Intermediate valence in alloys of SmS with SmP

D. C. Henry,* K. J. Sisson,† W. R. Savage, and J. W. Schweitzer
Department of Physics and Astronomy, The University of Iowa, Iowa City, Iowa 52242

E. D. Cater
Department of Chemistry, The University of Iowa, Iowa City, Iowa 52242
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Results are presented for the lattice parameter and magnetic susceptibility as a function of temperature for a series of solid solutions of SmS with SmP. At room temperature the $SmS_{1-x}P_x$ alloys with $x \geqslant 0.06$ exhibit a metallic appearance and a much smaller lattice constant and magnetic susceptibility as compared with SmS. For $x \geqslant 0.15$ the susceptibilities do not show a Curie-law divergence or magnetic ordering. These properties are consistent with the Sm ions being in a homogeneous intermediate-valence state similar to that of SmS under pressure. The intermediate valence estimated from the lattice parameter is 2.8 at $x = 0.06$ and increases toward the pure trivalent value with increasing phosphorous concentration. Also, the color of the alloys changes from gold to red to silver grey. The alloys with $0.03 < x < 0.06$ exhibit a varying mixture of two distinct phases, the gold intermediate-valence phase and the black phase characteristic of the $x < 0.03$ alloys. The properties of the black phase are consistent with a mixture of Sm^{2+} and Sm^{3+} ions where Sm ions with one or more P ions as nearest neighbors are trivalent. The $0.04 \leqslant x \leqslant 0.08$ alloys exhibit a transition from the gold phase to the black phase with decreasing temperature. This transition which is continuous at higher concentrations changes to a discontinuous one near $x = 0.06$ as seen in the temperature variation of the lattice parameter.

I. INTRODUCTION

Intermediate valence can be chemically induced in SmS by anion substitutions. This has been previously observed in the solid solutions of SmS with SmAs,[1-4] and SmS with SmSb.[5,6] The lattice parameter of $SmS_{1-x}As_x$ undergoes an abrupt decrease at an As concentration in the range from 5 to 10% which is accompanied by a color change from black to golden yellow. This transition is similar to the first-order semiconductor-to-metal transition in SmS under pressure at 6.5 kbar where there is a large isostructural volume decrease and a change in color from black to gold. Various studies have demonstrated that the Sm ion in SmS under pressure undergoes a transition from the divalent $4f^6$ configuration to a state which is a linear combination of the $4f^6$ and $4f^5$ configurations. Lattice-parameter[7] and room-temperature magnetic-susceptibility measurements[8] give an estimate of 2.7 for the Sm valence in the gold phase. A similar estimate is obtained from Mössbauer isomer-shift measurements[9] which also provide perhaps the most convincing evidence for a true quantum-mechanical admixture of the $4f^6$ and $4f^5$ configurations. The metallic character of SmS at room temperature in the gold phase has been established by resistivity[7,10] and optical[11,12] measurements.

In the case of $SmS_{1-x}As_x$ for $x \leqslant 0.05$, lattice constant, magnetization, and transport measurements[4]

have shown that there is a mixture of Sm^{2+} and Sm^{3+} ions where Sm ions with one or more As as nearest neighbors are trivalent. However, in the collapsed phase, $x \geqslant 0.1$, the Sm ions exhibit a homogeneous intermediate valence[3] in analogy with SmS under pressure. The Sm valence in $SmS_{1-x}As_x$ is estimated to be 2.8 at $x = 0.1$ and increases with increasing x until it reaches the pure trivalent state at a concentration between 40 and 70% As.[3,13]

The $SmS_{1-x}Sb_x$ solid solutions do not exhibit a collapsed gold phase.[5,6] This is due to the much larger size of the Sb ion in comparison with the As ion. The lattice constants of SmS, SmAs, and SmSb are 5.97, 5.92, and 6.27 Å, respectively. Nevertheless, there is evidence for intermediate valence in the $SmS_{1-x}Sb_x$ alloys and the estimated valence from the lattice constant[5] deviates significantly from the $2 + x$ value which is inherent in the ionic charge transfer associated with the substitution of a fraction x of trivalent Sb for divalent S.

