

TABLE I. KMgF_3 frequencies (in cm^{-1}) and symmetry of infrared modes obtained from K-K analysis of the reflection data for KMgF_3 and for MgF_2 .

ν_1	450	F_{1u}	MgF stretch
ν_2	295	F_{1u}	FMgF bend
ν_3	140	F_{1u}	K-(MgF ₃) stretch (lattice mode)

TABLE II. MgF_2 frequencies (in cm^{-1}) and symmetry of infrared modes obtained from K-K analysis of the reflection data for KMgF_3 and for MgF_2 .

ν_1	435	E_u	MgF stretch
ν_2	405	E_u	MgF stretch—FMgF bend
ν_3	280	E_u	Pseudolattice modes where Mg moving one way and F in opposite
ν_4	265	A_{2u}	

around the magnesium atoms and the lattice is consequently made up of interpenetrating unit cells. Hence, a mode in one cell which could be described as predominantly a stretching mode automatically gives rise to a predominantly bending mode in all the interpenetrating cells. Again a full description of the form of the vibrations must await a normal coordinate analysis for which the additional information regarding the frequencies of the infrared-inactive modes must be obtained from the Raman spectrum.

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Phase Transformation in Samarium Induced by High Pressure and Its Effect on the Antiferromagnetic Ordering

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Samarium undergoes a pressure induced phase transformation to double-hexagonal close-packed (La-type) structure at pressures around 40 kbar and temperatures near 300°C . It is retained metastably at atmospheric pressure. The new phase has a Néel temperature of 27°K as compared to 14.8°K noted for normal form of Sm. Pressure induced phase transformations observed in Gd, Sm, Ce, and La suggest that the sequence of polymorphic transformations under pressure in trivalent rare earths is in the order hcp \rightarrow Sm-type \rightarrow dhcp \rightarrow fcc.

WE wish to report a pressure induced phase transformation in samarium metal to the double-hexagonal close-packed (La-type) structure. The phase change is accompanied by a shift of the Néel temperature from 14.8°K to 27°K . This structural transformation in Sm, together with the recently reported pressure-induced phase change in hcp Gd^{2+} suggests that there might be a sequence of pressure-induced polymorphic transformations in the trivalent rare earths.

Bridgman³ was the first to measure resistivity and volume of Sm as a function of pressure; he found no unusual features. Recently, Stager and Drickamer⁴ have observed some minor deviations from normal behavior in the resistivity of Sm in the region 50 to 500 kbar.

In the present study, Sm was subjected to a pressure

of about 40 kbar in a piston cylinder apparatus at about 350°C , as well as at room temperature. The pressure medium was silicone oil (40 centistokes). A Teflon cell⁵ was used as the container for the oil and the cell was made to fit into a furnace assembly to facilitate heating. Because a large sample volume of about 1 cc was needed for magnetic studies, the furnace assembly was suitably dimensioned to fit into a 1-in.-diam and 2-in.-long pressure chamber. After the sample was subjected to the required pressure and temperature for about 15 min, temperature was reduced to ambient and pressure then released.

X-ray powder photographs of pressurized Sm were taken with $\text{CrK}\alpha$ radiation. The x-ray data (Table I) are consistent with the dhcp structure (La-type); the lattice constants are $a = 3.618 \pm 0.005 \text{ \AA}$, $c = 11.66 \pm 0.01 \text{ \AA}$. The density calculated from x-ray data is 7.555 g/cc for the dhcp phase as compared with 7.536

¹ J. M. Lock, Proc. Phys. Soc. (London) **B70**, 566 (1957).² A. Jayaraman and R. C. Sherwood, Phys. Rev. Letters **12**, 22 (1964).³ P. W. Bridgman, Proc. Am. Acad. Arts Sci. **83**, 1 (1954).⁴ R. A. Stager and H. G. Drickamer, Phys. Rev. **133**, A830 (1964).⁵ S. Geller, D. B. McWhan, and G. W. Hull, Jr., Science **140**, 62 (1963).

TABLE I. X-ray data for pressurized Sm.

<i>hkl</i>	Spacing in Å	Intensity ^a
100	3.09	w
101	3.02	wm
004	2.91	vs
102	2.76	s
103	2.43	w
104	2.13	vw
105	1.87	m
110	1.809	m
106	1.650	s
114	1.536	ms
202	1.511	w
107	1.468	w
008	1.458	ms

^a s = strong, m = medium, w = weak, and v = very.

g/cc⁶ for the normal form of Sm. Conversion to the new form appeared to be complete when the temperature was maintained at 350°C while the sample was under pressure. When Sm was pressurized to 40 kbar at room temperature, conversion was incomplete, and the x-ray powder lines were broad. Unlike the pressure induced Sm-type Gd, the dhcp form of Sm is stable to liquid-helium temperatures. Reversion to the normal form took place on heating to about 600°C; there was no noticeable change on heating at 350°C for a few hours.

