Bishop and J. D. Reppy, Phys. Rev. Lett. 40, 1727 (1978); Emilia Webster, Grant Webster, and Marvin Chester, Phys. Rev. Lett. 42, 243 (1979).
[12]C. C. Tsuei, W. L. Johnson, R. B. Laibowitz, and J. M. Viggiano, Solid State Commun. 24, 615 (1977); C. C. Tseui, J. M. Coey, and S. von Molnar, Phys. Rev. Lett. 41, 664 (1978).
[13]P. M. Horn and R. D. Parks, Phys. Rev. B 4, 2178 (1971).
[14]T. Worthington, P. Lindenfeld, and G. Deutscher, Phys. Rev. Lett. 41, 316 (1978).
[15]N. F. Mott and E. A. Davis, *Electronic Processes In Noncrystalline Materials* (Clarendon, Oxford, 1979), 2nd ed., p. 31.
[16]B. A. Huberman and S. Doniach, Phys. Rev. Lett. 43, 950 (1979).
[17]S. A. Wolf, D. U. Gubser, and Y. Imry, Phys. Rev. Lett. 42, 324 (1979).

Specific Heat of Insulating Spin-Glasses, (Eu,Sr)S, near the Onset of Ferromagnetism

D. Meschede and F. Steglich[(a)]
II. Physikalische Institut der Universität, 5000 Köln, West Germany

and

W. Felsch
I. Physikalische Institut der Universität, 3400 Göttingen, West Germany

and

H. Maletta and W. Zinn
Institut für Festkörperforschung, Kernforschungsanlage Jülich, 5170 Jülich, West Germany
(Received 7 May 1979)

The specific heat, $C(T)$, of the insulating spin-glass $Eu_xSr_{1-x}S$ with $x = 0.40$ exhibits a linear term γT and no singularity at T_f, like metallic spin-glasses. A new term, δT^{-2}, is found which may arise from totally decoupled clusters created by frustration. The field dependence, $\gamma(B)$ and $\delta(B)$, show maxima. With $x = 0.54$ the behavior is similar. $C(T,B)$ and $\chi(T,B)$ there indicate the spin-glass phase to be supressed at $B = 1$ T.

A characteristic property of metallic spin-glass systems is the (nearly) linear thermal variation of the magnetic specific heat, $C(T)$, at low T, together with the observation of a broad maximum of C above the freezing temperature T_f but a lack of a pronounced anomaly at T_f.[1] Recent numerical calculations by Walker and Walstedt[2] confirmed the linear dependence of $C(T)$.

Recently, the insulating compounds (Eu, Sr)S were found to show the same magnetic behavior[3] as is well established for metallic spin-glasses. The oscillating Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction mediated by the conduction electrons is now replaced in (Eu, Sr)S by the well-known competing nearest- and next-nearest-neighbor exchange interactions.[4] An interesting detail of its magnetic phase diagram has been discovered by neutron diffraction experiments,[5] showing upon cooling a spin-glass state to exist below the ferromagnetic phase within a concentration regime above the "multicritical" point at $x_c = 0.51$. In this Letter we present the first calorimetric studies of $Eu_xSr_{1-x}S$ single crystals with concentrations below ($x = 0.40$) and slightly above ($x = 0.54$) x_c. One advantage of this system is the lack of an electronic contribution to the specific heat. Since, in addition, below 10 K the lattice contributes less than 0.3%, the measured specific heat is nearly identical with the magnetic part.

The specific heat was determined between 0.3 and 10 K at magnetic fields $0 \leq B \leq 1.0$ T by a quasistatic method as described in detail elsewhere.[6] A pair of carbon resistors (Allen-Bradley, 10 Ω and 180 Ω) were used as sample thermometers, which covered the ranges 0.3–1.5 K and 1.2–10 K, respectively. They were calibrated against ^{3}He and ^{4}He vapor pressure and (for $T > 4.2$ K) against a precalibrated Ge resistor. The magnetoresistance of these thermometers never exceeded $\Delta R/R(B=0) \approx 2\%$ in the present experiments. This introduced a maximum error of the specific heat, which was confined to 0.5% and could therefore be neglected in the data analysis (compare Ref. 6). The results of the specific heat were compared to the low-frequency (117

Hz) differential magnetic susceptibility, which was measured using a conventional mutual-inductance method and superposing static magnetic fields up to 1.0 T.

