9-1-2001

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EUROPHYSICS LETTERS 1 September 2001

Europhys. Lett., **55** (5), pp. 732–738 (2001)

Off-diagonal exchange-induced transverse and field-induced spin-flop order in the diluted metamagnet $Fe_{0.85}Mg_{0.15}Br_2$

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(received 9 February 2001; accepted in final form 21 June 2001)

PACS. 75.25.+z – Spin arrangements in magnetically ordered materials (including neutron and spin-polarized electron studies, synchrotron-source X-ray scattering, etc.).

PACS. 75.30.Kz – Magnetic phase boundaries (including magnetic transitions, metamagnetism, etc.).

Abstract. – Specific heat and Faraday rotation magnetometry were used to determine the axial magnetic phase diagram of the dilute hexagonal antiferromagnet $Fe_{0.85}Mg_{0.15}Br_2$. In contrast to metamagnetic pure $FeBr_2$, the first-order line of transverse phase transitions, $H_1(T)$, is disconnected with the antiferro-to-paramagnetic phase line $H_c(T)$ and extends down to $H_t = 0$ at $T_t \approx 8.7\,K$. This is attributed to symmetric off-diagonal exchange in the presence of structural disorder. Moreover, a spin-flop phase emerges beyond $H_c(T)$ up to a bicritical point ($T_b \approx 9.3\,K$, $\mu_0 H_b \approx 1.3\,T$).

The magnetic phase diagram of the layered hexagonal antiferromagnetic (AF) insulator $FeBr_2$ (space group $D_{3d}^3 = P\bar{3}m1$, Néel temperature $T_N = 14.1\,K$) has attracted appreciable new interest after the discovery of anomalous fluctuations of the field-induced magnetization along a "non-critical phase line", $H_-(T)$ [1], which lies below the well-known [2] AF-to-paramagnetic (PM) phase line $H_c(T)$. Both of them meet in a multicritical point (MCP) at $T_m = 4.6\,K$, below which $H_c(T)$ becomes first-order [3]. Later on, a first-order phase line $H_1(T)$ was additionally discovered in the vicinity of $H_-(T)$ by means of specific-heat measurements [4]. Peculiarly, both phase lines seem to have quite different origins. On the one hand, $H_-(T)$ recently [5] turned out to be due to large fluctuations of the magnetization in that magnetic sublattice, in which the external and the exchange fields are nearly compensating (see inset to fig. 1a). On the other hand, $H_1(T)$ is due to order-disorder transitions of transverse spin components, which are completely absent, *e.g.*, in the related classic metamagnet

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$FeCl_2$ [2]. This became apparent from vector SQUID magnetometry [6] and neutron scattering experiments [7] and has been explained in terms of symmetric non-diagonal exchange interaction predicted for the trigonal point group of $FeBr_2$ [8]. As depicted by the tentative spin orientations shown in fig. 1a, a net intraplanar ferromagnetic (FM) moment appears when cooling to below $H_1(T)$ at the AFII-AFI phase transition.

Despite very ambitious theoretical and computer simulation efforts [9] the phase diagram of $FeBr_2$ as shown in fig. 1a has never fully been clarified. Very probably this deficiency is due to the neglect of properly taking into account the proposed [8] symmetric non-diagonal exchange interaction. Indeed, this appears difficult, since its contribution to the free energy vanishes in the case of a $\boldsymbol{q} = 0$ Néel-type ground state, as pointed out by Mukamel [8] and confirmed by ourselves [7]. Hence, in order to activate the off-diagonal exchange, one has to consider mechanisms of local symmetry breaking. One of these might be domain wall-induced disorder due to intraplanar secondary anisotropy [7]. Another source of disorder can reside in stacking faults, which seem to be quite frequent in $FeBr_2$-like systems [10]. They break the translation symmetry in real samples of $FeBr_2$ and may thus enable non-diagonal exchange to a certain extent. In order to enhance this tendency it appears tempting to increase the randomness, *e.g.*, by alloying with diamagnetic $MgBr_2$. This prediction is confirmed very drastically in our present study on the disordered diluted compound $Fe_{0.85}Mg_{0.15}Br_2$. In this letter we show for the first time that 15% diamagnetic dilution is sufficient for the phase line $H_1(T)$ to reach the limit $H = 0$, while the metamagnetic (spin-flip) transition is completely replaced by a spin-flop (SF) one. At a lower dilution, $Fe_{0.95}Mg_{0.05}Br_2$ [11], the spin-flip transition is already partially replaced by a SF one, but $H_1(T)$ still terminates at a critical endpoint, $H_{\mathrm{CEP}} > 0$, as in $FeBr_2$.

