PHYSICAL REVIEW B VOLUME 35, NUMBER 13 1 MAY 1987

Magnetic phase transitions close to the bicritical concentration in EuS_ySe_{1-y}

K. Westerholt and Th. Wegmann
Institut für Experimentalphysik IV, Ruhr Universität, D-4630 Bochum, West Germany
(Received 29 December 1986)

The critical behavior of the magnetic phase transitions for concentrations very close to the bicritical point in the solid-solution system EuS_ySe_{1-y} are analyzed by specific-heat, susceptibility, and magnetization measurements. At the ferromagnetic side of the bicritical point one observes nonuniversal critical behavior which asymptotically crosses over toward three-dimensional Heisenberg behavior. At the antiferromagnetic side of the bicritical point an order–improper-disorder transition with an antiferromagnetically ordered state below the ordering temperature and purely ferromagnetic fluctuations above the ordering temperature is observed.

The critical behavior at phase transitions close to multicritical points is of great current interest in magnetism. Two well-characterized multicritical points are known in magnetic systems, namely, the bicritical and the tricritical point in uniaxial antiferromagnets.[1,2] In randomly mixed magnetic systems many other multicritical points exist (see, e.g., Refs. 3 and 4), but the critical behavior in these systems has rarely been studied in detail up to the present.

In this Rapid Communication we report on magnetic phase transitions in the system EuS_ySe_{1-y} for concentrations very close to the bicritical concentration $y_b \simeq 0.10$. As shown in Fig. 1, EuSe with applied hydrostatic pressure and the mixed system EuS_ySe_{1-y} both exhibit a bicritical point where one first-order phase line (p→ af) and two second-order phase lines (p→ f and f→ af) meet. When plotted as a function of the lattice parameter (Fig. 1, second scale) the magnetic phase diagrams of EuSe with pressure and EuS_ySe_{1-y} are very similar. Contrary to most other mixed magnetic systems the lattice-parameter dependence of the exchange interactions[5,6] determines the magnetic phase diagram of EuS_ySe_{1-y}, the distribution of the exchange interactions is of negligible influence.

It should be mentioned that the magnetic order close to the bicritical point in EuS_ySe_{1-y} depends sensitively on the preparation conditions. In our previous magnetic phase diagram of EuS_ySe_{1-y} [Fig. 1(c), see Refs. 6 and 7] measured on single crystals prepared at 2200 °C an intermediate spin-glass phase close to the bicritical point occurred. We were able to prepare samples with much better quality concerning the stoichiometry and the concentration of impurities by long-time annealing of the starting material at much lower temperatures, namely 1200 °C. These samples exhibit sharp phase transitions for concentrations very close to the bicritical point [Fig. 1(b)], which is a prerequisite for the present analysis of the critical behavior.

The stable magnetic phases close to the bicritical point in EuS_ySe_{1-y} and EuSe with pressure are the antiferromagnetic state of the second kind and the ferromagnetic state, as has been determined by NMR experiments.[8,9] Thus the sum of the numbers of spin degrees of freedom of the ordered magnetic phases close to y_b is $n=11$ ($n_1=3$ for the ferromagnetic and $n_2=8$ for the antiferromagnetic phase), the bicritical behavior is described by the biconical fixed point in the renormalization-group treatment of bicritical behavior in Refs. 10 and 11.

In Fig. 2 we show the results of the low-field ac-susceptibility measurements on four samples of EuS_ySe_{1-y}; the two samples with $y=0.10$ have the same nominal composition but slightly different lattice parame-

