ulations, the optical data allow us to distinguish Γ_3 (z-polarized) transitions from Γ_2 or Γ_4 transitions, and hence partially to determine the symmetry of the crystal field states. For example, $^3P_0$ has Γ_1 symmetry and the transitions at 4808, 4868, and 4882 Å are (x,y), z, and (x,y) polarized, respectively. Thus the 4868-Å line originates on a Γ_3 substate of $^3H_4$, while the other two originate on Γ_2 or Γ_4 substates. The above analysis can be extended to identify the transformation properties of many of the excited states. The additional information provided by the site preference results, together with the forbiddenness of transition between states of the same symmetry,[11] imposes stringent limitations in the calculations of the crystal field parameters which have not been considered heretofore.

Our sensitivity was low compared with what can be obtained using well-known modulation techniques by which polarization ratios of 10^{-5} can be measured.[12,13] Hence, the optical dichroism of the crystal can be used, in principle, to determine differences in the site population distributions as small as a few parts in 10^5. The results presented here and in Ref. 5 indicate that the largest site selectivity is obtained for ions whose radii differ most from Y^{3+}.[14] The measurement of the site selectivity may provide a detailed probe for studying the dynamics of the flux crystal growth process.

We are grateful to L. Kopf for technical assistance, and to R. C. Miller and R. Wolfe for comments on the manuscript.

[1]The uniaxial anisotropy of the magnetic garnets forms the basis for the use of these materials in magnetic-bubble domain memory technology. See, for example, A. H. Bobeck, E. G. Spencer, L. G. Van Uitert, S. C. Abrahams, R. L. Barnes, P. H. Smith, and R. M. Walters, Appl. Phys. Lett. 17, 131 (1970).

[2]R. C. LeCraw, R. Wolfe, A. H. Bobeck, R. D. Pierce, and L. G. Van Uitert, J. Appl. Phys. 42, 1641 (1971).

[3]A. Rosencwaig, W. J. Tabor, and R. D. Pierce, Phys. Rev. Lett. 26, 779 (1971).

[4]H. Callen, Appl. Phys. Lett. 18, 311 (1971).

[5]R. Wolfe, M. D. Sturge, F. R. Merritt, and L. G. Van Uitert, Phys. Rev. Lett. 26, 1570 (1971).

[6]S. Geller and M. A. Gilleo, J. Phys. Chem. Solids 3, 30 (1957).

[7]G. F. Koster, J. O. Dimmock, R. C. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups*, (Massachusetts Institute of Technology Press, Cambridge, Mass., 1963), p. 36.

[8]M. J. Weber, J. Chem. Phys. 48, 4774 (1968).

[9]L. G. Van Uitert, W. H. Grodkiewicz, and E. F. Dearborn, J. Amer. Ceram. Soc. 48, 105 (1965).

[10]L. G. Van Uitert, W. A. Bonner, W. H. Grodkiewicz, L. Pictroski, and G. J. Zydzik, Mater. Res. Bull. 5, 825 (1970).

[11]R. A. Buchanan, J. J. Pearson, and G. F. Herrmann, Solid State Commun. 7, 195 (1969).

[12]L. F. Mollenauer, D. Downie, H. Engstrom, and W. B. Grant, Appl. Opt. 8, 661 (1969).

[13]S. N. Jasperson and S. E. Schnatterly, Rev. Sci. Instrum. 40, 761 (1969), and 41, 152 (1970).

[14]A set of effective rare-earth radii has been calculated by G. P. Espinosa, J. Chem. Phys. 37, 2344 (1962).

Nonmagnetic 4*f* Shell in the High-Pressure Phase of SmS†

M. B. Maple and D. Wohlleben
Institute for Pure and Applied Physical Sciences, University of California, San Diego, La Jolla, California 92037
(Received 19 May 1971)

The magnetic susceptibility of SmS indicates a discontinuous and hysteretic magnetic transition at 6 kbar. The ground state of the 4*f* shell in the metallic high-pressure "collapsed" phase is nonmagnetic, contrary to Hund's rules. Nonmagnetic behavior of the 4*f* shell is correlated with an intermediate valence in SmS, SmB_6, and α-Ce. It is suggested that in such intermediate-valence phases at $T = 0$ the 4*f* shell is demagnetized in the sense of the Friedel-Anderson model as modified by Hirst.