Unfortunately, for the composition $x = 0.05$ the difference of the AF phases below and above the H_1 line is unclear, since AFI and AFII merge into one another in zero applied field. Only at $x = 0.15$ we clearly identify two successive phase transitions referring to different order parameters. Preliminary experiments of elastic neutron scattering [12] reveal axial AF and transverse FM spin ordering, respectively, via the intensities of the Bragg peaks (1, 0, 1/2) and (2, 0, 0). While the structure factor of the axial AF (1, 0, 1/2) Bragg reflection starts to rise below $T_{\mathrm{N}} = 12.1\,\mathrm{K}$, another phase transition-like increase is observed on the (2, 0, 0) Bragg reflection at $T_1 = 10.1\,\mathrm{K}$. It probably signifies planar FM ordering. T_{N} and T_1 roughly agree with the values obtained from our present caloric and magnetometric data (see below). Less clear information is obtained from the neutron study at finite field because of experimental difficulties, mainly due to poor sample quality [12].

The experiments were carried out on Bridgman-grown samples with nominal composition $Fe_{0.85}Mg_{0.15}Br_2$ as-cleft parallel to planes perpendicular to the hexagonal c-axis with thickness $t \approx 0.2\,\mathrm{mm}$. Specific-heat measurements were performed with an automatic microcalorimeter (Oxford Instruments, *MagLab*) on a sample with mass $m \approx 8\,\mathrm{mg}$ in applied axial fields up to $\mu_0 H = 8\,\mathrm{T}$ and at temperatures $1 \leq T \leq 14\,\mathrm{K}$. Faraday rotation (FR) magnetometry was carried out in axial magnetic fields up to $\mu_0 H = 5\,\mathrm{T}$ at a light wavelength $\lambda = 670\,\mathrm{nm}$.

Figure 2 (curves 1–10) shows the temperature dependence of the magnetic specific heat, c_{m}, for various axial magnetic fields, $0 \leq \mu_0 H \leq 3\,\mathrm{T}$, after subtracting the diamagnetic lattice background measured separately in zero external field on a sample of $MgBr_2$. At $H = 0$ (curve 1) a prominent λ-shaped anomaly due to the AF-to-PM phase transition is observed at $T_{\mathrm{N}} = 10.80 \pm 0.05\,\mathrm{K}$. At $H > 0$ it shifts towards lower temperatures along the phase line $H_{\mathrm{c}}(T)$ (fig. 1b). While its shape becomes more symmetric at intermediate fields, $0.5 \leq \mu_0 H \leq 1.0\,\mathrm{T}$, rounding at $\mu_0 H > 1\,\mathrm{T}$ seems to indicate another kind of transition or even loss of long-range order.

The low-field behavior clearly hints at the now classic crossover to random-field criticality,