In Fig. 1, the specific heat per Eu atom in a.u., C^*/k_B, is shown for the two samples. We discuss the zero-field measurements first. The inset on the left in Fig. 1 shows the temperature dependence of C^* of $Eu_{0.40}Sr_{0.60}S$. Static susceptibility measurements in low fields[3] revealed a maximum in χ for $x = 0.40$ at $T_f = 1.7$ K. In fact, the specific-heat curve for $x = 0.40$ displays the characteristics of metallic spin-glasses: a broad maximum at 3.1 K well above T_f, no singularity at T_f, and a linear variation with temperature below T_f. At low temperatures, however, a distinct deviation from this behavior is observed. This is is better seen in a plot of C^*/k_BT vs T (main part of Fig. 1). Below 0.45 K, the data follow a straight line when plotted in the form C^*T^{-1} vs T^{-3}, i.e., they can be fitted with the relation

$$C^* = \gamma T + \Delta^2 T^{-2}, \quad (1)$$

where $\gamma/k_B = 0.49 \pm 0.01\ K^{-1}$ and $\Delta^2/k_B = (2.6 \pm 0.4) \times 10^{-3}\ K^2$. The same fit can be achieved with $Eu_{0.54}Sr_{0.46}S$ in the same temperature regime. This sample shows a double transition, namely, at $T_c = 5.0$ K (also reflected by the broad specific heat maximum, c.f. Fig. 1) and at $T_f = 2.0$ K.[5] In this case the fit yields $\gamma/k_B = 0.32 \pm 0.01\ K^{-1}$ and $\Delta^2/k_B = (1.2 \pm 0.3) \times 10^{-3}\ K^2$.

We note that above 0.45 K, the data for both samples lie above the straight lines in the C^*T^{-1} vs T^{-3} plot. This is reflected for the sample with $x = 0.54$ by a flat minimum in the C^*T^{-1} vs T plot of Fig. 1. We believe that this might indicate the existence of an additional term $\propto T^2$ in Eq. (1), as was recently detected in the low-temperature ($B = 0$) specific heat of the metallic spin-glass *Cu*Mn.[7]

The term $\Delta^2 T^{-2}$ hints at a Schottky anomaly well below the temperature limit of these experiments. For both samples, this term exceeds the nuclear specific heat, $\Delta_N^2 T^{-2}$, which is due to the hyperfine splitting of the ^{151}Eu and ^{153}Eu nuclei. With a hyperfine field[8] of ≈ 30 T one estimates $\Delta_N^2/k_B \approx 3.8 \times 10^{-4}\ K^2$.

Next we discuss the nature of the spin-glass phase in (Eu, Sr)S by studying the specific heat in applied magnetic fields. For this system the

