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Evidence of a first order magnetic phase transition in FeI_2 by neutron scattering

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Résumé. — La diffusion des neutrons par les réflexions de Bragg magnétiques dans FeI_2 subit une discontinuité à $T_c = 8,95$ K. A cette température le paramètre d'ordre chute de 0,83 à zéro, mettant en évidence une transition de phase du premier ordre. Ce résultat est discuté à la lumière des prévisions du groupe de renormalisation pour les systèmes avec $n \geq 4$. On remarque en outre que ce comportement pourrait indiquer l'existence d'une autre structure magnétique au-dessus de T_c .

Abstract. — Neutron scattering by magnetic Bragg reflections in FeI_2 is found to exhibit a sharp discontinuity at $T_c = 8.95$ K. At this temperature the order parameter abruptly falls from 0.83 to zero revealing an unsuspected first order transition. This result is discussed in the light of renormalization-group predictions for phase transitions in systems with $n \geq 4$. It is also pointed out that this behaviour could be an indication of the possible existence of a different magnetic structure above T_c .

1. Introduction. — FeI_2 crystallizes in the CdI_2 layer type hexagonal structure which has the $\text{P3ml}(\text{D}_3^3\text{d})$ space group symmetry.

Susceptibility measurements [1-3] have shown an anomaly at $T_N = 9.3$ K characteristic of an antiferromagnetic ordering with spins along the c -axis. The high temperature behaviour of χ was shown to exhibit a Curie-Weiss law with negative θ [2-3] suggesting that, contrary to FeCl_2 , antiferromagnetic interactions predominate in FeI_2 . On the other hand an anomaly in the specific heat was detected at

$$T_N = 8.9 \pm 0.1 \text{ K [4]}.$$

Since then it was assumed that FeI_2 was similar to FeCl_2 and FeBr_2 and that it undergoes a second order transition from the antiferromagnetic to the paramagnetic phase.

In this paper, measurements of the temperature dependence of the neutron elastic magnetic scattering in FeI_2 are reported which clearly show that in fact this compound undergoes a first order magnetic transition at $T_c = 8.95 \pm 0.05$ K.

2. Magnetic structure and reciprocal space. — The low temperature magnetic structure has been determined by neutron diffraction [5] and is shown in figure 1a. Though this structure was originally described with a 16 Fe^{++} ion orthorhombic cell ($A = 2a\sqrt{3}$, $B = a$, $C = 4c$) one can easily be convinced that it could as well be described with the 4 Fe^{++} ion monoclinic cell shown on figure 1a with $\mathbf{a} = \mathbf{A}$, $\mathbf{b} = \mathbf{B}$, $\mathbf{c} = 1/4 \mathbf{A} + 1/2 \mathbf{B} + 1/4 \mathbf{C}$ ($\mathbf{c} = (111)$ in the hexagonal cell). Nevertheless for convenience we shall use throughout this paper the conventional 16 Fe^{++} cell to index both direct and reciprocal spaces. The reason why the magnetic cell cannot be reduced to a 2-ions cell as in ordinary antiferromagnets is displayed on figure 1a : the planes with parallel spins do not order in the usual sequence $+-+-$ but in a $++--$ sequence.

According to our convention the reciprocal space (Fig. 1b) will be described by the orthogonal vectors

$$\left\{ \mathbf{A}^* = \frac{1}{2a\sqrt{3}} \mathbf{i}, \quad \mathbf{B}^* = \frac{1}{a} \mathbf{j}, \quad \mathbf{C}^* = \frac{1}{4c} \mathbf{k} \right\}.$$

The two reciprocal vectors $\mathbf{a}^*$ and $\mathbf{c}^*$ of the primitive

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Fig. 1. — a) Magnetic structure and the four Fe²⁺ cell of FeI₂. Black (white) circles are for up (down) magnetic moments. b) Reciprocal lattice of FeI₂. *a**, *b**, *c** are the reciprocal vectors of the four Fe²⁺ cell. White circles are lattice points with zero structure factors.

cell are in the *xz* plane of figure 1b. Because of the regular position of the four Fe²⁺ in the cell, only half of the magnetic reciprocal points have non-zero structure factors, the two most accessible ones being (10 $\bar{1}$) and (103).

