Smeared antiferromagnetic phase transitions and spin-glass properties in $Eu_xSr_{1-x}Se$

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We report specific-heat and susceptibility measurements on $Eu_xSr_{1-x}Se$ samples in the concentration range $0.5 \geq x \leq 1.0$. For $x \geq 0.85$, smeared first-order antiferromagnetic transitions are observed; for $x \leq 0.7$, the system shows typical spin-glass properties. In the intermediate concentration range the phenomena characteristic for antiferromagnetic and spin-glass ordering coexist.

INTRODUCTION

The magnetic ordering in systems with structural or compositional random disorder is a field of great current interest in theory and experiment. The activities follow two main directions: (1) the spin-glass problem and (2) the magnetic phase transitions, magnetic excitations, and ground-state properties in random magnetic systems with magnetic long-range order. Both phenomena can often be studied in the same solid solution system at high and low degrees of dilution, respectively; in the intermediate concentration range they can coexist. The reentrance behavior of the spin-glass state in many spin-glass systems is a well-known example.

In this paper we present an experimental study of the magnetic properties of the antiferromagnet EuSe when diluted with diamagnetic SrSe. The system $Eu_xSr_{1-x}Se$ has not been discussed much in the literature until now, contrary to its ferromagnetic counterpart $Eu_xSr_{1-x}S$, which has been studied in great detail in recent years[1] and is nowadays regarded as the standard system for spin-glass properties in insulating compounds. The main aim of this paper is to show that a very similar spin-glass phase also exists in the dilute antiferromagnet EuSe. We have published some preliminary results on $Eu_xSr_{1-x}Se$ in Ref. 2, and NMR results on $Eu_xSr_{1-x}Se$ at high Eu concentrations have been published by Kojima, Hihara, and Kamigaichi.[3]

We study here the $Eu_xSr_{1-x}Se$ system from both points of view mentioned above, i.e., we analyze the antiferromagnetic transitions at low Sr dilution and the spin glass properties at higher Sr concentrations. EuSe is a Heisenberg antiferromagnet with rather complex magnetic behavior; see Refs. 4 and 5 for recent reviews. In the Eu-chalcogenide series (EuO, EuS, EuSe, and EuTe), EuO and EuS are ferromagnets with transition temperatures, of 67 and 16.5 K, respectively, EuTe is a stable Heisenberg antiferromagnet with a Néel temperature of 9.6 K, and EuSe is a metastable antiferromagnet with a very low Néel temperature of 4.6 K and complex multiphase behavior below T_N. An applied pressure of 4 kbar or an applied magnetic field of 3 kG make EuSe ferromagnetic.

The metastability of the antiferromagnetic state in EuSe is due to the fact that the two main exchange interactions in the Eu chalcogenides, namely, the ferromagnetic exchange between nearest Eu neighbors J_1 and the antiferromagnetic next-nearest-neighbor exchange J_2 have nearly the same magnitude. When either J_1 or J_2 are dominating, as in EuS and EuTe, ferromagnetism or antiferromagnetism is the stable magnetic ground state.

The antiferromagnetic transition in EuSe is of the first-order type.[4] Now, the influence of random impurities on a first-order transition is definitely different from that on a second-order phase transition. In second-order phase transitions the correlation length at the transition temperature becomes infinite and on the length scale of the correlation-length concentration fluctuations are irrelevant and the transition remains sharp.[6] In first-order transitions the correlation length remains finite at the transition temperature and the concentration fluctuations are relevant.[7,8] From rather general energy and scaling considerations it is shown[8] that in a system with a first-order transition random impurities lead to a smearing or rounding of the transition in the dimension $d=3$. The system is expected to break up into domains with a distribution of ordering temperatures. The spatial extent of the domains is of the order of the correlation length at the ordering temperature or larger. Renormalization-group techniques have also been applied to first-order phase transitions.[9] Consistent with the results of Ref. 8 it is predicted that no long-range order should exist for a Heisenberg three-dimensional (3D) system with random impurities; the lower critical dimension is larger than 3. Formally the derivation of this result is equivalent to the well-known random-field problem in second-order phase transitions.

Experimentally the influence of random impurities on first-order transitions has rarely been studied systematically, although the sensitivity of the first-order character of a transition against any type of impurities is a well-known experimental fact.

SAMPLE PREPARATION AND EXPERIMENTS

The $Eu_xSr_{1-x}Se$ samples were prepared following the method described in detail in Ref. 10. For the present analysis we used samples in the form of sintered polycrystalline pellets, annealed at 1600 °C in sealed Mo crucibles for several hours. X-ray structure analysis revealed pure NaCl-type structure in the whole concentration range, the lattice parameter slightly increasing with the Sr concentration (Fig. 1).

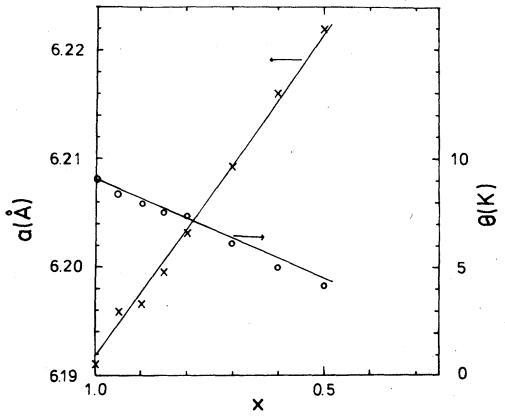

FIG. 1. Lattice parameter (crosses and left-hand scale) and paramagnetic Curie temperatures (open circles and right-hand scale) as a function of the Eu concentration x in $Eu_xSr_{1-x}Se$.

The specific-heat measurements were done by conventional heat-pulse technique. Some experimental details are given in Ref. 11. The ac susceptibility was measured by a mutual inductance bridge; when nothing else is specified in the figures the frequency was 87 Hz and the amplitude of the driving field 1 Oe. For the analysis of the frequency dependence of the susceptibility cusp up to 110 kHz an inductance bridge of the Wheatstone type[12] was used. For the susceptibility measurements the samples were ground into spherical shape with a total weight of about 30 mg; for the analysis of the field-dependent susceptibility, samples with the shape of thin platelets were used instead to avoid the necessity of correcting the demagnetizing field.

