

## Magnetic susceptibility of alloys of SmAs with SmS

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Results are presented for magnetic-susceptibility measurements on the solid solutions  $\text{SmS}_{1-x}\text{As}_x$  for  $x \geq 0.7$ . The SmAs compound exhibits an antiferromagnetic transition at  $T_N = 2.0$  K and this transition is also observed in the  $x = 0.95$  alloy at the same temperature although there is a significant enhancement of the susceptibility at low temperatures. For  $x \leq 0.90$  the antiferromagnetic transition is not observed. There appears to be a crossover from the antiferromagnetic state to a state where the moment is frozen out. Room-temperature lattice parameter and magnetic-susceptibility measurements indicate that the Sm valence is approximately pure trivalent for  $x \geq 0.7$  and only shows intermediate valence at lower As concentrations.

### I. INTRODUCTION

The solid solutions of SmS with SmAs exhibit a large decrease in the lattice constant and a color change from black to gold with increasing SmAs at concentrations in the range from 5 to 10%.<sup>1</sup> This transition is similar to the transition in pure SmS under pressure at 6.5 kbar where various studies have demonstrated that the Sm ion undergoes a transition from the divalent state to a state with an intermediate valence estimated to be 2.8 from the lattice parameter. Several investigations<sup>2-5</sup> have explored the question of intermediate valence in the  $\text{SmS}_{1-x}\text{As}_x$  system and one now has a rather complete picture. For small As concentrations ( $x \leq 0.05$ ) where the alloys are black, experiments are consistent with there being a mixture of  $\text{Sm}^{2+}$  and  $\text{Sm}^{3+}$  ions where Sm ions with one or more As as nearest neighbors are trivalent. For larger As concentrations ( $x \geq 0.1$ ), the Sm ions have a homogeneous intermediate valence similar to SmS under pressure. The Sm valence is estimated to be 2.8 at  $x = 0.1$  and increases with increasing  $x$  until it reaches 3 at approximately 70% SmAs. In the intermediate range of compositions,  $0.05 < x < 0.1$ , it appears that the two phases can coexist and one observes a transition from the gold to the black phase with decreasing temperature.

Intermediate valence induced by anion substitution in SmS has also been observed in the solid solutions  $\text{SmS}_{1-x}\text{Sb}_x$ ,<sup>6,7</sup> and  $\text{SmS}_{1-x}\text{P}_x$ .<sup>8</sup> The properties of the

solid solutions of SmS with SmP are very similar to those of the alloys with SmAs. However, the  $\text{SmS}_{1-x}\text{Sb}_x$  solid solutions do not exhibit a transition to a collapsed gold phase. This is probably owing to the much larger size of the Sb ion in comparison with the As and P ions. Nevertheless there is evidence for intermediate valence and the estimated valence from the lattice constant deviates significantly from the  $2+x$  which is inherent in the ionic charge transfer associated with the substitution of a fraction  $x$  of trivalent Sb for the divalent S.

One of the most interesting properties of SmS in the collapsed intermediate valence phase is the nonmagnetic character of the Sm ion as evidenced by magnetic-susceptibility measurements. The susceptibility in the intermediate valence phase shows neither a low-temperature divergence nor an antiferromagnetic transition, but instead it saturates to a constant value as the temperature goes to zero. This is in spite of the fact that the valence corresponds to a mixing of the  $4f^6$  configuration of  $\text{Sm}^{2+}$  and the  $4f^5$  configuration of  $\text{Sm}^{3+}$  where, although the  $4f^6$  configuration has a nonmagnetic  $^7F_0$  ground state, the ground state for the  $4f^5$  configuration has a magnetic moment corresponding to a  $^6H_{5/2}$  state which is split into a  $\Gamma_7$  doublet and a  $\Gamma_8$  quartet by the cubic crystal field. This absence of magnetic order and local moments at low temperatures appears to be characteristic of intermediate valence behavior when the ground state of one of the valence states being mixed is nonmagnetic.