3. Experimental. — The experiments were performed on the triple-axis spectrometers situated on the H1 cold neutron beam of the L.L.B. at Saclay and on the IN2 thermal beam of the I.L.L. at Grenoble in conjunction with inelastic measurements which are reported elsewhere [6]. The FeI₂ single crystal was a platelet of $3 \times 20 \times 10 \text{ mm}^3$ cut from a boule grown by S. Legrand at Saclay using the Bridgman technique. It was mounted with the *c*-axis horizontal in a pumped ⁴He variable temperature cryostat.

The elastic intensities scattered by the (10 $\bar{1}$) and (103) magnetic reflections were carefully measured as a function of temperature especially in the vicinity of the critical temperature, where the thermal spin equilibrium takes quite along to be established. Figure 2a shows the results obtained for both reflections when the temperature is first increased from 1.5 K to 12 K and then lowered to 1.5 K. For temperatures lower than 5 K there is no temperature dependence of the intensities.

Fig. 2. — a) Magnetic Bragg intensities as a function of temperature. b) The temperature dependence of the order parameter of FeI₂ compared with that of FeCl₂ and with two theoretical laws for a second order transition.

In order to determine the origin of the non-reversibility of the intensity, we made several thermal cycles which show that :

i) There is no long-time training : once the thermal equilibrium is reached the intensity remains stable up to one day.

ii) There is no hysteresis for cycles which do not cross *T_c* : At a given temperature the intensity does not depend on whether it has been reached by increasing or decreasing the temperature.

iii) The intensities observed after heating above T_c and then cooling down can be smaller or greater than the initial value and seem randomly distributed.

These observations lead us to the conclusion that there were several magnetic domains in the crystal. As the temperature is lowered through T_c the crystal is randomly shared between domains and since the experiment sees only one of them, the intensity contains a random factor which changes each time one crosses T_c .

This explanation implies that the various curves should merge into a single curve if the intensities are scaled to their low temperature limits. This is actually the case, as shown on figure 2b where the order parameter η ($\eta \cong \sqrt{I(T)/I(0)}$), is plotted as a function of temperature. In particular no hysteresis in the value of T_c could be detected within the accuracy of our measurements (~ 0.05 K). From the same curve it can be seen that the order parameter falls from 0.83 to zero in a range smaller than 0.05 K. This is clearly sharper than what could be expected for a 3d ordering via a second order transition. This is illustrated on figure 2b where for comparison have been plotted the experimental results obtained in FeCl_2 [7] and the two theoretical power laws

$$\eta = B \left(1 - \frac{T}{T_c} \right)^\beta$$

with $\beta = 0.312$, $B = 1.52$ (Ising $d = 3$) and $\beta = 0.36$, $B = 1.25$ (Heisenberg $d = 3$) [8].

4. Order parameter of FeI_2 . — As previously seen, the shortest magnetic reciprocal vector with non-zero structure factor is $\mathbf{k}_1 = (10\bar{1})$. The star of $\mathbf{k}_1$ consists of the six vectors $\mathbf{k}_1$ to $\mathbf{k}_6$ generated by the following six symmetry elements of the paramagnetic group $\{1, C_3, C_3^{-1}, \bar{1}, S_6, S_6^{-1}\}$:

$$\begin{aligned} \mathbf{k}_1 &= (10\bar{1}) & \mathbf{k}_2 &= (\bar{1}\bar{2}1) & \mathbf{k}_3 &= (\bar{1}\bar{2}\bar{1}) \\ \mathbf{k}_4 &= (\bar{1}01) & \mathbf{k}_5 &= (\bar{1}\bar{2}1) & \mathbf{k}_6 &= (\bar{1}\bar{2}\bar{1}) \end{aligned}$$

It must be emphasized that in the case of FeI_2 , k_4 to k_6 are actually elements of the star although they are related to the three first k_i by

$$\mathbf{k}_{i+3} = -\mathbf{k}_i \quad (i = 1, 2, 3).$$

This is because $2k_i$ is not a nuclear reciprocal vector as it is in the case of the $+-+--$ ordering.