The magnetic-field-dependent ac susceptibility was measured continuously during sweeping the dc field of the superconducting selenoid. For these measurements the frequency of the ac driving field was 997 Hz. The magnetization measurements at low temperatures were done by the same equipment. An electronic fluxmeter was used to integrate the voltage generated in the secondary coils during sweeping of the magnetic field. For the determination of the paramagnetic Curie temperatures standard Faraday technique with a magnetic field of 10 kG was used.

RESULTS

Paramagnetic Curie temperatures give immediate information about the magnetic exchange interactions. The Curie temperatures of $Eu_xSr_{1-x}Se$ determined from the magnetic susceptibility between 50 and 300 K are plotted in Fig. 1. The values of the paramagnetic Curie temperatures are close to the straight line which holds for concentration-independent exchange interactions; at higher Sr solution the values fall slightly below the straight line. This is probably caused by the lattice expansion with increasing Sr and reflects the distance dependence of the exchange integrals.

Specific heat

In Figs. 2(a)–2(c) we summarize the results of our specific-heat measurements. Figure 2(c) gives an enlarged view of the specific heat close to the transition for the samples of Fig. 2(a). The figures show only the magnetic part of the specific heat; the lattice contribution has been subtracted by fitting a Debye T^3 law at $T=20$ K. The contribution of the lattice is typically 30% of the magnetic specific heat at 10 K and very small compared to the magnetic contribution close to the ordering temperatures.

The first-order character of the magnetic phase transition in EuSe is apparent in Fig. 2(c). Within the experimental resolution the specific heat has a discontinuity at 4.64 K and the measured specific heat changes by a factor of nearly 100 within a temperature interval of 4 mK. At 1.8 K there is another sharp peak in the specific heat of EuSe. It belongs to a transition between two different antiferromagnetic structures. Above 1.8 K the magnetic lattice is of ↑↑↓↓ type; below, it is ↑↓↑↓, where ↑ and ↓ give the spin direction of neighboring Eu(111) planes.[5] Dependent on the temperature and the thermomagnetic history of the sample these two antiferromagnetic structures and the ferrimagnetic structure ↑↑↓ are the magnetic ground state in EuSe. These structures may even coexist in a limited temperature range.[13]

When replacing 5% of Eu by Sr the specific-heat value at the maximum is reduced by a factor of about 20, and compared to EuSe the specific-heat peak appears strongly smeared; see especially Fig. 2(c). Guided by theory we attribute this smearing to a distribution of Néel temperatures. Assuming a Gaussian distribution of Néel temperatures one estimates a half-width of about 160 mK for $Eu_{0.95}Sr_{0.05}Se$. With the Sr concentration increasing further one observes a progressive smearing of the transition; only the samples $Eu_{0.90}Sr_{0.10}Se$ and $Eu_{0.85}Sr_{0.15}Se$ still have a narrow peak. For these samples one derives a half-width of about 300 and 800 mK for the distribution of Néel temperatures. For lower Eu concentrations very broad specific-heat peaks are observed, an interpretation as a smeared antiferromagnetic transition would lead to a very unrealistic width of the Néel temperature distribution here. We think this description is not valid here. The magnetic measurements discussed below show that the borderline between the smeared antiferromagnetic and the spin-glass is close to the Eu concentration $x=0.80$. Actually the shape of the specific-heat curves for the samples $Eu_xSr_{1-x}Se$ with $x \leq 0.80$ is very similar to the one observed in the spin-glass of $Eu_xSr_{1-x}S$.[14]

Similar to second-order phase transitions the measured specific heat for the Sr-diluted samples is continuous at the ordering temperature, but quantitatively the form of the specific-heat curve is inconsistent with a second-order phase transition. Neglecting corrections, the specific heat for a second-order phase transition is described by

$$c_> = At^{-\alpha} + B \quad \text{for } T > T_c \ ,$$

$$c_< = A't^{-\alpha} + B' \quad \text{for } T < T_c \ ,$$

with the reduced temperature t, the critical exponent α, the amplitudes A and A', and the nonuniversal constants B and B'. For a Heisenberg 3D magnet $\alpha < 0$ and $B = B'$

