Eur. Phys. J. B **10**, 465–473 (1999)

THE EUROPEAN PHYSICAL JOURNAL B

EDP Sciences

Spin-ordering in S = 1 anisotropic Heisenberg models with nondiagonal spin exchange

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Received 24 January 1999

Abstract. The properties of $S = 1$ anisotropic Heisenberg models with nondiagonal exchange between axial and planar spin components are investigated using Monte Carlo techniques. The quantum nature is taken into account in a semi-classical approximation. The ordering of the spins when applying an external field with axial and planar components is discussed. It is argued that the quantum nature of the spins and the nondiagonal exchange may explain the peculiar shape of the magnetic specific heat of $FeBr_2$ as well as the weakly first–order phase transition observed in the same compound when a tilted field is applied.

PACS. 75.10.-b General theory and models of magnetic ordering – 75.30.Kz Magnetic phase boundaries (including magnetic transitions, metamagnetism, etc.) – 75.40.Mg Numerical simulation studies

1 Introduction

Metamagnets of Ising type display a field–induced phase transition from an antiferromagnetic phase to a (saturated) paramagnetic phase, the transition being of first order at low temperatures and of second order at high temperatures [1,2]. The first and second order transition lines meet at a tricritical point. The layered antiferromagnet $FeCl_2$ is generally considered to be the textbook example of this kind of antiferromagnets with a strong uniaxial anisotropy [3].

Recently, there has been a renewed interest in the layered hexagonal antiferromagnet $FeBr_2$ [4–12]. In the ordered phase of $FeBr_2$ the spins of the iron ions are aligned ferromagnetically in the triangular layers, the layers being stacked antiferromagnetically along the c–axis. Adjacent iron layers are separated by two nonmagnetic bromide planes.

Investigations of de Azevedo *et al.* [4] revealed noncritical anomalies in the antiferromagnetic phase of $FeBr_2$ below the transition line to the paramagnetic phase, *e.g.* maxima or shoulders in the temperature derivatives of the magnetization at constant axial fields. The ingredients crucial for the existence of these noncritical spin fluctuations are the effectively weak ferromagnetic intralayer couplings and the large number of interlayer nearest neighbors (due to the superexchange mediated by the bromide planes) [5,6,9].

Surprisingly, measurements of the magnetic specific heat [7] revealed a sharp peak superposed on a broad shoulder or maximum below the transition to the paramagnetic phase, in contrast to Monte Carlo simulations of Ising metamagnets [5–7,9] showing only a noncritical shoulder or maximum. The peculiar shape of the specific heat of $FeBr_2$ was tentatively interpreted [7,8] as the signature of a new phase transition between two different antiferromagnetic orderings of the z–components of the spins. This new transition line was supposed to result from the decomposition of the tricritical point into a bicritical point and a critical end point, a possible scenario emerging from the mean field treatment of Ising metamagnets [1]. Remarkably, however, such a decomposition of the tricritical point has not been observed in Monte Carlo simulations of three-dimensional Ising antiferromagnets [13,6,14]. Furthermore, there are no indications of an antiferromagnetic–antiferromagnetic phase transition in the magnetometric measurements in an axial magnetic field [4,11].

Recent investigations in an external field with an axial and a planar component have shown evidence for jumps in the magnetization parallel and perpendicular to the field [12]. The authors suggest that this transition–like phenomenon may involve a nondiagonal exchange between the axial and planar components of the spins.

Hitherto, theoretical progress in understanding the properties of $FeBr_2$ has mainly been achieved by analyzing simplified spin 1/2 Ising antiferromagnets [5–7,9,15]. However, the lowest state of an iron ion in $FeBr_2$ is a triplet consisting of a lowest doublet and a singlet [16]. Therefore, in reference [9], anomalies of the magnetization and the specific heat have also been studied in $S = 1$ models.

In the present work, I shall present a Monte Carlo study of $S = 1$ anisotropic Heisenberg models which include a nondiagonal exchange term between axial and planar spin components. The quantum nature of the $S = 1$

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spins will be taken into account in a semi–classical approximation. Especially, I shall give a possible explanation of the peculiar shape of the specific heat of $FeBr_2$ and discuss the spin–ordering in an axial and in a nonaxial field.

The paper is organized in the following way: in Section 2 the anisotropic $S = 1$ Heisenberg models are introduced and the semi–classical approximation used in the simulations is discussed. Section 3 deals with the properties of ferromagnetic and antiferromagnetic models on a tetragonal lattice. These simplified models are studied in order to investigate the effects of (1) the semi–classical approximation, (2) different couplings between planar and axial spin components, and (3) an external planar field component. In Section 4 a realistic model for $FeBr_2$, both in an axial and in a tilted field, is discussed and the findings are compared to the experiments. Some of the results of this Section have already been published in a brief report [17]. A short summary concludes the paper.

2 The models

The low-temperature properties of $FeBr_2$ (space group D^3_{3d}) may be described by the effective $S = 1$ Heisenberg Hamiltonian [18–20,9]

$$\mathcal{H} = -\sum_{\alpha>\beta} J_{\alpha\beta}\left\{\frac{1}{\eta}S^z_\alpha S^z_\beta + S^x_\alpha S^x_\beta + S^y_\alpha S^y_\beta\right\} - \sum_\alpha D\,(S^z_\alpha)^2 - \sum_\alpha \left[H_x S^x_\alpha + H_z S^z_\alpha\right] + \mathcal{H}_{nd}(J_{xz}) \quad (1)$$

defined on a three-dimensional hexagonal lattice consisting of a layered system of triangular lattice planes stacked along the c–axis. Two different sets of interactions $J_{\alpha\beta}$ have been derived from inelastic neutron scattering studies [18,19]: the ferromagnetic nearest neighbor interaction in the triangular layers perpendicular to the c–axis (corresponding to the z–direction), J_1, is weakened by antiferromagnetic in–layer couplings, extending either up to next-nearest neighbors [18], J_2, or up to third neighbors [19], J_3. Every spin is coupled antiferromagnetically with the strength J' to ten spins in the neighboring layer [15]. The constant η describes the anisotropy in the exchange interactions.

