Pressure-Induced Phase Transformations and Magnetic Ordering in Some Intra-Rare-Earth Alloys and Samarium

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Intra-rare-earth alloys in the system La-Y, La-Gd, Ce-Y, Gd-Y, and also the Sm-type PrY, NdY, NdTm, NdGd, $Ce_{0.30}Gd_{0.70}$, and $Ce_{0.45}Ho_{0.55}$, have been investigated at 40 kbar and 450°C. Pressure-induced phase transformation in the sequence hcp → Sm-type → dhcp → fcc seems to be a rule in these alloy systems, with the exception of Ce-Y. In all cases the high-pressure phase is retained metastably on release of pressure and temperature to the ambient. The similarity between the effect of alloying a hcp rare-earth metal from Gd to Lu or Y, with a lighter rare earth, and the effect of pressure on the former, is pointed out, and certain consequences arising therefrom are discussed. In the Ce-Y system decomposition to γ-Ce and α-Y was observed for two compositions, CeY and $Ce_{0.75}Y_{0.25}$ at the pressure and temperature conditions stated. This decomposition is interpreted as the result of $4f$-$5d$ electron promotion in Ce and the consequent size incompatibility preventing the alloy structure from being stable. Magnetic behavior of $LaGd_3$ and NdTm in their normal Sm-type structure and the pressure-induced dhcp structure, and also of the La-Gd alloys in their hcp and pressure-induced Sm-type structure, are reported. In the former two alloys the high-temperature susceptibility anomalies present in the Sm-type phase appear to be absent in the dhcp phase. Both forms however seem to be ordered at low temperatures (1–4°K) with incomplete cancellation of the moments. The La-Gd alloys are all ferromagnetic when in hcp form. In analogy with the behavior under pressure of the Sm form of Gd, it is presumed that the pressure-induced Sm form of La-Gd alloys would order antiferromagnetical. An unambiguous determination of the magnetic behavior of the Sm form is complicated by reversion to the hcp structure on cooling. Some evidence is presented to show that this somewhat unusual reversion of a metastably retained phase on cooling may be connected with magnetic ordering, and it is suggested that the exchange magneto-elastic strain energy associated with a magnetic transition could provide the driving force for the Sm-type → hcp transition. It is suggested that the magnetic-susceptibility anomalies observed in the normal as well as in the pressure-induced dhcp forms of Sm metal are connected with the ordering of the cubic-site layers (c) and the hexagonal-site layers (h) at different temperatures.

INTRODUCTION

PRESSURE–induced phase transformations in Gd [1] to the Sm-type structure, in Sm [2] to the double-hexagonal-close-packed (dhcp) structure have been reported. While the high-pressure phases were retained metastably at atmospheric pressure and room temperature in both cases, the Gd showed a rapid reversion to the hcp form on cooling. Magnetic studies over a limited temperature range at ambient pressure and subsequent study by McWhan and Stevens[3] at high pressure suggested that in the Sm-form, Gd undergoes an antiferromagnetic ordering.

The aforementioned studies stimulated our interest in the intra-rare-earth binary alloys, involving a lighter rare earth (La, Ce, Pr, and Nd) and a hexagonal-close-packed (hcp) heavier rare-earth element (Gd to Lu) or Y. These alloys have been shown[4–9] to crystallize in the Sm-type structure at some intermediate composition, while the compositions on the heavier and lighter rare-earth side have the hcp and the dhcp structures, respectively. In the entire range there is solid solution and the constituent atoms are disordered. It occurred to us that these alloys might undergo the same pressure-induced transformation sequence as that found in the rare earth metals,[2] and the effect of addition of a lighter rare earth to the heavier one and the effect of pressure on the latter act in the same direction. Further, we anticipated that the pressure-induced Sm-form of Gd could be retained down to the lowest temperature with the addition of La.

We have investigated alloys in the La-Y, La-Gd, Ce-Y, Gd-Y Systems, as also PrY, NdY, NdTm, NdGd, $Ce_{0.30}Gd_{0.70}$, and $Ce_{0.45}Ho_{0.55}$, all of which have the Sm-type structure.

Since pressure induced phase changes in the rare earth systems offer the possibility of studying the effect of crystal structure on magnetic ordering, we have studied a few alloys in the Gd-La system and NdTm both in their normal and pressure induced structures. In the Gd-La system, all the alloy compositions studied were on the Gd-rich side and had the hcp structure except $LaGd_3$ which had the Sm-type structure. The results will be presented and discussed.