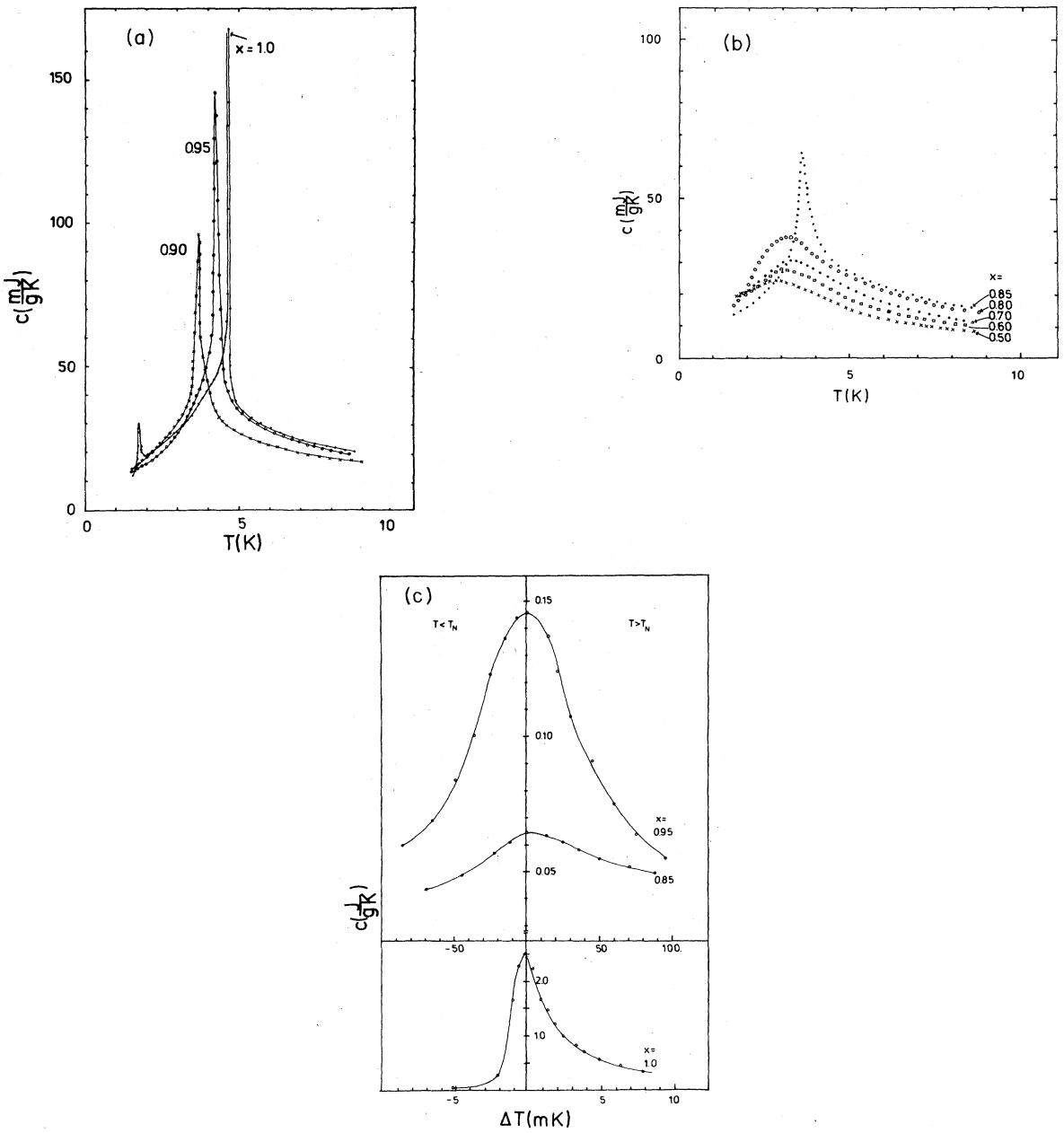

FIG. 2. Magnetic specific heat of samples $Eu_xSr_{1-x}Se$ as function of the temperature with the contractions (a) $x=0.90$, 0.95, and 1.0 and (b) $x=0.50$, 0.60, 0.70, 0.80, and 0.85. (c) Enlarged part of (a) for temperatures close to the transition; note the different scales for the specific heat and the temperature difference for the upper and lower part of the figure.

holds, for the universal amplitude ratio A/A' one expects a value close to 1.5; see measurements on EuS (Ref. 15) and EuTe (Ref. 16) as an example. The amplitude ratio gives rise to the typical asymmetric specific-heat anomaly for a second-order 3D transition with the slope of the specific heat towards higher temperatures steeper than towards lower temperatures.

For the samples in Fig. 2(c) one has a symmetric peak for the concentration $x=0.90$ and just the reverse asymmetry for $x=0.85$. A comparison with the results on EuSe shows that this type of asymmetry is a remnant of the discontinuity of the specific heat at the first-order transition. We regard this result as a strong indication that the Sr-diluted samples undergo a smeared first-order transition.

ac susceptibility

The results of the ac susceptibility analysis are shown in Figs. 3(a) and 3(b). At the first-order transition the susceptibility of EuSe drops off sharply. At 2 K there is another susceptibility peak. It belongs to the transformation $\uparrow\uparrow\downarrow\downarrow \rightarrow \uparrow\downarrow\uparrow\downarrow$ as mentioned above.

The ac susceptibility of the sample $Eu_{0.95}Sr_{0.05}Se$ has a

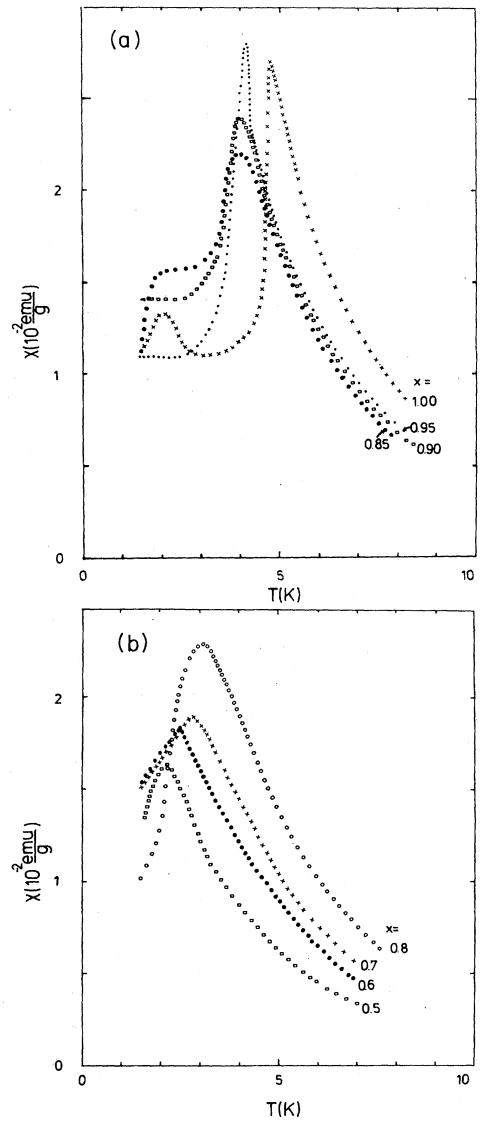

FIG. 3. Magnetic susceptibility for samples $Eu_xSr_{1-x}Se$ as function of temperature, with the concentrations (a) $x=0.85$, 0.90, 0.95, and 1.00 and (b) $x=0.5$, 0.6, 0.7, and 0.8.

very peculiar form. At the mean Néel temperature of 4.21 K as given by the position of the specific-heat maximum, the susceptibility has a kink [see arrow in Fig. 3(a)] and increases sharply below, before dropping off similar to EuSe. From the discussion of the magnetic phase diagram below we suppose that the ferrimagnetic state ↑↑↓ coexists with the antiferromagnetic state ↑↓↑↓ for a narrow temperature interval below T_N. At temperatures below 3 K the susceptibility is temperature independent, and there is no change of the magnetic structure down to 1.4 K.