Since the lattice constant of SmP is 5.77 Å one expects the alloys of SmS with SmP to have properties very similar to those of the alloys of SmS with SmAs. The electronic properties of the samarium pnictides SmP, SmAs, and SmSb are similar with all of the compounds showing semimetallic behavior. Therefore, the substitution of phosphorous for sulfur in SmS should produce the collapsed gold phase at a very small concentration of phosphorous. We report

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measurements of the temperature dependence of the lattice parameter and magnetic susceptibility of $SmS_{1-x}P_x$ solid solutions. The purpose of this study is to investigate the transition to intermediate valence in the $SmS_{1-x}P_x$ alloys and make comparison with previous studies of the $SmS_{1-x}As_x$ alloys.

II. MATERIALS AND EXPERIMENTAL METHODS

The alloy samples for this investigation were prepared from mixtures of SmS and SmP. The initial reaction of the elements to form the compounds was carried out in sealed Vycor tubes initially evacuated to 10^{-6} Torr. The tubes were heated at a rate of 1 degree per minute to 500 °C and held there for 16 hours. The temperature was then raised to 750 °C and maintained for 4 hours in the case of the SmS and for 15 days in the case of the SmP where the much longer period was required for complete reaction. The products of these reactions were mixed in the required proportions, ground to a fine powder in an inert atmosphere, and pressed into pellets at 3000 psi pressure. The pellets were sealed into tantalum capsules which were welded closed under vacuum. The capsules were heated in an induction furnace to 1900 °C for 1 hour in a vacuum, and then quenched to ambient temperature by the introduction of helium gas into the furnace.

The sintered pellets of the $SmS_{1-x}P_x$ samples with phosphorous concentrations $x \geq 0.08$ were polycrystalline and of uniform color and luster, with the color changing from yellow gold, to red, to blue, to silver grey with increasing phosphorous concentration. With phosphorus concentrations in the range $0.03 \leq x \leq 0.06$, the pellets consisted of a mixture of black and gold material. The $x = 0.03$ sample appeared almost entirely black with traces of gold, and the samples with $x = 0.04$ were mostly black with small (0.2 mm) flecks of gold material scattered throughout. The $x = 0.05$ samples appeared to have equal proportions of the black and gold phases, while the $x = 0.06$ samples were almost entirely gold in color. When immersed in liquid nitrogen the $0.03 \leq x \leq 0.06$ samples all exhibited some degree of shattering as the gold phase converted to the black phase. Upon warming to room temperature the gold phase was again observed. A similar explosive transition occurs in the $SmS_{1-x}As_x$ system[1] and in certain trivalent rare-earth substituted SmS.[14] The measurements reported in this investigation were performed on samples that had been subjected to repeated thermal cyclings.

X-ray powder diffraction patterns confirmed the NaCl-type crystal structure expected for the $SmS_{1-x}P_x$ solid solutions. The samples with the phosphorus concentrations $0.03 \leq x \leq 0.06$ showed two phases with significantly different lattice constants corresponding to the black and gold phases.

However, in two cases the x-ray patterns showed more than one black phase which was attributed to the phosphorous concentration not being uniform. Therefore results of measurements on these two samples are not reported. The x-ray patterns also showed Sm_2O_2S to be present in most of the samples with the amount generally increasing with the phosphorous concentration of the sample. The percentage of Sm_2O_2S was estimated from the relative intensities of the x-ray diffraction lines for Sm_2O_2S and alloy, calibrated by measurements on mixtures with known additions of Sm_2O_2S. The oxysulfide concentration was less than 2% for all samples except for the $x = 0.30$ alloy and one of the $x = 0.40$ alloys where the Sm_2O_2S concentrations were near 4%. The presence of the oxysulfide leads to an uncertainty in the true composition of an alloy and therefore the compositions reported represent nominal atomic percents.