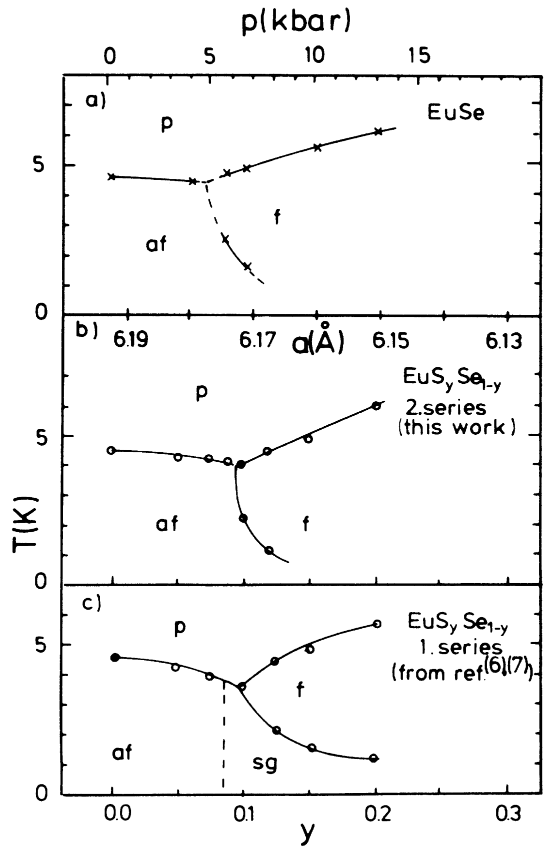

FIG. 1. Magnetic phase diagram of (a) EuSe with applied pressure and (b) and (c) two series of EuS_ySe_{1-y} samples (see main text). The lattice parameter scale refers to all three figures (p represents the paramagnetic state, af the antiferromagnetic state, f the ferromagnetic state, and sg the spin glass).

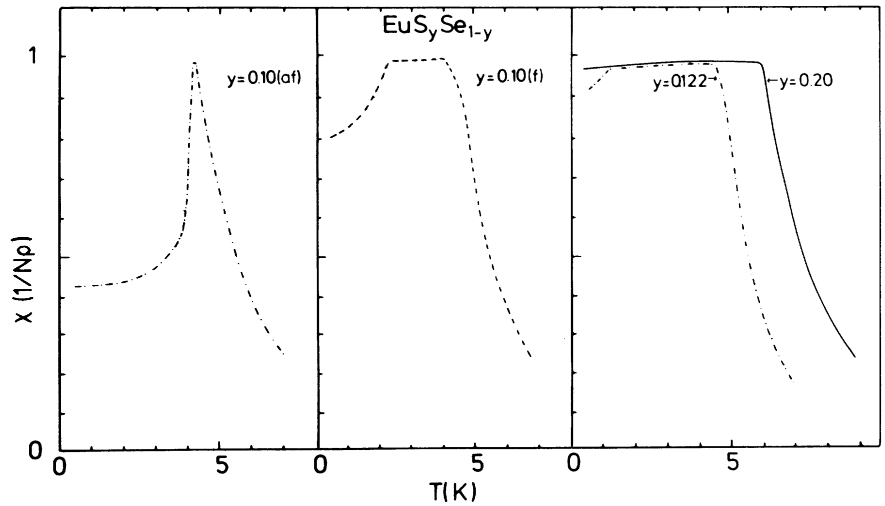

FIG. 2. ac susceptibility ($\nu = 33\ \mathrm{s}^{-1}$, $H = 1$ Oe) vs temperature for samples EuS_ySe_{1-y} (N and ρ denote the demagnetizing factor and the density, respectively).

ters [see Fig. 1(b)] and belong to the ferromagnetic (f) and the antiferromagnetic (af) phase very close to y_b, respectively. The susceptibility of all samples in Fig. 2 reaches the plateau defined by the reciprocal demagnetizing factor, indicating that the susceptibility diverges at the phase transition. One should note that this also holds for the $EuS_{0.10}Se_{0.90}$ sample which orders antiferromagnetically. In Fig. 3 the critical behavior of the susceptibility is analyzed via Fisher-Kouvel plots by numerical differentiation of the susceptibility in Fig. 2. For the sample $y = 0.20$ one derives a susceptibility exponent in good agreement with the three-dimensional (3D) Heisenberg value $\gamma = 1.39$. For the other two ferromagnets with a concentration closer to y_b the critical behavior changes markedly, one observes an effective susceptibility exponent $\gamma_{\mathrm{eff}} = 1.54$ and 1.74 for the samples with $y = 0.122$ and $y = 0.10$ (f), respectively; in addition, for the sample with $y = 0.10$ (f) one finds a crossover to an exponent close to the 3D-Heisenberg value at low reduced temperatures. Interestingly the direct susceptibility of the antiferromagnetic sample with $y = 0.10$ (af) is found to diverge with an effective exponent $\gamma_{\mathrm{eff}} = 1.37$.

