Calorimetric study of small clusters and single magnetic ions in dilute (*Sr*,Eu)S

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The specific heat of insulating $(Sr_{1-x}Eu_x)S$ with $0.017 \leq x \leq 0.07$ was measured between 0.04 and 2 K. The magnetic specific heat C_M consists of two contributions: a roughly constant term C_M^P between 0.3 and 1.2 K, which can be explained as arising from exchange coupled Eu^{2+} pairs and small clusters. At lower temperatures where C_M^P drops exponentially to zero, the contribution from the remaining isolated Eu^{2+} spins becomes important. The freezing of these single spins at $\simeq 0.01$ K gives rise to a T^{-2} term of C_M.

I. INTRODUCTION

Dilute magnetic isulators have become of interest recently in the context of spin-glasses. In *metallic* spin-glasses, it is generally agreed upon that the oscillatory Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction between magnetic impurities mediated by the conduction electrons plays an important role in determining the spin-glass properties, i.e., susceptibility cusp and remanence. Yet there exist also a number of *insulators* which show spin-glass-like behavior. In particular, the system $(Sr_{1-x}Eu_x)S$ has been studied extensively. In this system the exchange interaction between nearest neighbors of Eu^{2+} (J_1) is ferromagnetic while that between next-nearest neighbors (J_2) is antiferromagnetic with $J_2/J_1 \simeq -0.5$. (Keeping in mind that for Eu^{2+} $L=0$ and $S=\frac{7}{2}$, we omit the ion charge hereafter for brevity.)

For dilute $(Sr_{1-x}Eu_x)S$, $x \lesssim 0.05$, it has been shown that the (intracluster) dipolar interaction is sufficiently strong to block exchange coupled small clusters (predominantly pairs, but also triples, quartets, etc.).[1-3] The blocking of pairs leads to a maximum in the ac susceptibility χ^{ac} around $T_P = 0.1$ K. A second maximum in χ^{ac} occurring[3,4] at a still lower temperature $T_I (\simeq 0.01$ K) is interpreted as arising from freezing of single isolated spins due to intercluster dipolar interactions. The temperatures T_P and T_I are roughly independent of x but depend on the ac measuring frequency.

At moderate and high Eu concentrations $(0.05 \lesssim x \leq x_c = 0.51)$ (*Sr*, Eu)S displays many of the features well known from metallic spin-glasses,[5,6] in particular a susceptibility maximum at a "freezing temperature" T_f which is proportional to concentration. This is attributed to the competing interactions J_1 and J_2. Recently, it has been possible to model the spin-glass-like properties of (*Sr*, Eu)S by starting from a more realistic site-disorder problem[7] than the usual Edwards-Anderson-type bond-disorder approach. However, it has not been possible to explain in this model the frequency dependence of χ^{ac} also found[2,5,6] in this concentration regime. This frequency dependence of χ^{ac} and hence of T_f, however, is different from that for T_P for (*Sr*, Eu)S with $x \lesssim 0.05$. In fact, the different frequency dependencies originally helped to reveal the two concentration regimes,[2] i.e., "pair blocking" and "spin-glass" regime.

Very recently, Meschede *et al.*[8] reported on a specific-heat study of $(Sr_{1-x}Eu_x)S$ with $x = 0.4$ and 0.54, i.e., below and just above the critical concentration x_c for the onset of ferromagnetism. Again, the magnetic specific heat C_M resembles that of metallic spin-glasses: a low-temperature linear term extends well beyond T_f and a broad maximum occurs at $T \simeq 2T_f$. At the lowest temperature of that experiment ($T = 0.3$ K) there is an anomalous contribution to C_M which is too large to be accounted for by hyperfine splitting of the Eu nuclei.[8]

It was the aim of the work presented here to undertake a calorimetric study at low concentrations and low temperatures in order to obtain more insight into the blocking of pairs and single impurities due to the dipolar interactions. In brief, the present study reveals that the magnetic contribution to the specific heat of dilute (*Sr*, Eu)S consists of two parts, one of which can be explained by taking pairs of Eu nearest neighbors and small clusters into account. The other is probably associated with the "freezing" of single spins.

