

(Nd-glass laser),  $k_0L \approx 10^3-10^5$ , and  $(c/v_e)^2 \approx 10^3$ ,  $l/L$  is less than unity for  $k_0L\eta(0) = 70$ , provided that other nonlinear effects have not set in to further limit the growth.

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<sup>1</sup>F. W. Perkins and J. Flick, Phys. Fluids 14, 2012 (1971), and references contained therein.

<sup>2</sup>M. W. Goldman and D. F. DuBois, Phys. Fluids 8, 1404 (1965); R. E. Kidder, in *Physics of High Energy Densities, Proceedings of the International School of Physics "Enrico Fermi," Course XLVIII*, edited by P. Caldirola (Academic, New York, 1971); L. M. Gorbunov, Zh. Eksp. Teor. Fiz. 55, 2298 (1968) [Sov. Phys. JETP 28, 1220 (1969)].

<sup>3</sup>M. N. Rosenbluth, Phys. Rev. Lett. 29, 565 (1972).

<sup>4</sup>C. S. Liu, M. N. Rosenbluth, and R. B. White, to be published.

<sup>5</sup>D. W. Forslund, J. M. Kindel, and E. L. Lindman, Phys. Rev. Lett. 30, 739 (1973); W. L. Kruer, K. G. Estabrook, and K. H. Sinz, UCRL Report No. UCRL-74676, 1973 (unpublished).

<sup>6</sup>M. Mostrom, D. Nicholson, and A. N. Kaufman, to be published.

<sup>7</sup>A. A. Galeev, G. Laval, T. M. O'Neil, M. N. Rosenbluth, and R. Z. Sagdeev, Pis'ma Zh. Eksp. Teor. Fiz. 17, 48 (1973) [JETP Lett. 17, 35 (1973)].

## Temperature-Induced Explosive First-Order Electronic Phase Transition in Gd-Doped SmS

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We have found a reversible temperature-induced explosive first-order electronic phase transition, with decreasing temperature at atmospheric pressure, in  $\text{Sm}_{1-x}\text{Gd}_x\text{S}$  for  $0.16 \leq x < 0.22$ . The shiny golden-yellow metallic crystal disintegrates to a black powder. The transition is isostructural, but the unit cell expands from  $a \approx 5.68$  to  $5.82$  Å. The Sm ion in the black phase is characterized by an intermediate valence of  $\sim 2.45$ . We present a phase diagram showing the stability regions in the  $T$ - $x$  plane and discuss a plausible driving mechanism for the transition.

A pressure-induced first-order isostructural semiconductor-to-metal transition due to  $4f$ -electron delocalization was recently reported in pure SmS at 6.5-kbar pressure at room temperature.<sup>1</sup> With a view to lowering this transition pressure we studied the effect of Gd substitution for the Sm ion in SmS. Since the lattice constant of GdS is substantially smaller than that of SmS, 5.563 Å compared to 5.97 Å for pure SmS, Gd substitution may be expected to have the same effect as applying pressure. Accordingly, we find that Gd substitution lowers the transition pressure and, further, that concentrations in excess of 15 at.% Gd stabilize the "collapsed" metallic phase at atmospheric pressure. The lattice parameter abruptly decreases to 5.68 Å near this concentration, and the samples exhibit a golden-yellow metallic reflectivity. We have discovered that this metallic phase when cooled exhibits an explosive first-order phase transition at ambient pressure in which the bright shiny sample disintegrates into a black powder. The black phase

has the NaCl-type structure and is characterized by an intermediate valence of 2.45 for the Sm ion due to a partial localization of the electrons on the  $4f$  band of Sm. We believe that the driving force for the transition is the following: The  $4f$  level of Sm moves towards the Fermi level when temperature is lowered, resulting in fractional occupation of the level. This causes expansion of the lattice, which in turn increases the overlap of the  $4f$  level with the Fermi level. This bootstrapping drives the transition.

Samples were made by reacting appropriate amounts of Sm and Gd with S in an evacuated quartz tube at 500°C for 15 h, followed by heat treatment at 900°C for 2 h, and then melting the reacted material in a sealed evacuated tantalum tube. The material thus prepared was well crystallized and appeared black in color when the Gd concentration was  $\leq 15$  at.%. At higher concentrations of Gd the samples have a metallic golden-yellow luster. X-ray powder photographs were taken to obtain the lattice parameters and to con-

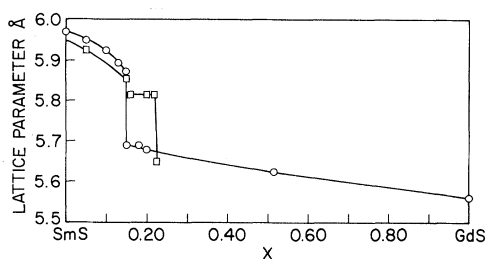


FIG. 1. Lattice-parameter data as a function of Gd concentration at 298°K (circles) and 4.2°K (squares). The parameter is independent of concentration in the range  $15 < x < 22$  at. %.

firm the NaCl-type structure. In some samples, especially at concentrations above 15 at. % Gd, very weak extra lines were found, and these were identified as belonging to  $Gd_2O_3S$ .