Recently, pressure-induced semiconductor-metal transitions were discovered in SmTe, SmSe, and SmS.[1,2] A large volume decrease (~10–20%) in the transitions without change of crystal structure indicates an electronic valence change of the Sm ions which should have a profound influence on their magnetic behavior. By susceptibility measurements under pressure we have found a first-order magnetic phase transtion in SmS, as expected from the resistivity measurements of Jayaraman *et al.*[2] Quite unexpectedly, however, the Sm ions do not carry localized magnetic moments after the pressure-induced valence change. This finding, taken

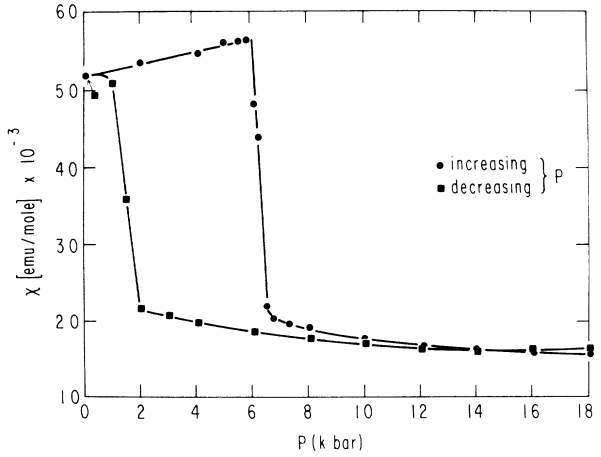

FIG. 1. Magnetic susceptibility of SmS versus pressure at room temperature.

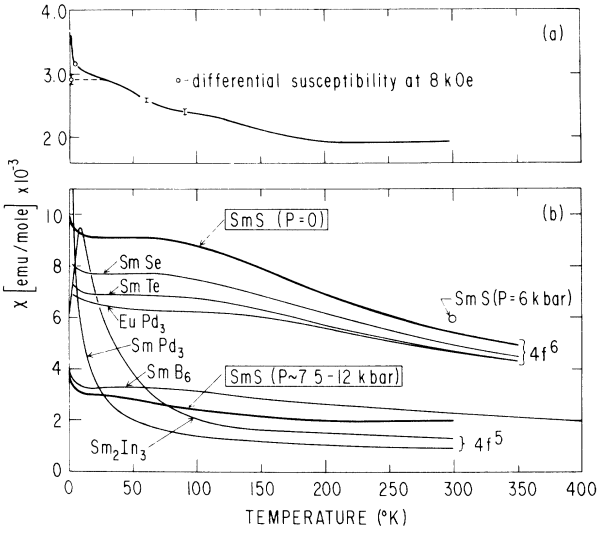

FIG. 2. (a) Temperature dependence of the susceptibility of SmS in the collapsed high-pressure phase. The pressure was 12 kbar at 300°K and 7.5 kbar at liquid-helium temperatures. (b) Comparison of $\chi(T)$ for ions in the $4f^6$ and $4f^5$ configuration with "collapsed" SmS and SmB_6. (SmS, SmSe, SmTe, Ref. 4; SmB_6, Ref. 5; Sm_2In_3, Ref. 6; $SmPd_3$, $EuPd_3$, Ref. 7.)

together with the puzzling behavior of nonmagnetic SmB_6 and with α-Ce, seems to indicate that under certain conditions the magnetic moment of rare-earth metals can be just as unstable as that of transition metals.

The polycrystalline samples were from the lots used in the resistivity study.[1,2] A detailed description of our measurements of weak paramagnetic susceptibilities under pressure is given elsewhere.[3]

Figure 1 shows the susceptibility of SmS between 0 and 18 kbar at room temperature. Initially, the susceptibility increases at a rate $d\chi/dP = +(78.3 \pm 7) \times 10^{-6}$ emu/mole kbar. At 6 kbar it drops by 65% within 0.5 kbar and then decreases further, but at a much slower and decreasing rate. The reverse transition occurs at a very much reduced pressure between 2 and 1 kbar.[2]

Room-temperature susceptibility measurements on SmSe and SmTe showed only a small pressure effect up to 18 kbar. An initial increase of χ was observed with $d\chi/dP = 17 \times 10^{-6}$ and 2.2×10^{-6} emu/mole kbar for SmSe and SmTe, respectively. In both cases $\chi(P)$ flattens out near 15 kbar.

