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The impact of fourth-order exchange interactions on the critical temperatures of $Eu_xSr_{1-x}S$ and $Eu_xSr_{1-x}Te$

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Abstract

The Curie phase line $T_C(x)$ of the diamagnetically diluted ferromagnets $Eu_xSr_{1-x}S$ and the Néel phase line $T_N(x)$ of the diamagnetically diluted antiferromagnets $Eu_xSr_{1-x}Te$ are analysed empirically on the basis of a mean-field approximation. Experimental data for the transition temperatures are collected from neutron scattering, magnetic specific heat and susceptibility measurements. Neither phase line, $T_C(x)$ or $T_N(x)$, is proportional to the concentration x of the magnetic atoms. It is shown that the deviations from linearity correlate with the fourth-order interaction sum in the paramagnetic phase. We therefore also ascribe the nonlinear x dependence of both phase lines to fourth-order interactions. Furthermore, our zero field neutron scattering measurements show that even for the strongly diluted $Eu_xSr_{1-x}S$ samples the order parameters exhibit a T^2 Bloch law at low temperatures instead of a $T^{3/2}$ law. The T^2 law is a characteristic signature of fourth-order interactions in 3D materials with half-integral spin. It is also observed that the critical exponent β of the order parameter changes from $\beta = 0.5$ for $x = 1$ towards $\beta = 1$ at about $x \leqslant 2/3$. This confirms that a new universality class is reached for a random distribution of magnetic moments. However, all phase transitions are first order and the critical power law applies only for the continuous part of the rise in the order parameter.

1. Introduction

In this communication we mainly address the question to what degree the magnetic transition temperatures of EuS and EuTe are affected by fourth-order exchange interactions, i.e. biquadratic, three-spin and four-spin interactions. Up to now we evaluated the strength of these interactions only in the high temperature limit on account of the Curie–Weiss temperature Θ_3 of the cubic susceptibility $\chi_3(T)$ [1, 2]. In order to investigate the impact of fourth-order interactions on the critical temperature it is essential to extend measurements to the mixed composition series $Eu_xSr_{1-x}S$ and $Eu_xSr_{1-x}Te$ in which the magnetic constituent is diamagnetically diluted with the isomorphous materials SrS and SrTe, respectively. In this

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way the relative weight of biquadratic, three-spin and four-spin interactions can be varied and a decomposition into the individual interaction processes becomes possible [2, 3].

For the diamagnetically diluted ferromagnetic solid solutions $Eu_xSr_{1-x}S$ we observed earlier that the Curie–Weiss temperature $\Theta_1(x)$ of the linear susceptibility $\chi_1(T, x)$ is a nonlinear function of composition x and can be described by

$$\Theta_1(x) = 14.5x + 7.3x^2. \tag{1}$$

Later it was shown [2] that the quadratic x-dependence is essentially due to ferromagnetic three-spin interactions while the linear coefficient of 14.5 K is given by a weighted sum of bilinear and biquadratic interactions. This interpretation could be confirmed by a comparison of the coefficients of equation (1) with the corresponding coefficients of the Curie–Weiss temperature $\Theta_3(x)$ of the cubic susceptibility $\chi_3(T, x)$

$$\Theta_3(x) = -19.2x + 21.9x^2. \tag{2}$$

In contrast to $\Theta_1(x)$, which is given by all interactions, $\Theta_3(x)$ is given exclusively by fourth-order interactions [2]. As a consequence, the coefficients of equation (2) show that biquadratic interactions are antiferromagnetic and three-spin interactions are ferromagnetic in $Eu_xSr_{1-x}S$. Four-spin interactions would give a term $\sim x^3$ but could not be identified experimentally and seem to be weak. Moreover, a comparison between the quadratic coefficients of equation (2) and equation (1) shows that three-spin interactions affect the Curie–Weiss temperature $\Theta_1(x)$ of the linear susceptibility with a reduced weight only.

The aim of the present experimental work is to investigate empirically whether a similar analytic description as for $\Theta_1(x)$ given in equation (1) is also possible for the critical temperatures $T_C(x)$. Earlier computer simulation investigations of the experimental $T_C(x)$ data of $Eu_xSr_{1-x}S$ considered only bilinear interactions to nearest and next-nearest neighbours [4]. It is evident that neglecting contributions from fourth-order interactions to $\Theta_1(x)$ and to $T_C(x)$ not only leads to wrong bilinear coupling parameters but also to a non-realistic spin dynamics. Modelling the experimental $T_C(x)$ curve of $Eu_xSr_{1-x}S$ with Monte Carlo methods resulted in a ratio between nearest (J_1) and next-nearest (J_2) neighbour bilinear coupling constants of $J_2 \approx -0.5J_1$. In an attempt to test this relation with an independent method, spin wave dispersion measurements were performed on EuS single crystals [5]. These neutron scattering data were also analysed assuming only bilinear Heisenberg interactions. They confirmed that interactions are restricted essentially to nearest and next-nearest neighbours but the experimental temperature dependence of the spontaneous magnetization was not correctly reproduced using the fitted low temperature values for J_1 and J_2. This indicates that the spin dynamics deviates, in fact, from that assumed.

A number of mean-field calculations have been carried out [6–9] on the modifications which the inclusion of fourth-order exchange interactions introduces on the magnetic ordering phenomena. Since these mean-field calculations cannot be expected to be quantitatively correct we proceed here along empirical lines. It is hoped that the conclusions obtained in this work may be of use for the development of an exact theory.

The analysis of the critical temperatures $T_C(x)$ and $T_N(x)$ is a more complicated task than the analysis of the Curie–Weiss temperatures presented in equations (1) and (2) for $\Theta_1(x)$ and $\Theta_3(x)$. First, in contrast to the Curie–Weiss temperatures which can be measured for all x-values, a true long range magnetic order seems to be limited in both composition series to $\sim 0.5 < x < 1$ [10, 11]. This restricts the observable x-range for Néel and Curie temperature accordingly and limits the accuracy of a polynomial fit. Second, in both composition series changes in spin structure occur at a critical composition x_c, which is $x_c \cong 0.88$ for $Eu_xSr_{1-x}S$ and $x_c \cong 0.85$ for $Eu_xSr_{1-x}Te$ [12]. As a consequence, $T_C(x)$ and $T_N(x)$ can be expected to have a different analytic behaviour in the two composition regions.

We should explain this feature in some more detail. The two Curie–Weiss laws for linear and cubic susceptibility obtained in mean-field theory [2] can be interpreted as a high temperature indication of the occurrence of two order–disorder phase transitions. This view is confirmed as essentially correct by the observation of a second ordering transition in many magnetization and neutron scattering experiments on different Eu and Gd compounds [12–15]. Consistently, this additional phase transition is antiferromagnetic if $\Theta_3 < 0$ and ferromagnetic if $\Theta_3 > 0$. We have attributed a second order parameter, called O_4, to this ordering process [12–14]. The transition temperature of this order parameter is Θ_3—in the mean field approximation—and is characterized by a divergence of the cubic susceptibility χ_3 [13].