In Fig. 1 the lattice parameter obtained at 298 and 4.2°K is plotted as a function of Gd concentration. The lattice parameter at 298°K decreases with Gd concentration and the decrease is non-linear. At about 15 at. % Gd there is an abrupt change from 5.875 to 5.68 Å. When this sample is powdered in an agate mortar, there is a partial change in color and the x-ray powder photograph shows lines belonging to two NaCl-type phases with lattice parameters of 5.875 and 5.68 Å; the lines belonging to the latter phase are the stronger. Thus the operation of grinding is sufficient to collapse the lattice. At 16 at. % Gd, only one NaCl-type phase, with  $a = 5.68$  Å, appears. Further additions of Gd cause only a small decrease in the lattice parameter, and the samples show the characteristic metallic golden-yellow reflectivity.

Samples containing Gd in the range  $15 < x < 22$  at. %, when cooled at ambient pressure, exhibit a spectacular, strongly first-order phase transition. The lustrous golden-yellow metallic looking crystal disintegrates explosively to a black powder. On warming, the black powder gradually turns golden. The transition temperature decreases with increasing Gd content, and no transition is observed when the concentration of Gd is greater than 22 at. %. A low-temperature x-ray diffraction study of the transition shows that the structure of the low-temperature-phase is also NaCl-type, but a sudden expansion of the lattice from  $a \approx 5.68$  to  $a = 5.82$  Å ( $\Delta V/V = 7.5\%$ ) takes place. The explosive character of the transition is due to this sudden expansion of the lattice. The transition temperatures obtained on cooling, from x-ray diffraction studies,<sup>2</sup> are plot-

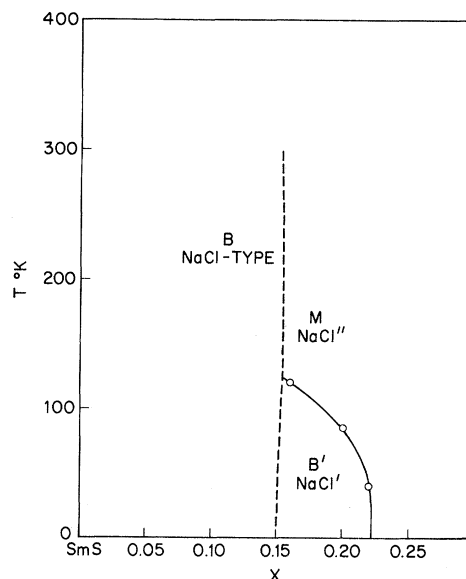
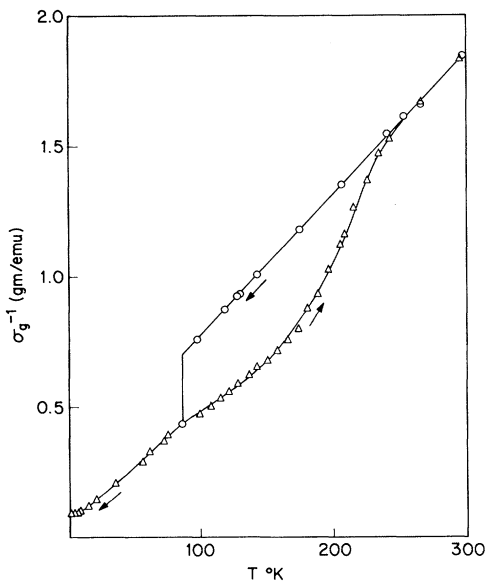


FIG. 2. Phase-stability regions in the  $T$ - $x$  diagram for  $Sm_{1-x}Gd_xS$ .

ted against Gd concentration in Fig. 2. Since we did not observe any transition in samples containing 15 and 16 at. % Gd on heating up to 600°K, we believe that the boundary between the  $B$  and the  $M$  phase<sup>3</sup> is very steep. Again, we failed to observe any transition from the  $B$  to  $B'$  phase when samples containing 14 and 15 at. % Gd were cooled down to 4.2°K, and hence this phase boundary must also be very steep. That this phase boundary must exist is clear from the lattice-parameter data obtained at 4.2°K (see Fig. 1). The lattice parameter at 4.2°K decreases from 5.85 to 5.82 Å in going from 15 to 16 at. % Gd. The  $B'$  phase has a narrow range of stability and is characterized by a lattice parameter  $a = 5.82$  Å. The latter is independent of the Gd concentration.

