

Magnetic phase diagram of $\text{Eu}_x\text{La}_{1-x}\text{S}$

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The magnetic phases of the solid-solution system $\text{Eu}_x\text{La}_{1-x}\text{S}$ are analyzed by ac susceptibility, magnetization, and specific-heat measurements. The dominant contribution to the exchange interactions $\text{Eu}_x\text{La}_{1-x}\text{S}$ is of the Ruderman-Kittel-Kasuya-Yosida (RKKY)-type; the effective RKKY interaction changes from ferromagnetic to antiferromagnetic at $x=0.45$. The system orders ferromagnetically for $x \geq 0.5$; at low La dilution the ferromagnetic phase is inhomogeneous below the Curie point. For the diluted ferromagnetic range we derive critical exponents $\alpha \simeq -1$ and $\gamma \simeq 2$ for the specific-heat and the susceptibility exponent, respectively. In the low-temperature specific heat there is a change from a $T^{3/2}$ law for low dilution toward a linear T dependence for higher dilution. For $x \leq 0.5$ the system exhibits spin-glass phenomena. In a narrow concentration range, a spin-glass phase with two freezing temperatures and a strong dependence on the atomic short-range order exists.

INTRODUCTION

The study of randomly diluted ferromagnets and of spin glasses is of great current interest in magnetism. Even after ten years of intense research the spin-glass phenomenon is not well understood and the influence of random disorder on the excitations, phase transitions, and ground states of systems with magnetic long-range order is a growing field in theory and experiment.

In this paper we present experimental results on the solid-solution system $\text{Eu}_x\text{La}_{1-x}\text{S}$, which has not been studied in detail until now. In the first part of the paper we will study the ferromagnetic solid-solution range $x \geq 0.5$, with emphasis on the critical behavior at the phase transition and on the magnetic excitations at low temperatures. In the second part of the paper we will study the concentration range $x \leq 0.5$, where interesting spin-glass phenomena are observed.

The system $\text{Eu}_x\text{La}_{1-x}\text{S}$ under discussion here is similar to the well-known spin-glass system $\text{Eu}_x\text{Sr}_{1-x}\text{S}$, which has been studied in great detail in recent years.¹⁻³ Due to the model character of $\text{Eu}_x\text{Sr}_{1-x}\text{S}$, it can be shown by Monte Carlo simulation techniques⁴ that the competition between the ferromagnetic and the antiferromagnetic exchange interaction causes the breakdown of long-range order at the concentration $x=0.5$. We have found a direct experimental confirmation of the dominant importance of the competing interactions within the quaternary system $\text{Eu}_x\text{Sr}_{1-x}\text{S}_y\text{Se}_{1-y}$, where the spin-glass phase shifts to higher Eu concentrations with increasing ratio of the antiferromagnetic to ferromagnetic exchange.^{5,6}

In a preliminary analysis of the susceptibility of $\text{Eu}_x\text{La}_{1-x}\text{S}$ (Ref. 7), we have found very high critical susceptibility exponents, $\gamma \simeq 2$, within the ferromagnetic concentration range, similar to the results for the dilution system $\text{Eu}_x\text{Sr}_{1-x}\text{S}_{0.50}\text{Se}_{0.50}$.⁸ In a detailed analysis of the critical behavior of this insulating dilution system in Ref. 8, we have analyzed the critical exponents α , β , γ , and δ

by measurement of the specific heat and magnetization. The critical exponents were found to be concentration dependent; for x close to the critical concentration, $\alpha \simeq -1$, $\beta \simeq 0.5$, $\gamma \simeq 2$, and $\delta \simeq 5$. The scaling relations were fulfilled in the whole solid-solution range. These results demonstrate that new critical exponents in a system with random disorder exist.

In the theoretical literature the critical behavior of random systems is still rather controversial.⁹⁻¹¹ In Refs. 9 and 11 it was concluded that the critical behavior should not change in a system with a random distribution of the exchange interactions. In Ref. 10 a definite change of the critical behavior with the amount of dilution was predicted.

Since the exchange interactions in $\text{Eu}_x\text{La}_{1-x}\text{S}$ are definitely different from those in the insulating compounds analyzed in Refs. 7 and 8, namely, predominantly ferromagnetic and long range compared to strongly competing and short range, the similarity of the exponents in both systems indicates the universality of these new exponents in random systems.

The properties of EuS and EuSe diluted with trivalent rare-earth ions have been already studied in some detail.¹²⁻¹⁵ The trivalent rare-earth ions (X) contribute one conduction electron per ion in the solid-solution systems $\text{Eu}^{2+}_x\text{X}^{3+}_{1-x}\text{S}$; thus, the solid-solution systems become metallic with a metal-semiconductor transition at $x \simeq 0.95$. In the concentration range about the metal-insulator transition, very interesting transport phenomena exist close to the ferromagnetic Curie temperature.^{12,13} The electrical resistivity increases by several orders of magnitude at T_c and is strongly suppressed by an applied magnetic field. This finding has been interpreted by models of the magnetic polaron state¹² or the magnetic impurity state.¹⁴ In both models, close to T_c the $5d$ electron is trapped by magnetic interactions, and spin-polarizes the surrounding $4f$ spins into a ferromagnetic alignment.

The $\text{Eu}^{2+}_x\text{X}^{3+}_{1-x}\text{S}$ systems have served as model systems for testing the Ruderman-Kittel-Kasuya-Yosida (RKKY) model.¹⁵ It is known from this work that the effective exchange induced by the conduction electrons is ferromagnetic at low conduction-electron concentration and changes sign close to $x=0.5$.

In recent years, Mössbauer, magnetization, and specific-heat measurements of the solid-solution system $\text{Eu}_x\text{Gd}_{1-x}\text{S}$ have been published.^{16,17} This system is similar to $\text{Eu}_x\text{La}_{1-x}\text{S}$ as far as the electronic band structure is concerned; magnetically, it is more complex since GdS is antiferromagnetic. For concentrations close to $x=0.5$, a spin-glass phase has been observed. Especially, the diluted antiferromagnetic phase of $\text{Eu}_x\text{Gd}_{1-x}\text{S}$ exhibits complicated behavior which is not well understood, e.g., a $T^{3/2}$ dependence of the low-temperature specific heat and a strong smearing of the antiferromagnetic phase transitions.

In order to get a detailed understanding of the magnetic order in $\text{Eu}_x\text{La}_{1-x}\text{S}$, we apply several experimental methods. The complex frequency-dependent susceptibility is the most important method for distinguishing the different magnetic phases. Low-field measurements made with a sensitive superconducting quantum interference device (SQUID) magnetometer give the susceptibility and magnetization in the limit $\omega \rightarrow 0$. The specific heat is a valuable technique for distinguishing magnetic phase transitions and freezing processes, since it measures mainly the magnetic short-range correlations. In a forthcoming paper¹⁸ a detailed Mössbauer study on the same samples is reported. Mössbauer spectroscopy, as a local method, probes the spin dynamics and the magnetic short-range order.