Lattice-parameter measurements at room temperature were obtained with a Guinier—de Wolff focusing camera using Cu $K\alpha$ radiation and an internal ThO_2 standard. The uncertainties in the lattice parameters obtained were ± 0.005 Å or less. The measurement of the temperature dependence of the lattice parameter of several of the samples between 70 and 400 K was carried out with a liquid-nitrogen cryostat adapted for use with a 114.6-mm Debye-Scherrer cylindrical powder camera. Silicone grease was used to bind the sample to the sample holder which was a copper wire that was cooled by conduction. The temperature was controlled with a Fisher proportional temperature controller which maintained the temperature with a stability of ± 2 K or better. The sample temperature was measured with a copper-Constantan thermocouple that was soldered to the sample holder. To establish that the sample was at the same temperature as the sample holder, the lattice parameter of KCl was determined at 80 K and compared with the published value. These agreed within experimental uncertainties. Temperatures below 77 K were obtained by pumping on the liquid-nitrogen reservoir. The lattice parameters reported were obtained by a least-squares extrapolation to 90 ° of the parameters as a function of the square of the cosine of the diffraction angle. A minimum of four and usually five or six diffraction lines with Bragg angles greater than 60 ° were used in the extrapolation. The standard deviation in the lattice parameters are estimated to be less than ± 0.002 Å except for some measurements on the black phases where the lines were very weak.

The magnetic-susceptibility measurements were made using the Faraday method with apparatus that has been previously described.[15] Susceptibilities were measured in the temperature interval from 1.6 to 300 K. The temperature could be stabilized to within ± 0.3 K near room temperature and ± 0.1 K below 4 K. Typical errors associated with the measured susceptibilities have been found to be less than 1.5%.

III. ROOM-TEMPERATURE VALENCE

The room-temperature lattice parameters of the alloys of SmS with SmP are shown in Fig. 1 as a function of the phosphorous concentration. The pure SmS is a semiconducting material having the NaCl-type structure with a lattice constant of 5.970 ± 0.002 Å. For $0.03 \leq x \leq 0.06$, the $SmS_{1-x}P_x$ alloys show two NaCl-type phases, a black phase with a lattice parameter that decreases continuously from that of SmS with increasing x, and a gold phase with a much smaller lattice parameter which is nearly independent of the phosphorous concentration.

The variation of the lattice parameter with the phosphorous concentration in the black phase is similar to that observed by Holtzberg et al.,[4] for alloys of SmS with SmAs at small arsenic concentrations. For $SmS_{1-x}As_x$ alloys with $x \leq 0.05$, lattice constant, magnetization, resistivity, and Hall constant measurements are consistent with there being a mixture of $Sm^{2+}(4f^6)$ and $Sm^{3+}(4f^5)$ ions where Sm ions with one or more As as nearest neighbors are trivalent as originally suggested by Kasuya.[16] If the same picture applies to the $SmS_{1-x}P_x$ alloys, the expected lattice constant can be estimated from a linear interpolation which yields

$$[a(x)]^{black} = [1 - x - (1-x)^6]a(Sm^{3+}S)$$
$$+ (1-x)^6 a(Sm^{2+}S) + xa(SmP) \quad . \quad (1)$$

Here $(1-x)^6$ is the probability that a Sm ion has no P ions at nearest-neighbor sites, $a(SmP)$ is the lattice parameter of SmP, $a(Sm^{2+}S)$ is the measured lattice parameter of SmS, and $a(Sm^{3+}S) = 5.62$ Å is an estimate based on an interpolation from the lattice parameters of neighboring trivalent rare-earth sul-
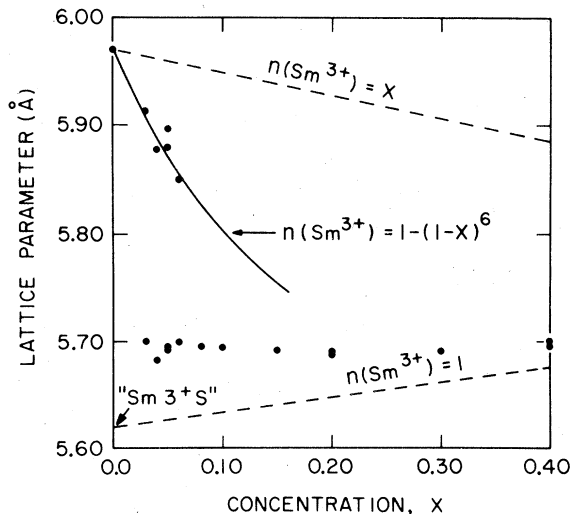
fides.[17] The solid curve in Fig. 1 is the calculated lattice parameter for the black phase in this picture and it is seen to be in good agreement with the measured values. The scatter of the black-phase parameters about the curve in Fig. 1 could represent errors in the compositions. Thus, it appears that the black phase corresponds to a mixture of Sm^{2+} ions and Sm^{3+} ions with an average valence of $3 - (1-x)^6$.

