Monte Carlo study of magnetic phase transitions in a model for $FeCl_2$

Laura Hernández
Laboratoire de Physique des Solides, Institut National des Sciences Appliquées, Département de Génie Physique, Complexe Scientifique de Rangueil, 31077 Toulouse CEDEX, France

H. T. Diep
Groupe de Physique Statistique, Université de Cergy-Pontoise 47-49 Avenue des Génottes, BP 8482, 95806 Cergy-Pontoise CEDEX, France

D. Bertrand
Laboratoire de Physique des Solides, Institut National des Sciences Appliquées, Département de Génie Physique, Complexe Scientifique de Rangueil, 31077 Toulouse CEDEX, France

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A Monte Carlo simulation of the critical behavior of a *quite realistic* model of $FeCl_2$ in a magnetic field has been performed. Our results show, in agreement with previous experimental ones, that in the temperature-field phase space, two regions of highly different critical behavior may be recognized. For values of temperature T higher than a certain tricritical temperature T_t, the transition is continuous. Conversely, for values of T lower than T_t the transition shows all the characteristics of a first-order one. The relative width of the first-order region was found to be $T_t/T_N \approx 0.87$, in excellent agreement with experimental results. We have studied the role played by competing interaction constants in the critical behavior of the system, and we have found that the presence of an antiferromagnetic and frustrated second-neighbor interaction, though small, is essential to reproduce the quantitative behavior of $FeCl_2$.

I. INTRODUCTION

Experimental results on $FeCl_2$ and $FeBr_2$, which may be roughly described as systems consisting of ferromagnetic planes coupled antiferromagnetically, show that they undergo a metamagnetic phase transition in an applied magnetic field, for temperature T lower than a tricritical temperature T_t above which it becomes continuous.[1–4]

Some theoretical Hamiltonian models showing a similar kind of behavior have been proposed. Harbus and Stanley[5] have performed a high-temperature series expansion on a simple cubic lattice Ising model with in-plane ferromagnetic coupling and antiferromagnetic coupling of the planes (the "meta" model) and on the "NNN model"[6] consisting of a simple cubic Ising lattice with isotropic antiferromagnetic nearest-neighbor (NN) and ferromagnetic second-neighbors (NNN) interactions.

Landau[7] has performed a Monte Carlo simulation of antiferromagnetic Ising simple cubic and simple square lattices with NN antiferromagnetic and NNN ferromagnetic coupling, also finding a tricritical behavior.

However all these models, though interesting from the theoretical point of view, cannot be taken as models of the measured "prototype" metamagnets: $FeCl_2$ or $FeBr_2$ as they considered only the simplest lattice structures, (square and simple cubic) and did not take into account important features appearing in these systems such as high anisotropy, triangular lattice planes, superexchange paths along the c axis, and in-plane frustrated second-neighbor interaction in competition with a nearest-neighbor one.

In this work we are interested in a three-dimensional (3D) Ising model of $FeCl_2$ that takes into account those outstanding features. Thus we have studied a layered system consisting of triangular lattice planes coupled antiferromagnetically, with competing in-plane interactions: ferromagnetic between NN and antiferromagnetic between NNN, the latter being frustrated in such a lattice [Fig. 1(a)]. We have also taken into account the superex-

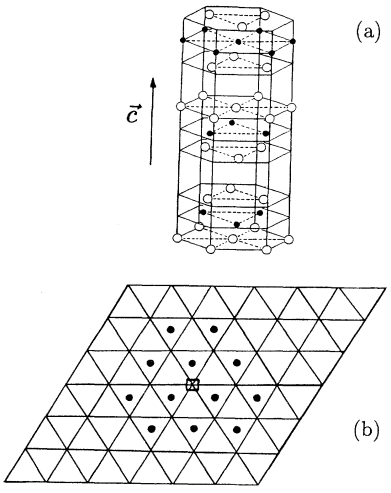

FIG. 1. (a) Crystalline structure of $FeCl_2$ (Ref. 12). ● Fe^{2+}; ○ Cl^-. (b) Top view of the 12 neighbors of an Fe^{2+} ion. □ the considered ion; ● neighbors in the adjacent plane below.

change path for the coupling between iron planes, which, following Anderson's rule,[8] leads to 12 NN in each one of the neighboring planes [Fig. 1(b)].

The article is organized as follows: In Sec. II we describe the system, the quantities studied, and some technical details on the Monte Carlo method used. In Sec. III we analyze our results and compare them with previous ones. Finally in Sec. IV we present our conclusions along with some suggestions for forthcoming work.