EXPERIMENTAL

The alloys were prepared by arc melting in an argon atmosphere appropriate amounts of the metals. They

[1] A. Jayaraman and R. C. Sherwood, Phys. Rev. Letters **11**, 22 (1964).
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[4] *The Rare Earths*, edited by F. H. Spedding and A. H. Daane, (John Wiley & Sons, Inc., New York, 1961).
[5] K. A. Gschneidner Jr., *Rare Earth Alloys*, (Van Nostrand, Inc., Princeton, New Jersey, 1961).
[6] J. Nachman, C. E. Lundin, and G. Rauscher, Technical Report No. 1, Contract No. NONR-3661(02), 1963 (unpublished).
[7] C. E. Lundin and J. F. Nachman, Technical Report No. 2, Contract No. NONR-3661(02), 1964 (unpublished).
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[9] R. M. Valletta (A. Daane), dissertation abstr. **20**, 3539 (1960).

were then heat treated at about 500°C for several days, in sealed evacuated quartz glass tubes. X-ray powder patterns revealed that the annealed samples were single-phase materials and had the structure expected for the composition. High-pressure experiments were carried out in a piston-cylinder apparatus. Samples were normally subjected to 40 kbar and 450°C for about 5 h. After this treatment, temperature was reduced to ambient and pressure released. The x-ray patterns of the specimens were then recorded. Magnetic-susceptibility measurements were carried out with a pendulum magnetometer[10] down to 1.4°K.

RESULTS

The compositions studied, their normal crystal structure, and the structure of the pressure induced phases are listed in Table I.

TABLE I. Composition and structure of the alloys studied.

Alloys	Normal phase	Pressure-induced phase
$La_{0.05}Gd_{0.95}$	hcp	Sm type
$La_{0.10}Gd_{0.90}$	hcp	Sm type
$La_{0.15}Gd_{0.85}$	hcp	Sm type+dhcp[a]
$La_{0.25}Gd_{0.75}$	Sm type	dhcp
$La_{0.30}Y_{0.70}$	hcp	no transition
$La_{0.40}Y_{0.60}$	hcp	Sm type
$La_{0.50}Y_{0.50}$	Sm type	dhcp
$Ce_{0.25}Y_{0.75}$	hcp	no transition
$Ce_{0.50}Y_{0.50}$	Sm type	decomposes to elements[b]
$Ce_{0.70}Y_{0.30}$	dhcp	decomposes to elements[b]
$Ce_{0.30}Gd_{0.70}$	Sm type	dhcp
$Ce_{0.45}Ho_{0.55}$	Sm type	dhcp
PrY	Sm type	dhcp
NdGd	Sm type	dhcp
NdY	Sm type	dhcp
NdTm[c]	Sm type	dhcp
$Gd_{0.90}Y_{0.10}$	hcp	Sm type
$Gd_{0.80}Y_{0.20}$	hcp	no transition

[a] Some dhcp phase is present.
[b] Decomposed to γ-Ce (fcc) and α-Y (hcp).
[c] The composition was definitely less rich in Tm than $Nd_{0.5}Tm_{0.5}$ as there was considerable loss of Tm because of its higher vapor pressure at the preparation temperature. In fact, the Sm-type phase is centered at the composition $Nd_{0.63}Tm_{0.37}$ with some solid solubility.

All the alloys with the Sm-type structure, except CeY, transformed to the dhcp structure and the respective high-pressure phases are retained at atmospheric pressure and room temperature. CeY broke down to the elements under the pressure and temperature conditions stated. Also, $Ce_{0.70}Y_{0.30}$ which has the dhcp structure decomposed to the elements. In Table II are presented the crystallographic data for the Sm-type phase and the pressure-induced dhcp phase. In the case of NdY, conversion to dhcp was only partial under the experimental conditions. The transformations are sluggish and the conversion to the high-pressure form is temperature- and time-dependent. Hence, no attempt was made to locate transition pressures. However, it would seem from the results that the latter increases in the sequence LaY<PrY<NdY.

[10] R. M. Bozorth, H. J. Williams, and D. E. Walsh, Phys. Rev. 103, 572 (1956).

TABLE II. Crystallographic data.

	Sm-type phase		La-type phase	
	a (Å)	c (Å)	a (Å)	c (Å)
$LaGd_3$	3.65±0.02	26.33±0.02	3.63±0.02	11.79±0.02
LaY	3.70±0.05	26.65±0.02	3.69±0.05	11.85±0.02
PrY	3.65±0.05	26.25±0.02	3.62±0.05	11.68±0.02
NdTm	3.50±0.05	26.00±0.02	3.60±0.05	11.50±0.02
NdGd	3.65±0.05	26.22±0.02	3.70±0.05	11.70±0.02
$Ce_{0.30}Gd_{0.70}$	3.66±0.05	26.24±0.02	3.55±0.05	11.77±0.02
$Ce_{0.45}Ho_{0.55}$	3.63±0.05	26.02±0.05	3.66±0.05	11.57±0.02