SAMPLE PREPARATION AND EXPERIMENTAL

Single crystals from the solid-solution series $\text{Eu}_x\text{La}_{1-x}\text{S}$ were grown in sealed tungsten crucibles by the Bridgman technique; details of the technique are described in Ref. 19. All samples had a sodium-chloride-type structure. Microprobe analysis showed that the real composition of the samples was close to the nominal composition. From the Mössbauer spectra (see Ref. 18), it was found that the crystals contain typically a few percent of Eu^{3+} . The lattice parameters of all samples of the present analysis are given in Fig. 1. Because of the smaller ionic radius of La^{3+} compared to Eu^{2+} , the lattice parameter decreases with increasing La concentration.

In the magnetic analysis we have found clear evidence that the atomic short-range order changes with annealing treatment in $\text{Eu}_x\text{La}_{1-x}\text{S}$. Motivated by this finding, we did a fine-structure analysis of the x-ray Bragg peaks as a function of concentration and annealing conditions. The influence of both concentration and annealing on the Bragg peaks was beyond the resolution of the conventional x-ray spectrometer. We suppose that the system has a tendency towards anticlustering (partial Eu-La ordering) and this type of atomic short-range order is very difficult to detect by standard x-ray techniques.

For the determination of the paramagnetic Curie temperatures, the susceptibility was measured in a magnetic

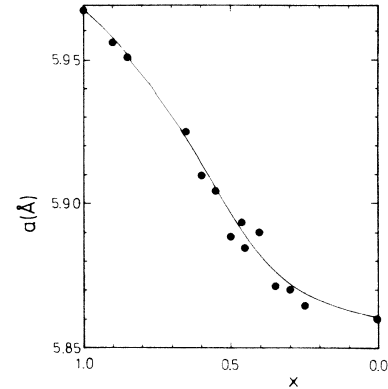


FIG. 1. Lattice parameter versus concentration for $\text{Eu}_x\text{La}_{1-x}\text{S}$.

field of 10 kOe by a standard Faraday balance. The ac susceptibility was measured by a mutual inductance technique; unless stated otherwise, the measurements were done at a frequency of 87 Hz. The dc magnetization was measured by a SQUID magnetometer with a field of 1 Oe trapped in the superconducting Pb shield. The specific-heat measurements were done by an adiabatic heat-pulse technique. For the measurements of the magnetic properties, the single crystals were ground into a spherical shape; all measurements for one concentration were done on the same sample.

RESULTS

Paramagnetic Curie temperatures

In Fig. 2 the paramagnetic Curie temperatures of $\text{Eu}_x\text{La}_{1-x}\text{S}$ are given. As the dashed line, we have plotted the paramagnetic Curie temperature predicted for an insulating system, using the lattice parameters of Fig. 1.

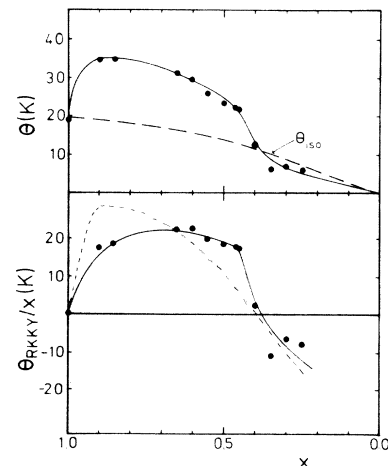


FIG. 2. Upper part: Paramagnetic Curie temperatures versus concentration for $\text{Eu}_x\text{La}_{1-x}\text{S}$; the dashed line gives the paramagnetic Curie temperatures Θ_{iso} expected for an insulating system. Lower part: RKKY part of the interaction scaled by the concentration (solid dots and solid curve) and theoretical curve (dashed curve) as described in the main text.

The Curie temperatures for an insulating dilution system can be calculated from the known lattice-parameter dependence of the exchange interactions J_1 and J_2 in the Eu chalcogenides.²⁰ The RKKY exchange is proportional to the difference of the two curves. This part of the exchange interactions, scaled by the concentration x , is given in the lower half of Fig. 2. The conduction-electron exchange is strong and ferromagnetic down to $x=0.45$, then it drops off sharply towards antiferromagnetic values for $x < 0.35$.

The dashed curve in the lower part of Fig. 2 is the concentration dependence of the paramagnetic Curie temperatures calculated by RKKY theory using the standard formula for the paramagnetic Curie temperature¹⁵

$$\Theta = \frac{3\pi^2 n^2 \Gamma^2 (g-1)^2 J(J+1)}{4k_B \epsilon_F} \sum_i F(2k_F r_i), \quad (1)$$

n being the conduction-electron concentration, Γ the exchange constant, $F(2k_F r_i)$ the RKKY function $F(x) = [x \cos(x) - \sin(x)]/x^4$, and the other parameters having their usual meaning. The sum is taken over all neighbors at distance r_i from the origin.

We have fitted the prefactor in Eq. (1) and assumed a degeneracy of the conduction band, $d=4$ (Ref. 15); the conduction-electron concentration n was calculated from the nominal composition. The overall fit is quantitatively rather bad but qualitatively gives the essential features of the experimental curve, namely, a positive paramagnetic Curie temperature for high Eu concentrations and a change towards negative values at $x=0.4$.

FERROMAGNETIC CONCENTRATION RANGE

In $\text{Eu}_x\text{La}_{1-x}\text{S}$, a ferromagnetic phase and a spin-glass phase exist for $x \geq 0.50$ and $x \leq 0.50$, respectively; these two phases will be discussed successively. The ferromagnetic phase is characterized by a plateau in the low-field magnetization determined by the reciprocal demagnetizing factor, as shown in Figs. 3 and 6.

For Eu concentrations $x \geq 0.85$ in Fig. 3, the ac susceptibility below the Curie temperature is temperature independent, as is characteristic for soft ferromagnetic materials with a very high susceptibility in the ferromagnetic state. The static low-field susceptibilities defined by m/h (SQUID magnetization m and applied field h) give identi-

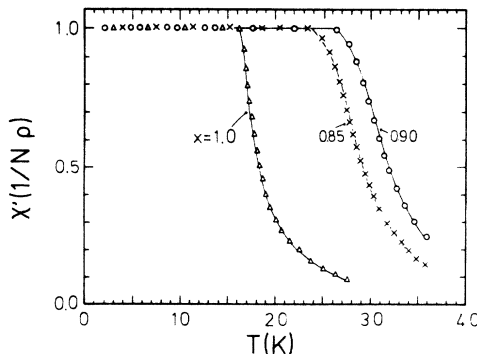


FIG. 3. Real part of the susceptibility as a function of temperature for samples $\text{Eu}_x\text{La}_{1-x}\text{S}$, with x given in the figure.

cal curves, apart from details close to T_c (see below). The ferromagnetic Curie temperatures of the La-diluted samples are about 10 K above that of EuS; this is due to the strong ferromagnetic RKKY exchange.

