE 4

X-ray data for HoAl$_3$-type TbAl$_3$

hkl	d (Å) cal.	d (Å) obs.	Intensity obs.	Intensity cal.	hkl	d (Å) cal.	d (Å) obs.	Intensity obs.	Intensity cal.
1 0 4	4.552	4.559	mw	71	2 0 23	1.345	1.344	mw	12
0 1 5	4.255	4.257	w	37	4 0 4	1.306	--	--	6
1 0 7	3.681	3.687	m	77	2 2 15	1.286	1.286	vs	43
0 1 8	3.422	3.425	m	64	4 0 7	1.278	--	--	10
1 1 0	3.047	3.053	s	100	0 4 8	1.266	1.264	m	10
1 0 10	2.972	2.982	w	15	2 1 22	1.264			6
0 1 11	2.779	2.773	mw	21	2 0 26	1.225	1.223	mw	5
2 0 2	2.611	2.616	mw	18	0 4 11	1.224			5
0 2 4	2.532	2.533	ms	54	3 2 4	1.200	1.198	mw	3
2 0 5	2.478	2.471	mw	30	0 0 30	1.199			6
0 0 15	2.398	2.397	vs	57	3 2 7	1.179	1.180	w	5
0 2 7	2.347	2.347	vs	77	2 3 8	1.169	1.168	w	5
2 0 8	2.276	2.274	vs	70	4 1 0	1.152	1.153	mw	10
0 2 10	2.128	2.127	mw	19	1 2 26	1.137	1.138	w	2
2 0 11	2.054	2.055	m	29	2 3 11	1.136			2
2 1 4	1.948	1.944	mw	15	1 1 30	1.116	1.116	mw	9
1 1 15	1.884	1.885	ms	50	4 1 15	1.038	1.039	m	7
2 1 7	1.860	1.861	mw	23	1 4 15	1.038			7
1 2 8	1.823	1.824	mw	21	4 0 22	1.027	1.027	mw	5
3 0 0	1.759	1.760	mw	20	0 4 23	1.008	1.008	w	5
2 1 10	1.745	--	--	6	2 4 4	0.991			6
1 2 11	1.702	1.703	mw	9	0 3 30	.991	0.990	mw	4
0 1 20	1.703			3	3 0 30	.991			4
1 0 22	1.562	1.556	w	6	2 4 7	.979	.981	mw	10
0 2 19	1.538	1.535	mw	11	4 2 8	.974	.974	mw	10
2 2 0	1.524	1.524	vs	40	3 2 22	.973			3
3 0 15	1.418	1.417	mw	9	4 2 11	.954	--	--	5
0 3 15	1.418			9	2 2 30	.942	.942	m	20
1 3 7	1.408	--	--	9	3 3 15	.935	--	--	7
3 1 8	1.392	1.390	m	8	0 2 37	.912	--	--	5
0 2 22	1.390			14	2 0 38	.891	--	--	5

TABLE 4 *(continued)*

X-ray data for HoAl$_3$-type TbAl$_3$

hkl	d (Å) cal.	d (Å) obs.	Intensity obs.	Intensity cal.	hkl	d (Å) cal.	d (Å) obs.	Intensity obs.	Intensity cal.
2 4 19	.882	--	--	6	5 1 22	.820	.819	w	5
6 0 0	.880	--	--	11	2 4 25	.820			4
3 4 8	.852	.852	mw	4	1 5 23	.811	.810	w	5
2 4 22	.851			11	1 3 37	.810			5
5 2 0	.845	--	--	8	4 2 26	.809	--	--	8
4 2 23	.841	.841	w	11	0 0 45	.799	--	--	6
1 4 30	.831	.830	mw	9	5 2 15	.797	.797	w	13
4 1 30	.831			9	2 5 15	.797			13
6 0 15	.826	.826	mw	13					
0 6 15	.826			13					

At 64 kbar, 5 min treatments gave conversion to the HoAl$_3$-type structure at temperatures from 800 to 1050°C. At 1240°C there was complete decomposition to DyAl$_2$. Giving a very fast (of the order of 1 s) very-high temperature (maximum about 1660°C) treatment, at 64 kbar, resulted in almost total conversion to the Cu$_3$Au-type structure. The minor phase present had the HoAl$_3$-type structure. It is interesting to note that the Cu$_3$Au-type phase prepared in this manner has a lattice parameter significantly smaller than that reported for the same phase prepared [5] by splat cooling samples at atmospheric pressure.