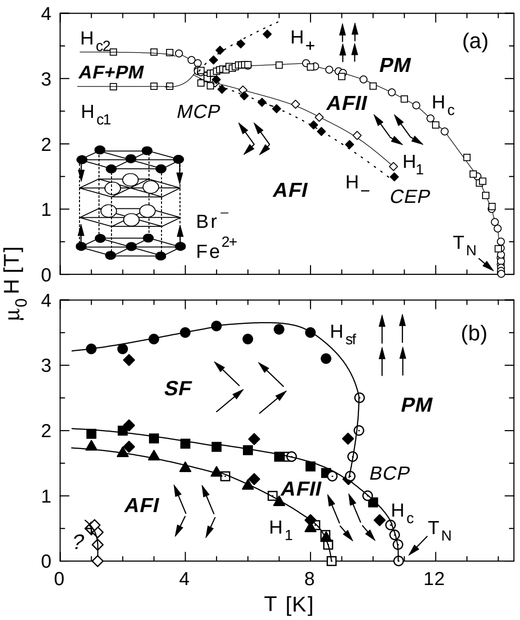

Fig. 1

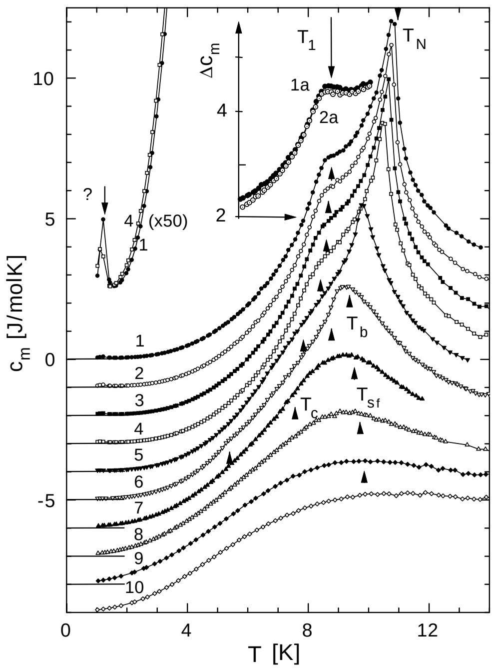

Fig. 2

Fig. 1 – H-T phase diagrams of $FeBr_2$ (a) and $Fe_{0.85}Mg_{0.15}Br_2$ (b) presented by interpolated lines and data points (see [1] and text, respectively, for details). H_c, H_{c1}, H_{c2}, H_1 and H_{sf} are phase boundaries, while H_- and H_+ denote non-critical fluctuation lines. Critical points (CEP, MCP, BCP), transition temperatures (T_N) and phases (PM, SF, AFI, AFII and an unknown one (?)) are indicated (see text). Tentative spin structures referring to adjacent Fe^{2+} layers are schematically sketched by arrows. The inset in (a) shows the unit cell with arrows indicating the conventional spin directions.

Fig. 2 – (a) Magnetic specific heat, c_m *vs.* T, of $Fe_{0.85}Mg_{0.15}Br_2$ measured at magnetic fields, $\mu_0 H = 0$ (curve 1), 0.25 (2), 0.4 (3), 0.55 (4), 1.0 (5), 1.3 (6), 1.6 (7), 2.0 (8), 2.5 (9) and 3.0 T (10), mutually shifted as indicated, after subtraction of the diamagnetic phonon background ($MgBr_2$). The transition temperatures T_c, T_1, T_{sf} and T_b are indicated by arrows (see text). The inset shows difference curves Δc_m *vs.* T for $\mu_0 H = 0$ (curve 1a) and 0.25 T (2a) after subtracting the AF anomaly at T_N. The low-T anomalies of curves 1 and 4 are shown at 50 × magnification within $1 \leq T \leq 3.4$ K.

which has been observed on numerous dilute axial antiferromagnets (DAFF) [13]. Figure 3 shows the specific-heat anomalies plotted semi-logarithmically against the respective reduced phase transition temperature, $0.005 < |T/T_c - 1| < 1$, for applied fields $0 \leq \mu_0 H \leq 1.0$ T. In the limits $\mu_0 H = 0$ (a) and 1.0 T (d) concave and convex curvatures, respectively, are encountered. They are due to power law behavior similar to that observed on pure $FeBr_2$ [3,4] in zero field (a), while rounding occurs in the high-field limit (d) owing to dynamic smearing and formation of metastable AF domain states [14]. For intermediate weak fields, $\mu_0 H = 0.25$ (b) and 0.55 T (c), straight lines indicate logarithmic anomalies. They confirm the well-known experimental issue of a critical exponent $\alpha \approx 0$ in a three-dimensional random-field Ising model system, a result which still lacks theoretical support [13].