The sudden expansion of the lattice in going from the  $M$  phase to the  $B'$  phase is a consequence of a discontinuous change in the valence state of Sm to a lower valence state. From a comparison of the measured lattice parameter of the  $B'$  phase with that of SmS and the metallic form of SmS ( $a = 5.97$  Å for  $Sm^{2+}S$  and  $a = 5.64$  Å for  $Sm^{3+}S$ ), we estimate the valence of Sm in the  $B'$  phase to be  $\approx 2.45$ . The change to a lower valence state is due to a partial localization of the conduction electron on the  $4f$  level of Sm, which may be expected to result in a loss of conductivity and hence lower the plasma frequency. The color change observed in the transition is a direct consequence of this.

Figure 3 shows the magnetic susceptibility as

FIG. 3. Magnetic data for  $\text{Sm}_{0.80}\text{Gd}_{0.20}\text{S}$ .

a function of temperature for  $\text{Sm}_{0.80}\text{Gd}_{0.20}\text{S}$ . The susceptibility is predominantly due to the Gd and increases abruptly at the phase transition to the  $B'$  phase. The thermal hysteresis associated with the  $M$  to  $B'$  transition is apparent from the data for cooling and warming cycles. It is clear that the transition is strongly first order and exhibits marked supercooling.

The electronic transition from the  $M$  to  $B'$  phase in Gd-doped SmS raises several interesting questions. (1) What is the driving mechanism of the transition? (2) Why has the Sm ion an intermediate valence of  $\approx 2.45$  in the  $B'$  phase? (3) Does the magnetic interaction arising out of the presence of Gd play a role? In seeking an answer to these questions one has to probe into the electronic band structure of these materials and the magnetic behavior of the system. Present optical-absorption<sup>4</sup> data suggest that in SmS the  $4f^6$  to  $6s-5d$  conduction-band energy separation is of the order of 60 mV.<sup>4,5</sup> Resistivity measurements<sup>6</sup> and magnetic-susceptibility<sup>7</sup> data on SmS under pressure strongly suggest that the Fermi level is tied to the  $4f$  level and the above energy separation narrows with pressure.<sup>6</sup> Hence in Gd-doped SmS the transition from the  $B$  to the  $M$  phase may be expected to take place at progressively lower and lower pressure with increasing Gd concentration, eventually leading to the stabilization of the latter phase at atmospheric pressure. This is actually observed.

To understand the  $M \rightarrow B'$  transition we pro-

pose the following. The  $4f$  level in the  $M$  phase we believe is a very narrow band lying above but very close to the Fermi level in the  $5d$  conduction band. When the temperature is lowered, the  $4f$  band lowers<sup>8</sup> and overlaps with the Fermi level, resulting in the localization of some fraction of the conduction electrons in the  $4f$  band. This fractional occupation of the  $4f$  band will change the valence state of the Sm ion towards a lower valence, and thereby give rise to an expansion of the lattice. The expansion of the lattice would push the Fermi level further into the  $4f$  band, resulting in further localization of the conduction electrons. A self-consistent physical circumstance of this nature would lead to instability and hence to a catastrophic electronic phase transition. However, the lattice expansion would limit itself in the presence of Gd because the latter ion is effectively equivalent to applying pressure on the system<sup>9</sup> and hence would counteract the force of expansion. We believe that the intermediate valence of the Sm ion in the  $B'$  phase is due to this circumstance. Also the range of stability of the  $B'$  phase would be determined by the energy balance between the energy gained in the localization of the electron in the  $4f$  band versus the elastic energy needed to expand the lattice. With increasing Gd concentration<sup>9</sup> the latter energy would exceed the former and above a critical concentration the  $M$  to  $B'$  transition would cease to take place even at  $0^\circ\text{K}$ .

The results of magnetic measurements presented in Fig. 3 show that the exchange interaction between Gd sharply increases at the transition. In both the  $M$  and  $B'$  phases the susceptibility follows the Curie-Weiss law, and the curves intercept the temperature axis on the negative side. This would seem to suggest antiferromagnetic coupling between the Gd ions in the  $B'$  as well as the  $M$  phase. We have, however, no direct evidence for antiferromagnetic ordering in the  $B'$  phase from the present temperature-susceptibility data.

As a test of the importance of magnetism in inducing the electronic collapse of SmS we have also investigated yttrium substitution, which compresses the lattice without introducing a local moment. The transition to the metallic state appears gradual in this case, and it takes nominally  $\sim 30$  at.% Y<sup>10</sup> to collapse the lattice to 5.69 Å. The resulting  $M$  phase at this concentration exhibits a continuous expansion on cooling (from 5.69 Å at 298°K to 5.74 Å at 4.2°K) and the color changes to black; these changes are reversible.