HoAl3 (mixture of HoAl3 and Cu3Au types)

In experiments of 4.5 h duration at a temperature of 770°C the entire sample assumed the HoAl$_3$-type structure at 22 kbar, and the Cu$_3$Au-type structure at 64 kbar. Conversion to the Cu$_3$Au-type structure was also completed by treatment at 64 kbar and 970°C for 5 min.

ErAl3 (Cu3Au-type)

Treatment at 64 kbar and 970°C for 5 min caused no observable changes.

Tm + 3Al

Synthesis at 64 kbar and 1240°C for 5 min resulted in the formation of Cu$_3$Au-type TmAl$_3$ with a minor phase of TmAl$_2$.

Lu + 3Al

This system was examined simply because the synthesis of LuAl$_3$ had not been previously reported. Synthesis at 62 kbar and 970°C for 60 min resulted in the formation of Cu$_3$Au-type LuAl$_3$, as expected. The X-ray spectrum, however, was of very poor quality with broad, fuzzy lines and attendant poor resolution in the back-angle region. Because of this, another experiment was conducted, this time at 59 kbar and 900°C for 16 h. The X-ray spectrum contained a much sharper and better-resolved set of lines characteristic of the Cu$_3$Au-type structure, but it also displayed 12 additional lines, which could be indexed cubic, with a = 5.154 Å.

One further experiment was made at 15 kbar and 880°C for 100 min. The X-ray spectrum of the product showed that the major phase was the cubic material, with a = 5.154 Å, but that minor phases of Cu_3Au-type $LuAl_3$, and elemental Al, were also present.

To date, the identity of this new cubic phase has not been determined.

TABLE 5

X-ray data for Cu_3Au-type $LuAl_3$

hkl	d (Å) cal.	obs.	Intensity obs.	cal.	hkl	d (Å) cal.	obs.	Intensity obs.	cal.
1 0 0	4.186	4.161	m	103	3 3 0	0.987	0.986	w	3
1 1 0	2.960	2.954	vs*	87	4 1 1	0.987			7
1 1 1	2.417	2.409	vs	100	3 3 1	.960	.959	m	18
2 0 0	2.093	2.089	ms	49	4 2 0	.936	.936	m	18
2 1 0	1.872	1.868	ms	46	4 2 1	.913	.912	mw*	13
2 1 1	1.709	1.706	m	34	3 3 2	.892	.892	vw	7
2 2 0	1.480	1.479	ms*	31	4 2 2	.854	.855	mw	20
3 0 0	1.395	1.394	m	4	5 0 0	.837	.837	vw	2
2 2 1	1.395			17	4 3 0	.837			8
3 1 0	1.324	1.322	mw	14	5 1 0	.821	.821	mw	9
3 1 1	1.262	1.261	vs	35	4 3 1	.821			19
2 2 2	1.208	1.207	mw	10	5 1 1	.806	.806	mw	28
3 2 0	1.161	1.160	w	9	3 3 3	.806			9
3 2 1	1.119	1.118	mw	17	4 3 2	.777	.777	mw	48
4 0 0	1.047	1.046	vw	5	5 2 0	.777			24
4 1 0	1.015	1.014	mw	7					
3 2 2	1.015			7					

*Interference from impurity.

The lattice parameter is about one-half that attributable to Mn_2O_3-type Lu_2O_3, but the X-ray spectrum for this form of Lu_2O_3 does not match the high-angle lines of the spectrum for the new material. Also, there are no lines present in the spectrum of the new material to indicate that the cell size should be doubled. Work is continuing on this problem and will be reported in due course.

TABLE 6

X-ray data for Cu_3Au-type $ScAl_3$

hkl	d (Å) cal.	d (Å) obs.	Intensity obs.	Intensity cal.	hkl	d (Å) cal.	d (Å) obs.	Intensity obs.	Intensity cal.
1 0 0	4.103	4.074	w	8	4 1 0	0.995	0.994	vw	0.3
1 1 0	2.901	2.888	w	7	3 2 2	0.995			0.3
1 1 1	2.369	2.360	vs	100	3 3 1	.941	.941	mw	16
2 0 0	2.051	2.045	m	47	4 2 0	.917	.917	mw	15
2 1 0	1.835	1.831	vw	3	4 2 1	.896	--	--	0.7
2 1 1	1.675	1.672	vw	2	4 2 2	.838	.837	mw	18
2 2 0	1.451	1.448	mw	28	4 3 0	.821	--	--	0.5
3 0 0	1.368	1.366	vw	0.2	5 0 0	.821			0.1
2 2 1	1.368			0.8	4 3 1	.805	.804	vw	1.1
3 1 0	1.298	1.296	vw	0.7	5 1 0	.805			0.6
3 1 1	1.237	1.235	mw	31	5 1 1	.790	.790	mw	29
2 2 2	1.184	1.183	w	9	3 3 3	.790			10
3 2 1	1.097	1.095	vw	0.8					
4 0 0	1.026	1.025	w	4					

