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Study of the valence transition in SmS induced by alloying, temperature, and pressure

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Lattice-parameter studies as a function of composition as well as temperature (4.7 to 900 °K) have been carried out on a number of trivalent rare-earth-substituted SmS ($Sm_{1-x}R_x^{3+}S$ where R = Ce, Pr, Nd, Gd, Tb, Dy, Ho, En, Tm, Lu) compounds. The data for the $Sm_{1-x}Gd_xS$ compounds show that the lattice parameter a decreases smoothly first and undergoes an abrupt decrease at a critical concentration of 15.5-at.% Gd. For $x < 0.15$ the material is black and for $x > 0.16$ it turns metallic golden yellow. The crystal structure remains NaCl type but the lattice contracts from 5.86 Å to a value of ~5.68 Å. At higher concentrations the change in a is smooth and small. This is typical of the behavior of the $Sm_{1-x}R_x^{3+}S$ compounds, with the exception of La-substituted ones. These effects are attributed to a change in the valence state of the Sm ion from 2^+ towards the 3^+ state and R^{3+} substitution is equivalent to application of pressure. The metallic-looking samples show a strong first-order transition on cooling (depending upon the composition) and exhibit anomalous thermal-expansion behaviors in the 300 to 900 °K temperature range, which are related to a change in the valence state, from 3^+ to the 2^+. Based on pressure and temperature data a phase-stability diagram in the $P-T$ plane for SmS, and in the $T-x$ plane for the $Sm_{1-x}Gd_xS$ system are presented. In the latter, three NaCl phases designated B', B, and M appear, of which the B (black) phase is the high-temperature phase, B' is stable at low temperature, and M is stable at intermediate temperatures. The phase-stability diagrams, the lattice-parameter variation with temperature, pressure, and alloying, and the intermediate valence state of Sm in these compounds are discussed in terms of the electronic structure of the phases involved. It is shown that the lattice-parameter data are extremely valuable and unique in providing clues as to what goes on in these materials on a microscopic scale.

I. INTRODUCTION

Recent pressure studies on[1,2] SmS have revealed that the Sm ion in this compound undergoes a pressure-induced first-order electronic transition at about 6.5 kbar at room temperature. The transition is isostructural (NaCl structure retained) but is accompanied by a large volume decrease, owing to a change in the valence state of the Sm ion from 2^+ towards the 3^+ state. High-pressure resistivity measurements[1] and optical studies[3] have established that the change of state involves the delocalization of a $4f$ electron from the Sm ion ($4f^65d^0$ to $4f^55d^1$). The high-pressure phase is metallic and has a brilliant golden-yellow luster. A more recent study[4] has shown that this metallic phase can be stabilized at atmospheric pressure by substituting Gd for the Sm in SmS. Above a certain critical concentration of Gd the lattice parameter of $Sm_{1-x}Gd_xS$ compounds undergoes an abrupt decrease (for $x > 0.15$ the unit-cell parameter a changes abruptly from 5.875 to 5.68 Å) and the material turns bright golden yellow in color. Interestingly, this metallic phase in the composition range $0.15 < x < 0.25$ exhibits a strongly first-order electronic transition at ambient pressure when the temperature is lowered and the golden-yellow metallic-looking material disintegrates to a black powder. Preliminary low-temperature x-ray crystallographic studies showed that the lattice expands abruptly at the transition.

These results suggested that it would be worthwhile to investigate in more detail the effect of temperature on the lattice parameter of $Sm_{1-x}Gd_xS$ compounds over a wide range of temperatures, as well as study the effect of a few other rare-earth substitutions. Accordingly, we have investigated the lattice parameter as a function of temperature from 4.2 to about 1000 °K. In this paper the results of this study are presented and their relevance to the question of mixed valence state is discussed.

II. MATERIALS AND EXPERIMENTS

Samples were prepared by the following procedure. Appropriate quantities of sulfur and the rare-earth metal in the form of chips were reacted in a sealed evacuated quartz tube (prior to sealing, the quartz tube was flushed several times with argon and evacuated to 10^{-3}-mm argon pressure) at about 600 °C for 18–24 h. This was followed by further reaction near 900 °C for 3–4 h. The charge thus reacted was thoroughly homogenized, sealed in a tantalum tube, and repeatedly melted by passing high current through the tantalum. (The tantalum tube was kept inside a vacuum chamber maintained at about 7×10^{-5} mm;

the temperatures attained were close to 2000 °C.) After this treatment power was shut off and the sample allowed to equilibrate to ambient temperature. The whole operation was performed under high vacuum. The material thus prepared was well crystallized and the x-ray powder photographs confirmed the NaCl-type structure expected for the compounds.

Lattice-parameter determination as a function of temperature was carried out with a Philips/Norelco diffractometer set at a scanning rate of $\frac{1}{4}$°/min. Copper radiation was used along with an internal standard consisting of silicon powder. For low-temperature determinations (298–4.2 °K) an Air Products and Chemicals Cryotip device with automatic temperature control was used. Silicone grease served as sample binder to the cryotip block. High-temperature measurements were made with a platinum-resistance-type heating strip mounted on a water-cooled stage specifically designed to fit the diffractometer. At elevated temperatures the diffraction compartment was continuously flushed with dry nitrogen gas to minimize possible reaction of the sample with the atmosphere. Least-squares lattice-parameter refinements were carried out using at the very minimum, six high-angle reflections, wherein Cu $K\alpha_1$ peaks were well resolved. The probable errors for the unit-cell edges did not exceed one part in 5000 for any of the phases. For the majority of samples lattice parameters were determined from the (220) and (200) reflections, at various temperatures. The Bragg angles for these reflections were adjusted for sample shift, thermal expansion of sample block, and the zero of 2θ, by monitoring the silicon standard peaks.

TABLE I. Lattice constants and color of $Sm_{1-x}R_x{}^{3+}S$ compounds (NaCl-type structure) studied. In Yb-doped SmS Yb is 2^+. (In general very weak x-ray powder lines of rare-earth oxysulfide are seen, especially at higher concentrations of R^{3+}.)

Compound	Lattice parameter (Å)	Color
SmS	5.97	Black
$Sm_{0.95}Gd_{0.05}S$	5.95	Black
$Sm_{0.9}Gd_{0.1}S$	5.925	Black
$Sm_{0.87}Gd_{0.13}S$	5.89	Black
$Sm_{0.85}Gd_{0.15}S$	5.87	Black
$Sm_{0.84}Gd_{0.16}S$	5.68	Golden-yellow
$Sm_{0.82}Gd_{0.18}S$	5.67	Golden-yellow
$Sm_{0.80}Gd_{0.20}S$	5.66	Golden-yellow
$Sm_{0.75}Gd_{0.25}S$	5.67	Golden-yellow
$Sm_{0.70}Gd_{0.30}S$	5.67	Golden-yellow
$Sm_{0.5}Gd_{0.5}S$	5.63	Golden-yellow
$Sm_{0.75}Ce_{0.25}S$	5.72	Golden-yellow
$Sm_{0.75}Pr_{0.25}S$	5.71	Golden-yellow
$Sm_{0.75}Nd_{0.25}S$	5.70	Golden-yellow
$Sm_{0.75}Dy_{0.25}S$	5.65	Golden-yellow
$Sm_{0.77}Ho_{0.23}S$	5.67	Golden-yellow
$Sm_{0.77}Er_{0.23}S$	5.67	Golden-yellow
$Sm_{0.75}Tm_{0.25}S$	5.66	Golden-yellow
$Sm_{0.75}Yb_{0.25}S$	5.89	Black
$Sm_{0.70}Lu_{0.30}S$	5.68	Golden-yellow
$Sm_{0.75}Y_{0.25}S$	5.72	Golden-yellow
$Sm_{0.70}Y_{0.30}S$	5.68	Golden-yellow