The second term in equation (1) describes a single–ion anisotropy with the easy axis of the spin along the z–axis, *i.e.* $D > 0$, whereas H_x and H_z are the planar and axial components of an applied external field. Finally, the last term, $\mathcal{H}_{nd}(J_{xz})$, is a nondiagonal intralayer exchange between axial and planar spin components with the strength J_{xz} [20], involving only products of pairs of spins. In order to illustrate this interaction, which is invariant when applying the symmetry elements of the trigonal point group, consider two neighboring in-layer sites, called 0 and 1, with the same value of y. The nondiagonal exchange may be written in the form [20]

$$\mathcal{H}_{nd}(J_{xz}) = \sum_{\langle\alpha\beta\rangle} H_{\alpha\beta}(J_{xz}) \quad (2)$$

where the sum is over nearest-neighbor in-layer sites $\langle\alpha\beta\rangle$. For the pair $\langle\alpha\beta\rangle = \langle 01\rangle$ this exchange takes the form [20]

$$H_{01} = -J_{xz}\left(S^z_0 S^x_1 + S^x_0 S^z_1\right). \quad (3)$$

The other terms in equation (2) are obtained by applying the appropriate symmetry elements transforming the pair $\langle 01\rangle$ onto $\langle\alpha\beta\rangle$.

As this model, defined on a hexagonal lattice, is rather complicated, it is preferable to study the effects of the semi-classical approximation, of the nondiagonal exchange, and of the planar field component first in simpler models. Therefore, I consider also the following $S = 1$ Heisenberg Hamiltonian defined on a tetragonal lattice:

$$\mathcal{H} = -J\sum_{ijk}\mathbf{S}_{ijk}\left(\mathbf{S}_{i+1\,jk} + \mathbf{S}_{i\,j+1\,k}\right) - J'\sum_{ijk}\mathbf{S}_{ijk}\mathbf{S}_{ij\,k+1} - D\sum_{ijk}\left(S^z_{ijk}\right)^2 - \sum_{ijk}\mathbf{H}\mathbf{S}_{ijk} + \mathcal{H}_{nd}(J_{xz}) \quad (4)$$

with $\mathbf{S} = (S^x, S^y, S^z)$ and $\mathbf{H} = (H_x, 0, H_z)$. Here i, j, k (corresponding to the a, b, c–directions respectively) label the lattice sites. The coupling in the layers, J, is ferromagnetic, whereas the coupling between adjacent layers, J', may be antiferromagnetic ($J' < 0$) or ferromagnetic ($J' > 0$). The single-ion anisotropy, $D > 0$, is considered in order to obtain ground states with nonvanishing z–components of the spins. This may alternatively be achieved by considering instead an anisotropy in the exchange interactions (yielding three-dimensional XXZ models).

For the tetragonal models, I will consider two different couplings between planar and axial spin components: (1) a term involving only products of pairs of spins, being invariant under the symmetry operations of the point group C_{4v} (this term can thus be considered to be analogous to the nondiagonal exchange term, see Eqs. (1-3), proposed for the description of $FeBr_2$),

$$\mathcal{H}^1_{nd}(J^1_{xz}) = -J^1_{xz}\sum_{ijk}\Big[S^z_{ijk}S^x_{i+1\,jk} - S^x_{ijk}S^z_{i+1\,jk} + S^z_{ijk}S^y_{i\,j+1\,k} - S^y_{ijk}S^z_{i\,j+1\,k}\Big], \quad (5)$$

or (2) a term involving products of squares of spins, being invariant under the symmetry operations of the space group,

$$\mathcal{H}^2_{nd}(J^2_{xz}) = -J^2_{xz}\sum_{\langle\alpha\beta\rangle}(S^z_\alpha)^2\left[\left(S^x_\beta\right)^2 + \left(S^y_\beta\right)^2\right], \quad (6)$$

where the sum is over nearest–neighbor in–layer sites.

I consider in the following $S = 1$ spins where the quantum nature is treated in a semi–classical approximation: the z–component is discretized and can only take the values 1, 0, or -1, whereas the spin length is fixed to be $|\mathbf{S}| = \sqrt{S\,(S+1)} = \sqrt{2}$. Hence, the spins rotate in the xy plane like a classical vector. The xy–components provide additional energy contributions as compared to the

$S = 1$ Ising model, even at low temperatures. Note that in reference [9] the spin length was fixed at 1, the spins thus having a planar component only if $S^z = 0$, yielding thermal properties similar to the $S = 1$ Ising model.

The ground states of the semi–classical antiferromagnetic hexagonal and tetragonal models are readily obtained provided the nondiagonal exchange constant is not too large. In small axial fields ($H_x = 0$ and $H_z < H_z^c = -2NJ'$, $N = 10$ for the hexagonal model and $N = 2$ for the tetragonal model), the antiferromagnetic phase, where the spins are aligned ferromagnetically in the layers, with an antiferromagnetic arrangement between subsequent layers, is stable. For larger fields ($H_z > H_z^c$ and $H_x = 0$) the axial spin components S^z order ferromagnetically, whereas the signs of the planar components (S^x and S^y) still change from layer to layer. Note that in absence of an ordering planar field the ground state is infinitely degenerate, as the angle between the planar spin components and, say, the x–axis is not fixed. Keeping H_z constant and applying a planar field, H_x, yields a stable phase where the xy–components of the spins are ordered in a spin–flop phase, in which the magnetization per layer in x–direction has the same value in each layer, whereas the y–components have different signs in adjacent layers but the same absolute value. For stronger planar fields the y–components finally vanish, leading to a ferromagnetic ordering of the planar spin components.