The measured susceptibility χ_{meas} in Fig. 3 is related to the true susceptibility χ_{tr} by the standard relation

$$\chi_{\text{meas}}^{-1} = \chi_{\text{tr}}^{-1} + N, \quad (2)$$

where the susceptibility is expressed in SI units and N denotes the demagnetizing factor.

For the spherical samples, $N = \frac{1}{3}$, whereas χ_{tr} is of the order of magnitude of 10^4 below T_c ; thus, any temperature dependence of χ_{tr} below T_c is strongly suppressed in χ_{meas} . But with the high intrinsic resolution of the ac susceptibility and the SQUID method of about 10^{-5} , one can resolve some details below T_c , which in the present case are very important.

In Fig. 4 we have plotted the ac susceptibility of the samples from Fig. 3 close to the ordering temperature on an enlarged susceptibility scale. For EuS, the Hopkinson maximum just below T_c is clearly resolved. For the La-diluted samples, one observes a very sharp peak at T_{c1} followed by a second one at T_{c2} about 4K below T_{c1} . This second peak is an indication of a second ferromagnetic transition; thus, the ferromagnetic phase seems to be inhomogeneous below T_{c1} . We show in Fig. 9 that the magnetic specific heat has a maximum close to T_{c2} .

The detailed analysis of the SQUID magnetization close to the Curie temperature supports this picture (Fig. 5). In EuS one observes a very sharp kink point, as expected for a homogeneous ferromagnet. At the kink temperature the spontaneous magnetization is given by H/N ; with a magnetic field of 1 Oe as in the present experiment the kink temperature is about 10^{-3} K below T_c .

For $\text{Eu}_{0.85}\text{La}_{0.15}\text{S}$ in Fig. 5, the magnetization increases continuously below T_{c1} and is approximately constant only below T_{c2} . This suggests that a homogeneous fer-

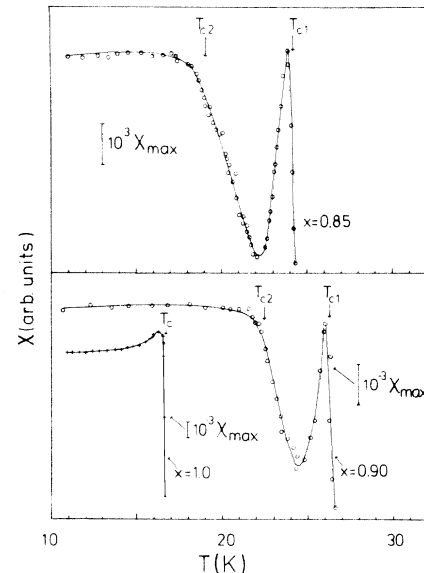


FIG. 4. Real part of the susceptibility close to the Curie temperature for the samples from Fig. 3 on an enlarged scale.

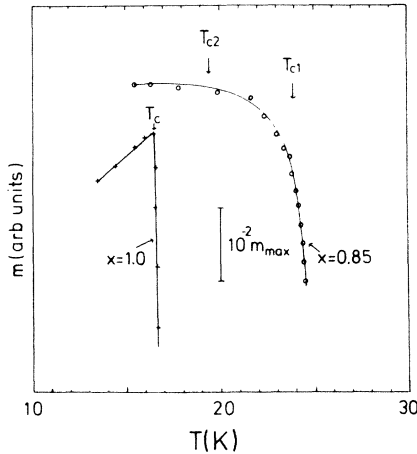


FIG. 5. Low-field SQUID magnetization on an enlarged magnetization scale for sample $\text{Eu}_x\text{La}_{1-x}\text{S}$, with x given in the figure.

romagnetic phase exists only below T_{c2} ; we will try to explain this interesting phenomenon in the discussion below.

In Fig. 6 the results for the ferromagnetic samples with lower Eu concentration are given. The magnetization has a plateau below T_c , whereas the ac susceptibility decreases with decreasing temperature. Fine structure below T_c , as in Fig. 4, does not exist. At about 10 K there is a further, steeper drop in χ . This is observed in many dilution systems at concentrations close to the breakdown of ferromagnetic long-range order; see, e.g., Ref. 2 for similar curves for $\text{Eu}_x\text{Sr}_{1-x}\text{S}$. Following the results of the infinite-range spin-glass models,²¹ this behavior is usually interpreted as a reentrance of the spin-glass state. In Fig. 6 one observes that the static magnetization does not show

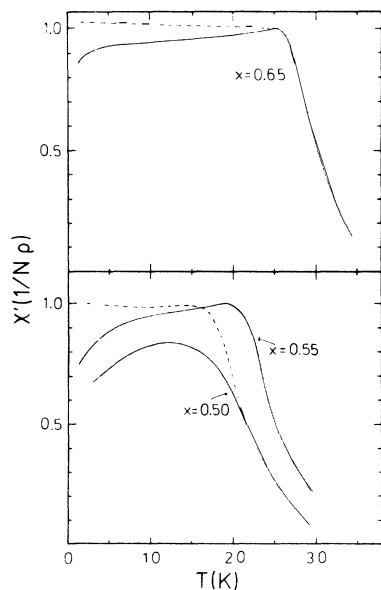


FIG. 6. Real part of the ac susceptibility (solid curves) and static susceptibility m/h from the SQUID magnetization (dashed curve) as a function of temperature for samples $\text{Eu}_x\text{La}_{1-x}\text{S}$, with x given in the figure.

any anomaly at low temperatures; thus, the reentrant behavior does not seem to exist in thermodynamic equilibrium in $\text{Eu}_x\text{La}_{1-x}\text{S}$. This is at variance with other systems, e.g., $\text{Fe}_x\text{Au}_{1-x}$, where reentrant behavior exists in the static low-field magnetization.²²

For the sample $\text{Eu}_{0.50}\text{La}_{0.50}\text{S}$ in Fig. 6 the ac susceptibility has a broad peak, with its maximum below the ferromagnetic saturation value, while the dc magnetization still exhibits a plateau. This sample is just at the borderline between the spin-glass and the ferromagnetic concentration range.