Conspicuously, the two branches of the logarithmic singularity do not have the same am-

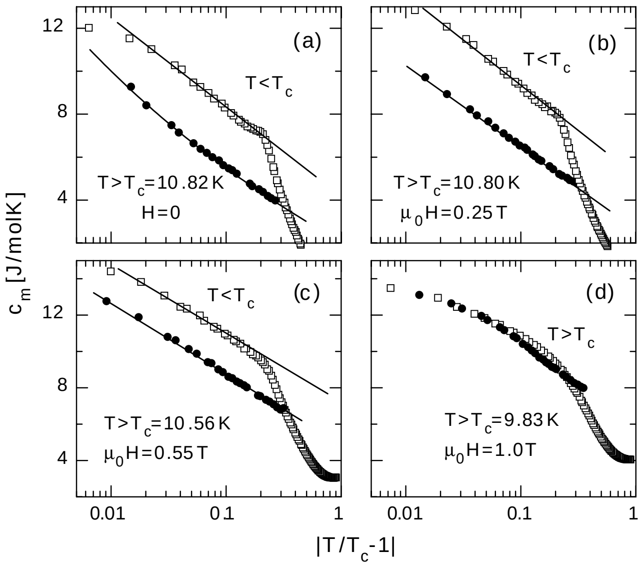

Fig. 3 – Semilogarithmic plots of the magnetic specific heat, c_{m} *vs.* $\log_{10}(|T/T_{\mathrm{c}}-1|)$, recorded at $\mu_0H = 0$ (a), 0.25 (b), 0.55 (c) and 1.0 T (d) (see fig. 2) interpolated by solid lines.

plitude as usually found with DAFF systems [13]. Obviously, the branches at $T < T_{\mathrm{c}}$ are enhanced by a low-T anomaly, which is clearly seen in the original curves of fig. 2 (arrows). The curves 1a and 2a in fig. 2 show these anomalies more clearly for $\mu_0H = 0$ and 0.25 T, respectively, after subtracting symmetric high-T anomalies. Slightly rounded peaks indicate temperatures T_1, which are attributed to the phase line $H_1(T)$ depicted in fig. 1b by open squares. Upon increasing the field the T_1 anomaly becomes gradually smeared and can be observed only up to $\mu_0H = 1.3$ T (curve 6).

Complementary data points are provided by the isothermal specific-heat measurements shown as semi-logarithmic plots in fig. 4. Here both anomaly lines, H_{c} and H_1, are indicated by peaks ($T > 5$ K) and points of inflexion ($T < 5$ K), respectively, in c_{m} *vs.* μ_0H (arrows in fig. 4; solid triangles and squares in fig. 1b). Interestingly, further inflexion points are observed at higher fields (arrows in fig. 4; solid circles in fig. 1b). Here we suspect the upper phase line of a spin-flop (SF) phase, $H_{\mathrm{sf}}(T)$, which is evidenced more clearly in magnetometric data to be discussed below (fig. 5). As a consequence, $H_{\mathrm{c}}(T)$ has to be considered as the lower phase line of the SF phase below the bicritical point (BCP) at $T_{\mathrm{b}} \approx 9.2$ K. This is indicated by two adjacent anomalies at T_{b} (peak) and T_{c} (inflexion point) in c_{m} (T, $\mu_0H = 1.3$ T) (fig. 2, curve 6). Consequently, the broad peaks encountered for $1.6 \le \mu_0H \le 2.5$ T are attributed to the balloon-shaped part of $H_{\mathrm{sf}}(T)$ (fig. 1b).