In the collapsed phase the Sm ions are expected to have a homogeneous intermediate valence similar to SmS under pressure. An estimate of the Sm valence $v(x)$ is given by[2]

$$v(x) = 2 + x + \frac{(1-x)a(Sm^{2+}S) + xa(SmP) - a(x)}{a(Sm^{2+}S) - a(Sm^{3+}S)} ,$$
$$(2)$$

where $a(x)$ is the measured lattice constant of the alloy. This estimate is based on a linear interpolation for the lattice constant assuming a mixture of Sm^{2+} and Sm^{3+} ions as is pictured for the black phase. However, it also gives a reliable estimate for the valence in the case of homogeneous intermediate valence.[2] The resulting estimate for the Sm valence at room temperature is shown in Fig. 2 as a function of the phosphorous concentration. The average valence in the black phase can be compared with the expected $3 - (1-x)^6$ which is the plotted curve. The intermediate valence in the collapsed phase is approximately 2.8 at its lowest phosphorous concentration and increases to 2.95 at $x = 0.04$. This behavior is very similar to that observed in the $SmS_{1-x}As_x$ alloys.[3]

FIG. 1. Lattice parameter of alloys as a function of the phosphorus concentration.
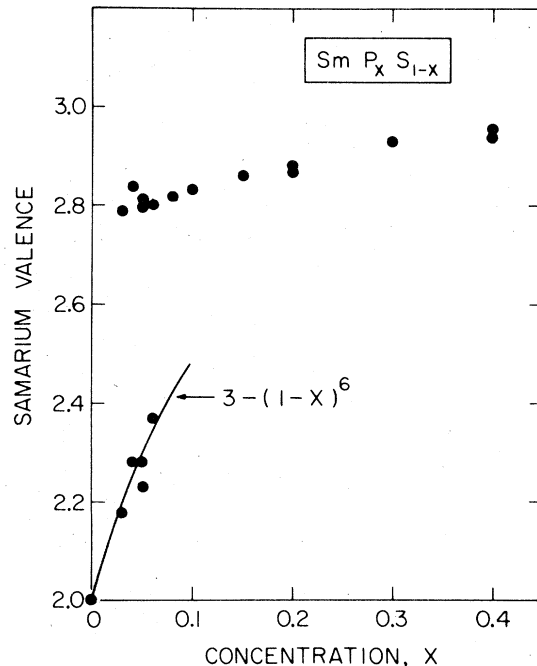

FIG. 2. Estimated samarium valence from lattice parameter as a function of the phosphorous concentration.

IV. MAGNETIC SUSCEPTIBILITIES

The magnetic susceptibilities of the $SmS_{1-x}P_x$ alloys have been measured in the temperature range from 1.6 to 300 K. Figure 3 shows the temperature dependence of the susceptibility of SmP, SmS, and several of their mutual solid solutions in order to illustrate the dependence on composition. The SmS susceptibility is well described[18] by an exchange enhanced Van Vleck susceptibility associated with the $Sm^{2+}(4f^6)\,^7F$ ions where the $J = 0$ ground state is separated by 420 K from the $J = 1$ excited state. The Curie-like rise in the susceptibility at low temperatures is attributed to small concentrations of Sm^{3+} ions and other magnetic impurities.[19] SmP exhibits a susceptibility which is characteristic of the $Sm^{3+}(4f^5)\,^6H$ ions in a cubic crystal field which interact by an exchange coupling of the spins. Such a model with reasonable values for the spin-orbit, crystal field, and exchange parameters yields excellent agreement with the measured susceptibilities of other samarium pnictides (SmAs, SmSb, SmBi) that we have prepared, and good agreement with our SmP except at low temperatures where the Curie law increase observed is somewhat larger than expected.[20]