III. LATTICE PARAMETER VERSUS CONCENTRATION

The rare-earth monosulfides appear to form solid solutions among themselves over the entire range of composition[5] and have the NaCl-type structure. When a R^{3+} ion replaces the Sm ion (the former is usually substantially smaller than the latter) in SmS, the lattice parameter decreases smoothly first and at a certain critical concentration abruptly contracts to a value close to 5.68 Å without involving any change in structure. The material also changes color abruptly at this point from black to metallic golden yellow. In Table I the room-temperature lattice parameters for the $Sm_xGd_{1-x}S$ compounds and the observed color of the material are given. In Fig. 1 plots of the lattice-parameter variation with composition at room temperature and 4.2 °K for the $Sm_{1-x}Gd_xS$ system are shown. At room temperature (298 °K) the lattice parameter undergoes a discontinuous change near 15 at.% Gd. The compound $Sm_{0.85}Gd_{0.15}S$ is black and has a lattice parameter of 5.875 Å. This material when powdered in an agate mortar turns golden and the x-ray powder photograph of the ground material shows two NaCl-type phases with lattice parameters of 5.875 and 5.68 Å (the pattern from the phase with the smaller a is the stronger of the two). The process of grinding strains the material sufficiently to cause the transition to the collapsed state. At about 16 at.% Gd the sample is metallic golden yellow in color and the lattice parameter is 5.68 Å. We believe that ~15.5 at.% Gd would be close to the critical concentration for the lattice

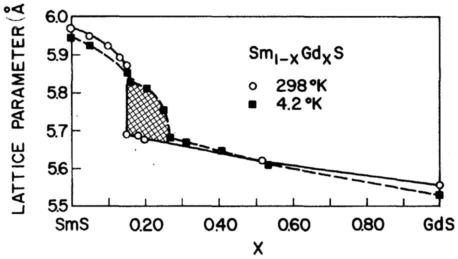

FIG. 1. Lattice-parameter data for $Sm_{1-x}Gd_xS$ compounds at 298 °K (open circles) and 4.2 °K (filled squares). The crossed region $0.16 < x < 0.27$ is the region of first-order phase transition observed on cooling.

collapse in the $Sm_{1-x}Gd_xS$ system at room temperature. At concentrations higher than 16 at.% Gd, the *a* parameter continues to decrease smoothly with increasing Gd content and reaches the value characteristic for pure GdS of 5.56 Å.

Also of interest are the lattice-parameter data taken at 4.2 °K as a function of x (Fig. 1). At 4.2 °K the lattice-parameter variation is anomalous in the region $0.16 < x < 0.27$. An abrupt decrease in *a* occurs around 27 at.% (estimated) Gd. In the region $0.16 \leq x < 0.27$ a strong first-order transition occurs on cooling the metallic-looking samples, which will be discussed in more detail in Sec. IV.

An abrupt change in the lattice parameter as well as color (black to metallic gold) at a critical R^{3+} concentration, followed by a smooth decrease in the lattice parameter to the value characteristic of the particular $R^{3+}S$ compound, is the general pattern of behavior for all the $Sm_{1-x}R_x^{3+}S$ compounds. With La, however, there does not appear to be any abrupt change either in the lattice parameter or in color.

IV. LATTICE PARAMETER VERSUS TEMPERATURE

The metallic golden-yellow $Sm_{1-x}R_x^{3+}S$ crystals (R = Ce, Pr, Nd, Gd, Tb, Dy, Ho) near the critical concentration undergo an explosive first-order transition when immersed in liquid N_2 and disintegrate to black powder. On warming, the black powder turns golden yellow in color and this transformation to the metallic state exhibits a marked thermal hysteresis. With Er and Tm substitution, the crystals show visible cracks and turn black, but the samples do not appear to disintegrate. Low-temperature x-ray diffraction patterns show that the structure remains unchanged as NaCl, the first-order transition in all the compounds, but the lattice parameter undergoes a discontinuous increase in the black phase (Fig. 2). In Fig. 3 the lattice-parameter variations with temperature for a number of $Sm_{1-x}Gd_xS$ compounds are shown for the range 300–4.2 °K. Compounds with nominal concentration in the range $0.15 < x < 0.22$ exhibit the explosive transition mentioned when immersed in liquid N_2, and correspondingly they show a discontinuous jump in the lattice parameter at temperatures above 77 °K. For 25 at.% Gd the discontinuous jump in the lattice parameter occurs just below liquid N_2 temperature. Near 30 at.% Gd, only a smooth variation in the lattice parameter is observed down to 4.2 °K. Thus there should be a concentration above which no first-order transition occurs, and we believe that this concentration is around 27 at.% (bracketed between 25–30 at.%) Gd for the $Sm_{1-x}Gd_xS$ compounds. The shaded region in Fig. 1 represents the compositions over which the first-order transition is observed.

The lattice-parameter variation with temperature for the range 300–4.2 °K shows other features that are noteworthy. Well below the critical concentration (viz. for $x = 0.05$) and at high Gd concentrations (e.g., $x > 0.40$) the lattice contracts with decreasing temperature. In the range $0.16 < x < 0.27$ a lattice expansion with decreasing temperature precedes the first-order transition. The effect is more pronounced the higher is the concentration of Gd (see Fig. 2 for $x = 0.25$). For $x = 0.30$ no abrupt change occurs, but the lattice contracts initially and then expands. The case of

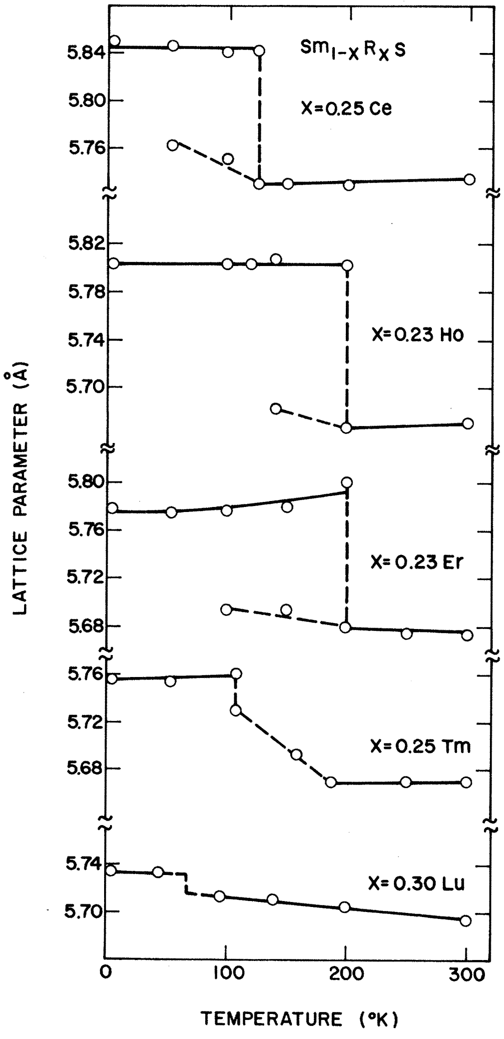

FIG. 2. Lattice-parameter–temperature data for some $Sm_{1-x}R_x^{3+}S$ compounds. Vertical broken lines mark the first-order transitions (wiggles on Y axis indicate break in scale). The compositions represent the nominal atomic percent R^{3+}. However, this may not be the true composition because their x-ray powder patterns show weak lines identifiable as R_2OS_2.