The specific-heat results for the same samples are shown in Fig. 4. Again the sample with $y = 0.20$ exhibits the characteristic specific-heat peak for a 3D Heisenberg magnet, but for the other two ferromagnetic samples [$y = 0.122$ and $y = 0.10$ (f)] the shape of the specific-heat curve is definitely different: A small narrow peak develops close to the ordering temperature and shifts toward lower reduced temperatures and gets smaller for $y \to y_b$. The antiferromagnetic sample [$y = 0.10$ (af)] exhibits a sharp peak in the specific heat, which again possesses an interesting fine structure. At $T_c = 4.24$ K, the ordering temperature determined from the divergence of the direct sus-

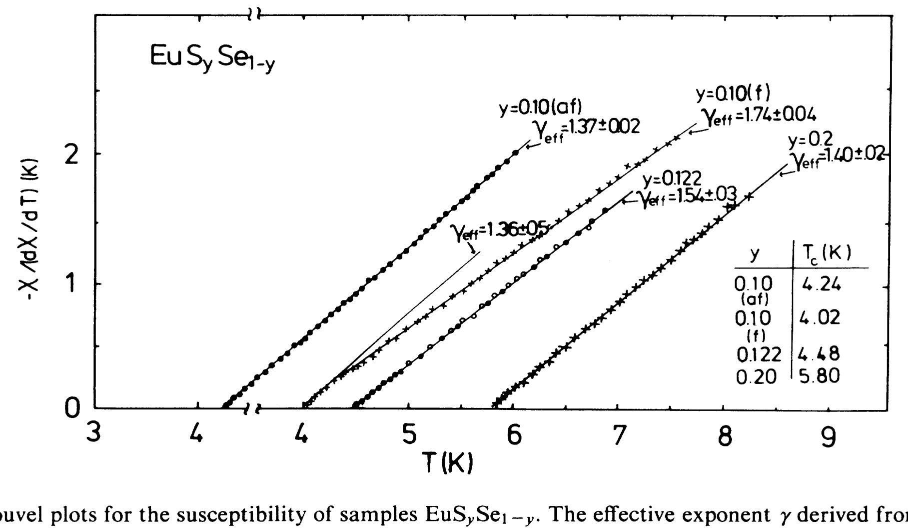

FIG. 3. Fisher-Kouvel plots for the susceptibility of samples EuS_ySe_{1-y}. The effective exponent γ derived from the slope is given in the figure. The magnetic ordering temperatures derived from the intersection with the T axis is given in the inset.

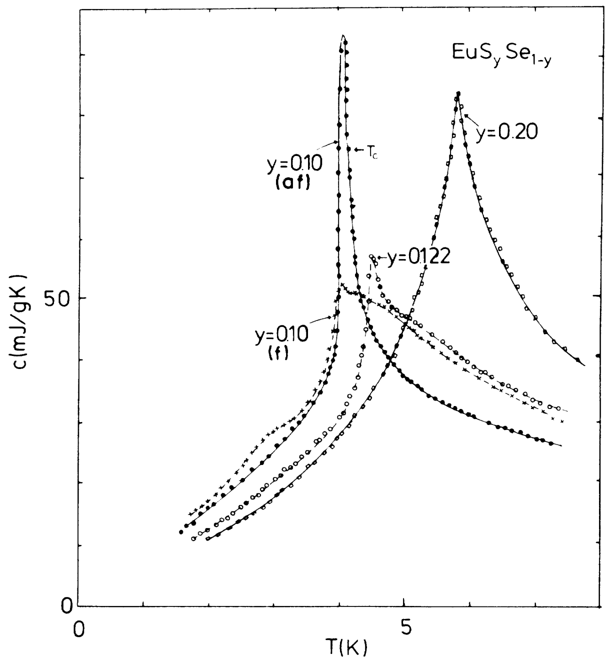

FIG. 4. Specific heat as a function of temperature for samples EuS_ySe_{1-y}. The arrow at the specific-heat curve of the sample $y=0.10$ (af) indicates the ordering temperature derived in Fig. 3.

ceptibility in Fig. 3, the specific heat shows a kink (see arrow in Fig. 4) and increases sharply toward lower temperatures. The maximum of the specific heat is reached at 4.15 K and correlates with the Néel temperature T_N as determined from the slope of the low-temperature side of the susceptibility in Fig. 2.