In the case of the alloys the susceptibility at sufficiently high temperatures is expected to be a linear combination of the Sm^{3+} and Sm^{2+} contributions weighted according to the average valence as has been observed in other intermediate-valence systems.[13,21] If one compares the room-temperature susceptibility to the linear interpolation

$$\chi(SmS_{1-x}P_x) = [1 - \epsilon(x)]\chi(SmS) + \epsilon(x)\chi(SmP) ,$$

then $2 + \epsilon(x)$ provides an estimate of the average valence. This estimate is in qualitative agreement with the estimate from the lattice constant. In the alloys where both the black and gold phases are present, $2 + \epsilon(x)$ should be compared with the average of the valences in the individual phases weighted by the relative amount of each phase.

The temperature dependence of the susceptibility of the $SmS_{1-x}P_x$ alloys with $x = 0.40$, where the intermediate valence is 2.95 as estimated from lattice constant and room-temperature susceptibility, is very similar to that of the pure trivalent SmP except at low temperatures. In this alloy one does not observe a Curie-law divergence as would be expected for Sm^{3+} ions that do not order at low temperatures. Furthermore there is no evidence for an antiferromagnetic transition in the alloy as has been observed in SmP at 1.7 K.[20] This nonmagnetic behavior at low temperatures seen in the $x = 0.40$ alloy is characteristic of the homogeneous intermediate-valence phase as found in SmS under pressure. The temperature dependences of the $x = 0.20$ and 0.15 samples are qualitatively simi-

lar. However, with the $x = 0.10$ alloys one begins to see an anomalous increase in the susceptibility below 100 K. This increase is more evident in the $x = 0.08$ and 0.06 alloys and occurs over a broad temperature interval at higher temperatures in the $x = 0.04$ alloy. Such an increase suggests a smaller average valence at low temperatures. This could correspond to a continuous change in the homogeneous intermediate valence, a discontinuous transition to the black phase, or some combination of both effects. In Sec. V, measurements of the temperature dependence of the lattice parameter are presented in order to clarify the picture.

At temperatures below 40 K the susceptibilities of the $x = 0.04$, 0.06, and 0.08 alloys exhibit a very large Curie-like temperature dependence. This behavior is consistent with the samples of low-phosphorous concentration being in the black phase at low temperatures since the black phase is pictured as a mixture of pure Sm^{2+} and Sm^{3+} ions. However, the observed rise at low temperature is several times greater in magnitude than would be predicted for the estimated concentration of Sm^{3+} ions. These low-concentration alloys clearly show superparamagnetic effects.

The susceptibilities of the $SmS_{1-x}P_x$ alloys with $0.3 \leq x \leq 0.06$ exhibit hysteresis in their temperature dependence. The data shown in Fig. 3 correspond to the temperature increasing. Figure 4 shows the observed thermal hysteresis in the case of a $x = 0.06$ alloy that had been cycled between room temperature and liquid-nitrogen temperature several times prior to the susceptibility measurement. The $x = 0.03$ alloy
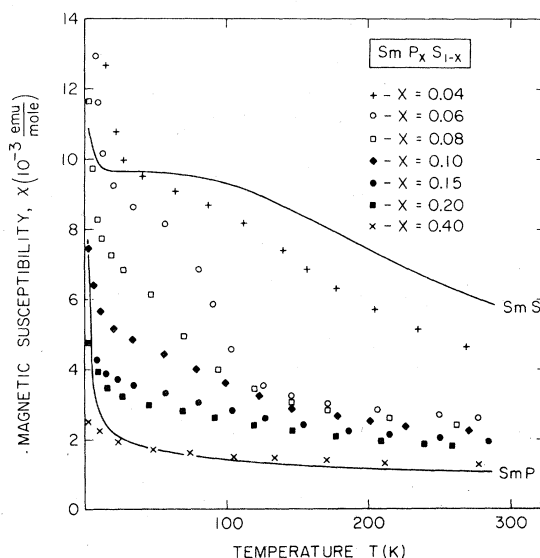

