

## Intermediate valence in alloys of SmSe with SmAs

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Results are presented for lattice-parameter and magnetic-susceptibility measurements on a series of solid solutions of SmSe with SmAs. The lattice parameter shows a continuous transition (collapse in excess of Vegard's law) with increasing SmAs concentration similar to the valence transition in SmSe under increasing pressure. The estimated average Sm valence increases from divalent to trivalent as the SmAs concentration increases from 0 to 70%. This behavior is compared with the previously observed first-order valence transition in the solid solutions of SmS with SmAs at 5 to 10 at. % SmAs. The magnetic susceptibilities of the  $\text{SmSe}_{1-x}\text{As}_x$  alloys with  $x < 0.1$  show a temperature dependence characteristic of a mixture of divalent and trivalent Sm ions. At higher concentrations of As the behavior is characteristic of Sm ions with intermediate valence.

### I. INTRODUCTION

Alloying with SmAs and SmP has proved to be a very effective method for inducing a valence transition in SmS at ambient pressure and temperature.<sup>1-6</sup> At a critical concentration in the range of 5 to 10 at. % of SmAs or SmP there is a first-order transition to a metallic intermediate-valence phase.<sup>7</sup> This transition is similar to the first-order semiconductor-to-metal transition in SmS under pressure at 6.5 kbars where there is a large decrease in the lattice parameter and a color change from black to gold. Experiments have indicated that dilute substitutions of trivalent As for the divalent S in SmS cause the six neighboring Sm ions to become trivalent but the extra electrons remain localized.<sup>4</sup> As the As concentration is increased there is an abrupt transition to a homogeneous intermediate-valence phase for the Sm ions with electrons delocalized into the conduction band.<sup>3</sup> Nearly identical behavior has been found in the alloys of SmP with SmS.<sup>6</sup> However, the substitution of another Sm mononictide, SmSb, does not induce a discontinuous transition in SmS.<sup>8</sup> This difference has been attributed to the much larger size of the Sb ion in comparison with the As and P ions.

The first-order character of the pressure-induced valence transition in SmS distinguishes it from the continuous transitions observed in SmSe and SmTe. There have been a number of attempts to account for this difference in terms of the fundamental physical parameters that characterize these compounds; however, this problem is still unresolved. With a view to provide more experimental information it is of interest to study alloys of SmSe and SmTe with the Sm mononictides. In

this paper we report lattice-parameter and magnetic-susceptibility measurements on alloys of SmSe with SmAs.

### II. EXPERIMENTAL METHODS

The  $\text{SmSe}_{1-x}\text{As}_x$  alloys were prepared in the following manner. Compounds of SmSe and SmAs were produced by reaction of the elements in sealed, evacuated Vycor tubes heated to 600 °C at a rate of five degrees per hour. The compounds were mixed in the required proportions for the alloys, pressed into pellets, and sealed under vacuum in tantalum capsules. The encapsulated samples were heated in an induction furnace to 1800 °C for 3 h and then quenched to ambient temperature. The alloy samples thus produced were sintered pellets with color ranging from black to blue to silver, with increasing As concentration.

Lattice-parameter measurements were obtained with a Guinier-de Wolff focusing camera. The diffraction patterns showed the samples to be single phase with the expected NaCl-type crystal structure. The uncertainties in the lattice parameters obtained were  $\pm 0.005 \text{ \AA}$  or less.

The magnetic-susceptibility measurements were made using the Faraday method with apparatus that has been previously described.<sup>9</sup> Random and systematic errors in the determination of the molar susceptibility are estimated to be less than 2%. Thermal stability associated with the apparatus is  $\pm 0.05 \text{ K}$  below 4.2 K,  $\pm 0.1 \text{ K}$  in the interval 4.2–100 K, and  $\pm 0.5 \text{ K}$  near room temperature.