The results of magnetization measurements are presented in Figs. 1 (Sm-form) and 2 (dhcp-form) for $LaGd_3$, and Figs. 3 (Sm-type) and 4 (dhcp-type) for NdTm. In the case of $LaGd_3$, a kink in the curve occurs at about 120°K for the Sm-form (See Fig. 1). The curve for NdTm shows a peak for the Sm-form at about 32°K (See Fig. 3). In either case, the curves for the dhcp-form appear to be smooth. Figure 5 is the data for the La-Gd alloys. The upper curves (1,2,3) are for the hcp phase for the three compositions, while the lower curves (4, 5, and 6) are for the pressure-induced Sm-type phases. In the hcp phase, all the three alloys exhibit ferromagnetic ordering. In the Sm-type phases the situation is complicated by reversion to the hcp structure.

DISCUSSION

Crystal Structure under Pressure

In the rare-earth metals, pressure-induced phase transformations have been shown to occur in the sequence hcp → Sm-type → dhcp → fcc.[2] The same sequence of transformations holds good for intra-rare-

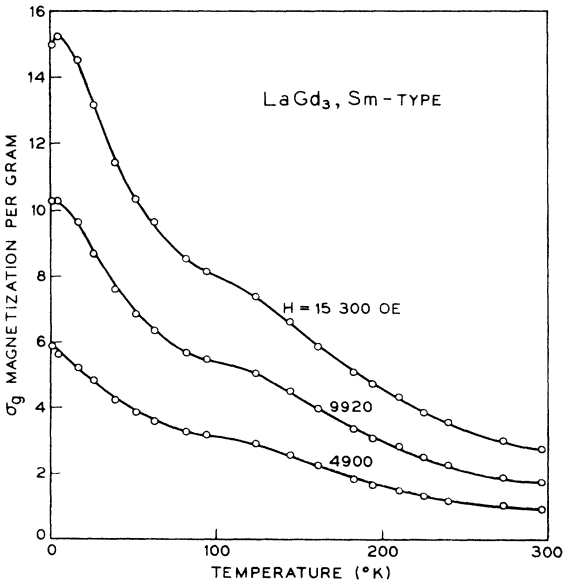

FIG. 1. Magnetic data for Sm-form of $LaGd_3$.

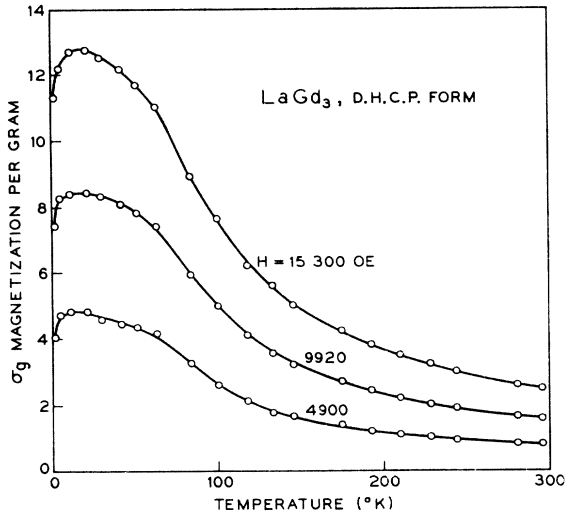

FIG. 2. Magnetic data for dhcp $LaGd_3$.

earth alloys; the hcp alloys transform to the Sm structure and those having the Sm-structure transform to the dhcp structure under pressure. It is well known that the c/a ratio is markedly different[4,5] for the lighter rare earths and the heavier rare earths; for the former it is near 1.62 and for the latter near 1.57. Samarium falls in between with a ratio of 1.60. Spedding *et al.*, and Beaudry *et al.*[11] have suggested that the Sm-type structure becomes stable at a critical c/a ratio near 1.61 in the case of intra-rare-earth alloys, with a discontinuous change in the ratio. McWhan[12] reports a similar effect with pressure in the case of Gd, Tb, Dy, and Ho. Thus, the effect of pressure on a hcp rare-earth metal and the addition of a lighter rare-earth metal to it have the same effect and act in the same direction; they bring about similar sequence of structures and both affect the c/a ratio similarly. Therefore it is reasonable to conclude that if in an alloy system the Sm-type phase is stable at some composition, the latter phase could also be produced by application of high pressure on the pure hcp end member. Thus, the existence of the Sm-type phase in the systems Y-Ce, Y-Pr, and Y-Nd and the occurrence of a pressure-induced hcp → Sm-type transformation in $Y_{0.10}Gd_{0.90}$ and $Y_{0.60}La_{0.40}$ indicates that pure Y would transform to the Sm-type structure at some high pressure. Whereas Gd transforms at moderate pressures (25 kbar at room temperature[13]) to the Sm type, Y would transform at pressures probably an order of magnitude higher or more; under the above experimental conditions, $Y_{0.20}Gd_{0.80}$ and $Y_{0.70}La_{0.30}$ do not transform to the Sm-type as addition of Y apparently increases the transition pressure rapidly. Spedding *et al.*[11] have pointed out that Y, although very similar to Gd in atomic volume, behaves differently and is more similar to Dy, Ho, Er, or Tm in its structural properties, viz., c/a ratio of 1.57. Lundin[8] arrives at the same conclusion from a study of the range of stability of the Sm-type phase in the intra-rare-earth alloys involving Y. In high-pressure behavior also, Y seems to reflect this tendency, for it is expected to transform to the Sm-type structure at a much higher pressure compared to Gd. Since the Sm-type phase occurs for all the heavy rare earths[8] when alloyed with La to Nd, transformation to the Sm-type and dhcp structures may very well be anticipated for all of them at high