The susceptibility curves for the two samples $x=0.90$ and 0.85 are similar to EuSe but have a definitely smeared structure. The sharp peak at T_N of EuSe has changed towards a smooth maximum. This finding supports the interpretation of the specific-heat results that the samples undergo a smeared antiferromagnetic phase transition. The mean Néel temperatures as derived from the position of the specific-heat maximum correlate with the maximum of $d\chi/dT$, as in normal antiferromagnets. The sample $Eu_{0.85}Sr_{0.15}Se$ exhibits a sharp decrease of the susceptibility at 2.1 K. This indicates a change of the magnetic structure but we do not know the microscopic process.

It should be noted that the shape of the susceptibility curves is very different from mean-field behavior. Below the transition the susceptibility decreases sharply by a factor of about 2 and then gets temperature independent, if one disregards the magnetic transitions in EuSe and $Eu_{0.85}Sr_{0.15}Se$ below T_N. The sharp decrease of the susceptibility at the ordering temperature can be explained following Kovalenko and Nagaev[4] assuming that the short-range order above the Néel temperature is ferromagnetic, i.e., the phase transition is from ferromagnetic disorder towards antiferromagnetic order.

The temperature independence of the susceptibility below T_N could be interpreted by assuming that the whole polycrystalline sample is in the spin-flip state with the magnetization perpendicular to the applied magnetic field. But the applied field is only 1 Oe, thus using the standard formula for the spin-flip field H_{SF}:

$$H_{SF}=(2H_eH_a)^{1/2}\ .$$

With the anisotropy field H_a and the intersublattice exchange field H_e, this would mean an upper limit for the anisotropy field H_a of 1 mOe. We have estimated the exchange field H_e as being identical to the metamagnetic transition-field strength towards the ferromagnetic state from Fig. 7. Although the $S=\frac{7}{2}$ ground state of Eu is isotropic this is an unrealistically low value, for EuTe a H_a of 8 Oe was derived.[17] Thus the samples are not in the spin-flip state; the temperature independence of the susceptibility must have another explanation beyond the description by mean-field theory.

The susceptibility curves for the samples $x\leq 0.80$ in Fig. 3(b) are definitely different than those for the higher concentrations. $Eu_{0.80}Sr_{0.20}Se$ has a very broad peak symmetric in temperature; for lower concentrations the peak sharpens up again and has a shape similar to spin-glasses. There is no longer any resemblance with the antiferromagnetic peak of EuSe. As usually observed in spin-glasses the temperature of the susceptibility maximum is below the specific-heat maximum temperature. For the smeared antiferromagnetic transitions at higher Eu concentrations just the reverse was found. Thus we suppose that close to $x=0.80$ the magnetic ground state changes from antiferromagnetic towards the spin-glass. For a further support of this assumption we have analyzed the frequency dependence of the susceptibility. Frequency shifts of the ac-susceptibility maximum is a further characteristic feature of insulating and metallic spin-glasses. The results of the analysis are summarized in Fig. 4.

The sample $Eu_{0.85}Sr_{0.15}Se$, which we have assigned to the smeared antiferromagnetic phase above, does not show a frequency shift within the precision of the measurement. For the samples with lower Eu concentration there is a frequency shift. For all samples in Fig. 4 the frequency dependence saturates below 100 Hz. Above 100 Hz the frequency shift of the reciprocal freezing temperature is

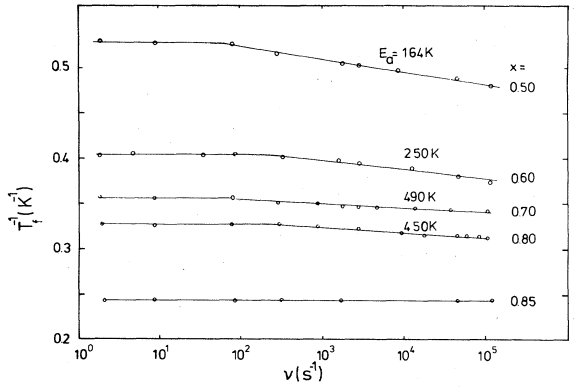

FIG. 4. Reciprocal freezing temperature as function of the frequency of the ac field. Each curve is labeled by the concentration x in $Eu_xSr_{1-x}Se$ and the activation energy E_a as derived from the Arrhenius law.

linear on a logarithmic frequency scale, and the slope is increasing with the Sr dilution. This finding is very similar to what has been observed in $Eu_xSr_{1-x}S$ in the spin-glass phase below $x_c=0.5$.[18] The slopes in Fig. 4 can be fitted by an Arrehnius law thus defining an activation energy E_a:

$$E_a=-k_b T_f^{-1}\frac{d(\ln\nu)}{d(T_f^{-1})} .$$

The activation energy E_a thus derived is given in Fig. 4. The values compare well with those derived for $Eu_xSr_{1-x}S$,[18] e.g., for the sample $Eu_{0.50}Sr_{0.50}Se$ we get $E_a=164$ K and for $Eu_{0.40}Sr_{0.60}S$ an E_a of 204 K is derived in Ref. 18.

The microscipic model leading to the Arrehnius law is the blocking of ferromagnetic clusters in anisotropic dipolar fields, but this model has no justification in diluted antiferromagnets where ferromagnetic clusters probably do not exist.