### III. ESTIMATED VALENCE

The measured room-temperature lattice parameters of the solid solutions  $\text{SmSe}_{1-x}\text{As}_x$  are shown

in Fig. 1 as a function of the SmAs concentration. For  $x \geq 0.1$  there is a significantly greater decrease in the lattice parameter than what would result from the purely ionic charge transfer inherent in the substitution of trivalent As anions for the divalent Se anions. For comparison, the upper dashed curve gives the lattice parameter from Vegard's law under the assumption that each As substituted for Se converts one divalent Sm ion to a trivalent Sm ion. Thus there is evidence for a chemically induced continuous transition similar to the continuous transition to a metallic phase in pure SmSe under increasing pressure.

Also shown in Fig. 1 is an estimate of the Sm valence  $v(x)$  deduced from the lattice parameter by

$$v(x) = 2 + x + \frac{(1-x)a(0) + xa(1) - a(x)}{a(0) - a(\text{Sm}^{3+}\text{Se})}, \quad (1)$$

where  $a(x)$  is the measured lattice parameter of the alloy with SmAs concentration  $x$  and  $a(\text{Sm}^{3+}\text{Se}) = 5.84 \text{ \AA}$  is an estimated value based on an interpolation from the lattice parameters of neighboring trivalent rare-earth selenides. Although this formula is based on a linear interpolation for the lattice parameter assuming a mixture of  $\text{Sm}^{2+}$  and  $\text{Sm}^{3+}$  ions, it has been found to give a reliable estimate for the case of homogeneous intermediate valence.<sup>2</sup>

The average valence initially increases as if each As produces a trivalent Sm ion. The increase of the Sm valence with As concentration then be-

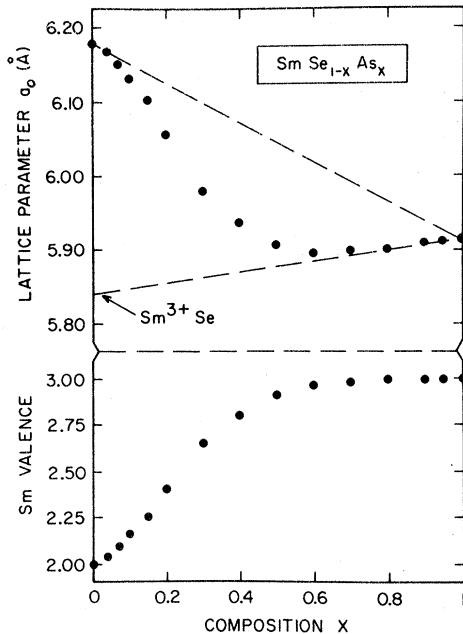


FIG. 1. Lattice parameter and estimated Sm valence as a function of the alloy composition.

comes greater reaching a maximum near  $x=0.2$ , and for  $x \geq 0.7$  the Sm is essentially trivalent.

#### IV. MAGNETIC SUSCEPTIBILITY

The measured magnetic susceptibilities of SmSe, SmAs, and several of their solid solutions as a function of the temperature from 2.0 to 300 K are shown in Fig. 2 in order to illustrate the dependence on composition.

The SmSe susceptibility can be described by a lattice of  $\text{Sm}^{2+}(4f^6)^7F$  ions having a nonmagnetic  $J=0$  ground state plus magnetic impurities to account for the Curie-like rise at low temperatures. The model Hamiltonian for the  $\text{Sm}^{2+}(4f^6)^7F$  lattice is

$$H = \lambda \sum_i \vec{L}_i \cdot \vec{S}_i - \sum_{i < j} J_{ij} \vec{S}_i \cdot \vec{S}_j, \quad (2)$$