We next want to characterize the ferromagnetic phase transitions in more detail by an analysis of the critical power laws of the susceptibility and the specific heat at the magnetic phase transition. For the evaluation of the susceptibility exponent γ , we use the method proposed by Kouvel and Fisher.²³ From the asymptotic power law of the susceptibility

$$\chi = A(T - T_c)^{-\gamma}, \quad (3)$$

one gets by derivation

$$-\chi/(d\chi/dT) = \gamma^{-1}(T - T_c);$$

thus, plotting the left-hand side of Eq. (3) against T , one obtains the ferromagnetic Curie temperature by extrapolation and the critical exponent γ from the slope.

In Fig. 7 we show the results of this analysis. For EuS one gets a critical exponent $\gamma = 1.38$, i.e., very close to the theoretical three-dimensional value $\gamma = 1.39$. For the samples, $\text{Eu}_{0.85}\text{La}_{0.15}\text{S}$ and $\text{Eu}_{0.65}\text{La}_{0.35}\text{S}$, one gets ferromagnetic Curie temperatures of 23.8 and 24.8 K and γ values of 2.18 and 2.20, respectively.

In Fig. 8 we show the temperature dependence of the effective exponent γ on a reduced temperature scale. The critical power law with a well-defined exponent can be followed down to a reduced temperature of about 5×10^{-3} ; the crossover towards the Landau range starts at a reduced temperature of about 10^{-1} in EuS. In $\text{Eu}_{0.65}\text{La}_{0.35}\text{S}$ we observe a very broad critical range extending up to a reduced temperature of 3×10^{-1} .

For the ferromagnetic sample $\text{Eu}_{0.55}\text{La}_{0.45}\text{S}$ in Fig. 7, the Fisher-Kouvel plot reveals that no pure critical power law exists; a ferromagnetic Curie temperature and a criti-

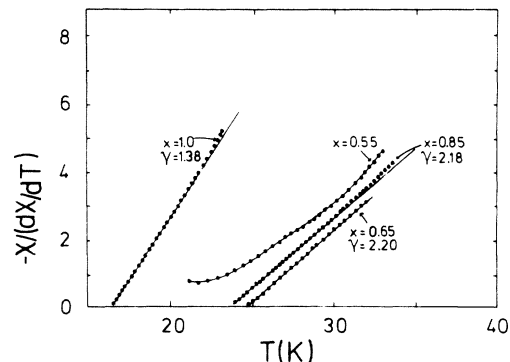


FIG. 7. Susceptibility divided by its thermal derivative as a function of temperature for samples $\text{Eu}_x\text{La}_{1-x}\text{S}$, with x and the critical exponent γ given in the figure.

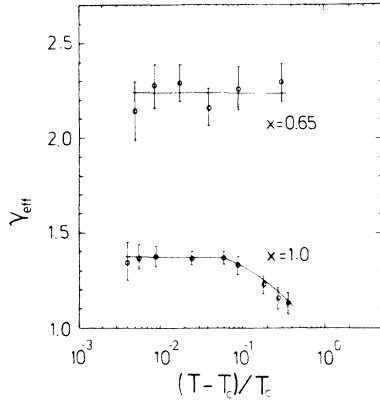


FIG. 8. Effective critical exponent γ versus the reduced temperature for $\text{Eu}_{0.65}\text{La}_{0.35}\text{S}$ and EuS .

cal exponent cannot be defined in an unambiguous manner. We have observed a similar deviation from a pure power law in the susceptibility of the diluted insulating compounds analyzed in Ref. 7.

The magnetic specific heat of two La-diluted samples in the ferromagnetic regime is given in Fig. 9. The lattice specific heat has been subtracted assuming a Debye T^3 law; the Debye temperature was calculated from the Debye temperature $\Theta = 279$ K of EuS (Ref. 24) using the Debye-model result $\Theta \propto \sqrt{M}/a$ with the lattice parameter a and the molecular weight M . The conduction-electron specific heat is small compared to the magnetic specific heat and can be neglected.

The magnetic specific heat has a smooth peak for both samples. For $x=0.85$, the maximum correlates with T_{c2} in Fig. 4; at T_{c1} , the ferromagnetic Curie temperature determined from the Fisher-Kouvel plots, there is no anomaly in the specific heat within the resolution of the experiment. This result suggests that only a fraction of the Eu spins takes part in the ferromagnetic phase transition at T_{c1} ; most Eu spins order at T_{c2} .

For the sample $\text{Eu}_{0.65}\text{La}_{0.35}\text{S}$, the temperature of the specific-heat maximum agrees with the ferromagnetic

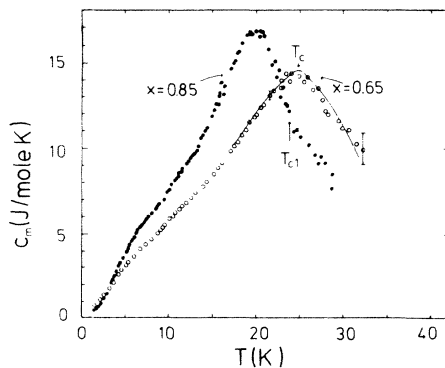


FIG. 9. Magnetic specific heat as a function of temperature for sample $\text{Eu}_x\text{La}_{1-x}\text{S}$, with x given in the figure. For the sample $x=0.65$, the solid curve is a fit following Eq. (5), with the parameters $T_c = 24.8$ K, $\alpha = -1.3$, $A = 30$, $A' = 24.5$, and $B = 14.8$ (units J/mole K).

Curie temperature determined from the divergence of the susceptibility, as expected for homogeneous ferromagnetism. We have observed similar smooth specific-heat curves for diluted ferromagnets $\text{Eu}_x\text{Sr}_{1-x}\text{S}_y\text{Se}_{1-y}$ (Ref. 8); similar curves have also been published for $\text{Eu}_x\text{Sr}_{1-x}\text{S}$.²⁵ The specific heat at the magnetic phase transition is described by the standard specific-heat formula

$$c_{>} = A/(T - T_c)^{-\alpha} + B \text{ for } T > T_c, \quad (4)$$

$$c_{<} = A'/(T_c - T)^{-\alpha} + B \text{ for } T < T_c.$$

The smooth specific-heat peak in Fig. 9 is consistent with a very low value for the specific-heat critical exponent α (Refs. 8 and 9). From the scaling relation $\alpha = 2 - \gamma(\delta + 1)/(\delta - 1)$, one calculates $\alpha = -1.3$ with the exponent $\gamma = 2.2$ derived for $\text{Eu}_{0.65}\text{La}_{0.35}\text{S}$ and assuming $\delta = 5$ (Ref. 8).

The drawn line in Fig. 9 shows a least-squares fit with $\alpha = -1.3$ fixed; one gets a reasonable fit with the parameters given in the subscript of the figure.