Equation (2) shows that for the $Eu_xSr_{1-x}S$ samples Θ_3 changes its sign at $x_c \cong 0.88$. For $x < x_c$ Θ_3 is negative, meaning that O_4 is antiferromagnetic but for $x > x_c$ Θ_3 is positive and O_4 is ferromagnetic [13]. In other words, antiferromagnetic biquadratic interactions dominate for small Eu concentrations but ferromagnetic three-spin interactions dominate for large Eu concentrations. A similar situation is observed also in $Eu_xSr_{1-x}Te$ [12]. Since the critical temperature of the conventional order parameter O_2 is defined by all interactions it can be expected to respond in some way to the change in spin order of O_4 at x_c. In fact, $T_C(x)$ and $T_N(x)$ exhibit a small change in slope at x_c.

We should admit that a long range magnetic order associated with O_4 was verified using the microscopic method of neutron scattering only for some materials for which the spin order of O_2 and O_4 is of the same type. Examples are EuS and EuO, for which O_2 and O_4 are ferromagnetic [13], and $Eu_{0.75}Sr_{0.25}Te$, for which the two order parameters are antiferromagnetic [3]. In those cases both order parameters give rise to the same set of Bragg lines and can be distinguished only with investigations using a magnetic field: in $Eu_{0.75}Sr_{0.25}S$ the critical field $B_c^{\perp}$ associated with O_4 is identified by a sudden relative decrease of the antiferromagnetic scattering intensities as a function of increasing field [3] while in EuS and EuO the existence of ferromagnetic O_4 is noticed by a spontaneous magnetization component transverse to an applied magnetic field [13]. If O_2 and O_4 have different ordering types the ordered moment of O_4 is usually very small and often beyond the sensitivity limits of neutron scattering. This is obvious for antiferromagnets with ferromagnetic O_4 such as GdAg, GdS, EuTe. According to susceptibility measurements the ferromagnetic moment of O_4 can be estimated to be only a few per cent of the absolute moment in these antiferromagnets. One exception is GdMg having ferromagnetic O_2 and antiferromagnetic O_4 [14]. Surprisingly, both order parameters have a saturation moment of as large as $\sim 5\ \mu_B$ and are easily distinguished since they contribute to different sets of Bragg reflections [15].

In the following we investigate the critical temperatures of O_2. The critical temperatures of O_4 are much more difficult to identify experimentally and are frequently overlooked. For the $Eu_xSr_{1-x}S$ samples very accurate $T_C(x)$ data are obtained by a combination of earlier specific heat results [16] with the present zero-field neutron scattering investigations. Our analysis confirms conclusions obtained in previous publications [1–3, 14] that fourth-order interactions are sizable but due to the different signs of biquadratic and three-spin interactions they affect the critical temperatures of the compact materials EuS and EuTe only slightly. Instead, they change the spin dynamics fundamentally at all temperatures: in the spin wave regime fourth-order interactions give rise to particular Bloch exponents for the temperature dependence of the order parameter [17]. For materials with half-integral spin and three-dimensional (3D) interactions a T^2 Bloch law was found empirically [12]. This law is confirmed here to hold even for the most diluted $Eu_xSr_{1-x}S$ sample with $x = 0.63$. On the other hand, fourth-order interactions change the critical behaviour also decisively. In agreement with mean-field predictions it was observed in [18] that the order–disorder phase transition is mostly first order in the sense that the order parameter is discontinuous. Our neutron scattering investigations

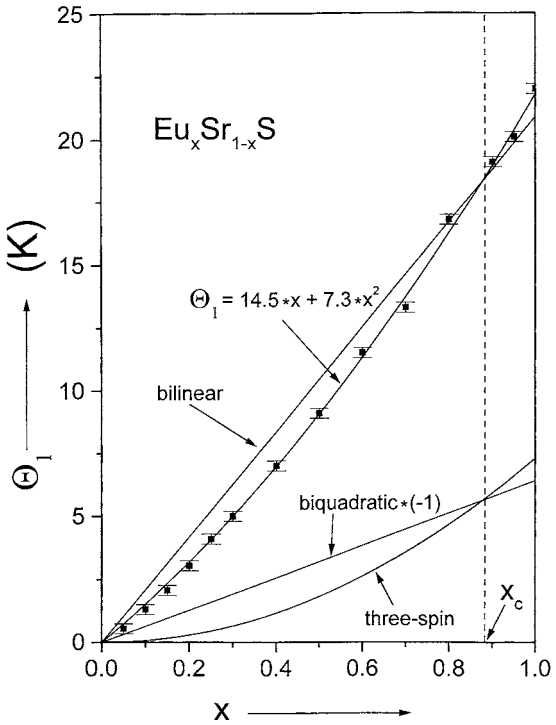

Figure 1. Decomposition of the experimental Curie–Weiss temperatures $\theta_1(x)$ of the linear susceptibility $\chi_1(T, x)$ of $Eu_xSr_{1-x}S$ powder samples into bilinear, biquadratic and three-spin interactions. Knowing that at $x_c = 0.88$ biquadratic and three-spin interactions cancel the bilinear contribution to the linear coefficient of 14.5 K is given by 20.9 K. The difference of -6.4 K is due to biquadratic interactions. The quadratic coefficient of 7.3 K is exclusively due to ferromagnetic three-spin interactions. Four-spin interactions ($\sim x^3$) are not identified.

confirm this behaviour for all the four measured $Eu_xSr_{1-x}S$ samples with $x = 0.95$, 0.8, 0.7 and 0.63.

2. Experiment

2.1. $Eu_xSr_{1-x}S$

The Curie–Weiss temperature $\Theta_1(x)$ of the linear susceptibility $\chi_1(T, x)$ of the diamagnetically diluted $Eu_xSr_{1-x}S$ ferromagnets shows very clearly the importance of three-spin interactions in the paramagnetic phase. The experimental data of figure 1 are well described by equation (1). According to the wet chemical procedure used to prepare the powder samples measured in this experiment [19] we can be sure that Eu and Sr atoms are distributed statistically. This is an important prerequisite for an interpretation of the experimental coefficients in equation (1) in terms of second-order and fourth-order interaction strengths [20].

Taking a random distribution of Eu and Sr atoms for granted, the linear coefficient in equation (1) is given by a superposition of conventional bilinear (Heisenberg) interactions and by biquadratic interactions while the quadratic coefficient is given exclusively by three-spin interactions [2]. Four-spin interactions would give a term $\sim x^3$ and seem to be much weaker.

We can roughly separate the linear coefficient of 14.5 K in equation (1) into contributions from bilinear and biquadratic interactions. As we know from measurements of the cubic susceptibility $\chi_3(T, x)$, ferromagnetic three-spin interactions and antiferromagnetic biquadratic interactions cancel at about $x_c \cong 0.88$ in $Eu_xSr_{1-x}S$ [1, 2]. Equation (2) summarizes the results of these investigations on account of the cubic Curie–Weiss constant $\Theta_3(x)$ and shows that $\Theta_3(x_c) = 0$. It is therefore reasonable to assume that the value of $\Theta_1 = 18.4$ K at $x_c = 0.88$ calculated by equation (1) is given exclusively by bilinear interactions. Hence, the bilinear part of $\Theta_1(x)$ is given by $\Theta_1^{bl}(x) = 20.9x$ in the mean-field approximation.