where  $\lambda$  is the spin-orbit coupling constant and  $J_{ij}$  is the isotropic exchange coupling between Sm spins at the  $i$  and  $j$  sites. Crystal-field effects are neglected since the cubic crystal field can not lift the degeneracy of the first excited state ( $J=1$ ) and is not expected to produce a significant change in the separation between  $J$  manifolds. The susceptibility of the  $\text{Sm}^{2+}$  lattice was calculated within the molecular-field approximation using all the  $J$  manifolds. Details of the susceptibility calculation are given in the Appendix. The resulting expression depends on the parameters  $\lambda$  and  $J = \sum_i z_i J_i$ , where  $z_i$  is the number of Sm  $i$ th equivalent neighbors and  $J_i$  is the appropriate exchange interaction. For the contribution from magnetic impurities we assume a simple Curie-law susceptibility which should be valid at lower temperatures independent of the particular species of ions present and their local environments.

The SmSe susceptibility data were compared with the expression

$$\chi(T) = (1 - c) \chi(\text{Sm}^{2+}, T) + R \frac{N_A \mu_B^2}{3kT}, \quad (3)$$

where  $\chi(\text{Sm}^{2+}, T)$  is the  $\text{Sm}^{2+}$  lattice contribution,  $1 - c$  is the fraction of  $\text{Sm}^{2+}$  present, and  $R$  is the coefficient of the Curie term. A least-squares fit of the SmSe susceptibility data between 2.0 and 300 K was used to determine the parameters  $J$ ,  $c$ , and  $R$  with the spin-orbit parameter  $\lambda$  set equal to the free-ion value of 422 K (36.4 meV). The susceptibility could be fitted within 0.3% and the resulting estimates are

$$J = 4.8 \pm 0.5 \text{ K } (0.41 \pm 0.04 \text{ meV}),$$

$$c = 0.03 \pm 0.01,$$

and

$$R = 0.014 \pm 0.005.$$

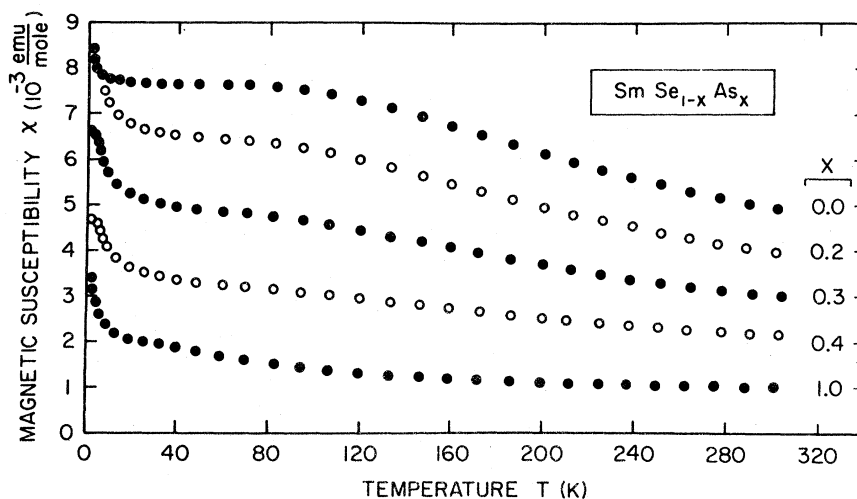


FIG. 2. Magnetic susceptibility as a function of temperature for SmSe, SmAs, and several of their solid solutions.

This would suggest, since the SmSe has the stoichiometric composition, that 3% of the Sm ions are trivalent. For  $\text{Sm}^{3+}$  ions one expects an effective magnetic moment  $\mu_{\text{eff}}$  between 0.41 and 0.85 where the upper limit is appropriate to the free-ion  $J = \frac{5}{2}$  ground state and the lower limit corresponds to a doublet ground state resulting from a cubic crystal-field splitting of the  $J = \frac{5}{2}$  manifold. Identifying the Curie-law contribution with  $\text{Sm}^{3+}$  ions, i.e.  $R = c\mu_{\text{eff}}^2$ , one obtains a best-fit value of 0.68 for  $\mu_{\text{eff}}$  which is consistent. However, other data argue against this interpretation. When susceptibility data for similarly prepared SmS samples are fitted to Eq. (3) one obtains

