Domainlike Antiferromagnetic Correlations of Paramagnetic $FeCl_2$: A Field-Induced Griffiths Phase?

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Domainlike antiferromagnetic correlations are detected by SQUID measurements of the low-frequency susceptibility in the metamagnet $FeCl_2$ when exposed to an axial magnetic field H at temperatures $T_c(H) \leq T \leq T_N$. A distinct change of curvature of χ'' vs T appearing at T_N is explained in terms of fluctuating distributions of demagnetizing fields and, hence, transition temperatures. The field-induced dynamic domain phase—an analog of the Griffiths phase predicted for a ferromagnet with dilution x within $T_c(x) \leq T \leq T_c(0)$—is confirmed by elastic light scattering experiments.

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The Griffiths phase conjecture [1] is based on the idea of "local" phase transitions (PTs) in a diluted system due to the finite probability of arbitrarily large pure and differently diluted clusters. For a ferromagnet with diamagnetic dilution x, the magnetization is expected to be a nonanalytic function of the magnetic field for any temperature T within the so-called Griffiths phase $T_c(x) \leq T \leq T_c(x=0)$. On the one hand, if x does not exceed the percolation limit x_p, static critical behavior characterizes the global PT at $T_c(x) \geq 0$. On the other hand, anomalies, if any [2], are expected within the Griffiths phase. To the best of our knowledge, however, there is no convincing experimental evidence of its very existence up to now. For example, the wide temperature regime of extreme slowing down of the dipolar relaxation in the relaxor ferroelectric $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) has tentatively been attributed to a Griffiths phase [3]. However, this interpretation is seriously cast in doubt by invoking random-field mechanisms to be responsible for the diffuse PT of PMN [4]. An experimental hint at a dynamical signature of the Griffiths phase in the dilute Heisenberg antiferromagnet $KMn_{0.3}Ni_{0.7}F_3$ was derived from inelastic neutron scattering experiments [5]. Also, recent Monte Carlo studies of diluted Ising ferromagnets [6] suggest that dilution merely changes the temporal decay of the spin autocorrelation function. However, clear experimental verification of this subtlety is still lacking.

A more favorable situation seems to be encountered in the present investigation of a new Griffiths phaselike phenomenon. It is connected with quasicritical fluctuations of a uniaxial antiferromagnet (AF), $FeCl_2$, in the presence of an applied axial magnetic field H_a. Within the temperature regime $T_c(H_a) \leq T \leq T_c(H=0) \equiv T_N$ we observe anomalous contributions to the magnetic loss function, χ'', at low frequencies, $0.1 \leq f \leq 10$ Hz. In particular, a kinklike change of $(\partial\chi''/\partial T)_H$ is observed at $T=T_N$. We suggest that fluctuating demagnetizing fields locally diminish the applied field such that internal fields H drive local PTs at $T_c(H)$, where $0 \leq |H| \leq H_a$. Hence, analogously to the Griffiths scenario of the diluted ferromagnet [1] we expect local AF PTs throughout the above temperature regime, which is conventionally denoted as paramagnetic. In contrast with the Griffiths phase, which is due to a static distribution of local concentrations x_1 with $0 \leq x_1 \leq x$, however, a dynamic distribution of local fields $0 \leq |H| \leq H_a$ is involved. This is accounted for in our interpretation, which considers fluctuating domainlike AF correlations giving rise to the observed contributions to χ'' at low frequencies.

The occurrence of domainlike fluctuations above an ordering temperature T_c is well known from uniaxial ferromagnets (FMs), where demagnetizing fields couple to fluctuations of the FM order parameter (OP) [7-9]. The situation is more complicated in the case of AFs in an external magnetic field. The internal field, which is a superposition of the external and the demagnetizing field, couples indirectly to the AF OP, $\boldsymbol{\eta}$, via the FM secondary OP, $\mathbf{m}$. Hence, it is not easy to determine the influence of the demagnetizing field on the AF order parameter. Moreover, the internal field is strongly inhomogeneous. This is obvious in the case of $FeCl_2$, where AF and quasi-FM ("saturated paramagnetic") phases coexist at the metamagnetic PT (Fig. 1) [10]. Conventionally, this takes place at an internal field $H_c = H_a - NM$ being constant within $H_{c1} \leq H_a \leq H_{c2}$, where M gradually increases from the low AF to the high PM value and N is the demagnetization factor, $0 < N \leq 1$. Nonuniform N values have to be accounted for if the sample is not a homogeneous ellipsoid [11]. As a rule the demagnetizing field is smaller near the edge of the sample than at the center. However, owing to the inhomogeneous domain configuration of the mixed phase [10] additional inhomogeneity of the internal field is encountered. In analogy with the behavior of Ising FMs [7-9], we assume that this inhomogeneity becomes dynamic above the PT, $H_a > H_{c2}$. Hence, fluctuations of the FM OP characterize the adjacent PM regime via fluctuating demagnetizing fields which induce domainlike correlations of the AF OP. They are the basic ingredients of the newly detected "field-induced Griffiths phase," which extends up to T_N.