II. EXPERIMENTAL DETAILS

The single crystals of (*Sr*, Eu)S for the present investigation were the same as previously used for magnetic measurements.[1,2,4] The samples had nominal compositions of $x = 0.017$, 0.03, and 0.07. The concentration was checked by determining the saturation magnetization M_s. M_s was obtained from the asymptotic $1/H$ behavior of the high-field magnetization at $T \simeq 0.05$ K.[1] The concentrations were found to be approximately correct except for the nominal $x = 0.03$ sample, where the saturation value M_s yielded $x = 0.023$. In the following we will only use this magnetically determined concentration.

The specific-heat measurements were carried out in a double stage adiabatic demagnetization cryostat with a transient method described in detail elsewhere.[9] The samples — each weighing 20 to 50 mg — were pressed with a copper disk against a copper sample holder which carried a Pt-W heater and a doped Si thermometer. For $x = 0.017$ and 0.07, the crystals were very small (10 to 20 mg). Therefore, for these concentrations a few crystals (2–4) were measured together using a specially adapted copper disk to accommodate the slightly different heights. The addenda — while small at low temperatures — contributed as much as 90% to the total heat capacity at 1 K for the most dilute samples.

III. RESULTS

Figure 1 shows the specific heat C versus temperature T for the three (*Sr*, Eu)S samples investigated. The arrows indicate the freezing temperature T_f for $x = 0.07$ and the pair blocking temperature T_P for $x = 0.023$ and 0.017, respectively (for a frequency of 7.1 Hz).[4] We first note that no anomaly in C is observed at either T_f or T_P. The specific heat shows a rather large roughly constant contribution which is most prevalent for $x = 0.07$ where it extends over almost one order of magnitude in temperature. We note that this constant contribution increases *faster* than linearly with concentration. For $x = 0.07$, the specific heat then passes through a shallow minimum upon lowering the temperature.

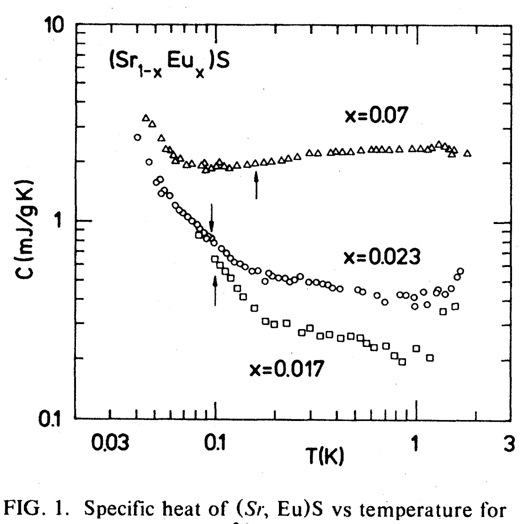

FIG. 1. Specific heat of (*Sr*, Eu)S vs temperature for three concentrations of Eu^{2+}. Arrows indicate freezing temperature T_f (for $x = 0.07$) and pair blocking temperature T_P (for $x = 0.017$ and 0.023), after Ref. 4.

At still lower temperatures, C rises as T decreases, approaching roughly a $C \sim T^{-2}$ behavior around 50 mK. A similiar behavior is observed also for the more dilute samples, although there no minimum occurs. Below 0.1 K, C increases somewhat *less* than linearly with concentration. We mention that C is appreciably larger than to be expected from the T^{-2} Schottky tail due to the nuclear hyperfine splitting. At high temperatures ($T > 1$ K) the rise in C for the more dilute samples is readily identified with the lattice contribution.

IV. DISCUSSION

The total specific heat of (*Sr*, Eu)S is comprised of three contributions:

$$C = C_M + C_D + C_N \ ,$$

where the subscripts denote the magnetic term, the lattice term, and the nuclear hyperfine term, respectively.

Before commenting in detail, we want to discuss the salient features of the specific heat of (*Sr*, Eu)S. The large temperature-independent contribution is of magnetic origin and will be attributed to pairs and small clusters. As already mentioned, below 0.1 K an additional specific-heat contribution proportional to T^{-2} but exceeding C_N is observed. We believe that this contribution arises from the freezing of the remaining degrees of freedom of single Eu impurities.