$$J = 13.8 \pm 0.5 \text{ K } (1.19 \pm 0.04 \text{ meV}),$$

$$c = 0.001 \pm 0.005,$$

and

$$R = 0.021 \pm 0.005.$$

We see that the coefficient of the Curie term in SmS is about the same as in SmSe while the value for  $c$  precludes any appreciable concentration of  $\text{Sm}^{3+}$  in the SmS samples. We have considerable confidence in the physical significance of these estimates since Eq. (3) is expected to describe adequately the data and our best-fit estimate of 1.19 meV for the exchange parameter  $J$  in SmS is in excellent agreement with a value of 1.20 meV from inelastic neutron scattering measurements.<sup>10</sup> Therefore, the most reasonable explanation for the Curie term in SmS is superparamagnetism associated with small concentrations of unknown magnetic impurities, and it is likely that such impurities make the major contribution to  $R$  in SmSe. A speculative interpretation of the very large value for  $c$  in

SmSe is that associated with vacancies there is the creation of  $\text{Sm}^{3+}$  ions which exhibit a reduced effective moment owing to the interaction between the ions. This explanation is suggested by the observation that SmSe samples heated to 2100°C during preparation have an appreciably larger lattice constant than the samples used for the susceptibility studies which were heated to 1800°C.

The estimate for the exchange parameter  $J$  in SmSe is consistent with a previous estimate<sup>11</sup> from susceptibility measurement when that estimate is adjusted for a different choice for the value of the spin-orbit parameter. We find that if we allow our fit to also determine the spin-orbit parameter it agrees with the free-ion value of 422 K in SmS and SmSe, and therefore we believe this is the proper choice. Furthermore this choice is consistent with the inelastic neutron scattering measurements of SmS.<sup>10</sup>

Since the lattice constant of the  $\text{SmSe}_{1-x}\text{As}_x$  alloys initially decreases as if each As substitution produces a trivalent Sm ion, it is of interest to also compare with Eq. (3) the susceptibility data for the alloys with low concentrations of As. For alloys with As concentrations up to 10% we find that the data can be fit within 1%. The three parameters  $J$ ,  $c$ , and  $R$  increase with increasing As substitution. The estimated values in the 10 at. % As alloys are

$$J = 8.7 \pm 1.0 \text{ K } (7.5 \pm 0.9 \text{ meV}),$$

$$c = 0.15 \pm 0.02,$$

and

$$R = 0.019 \pm 0.005.$$

Thus, there is an appreciable increase in the exchange parameter as compared with pure SmSe.

The value for  $c$  is consistent with the estimate of 16%  $\text{Sm}^{3+}$  from the lattice-parameter measurement and  $R$  shows a small increase indicating a possible small Curie-law contribution from the increased  $\text{Sm}^{3+}$  concentration. If one identifies the increase in  $R$  over its value in SmSe with the increased  $\text{Sm}^{3+}$  concentration, one finds an effective magnetic moment of 0.2 for the  $\text{Sm}^{3+}$  ions. Such a very small  $\mu_{\text{eff}}$  could be the result of either interactions between  $\text{Sm}^{3+}$  ions or intermediate-valence effects. However, since the fits are so good it is unlikely that there is appreciable intermediate valence. At higher As concentrations the fits become unacceptable.

For all the alloys the susceptibility at sufficiently high temperatures is expected to be a linear combination of the  $\text{Sm}^{3+}$  and  $\text{Sm}^{2+}$  weighted according to the average valence as has been observed in other intermediate-valence systems.<sup>5,6,12</sup> If one compares the room-temperature susceptibility to the linear interpolation

$$\chi(\text{SmSe}_{1-x}\text{As}_x, T) = [1 - \epsilon(x)]\chi(\text{SmSe}, T) + \epsilon(x)\chi(\text{SmAs}, T), \quad (4)$$

one obtains an estimate for the valence of  $2 + \epsilon(x)$ , which is in qualitative agreement with the estimate from the lattice-constant measurements.