$x = 0.15$ is somewhat special. There is a region of normal behavior, namely, contraction, and a region (160–100 °K) in which the lattice contracts somewhat anomalously, followed by an almost flat region at the very-low-temperature end. We will return to this behavior later in the paper.

In Fig. 4 the lattice-parameter variation with increasing temperature (300–900 °K) is shown for a few compositions. In the range $0.16 < x < 0.30$ the thermal expansion is unusually large compared to the expansion in samples with $x = 0.40$, or at concentrations less than $x = 0.14$. The thermal expansion of GdS, for instance, is found to be $\alpha = 12 \times 10^{-6}\,{}^{\circ}\mathrm{K}^{-1}$,[6] whereas the expansion in $\mathrm{Sm_{0.83}Gd_{0.17}S}$ would be slightly more than three times the above value. The golden phase does not show a first-order phase transition on heating and the x-ray diffraction peaks shift anomalously but continuously with increasing temperature. For the sample $x \sim 0.14$ (black) no evidence for the metallic phase is observed in the entire range and the lattice parameter decreases slightly with increasing temperature. In Fig. 5 the lattice-parameter data as a function of temperature from about 1000 down to 4.2 °K are shown for $\mathrm{Sm_{0.75}Y_{0.25}S}$, as well as $\mathrm{Sm_{0.70}Y_{0.30}S}$. In the case of the former compound the lattice expands anomalously on de-

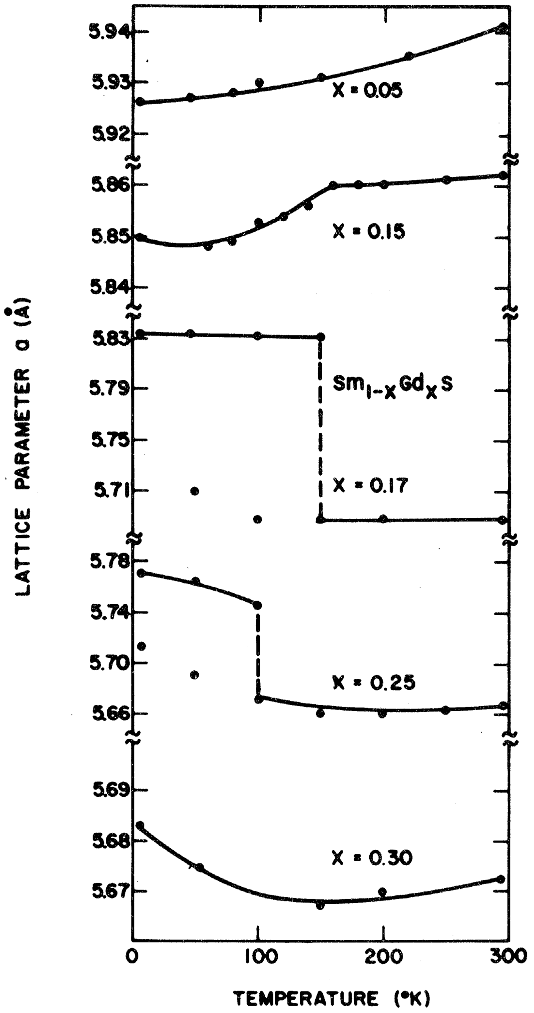

FIG. 3. Lattice parameter vs temperature for several $\mathrm{Sm_{1-x}Gd_xS}$ compounds. The compounds $x = 0.17$, 0.25, and 0.30 are metallic (*M* phase). The dashed line represents the first-order transition observed on cooling the *M* phase (see text). Wiggles on the *Y* axis indicate break in scale. Note also the anomalous thermal expansion (expansion on cooling) of the *M* phase. The compound with $x = 0.05$ shows normal behavior (contraction upon cooling).

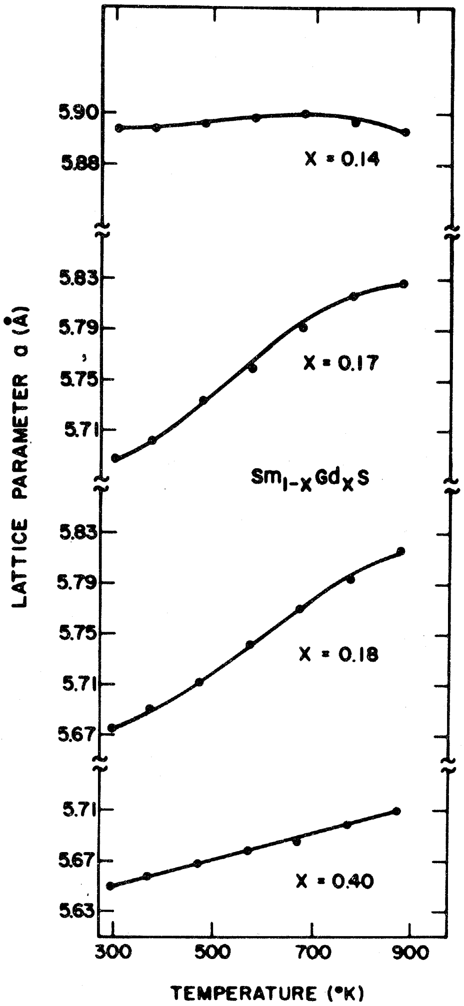

FIG. 4. Lattice parameter vs temperature for several $\mathrm{Sm_{1-x}Gd_xS}$ compounds. Metallic phases $x = 0.17$ and $x = 0.18$ show anomalously large thermal expansion on heating (see text for explanation) as compared to $x = 0.40$ or pure GdS, and the material turns black reversibly.

creasing as well as increasing temperature, with the minimum lattice parameter centered around 375 °K. This continuous and anomalous expansion behavior suggests that in the temperature traverse from 4.2 to 900 °K no first-order transition boundary is intersected in the above compounds.

V. RELATIONSHIP BETWEEN PRESSURE AND ALLOYING

Since the R^{3+} ions are substantially smaller than the Sm^{2+} ion, the effect of R^{3+} substitution for Sm in SmS is expected to exert a positive pressure on the SmS lattice. We demonstrate this in Fig. 6 for the $Sm_{1-x}Gd_xS$ system, wherein the transition pressure for the first-order electronic transition is plotted as a function of x. The transition pressures were determined at room temperature by visual observation of the abrupt change in color from black to bright golden yellow, in a hydrostatic pressure cell provided with sapphire windows. The effective pressure on the lattice is $6.5 - P_{tr}(x)$ kbar. It is clear from the data that substitution with the Gd ion is equivalent to applying positive pressure on the system. As noted earlier, the electronic transition exhibits a large pressure hysteresis. In the case of pure SmS the transition on increasing pressure occurs at about 6.5 kbar at room temperature, while the reverse transition does not take place until the pressure is down to 2 kbar. This pressure hysteresis seems to be unaffected over a wide temperature range (130–450 °K investigated). We found that a sample containing 10 at.% Gd reverses when pressure is released, while samples with 13, 14, and 15 at.% Gd stay golden yellow down to atmospheric pressure. There appears to be a 4-kbar hysteresis in pressure for the transition and this accounts for the metastable retention of the high-pressure phase of the 13-, 14-, and 15-at.%-Gd-doped SmS samples; their pressures of transition are less than 4 kbar and hence retained. *These metastably retained golden-yellow crystals undergo the explosive phase transition and disintegrate to a black powder on lowering the temperature.* Also, they transform to black powder through a first-order transition on heating ($Sm_{0.87}Gd_{0.13}S$ ~ 140 °C, $Sm_{0.86}Gd_{0.14}S$ ~ 220 °C, and $Sm_{0.85}Gd_{0.15}S$, $T > 350$ °C). The resulting black powder in either case has the same lattice parameter at room temperature, which is close to the value obtained on as-prepared samples.