For a quantitative discussion, we begin with an evaluation of the nuclear hyperfine term which is due to the hyperfine splitting of the ^{151}Eu and ^{153}Eu nuclei. In the high-temperature expansion of the corresponding Schottky specific-heat anomaly, the leading term neglecting quadrupolar effects is[10]

$$C_N = \frac{xR}{M} \sum_i a_i \frac{(I_i+1)}{3I_i} \left[\frac{\mu_i H_{\rm eff}}{k_B T} \right]^2 \equiv \frac{\alpha_N}{T^2} \ ,$$

where M is the molar mass of $(Sr_{1-x}Eu_x)S$, I_i is the nuclear spin, μ_i the nuclear moment, and a_i the relative abundance of the isotope i. With the values of $H_{\rm eff}$ in (*Sr*, Eu)S from Mössbauer measurements,[11] $H_{\rm eff} = 28.4$ T for $x = 0.07$ and 28.2 T for $x \simeq 0.02$, we can calculate α_N and compare it with the experimentally observed coefficient $\alpha_{\rm expt}$ as done in Table I. We see that $\alpha_{\rm expt}$ exceeds α_N by a factor of 3 to 5 hinting at an additional (magnetic) contribution C_M^l to C at low temperatures which also varies as T^{-2}: $C_M^l = \alpha_M T^{-2}$.

As has been mentioned in the Introduction, a second susceptibility maximum is observed at $T_l \simeq 10$ mK which has been attributed to the freezing of iso-

TABLE I. Analysis of coefficients of the low-temperature ($T < 0.1$ K) specific heat of (*Sr*, Eu)S. For notation, see text.

x	$\alpha_N(10^{-6}$ J K/g)	$\alpha_{expt}(10^{-6}$ J K/g)	$\alpha_M(10^{-6}$ J K/g)	$x_I(10^{-2})$	$\alpha_M^*(10^{-6}$ J K/g)
0.017	0.54	3.4[a]	2.9	1.25	2.9
0.023	0.73	4.0	3.3	1.51	3.5
0.07	2.16	7.0	4.8	1.90	4.4

[a]This number is rather uncertain because the specific heat was only measured down to 0.08 K for this sample.

lated spins due to the dipolar interaction.[3,4,12] We suggest that C_M^I is the high-temperature tail of an anomaly associated with this "dipolar spin-glass" freezing. This is supported by the following analysis of the concentration dependence of C_M^I.

As the freezing temperature T_I is found experimentally to be nearly concentration independent, α_M should be proportional to the concentration of isolated spins x_I. Here $x_I = x(1-x)^{18}$ because (*Sr*,Eu)S crystallizes in the NaCl structure with twelve nearest and six next-nearest Eu or Sr neighbors. α_M indeed scales with x_I, which is seen when calculating $\alpha_M^* = x_I(\alpha_M/x_I)_{x=0.017}$, i.e., fitting to the data for $x = 0.017$. The agreement between α_M and α_M^* is better than 10%, cf. Table I. This corroborates the previously found only weak concentration dependence of T_I.[3,4]

Eiselt *et al.*[3] suggested a mean-field model for the intercluster dipolar interaction to account for the susceptibility maximum at T_I. This interaction gives a preferred direction to the isolated spins which otherwise could rotate freely.[3] The calculated magnitude of T_I agrees well with experiment. However, the width Δ of dipolar fields in this model is proportional to x. This would lead to $T_I \sim x$ in contrast to experiment,[3,4] and, furthermore, $\alpha_M \sim \Delta^2 \sim x^2$ should vary stronger with concentration than observed in the present study. Finally, the frequency dependence of T_I remains unexplained.

As already noted before,[3] the discrepencies with experiment are probably due to the simple mean-field approximation of the dipolar interaction. At present, there is no theory to explain all the phenomena pertaining to the freezing of isolated spins at T_I.

Alternative to the interpretation in terms of the *intercluster* dipolar interaction given above, one could speculate that at these low temperatures one would have to take the superexchange coupling J_3 between third-nearest Eu neighbors into account. In fact, it has been suggested[13] that the exchange interaction in EuS might be of longer range than usually assumed when only considering J_1 and J_2. The statistically determined concentration of isolated spins with respect to J_3 is reduced to $x_{I,3} = x(1-x)^{42}$, as each Eu is surrounded by twenty-four possible third-nearest-neighbor sites in (*Sr*,Eu)S. If the susceptibility maximum at T_I originates from the blocking of J_3 clusters due to the *intracluster* dipolar interaction then T_I would be concentration independent as experimentally observed and could in addition conceivably depend on the measuring frequency.