In a more general sense the frequency dependence of the freezing temperature only reflects the complicated temperature dependence of the different relaxation processes in spin-glasses. The linear dependence of T_f^{-1} on the logarithmic frequency for a limited frequency range appears to be accidental. The very similar frequency dependence of the diluted antiferromagnet $Eu_xSr_{1-x}Se$ and the diluted ferromagnet $Eu_xSr_{1-x}S$ for comparable concentrations shows that the freezing of ferromagnetic clusters is not the dominant process at the freezing temperature.

Magnetic phase diagrams

The dependence of the equilibrium state of an antiferromagnet from an applied magnetic field gives valuable information about the microscopic parameters. For example, for uniaxial antiferromagnet a spin-flip transition and a transition spin-flip phase towards the high-field paramagnetic state can usually be observed. In the case of weak antiferromagnetic coupling and strong anisotropy first-order metamagnetic transitions towards the ferromagnetic state exist. In Ref. 17 the magnetic phase diagram of EuTe, representative for a normal antiferromagnet, is discussed in detail.

The magnetic phase diagram of EuSe is very different from that of a normal antiferromagnet. In Fig. 5 we show a magnetization curve for EuSe at low temperatures. With increasing magnetic field one observes two metamagnetic transitions. The first one at about 300 Oe is from the antiferromagnetic ground state↑↓↑↓ towards the ferrimagnetic state ↑↑↓ which has exactly $\frac{1}{3}$ of the ferromagnetic saturation magnetization. The second transition at 2.2 kG is from the ferrimagnetic state towards the ferromagnetic state. The first-order character of the transitions leads to a strong hysteresis of the magnetization curve not shown in the figure where we give only the increasing field cycle. The metamagnetic transitions can conveniently be observed by measuring the field dependence of the ac susceptibility. We extensively use this method for the detection of the transition fields, since this method has a much higher resolution. Figure 6(a) gives examples for EuSe; at the transition field the curves exhibit well-defined maxima. The phase diagram for EuSe thus derived in Fig. 7 is in good agreement with those previously published.[5,19] The existence of two different magnetic ground states ↑↓↑↓ (antiferromagnetic first kind) and ↑↑↓↓ (antiferromagnetic second kind) cannot be derived by magnetization measurements; this is a result from Mössbauer and NMR experiments.[3–5]

Note that the magnetic ground state in EuSe is ↑↑↓↓ down to 3 K and ↑↓↑↓ below 2 K; between 2 and 3 K the ferrimagnetic state is the ground state when the sample has been magnetized up before; in zero magnetic field ↑↑↓↓ exists down to 2 K.

The origin of the magnetic phase diagram of EuSe is still under discussion. It is reasonable that it results from the fact mentioned in the Introduction, namely, that the two strongest exchange interactions J_1 and J_2 are of nearly the same magnitude. For $J_1=-J_2$ a very special situation occurs: When one neglects all other magnetic interactions as dipolar interaction, higher-order exchange, or anisotropic exchange, the ferromagnetic, antiferromagnetic, and ferrimagnetic state are energetically degenerate. In this situation weaker interactions, which have negligi-

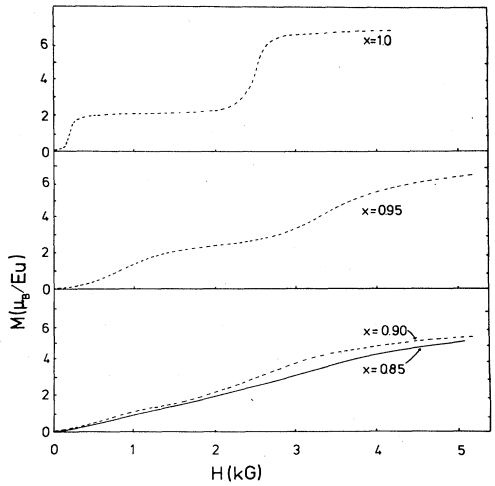

FIG. 5. Magnetization as function of magnetic field for samples $Eu_xSr_{1-x}Se$ with the concentration x given in the figure. The temperature was 1.6 K for all samples.