The difference between the experimental coefficient of 14.5 K and the bilinear coefficient of 20.9 K must be attributed to the biquadratic interactions. The biquadratic contribution to $\Theta_1(x)$ is, hence, $\Theta_1^{bq} = -6.4x$. The complete decomposition of $\Theta_1(x)$ into contributions from bilinear interactions, Θ^{bl}, biquadratic interactions, Θ^{bq}, and three-spin interactions, Θ^{3S}, is therefore

$$\Theta_1(x) = \Theta^{bl} + \Theta^{bq} + \Theta^{3S} = +20.9x - 6.4x + 7.3x^2. \tag{3}$$

This analysis shows that even though biquadratic and three-spin interactions are sizeable they do not contribute much to the high-temperature interaction sum, i.e. $\Theta_1(x)$, because of their different signs. This does not necessarily mean that they also affect the transition temperatures weakly. Depending on the spin structure the different interaction processes can be very differently weighted in the ordered state compared to the paramagnetic average.

The high-temperature interaction strengths as given by equations (1) and (3) should be reflected in a modified form also by the ordering temperatures $T_C(x)$. In particular a term quadratic in x due to ferromagnetic three-spin interactions should be observable. Using instrument D9 at ILL/Grenoble we have re-evaluated the Curie temperatures of four $Eu_xSr_{1-x}S$ single crystals with $x = 0.95$, 0.8, 0.7 and 0.63 by means of the ferromagnetic 1,1,1 neutron diffraction intensity. These measurements confirmed earlier critical temperature data obtained with specific heat measurements within a mean error of only ± 0.1 K [16]. Hence, we have rather precise $T_C(x)$ data for analysis (see figure 2). Fitting a polynomial to the $T_C(x)$ data for the composition range $x_c \leqslant 0.88$ for which the high-temperature fourth-order interaction sum is antiferromagnetic ($\Theta_3 < 0$) we obtain

$$T_C(x) = -2.95x + 21.7x^2 \qquad (x < x_c). \tag{4}$$

The statistical errors of both coefficients are ± 0.2. The result of equation (4) indicates that antiferromagnetic biquadratic interactions reduce the Curie temperature tremendously and even dominate over the ferromagnetic bilinear interactions according to the negative sign of the linear coefficient. Three-spin interactions are also much more important compared to the paramagnetic state (equations (1) and (3)) and make (or let) the Curie temperature steeply increase with increasing x.

Assuming that at $x_c = 0.88$ fourth-order interactions compensate each other and do not contribute at all to T_C we can easily obtain the mean-field phase line $T_C^{bl}(x)$ expected for the case where only bilinear interactions were present. According to equation (4) $T_C(x = 0.88) = 14.2$ K. The $T_C^{bl}(x)$ phase line is therefore given in the mean-field approximation by

$$T_C^{bl}(x) = +16.1x. \tag{5}$$

We now can calculate how strongly antiferromagnetic biquadratic interactions contribute to the experimental $T_C(x)$ phase line in the composition range $x < x_c$. This contribution is simply given by the difference between the total linear coefficients in equation (4) and the bilinear

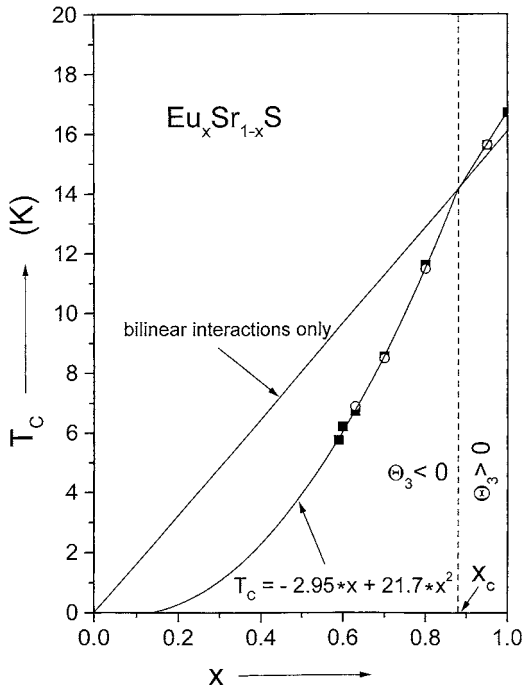

Figure 2. Phase diagram of $Eu_xSr_{1-x}S$ showing Curie temperatures $T_C(x)$ of the conventional order parameter O_2. Filled symbols are specific heat data from [16], open symbols are neutron scattering results of this work. Experimental errors correspond to the size of the symbols. At $x_c = 0.88$ antiferromagnetic biquadratic and ferromagnetic three-spin interactions cancel. This defines the expected Curie line due to bilinear interactions. For $x < 0.88$ the fitted coefficients of the rank-two polynomial show the strong influence of antiferromagnetic biquadratic and ferromagnetic three-spin interactions.

coefficient in equation (5), i.e. $T_C^{bq}(x) = -19.1x$. The decomposition of the observed $T_C(x)$ phase line into bilinear, biquadratic and three-spin contributions is therefore

$$T_C(x) = T_C^{bl}(x) + T_C^{bq}(x) + T_C^{3S}(x) = 16.1x - 19.1x + 21.7x^2 \qquad (x < x_c). \tag{6}$$

Of course, this is a qualitative estimate only. In particular, it must be questioned whether in an exact theory the three interaction processes contribute simply as additive as in equation (6) to the total transition temperature.

It is very surprising that biquadratic and three-spin interactions contribute with their full strength given by equation (2) to the Curie phase line in equation (6). Compared with the paramagnetic average given by equation (3) they are three times stronger in the ordered state. The strongly changing weight of the fourth-order interaction processes between the paramagnetic and the ordered state may provide a qualitative explanation for the first order character of the Curie transition and indicates furthermore that the spin order cannot be of the collinear ferromagnetic type.