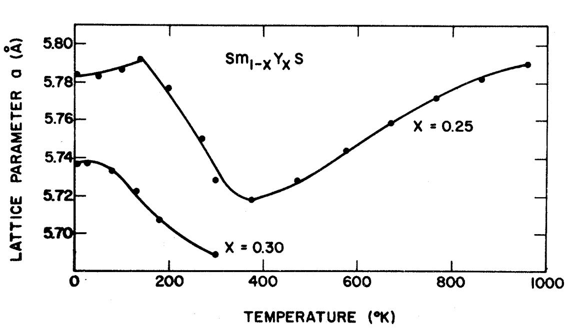

FIG. 5. Lattice parameter vs temperature data for two $Sm_{1-x}Y_xS$ compounds. The compound with $x = 0.25$ exhibits anomalous thermal-expansion behavior on cooling as well as heating. The x-ray diffraction peaks continuously shift with temperature and no evidence for a first-order transition is seen.

With Y doping similar lowering of the pressure of transition is observed, but, unlike Gd doping, the pressure hysteresis associated with the transition seems to be rather small. Samples in the black phase very near the critical concentration exhibit the reverse transition and the pressure hysteresis appears to be less than 1 kbar.

VI. PHASE STABILITY DIAGRAM

Based on the results of low-temperature as well as high-temperature x-ray studies a plausible phase stability diagram with T as the ordinate and concentration (x) as the abscissa is presented in Fig. 7 for the system $Sm_{1-x}Gd_xS$. It must be noted that this is not an equilibrium diagram. We have taken the appearance of two diffraction peaks in any sample, when cooled, as evidence for a

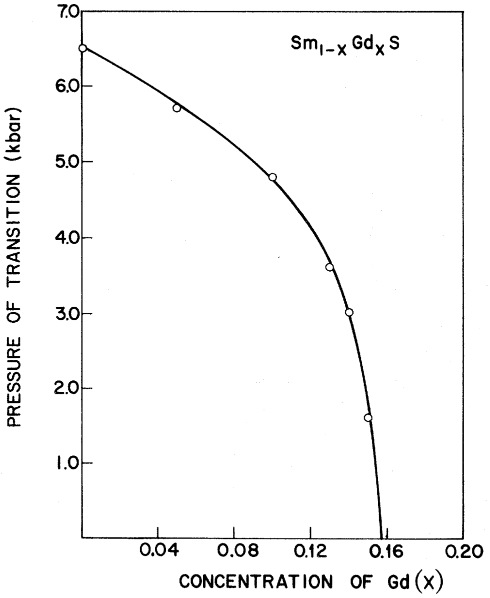

FIG. 6. Pressure of transition for $Sm_{1-x}Gd_xS$ alloys for the B-M transition as a function of Gd concentration. Substitution of Gd is equivalent to pressure. ($6.5 - P_{tr}$ is the effective pressure on the lattice due to Gd substitution.)

first-order transition. The temperature for the transition was chosen to be that temperature at which the intensity of the (220) peaks from both phases was equal. The phase stability diagram has three phases, designated as *B* for the normal phase, *M* for the metallic phase, and *B'* for the black phase usually resulting from the first-order transition, observed on cooling. We believe that the anomalous variation of the lattice parameter observed on cooling the sample with $x = 0.15$ (see Fig. 3) is due to the $B \rightarrow B'$ transition. It is extremely difficult to get reliable data on the $B \rightarrow M$ transition except the point at room temperature. Also, the $M \rightarrow B$ transition cannot be effected by heating the *M* phase because of the hysteresis associated with the $M \rightarrow B$ transition.

The semiconductor-to-metal transition boundary in pure SmS is very steep (~300°/kbar) and has a positive slope[7] (Fig. 9). If the substitution of Gd is strictly equivalent to positive pressure, the dT/dx phase boundary for the *B*-*M* transition in $Sm_{1-x}Gd_xS$ compounds should also be steep and positive. Our differential-thermal-analysis (DTA) experiments with samples close to the critical Gd concentration (15 at.%) show that the $B \rightarrow M$ transition produced by applying pressure is accompanied by evolution of heat. This signifies that the *B* phase in the $Sm_{1-x}Gd_xS$ compounds is the higher entropy phase and that the dT/dx of the *B*-*M* phase boundary must be positive.

The fact that the boundary for the first-order phase transition (*M* to *B'*) observed on cooling the *M* phase has negative dT/dx and a striking break in slope relative to the *M*-*B* boundary, and is accompanied by evolution of heat, strongly suggests that the *B'* phase must be different from the *B* phase. We have also obtained additional experimental evidence to show that the transition must be to a different *B* phase. Samples with the nominal composition $Sm_{0.85}Gd_{0.15}S$ are normally stable in the *B* phase but transform to the metallic golden-yellow (*M*) phase on application of about 1.5-kbar hydrostatic pressure at room temperature, and stay as *M* phase on releasing the pressure. In the experiments a pressure of about 2 kbar was applied on $Sm_{0.85}Gd_{0.15}S$ samples at different temperatures in the range 670–77 °K and pressure was released while holding the temperature constant. Then the temperature was allowed to return to the ambient and the samples were examined. The change of color (black $\rightleftarrows$ yellow) was used as an indicator to determine whether the transition *B* to *M* or *M* to *B* took place or not, after a specified *P* and *T* treatment. Samples came out golden yellow when *T* was held in the range 670–150 °K, and black when *T* was below 140 °K, suggesting that something different was happening in the lower-temperature region of the stability diagram. A smaller-pressure hysteresis at lower temperatures is hard to explain unless there is something totally different about the low-temperature part of the phase stability diagram. We therefore postulate the existence of a different *B* phase in the low-temperature part, which we have labeled as *B'* in the diagram.