We used a commercial SQUID magnetometer (Quantum Design MPMS 5S) to measure the temperature

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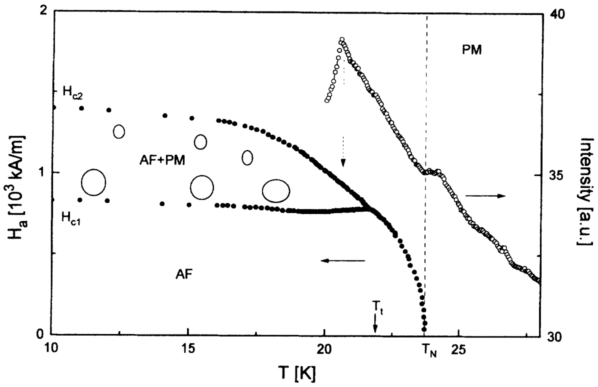

FIG. 1. H_a vs T phase diagram of $FeCl_2$ (solid circles) [19] with elliptical AF domain symbols (see text) in the AF+PM (transition fields H_{c1} and H_{c2}) and in the PM phase. Tricritical and Néel temperatures, T_t and T_N, are indicated by the arrow and vertical dashed line, respectively. Transmitted intensity of circularly polarized light at $H_a=955$ kA/m is presented by open circles.

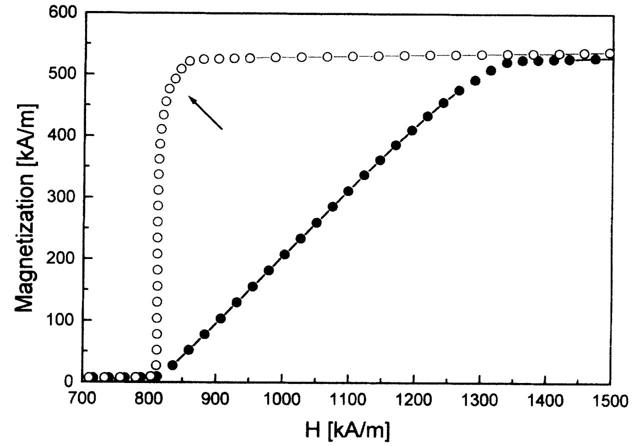

FIG. 2. Magnetization of $FeCl_2$ vs applied and internal fields H_a and H_i (solid and open circles, respectively) at $T=10$ K. Rounding close to the paramagnetic saturation is indicated by an arrow.

dependence of the in-phase and out-of-phase parallel magnetic susceptibility in the low-frequency range $0.1 < f < 10$ Hz at constant fields between $398 < H_a < 1592$ kA/m. A Bridgman-grown $FeCl_2$ crystal was prepared in a dry helium atmosphere to obtain a thin (0001) sheet of $3.4\times2.3\times0.28$ mm^3. In order to determine the Néel temperature T_N, we measured the temperature and field dependence of the magnetization at $H_a=0.8$ kA/m and $T=10$ K, respectively. The optical transmittivity of circularly polarized light at the wavelength $\lambda=670$ nm was measured as a function of $H_a \leq 10^3$ kA/m using a technique described previously [12].