At $x_c \cong 0.88$ the $T_C(x)$ curve exhibits a small but definite change in slope. Our rank-two polynomial fit to the $T_C(x)$ data for $x < x_c$ (see equations (4) and (6)) extrapolates to $T_C(x = 1) = 18.8$ K and is about 13% larger than the observed Curie temperature of EuS of 16.6 K. Note that the average error between the fit function given in equation (4) and the experimental Curie temperatures of the range $x < x_c$ is smaller than 1%. The obtuse kink the $T_C(x)$ curve exhibits at x_c indicates some change in spin structure of the conventional order

parameter O_2 induced by the change in spin order from ferromagnetic to antiferromagnetic of O_4. Fitting a polynomial of rank two onto the only two data points of the range $x > 0.88$ gives the approximative result

$$T_C(x) = 11.1x + 5.5x^2 \qquad (x > x_c = 0.88). \tag{7}$$

We can again separate the linear coefficient in equation (7) into contributions from bilinear and biquadratic interactions. Knowing that bilinear interactions are given by equation (5) for all compositions the biquadratic contribution is clearly -5.0 K. $T_C(x)$ can therefore be written as

$$T_C(x) = T_C^{bl}(x) + T_C^{bq}(x) + T_C^{3S} = 16.1x - 5.0x + 5.5x^2 \qquad (x > x_c). \tag{8}$$

Comparison between equation (8) and equation (3) shows that for $x > x_c$ $T_C(x)$ is nearly proportional to $\Theta_1(x)$ with $\Theta_1(x) \sim 1.30T_C(x)$. In other words, the ratio between the fourth-order interaction strength in the paramagnetic and in the ordered state corresponds to that one of the bilinear interactions. On the other hand, the ratio between the biquadratic and the three-spin coefficient in equations (2), (3), (6) and (8) is nearly constant (~ -0.88), indicating that both interaction types always act with the same relative strength.

We should note that the difference in spin structure between the composition range $x > x_c$ and $x < x_c$ is not yet sufficiently resolved. For $x > x_c$ the field parallel spontaneous magnetization component reaches the theoretical saturation value of 7 μ_B but there also exists a magnetization component transverse to the field. This component which was observed with neutron scattering and ac-susceptibility measurements performed perpendicular to the field [13], is attributed to the ferromagnetic order parameter O_4. On the other hand, for $x < x_c$ O_4 can be expected to be antiferromagnetic. In fact, the observed field parallel spontaneous magnetization component begins to fall below 7 μ_B for $x \leqslant x_c$ but no antiferromagnetic component was observed in our neutron scattering measurements, possibly due to intensity problems with this weak antiferromagnetic component.

2.2. $Eu_xSr_{1-x}Te$

The same analysis as for $Eu_xSr_{1-x}S$ is performed for the Néel line $T_N(x)$ in the $Eu_xSr_{1-x}Te$ phase diagram (see figure 3) and yields

$$T_N^{\parallel}(x) = 2.75x + 8.45x^2 \tag{9}$$

for the composition range $x_c \leqslant 0.85$. In this range antiferromagnetic O_4 was identified by magnetization measurements [12, 13] on account of a second critical field, $B_c^{\perp}$, but also with neutron scattering measurements [3]. In the neutron scattering experiments it is observed that the antiferromagnetic MnO type scattering lines exhibit a sudden intensity loss at $B_c^{\perp}$ as a function of an increasing magnetic field [3]. This is attributed to the disappearance of O_4 at $B_c^{\perp}$.

The Néel temperatures in figure 3 are taken from [21, 22]. As we know from experimental investigations of the cubic susceptibility $\chi_3(T, x)$ [1] the third-order Curie–Weiss temperature $\Theta_3(x)$ can be written as

$$\Theta_3(x) = -17.8x + 20.8x^2. \tag{10}$$

From equation (10) it turns out that antiferromagnetic biquadratic interactions and ferromagnetic three-spin interactions cancel at $x_c = 0.85$ in $Eu_xSr_{1-x}Te$. This allows us to calculate the Néel phase line, $T_N^{bl}(x)$, expected for the case where only bilinear interactions were present. Assuming that fourth-order interactions do not contribute to the Néel temperature at $x_c = 0.85$ we obtain from equation (9) $T_N(x = 0.85) = 8.4$ K and therefore in the mean-field approximation

$$T_N^{bl} = 9.9x. \tag{11}$$

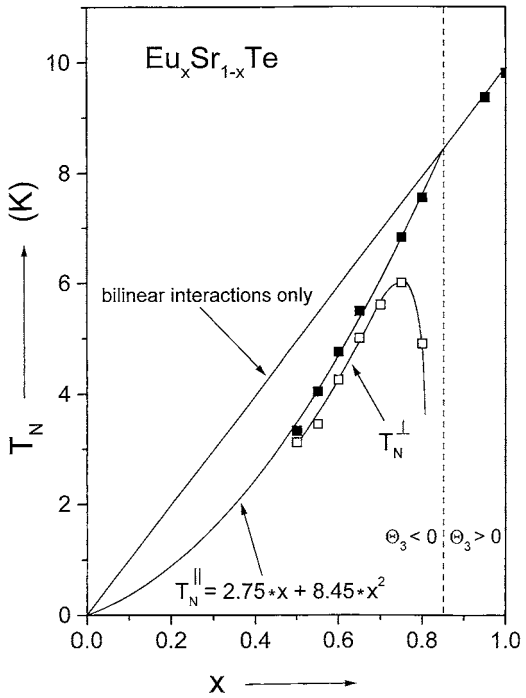

Figure 3. Phase diagram of $Eu_xSr_{1-x}Te$ showing the Néel line $T_N^{\parallel}(x)$ of the conventional order parameter O_2 and the Néel line $T_N^{\perp}(x)$ of the order parameter O_4. At $x_c = 0.85$ antiferromagnetic biquadratic interactions and ferromagnetic three-spin interactions compensate. The straight line $\sim x$ gives the expected Néel line without fourth-order interactions. For $x < 0.85$ fourth-order interactions strongly reduce $T_N^{\parallel}$. For $x > 0.85$ fourth-order interactions hardly contribute to $T_N^{\parallel}$.

Subtracting from the fitted linear coefficient of 2.75 the bilinear contribution of 9.9 K we obtain for the biquadratic coefficient -7.2. The complete decomposition of the observed $T_N(x)$ phase line into bilinear, biquadratic and three-spin interactions is therefore

$$T_N^{\parallel}(x) = T_N^{bl}(x) + T_N^{bq}(x) + T_N^{3S} = 9.9x - 7.2x + 8.5x^2 \qquad (x < x_c). \quad (12)$$

We observe again that the coefficients of biquadratic and three-spin interactions in equation (10) are proportional to the corresponding coefficients in equation (12), meaning that their relative strength is independent of the spin order type. This corresponds to the fact that the two interactions are members of the same class and, apparently, always act in a similar way.

In the composition range $0.85 \leqslant x \leqslant 1$ with a ferromagnetic fourth-order interaction sum ($\Theta_3 > 0$) a fit to the only two T_N data points gives very approximately

$$T_N^{\parallel} = 11.0x - 1.2x^2 \qquad (x > x_c). \quad (13)$$

Comparison of the linear coefficient of 11.0 K with the bilinear coefficient of 9.9 K in equation (11) together with the very small quadratic coefficient shows that fourth-order interactions affect the Néel temperature very little for $x > x_c$. Formally, the linear and quadratic coefficient in equation (13) show that antiferromagnetic biquadratic interactions contribute positively to T_N but ferromagnetic three-spin interactions contribute negatively to T_N. Such an effect on the Néel line we would intuitively expect. But considering the large experimental uncertainty we should not overstress the result in equation (13).