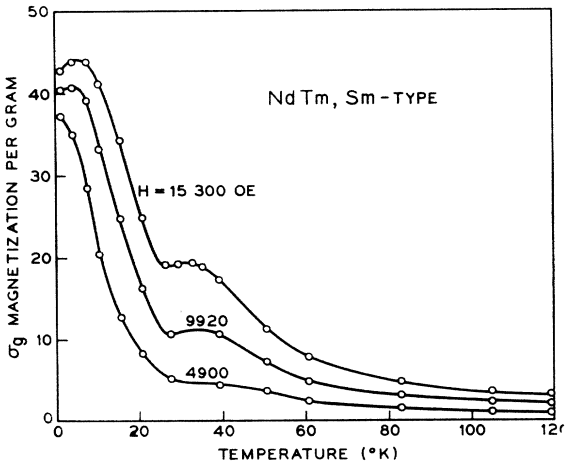

FIG. 3. Magnetic data for Sm-form of NdTm.

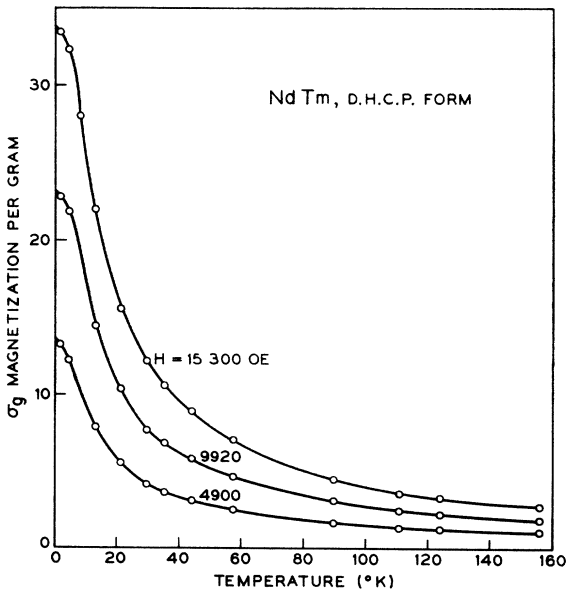

FIG. 4. Magnetic data for dhcp NdTm.

[11] F. H. Spedding, R. M. Valletta and A. H. Daane, Trans. Am. Soc. Metals **55**, 483 (1962); B. J. Beaudry, M. Michel, A. H. Daane, and F. H. Spedding, Atomic Energy Commission, Ames Research Laboratory, Contribution No. 1470 (unpublished).

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[13] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **82**, 95 (1953).