The continuous but anomalous thermal-expansion behavior of the golden-phase samples (at compositions especially close to the critical concentration) and the absence of any first-order phase transition on heating strongly suggest termination of the *M*-*B* phase boundary at a critical point. Indeed, this is to be expected, in analogy with the behavior of electronic transitions of similar nature in[8] Ce and in[9] Cr-doped V_2O_3; in Ce the γ- to α-Ce phase boundary and in Cr-doped V_2O_3 the metal-insulator transition (Mott transition) boundary terminate at a critical point. Accordingly, in the stability diagram in Fig. 7 we indicate by the dotted line a range of temperature in which the critical point could lie. At this time we are unable to specify the exact location of the critical point either in terms of composition or temperature, atm. pres-

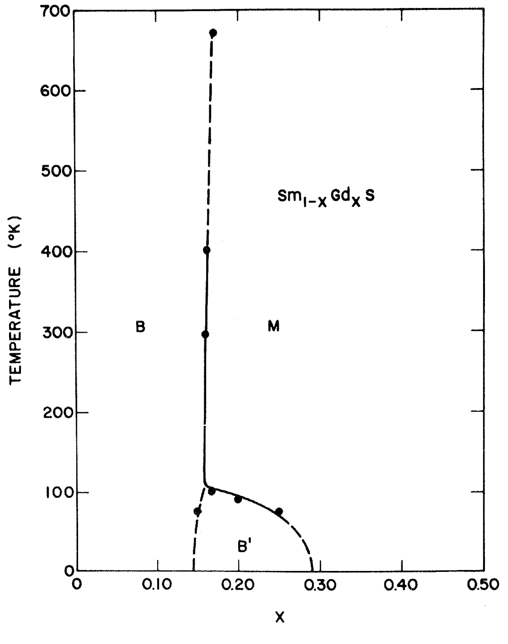

FIG. 7. Phase stability diagram for $Sm_{1-x}Gd_xS$ compounds in the *T*-*x* plane. *B* is the black phase, *M* the golden-yellow metallic phase, and *B'* the black phase resulting from the first-order transition on cooling the *M* phase. A critical point for the *B*-*M* phase boundary should lie within the limits of the dotted line. The slope of the *B*-*M* phase boundary is steep but has a positive dT/dx. The *M*-*B'* phase boundary has negative dT/dx (see text for explanation).

sure. However, we show in Fig. 8 data to justify the upper limit for the critical point. In a sample nominally $Sm_{0.85}Gd_{0.15}S$ two phases appeared during heating and their lattice parameters merged near 675 °K, which we believe is the upper limit.

VII. DISCUSSION

The present study raises several interesting questions which we will discuss in this section: (i) Does the so-called B' phase exist in the $Sm_{1-x}R_x^{3+}S$ compounds? (ii) If it exists, does magnetism of the substituted R^{3+} play a role? (iii) What role, if any, does the electronic structure of the substituted R^{3+} play in the transition? (iv) What conclusions can one draw from the results of the present investigation with regard to the metal-insulator transition in pure SmS?

(i). Based on the results of our pressure and temperature experiments, particularly with the $Sm_{0.85}Gd_{0.15}S$ compound, we have argued in Sec. VI that there is something different about the low-temperature part of the phase stability diagram, and the indications are in favor of a B' phase, which is distinct from the B phase.

Holtzberg[10] and Tao *et al.*[11] have invoked phase separation as the cause of the explosive transition and favor the idea of a miscibility gap in the system at low temperature. For a binary system such as the one we have here, a miscibility gap is a perfectly valid possibility. However, the interpretation that the explosive transition encountered in $Sm_{1-x}R_x^{3+}S$ compounds is due to phase separation runs into serious difficulties. In the present case phase separation due to a miscibility gap demands instantaneous diffusion of the R^{3+} ion into R^{3+}-lean and R^{3+}-rich regions at liquid nitrogen and still lower temperature. It is extremely unlikely that this will take place at such a low temperature. While the explosive aspect of the transition may be related to the existence of temperature and possibly some concentration gradient over a bulk sample, we find it difficult to attribute the cause of the transition to a phase separation into Gd-low and Gd-rich regions. Phase separation can occur during the preparation from the melt if we cool slowly through the subsolidus (provided there is a miscibility gap at moderate temperatures). Indeed, occasionally in some samples near the critical concentration we have seen the golden-colored phase coexisting with black phase. However, the way most of our samples were prepared was by cooling rapidly through the subsolidus region, and the material thus obtained was single phase.

(ii). The answer to the second point we raised, namely, whether magnetism of the R^{3+} ion plays a significant role, appears to be negative because the Y-substituted compounds according to Holtzberg[10] and Tao *et al.*[11] seem to behave very much like the Gd-substituted compounds, although the Y^{3+} ion is nonmagnetic.

(iii). Results with Yb-substituted compounds obtained by Bucher[12] indicate that the electronic structure of the *R*S compounds is very crucial. Although the lattice constant of YbS (5.68 Å) is almost the same as that of $Nd^{3+}S$ (5.69 Å), the effect of substitution of Yb and Nd in the SmS lattice is totally different. Whereas substitution of Nd causes a lattice collapse of SmS at about 15 at.% Nd, the lattice parameter of Yb-substituted compounds decrease smoothly to that of YbS, and the $Sm_{1-x}Yb_xS$ are all black. YbS is a semiconductor with a $4f$-$5d$ gap of nearly 1 eV and hence substitution of Yb results in a progressive widening of the gap of SmS and shifts the electronic transition to higher pressures. In pure YbS the electronic collapse occurs continuously in the range 150–200 kbar.[2] *We therefore believe that only compounds with favorable size factor and electronic structure can collapse the lattice of SmS and stabilize the high-pressure phase at atmospheric pressure.*

(iv). The equivalence of pressure and R^{3+} substitution appears to hold. Hence, from the behavior of $Sm_{1-x}R_x^{3+}S$ compounds we would be justified in deducing certain features of the P-T diagram of SmS and comparing them with what has been observed in SmS. We present the P-T stability diagram for SmS in Fig. 9 based on our resistivity measurements. On the basis of the equivalence

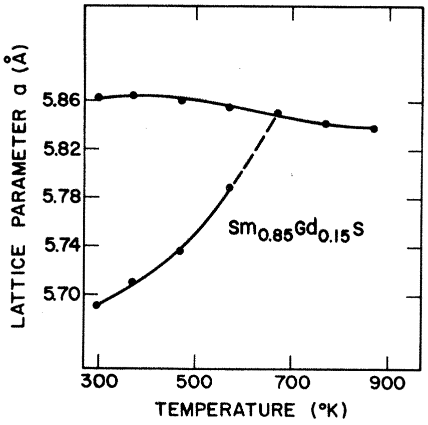

FIG. 8. Thermal-expansion data for a composition close to $Sm_{0.85}Gd_{0.15}S$. In this sample there were evidently two phases, one on the B side and another on the M-phase side. The B phase exhibits a small contraction on heating in the 400–900 °K, range while the M phase expands anomalously. The x-ray peaks from the two phases merge at about 675 °K (see text).

of pressure and R^{3+} substitution a phase boundary analogous to the M-B' phase boundary may be expected in the P-T field of SmS. In our experiments on SmS extending down to about 190 °K we have not seen clear-cut evidence for its presence. At lower temperature the friction correction in the piston-cylinder device becomes large, and further, the fluid medium freezes. Because of this freezing we lose the sharpness of the resistivity drop as well as the DTA signal, making a precise determination of the dT/dP difficult. In this connection experiments using gas pressure (He) would be rewarding, and the signs of dT/dP and ΔH should be checked. This should give an unambiguous answer to the existence or nonexistence of such a phase boundary. The semiconductor-metal boundary in SmS should terminate at a critical point.[13] Tonkov and Aptekar,[7] who delineated the semiconductor-metal phase boundary for SmS from DTA measurements, predict a critical point for SmS at about 700 °C and 7 kbar. This, of course, is an extrapolation based on the observed progressive narrowing of the pressure hysteresis of the semiconductor-metal transition and rests on the assumption that the critical point would be situated where the hysteresis interval closes. The anomalous thermal-expansion behavior of the M phase of both Gd- and Y-substituted compounds and the absence of any first-order transition on heating, as we already mentioned, are strongly indicative of critical termination of the B-M phase boundary in the alloy system. If this is the case, the termination of the semiconductor-metal phase boundary in SmS is a certainty and the estimate of Tonkov and Aptekar[7] is probably very realistic.

