PRESSURE-INDUCED PHASE TRANSFORMATION IN GADOLINIUM AND ITS EFFECT ON THE MAGNETIC BEHAVIOR

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We report in this Letter the pressure-induced transformation of hcp gadolinium to the samarium-type structure, metastably retained at room temperature under atmospheric pressure. Samarium has a unique close-packed metallic structure in which layers of atoms are arranged in the sequence *ABABCBCACA*. For the first time a transformation to this structure has been observed. Also, there is some evidence for the presence of lanthanum-type double-hexagonal close-packed arrangement in pressurized Gd samples. The magnetic behavior of these phases differ markedly from that of the normal Gd.

Gadolinium was first investigated under pressure by Bridgman[1] who observed an irreversible downward drift in resistance, and a break in volume in the region 20 000 to 25 000 kg/cm^2. Also, recent investigations[2] on the effect of pressure on the ferromagnetic Curie temperature gave anomalous results at these pressures, suggestive of a phase change. Neither of these studies shed any light on the nature of the transition involved.

In the present investigation, samples of gadolinium were pressurized to about 40 kbar in a piston cylinder apparatus at room temperature and at 400°C. Silicone oil (40 centistoke) was used as the pressure transmitting medium, and the oil was contained in a Teflon cell.[3] The latter was dimensioned to go into the furnace assembly used in differential thermal analysis runs,[4] to facilitate heating of the sample to the desired temperature.

For magnetic studies Gd (99+% purity) was machined to a cylinder 1/16 in. × 1/16 in., while for x-ray identification small fragments were found to be suitable. After about 15 minutes under pressure and temperature, temperature was reduced first and pressure released. Silicone oil was found to be well contained, and there appeared to be no deformation of the specimens.

X-ray powder photographs were taken with Cr K_α radiation. X-ray data (Table I) for Gd subjected to pressure at 400°C show that the predominant phase present fits perfectly the samarium-type ($R\bar{3}M$ - D_{3D}[5]) structure[5]; the lattice constants are $a = 8.92 \pm 0.01$ Å; $\alpha = 23.3 \pm 0.03°$. The lattice constants based on hexagonal cell are $a = 3.61 \pm 0.01$ Å; $c = 26.03 \pm 0.01$ Å. The density calculated from the x-ray data is 8.00 g/cc as compared to 7.895 for the hcp Gd. The volume difference at atmospheric pressure for the transition, computed from these data, is $\Delta V = 1.37\%$. Gadolinium with the Sm-type structure, on cooling below liquid nitrogen temperatures, transforms to the normal form.

In the x-ray pattern (Table I) there are faint additional lines (indicated by reference c) which do not belong to the Sm-type structure. These lines are appropriate to the double-hexagonal close-packed (La-type) structure. Because of overlap of many of the lines of this structure with that of the normal form of Gd and extreme faintness of the distinguishing reflections such as (10.3) and (10.5) of the dhcp structure, it is not possible to offer any precise data. X-ray photographs of Gd compressed at room temperature to 20-40 kbar show the normal hcp pattern except for an additional line at 3.03 Å. This could be the (10.1) reflection for the dhcp structure, but the (10.3) and (10.5) are not detectable. Since these structures are related, differing only in the stacking sequence, localized regions characteristic of both could be simultaneously present, and they may be responsible for the observed features.

It has been suggested that the complex crystallographic structures of the lighter rare earths La to Sm could be due to the smallness of the

Table I. X-ray data for pressurized gadolinium.

Spacing	*hkl*[a]	Intensity[b]	Spacing	*hkl*	Intensity
3.16*[c]		vw	1.87*[c]		vw
3.09	100	vw	1.80	$10\bar{1}$	s
3.04	110	vw	1.68	544	ms
2.88	333	vs	1.64*[c]		w
2.81	211	ms	1.597	554	ms
2.75*[c]		m	1.56*[c]		vw
2.68	221	ms	1.53	432, 220	vs
2.39	322	vw	1.515*[c]		w
2.25	332	w	1.496	311	w
2.13*[c]		vw	1.447	666	s
2.00	433	vw			

[a] *hkl* = Rhombohedral indexing.
[b] vw = very weak; w = weak; ms = medium strong; s = strong; vs = very strong.
[c] See text.

magnetic dipole-dipole interaction energy[6]; whereas in heavier rare earths this contributes a greater share to the bonding energy and supposedly stabilizes the hcp structure. Compression would normally be expected to decrease the metallic radius which, in turn, would increase the dipole-dipole interaction energy, since the latter is a function of $1/r^3$. Therefore, this situation would not favor the complex structures, unless pressure also affects the effective moment.

Another profitable line of inquiry would be to examine the effect of pressure and temperature on the axial ratio. Gadolinium has a c/a ratio of 1.59, which is intermediate between the light and heavy rare earths. The elastic constants might be such that the combined effect of pressure and temperature increases the axial ratio to values closer to those observed in lighter rare earths. This situation might favor the transformation of Gd to the complex structures.

Magnetic measurements were carried out with the pendulum magnetometer.[7] The magnetization versus absolute temperature at 15 300 oersteds is given in Fig. 1, for normal Gd (curve 1), for Gd pressurized at 25°C (curve 2), and for Gd predominantly in the Sm form (curve 3). The results of measurements on the latter are influenced by the presence of dhcp phase and possibly also hcp Gd. The data, however, clearly show that Gd in the Sm form has the lowest moment. The break in curve 3 reflects the transformation of the Sm form on cooling.

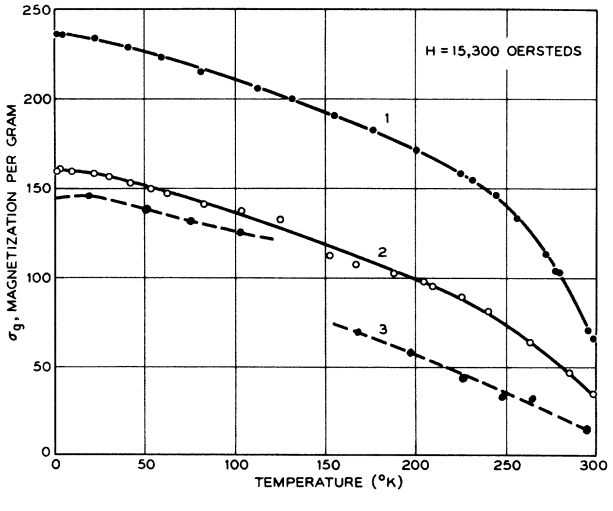

FIG. 1. Magnetic data for pressurized and nonpressurized samples of gadolinium.

In the La-Gd phase diagram,[8] alloys containing 75 to 83 at.% Gd have the Sm-type structure (δ phase), and these are reported to be antiferromagnetic.[9] Spiral structure[10] for normal Gd was proposed, but this has been questioned.[11] However, this does not rule out the possibility of a spiral-type magnetic ordering for Gd in the Sm form. When Gd is prepared purely in the Sm form as a single crystal, neutron diffraction will give a definitive answer on its magnetic structure.

The lower moments observed in Gd samples pressurized at room temperature could be caused by the presence of stacking arrangements other than that characteristic of hcp. Stacking fault energies are apparently low for Gd and deviations from *ABAB* sequence occur rapidly in the pressure range in which the anomalies were reported.

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