Magnetic properties of Eu substituted SmS

L. Hedman

Department of Solid State Physics, Royal Institute of Technology, Stockholm, Sweden

K. V. Rao and Y. Yeshurun

University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Our magnetic measurements on $Sm_{1-x}Eu_xS$ alloys in the temperature range 2–340K, indicate that the ferromagnetic transition temperature, T_C, dependence on the concentration of Sm follows the expectations from a simple dilution phenomenon. In the paramagnetic state the measured magnetic susceptibility and its temperature dependence can be described, at least to a first approximation, by a simple linear combination of the susceptibility due to Eu in its S = 7/2 state and the non-collapsed SmS.

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INTRODUCTION

Samarium and europium monosulfides are semiconductors, crystallizing in the NaCl-type structure, and have almost identical lattice parameter (SmS = 5.97Å, EuS = 5.96Å)[1]. In recent years their electrical, optical, and magnetic properties have been the subject of numerous studies[2] and these have established the divalency of the Sm and Eu ions in SmS and EuS. Also, recent high pressure studies[3] have shown that SmS undergoes a change in the valence state at ∿7 kbar pressure, due to the delocalization of 4f electron. However, no such transition has been encountered in EuS up to 300 kbar[4].

The valence transition in SmS can also be induced by trivalent rare earth substitution[4]. In this connection the effect of divalent ion substitution including Eu and Yb has been investigated[5]. With Eu substitution a valence change is not expected because of the identical size of Sm^{2+} and Eu^{2+} ions and this is borne out to be true. SmS and EuS are soluble in each other in all proportions and the respective ions stay divalent throughout the solid solution range. However, from resistivity, and magnetic susceptibility measurements on $Sm_{1-x}Eu_xS$, Samokhalov et al[6] have claimed that there is a valence change in Sm, at the Sm rich end. In order to resolve these conflicting results, we have performed precise magnetic susceptibility measurements on a few compositions of interest.

Our studies indicate that the T_C dependence on the concentration of Sm at the Eu rich end follows the expectations from simple dilution. In the paramagnetic region the measured magnetic susceptibility and its temperature dependence agrees with the additivity law for a mixture of Eu with S = 7/2, and divalent Sm.

EXPERIMENTAL DETAILS

The $Sm_{1-x}Eu_xS$ alloys studied for x=1, 0.75; 0.25; & 0.22 were taken from the same stock used in earlier pressure studies on this system[5]. Independent determination of the lattice parameters from X-ray studies on some of the alloys used in this study did not differ from those reported[5]. However, in the case of the alloys in the Sm-rich regime the concentration of the Sm ions deduced from the effective susceptibility found in the paramagnetic region differed slightly from the values reported in ref 5. This could well be due to some concentration inhomogenieties between the granules although from the same source. The magnetic susceptibility of samples with x=1 and 0.22 were measured between 4 and 340K according to the Faraday method using a Cahn RG electromechanical balance. The samples weighing about 0.01 gms were contained in a teflon can weighing about 0.12 gms. The applied field was kept low in the range of 2-3 KOe in order to prevent any possible sticking of the freely suspended samples at low temperatures. The field gradient was about 440 Oe/cm. The low temperature magnetization of all the samples was determined on much larger granules (20 to 150 mgms) using a standard PAR vibration sample magnetometer in applied fields upto 15 KOe. The high temperature susceptibility determined by the two experimental techniques showed no significant differences although clearly the Faraday technique gave data of much higher precision.

RESULTS AND DISCUSSIONS

i) Magnetic ordering at low temperatures: EuS is one of the well-studied ferromagnetic semiconductors, with a T_C around 16.5K, specially from a critical phenomena point of view. The critical exponents observed at the second order magnetic phase transition in this system have well characterized it to be that of a classical cubic Heisenberg type ferromagnet[7]. Magnetization studies on the EuS used in our alloy system agree with this description and yield a $T_C \simeq 16.2$K. Furthermore, from appropriate extrapolation of the measured high field magnetization (>10KOe) we obtain for the saturation magnetization, M_S, a value of 220 erg/gm Oe which is in close agreement with the value expected from an S = 7/2 state of the Eu spins.