Discussion

The results outlined in the previous section prove conclusively the effect of pressure on the crystal structures of the $LnAl_3$ series. In every case where a pressure-induced transformation occurs, the change is toward the more cubic structure. The conclusions that may be drawn from these results, however, must be re-examined in light of data regarding the volumes per formula unit of the compounds under study.

The argument that the size effect will cause pressure-induced transformations toward the more hexagonal structures was based on the prediction that increased hexagonal character will result in a smaller volume per formula unit [5, 6]. In fact, however, our experiments have shown that the opposite is true. Figure 1 shows a plot of volume per formula unit *vs*. Ln^{3+} ionic radius. Data from this study show, without exception, that increased hexagonal character results in a *larger* volume per formula unit. If data from other reports are considered, then the evidence is not quite so conclusive. The differences can possibly be explained by different methods of X-ray data work-up, in particular the differences attributable to methods of absorption correction, and the determination of lattice parameters for non-, cubic materials. It does not seem unreasonable to place good reliance on the self-consistent data from this laboratory.

It is reassuring, upon reflection, to find that the more hexagonal structures do have larger unit volumes, since this results in predictions of high-pressure behavior that are consistent with that which one would expect from a consideration of the compressibility data. The lanthanide elements are each more compressible than Al, so one would predict that high pressures should cause the larger lanthanides to behave more like the smaller ones. Since the smaller lanthanides form the more cubic structures, this means that high pressure should favor the cubic over the hexagonal structures -- exactly as is observed.

Unfortunately, however, this re-analysis of the size-effect prediction of high-pressure behavior of $LnAl_3$ structures renders this study ineffective in its stated objective. As the arguments now stand, both the 4*f*-bonding approach and the size-effect approach predict the observed behavior in $LnAl_3$ compounds under high pressure.
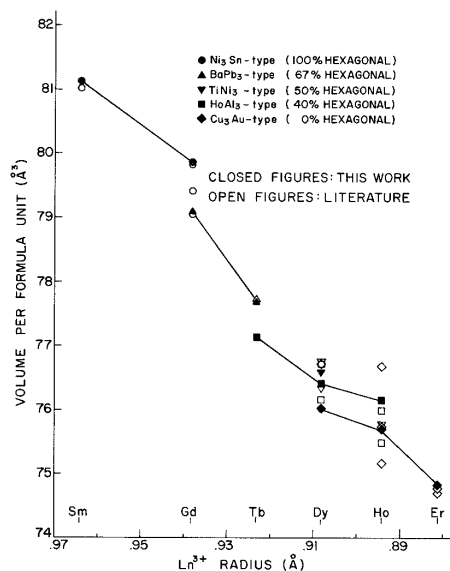
Fig. 1. Volume per formula unit *vs.* lanthanide ionic radius.

The interesting aspects of this study remain: (1) further confirmation that the application of high pressures and temperatures will convert materials from one polymorphic form to another related polymorphic form, according to predictions based on considerations of the relative compressibilities of the elements involved; (2) lack of success in preparing the $TiNi_3$-type structure for $TbAl_3$.

The second statement above requires further examination. A glance at Table 1 will reveal that the difference in hexagonal character between the $HoAl_3$- and $TiNi_3$-type structures is only 10 percent. Reference to Fig. 1 and Table 2 will show that the volumes per formula unit of $DyAl_3$ in the two structure types are quite close -- within less than three standard deviations of each other. If this latter property holds good for $TbAl_3$ also, then in all probability the energy contents of these two polymorphs are very close. This means that the conditions of preparation of $TiNi_3$-type $TbAl_3$ must be controlled in such a way that just enough energy is added to convert the $BaPb_3$-type polymorph to the $TiNi_3$-type material without inducing it to transform all the way to the $HoAl_3$-type. Obviously, our experiments were not successful in accomplishing this relatively delicate task. Presumably, lower pressures and/or temperatures for long periods of time will be required to produce $TiNi_3$-type $TbAl_3$ successfully.

Acknowledgements

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