The effect, at $T = 0$, of a strong nondiagonal coupling between spin components can be discussed for the tetragonal ferromagnetic model. For small absolute values of the nondiagonal exchange constant (be it J_{xz}^1 or J_{xz}^2, see Eqs. (5, 6)), the ground state is given by a ferromagnetic phase where the spins have both axial and planar components. Consider first the two–spin exchange with the coupling constant J_{xz}^1. Increasing $\left|J_{xz}^1\right|$ does not change the energy of the ferromagnetic phase, whereas the energy of a second phase, consisting of ferromagnetically coupled layers with a stripped pattern in every layer, is decreased, until, for $\left|J_{xz}^1\right| > \sqrt{2}J + \sqrt{2}/4H_x$, the stripped phase has, at $T = 0$, a lower energy than the ferromagnetic phase, thus forming the ground state. Note that the appearance of a new ground state at the threshold value does not depend on the sign of J_{xz}^1. If the second spin exchange with negative coupling constants J_{xz}^2 is considered, the energy of the ferromagnetic phase is increased when J_{xz}^2 decreases. For couplings $J_{xz}^2 < -\frac{D+H_z+\left(1-\sqrt{2}\right)H_x}{4}$ the ground state is given by a ferromagnetic phase where the spins have only a planar component. A positive coupling constant J_{xz}^2 does not yield a new stable phase. The ground state of the tetragonal antiferromagnetic model in presence of a nondiagonal spin exchange can be discussed in similar terms. In the following it is always supposed that the nondiagonal coupling constant does not exceed the threshold value which leads to a new ground state.

The thermal properties of the different models were investigated by simulating systems consisting of $L \times L \times L$ Heisenberg spins, with L ranging from 10 to 30. As the equilibration proved to be rather slow, the first 3×10^4 Monte Carlo steps per site were usually discarded. Simulations for up to 20 different realizations with different random numbers were performed in order to improve the statistics. Besides the energy E and the specific heat C, the different components of the magnetization per layer, $m_x(i)$, $m_y(i)$, and $m_z(i)$, and, for the antiferromagnetic models, related quantities such as the sublattice magnetizations, $\mathbf{M}_1 = \left(m_x^1, m_y^1, m_z^1\right)$ and $\mathbf{M}_2 = \left(m_x^2, m_y^2, m_z^2\right)$, referring to odd and even layers, were computed. Here, the odd, respectively even layers have the magnetization $m_z^1 = +1$, respectively $m_z^1 = -1$ at $T = 0$. The applied axial field points in the "+"–direction, *i.e.* it tends to destabilize the even layers.

The ground state was always used as starting configuration for the simulations. In absence of a planar field component, the state with $S^x = 0$ was chosen among the infinity of degenerate ground states. Note that in this case one encounters, after initial relaxation, a metastable state, in which the system remains, possibly, for a long time, the time depending on the size of the system and the temperature. The computed planar spin components are then supposed to be very close to their values in the thermodynamic limit.

3 Thermal properties of the tetragonal models

In this section, the thermal properties of the tetragonal ferromagnetic and antiferromagnetic models in a planar field (see Eq. (4)) are discussed. For a vanishing external field, the Hamiltonian of the antiferromagnetic model can be mapped in the usual way onto that of the ferromagnetic model. Therefore, I will in the following present for $H_x = 0$ simulations of the ferromagnetic model, the antiferromagnetic model being analyzed for $H_x \neq 0$.

Figure 1 shows the temperature dependent specific heat and the magnetization obtained for vanishing nondiagonal spin exchange for the ferromagnetic model, with $J = J'$, $D = 3J'$, and $H_x = 0$. The specific heat has a two peak structure, see Figure 1a: the peak at T_c is the critical peak resulting from the disordering of the z–components of the spins, whereas the low–temperature peak at T_{xy} follows from the disordering of the planar spin components. The magnetization data, see Figure 1b, show that the z–components, in absence of a coupling between planar and axial spin components, are not affected by this disordering.

This two peak structure of the specific heat should be compared to the specific heat of the classical anisotropic Heisenberg model showing only one maximum. For vanishing single–ion anisotropy the two peaks of the specific heat of the semi–classical model merge to a single peak located at the critical temperature of the corresponding classical isotropic Heisenberg model.

It is clear from Figure 1 that, due to the discretization of S^z and the presence of the single–ion anisotropy, the disorderings of the axial and planar spin components are largely decoupled. The z–components behave like $S = 1$ Ising spins and disorder at the critical temperature T_c

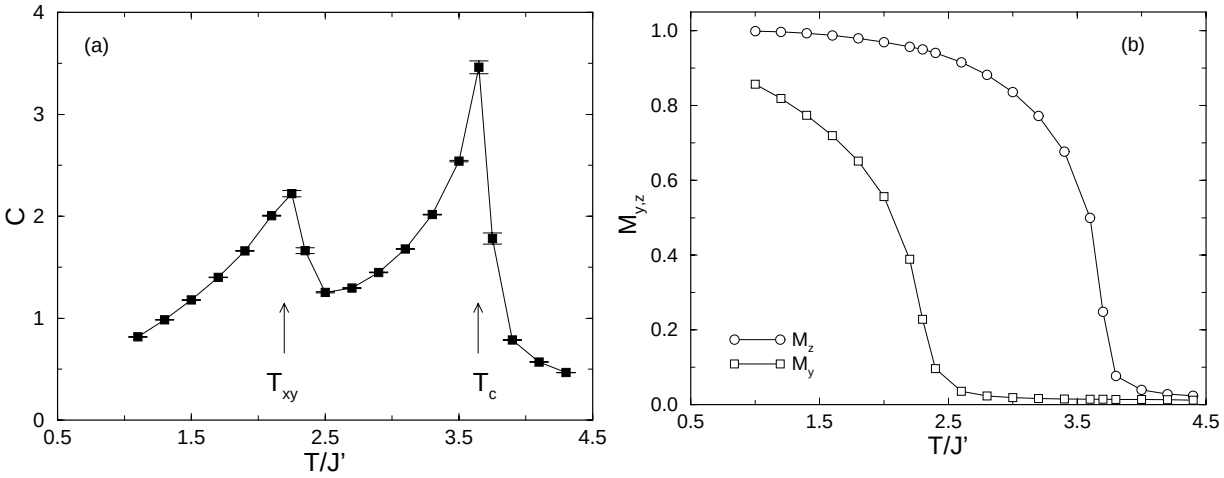

Fig. 1. Monte Carlo data of (a) the specific heat and (b) the components of the magnetization as function of the temperature for the $S = 1$ ferromagnetic Heisenberg model on a tetragonal lattice, with $J = J'$, $D = 3J'$, and $H_x = H_z = 0$. The system size is $L = 20$. Here and in the following figures, the Boltzmann constant is set equal to one.