We now turn to the discussion of the remaining contribution C_M^P to C_M. This is obtained by

$$C_M^P = C - \beta T^3 - \alpha_N T^{-2} - \alpha_M T^{-2} ,$$

where we assume a Debye temperature of $\Theta_D = 350$ K for EuS (Ref. 14) to account for the lattice contribution $C_D = \beta T^3$. The resulting $C_M^P(T)$ curves are shown in Fig. 2. For the $x = 0.07$ sample, C_M^P is nearly constant for temperatures between 0.3 and 1.2 K, exhibiting a very broad plateau centered around 0.8 K. Below 0.1 K, C_M^P decreases exponentially with decreasing temperature. A similar behavior is seen

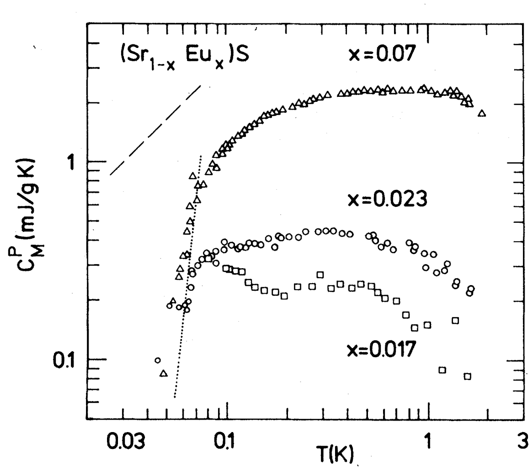

FIG. 2. Specific-heat contribution C_M^P of nearest-neighbor Eu pairs and small clusters vs temperature. Dashed line indicates extrapolation of the linear term $C_M = \gamma_M T$ for concentrated (*Sr*, Eu)S ($x = 0.4$), after Ref. 8. Dotted line illustrates an exponential rise of C_M^P.

for the $x=0.023$ sample. A plateau is also observed for $x=0.017$ although the scatter in the data is larger due to the relatively higher addenda contribution to the total heat capacity. For this most dilute sample, C_M^p appears to rise again as the temperature is lowered below 0.12 K, although this rise is almost within the scatter of the data. In the high-temperature range, the specific heat decreases approximately proportional to T^{-1}.

The behavior described above, in particular, the specific-heat plateau and the exponential drop of C_M^p, is remarkably different from what is observed in metallic spin-glasses, namely, a low-temperature linear term $C_M=\gamma_M T$ extending to $T>T_f$.[15] From scaling arguments the coefficient γ_M should be independent of concentration because $C_M/x=f(T/x)$, i.e., $C_M=f(T)$ independent of concentration as long as $C_M \sim T$.[16]

In concentrated (*Sr*, Eu)S where spin-glass properties are found such a linear term in C_M is indeed observed with $\gamma_M=0.033$ J/g K^2 for $x=0.4$.[8] This linear term is indicated as the dashed line in Fig. 2. Clearly, the specific heat C_M^p for all our samples is much smaller than $\gamma_M T$, although for $x \geq 0.07$ (*Sr*, Eu)S shows typical spin-glass maxima in the magnetic susceptibility with $T_f \sim x$.[4] Since the above scaling argument is based on the $1/r^3$ dependence of the RKKY interaction, it is not surprising that no simple scaling is observed for insulating (*Sr*, Eu)S. In fact, in dilute (*Sr*, Eu)S, the specific-heat value at the plateau varies faster than linearly with concentration, cf. Fig. 2. This hints at an influence of pairs and small clusters of Eu coupled by J_1 and J_2.

The statistically determined number of the different configurations of pairs and triples in (*Sr*, Eu)S can be calculated from the work of Eiselt *et al.*[3] We define the "cluster occupation ratio" r_n as the number of Eu spins belonging to any cluster which contains up to n spins, divided by the total number of Eu spins. As can be seen from Table II, for the two smaller concentrations investigated in the present work, the majority of Eu spins is isolated with respect to J_1 and J_2 — they contribute to C_M^i as discussed previously. Therefore the cluster contribution is relatively small. However for $x=0.07$, only 27% of the Eu spins have no nearest or next-nearest Eu neighbor. The corresponding large number of clusters accounts for the large term of C_M^p observed for this concentration.