The magnetic order of the very interesting antiferromagnetic $y=0.10$ sample is characterized in more detail in Figs. 5 and 6. Below the ordering temperature one observes first-order metamagnetic transitions at very low magnetic fields (Fig. 5). The metamagnetic transition field depends linearly on temperature and extrapolates toward about 4.2 K. The magnetic field dependence at the ordering temperature $T_c=4.24$ K can be well described by a law $M(H)\propto H^{1/\delta}$ with a critical exponent $\delta=4.7\pm0.2$ similar to a 3D Heisenberg ferromagnet. Motivated by this finding and the power law for the direct susceptibility above the ordering temperature in Fig. 3, we have plotted magnetization data above T_c in the scaled form expected for a ferromagnet (Fig. 6). Actually the data follow this type of scaling perfectly. This important result demonstrates that the magnetic fluctuations above the ordering temperature are dominantly ferromagnetic, although the ordered state is antiferromagnetic.

The results presented here show that interesting and new critical behavior exists close to the bicritical concentration in EuS_ySe_{1-y}. The critical behavior is strongly influenced by the bicritical point close by, only asymptotically for low reduced temperatures there is a crossover toward the normal critical behavior as determined by the phase line the sample finally reaches. This crossover is clearly observed in the susceptibility of the sample with $y=0.10$ (f) (Fig. 3) and gives rise to the narrow peaks in the specific heat for the two ferromagnetic samples in Fig. 4. Similarly, the kink in the specific heat of the antiferromagnetic $y=0.10$ sample can be interpreted as a crossover between a critical behavior determined by the bicritical point close by and the first-order antiferromagnetic phase line which the sample ultimately reaches.

Phenomenologically the phase transition of the antifer-

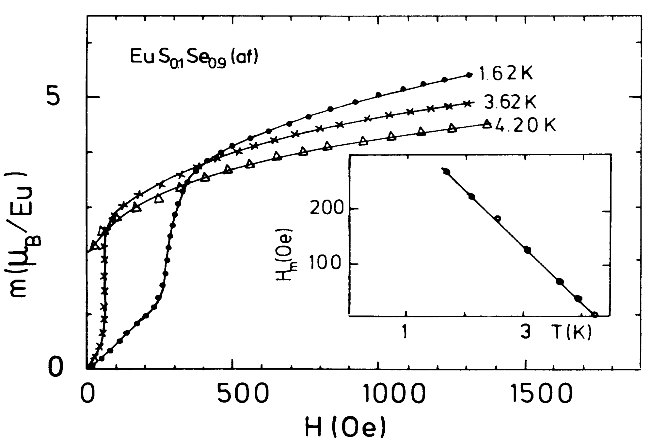

FIG. 5. Magnetization vs internal magnetic field at different temperatures for the sample $EuS_{0.10}Se_{0.90}$ (af). The inset shows the metamagnetic transition field strength as a function of temperature.

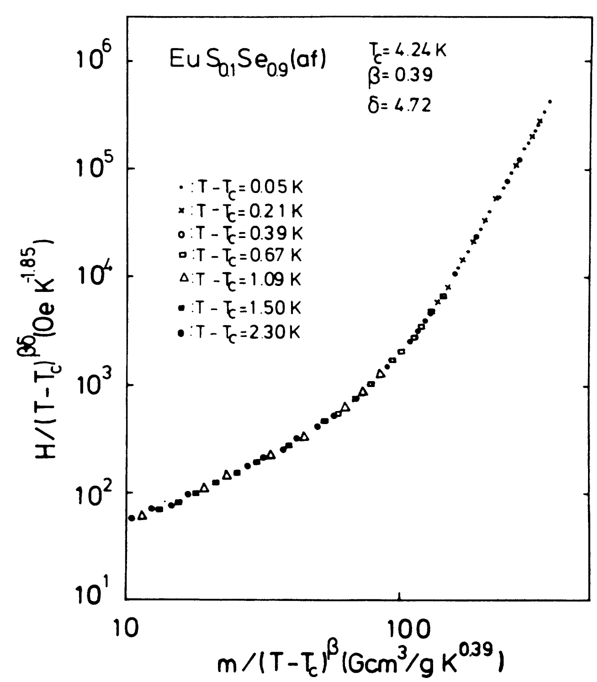

FIG. 6. Magnetization vs magnetic field in scaled form for temperatures above the ordering temperature for the sample $EuS_{0.10}Se_{0.90}$ (af). The ordering temperature and the critical exponents are given in the figure.