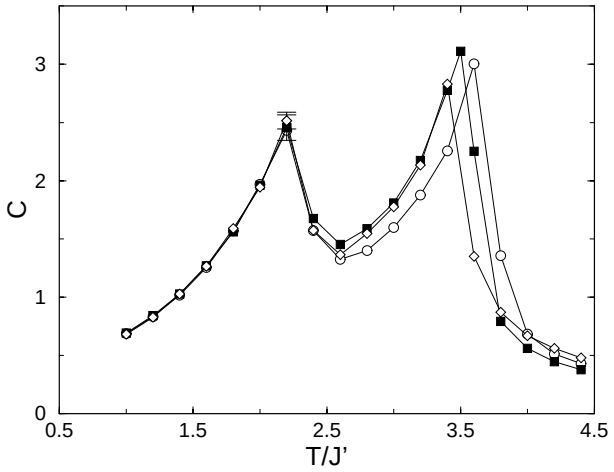

Fig. 2. Specific heat C of the ferromagnetic model as a function of temperature for the two different nondiagonal spin exchange terms given in equations (5) (coupling constant J^1_{xy}) and (6) (coupling constant J^2_{xy}), with $J = J'$, $D = 3J'$, and $H_x = H_z = 0$. Open diamonds: $J^1_{xy} = 0.5J'$. Filled squares: $J^2_{xy} = 0.5J'$. The data obtained without a nondiagonal coupling (open circles) are included for comparison. Systems with 10^3 spins are considered. Only error bars larger than the size of the symbols are shown.

(which increases with increasing value of D, yielding in the limit $D \longrightarrow +\infty$ the critical temperature of the 3d Ising model), whereas the xy–components form a classical three-dimensional plane-rotator disordering at the temperature [21] $T_{xy} = 2.2J'$ (setting the Boltzmann constant equal to one).

Note that the specific heat does not vanish when T approaches 0. This is an artefact of the classical nature of the planar spin components yielding $\lim_{T\to 0} C = 1/2$.

In presence of the nondiagonal two–spin exchange with coupling constant J^1_{xz} (Eq. (5)), the ordering temperature T_c of the axial spin components is decreased, see Figure 2. This results from the coupling, at temperatures above T_{xy}, of the ordered z–components to the disordered planar components, yielding additional fluctuations which lead to a decrease of the ordering temperature of the axial spin components. The value of T_{xy} is not affected by this nondiagonal spin–exchange, as long as $\left|J^1_{xz}\right|$ is not too large, see below. The spin exchange involving products of squares of spins (Eq. (6)) also leads to a decrease of T_c for negative values of J^2_{xz}. This second coupling is not so effective in destabilizing the ferromagnetically ordered z–components, yielding a smaller decrease of T_c.

If the strength of $\left|J^1_{xz}\right|$ is increased beyond a threshold value (being around 0.65 J' for $J = J'$ and $D = 3J'$), a jump in the axial component of the magnetization, M_z, is observed, see Figure 3a. This discontinuous change, which is induced by the disordering of the planar components, shows up as a sharp peak in the specific heat (Fig. 3b). At temperatures slightly above T_{xy} some orderness of the z–components still persists, *i.e.* $M_z \neq 0$. Increasing further the temperature, M_z increases until, at T_c ($= 3.1\ J'$ for the parameters of Fig. 3), the disordering of the z–components finally takes place, yielding a second peak in the specific heat. This behaviour of M_z may be better understood when the temperature, starting from the disordered high temperature phase, is decreased. At T_c, the z–components order at the usual second order phase transition. The increase of the ordering of the S^z spins at temperatures below T_c increases the effect of the nondiagonal exchange, yielding, after an initial slow rising, effectively a decrease of M_z, until, at T_{xy}, the planar components order. Note that in this case both T_c and T_{xy} are shifted to lower temperatures, the shift being larger for larger values of $\left|J^1_{xz}\right|$.

Interestingly, no jump in M_z occurs when the second spin exchange with coupling constant J^2_{xz} is considered.

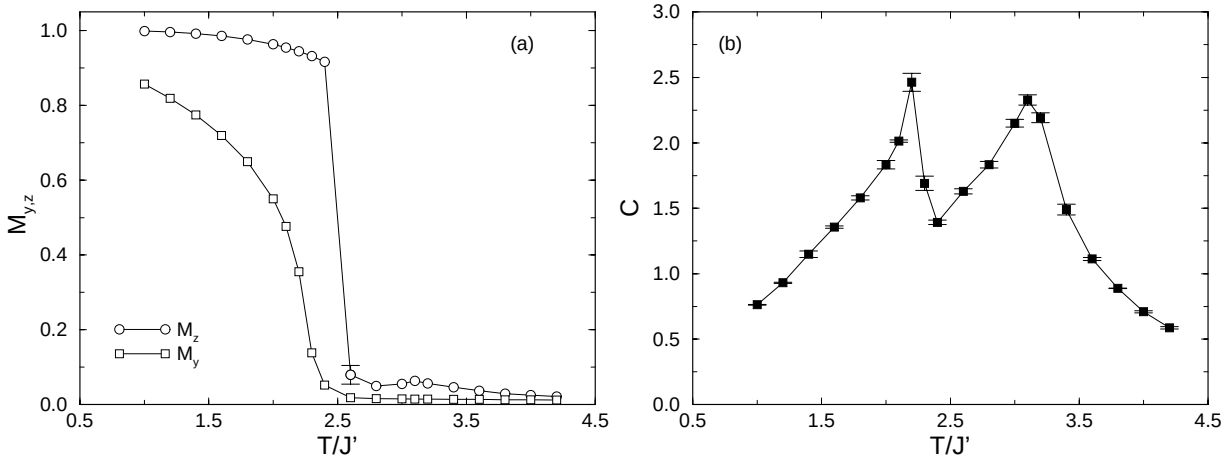

Fig. 3. Monte Carlo data of (a) the components of the magnetization and (b) the specific heat as function of the temperature obtained for the ferromagnetic model on a tetragonal lattice, with $J = J'$, $D = 3J'$, $H_x = H_z = 0$, and $J^1_{xz} = 0.7J'$. Systems with $20 \times 20 \times 20$ spins are simulated.