II. MODEL AND CALCULATION TECHNIQUES

A. The $FeCl_2$ model

We have studied a highly anisotropical 3D Ising system consisting of a stacking, along the c axis, of triangular lattice planes shifted one with respect to the other so as to reproduce the magnetic sites of Fig. 1(a).

This system may be described by the following Hamiltonian:

$$\beta\mathcal{H}=-\frac{J_1}{k_BT}\sum_{\langle \mathrm{NN}\rangle}s_is_j-\frac{J_2}{k_BT}\sum_{\langle \mathrm{NNN}\rangle}s_is_l -\frac{J'}{k_BT}\sum_{\langle \mathrm{NN}'\rangle}s_is_k-\frac{g\mu_BH}{k_BT}\sum_i s_i\ , \tag{1}$$

where $s_i=\pm1$ is an Ising spin, $\langle \mathrm{NN}\rangle$ and $\langle \mathrm{NNN}\rangle$ mean sums over NN and NNN in the plane perpendicular to the c axis, respectively, and $\langle \mathrm{NN}'\rangle$ means sum over interacting spins belonging the adjacent planes.

Several sets of interaction constants (J_1,J') or (J_1,J_2,J') have been proposed by fitting experimental data with different Hamiltonian models,[4,9,10] but all of them agree with the fact that the coupling between nearest neighbors in the plane is ferromagnetic, $(J_1>0)$, with a magnitude much larger than the antiferromagnetic coupling between the planes, $(J'<0)$, $|J_1|\gg|J'|$. Those authors proposing an antiferromagnetic coupling of second neighbors in the plane, $J_2<0$,[4,10] have found that $|J_1|/|J_2|\approx7$. This interaction $(J_2<0)$ is frustrated in a triangular lattice (it is not possible to satisfy all the bonds simultaneously[11]), and though small compared to the first-neighbors interaction, it plays an important role in the critical behavior of the system.

As J' is a superexchange interaction, mediated by the two nonmagnetic chlorine planes, we took into account all the equivalent superexchange paths,[8,12] which gives 12 "nearest neighbors" in each of the neighboring iron planes, instead of three NN as in previous works [see Fig. 1(b)].

In the following we use the notation

$$h(T)=\frac{g\mu_BH(T)}{k_B}\ ,$$

where $H(T)$ indicates the critical line in the (T,h) space. At 0 K the threshold magnetic field to change from the antiferromagnetic order of up and down planes to a saturated paramagnetic one is $h_c(0)=24|J'|/k_B$.

B. Calculation techniques

The system we mainly studied consists of 12 triangular planes of 18×18 sites, each with full periodic boundary conditions, but we have also tested for finite-size effects performing: (i) some runs changing the size of the system along the c axis, while leaving the size along the other directions constant ($18\times18\times6$ and $18\times18\times24$ lattices) and (ii) study of the T_t shift when the size of the system is globally changed in all directions ($6\times6\times6$, $12\times12\times12$, and $24\times24\times24$).

Averages were calculated using typically 5000 MCS/spin after having discarded other 5000 MCS/spin to equilibrate the system. Near the critical region runs up to 10 000 MCS/spin for averaging and 10 000 MCS/spin to equilibrate the system were performed to reduce the effect of critical slowing down. Data were generally taken isothermally with the field both increasing and decreasing, in order to test for irreversibility. Special attention was paid in the first-order region to simulate an actual sweeping in h, starting the simulation in the zones of stable order (ferromagnetic initial condition for high fields and antiferromagnetic one for very low fields) and taking always the output at h as the input for $h+\Delta h$.

In each run, we have calculated the following physical quantities: magnetization (m), staggered magnetization along the c axis (m_{st}), energy per spin (E), specific heat (c) by energy fluctuations, susceptibility (χ) by magnetization fluctuations, staggered susceptibility (χ_{st}) by staggered magnetization fluctuations, and Edwards-Anderson order parameter (q_{EA}).

III. ANALYSIS OF THE RESULTS

Unless stated otherwise the results discussed here correspond to a system having $J_1/k_B=10$ K, $J_2/k_B=-1.5$ K, and $J'/k_B=-0.5$ K. These values have been found experimentally when taking into account only three NN in each of the neighboring iron planes. Discussion on these values when taking into account 12 NN will be given later.