Thermal magnetic excitations in the ferromagnetic range

In Fig. 10 we have plotted the specific heat of the ferromagnetic samples of $\text{Eu}_x\text{La}_{1-x}\text{S}$ in comparison with that of EuS . For an isotropic ferromagnet, the dominant contributions to the magnetic excitations at low temperatures are long-wavelength spin waves with a quadratic dispersion law; they give a contribution

$$c = AT^{3/2} + BT^{5/2} \dots \quad (5)$$

to the low-temperature specific heat.

The low-temperature specific heat of EuS and

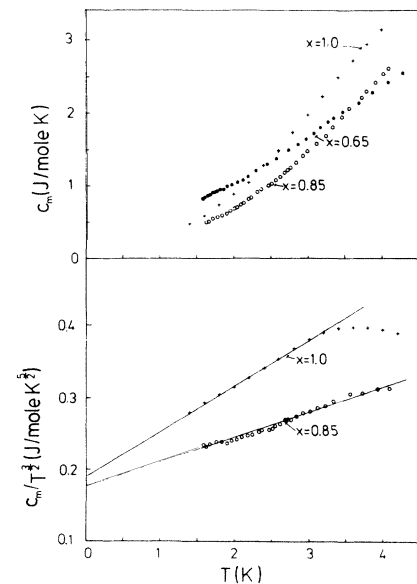


FIG. 10. Upper part: Specific heat as a function of temperature for samples $\text{Eu}_x\text{La}_{1-x}\text{S}$, with x given in the figure; EuS values were taken from Ref. 26. Lower part: Specific heat of the upper part plotted for the evaluation of A and B in Eq. (5).

$\text{Eu}_{0.85}\text{La}_{0.15}\text{S}$ is well described by Eq. (5) (see lower half of Fig. 10). The parameters are $A=0.19$ and 0.18 J/mole K and $B=0.068$ and 0.033 J/mole K for the two samples.

The specific heat of the diluted ferromagnet $\text{Eu}_{0.65}\text{La}_{0.35}\text{S}$, however, follows a linear T dependence (Figs. 10 and 18). The magnetic specific heat of this sample at low temperatures is high compared to EuS and $\text{Eu}_{0.85}\text{La}_{0.15}\text{S}$, reflecting its high density of states at low excitation energies.

The magnetic excitations of ferromagnets diluted at random have been studied theoretically in detail by the coherent potential approximation,²⁷ by computer simulation^{28,29} and by Green's-function methods.³⁰ At low dilution the density of states of the magnetic excitations derived theoretically is similar to that for the concentrated case; the spin-wave stiffness constant is expected to decrease linearly with the dilution. Thus, a $T^{3/2}$ law with A in Eq. (5) increasing with dilution should hold at low temperatures.

In the case of high dilution, however, at concentrations close to the breakdown of ferromagnetic long-range order, the theories predict a qualitative change of the excitation spectra. The density of states at low energies is strongly enhanced compared to that at higher energies. In Ref. 30 this feature has been interpreted as due to contributions of spin-wave excitations within finite clusters, which for topological reasons exist at higher dilution. These additional excitation modes dominate at low excitation energies and give rise to the characteristic change of the low-temperature specific heat. A numerical integration of the calculated excitation modes gives an approximately linear temperature dependence of the specific heat at low temperatures,^{29,30} in good qualitative agreement with our experimental result in Fig. 10.

Unlike most other ferromagnetic dilution systems, the mean magnetic interaction strength does not decrease with dilution in $\text{Eu}_x\text{La}_{1-x}\text{S}$. Actually, the sample $\text{Eu}_{0.65}\text{La}_{0.35}\text{S}$ has the highest ferromagnetic Curie temperature of the samples in Fig. 10. This fact makes the system very suitable for the study of the spin-wave modes in random lattices, since the spin-wave spectrum of the normal magnon modes should be approximately unchanged by the dilution. Thus, the high specific heat at low temperatures and the linear temperature dependence in $\text{Eu}_{0.65}\text{La}_{0.35}\text{S}$ suggests the existence of new local spin-wave modes.

Spin-glass phase

Below $x=0.50$, the system $\text{Eu}_x\text{La}_{1-x}\text{S}$ exhibits typical spin-glass phenomena. For the two samples in Fig. 11 the real part of the susceptibility has two peaks, which is very unusual and indicates the existence of two different freezing temperatures T_{f1} and T_{f2} . The dc magnetization has one broad peak with a maximum just below the value given by the reciprocal demagnetizing factor. The field-cooled dc susceptibility shown in Fig. 11 is higher than the ac susceptibility at low temperatures. This is usual in spin glasses, since the dc susceptibility probes all reversible and irreversible changes of the magnetization, whereas the ac susceptibility only gives the change of the magneti-

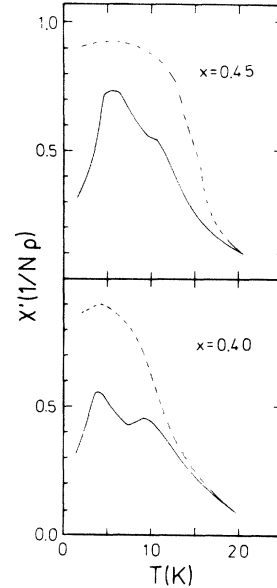


FIG. 11. Real part of the ac susceptibility (solid curve) and static susceptibility (dashed curve) as a function of temperature for samples $\text{Eu}_x\text{La}_{1-x}\text{S}$.

zation with a relaxation time smaller than the reciprocal measuring frequency. But contrary to the observation in the spin glasses AuFe or CuMg (Ref. 31), strong irreversibilities already exist far above the freezing temperatures.

For the concentration range $x \leq 0.35$, the real part of the ac susceptibility develops one rather sharp susceptibility peak similar to that of $\text{Eu}_x\text{Sr}_{1-x}\text{S}$ (Ref. 2) (Fig. 12). The dc field-cooled magnetization has a maximum at a somewhat lower temperature, as shown in Fig. 12 for one example. This again is different from the canonical spin glasses AuFe and CuMn , where the field-cooled magnetization is temperature independent below T_f (Ref. 3). The existence of a maximum in the static field-cooled susceptibility or in the ac susceptibility for $\omega \rightarrow 0$ has been observed in other spin glasses too³²⁻³⁴ and is discussed as a support of the existence of a true static phase transition at T_f .

In order to characterize the spin-glass phase in more de-

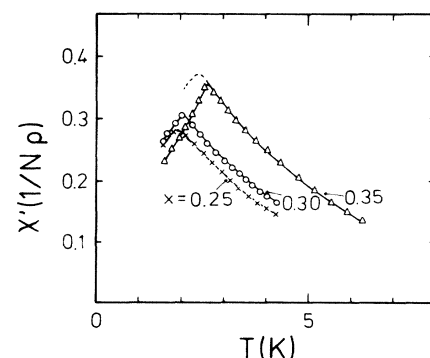


FIG. 12. Real part of the ac susceptibility (solid curve) and static susceptibility (dashed curve) as a function of temperature for samples $\text{Eu}_x\text{La}_{1-x}\text{S}$.

tail and elucidate especially the anomalous spin-glass phase with the two susceptibility maxima, we have analyzed the imaginary part of the susceptibility and the dependence of the susceptibility on the magnetic field and the frequency.