romagnetic $y=0.10$ sample belongs to the exotic class of order–improper-disorder transitions, where the long-range order below the ordering temperature has a periodicity different from the short-range order above the ordering temperature. To our knowledge the sample is the first example for a transition from antiferromagnetic order to ferromagnetic disorder. Several other compounds with order–improper-disorder transitions with different antiferromagnetic periodicities in the long-range order below and the short-range order above the transition temperature are known in the literature [CeSb (Ref. 12) and UAs (Ref. 13)]. The origin of the order–improper-disorder transition in these compounds is not clear, but it is assumed that a multicritical point, in these examples a generalized Lifschitz point, causes the anomalous phase transition. For our sample $EuS_{0.1}Se_{0.9}$ the existence of a multicritical point in the neighborhood is obvious; the order–improper-disorder transition originates from a crossover between bicritical and asymptotic antiferromagnetic behavior.

A phase transition as observed here has been predicted in a microscopic model of Nagaev,[14] and Nagaev and Kovalenko[15] which treats the influence of higher-order exchange interactions on the magnetic order of Heisenberg magnets. It is shown that an antiferromagnetic higher-order exchange interaction competing with a Heisenberg-type ferromagnetic exchange can induce a phase transition as observed experimentally in $EuS_{0.1}Se_{0.9}$.

It should be noted when comparing the results presented here to renormalization-group calculations of bicritical behavior (e.g., Refs. 10 and 11), that we did not try to test multicritical scaling or determine multicritical exponents. Actually this would be very difficult experimentally in EuS_ySe_{1-y} or any other mixed magnetic system, since the concentration cannot be varied continuously. Nevertheless, the study of normal phase transition, as we have done, can be an interesting subject on its own, close to multicritical points in mixed magnetic systems.

[1]Ian D. Lawrie and S. Sarbach, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. Green (Academic, London, 1984).

[2]R. M. Hornreich, in *Magnetic Phase Transitions,* edited by M. Ausloos and R. J. Green (Springer-Verlag, New York, Tokyo, 1983).

[3]S. Fishman and A. Aharony, Phys. Rev. B **19**, 3776 (1979); **21**, 280 (1980).

[4]A. Ito, Hyperfine Interact. **27**, 81 (1986).

[5]W. Zinn, J. Magn. Magn. Mater. **3**, 23 (1976).

[6]K. Westerholt and H. Bach, J. Phys. F **12**, 1227 (1982).

[7]K. Westerholt, A. Eiling, and H. Bach, J. Magn. Magn. Mater. **28**, 214 (1982).

[8]T. Hihara, K. Kojima, S. Nishisawa, K. Hiraoka, and F. Kamiguichi, J. Magn. Magn. Mater. **31-34**, 429 (1983).

[9]K. Hiraoka, T. Hihara, K. Kojima, and F. Kino, Solid State Commun. **52**, 479 (1984).

[10]M. E. Fisher and D. R. Nelson, Phys. Rev. Lett. **32**, 1350 (1974).

[11]J. M. Kosterlitz, D. R. Nelson, and M. E. Fisher, Phys. Rev. B **13**, 412 (1976).

[12]B. Hälg, A. Furrer, W. Hälg, and O. Vogt, J. Phys. C **14**, L967 (1981).

[13]S. K. Sinka, J. H. Lander, S. M. Shapiro, and O. Vogt, Phys. Rev. Lett. **45**, 1029 (1980).

[14]E. L. Nagaev, *Physics of Magnetic Semiconductors* (Mir, Moscow, 1983).

[15]E. L. Nagaev and A. A. Kovalenko, Pis'ma Zh. Eksp. Teor. Fiz. **29**, 449 (1979) [JETP Lett. **29**, 493 (1979)]; Solid State Commun. **38**, 1121 (1981).