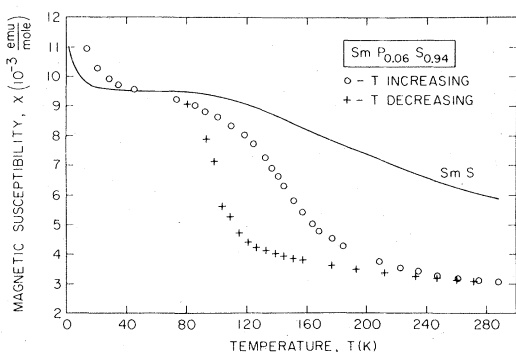FIG. 3. Magnetic susceptibility as a function of temperature for SmS, SmP, and several of their solid solutions.

FIG. 4. Magnetic susceptibility of the $SmS_{0.94}P_{0.06}$ alloy as a function of increasing and decreasing temperature.

showed very little hysteresis, while the $x = 0.04$ and 0.05 alloys were similar to the $x = 0.06$ alloy. Hysteresis was also observed in the susceptibility of the $SmS_{1-x}As_x$ alloy system.[1]

V. TEMPERATURE DEPENDENCE OF LATTICE PARAMETER

The lattice parameters of SmS, SmP, and several of the alloys were measured in the temperature range from 70 to 400 K. The linear thermal expansion coefficients for SmS and SmP were found to be 13×10^{-6} and 9.7×10^{-6}, respectively, for temperatures above 150 K. In Fig. 5 the variation in the lattice parameter with temperature is shown for the $x = 0.06$, 0.08, and 0.20 $SmS_{1-x}P_x$ alloys. The lattice constant of the $x = 0.20$ alloy exhibits a uniform con-
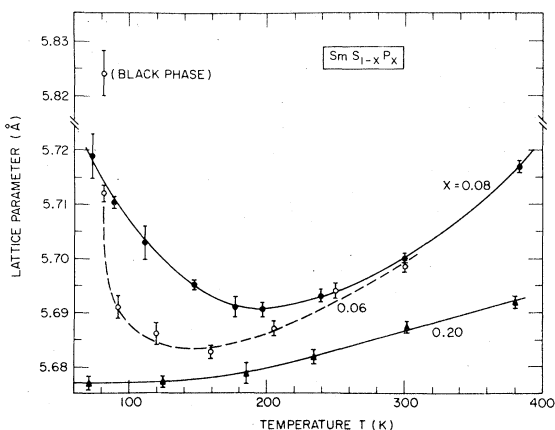

FIG. 5. Lattice parameter as a function of temperature for several of the alloys in the gold phase.

traction with decreasing temperature similar to SmS and SmP and an expansion coefficient equal to that of SmS. However, the $x = 0.06$ and 0.08 alloys have expansion coefficients almost twice that of SmS at temperatures above 250 K and show an expansion with decreasing temperature at lower temperatures. This expansion is continuous in the $x = 0.08$ alloy down to the lowest measured temperature. In the case of the alloy with $x = 0.06$, the lattice constant increases rapidly below 100 K and at 81 K two phases are clearly seen. At higher temperatures there was insufficient material in the black phase to measure the lattice constant, but at 81 K the diffraction lines corresponding to the larger lattice constant (black phase) were much more intense than those corresponding to the smaller lattice constant (gold phase). This behavior is consistent with the visual observation of a gold to black transition when the $x = 0.06$ alloy was immersed in liquid nitrogen.

The rapid increase in the susceptibility of the $x = 0.06$ alloy observed near 100 K with decreasing temperature as shown in Fig. 4 is clearly associated with the transition from the gold to the black phase. A comparison of Fig. 4 with Fig. 5 shows that the transition occurs at a temperature 10 to 15 K lower in the x-ray measurements. The lower transition temperature is probably the result of mechanical strains in the sample caused by the silicone binder since we also observe a significant broadening of the diffraction lines as the temperature decreases.