The initial increase of the susceptibility with pressure correlates with the increase of the zero-pressure susceptibility in the sequence SmTe, SmSe, SmS which was found by Bucher *et al.*[4] [Fig. 2(b)]. This effect was traced quantitatively to a decrease of the multiplet splitting of the $4f^6$ configuration, i.e., to increased screening of the nuclear charge, believed to occur because of increasing hybridization of the $4f$ states with d states across the decreasing energy gap.

Figure 2(a) shows the temperature dependence of the isofield susceptibility (8 kG) in the high-pressure phase of SmS. The pressure was 12 kbar at room temperature whereas a superconducting lead manometer indicated a pressure of 7.5 kbar at liquid-helium temperatures. This pressure loss is believed to be due to freezing of the pressure transmitting fluid.

The susceptibility depends only weakly on temperature. The tail at the lowest temperatures is due to saturable local moments since the differential susceptibility at 8 kG at the lowest temperature (0.4°K) equals the value of the susceptibility near 30°K. The saturable moment is $M_0 = 8.5$ emu/mole, much smaller than the saturation moment of Sm in the $4f^5$ configuration with a $^6H_{5/2}$ ground state (4×10^3 emu/mole). Since the magnitude of the low-temperature susceptibility tail is the same as in the atmospheric-pressure measurements of Bucher *et al.*,[4] [Fig. 2(b)], we attribute this tail to rare-earth impurities, whose magnetic moments remain unaffected by the magnetic transition of the Sm ions.

During the cooldown, a systematic error, monotonic in temperature, was ±3% between 30 and 100°K and ±0.5% elsewhere. The statistical error is much smaller, about 0.1%. In view of the small statistical error and the mono-

tonic rise of χ throughout the cooldown below 200°K it can be stated unambiguously that there is *no antiferromagnetic transition* between 200 and 1°K that would cause more than a 0.1% drop of the susceptibility or a small kink over an interval of a few degrees Kelvin. In particular we searched repeatedly and unsuccessfully for a transition below 30°K, the range of the ordering temperatures of some other monochalcogenides with trivalent rare-earth ions. The saturation of the susceptibility to a constant value near $T \to 0$ implies that *the ground state of the* Sm *ions in this phase is nonmagnetic,* contrary to the behavior of trivalent Sm. A similar phenomenon was observed previously in SmB_6.[5]

In Fig. 2(b) curves of susceptibility versus temperature for various materials with $4f^5$ or $4f^6$ configurations are collected for comparison. The compounds with $4f^6$ configurations (nonmagnetic $^7F_0$ ground state) saturate at low temperature. The materials with a $4f^5$ configuration (magnetic Kramer's ion ground state) show either a low-temperature divergence of the susceptibility or an antiferromagnetic transition. The susceptibility of SmS in the collapsed phase and of SmB_6 is intermediate between the $4f^6$ and $4f^5$ configurations above ~ 100°K but saturates to a constant value as $T \to 0$.

We wish to point out a striking correlation between SmS and Ce,[8] in their collapsed high-pressure phases, and SmB_6 at atmospheric pressure: (1) All three materials exhibit an unusual intermediate-valence state of the rare-earth ion. (2) All three materials are nonmagnetic in the sense that there is no indication of a local moment near $T = 0$ and only a weak decrease of the susceptibility above a temperature of the order of 100°K.

In the rare-earth monochalcogenides and borides the lattice constants vary linearly with the "radius" of the $4f$ shell.[9,10] The radius yields the valence consistent with the magnetic behavior. A measure of *intermediate* valence ϵ_a, defined in Table I, is of order 70% for the three materials. In the case of SmB_6 this value is corroborated by the Mössbauer isomer shift,[11] and by soft-x-ray absorption.[12] We infer that the "collapsed" phase of SmB_6 happens to be stable at atmospheric pressure, and in this sense the states of the Sm ions in SmB_6 at atmospheric pressure and in SmS above 6 kbar belong in the same class, calling for a common model.