Summarizing the results of this section it appears empirically possible to explain the deviations of the observed phase lines $T_C(x)$ and $T_N(x)$ from the simple mean-field

proportionality $\sim x$ by fourth-order exchange interactions. These interactions affect the transition temperatures not necessarily according to their strength in the paramagnetic phase. Depending on the spin structures of O_4 and O_2 the impact of fourth-order interactions on the critical temperature of O_2 can be much stronger but also much weaker than on the paramagnetic Curie–Weiss temperature Θ_1. This observation seems to be logically connected with the fact that fourth-order interactions make the conventional phase transitions first order. On the other hand, the assumption that without fourth-order interactions the phase lines are essentially proportional to the concentration of the magnetic atoms appears to be a reasonable first-order approximation. Using this assumption the remarkable systematics is obtained that the relation between biquadratic and three-spin interactions (-0.88 for $Eu_xSr_{1-x}S$) is constant for all spin structures occurring in the phase diagram. As a generalization, in mixed materials any deviation of the order–disorder phase line from a linear composition dependence $\sim x$ may indicate the existence of fourth-order interactions. This is, of course, correct only if the microscopic interaction parameters do not change with composition.

2.3. Investigation of the T^2 law

For many isotropic 3D ferromagnets and antiferromagnets with half-integral spin it was observed that the deviation of the order parameter from its saturation values at absolute zero is given by a T^2 law [12, 14, 17]. Interestingly, the T^2 law is independent of the spin order type and holds over a temperature range of typically $T \leqslant 0.65T_{crit}$ but for some materials up to $T \leqslant 0.8T_{crit}$. Since results for $Eu_xSr_{1-x}Te$ have been reported earlier [3] we discuss here only $Eu_xSr_{1-x}S$.

The $T^{3/2}$ Bloch law predicted for the Heisenberg ferromagnet [23] is not confirmed for the ferromagnets EuS, EuO and $CrBr_3$ [12, 17]. We explain this by the changed spin dynamics due to fourth-order exchange interactions [12]. Since the T^2 law is observed also in experiments such as zero-field NMR which do not distinguish between O_2 and O_4 it can be concluded that it is common to both order parameters. This was shown explicitly for GdMg [13, 14] having ferromagnetic O_2 and antiferromagnetic O_4. In this case both order parameters are easily distinguished on account of different sets of Bragg reflections.

In figure 4 we show the normalized magnetic moments for four $Eu_xSr_{1-x}S$ single crystals obtained from the integrated 1,1,1 scattering intensities as a function of the squared absolute temperature. In contrast to magnetization measurements zero-field neutron scattering has the advantage of avoiding the ambiguity normally associated with the extrapolation to an internal field of zero. It can clearly be seen in figure 4 that the T^2 law holds even for the most diluted sample with $x = 0.63$.

Nuclear magnetic resonance, NMR, is the most accurate method in magnetism but, unfortunately, it is less suited for the evaluation of the averaged polarization in mixed crystals. Due to the high resolution of this method and the short range of the transferred hyperfine fields very complicated NMR spectra result in mixed materials from which the configuration average is difficult to obtain. Practically, application of NMR is restricted to the pure materials. In figure 5 we have plotted the ^{153}Eu zero-field NMR resonance frequencies of EuS collected from two different literature sources [24, 25] against the square of the absolute temperature. Both data sets agree very well. It can be seen that the T^2 law holds up to a temperature of more than 0.7 of the Curie temperature (upper scale). In those zero-field measurements it is not clear which combination of the two ferromagnetic order parameters is measured. It is therefore useful to compare the T^2 coefficient obtained by NMR with that obtained in conventional magnetization measurements. Although the extrapolation of the magnetization curves to an internal field of zero cannot be made unambiguously and implies systematic errors,

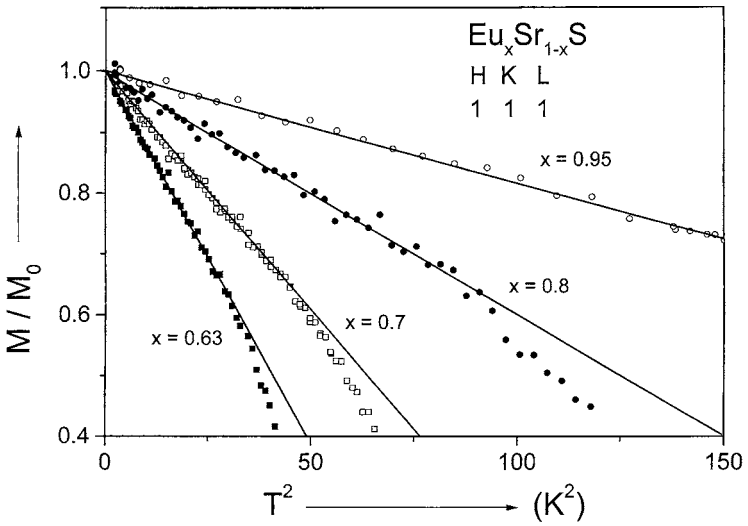

Figure 4. Normalized spontaneous magnetizations obtained from integrated 1,1,1 Bragg scattering intensities as a function of squared absolute temperature. For all $Eu_xSr_{1-x}S$ samples the T^2 law expected for isotropic magnetic materials with three-dimensional interactions and half integral spin [12, 17] is confirmed.

both methods give very precisely the same value of $0.014\,13 \pm 0.000\,05\ \mu_B\ K^{-2}$. This could mean that both methods measure nearly the same combination of both ferromagnetic order parameters in EuS [12, 13].

In figure 6 we present the composition dependence of the T^2 coefficient. These data reveal the changing spin order at $x_c = 0.88$ more clearly than the $T_C(x)$ data. Closed symbols are neutron scattering results while open symbols are from conventional, i.e. field parallel, magnetization measurements. Both data sets agree very well which is not self-evident. Since the T^2 coefficient is characteristic for the spin dynamics in the presence of fourth-order interactions, the strong change at $x_c = 0.88$ shows the changing importance of these interactions associated with the changing spin order at x_c. This is in keeping with the conclusions drawn from the analysis of the $T_C(x)$ phase line (compare equations (6) and (8)).

2.4. Critical magnetic behaviour

In order to obtain accurate critical temperature values for the $Eu_xSr_{1-x}S$ single crystals using neutron scattering the critical temperature range must be investigated in detail. Evaluation of the critical temperature by an extrapolation of the order parameter down to zero is complicated by the fact that magnetic Bragg intensities decrease strongly on approaching the critical temperature. On the other hand, critical diffuse scattering intensities increase strongly on approaching the critical temperature from the paramagnetic side. This masks the critical behaviour of the order parameter near T_C. Using standard line profile fit programs to evaluate the integrated scattering intensities, the transition between the fitted Bragg intensities below T_C and the fitted critical diffuse scattering intensities above T_C can be noticed as an inflection point at T_C. If the Bragg line is rather narrow such that the integration interval can be kept small critical diffuse scattering is pronounced only in the immediate temperature range above T_C. Figure 7 gives an example for this. Shown is the calibrated magnetic moment obtained from the 1,1,1 scattering intensities of $Eu_{0.95}Sr_{0.05}S$ as a function of temperature.