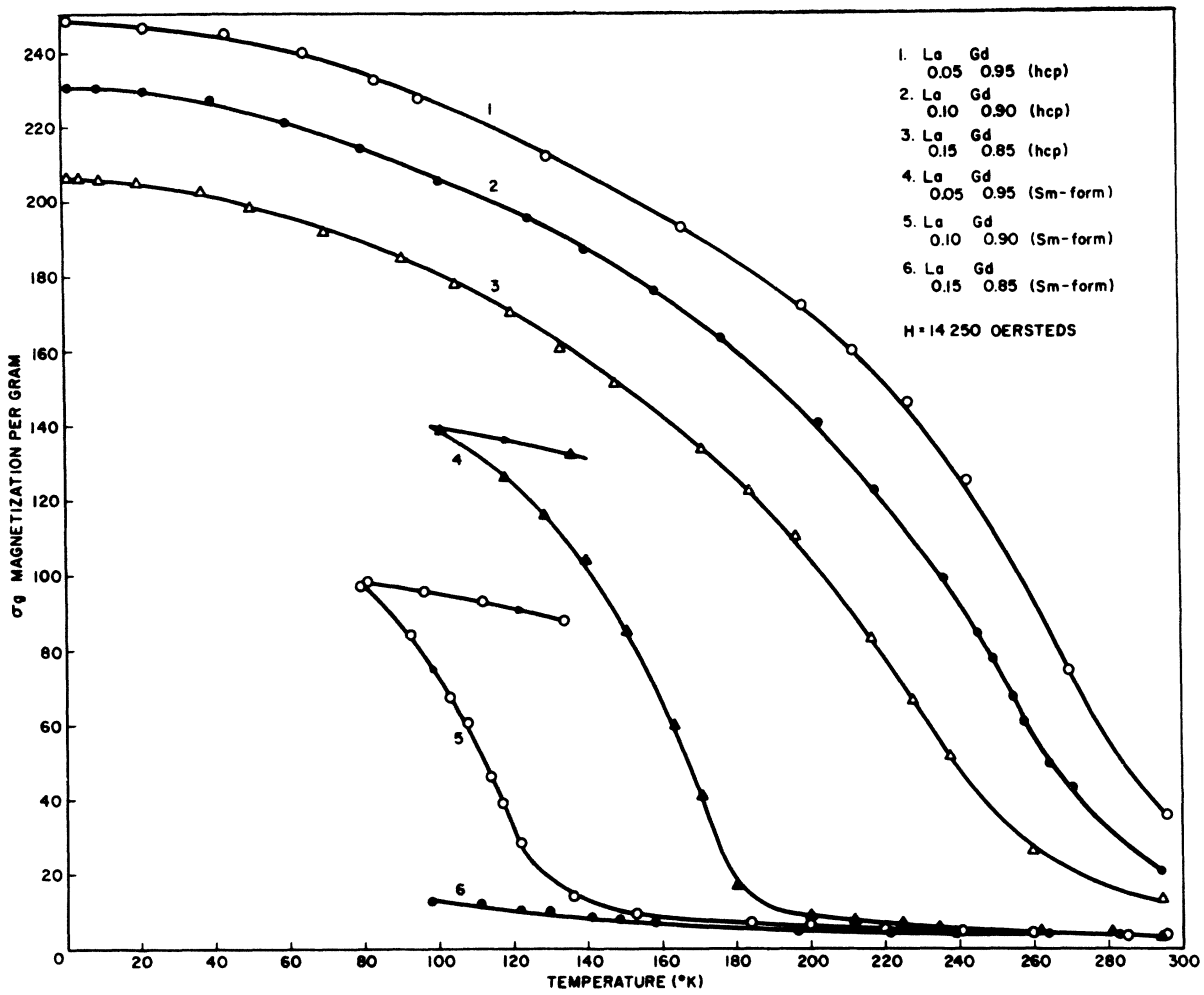

FIG. 5. Magnetic data for the hcp and Sm-type phase of La-Gd alloys.

pressures. McWhan and Stevens[3] have found evidence for hcp to Sm-type transition in Tb, Dy, and Ho. Perez-Albuerne *et al.*[14] have reported anomalies in the lattice constants in Ho, Er, and Tm at high pressures. These anomalies and some of the resistivity anomalies reported by Stager and Drickamer,[15] who have investigated a number of hcp rare-earth metals in the range 1–700 kbars, is very likely to be due to the occurrence of these transitions.

Electronic Transition in Ce and Its Effect on the Alloy Structure

The decomposition of CeY (Sm-type) and $Ce_{0.70}Y_{0.30}$ (dhcp) to γ-Ce (fcc) and α-Y (hcp) can be rationalized as follows: The Ce atoms which are normally trivalent in these alloys, under the influence of pressure and temperature, become quadrivalent due to $4f \rightarrow 5d$ electron promotion[16,17] and consequently undergo a reduction in size. The change in the metallic radius accompanying such a transformation has been shown to be 1.842 to 1.71 Å in the case of pure Ce.[16,17] Apparently, under the influence of temperature at high pressure the collapsed Ce atoms diffuse through the alloy and cluster to form regions of α-Ce which reverts to γ-Ce on release of pressure, giving a mixture of γ-Ce and α-Y. Our results suggest that neither the Sm-type structure nor the dhcp structure in the Ce-Y system is stable at high pressures and instead only α-Ce and α-Y exists. A corollary of this is that beyond a certain critical radius ratio for the constituent atoms, neither the Sm-type nor the dhcp structure could be stable. In Table III are given the radius ratios (based on metallic radius) of the lighter rare-earth to the

[14] E. A. Perez-Albuerne, R. L. Clendenen, R. W. Lynch, and H. G. Drickamer, Phys. Rev. **142**, 392 (1966).
[15] R. A. Stager and H. G. Drickamer, Phys. Rev. **133**, A830 (1964).
[16] A. W. Lawson and T. Tang, Phys. Rev. **76**, 301 (1949).
[17] A. F. Schuch and J. H. Sturdivant, J. Chem. Phys. **18**, 145 (1950).