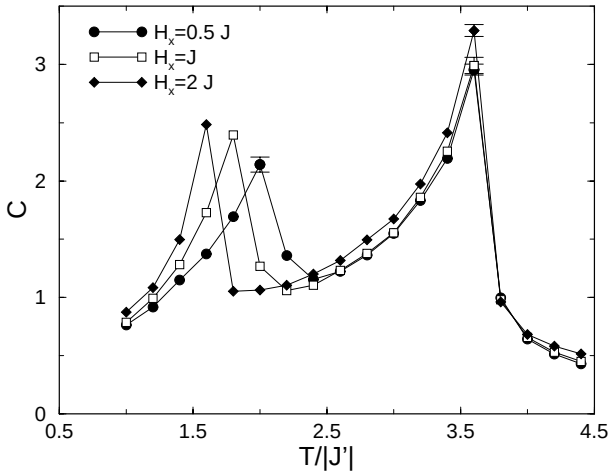

Fig. 4. The temperature dependent specific heat obtained for the antiferromagnetic $S = 1$ Heisenberg model defined on a tetragonal lattice when planar fields with different strengths are applied, with $J = -J'$, $D = -3J'$, and $H_z = 0$. Nondiagonal couplings between axial and planar spin components are not considered. The system size is $L = 20$. Only error bars larger than the size of the symbols are shown.

For all values of J^2_{xz} yielding the ferromagnetic ground state with both planar and axial spin components, see above, M_z changes continuously at T_{xy}.

Figure 4 shows the specific heat of the antiferromagnetic tetragonal model obtained when planar fields with different strengths are applied and only diagonal couplings are considered. Increasing the value of H_x moves T_{xy} to lower temperatures, whereas T_c is not changed. In presence of a planar field unusual strong finite–size effects are observed when the planar spin components disorder, making it necessary to simulate at least systems of length $L = 20$ in order to get a reliable estimate of T_{xy}. These strong finite–size effects are due to the presence of the $S^z = 0$ states and do not show up for the corresponding classical plane–rotator, as I checked. Finally, one should notice that, in presence of the nondiagonal coupling (5) with the strength J^1_{xz}, the total magnetization in z–direction again changes discontinuously for values of $\left|J^1_{xz}\right|$ larger than the threshold value, which seems not to depend on the value of H_x.

4 Thermal properties of the hexagonal model

Most of the features discussed in the previous Section for the tetragonal models are also encountered if the realistic hexagonal model (1) for $FeBr_2$ is considered [17]. In the following I will not reiterate the discussion on the values of the diagonal couplings of the spins (the interested reader is referred to Ref. [9]) and choose a set of parameters, based on inelastic neutron scattering experiments [18,19], for which pronounced anomalies in the magnetization data and in the specific heat data are observed [9]: $J_1 = -16.75J'$, $J_2 = 0$, $J_3 = -0.29J_1$, and $\eta = 0.78$.

Figure 5 shows the specific heat and the sublattice magnetizations obtained for strong single–ion anisotropy D and vanishing nondiagonal interactions, with $H_z = -18J'$ and $H_x = 0$. The temperature dependent specific heat $C(T)$ has a three peak structure: the peak at T_c is the critical peak resulting from the disordering of the z–components of the spins. Going to lower temperatures, one encounters first the anomaly due to the noncritical spin fluctuations. This peak does not correspond to a sharp phase transition and does not show a significant size dependency, in contrast to the critical peak at higher temperatures [9]. Both peaks are present when computing the specific heat of Ising metamagnets and involve solely S^z. The third peak, again, results from the disordering of the planar spin components, see Figure 5b.

The presence of the nondiagonal spin exchange moves both T_c and the anomaly to lower temperatures, see Figure 6a, whereas T_{xy} only decreases, moderately, for large

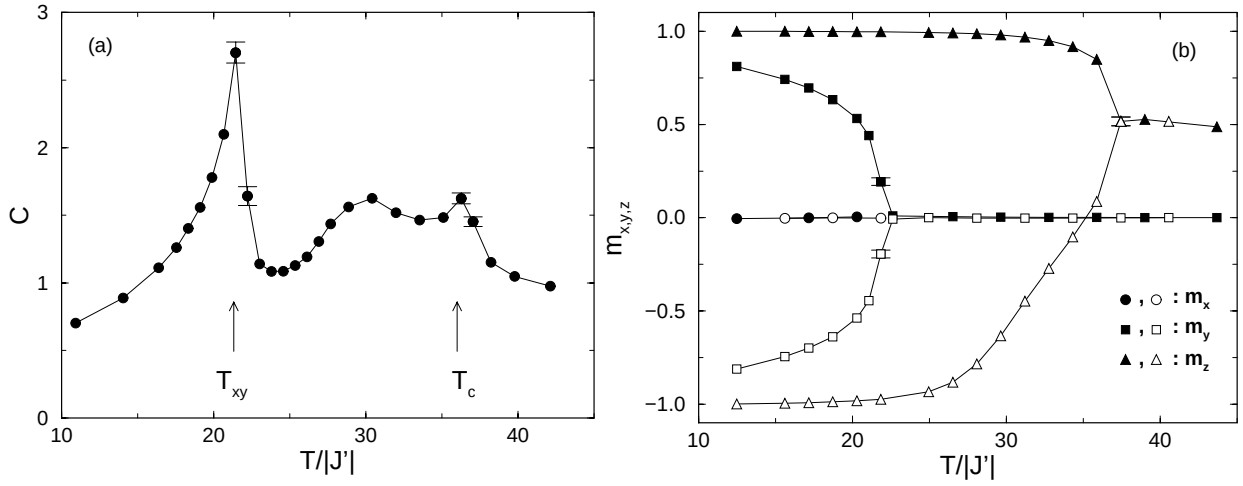

Fig. 5. Monte Carlo data of (a) the specific heat and (b) the components of the magnetization per layer in odd (full symbols) and even (open symbols) planes as function of the temperature for the $S = 1$ anisotropic Heisenberg model on the hexagonal model in an axial field $H_z = -18J'$, with $D = -32.4J'$ and $J_{xz} = 0$. Systems with $20 \times 20 \times 20$ spins are simulated. Error bars are only shown when they are larger than the sizes of the symbols.