The SF phase is most clearly identified in Faraday rotation curves Θ *vs.* μ_0H, as measured, *e.g.*, at $T = 2.20$ K in fig. 5a. After a steep increase peaking at $\mu_0H_{\mathrm{c}} = 2.07$ T the signal rises linearly over a fairly wide range of fields up to $\mu_0H_{\mathrm{sf}} = 3.08$ T. Additionally, at $\mu_0H_1 = 1.76$ T a kink of the derivative curve indicates the AFI-AFII transition at H_1. All of these data points (arrows in fig. 5a; solid diamonds in fig. 1b) fit satisfactorily with the phase lines obtained so far. It should be mentioned that the slope of the magnetization curve in the SF phase does not extrapolate to $\Theta = 0$ as $\mu_0H \to 0$. This non-classic behavior is a consequence of the transverse AF spin components existing already in the low-field AF phases (see below). Since these

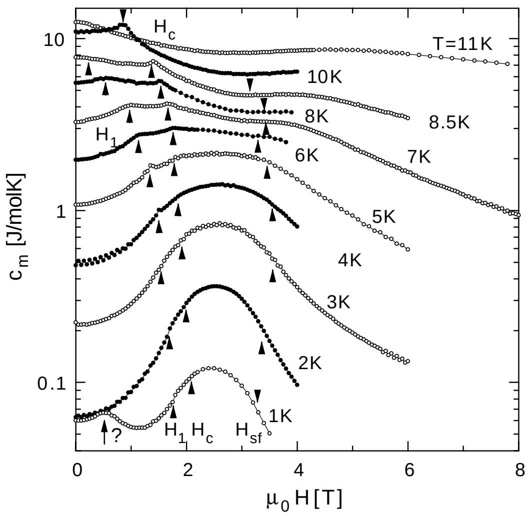

Fig. 4 – Semilogarithmic plot of the magnetic specific heat, $c_{\rm m}$ *vs.* $\mu_0 H$, measured at various temperatures $1 \leq T \leq 11.0\,\mathrm{K}$ as indicated. The phase transition fields, $H_{\rm c}$, H_1 and $H_{\rm sf}$, are indicated by arrows (see text).

components are essentially maintained at the AFII-SF transition, while the axial moments flip into the same $+z$ direction, the axial moment M_z rises more steeply than expected for a classic AF-SF transition.

Additional information is provided by isomagnetic FR curves, Θ *vs.* T, as shown in fig. 5b for $\mu_0 H = 0.63$, 1.35 and 1.83 T. As is well known [15], the derivatives, $\mathrm{d}\Theta/\mathrm{d}T$, are peaking at temperatures, which (arrows in fig. 5b; solid diamonds in fig. 1b) fit well with the phase line $H_{\rm c}(T)$. Further anomalies are observed at $T_1 = T(H_1)$ and indicated analogously. It should be mentioned that our present data qualitatively agree with those from a previous FR study on $\mathrm{Fe}_{0.85}\mathrm{Mg}_{0.15}\mathrm{Br}_2$ where, however, only one AF phase apart from the SF and PM ones was considered [15]. Further, as mentioned above, the occurrence of transverse FM spin components at $T < T_1$ has recently been verified by means of elastic neutron scattering in the limit $H = 0$ [12].

The present results are in agreement with our previous hypothesis of an order-disorder transition of the $m_{\rm s} = 0$ spin components of the Fe^{2+} ions when crossing the $H_1(T)$ phase line from above [6]. The planar spin ordering probably originates from the symmetric off-diagonal exchange [6–8], $-J(S_x^i S_z^j + S_x^j S_z^i)$, between axial and planar spin components, S_z and S_x, respectively. By virtue of ferromagnetic coupling the secondary order parameter, $\langle S_x \rangle$, appears discontinuously at the critical field $H_1(T)$. While this transition requires the field-induced order parameter $\langle S_z \rangle$ to be large enough in the pure compound, FeBr_2, the diluted system $\mathrm{Fe}_{0.85}\mathrm{Mg}_{0.15}\mathrm{Br}_2$ contains sufficiently symmetry-breaking disorder for activating the transition into phase AFI at $H = 0$ and $T < T_1$. As shown in fig. 2, the specific-heat anomalies due to these transitions have quite large precursor "tails" (curves 1a and 2a), which probably affect also the critical behavior at $T_{\rm N}$ [7].