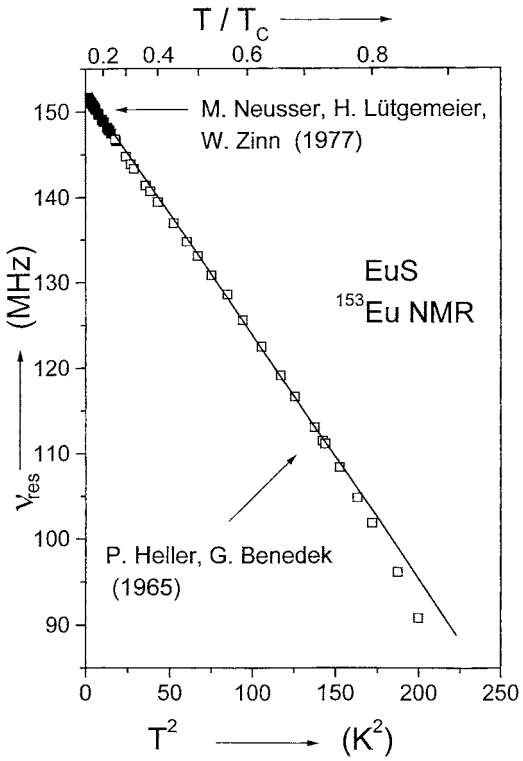

Figure 5. Zero-field ^{153}Eu NMR frequencies of EuS from two literature sources [24, 25] as a function of squared absolute temperature. NMR resonance frequencies sample the hyperfine field at the Eu nucleus which is proportional to the spontaneous magnetization. The T^2 Bloch law holds up to 0.75 of the Curie temperature.

The weak nuclear scattering contribution to the 1,1,1 intensity is only about 0.1 of the saturation intensity for $T \to 0$ and was subtracted before. In the following data processing we let T_C be fixed to the visible inflection point instead of treating T_C as an adjustable fit parameter. The rather sharp transition between the ferromagnetic Bragg intensities and the diffuse scattering intensities can be seen clearly in figure 7. The Curie temperature is therefore defined as $T_C = 15.5 \pm 0.05$ K with an error given by the temperature increments of typically 0.1 K between successive measurements. This value agrees well with 15.63 K obtained by specific heat measurements [16].

It can be seen that critical diffuse scattering affects only the first few data points above T_C. Since these intensities are considerably weaker for $T < T_C$ we refrained from correcting the Bragg intensities for the small diffuse scattering contributions. To evaluate the critical exponent β of the spontaneous magnetization we plot the magnetic moment data of figure 7 against $(T_C - T)^\beta$ using suitable test values for β. Figure 8 shows that the mean field value $\beta = 0.5$ evidently describes the results better than the Heisenberg value $\beta = 0.367$ [26]. To demonstrate this a curved line labeld by $\beta = 0.367$ is added, which indicates how the straight line drawn through the experimental points would be bent if the data were alternatively plotted against $(T_C - T)^{0.367}$. Note that the horizontal error bars give the uncertainty in defining T_C. The straight line fitted to the experimental points in figure 8 has been transferred to the linear temperature scale in figure 7 and is labelled by $\beta = 0.5$.

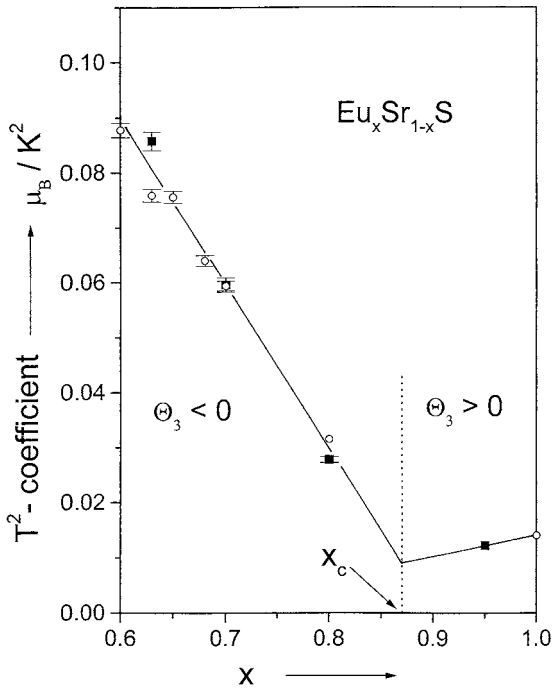

Figure 6. T^2 coefficients of spontaneous magnetization of $Eu_xSr_{1-x}S$ obtained from data analyses according to figures 4 and 5 as a function of composition. The strong change at $x_c = 0.88$ is attributed to the changing importance of fourth-order interactions (see discussion of figure 2). Filled symbols are from neutron scattering, open symbols are from magnetization measurements.

According to our data analyses following the procedure shown in figures 7 and 8 for $x = 0.95$ the Curie transitions of all investigated samples of the $Eu_xSr_{1-x}S$ composition series turned out to be first order. This is hardly recognized in the original scattering data in figure 7. A first-order transition observed with neutron scattering conforms to recent magnetization studies on EuS and EuO, which also suggested first-order transitions for these materials [18]. Also mean-field calculations predict first-order transitions if fourth-order interactions are sufficiently strong [6–9]. We should note that only the order parameter is discontinuous but that susceptibility [18] and correlation length [27] diverge rather normally.

To add one further example we show in figure 9 a log–log plot of the ordered magnetic moment of $Eu_{0.8}Sr_{0.2}$ against $T_C - T$ after subtraction of the discontinuity at T_C. The Curie temperature was again fixed to the inflection point of the integrated scattering intensities as a function of temperature. In order to evaluate the discontinuity of the order parameter at T_C the magnetic moment data are plotted against $(T_C - T)^\beta$ using an approximate value of β. This allows one to evaluate Δm by way of extrapolation $(T_C - T)^\beta \to 0$ (compare figure 8). It is very surprising that nearly the same discontinuity value of $\Delta m \sim 0.2 \cong 1.4\ \mu_B$ results for all $Eu_xSr_{1-x}S$ samples.

We should note that in contrast to the $Eu_{0.95}Sr_{0.05}S$ sample the order parameter O_4 of the $Eu_{0.8}Sr_{0.2}S$ sample is antiferromagnetic. We can therefore be sure that the 1,1,1 Bragg intensity samples O_2 individually. On the other hand, the influence of ferromagnetic O_4 decreases very fast with diamagnetic dilution and seems to be nearly negligible for the $Eu_{0.95}Sr_{0.05}S$ sample.