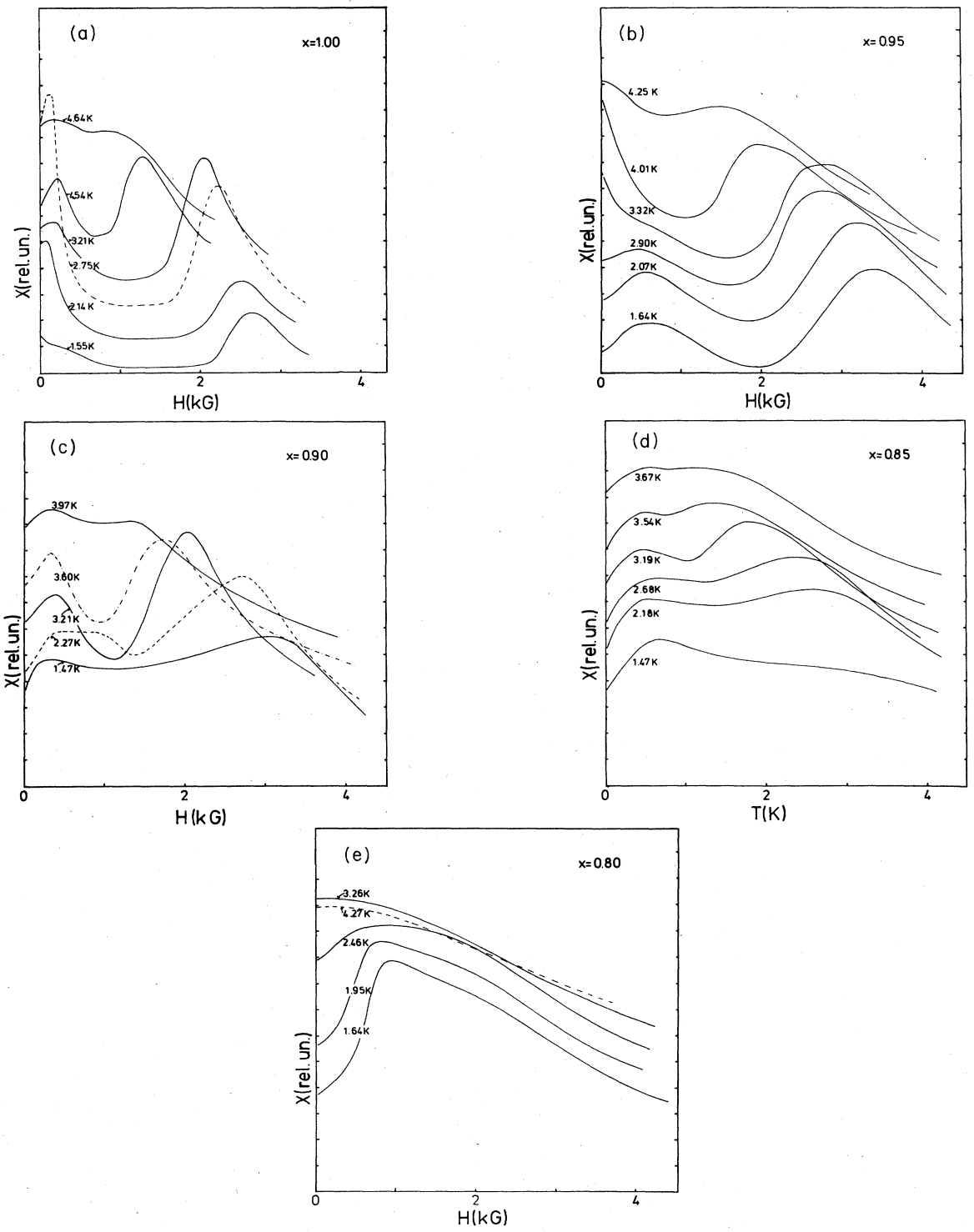

FIG. 6. ac susceptibility at constant temperature as function of the applied magnetic field with the concentration x given in the figures. For the sake of clarity each curve in one figure has been shifted upwards by one unit on the relative scale compared to the previous curve, starting with the curve at the lowest temperature.

ble influence when either J_1 or J_2 are dominating, determine the magnetic structure.

In Ref. 20 it is proposed that the magnetoelastic coupling leads to a modulation of the distance between the Eu(111) planes and thus stabilize the magnetic structure. A modulation with an expansion between planes of antiparallel spins and a contraction between planes with parallel spins should stabilize the ↑↑↓↓ structure. The other approach[4] assigns the metastability of the magnetic structures in EuSe to the existence of non-Heisenberg

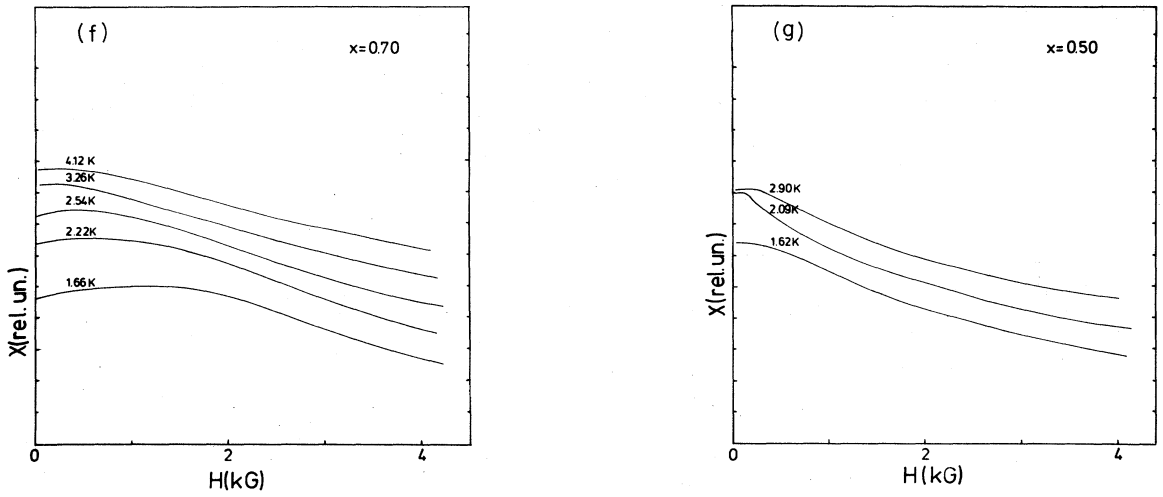

FIG. 6. (*Continued*).

higher-order exchange interactions, e.g., a biquadratic exchange $J(\mathbf{S}_1\cdot\mathbf{S}_2)(\mathbf{S}_1\cdot\mathbf{S}_2)$. The different temperature dependence of the Heisenberg and the non-Heisenberg effective-exchange fields then leads to a change of the magnetic ground state with temperature as observed in EuSe. This theory has, in addition, a straightforward explanation for the first-order character of the transition.

Coming back to the question of central interest in this paper, we show magnetization and field-dependent susceptibility curves for the Sr-diluted samples in Fig. 5 and Figs. 6(b)—6(g). For the sample $Eu_{0.95}Sr_{0.05}Se$ the magnetization curve is very similar to EuSe indicating two transitions from the antiferromagnetic state towards the ferrimagnetic state and from the ferrimagnetic state towards the ferromagnetic state. But the transitions are strongly smeared. The susceptibility possesses two well-defined maxima [Fig. 6(b)] and thus a magnetic phase diagram similar to EuSe can be derived (Fig. 7). The position of the susceptibility maxima define the mean metamagnetic transition fields.

With the Sr concentration increasing further one observes a strongly increasing smearing of the metamagnetic transitions. For the sample $Eu_{0.90}Sr_{0.10}Se$ one still can detect the two transitions in the magnetization; for $Eu_{0.85}Sr_{0.15}$ the transitions can hardly be resolved any more in the magnetization, but the susceptibility still possesses two well-defined maxima [Fig. 6(d)]. The magnetic phase diagrams of these two samples are also given in Fig. 7.