In SmAs where the Sm is trivalent 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. The Curie-law behavior associated with the  $\Gamma_7$  doublet terminates in an antiferromagnetic transition near 2.0 K. The paramagnetic susceptibility of SmAs can be quantitatively described in terms of the model

$$H = \lambda \sum_i \vec{L}_i \cdot \vec{S}_i - \sum_{i < j} J_{ij} \vec{S}_i \cdot \vec{S}_j + H_{\text{CEF}}, \quad (5)$$

where  $H_{\text{CEF}}$  is the cubic-crystal-field Hamiltonian. The susceptibility could be fitted to within 1% to the expression

$$\chi(T) = \chi(\text{Sm}^{3+}, T) + \chi_0, \quad (6)$$

where  $\chi(\text{Sm}^{3+}, T)$  is the contribution from the model Hamiltonian for the  $\text{Sm}^{3+}$  lattice calculated within the molecular-field approximation using the  $J = \frac{5}{2}$  and  $\frac{7}{2}$  multiplets and  $\chi_0$  is a temperature-independent contribution due primarily to the diamagnetism of the ion cores and filled bands.  $\chi(\text{Sm}^{3+}, T)$  depends on the spin-orbit parameter  $\lambda$ , the exchange parameter  $J$ , and the crystal-field parameters  $A_4\langle r^4 \rangle$  and  $A_6\langle r^6 \rangle$ . The resulting least-square-fit estimates are

$$\lambda = 418 \pm 10 \text{ K}, \quad J = -1.9 \pm 0.5 \text{ K},$$

$$\chi_0 = -82 \pm 20 \times 10^{-6} \text{ emu/mole}, \quad A_4\langle r^4 \rangle = 125 \pm 15 \text{ K},$$

and

$$A_6\langle r^6 \rangle = 9 \pm 5 \text{ K}.$$

These estimates are reasonable as has been previously discussed,<sup>13</sup> and therefore we believe that SmAs is well understood in terms of a lattice of  $\text{Sm}^{3+}$  ions. One might expect Eq. (6) to be also applicable to the  $\text{SmSe}_{1-x}\text{As}_x$  alloys with  $x \geq 0.7$  where the Sm is estimated to be trivalent from the lattice-constant measurements. However, we could not obtain good fits for the alloys. This was also the case with the previously studied  $\text{SmS}_{1-x}\text{As}_x$  alloys.<sup>5</sup>

The magnetic-susceptibility data for several of the  $\text{SmSe}_{1-x}\text{As}_x$  alloys below 10 K are shown in Fig. 3 in order to illustrate the behavior near the Néel temperature of SmAs. With increasing Se substitution for As the peak associated with the antiferromagnetic transition broadens and shifts to higher temperatures. Once the Se concentration is sufficiently large that the average valence deviates from pure trivalence there is little evidence

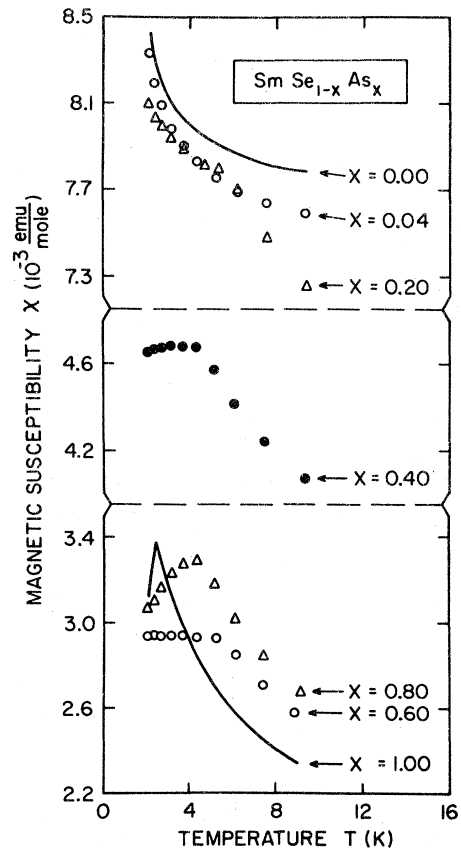


FIG. 3. Low-temperature magnetic susceptibility for several alloys in the  $\text{SmSe}_{1-x}\text{As}_x$  system.