TABLE III. Radius ratio for the intra-rare-earth alloys.

	La	Ce^{3+}	Ce^{4+}	Pr	Nd
Y	1.06	1.01	0.956	1.032	1.028
Tm	...	...	...	...	1.034
Ho	1.053	1.03	0.968	...	1.022
Gd	1.041	1.01	0.945	...	1.01

heavier rare-earth element and Y, for several alloys crystallizing in the Sm-type structure. For Gd which transforms under pressure to the Sm-type structure, the ratio is unity. In the case of Ce^{4+} (see Table III) the radius ratio would be substantially lower than unity and under these conditions instability sets in.

Gschneidner[18] *et al.* have shown that the transition pressure of γ-Ce $\rightarrow$ α-Ce transformation is raised by Y and rare-earth additions. The absence of decomposition in $Ce_{0.25}Y_{0.75}$, $Ce_{0.30}Gd_{0.70}$, and $Ce_{0.45}Ho_{0.55}$ must be attributed to the nonoccurrence of $Ce^{3+} \rightarrow Ce^{4+}$ transformation, this evidently being at pressures higher than the present experimental conditions. If the hcp $\rightarrow$ Sm-type $\rightarrow$ dhcp sequence of transformation occurs in a particular case at a lower pressure relative to the valence transformation of the Ce atoms, pressure would induce the phase change in the sequence mentioned. This seems to be the case with $Ce_{0.30}Gd_{0.70}$ and $Ce_{0.45}Ho_{0.55}$, for they transform to the dhcp structure and do not decompose. For the $Ce_{0.25}Y_{0.75}$ alloy, apparently neither the hcp $\rightarrow$ Sm-type nor the Ce^{3+} to Ce^{4+} transition pressures were reached under the present experimental conditions, and hence no change is observed. However, the possibility remains for these alloys involving Ce that at some high pressure they decompose. Thus, we believe that at very high pressures, the Ce atoms in the intra-rare-earth Ce alloys would undergo the valence transformation and therefore, only α-Ce and one of the phases in the sequence hcp $\rightarrow$ Sm-type $\rightarrow$ dhcp $\rightarrow$ fcc phase of the heavier rare earth can exist in the entire compositional range.

MAGNETIC PROPERTIES

Sm-Type Alloys

The magnetic behavior of some Gd-La and Gd-Y alloys has been studied by Thoburn, Legvold, and Spedding.[19] According to these authors $LaGd_3$ has a poorly defined antiferromagnetic maximum at about 130°K. In our measurements on $LaGd_3$ (Sm-type), an anomaly in the magnetization curve is evident at about 120°K, and some kind of ordering (probably antiferromagnetic) takes place at this temperature. In the magnetization curve for the dhcp-form, no such anomaly is evident. The effective moment per Gd calculated from the susceptibility data in the paramagnetic region yields 8.45 and 8.8 Bohr magnetons for the Sm and dhcp forms of $LaGd_3$, respectively. The difference is probably not significant. The value of 8.45 for the Sm-form is in reasonable agreement with the value of 8.38 Bohr magnetons obtained by Thoburn *et al.*[19] The theoretical value for Gd is 7.94 Bohr magnetons. Roughan and Daane[20] who have also studied $LaGd_3$ (Sm-type) report an anomaly in the susceptibility at 130°K and calculate the contribution from Gd as 9.4μ_B from the measured susceptibility in the paramagnetic region. This is, however, in disagreement with the value of Thoburn *et al.* and the value obtained in the present investigation.

At 4.2°K the magnetization increases with the field and at 80 kG (our maximum) Gd is contributing 1.82 and 1.62μ_B to the moment in the Sm-form and dhcp form, of $LaGd_3$, respectively. Also, the magnetization curves show some remanence in both cases. It is therefore believed that at very low temperatures (4.2°K), both forms undergo magnetic ordering with incomplete cancellation of the moments.