$Sm_{0.75}Y_{0.25}S$ exhibits anomalous but continuous expansion of the lattice in the range 375–4.2 °K. This raises the interesting question whether this behavior is again due to a degeneration of a first-order M-B' transition boundary to a second-order one. According to Tao *et al.*,[11] the M phase of Y-substituted SmS exhibits an explosive transition on cooling, down to at least 80 °K. If there is a first-order region for the M-B' transition, then the existence of a second-order transition region has to be postulated to account for the thermal-expansion data we have presented in Fig. 5.

VIII. INTERMEDIATE VALENCE STATE

The lattice parameters that characterize the divalent $Sm^{2+}S$ and fully trivalent $Sm^{3+}S$ are, respectively, 5.97 and 5.62 Å. Any lattice parameter intermediate in value suggests an intermediate or mixed valence state for the Sm ion. Magnetic-susceptibility measurements under pressure[14] and the lattice parameter[2] have firmly established that in the high-pressure metallic phase of SmS the Sm ions do not assume the fully trivalent value of 5.62 Å but instead have 5.70 Å, indicating an intermediate valence close to 2.8. Likewise, the lattice-parameter data of the B' phase in the R^{3+}-substituted SmS indicate that in this phase also the Sm ions exist in an intermediate valence state, the extent of the latter depending upon the R^{3+} concentration (see the lattice-parameter data of $Sm_{1-x}Gd_xS$ compounds at 4.2 °K reproduced in Fig. 1). The interesting question is how does one picture an intermediate valence state. There are two ways in which such a state can be viewed. (a) The Sm ions are present as Sm^{3+} and Sm^{2+} ions, as distinct species (small ion and large ion) intimately mixed and completely disordered on an atomic scale. The valence does not fluctuate from one to the other state with time and stays static and spatially frozen. (b) Every Sm ion in the crystal fluctuates in time between the $4f^6 5d^0$ (Sm^{2+}) and $4f^5 5d^1$ (Sm^{3+})

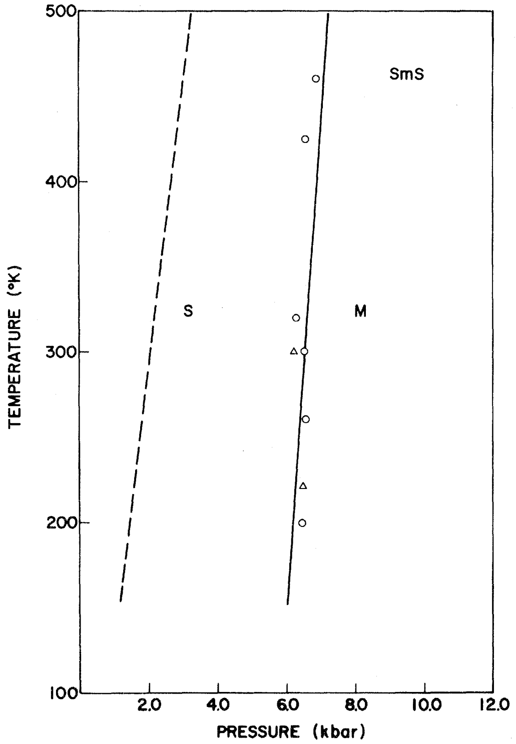

FIG. 9. P-T diagram for pure SmS. Open circles represent data obtained from the sharp drop in resistance upon increasing pressure at constant temperature (isotherm). Open triangles are data points from DTA measurements. Heat evolution in going from $S \rightarrow M$ proves dT/dP is positive. The dashed line is the reverse transition boundary. Note the large pressure hysteresis.

states on a rapid time scale, the relative time the electron spends in one of the two configurations determining the extent of the intermediate valence. In this situation the fluctuation rate may be so rapid that the lattice is not able to follow fully the electronic state and all the Sm ions stabilize at some intermediate size. This is a dynamic description that has been referred to as the interconfiguration fluctuation (ICF) model.[15] The ICF state is believed to have a period of $\tau \approx 10^{-12}$ sec. Admittedly, the x-ray diffraction technique cannot differentiate between the above-mentioned static and dynamic pictures and will show only a single characteristic set of diffraction lines appropriate to the NaCl-type structure. Recent x-ray photoelectron[16-18] (XPS) studies have shown that on the time scale $\tau \approx 10^{-16}$ sec (XPS is believed to have a probing time of 10^{-16} sec) Sm^{3+} and Sm^{2+} states are present in the *M* phase of $Sm_{1-x}R_x{}^{3+}S$ compounds. The XPS data by themselves do not prove that the ICF state exists in these materials, since both the static and dynamic situations would give rise to Sm^{3+} and Sm^{2+} spectrum. In this connection a direct Mössbauer study on the Sm ion in these materials would be of interest. In case the static situation prevails the Mössbauer resonance should show two resonances, whereas it is expected to show only a single resonance if the ICF state prevails. However, the magnetic-susceptibility data[14] that have been collected on the *M* phase of SmS and on some of the $Sm_{1-x}R_x{}^{3+}S$ compounds[11] have been interpreted on the basis of the ICF model; in particular, the nonmagnetic state of the Sm^{3+} is believed to be strongly in favor of the ICF state. The XPS results are consistent with this and hence the experimental situation as it stands now supports the ICF model.

IX. LATTICE PARAMETER, REFLECTIVITY, AND INTERMEDIATE VALENCE

Despite the limitation mentioned in Sec. VIII, the lattice parameter is a powerful and *direct indicator* of what is happening at the microscopic level in SmS as well as in R^{3+}-substituted SmS, under pressure and temperature. The lattice-parameter changes reflect changes in the size of the Sm ion, which in turn are directly related to changes in the valence state. Hence from lattice-parameter data, information regarding the $4f$-$5d$ character of the electronic wave functions can be inferred. Thus the anomalous thermal-expansion behavior at high temperature of the *M* phase of $Sm_{1-x}Gd_xS$ in the region 300–900 °K (see Fig. 4) must be due to a progressive localization of the conduction electron on the $4f^6$ states and consequent change in the valence of the Sm ions continuously towards the divalent state. The closer x is to the critical concentration the greater is the expansion. The anomalous thermal expansion strongly suggests that even in the *M* phase the $4f^6$ states are quite well defined and lie very close to the Fermi energy (E_f) and become thermally populated with increasing T. This, of course, would drive the *d* band higher up in energy, causing further localization. The reason a first-order transition does not occur is evidently connected with the existence of a critical point nearby. At high concentrations of Gd the $4f^6$ states may be expected to lie sufficiently far above E_f for the thermal expansion to become normal. This is clear from the data shown in Fig. 4 for $x = 0.40$ Gd. (Even in this case α is still somewhat larger than for pure GdS.)