for an antiferromagnetic transition or a Curie-law divergence.

The susceptibility of the alloys with As concentrations in the range of 30 at. % to 60 at. % is typical of intermediate-valence behavior as seen in SmS under pressure. We have attempted to fit the susceptibility of these alloys to a generalization of Eq. (4) which introduces phenomenologically<sup>14</sup> a characteristic energy scale  $kT_f$  by replacing the temperature  $T$  by  $T + T_f$ :

$$\chi(\text{SmSe}_{1-x}\text{As}_x, T) = [1 - \epsilon(x)]\chi(\text{SmSe}, T + T_f) + \epsilon(x)\chi(\text{SmAs}, T + T_f). \quad (7)$$

The parameter  $kT_f$  is usually identified with the width of the  $4f$  band due to hybridization; however, there is no convincing theoretical treatment of intermediate valence to justify the prescription contained in Eq. (7). We find that in the case of the  $0.3 \leq x \leq 0.6$  alloys the data for  $T \geq 20$  K can be fitted within 1% to Eq. (7) with  $T_f \sim 50$  K and  $\epsilon(x)$  having values about 0.1 less than the estimates from the lattice parameters. The best-fit value for  $T_f$  depends strongly on the range of low-temperature data used in the fit. As lower-temperature data are used, the value of  $T_f$  increases but the fit deteriorates rapidly as to make the parameter estimate meaningless. Therefore, the 50 K for  $T_f$  represents an order-of-magnitude estimate which is similar to the 100 K which has been estimated for the energy scale appropriate to SmS under pressure.<sup>14</sup>

It is not surprising that the prescription of Eq. (7) is inadequate to describe the data over the temperature range studied. A full theoretical description of intermediate valence is necessary for detailed analysis of such data. However, we feel that the large  $T_f$  we find is convincing evidence for intermediate valence as opposed to a mixture of divalent and trivalent Sm ions in the alloys with As concentrations between 30 at. % and 60 at. %. In analyzing our data we have ignored the possibility that the effective valence might be a function of temperature since this would introduce more uncertain parameters. However, there seems to be some evidence for this in the  $x=0.2$  alloy whose susceptibility shows an anomalous increase below 20 K suggesting a transition to a lower-average-valence phase possibly consisting of a mixture of divalent and trivalent Sm ions. The  $T_f$  estimate and the color of the alloy at room temperature indicate intermediate valence at  $T > 20$  K. Also, there is an unresolved question concerning the retention of the antiferromagnetic correlations in the intermediate-valence alloys. As seen in Fig. 3 the susceptibilities of the  $x=0.4$  and 0.6 alloys exhibit an abrupt saturation near 4 K. This would

suggest that antiferromagnetic correlations are not completely suppressed in the intermediate-valence phase.

## V. DISCUSSION

The most important result from this study is the observation that alloying SmSe with SmAs produces a continuous transition to an intermediate-valence phase. Thus the distinction between SmS and SmSe in the order of the valence transition when induced by applied pressure is also observed in the chemically induced transition resulting from the substitution of trivalent As anions.