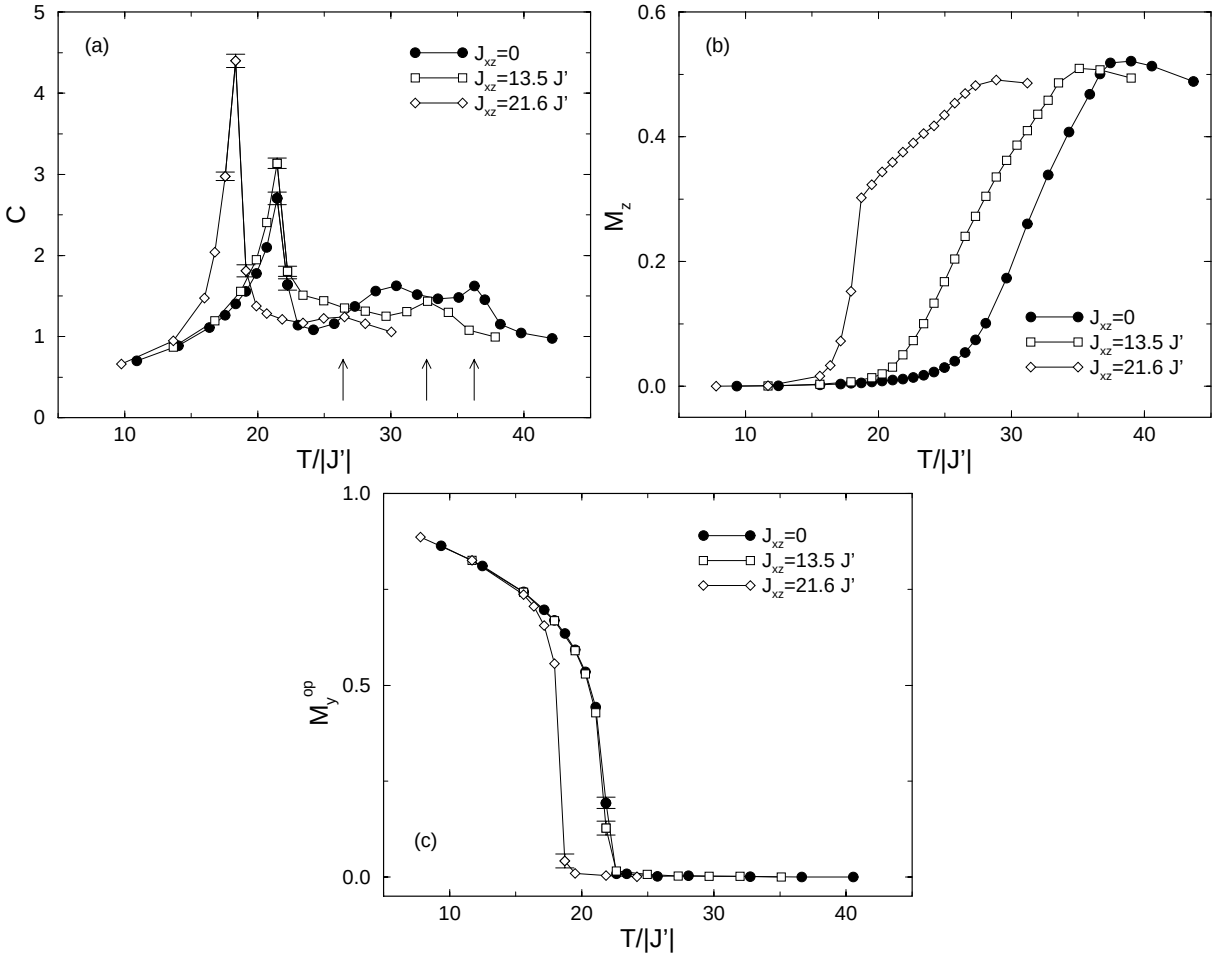

Fig. 6. Temperature dependence of (a) the specific heat (the arrows indicate the critical temperatures, T_c), (b) the total magnetization in z–direction, and (c) the order parameter of the planar spin components for different values of the nondiagonal spin exchange between the planar and the axial spin components for the hexagonal antiferromagnetic model, with $D = -32.4J'$ and $H_z = -18J'$. Systems with $20 \times 20 \times 20$ spins are considered. Only error bars larger than the size of the symbols are shown.

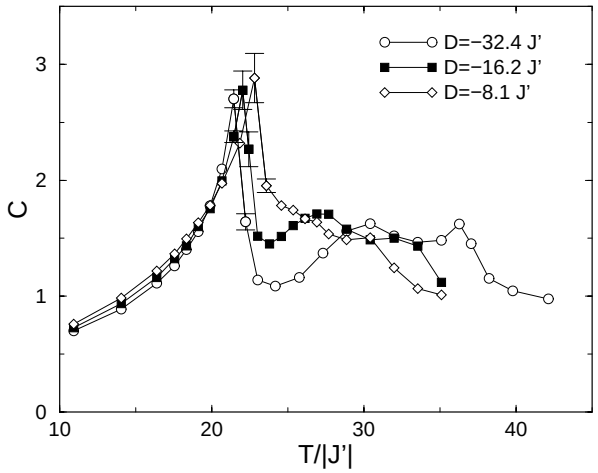

Fig. 7. The specific heat C as a function of temperature for different values of the single–ion anisotropy, with $J_{xz} = 0$ and $H_z = -18J'$. The system size of the simulated antiferromagnetic hexagonal model is $L = 20$. Error bars are only shown when they are larger than the sizes of the symbols.