The temperature variation of the lattice parameter of the black phase in the $x = 0.03$, 0.04, and 0.05 alloys is similar to that of SmS. However, the diffraction lines were generally too broad for a precise determination of the lattice parameters. The broad lines could be the result of variations in the phosphorous concentration which would help explain the coexistence of the black and gold phases over a range of nominal compositions from 3 to 6% phosphorous. However, the systematic dependence of the lattice parameter of the black phase on the nominal composition seen in Fig. 1 suggests that any variation in the composition must be quite small.

In the gold phase the lattice parameters of the $x = 0.04$ and 0.05 alloys exhibit a temperature dependence similar to that of the $x = 0.06$ alloy with minima at about 140 K. However, the increase below 140 K is very small for these alloys. The $x = 0.04$ and 0.05 alloys appear to undergo discontinuous transitions to the black phase with decreasing temperature over a wide range of temperatures. These observations suggest that the concentration of 6% phosphorus is very near the critical composition where the transition goes from being continuous to discontinuous. In the case of the alloy with 3% phosphorus there were insufficient gold-phase diffraction lines to study the variation of the lattice constant with temperature.

VI. CONCLUSIONS

The results of the magnetic-susceptibility and lattice-parameter measurements on solid solutions of SmS with SmP have demonstrated the similarity of this alloy system to the previously studied alloys of SmS with SmAs.[1-4] This is as expected, since SmP and SmAs have simlar electronic properties and lattice parameters. The interpretation of the low-As-concentration alloys in terms of local-environmental effects[4,16] which produce a mixture of Sm^{3+} and Sm^{2+} ions also provides a consistent description of the $SmS_{1-x}P_x$ alloys in the black phase. For $x \geq 0.06$ the $SmS_{1-x}P_x$ alloys exhibit at room temperature a metallic appearance and a much smaller lattice constant and susceptibility than SmS. These properties are consistent with the Sm ion in an intermediate-valence state as in the case of SmS under pressures greater than 6.5 kbar. Intermediate valence seems to occur at a slightly smaller concentration of P than As which is expected, due to the smaller size of the P ion. At $x = 0.06$ the intermediate valence of the Sm ions is approximately 2.8 and the valence increases towards the pure trivalent state with increasing phosphorous concentration.

For $x \geq 0.15$ the alloys exhibit intermediate valence down to the lowest temperatures measured as evidenced by the fact that susceptibilities do not show a Curie-law divergence or magnetic ordering. Also, the lattice parameters exhibit the normal contraction with decreasing temperatures. Alloys with phosphorus concentrations between 4 and 8% show temperature variations of the susceptibility and lattice parameter that indicate a transition from the intermediate-valence phase to the inhomogeneous mixed-valence phase with decreasing temperature. The transition is continuous in the $x = 0.08$ alloy and becomes discontinuous near $x = 0.06$. The discontinuous character of the transition is not apparent in the susceptibility results since individual crystals of the sample exhibit different transition temperatures. This variation in transition temperature could be the result of strains, impurities, or variations in composition.

The behavior of the alloys $SmS_{1-x}As_x$ and $SmS_{1-x}P_x$ as a function of the concentration x is very similar to the behavior of SmS as a function of pressure. In both cases there is a transition from a phase where the Sm $4f$ electrons exhibit the full atomic correlations and interactions between $4f$ electrons on different atomic sites may be treated as perturbations to a phase where mixing of the $4f$ electrons with the itinerant conduction-band electrons is the essential feature. The main difference is that the low-pressure phase of SmS is a homogeneous state where all Sm ions are in the $4f^6$ configuration whereas the localized atomic state of the Sm ion in the alloy is determined by the local environment.

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*Present address: Dept. of Phys., Gustavus Adolphus College, St. Peter, Minn. 56082.

†Present address: Dept. of Phys., Univ. of Cincinnati, Cincinnati, Ohio 45221.

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