A detailed model has recently been developed for the nonmagnetic ground state of SmB_6[13] which assumes two kinds of Sm ions to coexist independent of temperature and time. The peculiar configuration ratio, 7:3, was thought to arise from the rigidity of the boron lattice.[13] This now seems unlikely, since there is a great difference in the volume changes $\Delta V/V$ associated with the transition from Sm^{2+} to $Sm^{(2+\epsilon)+}$ in SmB_6 and SmS (Table I), while the fractional valences are the same and equal to that of α-Ce. This suggests a more general reason for the stability of the intermediate valence, which we believe to arise from an interplay of conduction electrons with the unstable $4f$ shell.

The following discussion is based on a recent modification of the Friedel-Anderson model by Hirst[14] for the case of well-localized partially filled shells. Hirst argues that correlations between the local electrons within the shell strong-

TABLE I. The lattice constants $a_{n+\epsilon}$ of nonmagnetic Ce, SmS, and SmB_6 are intermediate between those for integral valence n and $n+1$. The numbers $\epsilon_a \equiv (a_n - a_{n+\epsilon})/(a_n - a_{n+1})$, ϵ_M, and ϵ_X are measures of the intermediate valence as determined by lattice constant (a), Mössbauer (M), and soft x-ray absorption (X) analysis. $\Delta V/V$ is the volume change associated with the transition from integral valence n to the nonmagnetic (collapsed) phase with valence $n+\epsilon$. The lattice constants of the phases which are stable at 300°K and atmospheric pressure are in italics. The asterisks denote interpolated values.

	n	a_n (Å)	$a_{n+\epsilon}$ (Å)	a_{n+1} (Å)	ϵ_a (%)	ϵ_M (%)	ϵ_X (%)	$\Delta V/V$ (%)
Ce	3	5.20*[a]	4.85[a]	4.67*[a]	66 ± 6	···	···	20
SmS	2	*5.97*[b]	5.70[c]	5.62*[b]	77 ± 6	···	···	13.5
SmB_6	2	4.180*[a]	*4.130*[a]	4.115*[a]	77 ± 8	65 ± 10[d]	65 ± 5[e]	3.6

[a]Ref. 9.
[b]Ref. 10.
[c]Ref. 2.
[d]Ref. 11.
[e]Ref. 12.

ly favor an integral occupation number of the shell. Coexistence of two configurations with different occupation numbers n is only possible if the excitation energy $E_n - E_{n-1}$ between the lowest two configurations is smaller than an energy of the order of the width Δ of the virtual bound state ($\Delta \approx 10^{-2}$ eV in rare earth metals).[15] The excitation energy, determined by the state of the lattice, can range between zero and several electron volts, and is normally very much larger than Δ in rare earth metals.

We now assume that pressure changes the excitation energy, and that in some exceptional cases $E_n - E_{n-1}$ is small and can be driven from larger to smaller than Δ. Then interaction with the conduction electrons can cause transitions between a configuration with n $4f$ electrons and one with $n-1$ $4f$ electrons with the additional electron in the conduction band. Since the systems under consideration have one $4f$ shell per formula unit, the transfer of this electron (or a fraction ϵ thereof) into the conduction band requires a dramatic increase $\Delta E_F(\epsilon)$ of the Fermi energy. ΔE_F first impedes a transition to the mixed configuration state. After the transition, the two levels, degenerate within this width Δ, overlap the Fermi level at intermediate valence ϵ. Further lowering of E_{n-1} with respect to E_n with increasing pressure will cause further electron transfer from E_n, which has a very high effective density of states Δ^{-1}, to the conduction band with low density of states, raising the Fermi level rapidly while increasing ϵ slowly and keeping E_n and E_{n-1} degenerate within Δ. Thus over a certain pressure range the two levels are tied to the Fermi level, which stabilizes the intermediate valence.