Magnetic measurements were carried out with the pendulum magnetometer.⁷ The magnetization versus absolute temperature at 15 300 Oe is given in Fig. 1 for Sm in the dhcp form (curve 1) and in the normal form (curve 2). Results of our measurements on the normal form are in agreement with those of Lock,¹ the sharp decrease in magnetic susceptibility characteristic of the antiferromagnetic ordering occurring at 15°K. For dhcp Sm, this temperature (Néel point) has shifted to 27°K. In the temperature range above 140°K the two curves tend to superpose, but some deviations occur below this temperature. The susceptibility maximum, of the dhcp Sm is less than that of the normal form. No noticeable difference either in the location or in the height of the maximum was detected after annealing the pressurized sample for 20 h at 250°C. Further, there is a kink in the curve between 100 and 120°K. The origin of the latter two effects is not clear.

The structure of samarium is a close packed stacking arrangement of atomic layers in the sequence *ABABCBCACABAB*... The pressure induced polymorph which has the dhcp structure is also close packed, but has a different stacking sequence, namely, *ABACABAC*... In transformation from Sm type to dhcp as in Sm, or from hcp to Sm type as in Gd, two-

⁶ *The Rare Earths*, edited by F. H. Spedding and A. H. Daane (John Wiley & Sons, New York, 1961), p. 182.

⁷ R. M. Bozorth, H. J. Williams, and D. E. Walsh, *Phys. Rev.* **103**, 572 (1956).

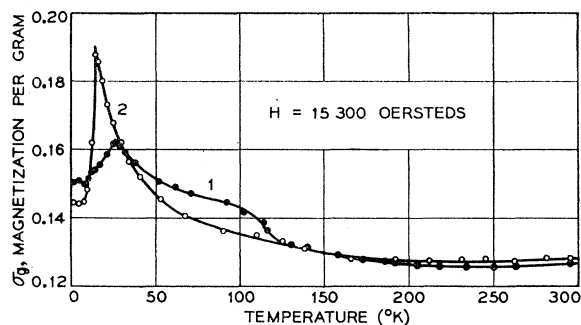


FIG. 1. Magnetic data for Sm in the dhcp form (curve 1) and in the normal form (curve 2).

thirds of the atomic layers must shift position and in either case it is seen that temperature aids pressure in effecting the transformation, the thermal energy evidently supplying the necessary activation. Also, the much greater stability range of the high pressure polymorph of Sm (dhcp), compared with the pressure induced polymorph of Gd seems rational. In the former case, the number of atomic layers that must readjust for reversion to the normal form is twice that required for the reversion of Sm-type Gd to the hcp form.

Double-hexagonal close-packed La⁸ and Ce⁹ transform to fcc structure on compression at room temperature because of the higher density of the latter phase. Praseodymium normally crystallizes in the dhcp arrangement, but Klemm and Bommer¹⁰ reported fcc structure for Pr, with a calculated density slightly greater than that of the dhcp form. It is not clear whether some impurity stabilized this phase. However, the higher density found for the fcc modification suggests the possibility that it could exist as a high-pressure phase even in pure Pr. The weight of experimental evidence seems to indicate that the polymorphic transitions under pressure in trivalent rare earths is in the order hcp → Sm-type → dhcp → fcc.

In our experiments on rare earth elements, to the right of Gd (Tb, Dy, Ho, Er) we did not observe any phase transition following treatment at 40 kbar pressure and 350°C. No phase transformation of Pr or Nd was observed under the same conditions. It is probable that in these cases higher pressures and possibly higher temperatures are needed.

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⁸ D. B. McWhan, P. W. Montgomery, H. D. Stromberg, and G. Jura, Lawrence Radiation Laboratory Report No. UCRL 9808, 1961 (unpublished); D. B. McWhan and W. L. Bond (to be published).

⁹ K. A. Gschneidner, Jr., R. O. Elliott, and R. R. McDonald, *Phys. Chem. Solids* **23**, 555 (1962).

¹⁰ W. Klemm and H. Bommer, *Z. Anorg. Allgem. Chem.* **231**, 138 (1937).