The same type of analysis but for $Eu_{0.63}Sr_{0.37}S$ is shown in figure 10. For this strongly diluted sample the critical exponent has changed to $\beta = 1$. Smaller indications for this change

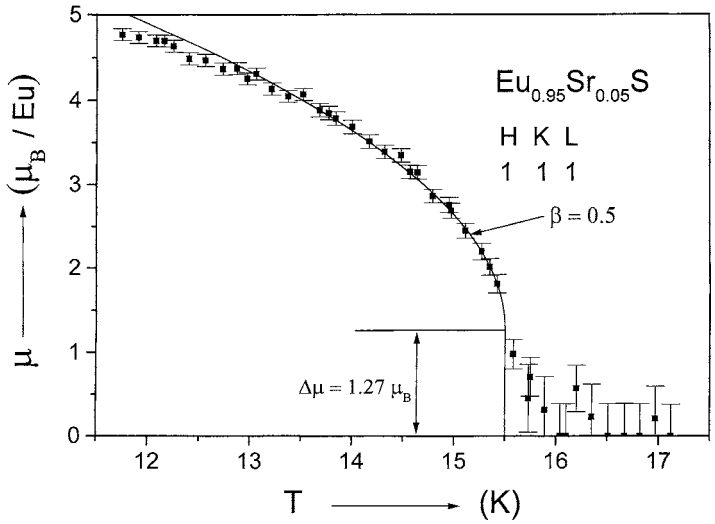

Figure 7. Ordered magnetic moment per Eu atom evaluated from the integrated 1,1,1 Bragg scattering intensity of $Eu_{0.95}Sr_{0.05}S$ as a function of temperature. The inflection point is characteristic for the change from Bragg scattering to critical diffuse scattering and is taken as the Curie temperature. With this choice of T_C a first-order transition with a discontinuity of the order parameter of $\Delta\mu = 1.27\ \mu_B$ results. Further continuous increase of magnetization is described by a critical power law with mean-field critical exponent of $\beta = 0.5$.

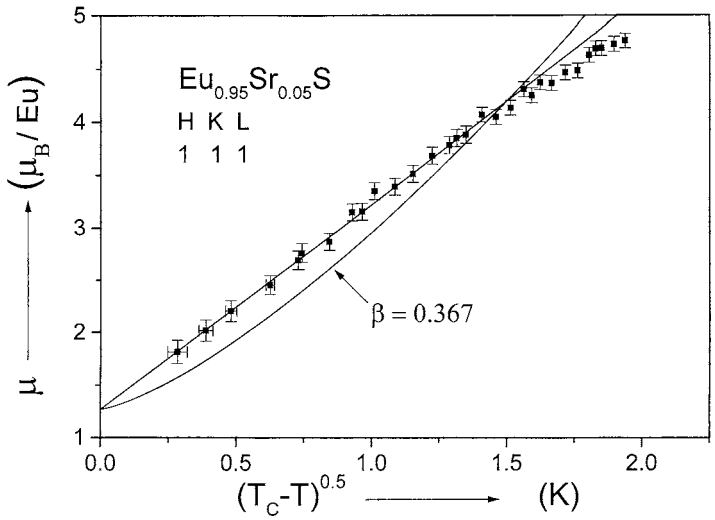

Figure 8. Magnetic moment data as shown in figure 7 against $(T_C - T)^{0.5}$. The curve labelled by the Heisenberg exponent $\beta = 0.367$ shows how the straight line fitted through the experimental points would be bent if the data were plotted alternatively over $(T_C - T)^{0.367}$. A discontinuity of 1.27 μ_B/Eu can be extrapolated for $T \to T_C$.

are already observed for the sample with $x = 0.7$. We interpret this result as a transition to a new universality class for a random distribution of magnetic moments [28, 29]. The value of $\beta = 1$ must be considered as characteristic for half-integral spin. The corresponding value for integral spin remains to be measured.

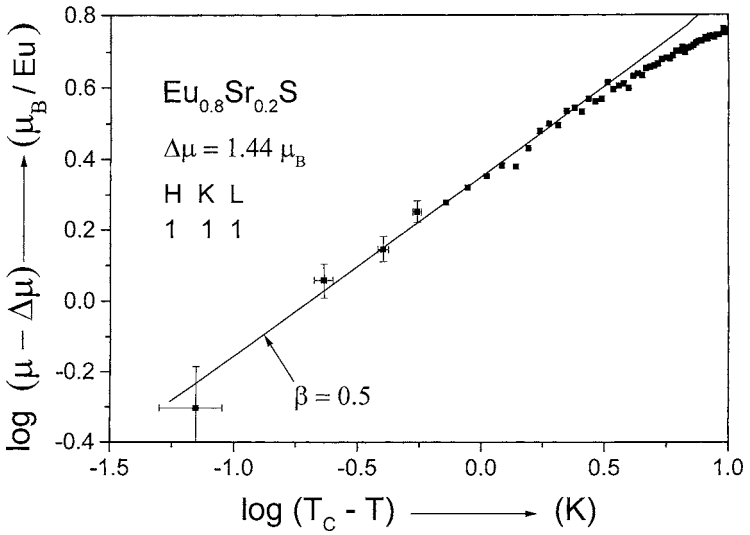

Figure 9. Log–log plot of ordered moment derived from 1,1,1 neutron scattering intensity against $(T_C - T)$ for $Eu_{0.8}Sr_{0.2}S$ after subtraction of a discontinuity of $\Delta\mu = 1.44\ \mu_B$/Eu. The value of the discontinuity is obtained in a graphical way as shown in figure 8.

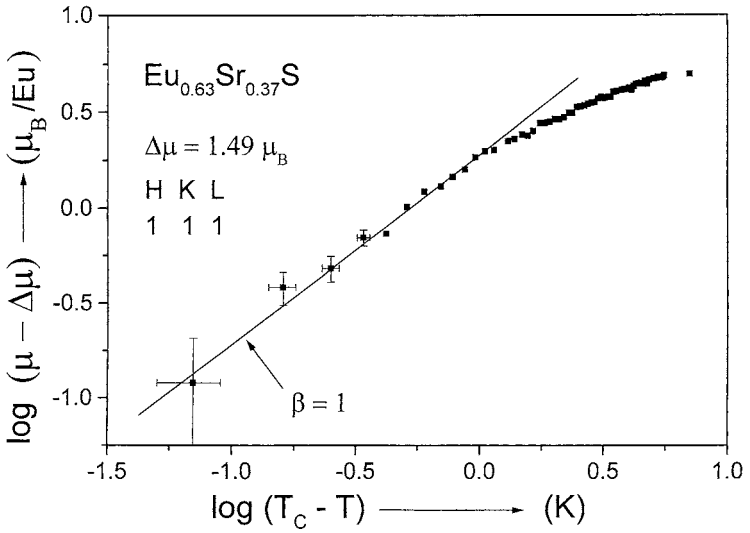

Figure 10. Log–log plot of ordered magnetic moment against $(T_C - T)$ for $Eu_{0.63}Sr_{0.37}S$ after subtraction of a discontinuity of $\Delta\mu_B = 1.49\ \mu_B$. For this strongly diluted ferromagnet a change to a critical exponent of $\beta = 1$ is observed.