Since SmSb and SmAs magnetically order in an antiferromagnetic state at low temperatures with  $T_N = 2.8$  K for SmSb and 2.0 K for SmAs, one can expect to observe a competition between magnetic ordering and the demagnetization associated with intermediate valence in the solid solutions with SmS. Indeed magnetic susceptibility measurements<sup>6,7</sup> of  $\text{SmS}_{1-x}\text{Sb}_x$  alloys have shown that the antiferromagnetic transition disappears when the SmS concentration is sufficient to cause the Sm valence to deviate from its trivalent value in SmSb. At a substitution of 5% S for Sb, where the estimated Sm valence is still pure 3+, the low-temperature susceptibility although significantly enhanced as compared with that of pure SmSb clearly shows a sharp cusp at 2.8 K which is also the Néel temperature in pure SmSb. However, for increasing S substitution where the estimated Sm valence begins to deviate from the trivalent value, there is a significant rounding of the cusp at 2.8 K such that with concentrations of SmS as large as 25% there is no longer any feature at 2.8 K.

These results suggest that it would be worthwhile to make a similar investigation of the magnetic susceptibility of the  $\text{SmS}_{1-x}\text{As}_x$  alloys with SmS concentrations such that the Sm valence just deviates from pure 3+ in order to see the effect on the antiferromagnetic transition observed in SmAs. Accordingly, we have measured the low-temperature magnetic susceptibility of alloys with SmS concentrations between 0 and 30%. Also, in order to estimate the Sm valence, we have made room-temperature lattice-constant and magnetic-susceptibility measurements. In this paper, the results of this study are presented and comparisons are made with the previous study of the  $\text{SmS}_{1-x}\text{Sb}_x$  alloys.

## II. EXPERIMENTAL METHODS

The compounds SmS and SmAs were initially formed by reaction of the elements in sealed, evacuated Vycor tubes heated slowly to 500 °C. The products were finely ground, mixed proportionately, and pressed into pellets to form the  $\text{SmAs}_x\text{S}_{1-x}$  solid solutions. The pellets were sealed under vacuum in tantalum capsules, heated inductively to 1800 °C for 1 hour, and then quenched to ambient temperature. The alloys appeared as homogeneous products with color ranging from gold, through red, to silver with arsenic concentration increasing from 20% to 100%.

X-ray diffraction patterns obtained with a Guinier-de Wolff focusing camera (generally  $\pm 0.005$  Å) confirmed the NaCl structure expected of the alloys. Two faint lines, identified as  $\text{Sm}_2\text{O}_2\text{S}$ , were observed in the patterns of some intermediate composition alloys.

Magnetic susceptibility values were obtained using

apparatus described elsewhere.<sup>9</sup> Thermal stability is  $\pm 0.1$  K in the interval 4.2–100 K, improving to  $\pm 0.05$  K below 4.2 K. Random and systematic errors in the determination of molar susceptibility are expected to be within 2%.

## III. ESTIMATED VALENCE

The measured room-temperature lattice parameters and magnetic susceptibilities of the  $\text{SmS}_{1-x}\text{As}_x$  alloys as a function of As concentration are given in Table I. The lattice parameters were used to estimate the Sm valence at a given composition assuming a model of hard-sphere mixing of  $\text{Sm}^{2+}$ ,  $\text{Sm}^{3+}$ ,  $\text{S}^{2-}$ , and  $\text{As}^{3-}$  ions. Designating  $a_2$  and  $a_3$  as the lattice parameters of  $\text{Sm}^{2+}\text{S}$  and  $\text{Sm}^{3+}\text{S}$ , respectively, the Sm valence  $\nu(x)$  is given by<sup>2</sup>

$$\nu(x) = 2 + x + \frac{a_2 - a(x) - x[a_2 - a(x=1)]}{a_2 - a_3} \quad (1)$$

where  $a(x)$  is the measured lattice parameter. For  $a_2$  we use the measured lattice constant for SmS while for  $a_3$  we use 5.62 Å which is an estimate based on an interpolation from the lattice parameters of the trivalent rare-earth sulfides. This estimate of the dependence of the Sm valence on As concentration is listed in Table I under the heading  $\nu_a$ .