Figure 1 is a plot of the temperature dependence of the magnetization in fields from 0.1 to 10KOe for the $Sm_{25}Eu_{75}S$ alloy. The low field data clearly exhibit the characteristic "kink" expected close to T_C below which the demagnetization factor limits the measured magnetization.

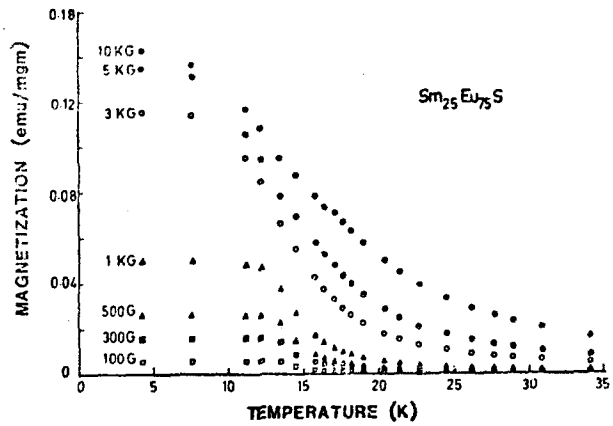

Fig. 1 Temperature dependence of the magnetization of $Sm_{25}Eu_{75}S$ below 35K in applied fields up to 10 KG.

A general method to establish the nature of the magnetic transition is to employ the scaling laws to obtain a simple form of the magnetic equation of state[8] in the

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critical region given by

$$M/|t|^{\beta} = m' \left(H/|t|^{\beta\delta} \right) \qquad (1)$$

where $t = (T-T_C)/T_C$. β, and δ are the well known critical exponents that characterize the ferromagnetic transition. If we take $y = H/|t|^{\beta}$, then m' has two branches m'_+ for $t > 0$, and m'_- for $t < 0$. Thus by choosing the correct parameters for T_C, β, and δ all the data points of the magnetic isotherms should collapse into two branches in an " m' vs y " plot as shown in fig 2. From

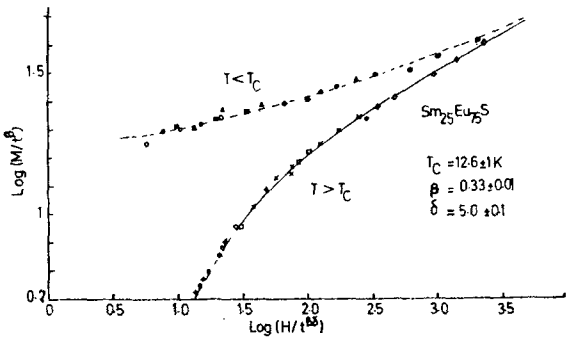

Fig. 2 Data collapsing of the magnetic isotherms according to the dictates of the scaling laws around the magnetic transition for $Sm_{25}Eu_{75}S$.

such a fit we find that the best set of parameters give the Heisenberg like exponents $\beta = 0.33 \pm 0.01$, and $\delta = 5.0 \pm 0.1$, and $T_C = 12.6 \pm 1$K. The value of T_C thus found appears to extrapolate well into the T_C vs conc plot observed by Samokhvalov et al[6]. Again from a high field data extrapolation we obtain for the saturation magnetization, M_S a value of 150.9 ergs/gm Oe implying an effective moment of about 7 Bohr magnetons for this concentration of Eu.

The low field temperature dependence of the magnetization for $Eu_{25}Sm_{75}S$ is shown in fig 3, which indicates a possible ferromagnetic transition around 4K. Similar

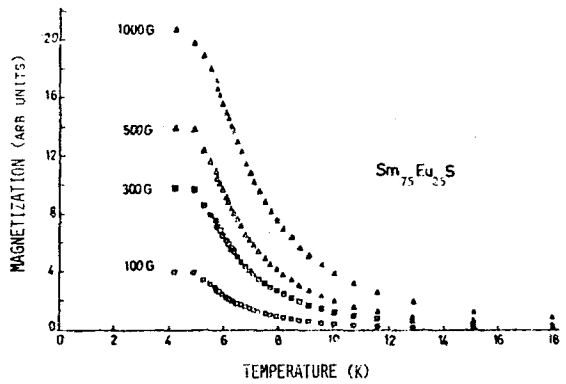

Fig. 3 Temperature dependence of the magnetization at low applied fields (0.1 to 1KG) around the magnetic transition in $Sm_{75}Eu_{25}S$.