The contribution C_M^p arises because of the thermal excitation of the clusters. Since data on the energy splittings of the different types of clusters in (*Sr*, Eu)S are not available, we limit ourselves to a qualitative account. For all concentrations, the exponential rise of C_M^p with temperature sets in at $\simeq 0.05$ K. Therefore it is suggestive to associate this rise with the excitation of ferro- or antiferromagnetic pairs: The calculated splitting of exchange coupled pairs is of the same order of magnitude as J,[17,18] and for EuS, $J_1/k_B=0.22$ K and $J_2/k_B=-0.11$ K.[13] From the values of r_n (Table II) one infers that for $x=0.017$ and 0.023 C_M^p must be mainly due to a superposition of two Schottky-like anomalies arising from ferromagnetic and antiferromagnetic pairs. For antiferromagnetic pairs the specific heat has been calculated by Smart.[17] For spin values exceeding $S=\frac{1}{2}$, the specific-heat maximum is much wider than the usual Schottky anomaly while the low-temperature rise is practically unchanged. The same should be true also for ferromagnetic pairs. Considering the large spin value $S=\frac{7}{2}$ of Eu^{2+}, the wide plateau in C_M^p can at least qualitatively be understood. For $x=0.07$ the plateau in C_M^p extends to still higher temperatures. This hints at the growing influence of larger clusters ($n>2$) on C_M^p. In fact, for this concentration $r_2=0.45$ and $r_3=0.57$ only.

Finally, we want to consider the contribution S^P of pairs and small clusters to the magnetic entropy. For $T\rightarrow\infty$, $S^P=x(1-x_I)(R/M)\ln(2S+1)$ because S^P is equal to the total entropy of those Eu spins which at low temperatures belong to any cluster with $n>1$. S^P is compared in Table II to the contribution S_M^p which is determined by integrating the experimental C_M^p/T curves up to 1.8 K. The agreement between S_M^p and S^P is rather good; i.e., most Eu spins are already free at 1.8 K. This finding is in agreement with the rather small values of J_1 and J_2 as determined from mean-field theory.

TABLE II. Cluster occupation ratios r_n $(n=1,2,3)$ and entropy due to clusters as determined by theory (S^P) and from experiment (S_M^p).

x	r_1	r_2	r_3	S^P (mJ/g K)	S_M^p (mJ/g K)
0.017	0.73	0.93	0.98	0.645	0.77
0.023	0.66	0.88	0.95	1.12	1.29
0.07	0.27	0.45	0.57	7.12	6.43

V. CONCLUSION

The magnetic specific heat of (Sr, Eu)S has been shown to consist of two parts. Firstly, at low temperatures $T < 0.1$ K, C_M is dominated by a contribution from single Eu spins which are frozen at still lower temperatures as evidenced by the susceptibility maximum at $T_l = 0.01$ K. This contribution C_M^l which varies as T^{-2} with temperature indicates that a considerable degree of entropy is already removed from the system of isolated spins at $T \simeq 0.05$ K. The observed concentration dependence for C_M^l is in agreement with the concentration *independence* of T_l. This behavior of T_l itself is not understood at present — it might reflect the influence of J_3 at very low temperatures — and deserves further exploration. Furthermore, it should be very interesting to eventually observe very low-lying excitations of the "dipolar spin-glass" below T_l.

The second (complimentary) contribution to C_M which is prevalent at $T > 0.1$ K stems from superparamagnetic clusters, i.e., pairs, triples, etc., of Eu nearest and next-nearest neighbors which are exchange coupled via J_1 and J_2. One major point is that for the $x = 0.07$ sample, no indication of a linear term was found, although susceptibility measurements reveal $T_f \sim x$ as for canonical spin-glasses.[4] However, the plateau of C_M^P extends to higher temperatures for the $x = 0.07$ sample than for the more dilute ones, also the shallow maximum in C_M^P is seen at $T \simeq 0.8$ K for $x = 0.07$, considerably higher than that at $T \simeq 0.3$ K for $x = 0.023$. This hints at the growing influence of triples, quartets, etc. There is some controversy as to exactly where to place the boundary between pair blocking regime (as evidenced by a concentration-independent T_P) and spin-glass regime ($T_f \sim x$), primarily based on different experimental findings for the $x = 0.1$ (Sr, Eu)S samples.[2,3,6,19] This might perhaps be attributed to the different types of samples investigated.[19] The present study shows the prevalent influence of pairs and small clusters on the specific heat at and above T_P for concentrations up to $x = 0.07$. It furthermore shows that the exchange forces leading to cluster formation are mostly broken thermally at 1.8 K. This puts some doubts on the assumption of rigid clusters for $T \lesssim 1$ K. It should be most interesting to extend the present measurements to higher concentrations in order to study the evolution of the linear specific-heat term present in highly concentrated (Sr, Eu)S near the onset of ferromagnetism.

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