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SYNTHESIS OF LANTHANIDE-IRON LAVES PHASES AT HIGH PRESSURES AND TEMPERATURES

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ABSTRACT

High pressures and temperatures were used to synthesize the previously unknown compounds $PrFe_2$, $NdFe_2$ and $YbFe_2$. These compounds have the cubic $MgCu_2$-type structure with lattice parameters 7.467, 7.452 and 7.239 A respectively. The relative importance of 4f bonding and size effects in the formation of LFe_2 compounds (L = lanthanide) is discussed.

Introduction

The lanthanide compounds of general formula LFe_2 (L = lanthanide) have been studied by a number of investigators (1-15). The known compounds in this series are isomorphous with a cubic Laves-phase structure of the $MgCu_2$-type. There are eight formula weights per unit cell, and the space group is Fd3m. None of the previous investigators has reported the synthesis of $LaFe_2$, $PrFe_2$, $NdFe_2$, $EuFe_2$ or $YbFe_2$, and some (6, 11, 13-14) report that attempts to prepare these compounds by high-temperature methods were unsuccessful.

Recently H. T. Hall (16) suggested that high-pressure synthesis methods may be useful in preparing otherwise unknown lanthanide compounds when certain conditions are met. These conditions are, first, that the compounds must be unknown for the lower molecular weight lanthanides, second,

that the lanthanide component must be more compressible than the non-lanthanide, and, third, that the increase in radius of the lanthanide component be primarily responsible for the premature termination of the series. Under these circumstances the application of high pressure will create a condition suitable for a successful synthesis by reducing the radius of the lanthanide to a greater degree than that of the non-lanthanide. Since the LFe_2 series seems to meet these conditions, high-pressure techniques were applied to the synthesis of the unknown members of this series.

Experimental

The tetrahedral anvil press developed by Hall (17-18) was used to generate the high pressures and temperatures needed for this work. Details of the pressure and temperature calibrations, the sample geometry, and details of the experimental procedure have been described elsewhere (19).

Powders of La (under oil) and Fe as well as ingots of Yb and Lu were obtained from Research Organic/Inorganic Chemical Corporation, Sun Valley, California. The other lanthanides (Pr, Nd, Sm, Gd, Tb, Ho) were obtained in ingot form from Research Chemicals Incorporated, Phoenix, Arizona.

The ingots were filed and those filings that passed a 100-mesh sieve were used. Each synthesis run was prepared from a stoichiometric mixture of the appropriate powders. No oxide contamination was observed in the powder X-ray spectra taken during the course of this study.

X-ray data were taken using a G. E. XRD-5 with a Debye-Scherrer powder camera of 143.2 mm diameter. Samples were crushed and without further preparation X-rayed in 0.5 mm glass capillaries which were rotated during exposure. Copper (λ = 1.54178 Å) and chromium (λ = 2.29092 Å) radiation were used as circumstances dictated. The Nelson-Riley extrapolation method (20) was used to determine the lattice constants.

Results

Although the syntheses were made from 1:2 L/Fe mixtures, none of the reaction products was free of impurity. In each case the X-ray spectrum showed minor lines which could not be identified. In determining the minimum pressure required to prepare a given compound, the synthesis was

considered successful if the most intense lines characteristic of the $MgCu_2$-type structure were present in the X-ray spectrum of the product.

The new compounds successfully prepared were $PrFe_2$, $NdFe_2$ and $YbFe_2$. Conditions as severe as 90 kbars at 1350°C for 5 minutes and 69 kbars at 1050°C for 60 minutes failed to cause any detectable reaction in the La-Fe runs. Several runs at various temperatures and pressures (up to 69 kbars) resulted in reactions between Eu and Fe, but X-ray spectra of the products showed no evidence of the $MgCu_2$-type structure. Previously known compounds prepared for comparison with the literature include $SmFe_2$, $GdFe_2$, $TbFe_2$, $HoFe_2$ and $LuFe_2$.

Lattice parameters and synthesis data for the compounds prepared in this study are shown in Table 1 along with some of the more recent literature

TABLE 1

Synthesis Data and Lattice Parameters

Compound	Min. Pressure Req. for Prep. at 1000°C (kbar)	Lattice Parameters (Å) This Work	Literature (13)	(14)	(15)
$PrFe_2$	32-35	7.467(4)			
$NdFe_2$	20-28	7.452(5)			
$SmFe_2$		7.415(4)	7.401		7.417
$GdFe_2$		7.394(5)	7.376	7.390	7.396
$TbFe_2$		7.345(6)	7.341	7.341	7.347
$HoFe_2$		7.303(6)	7.287	7.306	7.304
$YbFe_2$	<6	7.239(5)			
$LuFe_2$		7.229(4)		7.217	

data for the previously known compounds. The numbers in parantheses following our lattice parameters represent the standard deviation in the last significant figure. The pressures shown in the second column represent for each new compound the pressure of the last unsuccessful synthesis to the pressure of the first successful synthesis. Each run above the higher of these pressures (with temperature at 1000°C or higher) resulted in successful synthesis. The synthesis of $YbFe_2$ was successful down to the lowest pressure attainable in our apparatus (about 6 kbar). Table 2 shows the X-ray

data for the new compounds.