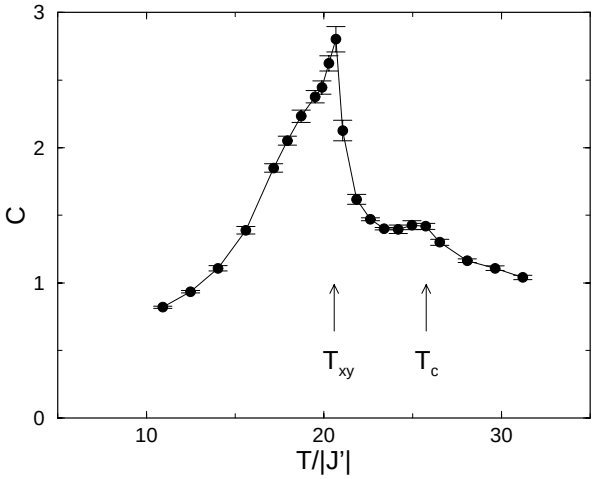

Fig. 8. Temperature dependent specific heat C of the hexagonal model with $J_{xz} = 16.2J'$, $D = -8.1J'$, and $H_z = -18J'$, for systems with $20 \times 20 \times 20$ spins.

values of J_{xz}. The anomaly in the specific heat approaches the xy–peak, its height being reduced, when J_{xz} is increased, and finally merges with the T_{xy} peak. Again, a threshold value exists for $|J_{xz}|$, at about 18 J', beyond which the total magnetization in z–direction, $M_z = \left(m_z^1 + m_z^2\right)/2$, changes discontinuously, see Figure 6b. The disordering of the planar components at T_{xy} is then also clearly discontinuous, as can be seen in the jump of the order parameter $M_y^{\rm op} = \left(m_y^1 - m_y^2\right)/2$, see Figure 6c. Note that the effect of J_{xz} does not depend on its sign.

Changing the value of the axial field H_z does not change T_{xy} if $J_{xz} = 0$. For nonvanishing nondiagonal couplings, however, the position of the xy–peak is shifted to lower temperatures when the axial field strength is increased.

Figure 7 shows the influence of the single-ion anisotropy D on the specific heat for $J_{xz} = 0$. Decreasing D, the $T_{\rm c}$ peak and the anomaly are moved to lower temperatures, whereas T_{xy} is slightly increased. A similar behavior is found for $J_{xz} \neq 0$, as shown in Figure 8 for $J_{xz} = 16.2J'$ and $D = -8.1J'$. For this choice of the parameters, the noncritical spin fluctuations appear at lower temperatures than the disordering of the planar spin components. The resulting specific heat has a peculiar shape consisting of a broad shoulder, the anomaly, and a superposed peak, the T_{xy} peak. This shape is reminiscent of the magnetic specific heat of $FeBr_2$ and will be discussed in more details below.

Applying an additional planar field component, H_x, leads to a spin–flop phase in the xy–components at $T = 0$: the y–components of the layer magnetization have opposite signs in the different sublattices but the same absolute value, whereas the x–components are the same in every layer. As the axial field tends to stabilize the odd or "+" layers and to destabilize the even or "−" layers, the absolute values of m_y^1 and m_y^2 are close but not identical at temperatures $T > 0$.

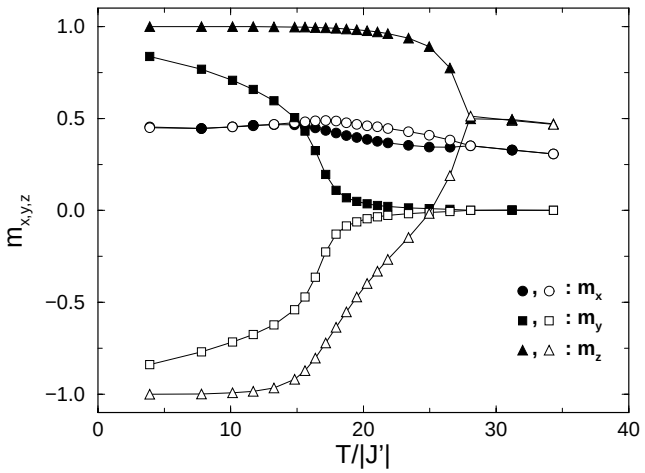

Fig. 9. The components of the magnetization per layer in odd (full symbols) and even (open symbols) planes as function of temperature in presence of a planar field component, $H_x = 0.75H_z$, with $J_{xz} = 16.2J'$, $D = -8.1J'$, and $H_z = -18J'$. Hexagonal systems with $30 \times 30 \times 30$ spins were simulated.

Figure 9 shows the different sublattice magnetizations for $J_{xz} = 16.2J'$, $D = -8.1J'$, and $H_x = 0.75H_z$, *i.e.* a field with axial and planar components is considered. At low temperatures, the antiferromagnetic ordering of the axial spin components and the spin–flop ordering of the planar spin components is clearly seen. When the system is heated, a drastic change in the y–component of the layer magnetization takes place at T_{xy} well below $T_{\rm c}$. For the chosen parameters, the change in the y–components is continuous. For values of $|J_{xz}|$ larger than the threshold value, *e.g.* $J_{xz} = 21.6J'$, this change occurs through a jump in the layer magnetization leading to a first–order transition. At first it may be surprising that the y–components (and also the x–components) of the sublattice magnetization are not equal at temperatures above

T_{xy} and below T_c, see Figure 9. In fact, this is explained by the finite value of the axial field H_z which tends to destabilize the z–components in the "$-$" layers, thus leading to different sublattice magnetizations in the different layer types. As a result the y–components do not vanish at the phase transition at T_{xy}, but take a small value which is different for the two layer types. Only when the z–components of the sublattice magnetizations are equal, at T_c, do the y–components vanish and the x–components take the same value. This effect is also observed when applying a field with axial and planar components to the tetragonal antiferromagnetic model discussed in the previous Section.

Increasing the value of the planar field moves T_{xy} to lower temperatures, as it is also the case for the tetragonal antiferromagnetic model. Furthermore, the specific heat seems to loose its peculiar shape for large values of H_x. At least for the temperature resolution used in the present study, only one, rather broad, peak is seen instead of the shoulder or maximum with a superposed sharp peak which is observed for $H_x = 0$.

The presented data indicate that the quantum nature of the $S = 1$ spins has to be taken into account in a theoretical description of the low temperature behaviour of $FeBr_2$. The semi–classical approach adopted in the present work leads to different disordering temperatures for the planar and the axial spin components. Hence, the anomaly and the low-temperature xy peak are not intimately related. The modification of, for instance, the exchange J_{xz} or the degree of Ising-like anisotropy D changes their respective positions and may lead in an axial field to specific heat data having the peculiar shape of the magnetic specific heat of $FeBr_2$, see Figure 8. One should notice that, in order to obtain this peculiar shape with the considered set of diagonal coupling constants, the single–ion anisotropy has to be decreased considerably as compared to the values obtained from inelastic neutron scattering measurements. Nevertheless, one must keep in mind that both D and the strengths of the diagonal couplings were derived from the experiments without taking a possible nondiagonal spin exchange into account [18,19].