Both electronic and lattice contributions to the free energy can be important in determining the character of the valence transition, and there is still uncertainty in accounting for the first-order transition in SmS and the continuous transition in SmSe with pressure. SmS and SmSe are semiconductors with very similar electronic structures except that the gap for exciting an electron from the  $4f$  level into the conduction band [ $4f^6 - 4f^5 5d(t_{2g})$ ] is much larger in SmSe. Experimental estimates<sup>15</sup> for the excitation energies are 0.06 to 0.25 eV in SmS and 0.46 in SmSe. Also, whereas the bottom of the conduction band in SmS has  $5d(t_{2g})$  character, it is likely that there is considerable  $6s$  character at the bottom in SmSe. Recently, Jayaraman and Maines<sup>16</sup> have suggested that, owing to the  $5d-6s$  hybridization at the bottom of the SmSe conduction band, the density of states at the Fermi energy might be too small to permit a first-order transition. Clearly a smaller density of states at the Fermi energy implies a larger increase in the energy with the number of electrons transferred to the conduction band which must favor a gradual transition regardless of the mechanism that is assumed to drive the transition. Earlier speculation on the explanation for the order of the transition has concentrated on the mechanisms that can accelerate the transition. These have been reviewed most recently by Robinson<sup>7</sup> and Jayaraman and Maines.<sup>16</sup> The compression shift mechanism of Hirst<sup>17</sup> and related generalizations by Varma and Heine<sup>18</sup> and Penney and Melcher<sup>19</sup> as well as Falicov-Kimbal-type Coulomb effects<sup>20-22</sup> can produce continuous or discontinuous transitions. Unfortunately it is impossible to distinguish from experiments which of these mechanisms is the dominant one or to decide whether the parameters required to reproduce the correct order of the transitions have a microscopic justification.

Chemical alloying certainly does not simplify the description of the phase transition and therefore one would not have been able to confidently

predict the order of the transition in  $\text{SmSe}_{1-x}\text{As}_x$  from the fact that it is first order in the  $\text{SmS}_{1-x}\text{As}_x$  and  $\text{SmS}_{1-x}\text{P}_x$  alloys. It is of interest to compare in some detail our results for the  $\text{SmSe}_{1-x}\text{As}_x$  alloys with the information that has been obtained from several studies of the  $\text{SmS}_{1-x}\text{As}_x$  and  $\text{SmS}_{1-x}\text{P}_x$  systems.<sup>1-6</sup> Since P and As are trivalent one expects them to act as acceptor impurities in the Sm monochalcogenides with each impurity converting one divalent Sm into a trivalent Sm ion. In the case of SmSe our observations on the dilute As alloys are consistent with this picture. However, for the case of SmS both As and P produce a more complicated "molecular" impurity state<sup>23</sup> where all six nearest neighbors of the substituted anion are trivalent. This is deduced from the observation that the average Sm valence in SmS varies as  $3 - (1-x)^6$  with the As or P concentration  $x$  for  $x \leq 0.05$  where electron localization is suggested by the transport measurements. This difference between the SmS and SmSe dilute alloys can be qualitatively understood in terms of the larger excitation gap in SmSe which implies a more stable divalent Sm configuration. One can speculate that the inhomogeneous mixture of divalent and trivalent Sm ions in the dilute alloys is the result of insufficient interatomic hybridization between the Sm 4*f* and 5*d* states.<sup>24</sup> The hybridization depends on the excitation gap, so one would expect to observe the inhomogeneous mixed-valence phase at higher As concentrations in the SmSe alloys. This is found in the susceptibility data where the mixed state can be identified by the Curie-like increase at low temperatures.

As the As concentration increases the presence of trivalent Sm ions<sup>16</sup> and the hybridization of the Sm 4*f* states with the As valence states<sup>23</sup> both tend to reduce the excitation gap. This will permit the transition to the intermediate-valence phase. In the  $\text{SmS}_{1-x}\text{As}_x$  and  $\text{SmS}_{1-x}\text{P}_x$  alloys there is a first-order transition in which the average valence changes from 2.3 to 2.8 approximately. In the case of the  $\text{SmSe}_{1-x}\text{As}_x$  alloys one can speculate that the As concentration required to reduce the gap to the value where the transition occurs in SmS is such that the average valence is already 2.5 or greater. In that case, a discontinuous collapse is unlikely.