Figure 2 shows the magnetization M versus applied field H_a (solid circles) and the corresponding curve corrected for demagnetization (open circles) for $FeCl_2$ at $T=10$ K. The mixed phase region contains a field interval of constant slope. Its reciprocal value, $N=0.92$, is used as the effective demagnetizing factor. The corrected curve M vs H_i shows the expected steplike first-order transition at $H_i=812$ kA/m. However, before M reaches the saturation value there is obvious rounding of the curve (arrow). This was observed previously on $FeCl_2$ [13], and is certainly not due to the nonellipsoidal shape of our sample [14]. We rather believe the diminishing of the magnetization at H_{c2} to be due to fluctuations of $\mathbf{m}$. They create a fluctuating demagnetizing field which locally allows for AF order and hence reduces the total magnetization. Its Fourier transform as determined from Maxwell's equations in the magnetostatic approximation [8] reads $\mathbf{h}(\mathbf{q})=-[\mathbf{q}\mathbf{m}(\mathbf{q})]\mathbf{q}/q^2$ with the wave vector $\mathbf{q}$ and $\mathbf{m}(\mathbf{q})$ the Fourier transform of the magnetization $\mathbf{M}(\mathbf{r})$. With increasing external field the magnetization fluctuations decrease and the local AF correlations vanish. In real space this means that the magnetization becomes more homogeneous with increasing field. Hence $-\mathrm{div}\mathbf{M}$, the source of the demagnetizing field, decreases. The static ($H_{c1} < H < H_{c2}$) and dynamic ($H \gtrsim H_{c2}$) AF correlations are symbolized in Fig. 1 by ellipsoids with solid and dotted margins, respectively.

Figure 3(a) shows the out-of-phase component χ'' of the ac susceptibility versus temperature at constant frequency $f=5$ Hz and field values $H_a=955$ (curve 1), 1432 (2), and 1592 kA/m (3). There is an obvious change in curvature of the χ'' vs T curves. The inset (curve 1') in Fig. 3(a) exemplarily shows the kinklike behavior of $d\chi''/dT$ vs T derived from curve 1. The straight lines are best linear fits to the data below and above $T=24$ K, respectively. They intersect at $T=23.9$ K, which lies very close to $T_N=23.7$ K as determined by the maximum of the temperature derivative of the low field magnetization [Fig. 3(a), curve 4]. Following curve 3 we see that the special role of the zero-field ordering temperature T_N is obvious even in the case that the system remains paramagnetic at all T (cf. Fig. 1).

Both positive and negative slopes, $d\chi''/dT$, are observed within the "Griffiths range" $T_c(H_a) \leq T \leq T_N$ when changing H_a or f [Fig. 3(b)]. Common features of all curves χ'' vs T are, apart from the change of curvature at T_N, monotonically decreasing tails at $T > T_N$ and increase by 1 order of magnitude at $T < T_c(H_a)$ [Fig. 3(b)]. For subtricritical field, $H_a < 800$ kA/m, the Griffiths range is small (Fig. 1), and the plateaulike behavior of χ'' vs T is hard to resolve.

Surprisingly large dispersion characterizes the anomaly. As an example, Fig. 3(b) shows χ'' vs T data obtained with $H_a=1432$ kA/m at $f=1$ (curve 1), 0.1 (2), and 10 Hz (3). Only for the intermediate frequency, $f_0=1$ Hz, the change of curvature at T_N drives $d\chi''/dT$ positive below T_N. It remains negative and changes but little at T_N at adjacent "low" and "high" frequencies. In parallel the amplitude of the tail at $T > T_N$ maximizes at $f=f_0$

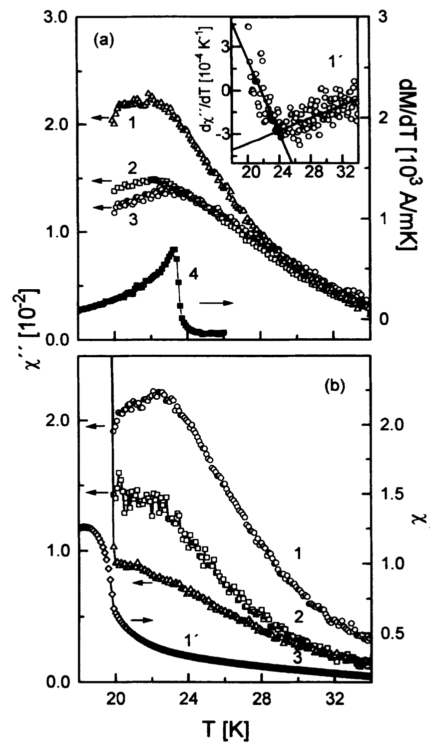

FIG. 3. Temperature dependence for $FeCl_2$ of (a) χ'' at $f=5$ Hz and $H_a=1592$ kA/m (curve 3, circles), 1432 kA/m (curve 2, squares), and 955 kA/m (curve 1, triangles), dM/dT at $H_a=0.8$ kA/m (curve 4, filled squares), and $d\chi''/dT$ (inset: curve 1′, referring to curve 1), and (b) χ'' at $H_a=955$ kA/m and $f=10$ Hz (curve 3, triangles), 1 Hz (curve 1, circles), and 0.1 Hz (curve 2, squares) and χ' at $H_a=955$ kA/m and $f=1$ Hz (curve 1′).

and sensitively decreases for $f \lesssim f_0$. For $f > 10$ Hz it becomes too weak to resolve a detectable anomaly at T_N. Finally, it should be noticed that the in-phase susceptibility, χ' vs T, does not show any anomaly at T_N [Fig. 3(b), curve 1′].