On the basis of this model we envision the collapsed phase of the two Sm compounds as having in time average 0.7 electron in the conduction band and 5.3 electrons in the $4f$ shell. However, on a sufficiently short time scale ($\tau < \hbar/\Delta$) a shell is in either one or the other of the two configurations since $\Delta \ll E_c$, where E_c is the intraconfigurational correlation energy on the order of several electron volts. The magnetic moment on a given shell fluctuates between the values on the two configurations with a frequency $\omega_{sf} \leq \Delta/\hbar$. At temperatures $\hbar\omega_{sf} < kT \ll E_c$, i.e., on a measuring time scale faster than this fluctuation frequency, the susceptibility should reflect the statistical average of both configurations. This seems to be the case above 100°K in collapsed SmB_6 and SmS [see Fig. 2(b)]. However, at $T = 0$ this intrinsic moment fluctuation prevents magnetic ordering or a divergence of the susceptibility of the $4f^5$ configuration. From Fig. 2(b) one estimates $T_{sf} \sim 100$°K or $\omega_{sf} \sim 2 \times 10^{12}$ cps. Consistent with this value, the very fast soft-x-ray absorption experiment in SmB_6 (10^{-18} sec) can distinguish between the two configurations[12] whereas the slow Mössbauer experiment[11] (lifetime $\sim 10^{-8}$ sec) does not. In the limit $T = 0$ the situation is equivalent to the nonmagnetic state of the Friedel-Anderson model.[16] However, according to the Hirst modification of this model, in the nonmagnetic case the degenerate states at the Fermi level are two well-defined many-electron states and at sufficiently high pressure one may expect the shell to become magnetic again, with the susceptibility characteristic of the $4f^5$ configuration. This can in no way follow from the Friedel-Anderson model.

It remains to be seen whether or not the transport properties of SmB_6 are in conflict with this model. One might expect resonant scattering with a strong temperature dependence around $kT \sim \hbar\omega_{sf} \sim 100$°K similar to observations in metallic rare-earth dodecaboride compounds containing Yb.[17]

We are grateful to E. Bucher for supplying us with his samples. We acknowledge informative discussions with C. Ratto, T. Geballe, D. McWhan, E. Müller Hartmann, and B. T. Matthias and correspondence with L. L. Hirst.

†Work supported by the U. S. Air Force Office of Scientific Research, Office of Aerospace Research, under Grant No. AF-AFOSR-631-67-A.

[1]A. Jayaraman, V. Narayanamurti, E. Bucher, and R. G. Maines, Phys. Rev. Lett. 25, 368 (1970).

[2]A. Jayaraman, V. Narayanamurti, E. Bucher, and R. G. Maines, Phys. Rev. Lett. 25, 1430 (1970).

[3]D. Wohlleben and M. B. Maple, to be published.

[4]E. Bucher, V. Narayanamurti, and A. Jayaraman, J. Appl. Phys. 42, 1741 (1971).

[5]A. Menth, E. Buehler, and T. H. Geballe, Phys. Rev. Lett. 22, 295 (1969).

[6]K. H. J. Buschow, H. W. deWijn, and A. M. van Diepen, in Proceedings of the Seventh Rare Earth Research Conference, Coronado, Calif., 1968 (unpublished).

[7]W. E. Gardner, J. Penfold, and I. R. Harris, J. Phys. (Paris) Suppl. 32, C1-1139 (1971).

[8]M. R. MacPherson, G. E. Everett, D. Wohlleben, and M. B. Maple, Phys. Rev. Lett 26, 20 (1971).

[9]K. A. Gschneidner, *Rare Earth Alloys* (Van Nostrand, Princeton, N. J., 1961).

[10]A. Iandelli, in *Rare Earth Research*, edited by E. V.

Kleber (McMillan, New York, 1961), p. 135.
[11]R. L. Cohen, M. Eibschütz, and K. W. West, Phys. Rev. Lett. 24, 383 (1970), and J. Appl. Phys. 41, 898 (1970).
[12]E. E. Vainshtein, S. M. Blokhin, and Yu. B. Paderno, Fiz. Tverd. Tela 6, 2909 (1964) [Sov. Phys. Solid State 6, 2318 (1965)].
[13]J. C. Nickerson, R. M. White, K. N. Lee, R. Bachmann, T. H. Geballe, and G. W. Hull, Jr., Phys. Rev. B 3, 2030 (1971).
[14]L. L. Hirst, Phys. Kondens. Mater. 11, 255 (1970).
[15]J. G. Huber and M. B. Maple, J. Low Temp. Phys. 3, 537 (1970).
[16]B. Coqblin and A. Blandin, Advan. Phys. 17, 281 (1968); B. Coqblin, J. Phys. (Paris) Suppl. 32, C1-599 (1971).
[17]Z. Fisk, B. T. Matthias, and E. Corenzwit, Proc. Nat. Acad. Sci. 64, 1151 (1969).