magnetization data on $Eu_{22}Sm_{78}S$ indicates that any possible ferromagnetic transition can occur only below about 3K. Measurements of magnetic isotherms on this alloy were extended to lower temperatures, however, no definitive determination of T_C was possible. In fig 4 is plotted the observed T_C, and the saturation magnetization M_S calculated from our high fied data for the alloys studied. It is interesting to note that the general dependence of T_C on concentration is rather monotonic and indicates a simple dilution effect due to the addition of Sm. Both T_C, and M_S values extrapolate almost linearly to a possible 'percolation limit' of about 0.12 Eu which is the dilution limit one would expect on the basis of a simple estimate for the occurence of suitable nearest-neighbour pairs for Eu atoms in a NaCl type of crystal structure.

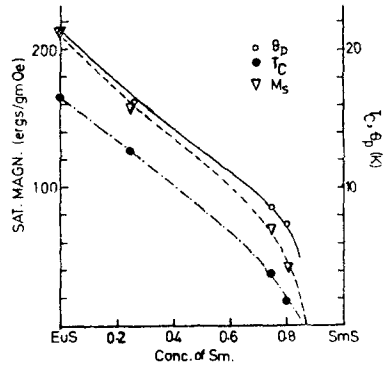

Fig. 4 Concentration dependence of the extrapolated saturation magnetization M_s at T = 0K, ferromagnetic transition temperature T_C, and the paramagnetic Curie temperature, θ_p, obtained from an analysis of the susceptibility data below 80K.

ii) Magnetic susceptibility at higher temperatures: We now discuss our analyses of the magnetic susceptibility data upto 340K. The ground state ($^7F_0$) of divalent Sm ions in the semiconducting phase is non magnetic. This leads to a Van-Vleck paramagnetism with a temperature independent contribution to the magnetic susceptibility of $\chi \simeq 50 \times 10^{-6}$ cm^3/gm for $t < 80$K. At higher temperatures, however, the susceptibility should decrease with temperature because of the thermal filling of the multiplet states[9]. This behaviour is Curie-Weiss like.

In the case of EuS, a simple Curie-Weiss Law of the type $\chi = C/(T-\theta)$, describes to within a precesion of 0.3% the temperature dependence of our measured χ in the range 100-340K. The calculated value for the effective Bohr magnetons (=7.97) deduced from the relation $p^2 = 3k_B C/N\mu_B^2$ (where k_B, N and μ_B are the well known constant parameters) is in good agreement with the theoretically expected value for g=2 and S= 7/2. The agreement of this independent determination of the effective magnetic moment with that obtained from our data in the magnetically ordered state is indeed quite satisfactory.

It is found from our data that except for the x=1 alloy our measured susceptibility cannot be meaningfully fitted into a single Curie-Weiss type law. In analyzing the measured total χ for the other alloys in the $Sm_{1-x}Eu_xS$ series, we have therefore adopted as a first approximation the simple possibility of a linear combination of the susceptibilities arising from non-collapsed SmS and an appropriate contribution from EuS. The results of our analyses on such a basis and the expectations from high pressure studies on these alloys support our above approach. The procedure adopted in such an analyses just described is then as follows: The measured susceptibility, χ, is fitted into a general expression of the type

$$\chi = x\,\chi_{Eu} + (1-x)\,\chi_{Sm} = x\,\frac{C_E}{(T-\theta_E)} + (1-x)\left[A_s + \frac{C_S}{(T-\theta_S)}\right] \qquad (2)$$

where x is the concentration of Eu in the alloy concerned. The values of A_S, C_S, and θ_S are assumed to be those of non-collapsed SmS as given in table I. It was found necessary to fit the data below 80K, and to those above 110K separately as illustrated in fig 5, due to the cross-over region arising out of the Van-Vleck susceptibility. The results of such a fitting for all the alloys studied are given in table I. It is important to point out that for every alloy both the low and high temperature fits give approximately the same value for C_E which agrees well with the theoretically expected value of 42810×10^{-6} K cm^3/gm for Eu in the 7/2 spin state. This strongly supports the validity of our