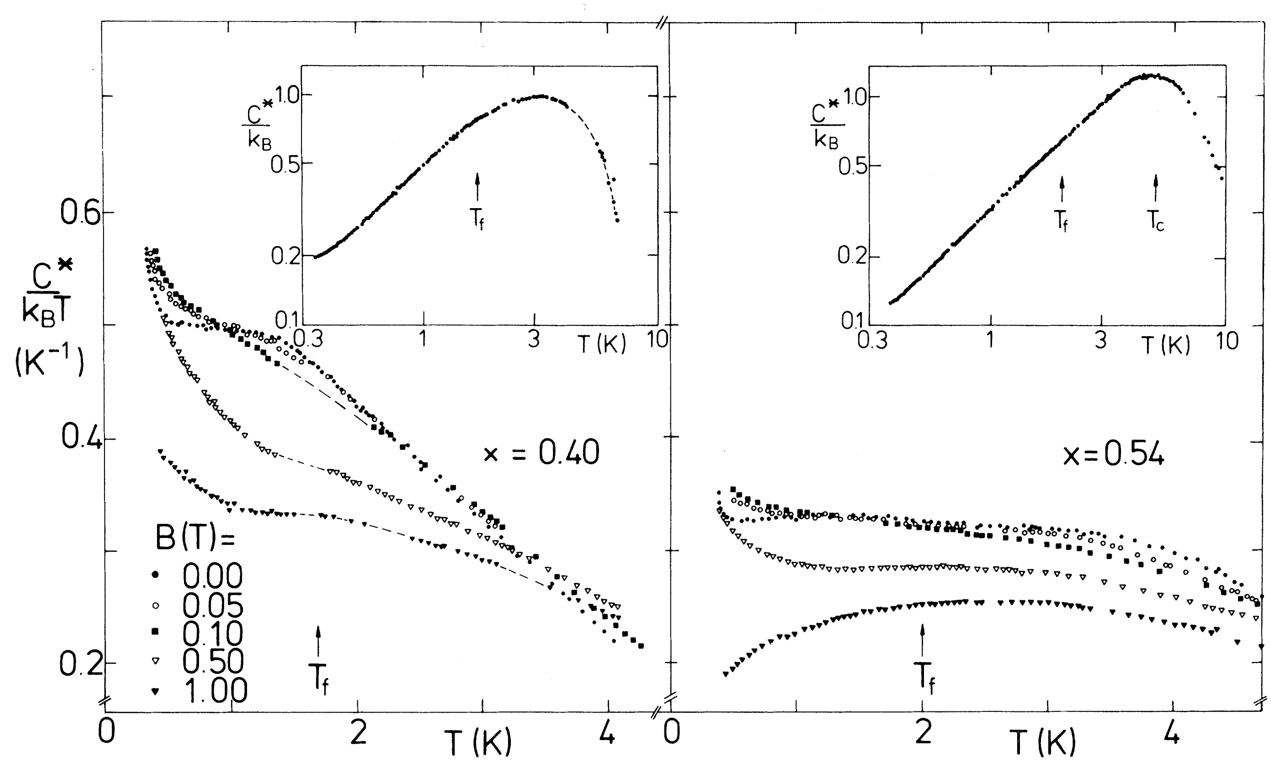

FIG. 1. Specific heat per Eu atom divided by k_BT vs temperature T in various applied fields B for $Eu_xSr_{1-x}S$ with $x = 0.40$ and $x = 0.54$. Insets show the zero-field specific heat on a log-log plot. The transition temperatures, T_f and T_c, taken from Refs. 3 and 5 are indicated by arrows.

field sensitivity of the susceptibility turned out[3] to be even more pronounced than in metallic spin-glasses. The temperature dependence of the specific heat of both samples measured at magnetic fields of 0.05, 0.10, 0.50, and 1.00 T is shown in Fig. 1, too. Like the $B=0$ data, these curves can again be reasonably well fitted (below $T=0.55$ K) by Eq. (1), with field-dependent coefficients $\gamma(B)$ and $\Delta^2(B)=\delta(B)+\Delta_N^2$, where $\Delta_N^2 \approx$ const because of the large hyperfine field[8] and, consequently,

$$C^*(B)=\gamma(B)T+\delta(B)T^{-2}+\Delta_N^2T^{-2}. \qquad (2)$$

The field dependences obtained for the coefficients γ and Δ^2 are shown in Fig. 2. The coefficient γ is comparable to that of the metallic spin-glass $La_{0.92}Gd_{0.08}Al_2$ with comparable T_f.[9] Above $B \approx 0.2$ T, $\gamma(B)$ decreases for both systems. However, in contrast to a slight increase of $\gamma(B)$ in small fields observed for (Eu, Sr)S, a strong initial suppression of this coefficient was observed in (*La*, Gd)Al_2 and attributed there to superparamagnetic effects.[9] For both samples in Fig. 2 $\Delta^2(B)$ is bigger than Δ_N^2 in the whole field range studied ($B \leqslant 1$ T) and passes through a maximum.

Figure 1 signalizes a qualitative change of the specific-heat curves of $Eu_{0.54}Sr_{0.46}S$ when B is changed from 0.50 to 1.00 T. In an applied field of 1.00 T the low-temperature behavior of C^* no longer follows Eq. (2), but shows fairly good straight-line behavior in a plot of C^*T^2 vs $T^{7/2}$ below $T=0.6$ K, i.e., fits with the relation common to ferromagnets in small fields, namely,

$$C^*=AT^{3/2}+\Delta^2T^{-2}. \qquad (3)$$

The constant $A/k_B=0.25\pm0.01$ $K^{-3/2}$ has to be compared with $A/k_B=0.03$ $K^{-3/2}$ for pure EuS,[10] and $\Delta^2/k_B=(2.0\pm0.7)\times10^{-3}$ K^2 again is larger than Δ_N^2/k_B. Obviously, such a field suppresses the low-temperature spin-glass phase in the sample with $x=0.54$ and induces ferromagnetic ordering.