TABLE 2

X-ray Data for New Compounds

		$PrFe_2$		$NdFe_2$		$YbFe_2$	
h k l	I/I_o	d(Obs)	d(Cal)	d(Obs)	d(Cal)	d(Obs)	d(Cal)
1 1 1	1	4.283	4.311	4.285*	4.303	4.167	4.179
2 2 0	6	2.630	2.640	2.622	2.635	2.552	2.559
3 1 1	10	2.244	2.251	2.239	2.247	2.179	2.183
2 2 2	3	2.149	2.156	2.143	2.151	2.085	2.090
4 0 0	1	N.O.	- -	N.O.	- -	1.806	1.810
3 3 1	1	1.710	1.713	1.710*	1.710	1.660	1.661
4 2 0	1	1.658*	1.670	1.644*	1.666	1.623*	1.619
4 2 2	5	1.522	1.524	1.519	1.521	1.477	1.478
5 1 1	5	1.436	1.437	1.434	1.434	1.393	1.393
4 4 0	5	1.319	1.320	1.316	1.317	1.280	1.280
5 3 1	3	1.263	1.262	1.256*	1.260	1.224	1.224
6 2 0	2	1.180	1.181	1.179	1.178	N.O.	- -

N.O. = Not Observed
All d values in angstroms

* Not used in lattice constant determination

Discussion

In this study, as in many others, Yb and Eu show their usual "anomalous" behavior. The lattice parameter that we found for $YbFe_2$ (see Table 1) indicates that the size of the Yb is such that a favorable synthesis condition should exist at atmospheric pressure. Nevertheless Mansey, Raynor and Harris (13) clearly state that their attempts to prepare $YbFe_2$ at atmospheric pressure did not succeed. This behavior is apparently associated with the tendency of Yb to exhibit divalent character. This same tendency in Eu is probably responsible for our lack of success in preparing $EuFe_2$.

The data in Table 1 show that increasing pressure is required for a successful synthesis as the size of the lanthanide increases. This suggests that the increasing size of the lanthanide component is primarily responsible for the previous lack of success in preparing $PrFe_2$ and $NdFe_2$. This could also explain our failure to prepare $LaFe_2$, i.e. La is apparently not

sufficiently reduced in size at 90 kbars to effect the synthesis. We realize, however, that other factors may come into play in the La-Fe system since, surprisingly, no binary La-Fe compound of any composition is known (14, 21).

Gschneidner (22-24) and others (25-28) have suggested that 4f bonding, rather than size effect, is a determining factor in the formation of certain lanthanide compounds. In a recent paper, Burzo (28) applied Gschneidner's arguments on this subject to the LFe_2, LCo_2 and LNi_2 series. By examining the difference between R_M (lanthanide radius in the compound) and R_{4f} (the lanthanide 4f shell radius) as a function of the lanthanide atomic number, he concluded that the smaller the value of $(R_M - R_{4f})$ the more the 4f electrons are exposed and the greater will be their contribution to the bonding. The value of $(R_M - R_{4f})$ is essentially constant from Lu down to Gd but decreases rapidly after Gd as the La end of the series is approached. This indicates that the 4f contribution to the bonding in the LFe_2 compounds is greatest for the earlier members of the series, decreases to Gd and then remains essentially constant from that point through Lu. Burzo further observes that R_M is smaller in the LFe_2 compounds than in pure lanthanide metals. This implies small L-L distances and thus indicates the existence of 4f bonding even in $LuFe_2$. He concludes finally that "in the compounds examined the contribution of the 4f electrons to the bonding is a predominant factor in the forming of the crystal cell."

If Burzo's conclusion is correct, then one might be tempted to say that 4f bonding is responsible for the lack of success in preparing $LaFe_2$, $PrFe_2$ and $NdFe_2$ at atmospheric pressure since these compounds would have the largest 4f bonding contribution of any in the series (with the exception of $CeFe_2$ which is unusual because of its tetravalent character). Because high pressure tends to increase the 4f contribution to the bonding (22), this would mean that high pressure should impede the formation of these compounds. Since our studies have shown the opposite effect, we conclude that an increase in 4f bonding does not account for the failure to prepare $LaFe_2$, $PrFe_2$ and $NdFe_2$ at atmospheric pressure.

Gschneidner (22) has suggested a test for determining whether 4f bonding or size effect is the determining factor in polymorphic changes

within a lanthanide compound series. If high pressure causes the heavier lanthanide compounds to behave more like the lighter ones, then 4f bonding plays an important part, but if the reverse occurs, size effects are the predominant factor. Applying this criterion to our findings, it is evident that size effects are the determining factor in the formation of LFe_2 compounds.

It should not be concluded that our experiments rule out the existence of 4f bonding in these compounds. It is entirely possible that 4f bonding does exist, but our work shows that, if it does, the effect is small. This conclusion is in accord with Gschneidner's earlier statements (22) that 4f bonding has no appreciable effect in lanthanide compound series which do not exhibit a polymorphic change. In accordance with this, we can also say that 4f bonding is probably not a significant factor in the formation of LCo_2 or LNi_2 compounds.

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