Another property which has bearing on the intermediate valence state and which is readily obvious, even to the unaided eye, is the change in reflectivity. The latter goes from bright metallic gold to black through a progression of colors, as the localization of the conduction electron on the $4f$ level proceeds. This property is related to the shift in the plasma frequency (ω_p) towards the infrared ($\omega_p^2 = 4\pi n e^2/m^*$), as n, the number of conduction electrons, changes with temperature. Samples which exhibit anomalously large thermal-expansion behavior show a progressive color change over from metallic gold to copper, bronze, purple, and to black as the electronic fraction localizing on the $4f^6$ states increases with temperature. Thus the color of the compounds observed in the reflectivity goes hand in hand with the thermal-expansion behavior and gives a quick qualitative picture of what is happening at the microscopic level.

X. ELECTRONIC STRUCTURE

From the results of our studies on SmS and its alloys we propose the following simple picture of the electronic state of the system under different circumstances. In Fig. 10 the electronic state of *B*, *M*, and *B′* phases of the $Sm_{1-x}Gd_xS$ compound is shown. In the *B* phase the Sm $4f^6$ configuration must lie below the Fermi level E_f, to be consistent with the divalent state of the Sm ion. Since Gd ions are trivalent they must contribute one extra electron, which should go into the $5d$ band (not shown in Fig. 10) of Gd.[19] The conductivity data show that heavily doped samples exhibit a positive temperature coefficient of resistivity. This makes the $Sm_{1-x}Gd_xS$ (for $x > 0.10$) compounds a degenerate semiconductor when in the *B* phase and the E_f in the latter must therefore lie in the $5d$ band of Gd, which at the concentrations in the present situation must still be a fairly narrow band. The $5d$ band of Sm, which constitutes the principal conduction band of the system, is largely empty. The $3p$ states of sulfur constitute the valence band and are also shown.

In the M phase, on the other hand, the Sm ions are nearly trivalent and hence the $4f^6$ configuration must have fewer electrons relative to the $4f^55d^1$ configuration. The way this is realized is through a large reduction in the lattice constant at the transition. The reduction in the lattice parameter lowers the energy of the $5d$ band and pushes it below the $4f^6$ configuration. An approximate calculation shows that for a 10% volume change in going from the B to M phase the $5d$-band edge should shift by about 0.5 eV (calculated from the deformation potential of −4.7 eV measured for SmS). This results in the shifting of the E_f to the $5d$ band of the Sm. Since the system is in the intermediate valence state, E_f must be tied to the $4f^6$ state and hence we believe that the latter lies in the proximity of E_f. This would be consistent with the anomalous thermal-expansion behavior of the M phase: The lattice will show an anomalous expansion because the Sm ions would move closer to the divalent state, when the $4f^6$ states are thermally populated.

In a recent paper Tao and Holtzberg[11] have presented results principally of their magnetic-susceptibility measurements taken over a wide temperature range and some lattice-parameter data on SmS alloys involving La, Y, and Gd substitutions. These results appear to be consistent with the findings discussed in this paper. They have proposed a model for the electronic structure of these alloys and have briefly discussed a plausible mechanism to explain the transitions from the metallic phase, observable upon increasing as well as decreasing temperature. The model invokes the multiplet structure of the $4f^6$ $(J=0, 1)$ resulting from the spin-orbit interaction and the crystal-field-split $4f^5$-$5d$ complex. In Fig. 10, we have a similar picture but have included E_f and the Fermi distribution function. We believe that the change in the latter function (indicated in Fig. 10 by the dashed line) with temperature cause changes in the occupation probability of the electrons in the various electronic states involved as temperature is varied, and initiates the transitions among the three relevant phases. The transition from M to B' can be rationalized as follows. When temperature is reduced the Fermi distribution tail [dashed line in Fig. 10(b)] would shift to lower energy, enhancing the occupation probability in the $4f^6$ $(J=0)$ state. This would then make the Sm ions go towards the divalent state, causing an expansion of the lattice which in turn would push the $4f^55d^1$ configuration to higher energies. Such a shift will dump more electrons into the $4f^6$ $(J=0)$ state and cause further expansion. This bootstrapping would lead to a catastrophic first-order transition from M to B'. On the other hand, raising the temperature will increase the occupation probability of the $4f^6$ $(J=1)$ state, which would also cause the lattice to expand and push the system in the same direction. Since the transition from M to B is found to be continuous, it must be the case that there are decelerating factors which make it go continuously rather than abruptly, when the M phase is heated (see the last paragraph of Sec. XI). Thus the M phase, because of its unique electronic structure, is un-

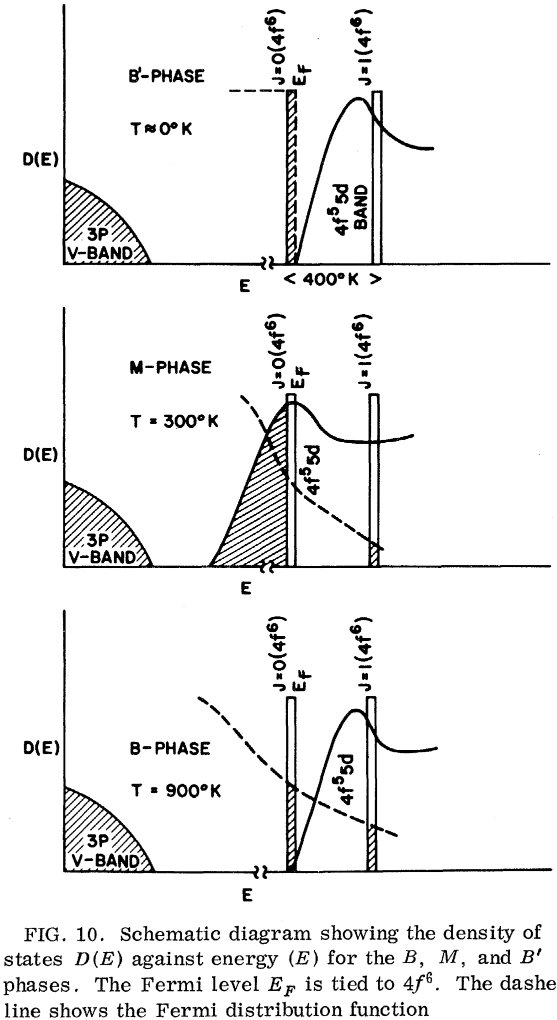

FIG. 10. Schematic diagram showing the density of states $D(E)$ against energy (E) for the B, M, and B' phases. The Fermi level E_F is tied to $4f^6$. The dashed line shows the Fermi distribution function $f_i = 1/(1+e^{(E-E_F)/kT})$. (Note change in energy scale.) See text for discussion of the transition from $M\rightarrow B$ and $M\rightarrow B'$, and the anomalous thermal-expansion behavior.

stable with respect to both high and low temperatures.