Since χ'' vs f is a measure of the distribution function of spin relaxation times, $\tau=(2\pi f)^{-1}$, our data seem to reveal a peak at $\tau_0=(2\pi f_0)^{-1}\approx 0.2$ s. Since τ_0 is large compared with single spin-flip times, $\tau \approx 10^{-10}$ s, it has to be attributed to preferentially formed large spin clusters. Their number, on the other hand, is rapidly decreasing as χ'' when cooling to below T_N. This is in accordance with the idea that an increasing number of "local" PTs takes place and more and more of the large clusters become quasistatic as T is lowered.

Presently there is no theory to predict the peculiar dependence of χ'' vs T on f. In this Letter we confine ourselves to explaining qualitatively the anomaly of $d\chi''/dT$ at T_N by considering the thermal decay of domainlike antiferromagnetic correlations in the paramagnetic phase. From the fluctuation-dissipation theorem it is known that χ'' is related to the power spectrum of the magnetization fluctuations [15]. These induce fluctuations of the AF OP by coupling of $\mathbf{m}$ to $\boldsymbol{\eta}$ at site $\mathbf{r}$ via the relation [16] $2\mathbf{m}(\mathbf{r})=(\mathbf{c}\cdot\nabla)\boldsymbol{\eta}(\mathbf{r})$, where $\mathbf{c}$ is the basis vector along [0001]. Hence, χ'' is also related to the autocorrelation function of the AF OP $S=\langle|\boldsymbol{\eta}(\mathbf{q})^2|\rangle$. One expects the proportionality $S\propto\chi''$, although χ is the ferromagnetic response. This explains, e.g., the steep increase of χ'' at the PM-AF PT [Fig. 3(b)]. $\boldsymbol{\eta}(\mathbf{q})=[\int\Delta\boldsymbol{\eta}\exp(-i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}]/V$ is the Fourier transform of the deviation $\Delta\boldsymbol{\eta}$ of the OP from its equilibrium value $\boldsymbol{\eta}_c$ integrated over the sample volume V. $\langle\cdots\rangle$ is the average obtained from Gaussian probability distribution. In the fluctuation regime of a PT one expects [15,17]

$$S=k_BT/V(\phi_{\eta\eta}+Dq^2)\,, \tag{1}$$

where $\phi_{\eta\eta}$ is the second derivative of the Landau expansion of the Gibbs free energy density at the point $\boldsymbol{\eta}=\boldsymbol{\eta}_c$. $D/2$ is the expansion coefficient of the gradient term. Note that $\phi_{\eta\eta}$ depends on the order of the phase transition and differs above and below the PT, respectively.

In the following we shall evidence a discontinuity of d^2S/dT^2 at T_N, which is equivalent to a kinklike behavior of χ'' vs T. Starting from the experimental observation of the rounded M vs H_i curve at fixed T (Fig. 2), we conjecture a fluctuating local distribution of different values of H_i at any fixed value of $H_a\geq H_{c2}$. This yields a continuous series of local PTs, which renders the entire sample paramagnetic only well above H_{c2}. A similar situation applies to a horizontal passage through the H_a-T phase diagram (Fig. 1). Here we expect a fluctuating local distribution of different values of H_i at any fixed value of $T\geq T_c(H_a)$. Owing to the unambiguous relationship $T_c=T_c(H_a)$ at the static phase boundary (Fig. 1), simultaneously a distribution of different PT temperatures within $T_c(H_a)\leq T_c\leq T_N$ is encountered. Within the concept of local transition temperatures [18] let $P(T,T_c)dT_c$ be the probability to find a critical temperature within the interval $[T_c,T_c+dT_c]$ at a given temperature T. Then we can introduce the ensemble average of the autocorrelation functions $S(T,T_c)$,