Finally, the alloys of SmS and SmSe with SmAs are very similar at the higher As concentrations. In both cases the antiferromagnetic ordering observed in SmAs is eliminated with decreasing As concentration.<sup>5</sup> In the range of compositions where the valence is intermediate the magnetic susceptibilities saturate at low temperatures. Also the metallic appearance and color of both alloys as a function of SmAs concentration are very similar

except below 40 at. % SmAs where the SmS alloys become red and then gold as the transition composition is approached. Therefore, we conclude that the alloys of SmSe with SmAs exhibit a continuous transition to an intermediate-valence state.

#### ACKNOWLEDGMENT

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#### APPENDIX

The paramagnetic susceptibility associated with the 4*f* electrons is given by

$$\chi(T) = -N\mu_B \frac{\langle L_x + 2S_x \rangle}{H}. \quad (\text{A1})$$

In the mean-field approximation the exchange interaction is replaced by

$$-J\langle S_x \rangle \sum_i S_{ix}. \quad (\text{A2})$$

This term together with the Zeeman interaction is treated perturbatively in calculating  $\langle L_x + 2S_x \rangle$  to first order in the applied field  $H$ . The resulting expression for the susceptibility is<sup>25</sup>

$$\chi(T) = -N\mu_B^2 \left( \sigma_{L+2S, L+2S} - \frac{J(\sigma_{L+2S, S})^2}{1 + J\sigma_{S, S}} \right), \quad (\text{A3})$$

where

$$\sigma_{A, B} = \sum_n \left( -\frac{\langle n|A_x|n\rangle\langle n|B_x|n\rangle}{kT} + 2 \sum_{n' \neq n} \frac{\langle n|A_x|n'\rangle\langle n'|B_x|n\rangle}{E_n^{(0)} - E_{n'}^{(0)}} \right) \frac{e^{-E_n^{(0)}/kT}}{Z}. \quad (\text{A4})$$

Here we have assumed that the unperturbed Hamiltonian describes noninteracting ions and therefore  $|n\rangle$  denotes the unperturbed eigenstates for the ion. Note that this expression is not applicable to the case of intermediate valence where, because of the hybridization with the conduction electrons, the unperturbed Hamiltonian is not a sum of single-ion terms.

For the lattice of  $\text{Sm}^{2+}(4f^6)^7F$  ions where the model of Eq. (2) is applicable, the eigenstates  $|n\rangle = |L=3, S=3, JM\rangle$  since the unperturbed Hamiltonian consists of the spin-orbit term only. Because of the small spin-orbit parameter it is necessary to include the first three  $J$  multiplets in order to calculate the susceptibility within 1% accuracy at room temperature.

For the lattice of  $\text{Sm}^{3+}(4f^5)^6H$  ions the unperturbed Hamiltonian consists of the cubic crystal-field term in addition to the spin-orbit term. For the

calculation of the susceptibility we used approximate eigenstates  $|n\rangle$  which were determined by diagonalizing the Hamiltonian in the subspace spanned by  $|L=5, S=\frac{5}{2}, JM\rangle$  with  $J=\frac{5}{2}$  and  $\frac{7}{2}$ . Since the separation between the  $J=\frac{5}{2}$  ground multiplet and the  $J=\frac{7}{2}$  multiplet is small ( $\sim 1400$  K), it is necessary to include the  $J=\frac{7}{2}$  multiplet in the cal-

ulation. There is a significant temperature-independent Van Vleck contribution associated with the excited multiplet and there are also appreciable admixtures of the  $J=\frac{7}{2}$  multiplet by the crystal-field and exchange terms. When the excited multiplet is included the effect of the crystal field depends on both  $A_4\langle r^4\rangle$  and  $A_6\langle r^6\rangle$ .

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