XI. SOME REMARKS ABOUT THE PHASE DIAGRAM

The phase stability diagram of SmS in the P-T plane and the T-vs-x diagram of the $Sm_{1-x}Gd_xS$ system invite some comments. From the phase stability diagrams it would be seen that the temperature ordering of the phases is in the sequence $B' \rightarrow M \rightarrow B$ with increasing T. We should like to point out that this ordering can originate from a delicate balance of a number of physical factors that contribute to the entropy. (i) In the B phase, which is stable at high temperature, the $4f^6$ states (including $J = 0$, 1, and 2) would all be populated substantially. (It is well known that this is the cause of Van Vleck paramagnetism in SmS.) Hence in this phase the spin-disorder contribution to the entropy is to be reckoned with. Such a contribution, however, does not exist in either the M phase, because the mixed valence state is nonmagnetic, or the B' phase, because in the latter the electrons occupy the $J = 0$ ($4f^6$) (nonmagnetic) ground state. However, the above picture can be criticized for two reasons. (a) Are $J = 0$, 1, and 2 of $4f^6$ good quantum numbers? (b) Even if they are good quantum numbers would the $J = 1, 2$ of $4f^6$ have a local moment if there is hybridization between the $4f$ and $5d$ states? These are valid criticisms to be reckoned with. (ii) Another possibility which is more likely to be responsible for the above temperature ordering is the lattice contribution to the entropy. The B phase with its much larger lattice constant (relative to the M phase) would have a smaller Debye Θ and hence the lattice contribution to the entropy at high temperature, which would be proportional to $(T/\Theta)^3$, could dominate over the combined electronic and lattice terms of the M phase. The lower entropy of the B' phase is then presumed to be due to the absence of electronic entropy and lowered contribution from the lattice term at low temperatures. This second possibility involving lattice contribution to the entropy appears more probable as an explanation of the temperature ordering of the three NaCl-type phases encountered in the system.

In the SmS system, the strong coupling of the electronic state with the lattice is a factor which acts self-consistently to accelerate the transition.[20] There are also decelerating tendencies, such as the rise in Fermi energy with the occupation of the $4f^5 5d^1$ configuration. As pointed out by Anderson and Chui[20] and Hirst,[15] it is the relative strength and balance between these two tendencies that is responsible for first- and second-order transitions in these systems.

XII. SUMMARY AND CONCLUSIONS

A variety of experiments under pressure, namely, resistivity, pressure-volume relationships, and optical studies, have shown that in a number of semiconducting rare-earth divalent monochalcogenides a transition to the metallic state involving $4f$ electron delocalization can be induced by pressure. These involve a change in the valence state from 2^+ towards the 3^+ state. This electronic transition takes place continuously in many systems but also discontinuously in some; e.g., in SmS at about 6 kbar at room temperature. Some recent studies have shown that the effect of pressure can be stimulated by substituting R^{3+} ions (including Y^{3+}) for Sm in SmS and the high-pressure metallic phase stabilized at atmospheric pressure. The metallic phase resulting from alloying as well as under pressure has an intermediate valence state. Temperature studies on the alloys have shown that in the system $Sm_{1-x}R_x^{3+}S$ there can be three NaCl-type phases, of which one is metallic with the Sm ion nearer to the 3^+ state and the other two appear black, have much larger lattice constants, and have the Sm ion closer to the divalent state. The so-called B-M phase boundaries in the alloy system and semiconductor-metal boundary in SmS have positive dT/dx and dT/dP, respectively, and there is strong evidence that they terminate at a critical point. (In these respects the phase transition is quite like that of the γ- to α-Ce phase boundary.) The M-B' phase boundary in the T-x plane has negative dT/dx. These phases show anomalous thermal expansion and first-order and continuous transition among themselves. Such effects are related to the changes in the occupation probability of the available electronic states [namely, the $4f^5 5d^1$, $4f^6 5d^0$ ($J = 0$) and $4f^6$ ($J = 1$)] caused by the changes in temperature. The temperature ordering of the phases in the phase stability diagram seems to be dictated by a delicate balance[21] between the different contributions to the entropy; i.e., lattice contribution, the electronic contribution, and possibly spin-disorder contribution. The behavior of the substituted systems is determined by the size as well as the electronic structure of the particular R^{3+} ion. We have also demonstrated the equivalence of pressure and R^{3+} substitution. Further, with substituted systems when the composition is near the critical x, the black phase (B) can be converted by application of pressure to the M phase and the latter retained on release of pressure at room temperature. This opens up the possibilities of performing many interesting experiments at the same composition on the same specimen, in different states (e.g., $Sm_{0.87}Gd_{0.13}S$ through $Sm_{0.85}Gd_{0.15}S$). We have also shown that lattice-parameter data provide one of the most powerful keys to understanding what is happening in these materials at the microscopic level and show that the valence state of Sm can be continuously varied from $2^+ \rightleftarrows 3^+$ under the combined effect of alloying and temperature. The alloy studies are also relevant to understanding the *P-T* behavior of SmS. Such studies predict a low-temperature nonmetallic phase for SmS distinct from the normal semiconducting phase.

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

[2] A. Jayaraman, A. K. Singh, A. Chatterjee, and S. Usha Devi, Phys. Rev. B 9, 2513 (1974).

[3] J. L. Kirk, K. Vedam, V. Narayanamurti, A. Jayaraman, and E. Bucher, Phys. Rev. B 6, 3023 (1972).

[4] A. Jayaraman, E. Bucher, P. D. Dernier, and L. D. Longinotti, Phys. Rev. Lett. 31, 700 (1973).

[5] Mutual solubility over the entire range of composition appears to be questionable in light of what has been found in the work reported in Refs. 11 and 12. There seems to be a region of phase separation near the critical concentration region for the electronic collapse, and this becomes apparent when slow cooling or annealing the sample at high temperatures. However, rapid quenching from the melt yields single phase.

[6] Yu. M. Goryachev and T. G. Kutsenok, High Temp.-High Pressure 4, 663 (1972).

[7] E. Yu. Tonkov and I. L. Aptekar, Fiz. Tverd. Tela. 16, 1507 (1974) [Sov. Phys.—Solid State 16, 972 (1974)].

[8] A. Jayaraman, Phys. Rev. 137, A179 (1965).

[9] A. Jayaraman, D. B. McWhan, J. P. Remeika, and P. D. Dernier, Phys. Rev. B 2, 3751 (1970).

[10] F. Holtzberg, AIP Conf. Proc. 18, 478 (1973).

[11] L. J. Tao, F. Holtzberg, and R. Tournier, Bull. Am. Phys. Soc. 19, 208 (1974); L. J. Tao and F. Holtzberg (unpublished).

[12] E. Bucher, Eur. J. Appl. Phys. (to be published).

[13] H. S. Wio, B. Alascio, and A. Lopez, Solid State Commun. (to be published).

[14] M. B. Maple and D. Wohlleben, Phys. Rev. Lett. 27, 511 (1971); AIP Conf. Proc. 18, 447 (1973).

[15] L. L. Hirst, J. Phys. Chem. Solids 35, 1285 (1974).

[16] J. L. Freeouf, D. E. Eastman, W. D. Grobman, F. Holtzberg, and J. B. Torrance, Phys. Rev. Lett. 33, 161 (1974).

[17] M. Campagna, E. Bucher, G. K. Wertheim, and L. D. Longinotti, Phys. Rev. Lett. 33, 165 (1974).

[18] R. A. Pollak, F. Holtzberg, J. L. Freeouf, and D. E. Eastman, Phys. Rev. Lett. 33, 820 (1974).

[19] W. M. Walsh, Jr., L. W. Rupp, Jr., E. Bucher, and L. D. Longinotti, AIP Conf. Proc. 18, 535 (1974).

[20] P. W. Anderson and S. T. Chui, Phys. Rev. B 9, 3229 (1974).

[21] A similar situation is known to exist in $AuGa_2$. H. T. Weaver, J. E. Schirber, and A. Narath, Phys. Rev. B 8, 5443 (1973).