The magnetic phase diagrams for the Sr-diluted samples in Fig. 7 are similar to EuSe; they differ, however, in some details. In $Eu_{0.95}Sr_{0.05}Se$ the susceptibility is very high below the Néel temperature and between 4 and 3.3 K only the peak for the ferrimagnetic-ferromagnetic transition can be observed. This is very similar to the susceptibility of EuSe in the temperature range of the ferrimagnetic ground state. We thus conclude that the ↑↑↓ state exists below T_N down to about 3 K. But the ↑↑↓ state is not pure below T_N. Since the susceptibility should then reach the value limited by the reciprocal-magnetization factor, it seems to coexist with the antiferromagnetic state. This interpretation is in agreement with the NMR results of Ref. 3. The NMR results furthermore have shown that the Sr-diluted samples always have the ↑↓↑↓ antiferromagnetic state. The non-Heisenberg state ↑↑↓↓ no longer exists.

The phase line ↑↑↓-↑↑↑ is about 500 Oe higher in $Eu_{0.95}Sr_{0.05}$ than in EuSe and approximately independent of the Sr dilution for lower Eu concentrations. The change of the magnetic phase diagrams with the Sr dilution can be attributed to the slight increase of the lattice parameter with the Sr concentration in Fig. 1. This will cause J_1 to decrease compared to J_2 and thus stabilize the Heisenberg ↑↓↑↓ ground state and the ↑↑↓ state compared to ↑↑↑.

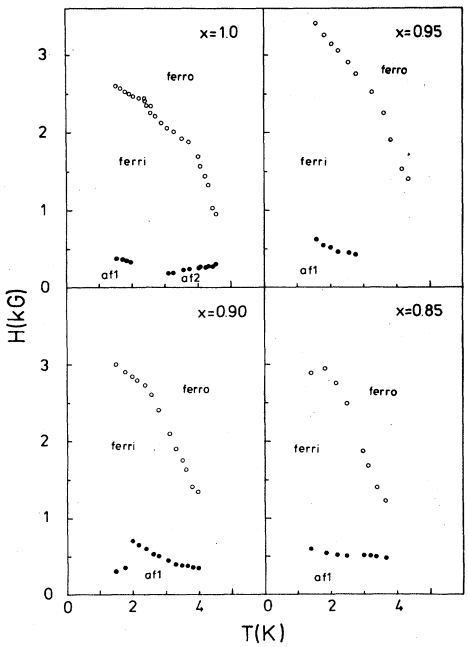

FIG. 7. Magnetic phase diagrams for samples $Eu_xSr_{1-x}Se$ with the concentration x given in the figure. af1 and af2, antiferromagnetic structure of 1- and 2-type; ferri, ferrimagnetic state; ferro, ferromagnetic state.

In summary, we find that the metamagnetic transitions characteristic for EuSe exist for the samples with the smeared antiferromagnetic phase transition also, and the mean metamagnetic transition fields seem to be determined by the mean exchange interactions. But one observes a strong smearing of the transitions. In principle, the same considerations explaining the smearing of the thermally driven first-order transitions can also be applied to the magnetic-field-driven first-order transitions. Determined by local concentration fluctuations domains undergo their field-induced transitions individually; the distribution of Néel temperatures in the thermally driven transitions corresponds to a distribution of magnetic transition fields in the magnetic-field-driven transitions.

In Figs. 6(e)—6(g) we show the results of the field-dependent susceptibility for the samples belonging to the spin-glass phase. $Eu_{0.80}Sr_{0.20}Se$, a sample with a frequency shift of the susceptibility peak, clearly has the structure in the susceptibility in Fig. 6(e) which results from strongly smeared metamagnetic transitions. Since a metamagnetic transition is a collective phenomenon of a large number of spins coupled rigidly, this result indicates that magnetic long-range order still exists. Thus in this sample both properties characteristic for spin-glasses and antiferromagnets coexist.

In the sample $Eu_{0.70}Sr_{0.30}Se$ in Fig. 6(f) the two susceptibility peaks cannot be resolved any more, but still at 1.66 K the maximum of the field-dependent susceptibility is at 2 kOe and this clearly is reminiscent of an antiferromagnetic structure. Only for the sample $Eu_{0.50}Sr_{0.50}Se$ is the susceptibility decreasing continuously with the magnetic field similar to other spin-glasses including $Eu_xSr_{1-x}S$.[18]

In Fig. 8 we present the magnetic phase diagram of $Eu_xSr_{1-x}Se$ emerging from the present analysis. We have plotted the phase-transition line between the smeared antiferromagnetic range and the spin-glass range as a dashed vertical line, but we want to stress that we think this transition is gradual and in a certain concentration range antiferromagnetic order and spin-glass order coexists.

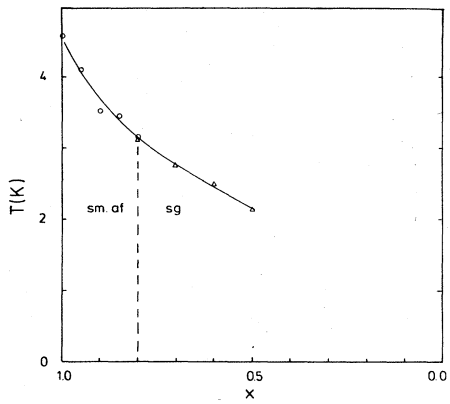

FIG. 8. Magnetic phase diagram of $Eu_xSr_{1-x}Se$. The open circles give the position of the specific-heat maximum in Fig. 2(a), the triangles denote the position of the ac-susceptibility peak in Fig. 3(b). sg, spin-glass range; sm af, smeared antiferromagnetic transitions.

DISCUSSION

We have presented experimental evidence for a smearing of the first-order magnetic phase transition in EuSe when diluting the Eu lattice by diamagnetic Sr. The smearing is observed in the thermally driven transition and it is especially strong in the magnetic-field-driven metamagnetic transitions.