An estimate of the Sm valence may also be deduced from the room-temperature susceptibility. If one assumes that the room-temperature susceptibility associated with the Sm ion is a linear combination of the  $\text{Sm}^{3+}$  and  $\text{Sm}^{2+}$  contributions, then one obtains<sup>10</sup>

$$\chi(\text{SmS}_{1-x}\text{As}_x) = \epsilon(x)\chi(\text{SmAs}) + [1 - \epsilon(x)]\chi(\text{SmS}) \quad (2)$$

where  $\epsilon(x)$  is related to the Sm valence  $\nu(x)$  by

$$\nu(x) = 2 + \epsilon(x) \quad (3)$$

The resulting values for the Sm valence are listed in Table I under the heading of  $\nu_x$ .

Both estimates are more appropriate for a system with  $\text{Sm}^{3+}$  and  $\text{Sm}^{2+}$  ions randomly distributed instead of a homogeneous intermediate valent state. Therefore, they provide only a qualitative picture of how the Sm valence changes with As concentration. Nevertheless, it is reasonable to conclude that the room-temperature Sm valence is near 2.8 for As concentrations slightly greater than that required to produce the collapsed phase and that the valence increases continuously to a pure trivalent value at a concentration somewhere between 55 and 90% As.

TABLE I. Lattice constants and magnetic susceptibilities at  $T = 300$  K for the  $\text{SmS}_{1-x}\text{As}_x$  alloys studied with estimates for the Sm valence. The  $\nu_a$  and  $\nu_x$  numbers are the estimates of the Sm valence as determined by the lattice constants and magnetic susceptibilities, respectively.

Composition $x$	Lattice Parameter $a$ (Å)	Magnetic Susceptibility $\chi$ ( $10^{-3}$ emu/mole)	Estimated Valence	
			$\nu_a$	$\nu_x$
0.00	5.96	5.58	2.00	2.00
0.20	5.74	1.94	2.83	2.80
0.40	5.77	1.43	2.91	2.91
0.55	5.80	1.19	2.95	2.96
0.70	5.83	1.06	2.99	2.99
0.80	5.86	1.03	2.99	2.99
0.90	5.89	1.015	3.00	3.00
0.95	5.90	1.01	3.00	3.00
1.00	5.92	1.005	3.00	3.00

#### IV. MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility as a function of temperature between 1.5 and 30 K is shown in Fig. 1 for the  $\text{SmS}_{1-x}\text{As}_x$  alloys with  $x = 1.00, 0.95,$  and  $0.80$ . The susceptibility of SmAs exhibits an antiferromagnetic transition at  $T_N = 2.0$  K. This transition is also clearly observed at the same temperature in the 0.95 alloy where the Sm valence is estimated to be pure trivalent. However, below 20 K the susceptibility of the 0.95 alloy is significantly enhanced in comparison with that of SmAs. The susceptibility of the 0.80 alloy is also enhanced for temperatures greater than 5 K, but below 5 K it becomes nearly temperature independent. In an attempt to understand the enhancement, we have tried to fit the paramagnetic susceptibility of the  $x = 0.95$  alloy to a theoretical expression that adequately describes the paramagnetic susceptibility of SmAs.

The model for SmAs consists of  $\text{Sm}^{3+} (4f^5) {}^6H$  ions in a cubic crystal field which interact by an iso-

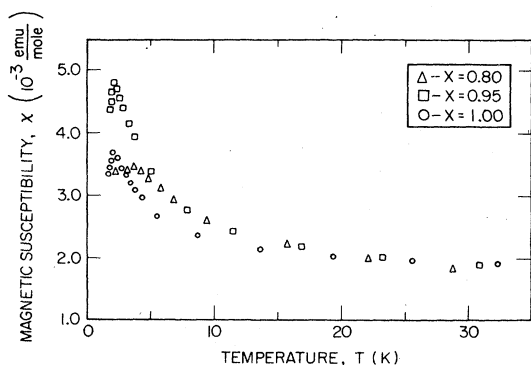


FIG. 1. Magnetic susceptibility vs temperature from 1.5 to 30 K for  $x = 0.80, 0.95,$  and  $1.00$  alloys in the  $\text{SmS}_{1-x}\text{As}_x$  system.