This interpretation is confirmed by investigating the magnetic susceptibility of (Eu, Sr)S in various static fields B (Fig. 3). For the zero-field curve in Fig. 3, the two transition temperatures, T_C and T_f, determined by neutron diffraction measurements[5] are indicated by arrows. The Curie temperature T_C coincides with the inflection point of $\chi(T)$, and T_f marks the onset of the steep decrease of χ at low T. With increasing field two maxima in $\chi(T)$ develop, corresponding to the transitions at T_C and T_f which shift toward opposite directions. At $B=1.00$ T only a very low and nearly constant $\chi(T)$ dependence is left indicating ferromagnetic instead of spin-glass ordering over the whole temperature range (0.3 K $\leqslant T \leqslant$ 10 K).

Our results provide an essential *distinction* between metallic spin-glasses (with long-range RKKY interaction) and insulating spin-glasses in

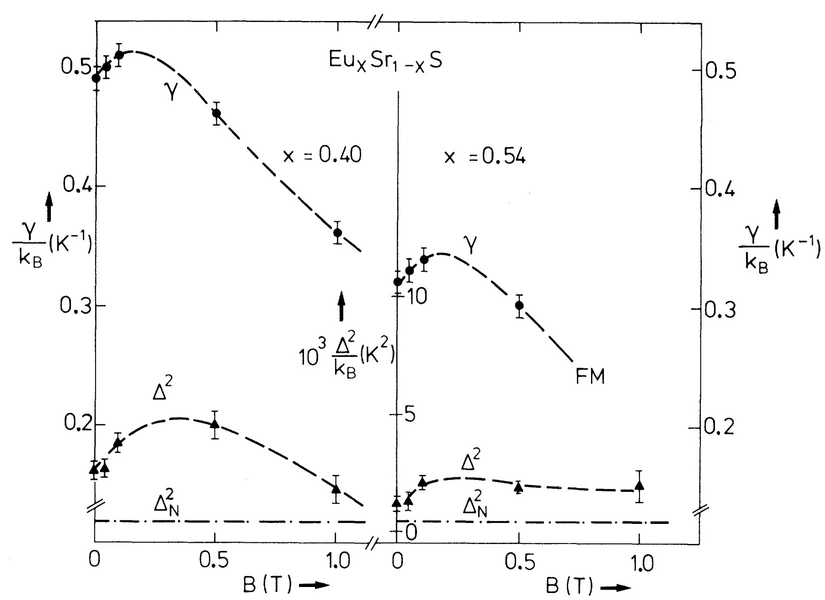

FIG. 2. Coefficient γ of the linear magnetic specific heat and coefficient Δ^2 of the T^{-2} term, both in units of k_B, as function of applied field B. The calculated values Δ_N^2 of the hyperfine term are indicated by dash-dotted lines.

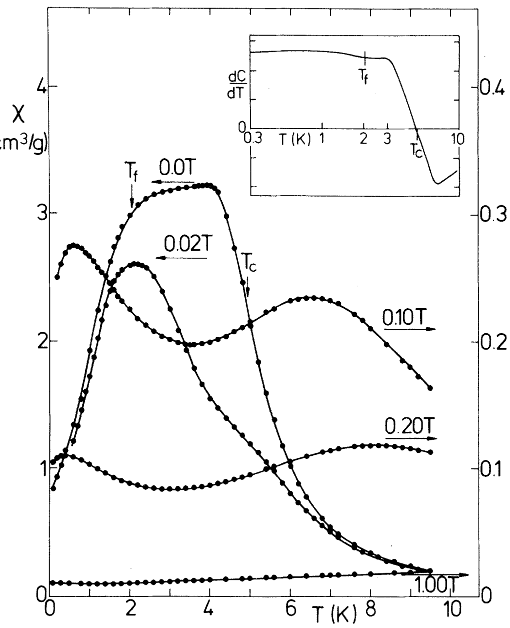

FIG. 3. Temperature dependence of the ac susceptibility in $Eu_{0.54}Sr_{0.46}S$ in various magnetic fields $B(T)$. Note the change of scale between $B = 0.02$ T and $B = 0.10$ T. The inset shows the temperature derivative of the specific heat for $B = 0$ of the same sample vs T on a logarithmic scale.