The analysis of our results shows clearly the existence of two regions of highly different critical behavior, in the (T,h) space, in agreement with previous experimental results.[1,3,4]

In Fig. 2, $m_{\mathrm{st}}(T)$ curves for different values of h in rising field are shown. For low values of h, (see curves a, b, c, d) the transition is smooth, and no hysteresis effect is observed. On the other hand, it is clearly seen that the fall of $m_{\mathrm{st}}(T)$ curves becomes steeper as h increases, turning into actual gaps with presence of metastable states for low critical temperatures (curves e, f, g, h of Fig. 2). This fact along with the large hysteresis effect observed in this region (not shown here) indicates that a crossover to a zone of first-order transitions has taken place.

The results obtained for the other physical quantities confirm this behavior; as an example, we show in Fig. 3, the specific heat curves as a function of T, for different fields. In Fig. 3(a) the broad peaks expected for the continuous region are observed. On the other hand, in Fig.

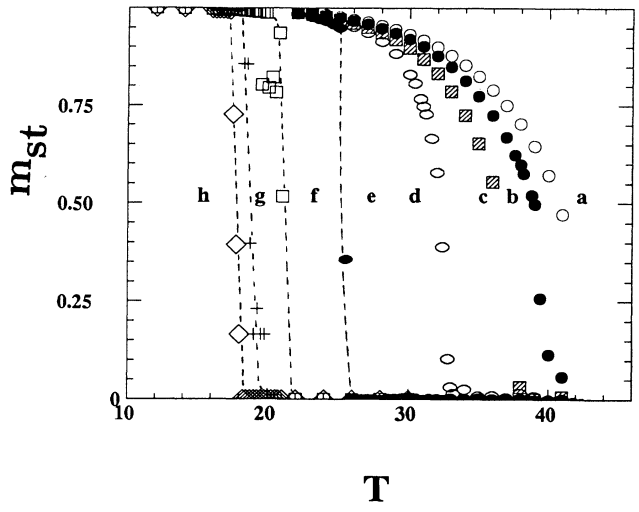

FIG. 2. m_{st} vs T (units of K) curves for different values of h in both, continuous and first order regions (data taken from rising field runs): (a) $h=8$ K; (b) $h=9$ K; (c) $h=10$ K; (d) $h=11$ K; (e) $h=12$ K; (f) $h=13.5$ K; (g) $h=14$ K; (h) $h=14.5$ K. Detailed T sweep is shown for $h=11$ K and $h=9$ K to show that no gap is actually present (see text for detailed comments). Unless stated otherwise, all lines are merely a guideline to the eye.

3(b) we observe *delta-like-function* curves whose peaks are very difficult to seize, in addition to wider peaks showing the thermal in-plane disorder at higher values of T.

The same differences in the behavior of χ and χ_{st} according to the considered region of the (T,h) plane are observed. Harbus and Stanley[5] have proposed that the tricritical point (TCP) could be determined using the fact that, in the continuous region, only χ_{st} shows a divergence, while χ has a finite peak and in the first-order region, both of them become divergent. As the aim of this work was not to locate the TCP with precision, we did not use a sweeping step ΔT small enough to see this effect; anyway we could observe that the χ_{st} peak in the continuous region is one order of magnitude higher than the χ one, while, in the first-order region, they both behave exactly in the same way.

Observing some snapshots of the crystal for different values of h and T, in the first-order region, one can see that the transition takes place by a sudden inversion of "down" planes. In decreasing field runs (ferromagnetic initial conditions), stacking fault occurs when the sweeping step in h is not small enough; thus, the value of the remanent magnetization is a finite-size effect.

In Fig. 4(a) the phase diagram is shown; in the low-T region, we observe that the critical line is split into two branches, obtained in rising and decreasing field, which corresponds to the hysteresis phenomenon.

Concerning the determination of the critical line $h_c(T)$ in the first-order region, different criteria can be found in the bibliography. The usual one, which consists of taking the half width of hysteresis is not always correct, as has been suggested by Creutz, Jacobs, and Rebbi.[13] It has been found that, for some systems,[14] the critical point is not placed in the middle of hysteresis gap. Hence, we prefer to show here the two branches corresponding to rising and decreasing field.