tropic exchange coupling of the spins. In the molecular-field approximation, the Hamiltonian for a single Sm ion is written

$$H = \lambda \bar{L} \cdot \bar{S} + H_{\text{CEF}} + 2\mu_B S_z H_{\text{ex}}, \quad (4)$$

where  $\lambda$  is the spin-orbit parameter,  $H_{\text{CEF}}$  is the cubic crystal-field Hamiltonian specified by the parameters  $A_4 \langle r^4 \rangle$  and  $A_6 \langle r^6 \rangle$ , and  $H_{\text{ex}}$  is the exchange-molecular field related to the exchange parameter  $J_{ff}$  by

$$2\mu_B H_{\text{ex}} = -J_{ff} \langle S_z \rangle. \quad (5)$$

Our calculation of the resulting paramagnetic susceptibility  $\chi_f(T)$  follows that of deWijn *et al.*<sup>11</sup> and uses all matrix elements within and between the  $J = \frac{5}{2}$  and  $J = \frac{7}{2}$  multiplets. It was found that one must use the full two-level matrix for an adequate description and that the inclusion of the  $J = \frac{9}{2}$  level is unnecessary since it produces only a 1% change in the susceptibility at 300 K for the values of the parameters appropriate for SmAs.

The measured susceptibility was compared with

$$\chi(T) = \chi_f(T) + \chi_0, \quad (6)$$

where  $\chi_0$  is a temperature-independent contribution due primarily to the diamagnetism of the ion cores and filled bands. A least-square fit of the SmAs susceptibility between 2.5 and 300 K was used to determine values for the parameters  $\lambda$ ,  $A_4 \langle r^4 \rangle$ ,  $A_6 \langle r^6 \rangle$ ,  $J_{ff}$ , and  $\chi_0$ . The susceptibility could be fit within 1% and the resulting parameter estimates are

$$\lambda/k = 415 \pm 15 \text{ K}, \quad A_4 \langle r^4 \rangle/k = 125 \pm 15 \text{ K},$$

$$A_6 \langle r^6 \rangle/k = 8 \pm 3 \text{ K}, \quad J_{ff}/k = -1.25 \pm 0.1 \text{ K},$$

and

$$\chi_0 = -90 \pm 20 \times 10^{-6} \text{ emu/mole}.$$

The estimates for  $\lambda/k$  and  $A_4\langle r^4\rangle/k$  are consistent with previous ones of  $401 \pm 5$  K and  $131 \pm 14$  K by Jones<sup>12</sup> from Knight-shift measurements. These Knight-shift data were insufficient to determine  $J_{ff}$  and the  $A_6\langle r^6\rangle$  parameter was not estimated since crystal-field effects arising from the  $J = \frac{7}{2}$  multiplet were ignored in the fit of the data. Our estimate for  $J_{ff}$  seems reasonable since  $T_N = 2.0$  K and the estimates for  $A_6\langle r^6\rangle$  and  $\chi_0$  are not unreasonable. Therefore, we believe the susceptibility of SmAs is well understood. However, it should be noted that Schottky anomalies observed in specific-heat measurements of SmP and SmSb have yielded values for  $A_4\langle r^4\rangle/k$  of  $103 \pm 4$  K and  $66 \pm 2$  K for SmP and SmSb, respectively, and suggest a value of  $89 \pm 5$  K for SmAs based on the assumption that  $A_4\langle r^4\rangle$  is inversely proportional to the fifth power of the lattice constant as observed in several of the rare-earth pnictides.<sup>13</sup> This estimate is inconsistent with our susceptibility results and the Knight-shift results as are the specific-heat estimates for SmP and SmSb with the Knight-shift measurements on these compounds.<sup>12</sup>

Our attempt to fit the susceptibility of the  $x = 0.95$  alloy with our calculated expression indicates that the crystal-field and  $\chi_0$  parameters are unchanged as compared with their values for SmAs while  $\lambda$  increases by 15% and  $J_{ff}$  becomes much less negative and perhaps even positive. However, the quality of the fit as indicated by the reduced  $\chi^2$  was a factor of 5 poorer than that of the fit for SmAs, and therefore the theoretical expression may not adequately describe the temperature dependence in the case of the alloy. Previously we had attributed a similar enhancement of the susceptibility in Sb-rich  $\text{SmS}_{1-x}\text{Sb}_x$  alloys to a decrease in the crystalline fields<sup>6,7</sup> since  $T_N$  did not change as in the present case, but our fits do not confirm this interpretation.