Following these results we reconsidered earlier neutron scattering data of the antiferromagnet EuTe obtained on instrument D10 at the Institute Laue–Langevin, Grenoble. We analysed the intensity data for the 1/2,1/2,3/2 data in the same way as for the 1,1,1 data of the $Eu_xSr_{1-x}S$ samples. Figure 11 shows that a very similar result is obtained: the Néel transition turns out to be first order and for the critical exponent β the mean-field value $\beta = 0.5$ is evidently the better alternative. The discontinuity of the order parameter has also a similar

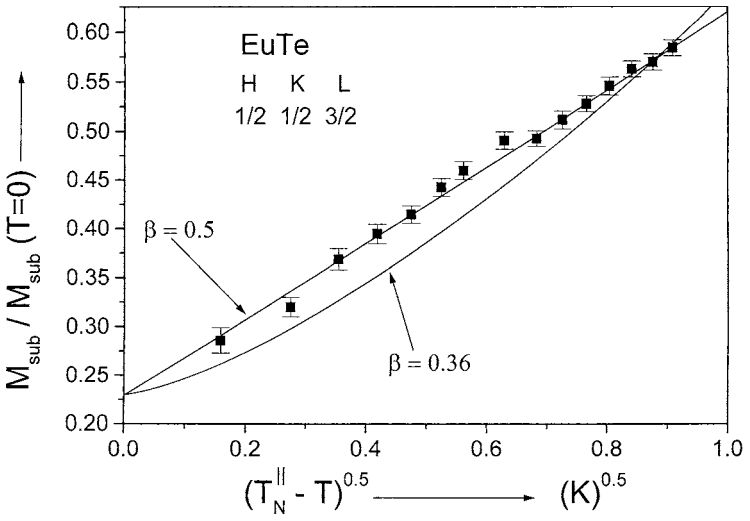

Figure 11. Normalized sublattice magnetization of EuTe in the critical temperature range against $(T_N^{\|} - T)^{0.5}$. The Néel temperature is first order with a discontinuity of the order parameter of ∼0.23. Further increase of order parameter is described by a critical power law with mean field critical exponent $\beta = 0.5$.

magnitude of ∼0.23. If the Néel temperature is treated as an adjustable parameter and the phase transition is assumed to be continuous a much smaller value will be fitted for β. In this way we obtained a critical exponent of $\beta = 0.29$ in an earlier publication [22]. This value is unexplained for an isotropic material with 3D interactions because it conforms neither to the Heisenberg nor to the mean-field model of critical behaviour. The analysis presented here has the great advantage of resulting in the well known mean-field value of $\beta = 0.5$. As was observed for GdMg the mean-field approximation is not a too simple model but turns out to be exact for isotropic magnetic materials with half-integral spin values [14]. This was not recognized as a general rule up to now because most isotropic magnets exhibit hard to identify first-order transitions. GdMg is an exceptional material in having a Curie transition of second order [14]. This allows one to observe the classical mean-field critical behaviour as seems to be characteristic for half-integral spin ($S = 7/2$). In [14] mean-field critical exponents were observed for the susceptibility ($\gamma = 1$), the spontaneous magnetization ($\beta = 0.5$) and the critical isotherm ($\delta = 3$) of GdMg.

3. Conclusions

For the diamagnetically diluted ferromagnets $Eu_xSr_{1-x}S$ a complete decomposition of the experimental Curie–Weiss temperature $\Theta_1(x)$ into contributions from bilinear interactions ($\sim x$), biquadratic interactions ($\sim x$) and three-spin interactions ($\sim x^2$) is presented. Knowing from measurements of the cubic susceptibility that antiferromagnetic biquadratic interactions and ferromagnetic three-spin interactions cancel at $x_c = 0.88$ a decomposition of the linear x coefficient into bilinear and biquadratic interactions is possible. A similar mean-field analysis for the critical temperature $T_C(x)$ must be performed separately for $x > x_c$ and $x < x_c$ because of spin structure changes due to the sign change of the fourth-order interaction sum at $x_c = 0.88$. Although this complication limits the accuracy of a polynomial fit to $T_C(x)$ it is observed that in both regions of the phase diagram the experimental $T_C(x)$ data can also

be approximated by a linear plus a quadratic x term. In other words, the observed deviations of the Curie line $T_C(x)$ from a simple linear x dependence can be explained in the same way as for $\Theta_1(x)$ by three-spin interactions. On the other hand, the mean field prediction that without fourth-order interactions $T_C(x)$ is simply proportional to the concentration of the magnetic atoms, x, seems to be reasonable. Using this assumption the remarkable systematics is obtained that the proportion between biquadratic and three-spin interactions is constant, i.e. independent of spin order. This means that the two interactions are always satisfied in the same way by the resulting spin structures and can be treated as proportional or equivalent.

We must assume that the appropriateness of mean-field theory for an analysis of $T_C(x)$ in materials with half-integral spin must be considered as a consequence of fourth-order interactions. These interactions affect the spin dynamics fundamentally and seem also to be responsible for the observed mean-field critical behaviour. At low temperatures quantum effects become, of course, important and a T^2 Bloch law is observed for the order parameter in materials with half-integral spin. In contrast to this, Bloch's original $T^{3/2}$ law was calculated assuming only Heisenberg interactions [23]. Even for the most diluted $Eu_xSr_{1-x}S$ sample with $x = 0.63$ the T^2 law is observed to hold. For the antiferromagnets $Eu_xSr_{1-x}Te$ the same behaviour was reported earlier [3].

The conventional ordering transitions of all $Eu_xSr_{1-x}S$ samples and of EuTe turned out to be first order in spite of no obvious latent heat [30]. First-order transitions observed with neutron scattering conform to recent magnetization studies on EuS and EuO [13] and to mean-field predictions [6–9].

A direct identification of the critical temperature is crucial for a reliable analysis of the critical behaviour. In neutron scattering experiments the transition temperature was often not measured directly but was obtained by extrapolating the order parameter from values as large as 0.3 down to zero [27]. This introduces a considerable ambiguity on the value of the critical temperature and on the type of critical magnetic behaviour. If the critical temperature is not precisely known nearly equivalent fits are possible either assuming a discontinuous phase transition with a following mean-field critical power law or assuming a continuous phase transition with a nearly Heisenberg β value. Here we fixed the ordering temperature to the obvious transition from Bragg to critical diffuse scattering intensities. Only for order parameter discontinuities of larger than $\sim$0.3 does the first-order character of the phase transition become obvious in the as-measured neutron scattering spectra. We consider it a justification of our analysis that the well known mean-field critical exponent $\beta = 0.5$ is obtained for all materials with half-integral spin. This conforms to the mean-field critical behaviour observed for GdMg, the only known isotropic 3D material having half-integral spin quantum number and a second-order Curie transition [14, 31].

A change from $\beta = 0.5$ to $\beta = 1$ is observed at a composition of about $x \sim 2/3$ in $Eu_xSr_{1-x}S$. This can be interpreted as a transition to a new universality class for a random distribution of the magnetic atoms [28, 29]. It would be very interesting to evaluate the corresponding critical exponent for materials with integral spin.

Acknowledgments

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