Davis and Bozorth[21] studied Tm metal and reported a maximum in the susceptibility curve indicative of antiferromagnetic ordering at about 60°K. According to them, Tm should be ferromagnetic below 22°K, as it shows a hysteresis loop. Jennings, Hill, and Spedding[22] have found a specific heat anomaly at 55°K in Tm metal, attributed to a magnetic ordering. Koehler, Cable, Wollan, and Wilkinson[23] studied by neutron diffraction the magnetic structure of Tm down to very low temperatures and have reported evidence for an oscillatory type antiferromagnetic configuration (spiral or helical type) below 55°K. The structure adopted by Tm at very low temperatures is a type of antiphase domain-type structure in which there is a net moment of 1.0 Bohr magneton, due to incomplete cancellation. For an alloy of 89.4% Tm-10.6% La[24] which is hcp, Koehler *et al.* found that the Néel temperature lowered to 36°K with the Curie point at 31°K. NdTm in the Sm-type structure would appear to be similar to Tm in magnetic behavior. From the anomaly in the magnetization curve (see Fig. 3), it is deduced that NdTm (Sm-type) orders antiferromagnetically at about 30°K. It exhibits a hysteresis loop at very low temperatures (our data were taken at 1.3°K) and is presumably, therefore, ferro- or ferrimagnetic. There does not appear to be any susceptibility anomaly indicative of ordering in the dhcp-form of NdTm near 30°K and the magnetization curve is quite smooth in this region (see Fig. 4). At very low temperatures (1.4°K), the dhcp

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[23] W. C. Koehler, J. W. Cable, E. O. Wollan, and M. K. Wilkinson, Phys. Rev. **126**, 1672 (1962); J. Appl. Phys. **33**, 1124 (1962).
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form also shows a hysteresis loop which would imply ferrimagnetic or ferromagnetic ordering. The effective moment P^2_{eff} calculated from the susceptibility data in the paramagnetic region for the two forms is about 68, which compares favorably with the theoretical value of 70.8 computed using $g(J(J+1))^{1/2}$ of 3.62 and 7.6 for tripositive Nd and Tm, respectively. Roughan and Daane[20] also report a susceptibility maximum at 28.5°K for the Sm-type phase.

Samarium

Lock[25] investigated the magnetic behavior of Sm metal and reported a sharp decrease in the susceptibility, characteristic of antiferromagnetic ordering at 15°K, and a kink in the curve between 110°K to 150°K. Anomalies in heat capacity have been reported by Jennings *et al.*[26] at 105 and 13.8°K. Features similar to those observed by Lock were obtained by Jayaraman and Sherwood[2] in the magnetization curve for the normal form of Sm. For the pressure-induced dhcp form there was a much more pronounced kink in magnetization around 100°K. Further, the peak occurring at the lower temperature was shifted to 27°K and was distinctly smaller in magnitude.

McWhan and Stevens[3] have suggested that the double peaks observed in the ac susceptibility of Sm-form of Gd, Tb, and Dy represent ordering of hexagonal (h) layers and cubic (c) layers at different temperatures, in analogy with the behavior of Nd. In Nd, neutron-diffraction studies[27] in the range of 1.6 to 20°K have shown that the hexagonal site layers (h) and the cubic site layers (c) present in the structure order at different temperatures, the former (h) at 19°K and the latter (c) at 7.5°K. We suggest that in the Sm metal also, the cubic and hexagonal layers order at different temperatures. The kink in the magnetization curve at the higher temperature (100–120°K) we believe is due to the ordering of the (c) layers and the low-temperature peak (27 and 14°K) associated with the ordering of (h) layers. The specific-heat measurements of Jennings *et al.* give a considerably higher entropy under the 105°K maximum in the C_P than that under the low-temperature maximum, which would seem to suggest the opposite sequence for the ordering. Our suggestion is based on the following facts. In the normal form (rhombohedral structure) the hexagonal-to-cubic-layer ratio is 3 to 1, while in the dhcp it is 1 to 1. Since the kink in the magnetization curve at the higher temperature is much more pronounced for the dhcp-form, it must be associated with the ordering of the cubic layers for, the ratio of (c) to (h) layers increases in going from the normal form to the dhcp-form of Sm. It would also follow that in the dhcp-form the peak associated with ordering of (h) layers should diminish in magnitude. This is precisely what is observed.

TABLE IV. Magnetic data on La-Gd alloys.

Alloy composition	Structure	Θ_f (°K)	Θ_N (°K)	Θ_p (°K)	Moment (μ_β)	Reversion temp. (°K)
Gd	hcp	293.2		317	7.55	
	Sm form		247[a]			
$La_{0.05}Gd_{0.95}$	hcp	275				
	Sm form			120	7.55	180
$La_{0.10}Gd_{0.90}$	hcp	258				
	Sm form			93	7.6	130
$La_{0.15}Gd_{0.85}$	hcp	240				
	Sm form			60	8.2	~60
$La_{0.25}Gd_{0.75}$	Sm form		~120	50	8.45	
	dhcp form			4	8.8	

[a] Reference 3.