At high enough field, $H > H_1$, the transverse FM moment becomes unstable to the benefit of the AF one [7], while the axial AF order parameter still persists in the phase AFII. Upon further increasing the field, however, the transverse AF ordering dominates at

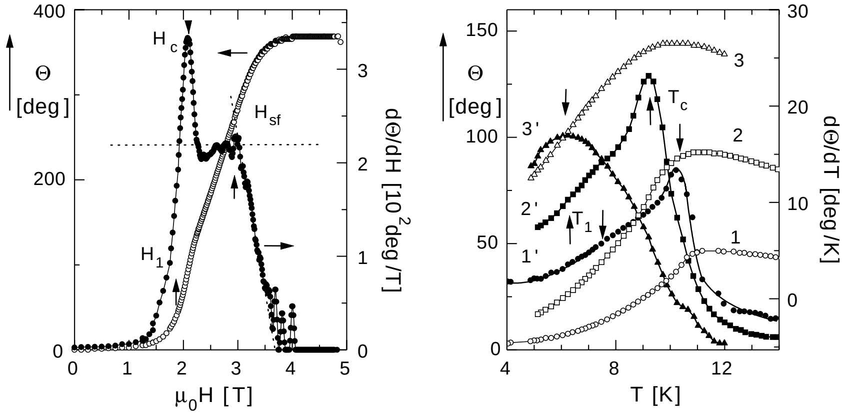

Fig. 5 – Faraday rotation, Θ (open symbols, left-hand scales), and its derivatives, $\mathrm{d}\Theta/\mathrm{d}\mu_0 H$ and $\mathrm{d}\Theta/\mathrm{d}T$, respectively (solid symbols, right-hand scales), recorded *vs.* $\mu_0 H$ at $T = 2.2\,\mathrm{K}$ (a) and *vs.* T at $\mu_0 H = 0.63$ (curves 1, 1′), 1.35 (2, 2′) and 1.83 T (3, 3′), respectively (b). H_1, H_c and H_{sf} (a) and T_1 and T_c (b) are indicated by arrows.

the expense of the axial one when entering the SF phase. Here the gradual bending-up of the spin components into the direction of the field, H_z, takes place until reaching the PM saturated phase at $H > H_{sf}$.

A future more complete theoretical treatment of the complex phase diagram of $Fe_{0.85}Mg_{0.15}Br_2$ will have to account for all of the different phases encountered at low T and increasing H. They are described by the order parameters L_a, L_t, M_a and M_t, where L, M, a and t designate AF, FM, axial and transverse, respectively. We propose all of the four order parameters to exist in the "parent" phase AFI. While in the two adjacent phases with transverse AF ordering, $L_t \neq 0$, the order parameters M_t and L_a successively vanish (AFII and SF, respectively), in the PM phase all order parameters, but the induced one, M_a, vanish.

We should finally mention another anomaly observed at very low T in $c_m(T)$ at $H \approx 0$ and in $c_m(H)$ at $T = 1\,\mathrm{K}$ (fig. 2 (enlarged curves 1 and 4) and 4, respectively; peaks designated by ?). These peaks seem to define another phase line in the H-T phase diagram (fig. 1b; open diamonds designated by ?). As seen in fig. 4, the entropy spent at this event is of the same order of magnitude as that found for the AFI-AFII-SF transition sequence at higher fields. The origin of this anomaly is presently unclear. It either characterizes another unexpected magnetic phase transition or might be due to a Schottky-type anomaly originating from unknown impurities.

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WK gratefully appreciates the hospitality while staying at RIKEN (Japan). The authors would like to thank O. PETRACIC and D. BERTRAND for discussions, and H. JUNGE for crystal growth. Thanks are due to Deutsche Forschungsgemeinschaft (KL306/25), Japanese Ministry of Education, Culture, Sports, Science and Technology and Hayashi Memorial Foundation for Female Natural Scientists.

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