The small group of $\mathbf{k}_1$ is $m(C_{1h}) = \{E, \sigma_y\}$, where σ_y is one of the three σ_d of $P\bar{3}m1$. The order parameter belongs to the one-dimensional irreducible representation Γ_2 of C_{1h} (transforming like R_z). It then follows that the ordering of FeI_2 is characterized by a six-component order parameter. This suggests that FeI_2 could be a further example of a physical system with a $n \geq 4$ order parameter which undergoes an order-disorder discontinuous phase transition [9-15].

5. Discussion. — Until the last few years, it was generally thought that most of the observed magnetic first order transitions could not be explained on purely magnetic grounds, and magnetoelastic couplings have often been proposed to explain them. In FeI_2 magnetoelastic effects could be expected, since the orbital contribution to magnetism is large in Fe^{++} . However, as previously mentioned, the similar compounds FeCl_2 and FeBr_2 exhibit a classical second order behaviour, which suggests that this coupling is too weak to alter the phase transition.

In their Renormalization Group analysis of four $n = 6$ systems, Mukamel *et al.* [12] found two classes of critical behaviour. In the first one (UO_2) the transition is predicted to be first order (as actually observed) while in the second one (TbD_2 , Nd , K_2IrCl_6) the transition is predicted to be second order.

Though FeI_2 and UO_2 both exhibit a first order transition it seems unlikely that they belong to the same class since UO_2 has an order parameter constructed from a star of three vectors each of them associated with two magnetization directions, while FeI_2 has a star of six vectors and an uniaxial magnetization. From this point of view FeI_2 could seem to be closer to the second class, however our experimental results are inconsistent with the predicted critical behaviour and especially with the critical exponent $\beta = 0.38$ which would mean a decrease of the order parameter smoother than for the $d = 3$ Heisenberg case (Fig. 2b).

This shows that a particular examination of the case of FeI_2 would be necessary to clarify whether a first order AF-P transition can be foreseen from the R.G. theory.

We shall now suggest an alternative explanation, which has not been considered so far, for the sudden drop of the magnetic elastic scattering. If there exists a second (II) magnetic phase between the low-temperature one (I) and the paramagnetic state, then a I-II transition could be easily understood to be first order even within the Landau theory. This is because the thermodynamic potential describing phase I has in this case to be invariant under the operations of the magnetic group of (II). Thus there is no restriction for the existence of third order terms which is sufficient for the transition to be first order. If the neutron experiment is performed on a single crystal it cannot be positively asserted that just above the transition temperature the sample is actually in the paramagnetic phase and not in a magnetically ordered phase (II) with a propagation vector $\mathbf{k}_{II} \neq \mathbf{k}_1$. Furthermore if the temperature interval for the existence of phase II is small, then the two transitions can be undistinguishable from macroscopic measurements such as specific heat or susceptibility. We think that such a situation occurs in MnBr_2 for which a first order transition at 2.16 K has been first reported [14]. Then it was argued that a first order AF-P transition could be anticipated from symmetry considera-

tions [16]. However optical measurements [17] revealed that the transition at 2.16 K was followed by a second one only 0.15 K above.

The existence of two successive phase transitions has been the subject of a renewed interest in the light of studies on the Lifshitz points [18-19].

In the case of FeI_2 , the possible existence of a new magnetic phase above $T_c = 8.95$ K is supported by a recent Monte-Carlo simulation of an Ising system having competing interactions between ferromagnetic nearest and antiferromagnetic next-nearest neighbours [20]. It was found that for sufficiently large values of $|J_2|/J_1$ the low temperature stable phase was $++--$ with a wave vector $\mathbf{k}_1$. This phase remains stable up to T_{c1} where the stable phase becomes sinusoidal with a temperature dependent $\mathbf{k}_H(T)$, and finally the system becomes paramagnetic at a higher temperature T_{c2} . Though the calculation was made for a lattice different from that of FeI_2 , it seems suitable as a first approach since it reproduces some of the most important characteristics of this compound.

i) Owing to its strong uniaxial single-ion anisotropy, FeI_2 can be rather well described by an Ising $S = \frac{1}{2}$ model.

ii) The low temperature magnetic phase of FeI_2 qualitatively looks like that of the model $(++--\text{sequence})$.

iii) It is now firmly established that the in-plane first neighbour and second neighbour interactions are respectively ferromagnetic and antiferromagnetic [21].

These considerations suggest that a careful experimental investigation of the magnetic structures just above T_c should be undertaken to investigate the possible existence of a sinusoidal phase.

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