One delicate experimental problem is the proof of the intrinsic origin of the smearing or, vice versa, the proof that macroscopic sample inhomogeneities are not the trivial reason for the observed smearing. From our experience with the chemically more complicated quaternary compounds $Eu_xSr_{1-x}S_ySe_{1-y}$ (Ref. 21) we would rule out this possibility. The critical behavior of the ferromagnetic second-order phase transitions can be followed typically down to a reduced temperature of 5×10^{-3} without a definite smearing; in EuSe with only 5% of Sr we get a smearing at $t=2\times10^{-2}$ already. With the preparation method applied here we expect Sr to be distributed at random on the Eu lattice, at least at low concentrations.

The intrinsic rounding of the transition is described in Ref. 8, and since these theoretical results are very informative for understanding the measurements, we partly reproduce them here. Magnetic clusters with a concentration deviating from the mean concentration by Δp will be unstable at a temperature ΔT_c from the mean transition temperature T_c with ΔT_c given by

$$\Delta T_c = p(1-p)^{1/2}\frac{dT_c(p)}{dp}l^{-d/2} - C\sigma T_c(p)l^{\lambda-d}/L(p)\ ,$$

where p is the concentration of the magnetic ions; T_c, the transition temperature; l, the diameter of the cluster; σ, the surface tension; L, the latent heat per site; and for Heisenberg 3D system $d=3$ and $\lambda=1$.

The first positive term is diminished by the second term, the surface term, describing the surface energy at the interface of the clusters. There is a typical domain width l^* for the characteristic domain size. It is of the order of magnitude of the correlation length at the transition temperature or larger.

The above formula contains microscopic parameters which are difficult to measure, e.g., σ, $L(p)$, and the geometry factor C, which measures the amount of interface formed during the transition. But qualitatively one expects a ΔT_c strongly increasing with the dilution and a characteristic domain size l^* strongly decreasing. Qualitatively $Eu_xSr_{1-x}Se$ exhibits this behavior.

The above formula can easily be generalized to the magnetic-field-driven metamagnetic transitions; one only has to replace T_c by the transition field H_m and then derives a transition width ΔH_m similar to the width of the transition temperatures ΔT_c. The different degree of smearing, e.g., $\Delta T_c/T_c \simeq 2\times10^{-2}$ and $\Delta H_m/H_m \simeq 2\times10^{-1}$ for the sample $Eu_{0.95}Sr_{0.05}Se$ can be attributed to the different microscopic parameters σ, L, and C.

A further very interesting finding in $Eu_xSr_{1-x}Se$ is the occurrence of a spin-glass phase at very high Eu concentrations $x\simeq0.8$; in $Eu_xSr_{1-x}Se$ the spin-glass phase in $Eu_xSr_{1-x}S$ exists up to a concentration $x=0.5$. Most

spin-glass systems known up to now are diluted ferromagnets or ferromagnets mixed with antiferromagnets; only until quite recently have spin-glass effects also been reported in some diluted antiferromagnets. The system $Ce_{1-x}Mn_xTe$ has been analyzed in detail,[22] and the results of this system compare well with our findings in $Eu_xSr_{1-x}Se$. In $Cd_{1-x}Mn_xTe$ a spin-glass phase exists for concentration $x < 0.6$; for higher Mn concentrations x a cluster antiferromagnet is observed. Unfortunately in $Cd_{1-x}Mn_xTe$ the development of magnetic long-range order can only be followed up to a concentration $x = 0.7$, since random mixed crystals can only be prepared up to this concentration.

A further example of spin-glass properties in diluted antiferromagnets is the spinell system $Zn(Cr_xGa_{1-x})_2O_4$.[23] Spin-glass ordering has also been detected in the compounds $GdAl_2$ (Ref. 24) and Mn_3Ge_2 (Ref. 25) when they are in the amorphous state; in the crystalline state these compounds are antiferromagnets.

The observation of spin-glass effects in diluted ferromagnets, diluted antiferromagnets, and mixed ferromagnets and antiferromagnets show that the spin-glass state is a rather general phenomenon in random systems. The cluster blocking model, which is the simplest approach to the spin-glass problem, does not account well for this fact. Antiferromagnetic clusters, if they exist in the spin-glass phase of diluted antiferromagnets, are coupled by exchange forces rather than anisotropic dipolar fields as assumed in the cluster blocking model.

By comparing the different systems exhibiting spin-glass effects it is found that competing interactions and randomness are necessary for spin-glass properties. $Eu_xSr_{1-x}Se$ fits very well with this rule. Even in EuSe the ferromagnetic exchange J_1 and the antiferromagnetic exchange J_2 and probably some weaker higher-order interactions are strongly competing. This competition causes the metamagnetic properties and the complex multiphase behavior of EuSe, and is probably also responsible for the occurrence of spin-glass properties at such high Eu concentrations in $Eu_xSr_{1-x}Se$ as reported here.

An interesting approach for the understanding of the spin-glass phase in $Eu_xSr_{1-x}Se$ is offered by the special characteristics of a first-order transition upon dilution. Theoretically it is expected that the system should break up into domains at the smeared phase transition. The size of the domains are expected to decrease strongly with the solution. Do the spin-glass effects set in below a certain cluster size or is the interface region between the clusters responsible for the spin-glass effects? We mention that we have found evidence for the coexistence of spin-glass effects and antiferromagnetic order for an intermediate concentration range. This could be assigned to the antiferromagnetic domains and the strongly frustrated interface regions, respectively.

An analysis of the magnetic short-range order in the spin-glass phase of $Eu_xSr_{1-x}Se$ either by neutron scattering or by an analysis of the transferred hyperfine fields by Mössbauer technique should give valuable additional information for answering these questions. We expect that antiferromagnetic short-range order prevails in $Eu_xSr_{1-x}Se$ similar to the ferromagnetic short-range order in the spin-glass phase of $Eu_xSr_{1-x}S$.[26]

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