The evolution of the temperature dependent specific heat of $FeBr_2$ with increasing axial fields is also of interest [7]. For small fields only one peak, the critical peak at T_c, has been observed. For larger fields, a shoulder with a superposed peak appears at lower temperatures. The shoulder evolves into a maximum with increasing fields whereas the superposed peak becomes sharper, the whole being shifted to lower temperatures. This large–field behavior is well rendered in the simulations, as shown in Figure 10. Indeed, the shoulder, resulting from the noncritical spin fluctuations, changes into a maximum when H_z is increased, whereas the xy–peak becomes sharper, the anomaly in the axial spin components and the disordering of the planar spin components both moving to lower temperatures. Note, however, that in the present model the disordering of the xy–components also takes place for small fields, see above.

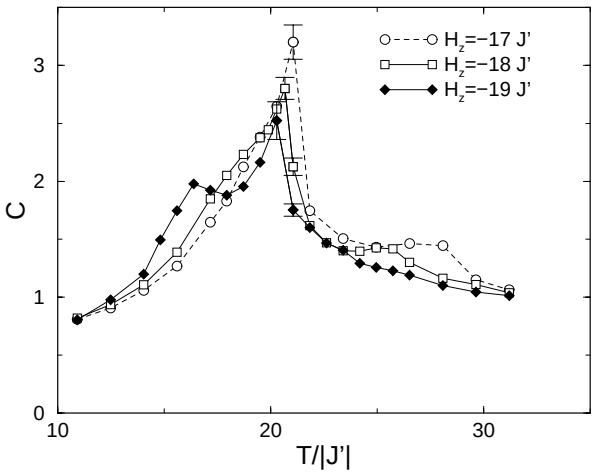

Fig. 10. Specific heat C *vs.* temperature as obtained from Monte Carlo simulations for different strengths of the axial field, with $J_{xz} = 16.2J'$, $D = -8.1J'$, and $H_x = 0$, for hexagonal systems with 20^3 spins. Error bars are only shown when they are larger than the sizes of the symbols.

The magnetization data resulting from the Hamiltonian (1) also compare favorable to the experiments. For example, without an applied planar field, the transverse spin–ordering at T_{xy} does not lead to a discontinuity of the axial magnetization (if J_{xy} is not too large, see above), in accordance with the magnetometric measurements [4], showing no jump in the axial magnetization despite a sharp peak in the specific heat. An additional planar field component yields a low-temperature spin–flop phase in the xy–components, which is compatible with the experiment [12]. The change in the y-component in the magnetization per layer may then occur through a continuous or a discontinuous phase transition, depending on the values of the parameters. Experimentally, one observes, in a tilted field, a "weakly first–order" transition [12], thus being supposedly at the border between these two scenarios.

One should bear in mind when applying the present results to $FeBr_2$ that the Hamiltonian (1) may not be complete. Indeed, the recent measurements in an nonaxial field [12] suggest the presence of in–plane anisotropy in $FeBr_2$, resulting, for example, from magnetoelastic couplings. Thus an anisotropy is not contained in the present Hamiltonian. Furthermore, one should recall that the treatment of the Heisenberg Hamiltonian is only approximative, due to the semi–classical approach adopted in Section 2, leading to a strong decoupling between planar and axial spin components.

Nevertheless, the present study shows the importance of the nondiagonal spin exchange and of the quantum nature of the $S = 1$ spins in describing the low-temperature properties of $FeBr_2$. Especially, the peculiar shape of the specific heat in an axial field may be traced back to a phase transition of the planar spin components, taking place, rather by chance, close to the anomaly of the axial spin components in the antiferromagnetic phase of $FeBr_2$.

5 Summary

Recent experimental investigations showed some intriguing transition–like phenomena in the magnetization and in the specific heat of the layered antiferromagnet $FeBr_2$. The observed transverse spin–ordering in a nonaxial field suggests the existence of a nondiagonal exchange between the planar and the axial spin components [12].

Motivated by these experiments, the properties of $S = 1$ anisotropic Heisenberg models (both on a tetragonal and on a hexagonal lattice) including nondiagonal spin exchange were investigated by Monte Carlo simulations. The quantum nature of the spins were taken into account in a semi–classical approximation, where S^z was discretized and the spin length fixed to be $|\mathbf{S}| = \sqrt{S(S+1)}$. Applied external fields with axial and planar components were considered.

These simulations showed that, besides the disordering of the axial spin components at high temperatures, a second phase transition involving the planar spin components takes place at lower temperatures. For the tetragonal models, the effects of two different nondiagonal spin exchange terms were discussed. It was shown that the nondiagonal coupling involving only products of two spins could induce, for large values of the coupling constant, a discontinuous change of the total axial magnetization at the ordering temperature of the planar spin components, whereas M_z always changed continuously when the second exchange term involving products of squares of spins was considered.

For the realistic antiferromagnetic model defined on a hexagonal lattice, which is supposed to describe the low–temperature properties of $FeBr_2$, the jump in the total magnetization in axial direction for strong nondiagonal couplings was always mirrored by a corresponding jump in the planar sublattice magnetizations. Furthermore, it was shown that the anomaly of the axial spin components in the antiferromagnetic phase [5,6,9] and the low–temperature peak resulting from the disordering of the planar spin components are not intimately related. In fact, the data suggest that the transition–like features in the specific heat (superposed peak on a shoulder or maximum) and in the magnetization (jumps in the magnetization observed in a tilted field) of $FeBr_2$ are well described if a nondiagonal coupling in the spin components and the quantum nature of the spins are taken into account. It seems, in the light of the present study, that the anomaly in the axial spin components in the antiferromagnetic phase and the disordering of the planar spin components occur in $FeBr_2$ closely one to the other rather by chance, yielding, for instance, the measured peculiar shape of the magnetic specific heat.

It is a pleasure to thank W. Selke for useful and stimulating discussions.

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