$$\langle S\rangle=\int_{T_c(H)}^{T_N}P(T,T_c')S(T,T_c')dT_c'\,,$$

where $P(T,T_c)>0$ is assumed if $T\leq T_N$. The second derivative of $\langle S\rangle$ at a fixed temperature T^* with $T_c(H_a)<T^*<T_N$,

$$\begin{aligned}\partial^2\langle S\rangle/\partial T^2|_{T^*}&=\int_{T_c(H)}^{T_N}[S\partial^2P/\partial T^2+2(\partial S/\partial T)(\partial P/\partial T)+P(\partial^2S/\partial T^2)]_{T^*}dT_c'\\&=g(T^*)+\int_{T_c(H)}^{T_N}[P(\partial^2S/\partial T^2)]_{T^*}dT_c'\,,\end{aligned} \tag{2}$$

contains two terms, which behave differently at $T^*=T_N$. Whereas $g(T)$ is very probably a continuous function, the second function is discontinuous at T_N. This is seen by using Eq. (1), which yields

$$\partial^2 S/\partial T^2|_{T^*} = f(T_c', T^*) + b(T_c', T^*)(\partial^2 \phi_{\eta\eta}/\partial T^2)_{T^*}, \quad (3)$$

where $f(T)$ is a function which contains no higher derivatives than $\partial\phi_{\eta\eta}/\partial T$, while $b(T)$ only depends on $\Phi_{\eta\eta}$. From Landau theory of second-order phase transitions we obtain $\phi_{\eta\eta} = mA_0(T/T_c' - 1)$ with $m = -2$ and $+1$ for $T < T_c'$ and $T > T_c'$, respectively, and, hence, $\partial^2\phi_{\eta\eta}/\partial T^2|_{T=T^*} \cong 3A_0/T_c'\delta(T^* - T_c')$ with Dirac's δ function and $A_0 = \text{const}$. Inserting this result into Eq. (3) and integrating,

$$\int_{T_c(H)}^{T_N} [P(\partial^2 S/\partial T^2)]_{T^*} dT_c' = h(T^*) + 3A_0 \int_{T_c(H)}^{T_N} P(T^*, T_c') b(T_c', T^*)/T_c'\delta(T^* - T_c') dT_c', \quad (4)$$

one immediately finds that $h(T)$ is continuous at T_N, whereas the second term behaves discontinuously. It vanishes at $T^* > T_N$, but becomes finite, $3A_0 P(T^*, T^*) \times b(T^*, T^*)/T^*$, if $T^* < T_N$. Hence, by inserting into Eq. (2) we see that $\partial^2\langle S\rangle/\partial T^2$ changes steplike at T_N by the amount $3A_0 P(T_N, T_N) b(T_N, T_N)/T_N$. This is the reason for the observed change of curvature in χ'' vs T at T_N.

Figure 1 illustrates this by a dashed vertical line. It separates the region of domainlike fluctuations from the usual PM phase with ordinary short-range AF correlations. Clearly this line is not a new phase boundary, but indicates that the PM phase of a real metamagnet needs a differentiated description.

This is corroborated by light scattering experiments. Figure 1 shows the transmitted intensity, I vs T, of circularly polarized light at $H_a = 955$ kA/m. The gradual increase of I when cooling from 28 to 20 K is an artifact due to slight displacements of the diaphragm attached to the sample with respect to the impinging laser beam. However, there is a distinct drop of I at T_N, which is due to the first formation of domainlike fluctuations. The scattering efficiency seems to be constant throughout the field-induced Griffiths phase since I vs T is parallel above and below T_N. A second, larger, drop of I is observed at $T \leq T_c(H_a)$. This is due to light diffraction caused by static domains of the mixed phase [12]. In contrast, the anomaly at T_N is caused by regions whose correlation lengths are probably smaller than the wavelength of the transmitted light.

In conclusion, our experiments seem to show that the paramagnetic phase of the prototypical metamagnet $FeCl_2$ has the signature of a field-induced Griffiths phase within $T_c(H) < T < T_N$ in analogy to the temperature region $T_c(x) < T < T_c$ predicted for diamagnetically diluted FMs. It is characterized by fluctuating regions of antiferromagnetic correlations. They are responsible for the observed features in the T dependences of the ac susceptibility and the transmittivity of circularly polarized light. Future work has to focus on a detailed understanding of the temperature dependence of the susceptibility and its complicated variation with H_a and f. Furthermore, it would be highly interesting to get direct information about antiferromagnetic correlations above $T_c(H)$ by using neutron scattering.

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