The TCP may be roughly obtained extrapolating these two branches to their point of junction. We have found $T_t/T_N \approx 0.6$ (T_N being the Néel temperature), which is rather small compared with the value obtained experimentally for $FeCl_2$, $T_t^{exp}/T_N^{exp}=0.886$.[4] This discrepancy can be solved by fitting experimental data taking into account 12 neighbors in each of the adjacent planes, instead of just taking the values obtained for only three. The resultant values of the interaction constants are then $J_1/k_B=10$ K, $J_2/k_B=-1.5$ K, and $J'/k_B=-0.107$ K. The simulations performed using these values give, qualitatively, the same behavior described above [see Fig. 4(b)]

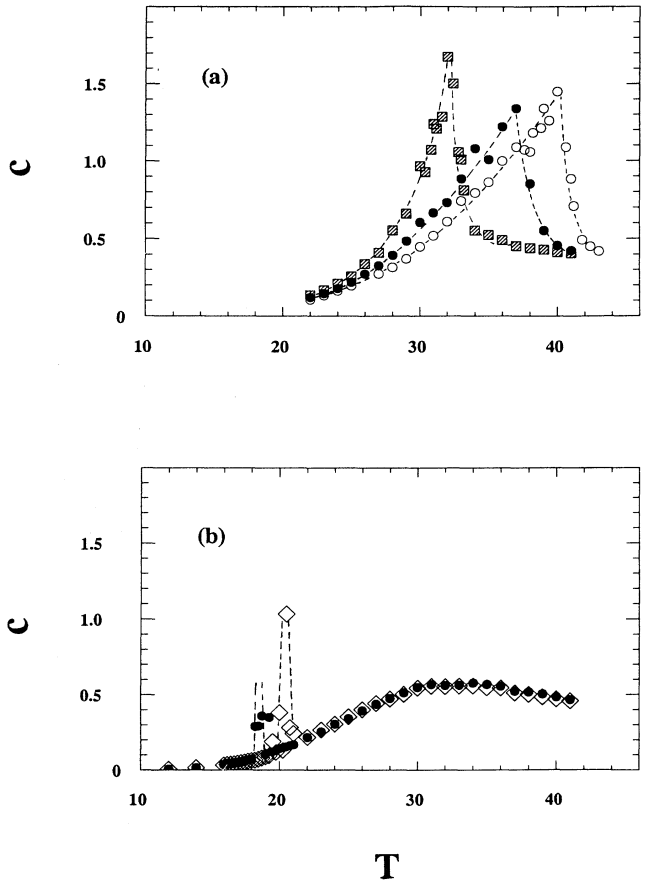

FIG. 3. (a) c (units of J/K spin) vs T (units of K), for different values of h; broad peaks, characteristic of continuous transitions can be observed. ○ $h=9$ K; ● $h=10$ K; □ $h=11$ K. (b) c vs T curves in the region of first-order transitions. ◇ $h=13.5$ K; ● $h=14$ K. At low temperatures the existence of a very sharp peak, corresponding to the first-order transition is indicated. Wider and lower peaks at higher temperatures correspond to thermal in-plane disorder. Data were taken from rising field runs.

and after a study of the shift of T_t with the lattice size we have found, for the $24\times24\times24$ lattice, $T_t/T_N\approx0.87$, which is in excellent agreement with the experimental value.[4] However, for this system, the Néel temperature was found to be $T_N=34$ K, larger than the experimental one, $T_N^{\rm exp}=23.5$ K. Nevertheless, this value is in agreement with the one found by Vettier,[4] based in a random-phase-approximation method: $T_N^V=33.7$ K and is quite better than the one given by mean-field theory, $T_N^{\rm MF}=39$ K. The discrepancy with experimental results found in the value of T_N may be understood recalling that the values of the interaction constants considered here were obtained by fitting neutron dispersion data to a Hamiltonian, which is different from (1). Then when replacing them into (1), only their respective ratios are accurate and not their actual values.