La-Gd Alloys

The magnetic data for the La-Gd alloys are summarized in Table IV where Θ_f, Θ_N, and Θ_p are, respectively, the ferromagnetic Curie temperature, Néel temperature, and paramagnetic Curie temperature. μ_β was calculated from magnetic susceptibility data obtained in the paramagnetic region. In the last column are given the observed temperatures for the reversion to the hcp structure, of the pressure-induced Sm-type phase. All the compositions when in the hcp-form show a transition to the ferromagnetic state (see Fig. 5). Our earlier magnetic susceptibility measurements[1] on the metastably retained Sm-form of Gd was complicated by the reversion to hcp structure on cooling. The expectation that the metastably retained Sm phase could be stabilized down to 1.4°K with some La in solid solution did not materialize because the pressure-induced Sm-form of La-Gd alloys also undergo a reversion to the hcp structure on cooling. The pressure-induced Sm-form of La-Gd alloys may be expected to show magnetic ordering similar to Gd. The drastic change in the susceptibility of the Sm-form is noteworthy (see Fig. 5) and reflects the very different magnetic behavior of this phase.

The temperature of reversion to the hcp structure and its dependence on the La concentration are shown in Fig. 6. Also plotted in the figure is the Θ_f the ferromagnetic Curie temperature of the hcp phase. The interesting point here is that the intersection of the line connecting the reversion temperature T_R with the temperature axis is precisely where the Sm-form of Gd would order antiferromagnetic at atmospheric pressure, as determined by the extrapolation of McWhan and Steven's[3] high-pressure data. This strongly suggests that the reversion to hcp-form in Gd and La-Gd alloys may be linked to the onset of a magnetic transition in the Sm-form.

In general, the transition from paramagnetic to the

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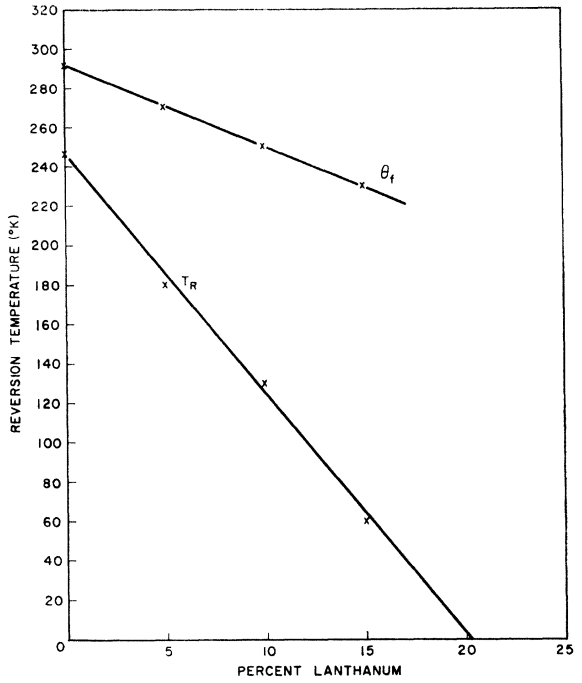

FIG. 6. Ferromagnetic Curie point of hcp La-Gd alloys and reversion temperature of the pressure induced Sm-type phase to the hcp structure.

ordered state is second order while antiferromagnetic (AF) to ferromagnetic (F) state is first order. It has been shown[28] that the exchange magnetoelastic energy is important in AF-F transitions and this often can lead to considerable lattice distortion. Darnell[29–31] has reported structural distortion in Dy and anomalous expansion coefficients for Tb at the AF-F transition. Also, in the majority of antiferromagnetics the fractional deformation of the lattice in the transition from paramagnetic to the antiferromagnetic state takes very large values.[32] It appears therefore, attractive to invoke a magnetic transition for providing the necessary driving force for reversion of Sm-type La-Gd alloys and Gd to the hcp structure. The transformation hcp $\rightleftarrows$ Sm-type represents a rearrangement of the atomic layers (from ABAB$\cdots\rightleftarrows$ ABABCBCAC, AB$\cdots$sequence) and the energy difference involved is very likely to be quite small. Indeed, it is a fact that mechanical straining such as cutting with a razor blade or filing brings about reversion to the hcp structure of the metastably retained Sm phase. Thus, that the magnetoelastic strain energy associated with a magnetic transition could provide the driving force though lattice distortion offers a rather convenient and plausible mechanism to explain away the reversion of the metastably retained Sm-form of Gd and La-Gd alloys on cooling. Alternatively it could be a martensitic transformation with a large pressure and temperature hysteresis, requiring a large driving force, but we believe that the coincidence of the extrapolated reversion temperature T_R to the Néel temperature of pure Gd (see Fig. 6) in the Sm-form is more than fortuitous and offers the main support for invoking the magnetoelastic energy to nucleate the transformation Sm-type $\rightarrow$ hcp.

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