The magnetic susceptibility measurements for several  $\text{SmS}_{1-x}\text{As}_x$  alloys near the Néel temperature of SmAs are shown in Fig. 2. The cusp associated with the antiferromagnetic transition seen in both SmAs and  $\text{SmS}_{0.05}\text{As}_{0.95}$  at 2.0 K is eliminated with only 10% S substituted for As. If all the Sm ions are trivalent, we expect that each S substitution will introduce an electron into the conduction band as is observed.<sup>3</sup> This should have a significant effect on the exchange coupling between the Sm spins. However, the saturation of the susceptibility for  $x \leq 0.9$  to a near constant value as  $T \rightarrow 0$  is a behavior characteristic of intermediate valence. It is surprising that this should occur for  $x > 0.7$  since the Sm valence as estimated by room-temperature measurements of the lattice constant and magnetic susceptibility is essentially pure trivalent. Also, one observes that the temperature at which the saturation takes place increases significantly with increasing S substitution. Therefore, the As-rich  $\text{SmS}_{1-x}\text{As}_x$  system behaves as

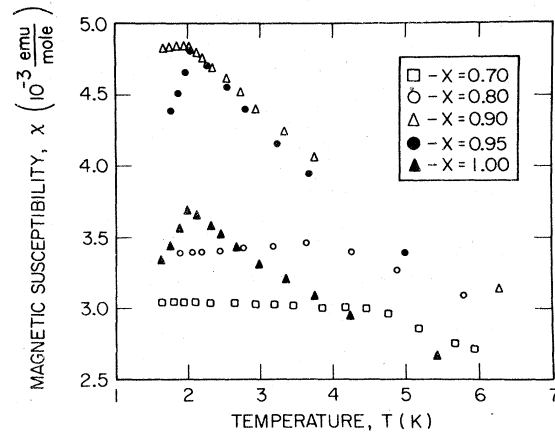


FIG. 2. Low-temperature magnetic susceptibility for several alloys in the  $\text{SmS}_{1-x}\text{As}_x$  system.

if there is a spin-fluctuation temperature which increases with S concentration. This increase was not observed in the  $\text{SmS}_{1-x}\text{Sb}_x$  alloys,<sup>6,7</sup> however. In that case the conduction-electron concentration remains fixed at about 0.1 for nearly the entire alloy composition range while the conduction-electron concentration in  $\text{SmS}_{1-x}\text{As}_x$  is approximately  $1 - x$  for the alloys studied.

## V. CONCLUSIONS

In SmAs where valence fluctuations are energetically unfavorable, the interactions between spins cause an antiferromagnetic transition which suppresses spin fluctuations. This is the usual situation in rare-earth compounds. The susceptibilities of rare-earth compounds that do exhibit intermediate valence are very similar to the susceptibilities of rare-earth impurity atoms in metals. The impurity problem is adequately described by the Anderson model<sup>14</sup> and this model is well understood.<sup>15,16</sup> The susceptibility may increase monotonically to a finite value as the temperature decreases or it may exhibit a broad maximum depending on the values of the various parameters.<sup>15</sup> Unfortunately, at present there is no satisfactory theory for concentrated rare-earth systems with intermediate valence and the impurity model is certainly not adequate for the description of the  $\text{SmS}_{1-x}\text{As}_x$  alloys owing to the interaction between spins. Nevertheless, in such a system we expect to observe a competition between the interactions between spins which stabilize the moments and the freezing out of this degree of freedom in the case of an impurity as the temperature goes to zero.

The valence of the Sm ion in the  $\text{SmS}_{1-x}\text{As}_x$  alloys with  $x \geq 0.7$  appears to be a pure trivalent state;

however, the difference in energy between the divalent and the trivalent states must be decreasing as  $x$  decreases since one clearly observes intermediate valence for  $x \leq 0.55$ . Also, the conduction-electron concentration is increasing as  $1 - x$ . Therefore, it is reasonable to assume that the effective coupling between the Sm moment and the conduction electrons increases with decreasing  $x$  and that this produces a crossover from the antiferromagnetic state to a state where the moment is frozen out. This appears to be what we are observing. However,

without a reliable microscopic theory these conclusions are quite speculative.

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