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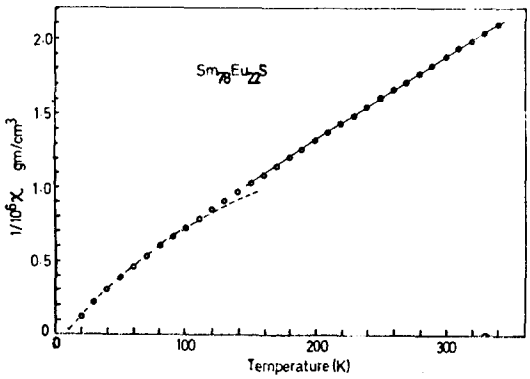

Fig. 5 *Temperature dependence of the inverse magnetic susceptibility of $Sm_{.78}Eu_{.22}S$ between 4 and 340K. The continuous and the interrupted lines are the high and low temperature fits as discussed in the text.*

approach of considering a simple linear combination of the contributions from the two constituents in the alloy system. Furthermore, the values obtained for the paramagnetic Curie temperature θ_E decreases monotonically with increasing Sm concentration almost following the trend exhibited in the concentration dependence of T_C, and specially M_s values as seen in fig 4. Also note that θ_E is positive and indicates a decreasing trend in ferromagnetic coupling between the Eu spins as we approach the Sm rich end.

These trends observed in the concentration dependence of θ_E, T_C, and M_s values are not in accordance with that reported by Samokhvalov et al[6] specially close to the the Sm-rich end of this system. In particular, no anomalous θ_p or T_c as reported by them is observed. However, our results seem to support the general conclusions by Jayaraman and Maines[5] from their pressure studies on these systems.

In an electronic structure representation for the mixed compound involving SmS and EuS, if the Sm-$4f^6$ level is placed close to the bottom of the conduction band, the Eu-$4f^7$ level will be located quite deep in the energy gap. We thus have in these mixed crystals two distinct 4f levels in the energy gap between the valence band and the bottom of the conduction band. Some $4f^6$ electrons may be delocalized at moderate pressures or perhaps in sample handling procedures. However, a reasonable explanation for the decrease in the resistivity as one approaches the Sm-rich end in these alloys (from about 330 ohm-cm to 0.1 ohm-cm) is a simple consequence of the fact that Sm $4f^6$ levels are much closer to the conduction band. With the substitution of Eu, the $4f^6$-5d gap increases in general solely due to the electronic structure of EuS and it does not induce any valence change in SmS.

Table I

Results of fitting the T-dependence of magnetic susceptibility data for $Sm_{1-x}Eu_xS$ according to equation 2 in the text. A_s,C_s, and θ_s are assumed to have the values of non-collapsed SmS. [a]For T< 80K, A_s=50 x10^{-6} cm^3/gm, C_s=θ_s=0; and for T> 100K, A_s=0, C_s=12900 x10^{-6} Kcm^3/gm, θ_s=-201K.

conc.	Range of fit	C_E 10^{-6} Kcm^3/gm.	θ_E	Maximum %-error
x=1[a]	130 - 340K	43200	21.4K	0.3
x=0.75[b]	31 - 82K	42735	15.7K	0.8
	109 - 315K	42735	13.4K	1.8
x=0.25[b]	25 - 78K	42120	8.8K	0.8
	101 - 253K	42120	8.1K	1.5
x=0.22[a]	30 - 80K	42225	7.5K	0.5
	130 - 340K	43560	9.8	0.4

a-measurements using a Faraday balance
b-vibration sample magnetometer data.
Note: C_F from the 4f-shell in Eu in EuS = 42820x10^{-6}Kcm^3/gm.

CONCLUSIONS

Thus, in conclusion, our susceptibility and low temperature magnetic studies simply describe the consequences of a dilution phenomenon on substitution of Eu in the magnetic properties os $Sm_{1-x}Eu_xS$ system.

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