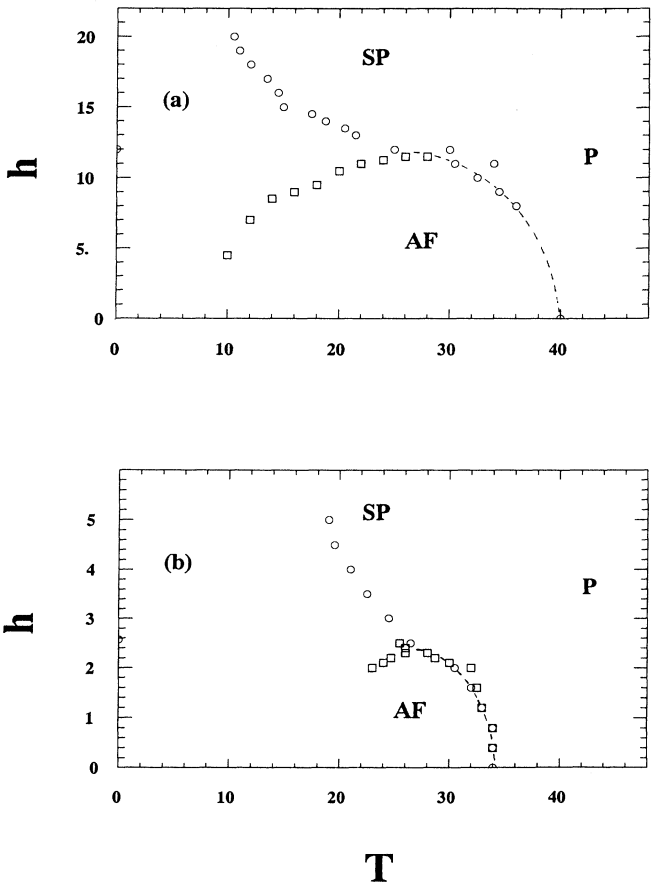

FIG. 4. (a) Phase diagram for a $18\times18\times12$ lattice with $J_1/k_B=10$ K, $J_2/k_B=-1.5$ K, and $J'/k_B=-0.5$ K. (b) Phase diagram for a $18\times18\times12$ lattice with $J_1/k_B=10$ K, $J_2/k_B=-1.5$ K, and $J'/k_B=-0.107$ K. At low T, the two branches correspond to, ○ rising field data, □ decreasing field data. The dashed line shows the region of continuous phase transitions. $h_c(0)$ is the exact value of the threshold field at $T=0$ K for the ferro-antiferromagnetic transition. *AF* antiferromagnetic phase, *SP* saturated paramagnetic (ferromagnetic) phase, *P* paramagnetic phase. T and h are both in units of K.

Our finite-size effect studies show that, as expected for this highly anisotropic system, size changes along the **c** axis are much more relevant than those along the other directions (i.e., results for $12\times12\times12$ are quite similar to those found for $18\times18\times12$).

We have also studied the influence of the antiferromagnetic and frustrated second-neighbors interaction in the plane. Taking $J_1/k_B=10$ K, $J_2/k_B=0$ K, and $J'/k_B=0.5$ K, we have observed that the system becomes very rigid: Quite high (low) values of h in rising (decreasing) field runs are needed to induce the antiferromagnetic-saturated paramagnetic transition and Néel temperature was found to be $T_N=54$ K. So it is clear that this interaction, though small compared to the first-neighbor interaction, introduces some degree of "intrinsic instability" to the system, which is essential to reproduce the actual critical behavior of $FeCl_2$.

IV. CONCLUSIONS

We have performed a Monte Carlo study of phase transition in a quite realistic model of $FeCl_2$, taking into consideration some of its outstanding features that had not been considered in previous theoretical studies: a stacking of triangular lattice planes, coupled antiferromagnetically, with competing interactions in the plane (one of them being frustrated in this lattice) and superexchange path for the antiferromagnetic coupling between neighboring planes.

We have determined qualitatively the phase diagram and we have found a crossover between a region of second-order phase transitions taking place at low h and high T and another one where the transitions are of first order at high h and low T; evidences confirming this behavior have been observed in all the studied physical quantities. The relative width of the first-order region is found to be $T_t/T_N\approx0.87$, in quantitative agreement with previous experimental results.[4]

In the first-order region, we have clearly found hysteresis, which is in contradiction with Jacobs and Lawrence,[1] who have only found hysteresis in pulsed field experiments, and in slight agreement with Carrara[9] who found a small amount of it in steady field experiments. This discrepancy can be explained by the fact that we considered an Ising model, which is known to show larger hysteresis effects than, for instance, a continuous spin model.[15]

We have also found that, when considering the actual magnetic structure of $FeCl_2$, the presence of an antiferromagnetic and frustrated second-neighbor in-plane interaction is essential to reproduce the behavior of this system.

The results of this work will serve as a solid basis to understand diluted systems like $Fe_xCl_2Mg_{1-x}$. Such systems (diluted anisotropic antiferromagnet in a field) are realization of random-field systems.[16]

Some experimental studies[17,18,19] and simple theoreti-

cal models[20–27] have been performed on systems of this kind, but the results obtained in this work lead us to believe that considering a frustrated second-neighbor competing interaction as well as a bigger number of interacting spins along the **c** axis will be of capital importance once dilution is considered.

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