The two-peak structure of χ is much more distinct in the imaginary part χ'' than in the real part χ' (Fig. 13) for the samples from the anomalous spin-glass phase. For the samples of Eu concentration $x=0.35$, one finds one sharp peak in χ'' , with the maximum just below the maximum in χ' , similar to what has been observed in the spin-glass phase of $\text{Eu}_x\text{Sr}_{1-x}\text{S}$.³⁵ The measurement of χ' at different frequencies for the anomalous spin-glass phase (Fig. 14) shows that the peak at 10 K shifts by about 1 K in the frequency range of Fig. 14, whereas the peak at 4 K only shifts by about 0.2 K. The relative amplitude of the two peaks decreases with the frequency.

The imaginary part of the susceptibility gives direct information of the magnetic relaxation times of the system. A broad distribution of relaxation times ranging from 10^{-12} s to hours is the most characteristic common feature of spin glasses. Allowing for a relaxation-time distribution $g(\tau)$ with a magnetic moment distribution $m(\tau)$, the following expression was derived for the imaginary part of the susceptibility in Ref. 36:

$$\chi''(\omega) = \int_0^\infty \frac{\omega \tau m(\tau)}{1 + \omega^2 \tau^2} g(\tau) d(\ln \tau), \quad (6)$$

where h is the amplitude of the oscillating magnetic field and ω is the measuring frequency. When $m(\tau)g(\tau) \approx \text{const}$ around the measuring frequency, the integration of (6) gives approximately

$$\chi''(\omega) = -\frac{\pi}{2} \frac{m(1/\omega)}{h} g(1/\omega), \quad (7)$$

i.e., the imaginary part of the susceptibility directly measures the spectral weight $m(\tau)g(\tau)$ of the relaxation processes at the measuring frequency. Thus, the strong maximum at 10 K in Figs. 13 and 14 indicates a strong relaxation at low frequencies, whereas the spectral weight of the

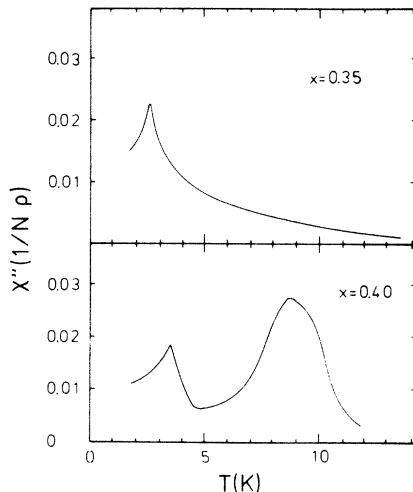


FIG. 13. Imaginary part of the ac susceptibility as a function of temperature for $\text{Eu}_x\text{La}_{1-x}\text{S}$.

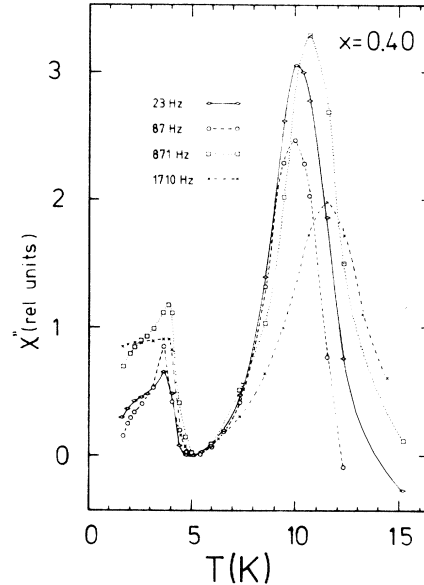


FIG. 14. Imaginary part of the susceptibility as a function of temperature for different frequencies for $\text{Eu}_{0.40}\text{La}_{0.60}\text{S}$.

relaxation processes for the freezing at 4 K is low in this frequency range.

In Fig. 15 we show the magnetic field dependence of χ' for spin glasses representative of the two spin-glass phases. For the sample with Eu concentration $x=0.35$, the susceptibility peak is smeared out as usual; for the sample with the double-peak structure one finds that a very small magnetic field of 4 Oe is sufficient to suppress the peak at 9 K. This strong dependence on the applied magnetic field is characteristic of ferromagnetic fluctuations being suppressed by the magnetic field.

The behavior of the susceptibility at T_{f1} , i.e., the strong

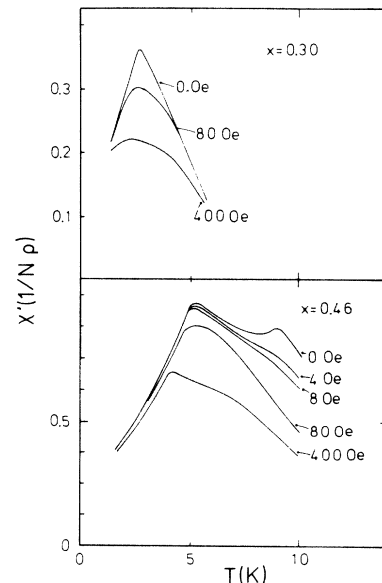


FIG. 15. Real part of the ac susceptibility as a function of temperature for two samples $\text{Eu}_x\text{La}_{1-x}\text{S}$ at different applied magnetic fields.

frequency and field dependence and the strong relaxation at low frequencies can tentatively be interpreted as a freezing of weakly coupled ferromagnetic clusters. A quite interesting additional finding concerning the origin of the two-peak structure in the susceptibility is its strong dependence on the annealing condition of the sample.

In Fig. 16 we display the susceptibility of a sample measured after different annealing processes. The sample was first annealed at 1200°C for 8 h and quenched to room temperature. The two-peak structure vanished completely and a peak very similar to those observed for the normal spin-glass phase at lower Eu-concentrations resulted. A further annealing at 500°C for 20 h did not change the susceptibility further. Afterwards, the sample was annealed just below the melting point at 1800°C for 2 h; now the two-peak structure occurs again and is even more distinct than in the as-prepared sample state.

The whole procedure is reversible and reflects the influence of a different atomic short-range order. The two-peak structure belongs to the sample state after quenching from high temperatures, i.e., to the state with the most random Eu-La distribution. The single peak occurs in the sample after long-time annealing at low temperatures, i.e., in the state with an atomic distribution close to thermal equilibrium. From the analysis of the x-ray fine structure, we suppose that in thermal equilibrium $\text{Eu}_x\text{La}_{1-x}\text{S}$ has a tendency towards Eu-La order. Thus, the anomalous two-peak structure occurs in the sample state with broader Eu-La distribution. In Fig. 17 we display the magnetic specific heat of spin-glass samples from the two spin-glass phases. As usual, in spin glasses there is no resolvable anomaly at T_f but a rather broad maximum at higher temperatures.