Nuclear-Orientation Studies of *La*Ce, *Au*Ce, and *Ag*Ce

J. Flouquet
Laboratoire de Physique des Solides associé au Centre National de la Recherche Scientifique, 91 Orsay, France
(Received 11 May 1971)

*La*Ce^{137m} alloys prepared by proton bombardment of La metal have been studied by orientation of the Ce^{137m} nuclei. From the variation of the anisotropy of the emitted γ rays with applied field, the Kondo temperature is estimated to be 0.1 K. *Au*Ce and *Ag*Ce have also been studied using the same technique. The results for the three systems are compared with those obtained by other methods.

For a rare-earth impurity in a metallic lattice, the coupling between the local spin J and the conduction electron s can be described by the Hamiltonian $H = \Gamma_{eff}\vec{J}\cdot\vec{s}$. There are two contributions to Γ_{eff}: a positive exchange term and an antiferromagnetic coupling due to the mixing between conduction and local electrons.[1] The existence of a resistance minimum for *La*Ce shows that apparently $\Gamma_{eff}<0$, while for *Mg*Ce,[2] with no resistance minimum, apparently $\Gamma_{eff}>0$. From resistivity measurements on *La*Ce, Kim and Maple,[3] Gey and Umlauf,[4] Sugawara and Eguchi,[5] and Wollan and Finnemore[6] find a Kondo temperature T_K less than 1 K, while Edelstein *et al.*[7] from susceptibility measurements estimate T_K to be about 20 K. Recently, Grobman[8] found an anomaly in the thermoelectric power near 20 K which had not been observed by Sugawara and Eguchi.[5] We present nuclear orientation measurements on *La*Ce alloys and compare them with the results obtained on *Au*Ce[9] and *Ag*Ce.

The *La*Ce alloy is obtained directly by proton bombardment of a La metal foil (99.9+% pure La provided by Koch Light). The 35-MeV incident protons form Ce^{137m} *in situ* by the $(p, 3n)$ reaction on La; 48 hours after irradiation the only activities visible were those of the 39-h half-life Ce^{137m} and Ce^{139}. The beam heating during bombardment may well affect the metallurgical state of the sample. The foil was point soldered onto a copper wire for thermal contact, and then cooled in an adiabatic demagnetization cryostat to temperatures between 12 and 30 mK. The anisotropy of the 255-keV γ rays from the radioactive nuclei was then measured as a function of applied field and temperature with fields from 1.5 to 25 kOe. Since La is a superconductor, possible reduction of flux penetration is an experimental problem. Sugawara and Eguchi[10] find a critical field $H_{c1}(0°K)$ of 400 Oe for the hexagonal α phase, but Mamiya, Fukuroi, and Tanama[11] find 1600 Oe for the cubic β phase. So since these values depend strongly on the sample purity, it is quite possible that flux penetration was reduced at the lowest fields (1500 Oe) for any parts of the sample in the β phase. This could lead to an overestimation of T_K in what follows. This estimation is also complicated by the presence of the two phases: In a site with hexagonal symmetry, a Ce ion is characterized by a highly anisotropic g factor and hyperfine coupling constant A, while in cubic symmetry, as long as the crystal-field splitting Δ is much greater than $g\mu_B H$, the ion has an isotropic g factor and hyperfine coupling constant. To simplify matters, we will assume in the analysis that the sample was entirely in the cubic β phase.

In a nuclear orientation experiment, the measured γ anisotropy can be directly related to the population of the nuclear sublevels of the parent[12] (in this case Ce^{137m}). When the nucleus is contained in a dilute paramagnetic impurity the difficulty is that there is in general no simple relation between the anisotropy and the magnetization M of the impurity[13]: The concept of a hyperfine