which the short range of the competing ferromagnetic and antiferromagnetic interactions results in a nonzero probability of a defect configuration where the cluster is "frustrated", i.e., decoupled from its environment concerning spin orientation. This case can be excluded for long-range RKKY interactions. If these "frustrated clusters" are subject to a magnetic field, they will contribute (at sufficiently high temperature) a Schottky-like δT^{-2} term to the specific heat of $Eu_xSr_{1-x}S$, where the coefficient δ is expected larger for the compound with the higher defect concentration $(1-x)$, as observed with $x = 0.40$ (see Fig. 2). The observation of such a δT^{-2} term even at $B = 0$ is probably caused by dipolar effects which were ignored in the kind of reasoning as given above.

Besides the new δT^{-2} term which is not known for metallic spin-glasses, two other important results of our study on $Eu_xSr_{1-x}S$ *confirm* the typical behavior of metallic spin-glasses: Firstly, no singularity is observed in the specific heat at T_f. (Only at the transition from ferromagnetic to spin-glass order of $Eu_{0.54}Sr_{0.46}S$ at $B = 0$ a tiny step in dC/dT is observed as shown in the insert of Fig. 3.) Secondly, there exists a linear term in the low-temperature specific heat. Since in $Eu_xSr_{1-x}S$ compounds no conduction electrons are present, the measured specific heat at low temperatures is nearly identical with the magnetic part. Compared with already studied metallic spin-glasses[1,7] with much lower concentrations of magnetic ions coupled by long-range RKKY interactions via the conduction electrons, we can now conlcude that a low-temperature specific heat being linear in T can be considered as a general property of spin-glasses, which is independent of the type of magnetic coupling and of the concentration of magnetic ions. This constitutes an interesting analogy to the dielectric and metallic glasses, where also linear dependences of $C(T)$ exist at low temperatures.[11] Thus the γT law of $C(T)$ seems, in fact, to be a universal property of disordered solids at low temperature.

It is a pleasure to thank H. Pink and K. J. Fischer for preparing the samples, and K. Binder, C. D. Bredl, H. von Löhneysen, and D. Stauffer for helpful discussions.

[a]Present address: Institut für Festkörperforschung, Technische Hochschule Darmstadt, D-6100 Darmstadt Germany.

[1]L. E. Wenger and P. H. Keesom, Phys. Rev. B 13, 4053 (1976).

[2]L. R. Walker and R. E. Walstedt, Phys. Rev. Lett. 38, 514 (1977).

[3]H. Maletta and W. Felsch, Phys. Rev. B 20, 1245 (1979).

[4]W. Zinn and J. Magn. Magn. Mater. 3, 23 (1976).

[5]H. Maletta and P. Convert, Phys. Rev. Lett. 42, 108 (1979).

[6]F. Steglich, Z. Phys. B 23, 331 (1976); C. D. Bredl, F. Steglich, and K. D. Schotte, Z. Phys. B 29, 327 (1978).

[7]W. H. Fogle, J. C. Ho, and N. E. Phillips, J. Phys. (Paris), Colloq. 39, C6-901 (1978).

[8]G. Crecelius, H. Maletta, H. Pink, and W. Zinn, J. Magn. Magn. Mater. 5, 150 (1977).

[9]C. D. Bredl, F. Steglich, H. v. Löhneysen, and K. Matho, J. Phys. (Paris), Colloq. 39, C6-925 (1978).

[10]O. W. Dietrich, A. J. Henderson, Jr., and H. Meyer, Phys. Rev. B 12, 2844 (1975).

[11]R. C. Zeller and R. O. Pohl, Phys. Rev. B 4, 2029 (1971); J. E. Graebner, B. Golding, R. J. Schutz, F. S. L. Hsu, and H. S. Chen, Phys. Rev. Lett. 39, 1480 (1977).