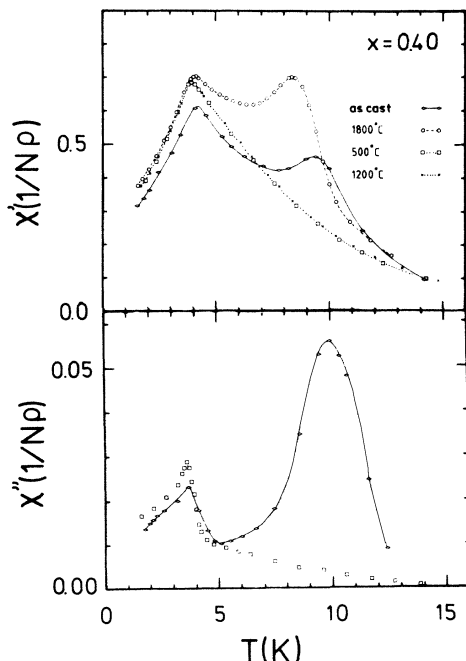


FIG. 16. Real and imaginary part of the ac susceptibility as a function of temperature for $\text{Eu}_{0.40}\text{La}_{0.60}\text{S}$ after different annealing treatments (see main text).

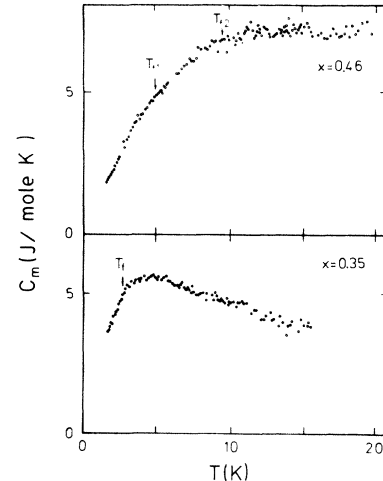


FIG. 17. Magnetic specific heat as a function of temperature for samples $\text{Eu}_x\text{La}_{1-x}\text{S}$.

In Fig. 18 we have plotted the low-temperature specific heat for the two spin-glass samples, together with the specific heat of one diluted ferromagnet. The linear dependence of the specific heat on the temperature is characteristic of spin glasses³⁷ and is well reproduced by the computer-simulation results.²⁹ Similar to the discussion of spin-wave modes in the diluted ferromagnets, it is assumed that local magnonlike modes in spin glasses give the dominant contribution to the excitations at low energies.

Magnetic phase diagram

The results of the preceding sections are summarized in the magnetic phase diagram, Fig. 19. One should discuss the magnetic phase diagram in combination with the concentration dependence of the exchange interactions in Fig. 2. The ferromagnetic Curie temperatures are nearly concentration independent in the range of strong and ferromagnetic RKKY exchange. At low conduction-electron concentrations, a ferromagnetic and a paramagnetic phase coexist just below T_c .

The breakdown of the ferromagnetic long-range order at $x=0.5$ is close to the change of sign of the RKKY interaction. For the spin-glass phase with two freezing tem-

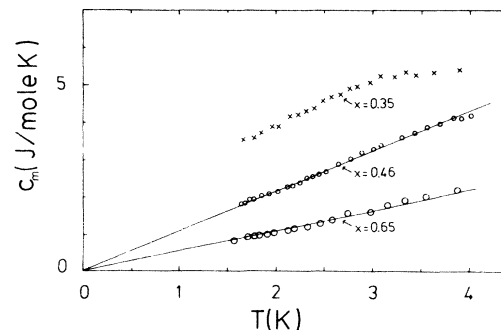


FIG. 18. Magnetic specific heat as a function of temperature for samples $\text{Eu}_x\text{La}_{1-x}\text{S}$.

peratures, the mean effective RKKY exchange is still ferromagnetic; for the spin-glass phase with normal behavior, the mean effective RKKY exchange is antiferromagnetic. The spin-glass phase *sg2* only exists in the sample state after quenching from high temperatures.

The magnetic phase diagram, Fig. 19, has some similarity with that of $\text{Eu}_x\text{Sr}_{1-x}\text{S}$ (Ref. 2). The critical concentration $x=0.50$ coincides; there is a "reentrance" and a spin-glass phase line meeting at the critical concentration.

DISCUSSION

Although there is some resemblance between the magnetic phase diagram of $\text{Eu}_x\text{Sr}_{1-x}\text{S}$ and $\text{Eu}_x\text{La}_{1-x}\text{S}$, the magnetic exchange interactions of the two systems are very different. In the ferromagnetic range the conduction-electron exchange interaction compensates for the dilution of the magnetic lattice. At the Eu concentration $x=0.6$, e.g., the La-diluted compound has a Curie temperature of 25 K, whereas $T_c=5.5$ K for the Sr-diluted compound

At low La dilution (10 and 15 at. % of La), we have observed a quite peculiar behavior at the ferromagnetic phase transition. The susceptibility reveals the existence of two transition temperatures T_{c1} and T_{c2} ; the maximum of the specific heat correlates with the lower temperature T_{c2} . We have concluded that between T_{c1} and T_{c2} the ferromagnetism is inhomogeneous; a paramagnetic and a ferromagnetic phase probably coexist. The magnetic polaron or the magnetic impurity model^{13,14} provide an explanation for this finding.

In this concentration range the conduction-electron concentration is low and the Fermi energy is close to the mobility edge. The anomalous transport properties at the magnetic ordering temperature prove that the trapping of electrons by the magnetic interactions still works in this concentration range.¹³ But the concentration of the impurity states is high; overlapping impurity states form an infinite percolating cluster. We assume that at T_{c1} the in-

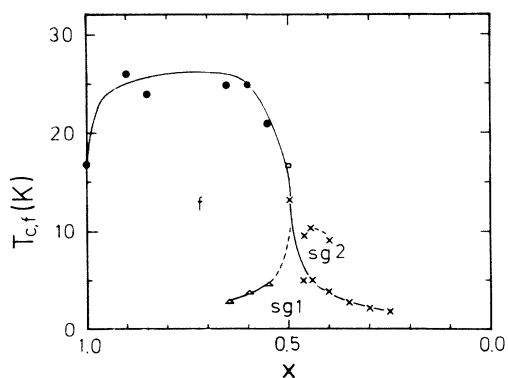


FIG. 19. Magnetic phase diagram of $\text{Eu}_x\text{La}_{1-x}\text{S}$. Solid dots: ferromagnetic Curie temperatures; open triangles: reentrance temperatures as determined from the ac susceptibility; crosses: freezing temperatures from the ac susceptibility. The open square gives the ferromagnetic Curie point determined from the SQUID magnetization. *f* denotes the ferromagnetic phase, *sg 1* and *sg 2* the two spin-glass phases.