It seems therefore possible that in some way the presence of  $5d$  and  $4f$  bands of the substituted rare-earth ion and the magnetism of the latter may play a role in the first-order phase transition discussed in this paper. Further detailed studies are in progress and the results will be published elsewhere.

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<sup>1</sup>A. Jayaraman, V. Narayanamurti, E. Bucher, and R. G. Maines, *Phys. Rev. Lett.* **25**, 1430 (1970).

<sup>2</sup>These transition temperatures were arbitrarily taken as the midpoints in the temperature intervals over which this phase change occurred for each sample. We believe that the existence of a temperature interval is mainly due to residual strain introduced during grinding and the extreme sensitivity of the transition temperature to strain. It is also possible that there is a narrow composition gradient which will contribute to this.

<sup>3</sup>The designations  $B$ ,  $B'$ , and  $M$  for the phases signify respectively the normal black phase, the black

phase stable at low temperature with lattice parameter  $a=5.82$  Å, and the golden-colored metallic phase.

<sup>4</sup>E. Kaldis and P. Wachter, *Solid State Commun.* **11**, 907 (1972).

<sup>5</sup>E. Bucher and F. DiSalvo, unpublished.

<sup>6</sup>A. Jayaraman, in Proceedings of the Indo-Soviet Conference on Solid State Materials, Bangalore, India, December 1973 (to be published).

<sup>7</sup>M. B. Maple and D. Wohlleben, *Phys. Rev. Lett.* **27**, 511 (1971).

<sup>8</sup>The lattice parameter of the  $M$  phase is independent of  $T$  between 225°K and the transition temperature ( $M \rightarrow B'$ ), signifying that with cooling there might actually be a slight expansion in volume counteracting the normal contraction. This would support the contention that the  $4f$  band lowers with decreasing  $T$  and becomes fractionally occupied.

<sup>9</sup>The lattice parameters of  $\text{Sm}_{0.84}\text{Gd}_{0.16}\text{S}$  and  $\text{Sm}_{0.78}\text{Gd}_{0.22}\text{S}$  are 5.68 and 5.66 Å, respectively. The lower lattice parameter for the latter is equivalent to greater positive pressure and hence higher compressional energy. Therefore, we are justified in assuming that the higher the Gd concentration the greater would be the elastic energy needed for expansion.

<sup>10</sup>There is a weak pattern in the x-ray powder photographs from  $\text{Y}_2\text{O}_3\text{S}$ . Because of this, the actual Y concentration in  $\text{Sm}_{1-x}\text{Y}_x\text{S}$  may be lower than the amount of Y added.

## Measurement of Lifetimes and Binding Energies of Atoms Adsorbed on Surfaces at Low Temperatures by a Rapid-Flash-Desorption Technique\*

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A dynamic method for measuring the characteristic lifetimes and binding energies of physisorbed atoms is described and results presented. We find for  $\sim 1.5$  monolayers of helium adsorbed on Constantan an isosteric binding energy of  $31 \pm 1^\circ\text{K}$  and a characteristic lifetime of  $(2 \pm 0.5) \times 10^{-7}$  sec. The velocity distribution of the desorbing atoms is found to be non-Maxwellian.

By means of low-temperature atomic beam techniques we have performed rapid-flash-desorption experiments in which  $\Delta T/\Delta t$  is greater than  $10^7$  °K/sec; complete desorption occurs in times as short as  $10^{-8}$  sec. For  $\sim 0.5$  monolayers of helium adsorbed on top of  $\sim 1.0$  monolayers of helium previously adsorbed on Constantan we find a binding energy  $E$  of  $31 \pm 1^\circ\text{K}/\text{atom}$ , equal to that simultaneously measured<sup>1</sup> by adsorption isosteres; and a characteristic lifetime  $\tau_0$ , for  $4^\circ\text{K} < T < 18^\circ\text{K}$ , of  $(2 \pm 0.5) \times 10^{-7}$  sec, 6 orders of magnitude longer than the Frenkel<sup>2</sup> value, but consistent with the trend shown in recent quantum-mechanical calculations by Bendow and Ying.<sup>3</sup> Nondimensional similarity parameters for this

system fall near the  $n=4$  resonance in the theory of Pagni and Keck,<sup>4</sup> which offers a classical explanation for long lifetimes. The observed velocity distribution differs from that of atoms effusing in a beam from a Maxwellian source by a factor of  $v^{-1}$ . This method has the advantage over isotherm,<sup>5</sup> isostere,<sup>6</sup> and quasi-steady-state<sup>7</sup> measurements in that in addition to the binding energy it gives the desorption velocity distribution and the characteristic lifetime  $\tau_0$  independently of the sticking coefficient and uncomplicated by desorption caused by gas bombardment or stray infrared radiation.<sup>8</sup> Besides being a contribution to the rapidly growing field of surface physics, these results have bearing