finite cluster with enhanced ferromagnetic exchange undergoes a ferromagnetic phase transition, whereas at T_{c2} the residual Eu spins join the ferromagnetic cluster. Remarkably, for the susceptibility, one derives a pure critical power law with an exponent $\gamma=2.2$ for the transition at T_{c1} . This can be explained by the very high susceptibility of the ferromagnetic phase compared to the coexisting paramagnetic phase. At higher conduction-electron concentrations the magnetic polaron or the magnetic impurity state are not stable any more, since the kinetic energy of the electrons counteracts trapping. Then, a phase transition with one well-defined ordering temperature is observed. We have studied the phase transition of the sample $\text{Eu}_{0.65}\text{La}_{0.35}\text{S}$ in some detail as a representative example for this concentration range.

The maximum of the specific heat and the divergence of the low-field susceptibility occur at the same temperature, as expected for a phase transition of a homogeneous system. The critical exponents which we have determined from the fit of the specific heat and the susceptibility are very different from those of the three-dimensional Heisenberg model, namely, $\alpha \approx -1$ and $\gamma \approx 2$. These values are similar to those derived for the diluted insulating Eu chalcogenides at concentrations close to the breakdown of ferromagnetic long-range order.^{8,9}

We mention that a crucial test for the validity of the critical exponents $\text{Eu}_{0.65}\text{La}_{0.35}\text{S}$, namely, the test of scaling relations and the existence of universal functions, is still lacking. A preliminary analysis³⁸ of the magnetization isotherms of this sample gave a value $\delta=4.7$ for the magnetization exponent at the ordering temperature; this is consistent with the scaling relations. But at variance with the results in Refs. 8 and 9, the modified Arrot plots are strongly curved at low magnetic fields and universal functions only exist for a limited range of magnetic fields.

Another unusual observation in the $\text{Eu}_x\text{La}_{1-x}\text{S}$ system is the spin-glass phase with the two susceptibility peaks and its peculiar dependence on the atomic short-range order which can be changed by different annealing procedures. The important influence of the atomic short-range order on the spin-glass properties and the ferromagnetism is a well-established experimental finding in metallic spin-glass systems.³⁹ Ferromagnetic Curie temperatures²² and spin-glass freezing temperatures⁴⁰ can definitely be shifted by a change of the atomic short-range order by annealing.

The occurrence of two freezing temperatures in one homogeneous sample has never been observed before, to our knowledge, and is of some importance for the understanding of the origin of the spin-glass freezing. Within the phase transition models for the spin-glass freezing predicting one single well-defined spin-glass ordering temperature, this phenomenon is difficult to understand. We think the two freezing temperatures reflect a magnetic inhomogeneity of the samples and propose the following microscopic model for the finding.

The exotic spin-glass phase exists in a narrow concentration range close to the change of sign of the RKKY interactions. A calculation of the RKKY sum following Eq. (1) assumes an infinite range of the exchange interactions and an identical spin polarization at each Eu site. A

more realistic model for a random system has to account for the finite range of the interactions, typically of the order of the electron mean free path and the random distribution of the nearest neighbors. The electron mean free path of typically 10 Å in $\text{Eu}_x\text{La}_{1-x}\text{S}$ makes the RKKY interaction effectively short range. The spin polarization at a lattice site then depends on the actual nearest-neighbor distribution, and one must expect a spin polarization with a certain distribution width. When the mean RKKY exchange interaction is close to zero, one should expect the coexistence of regions with ferromagnetic and antiferromagnetic effective exchange.

We assume that the freezing at the higher temperature T_{f1} indicates the formation of ferromagnetic clusters in the regions with effective ferromagnetic exchange, and that the lower freezing temperature T_{f2} belongs to a freezing within the regions with antiferromagnetic effective exchange. We have observed that the two-peak structure only exists in the crystal state with more random Eu-La distribution; in the annealed state with spatial Eu-La order it does not exist. Since the ferromagnetic-clusters formation is expected in regions rich in Eu, they are favored in the case of random distribution.

SUMMARY AND CONCLUSION

In this paper we have presented results on a dilution system $\text{Eu}_x\text{La}_{1-x}\text{S}$ and derived a magnetic phase diagram. In the ferromagnetic concentration range at low dilution, a spatially inhomogeneous conduction-electron spin polarization leads to an inhomogeneous ferromagnetic state for a limited temperature interval. The inhomogeneity of the ferromagnetic state becomes apparent in details of the susceptibility and the specific heat at the phase transition.

In the spin-glass range we find an inhomogeneous state

for a narrow concentration range too, which gives rise to a puzzling two-peak structure in the susceptibility. Here, we attribute the magnetic inhomogeneity to the coexistence of regions with effectively ferromagnetic and effectively antiferromagnetic RKKY exchange and a corresponding coexistence of ferromagnetic clusters and a spin-glass phase.

The study of the critical behavior at the ferromagnetic phase transition in the diluted ferromagnetic range revealed critical exponents comparable to those observed in the insulating diluted Eu chalcogenides. Thus, $\text{Eu}_x\text{La}_{1-x}\text{S}$ presents a further diluted ferromagnetic system with new critical exponents and γ values close to 2. In other metallic dilution systems, e.g., $\text{Fe}_x\text{Au}_{1-x}$ (Ref. 22) and $\text{Ni}_x\text{Cu}_{1-x}$ (Ref. 41), similar γ values have been reported. These results are in favor for the existence of a new universal fixed point in systems with random dilution, as supposed theoretically in Ref. 10.

In the diluted ferromagnetic range of $\text{Eu}_x\text{La}_{1-x}\text{S}$ close to the critical concentration $x_c=0.5$, we have observed a deviation from a pure power law in the susceptibility. The absence of a pure power law in the susceptibility seems to reflect the absence of true ferromagnetic long-range order. In a detailed neutron scattering analysis of $\text{Eu}_x\text{Sr}_{1-x}\text{S}$,⁴² it has been shown that the correlation length remains finite for ferromagnetic samples close to x_c . We have observed the absence of a pure power law in the susceptibility in the same concentration range.⁸

Finally, the analysis of the specific heat of the ferromagnets at low temperatures showed a change of the standard $T^{3/2}$ law at low dilution towards a linear T dependence at higher dilution, as predicted theoretically. The nearly concentration-independent ferromagnetic Curie temperatures in $\text{Eu}_x\text{La}_{1-x}\text{S}$ make the system very suitable for a more detailed study of the magnon modes responsible for the excess specific heat at low temperatures.

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