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MAGNETIC STRUCTURE OF FeI_2 BY NEUTRON DIFFRACTION EXPERIMENTS

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Phase transitions study of FeI_2 in high magnetic field parallel to the anisotropy axis has proved that FeI_2 has an antiferromagnetic structure (below $T_N = 9.3$ K) more complex than the two sublattices structure characteristic of $FeCl_2$ and $FeBr_2$.

We performed neutron diffraction experiments, at room temperature and at 4.2 K using a powder sample. The results show that FeI_2 has an antiferromagnetic structure similar to the structure proposed by Keohler for $MnBr_2$, but with spins oriented along the crystal anisotropy axis perpendicular to the Fe^{++} layers. This spin orientation is in accordance with the results of parallel and perpendicular susceptibilities study.

FeI_2 CRYSTALLIZES in the trigonal space group $P\bar{3}m1$. The unit cell contains one molecule with ions located in the following positions:

$1\ Fe^{++}$ at $1a$: 0 0 0

$2\ I^-$ at $2d$: $\frac{1}{3}\ \frac{2}{3}\ z.\ \frac{2}{3}\ \frac{1}{3}\ \bar{z}$ with $z \simeq \frac{1}{4}$

The values of a and c parameters are:

$$a = 4.03\ \text{Å} \quad \text{and} \quad c = 6.75\ \text{Å}.$$

A study of the principal susceptibilities (parallel and perpendicular to c axis) on a FeI_2 single crystal shows that, below $T_N = 9.3$ K, FeI_2 is antiferromagnetic with atomic magnetic moments parallel to the c axis.[1–3] Moreover, below T_N, the complex behavior, in a magnetic field parallel to the c axis of the magnetization,[2] compulsorily excludes for FeI_2 the two-sublattices structure characteristic of $FeCl_2$ and $FeBr_2$. In fact, the calculus, in molecular field approximation, shows that the main intralayers couplings are of antiferromagnetic type.

Therefore, a study by neutron diffraction has been undertaken to find the ordered magnetic structure of FeI_2 below Néel temperature.

The powder sample, prepared by crushing several single crystals in a dry and inert atmosphere, was enclosed in a cylindrical sealed quartz tube.

Figure 1 gives a part of neutron diffraction patterns obtained at room temperature and at 4.2 K. The diffusion peak observed in the background towards $2\theta = 16°$ comes from the quartz sample-holder.

The observed peaks at 293 K are only due to nuclear Bragg reflections. Table 1 allows to compare the observed and calculated intensities with nuclear scattering amplitudes:[4]

$$b_{Fe} = 0.95\ 10^{-12}\ \text{cm}$$

$$b_I = 0.53\ 10^{-12}\ \text{cm}$$

and z iodine parameter equal to 1/4

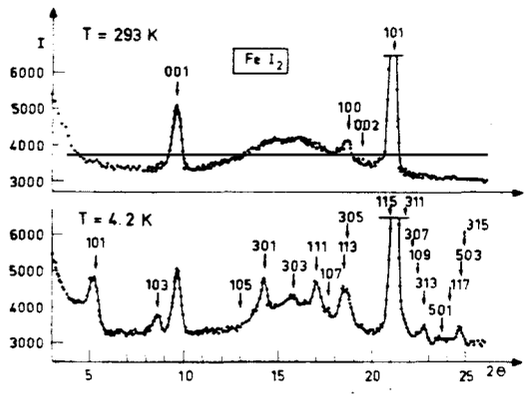

FIG. 1. Neutron diffraction patterns of FeI_2. (a) At room temperature: nuclear Bragg peaks are indexed in the trigonal crystal cell; (b) At 4.2 K: magnetic Bragg peaks indexed in the orthorhombic magnetic cell (See Fig. 2).

Table 1 *

hkl	I_N obs	I_N cal
001	131	128
100	31	21
002	0	< 1
101	316	317
102	189	246
003	7	14
110	229	159
111	77	66
103	92	121

The accordance between the observed and calculated intensities is good enough, though not excellent. Every attempt to improve this accordance by a fit of z parameter has proved fruitless. It was much more expectable to attribute the rather bad quality of the accordance to preferred orientations in the sample, due to the way it was prepared. The single crystals of FeI_2, in fact, are lamellar, and the powder specks coming from their crushing do not take haphazard orientations withing the sample holder. A second pattern carried out afterwards at room temperature with the same sample has confirmed this opinion: the intensities of these new nuclear Bragg reflections may differ from the first ones up to 20%.

* $I = \dfrac{jF_N^2}{\sin\theta \sin 2\theta}$ in barn/cell. The observed intensities have been normalized to the calculated intensities.

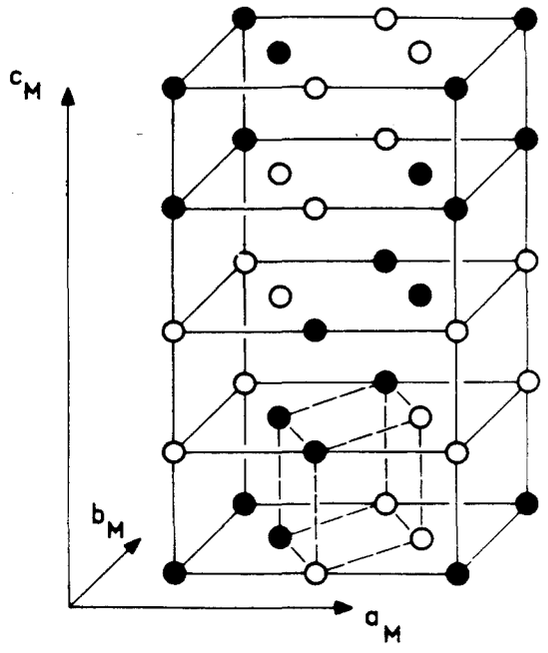

FIG. 2. Magnetic orthorhombic cell of FeI_2. Black and white circles represent magnetic ions with moments in opposite direction. The cristallographic cell is represented by dashed lines.

At 4.2 K, magnetic peaks appear while nuclear peaks (at least the isolated ones) have the same intensity as at room temperature. The magnetic reflections which appear, reveal that the magnetic Fe^{++} configuration is similar to Mn^{++} configuration found by Koehler[5] in $MnBr_2$. Figure 2, shows this configuration. Iodine ions are not represented, black and white circles correspond to magnetic ions with moments in opposite directions. The magnetic cell is orthorhombic and 16 times larger than crystallographic cell (represented by dashed lines on the figure).

On the other hand, the magnetic diffraction results prove that spins are oriented along the anisotropy axis in accordance with the study of magnetic properties (susceptibilities, magnetization behavior . . .). Table 2 compare magnetic intensities observed (we use the same normalization coefficient as for the observed nuclear intensities in Table 1) and calculated with an atomic magnetic moment value at 4.2 K equal

Table 2†

hkl	I_M obs.	I_M calc.
101	132	180
103	26	24
105	0	4
301	40	25
303	13	15
111	44	32
107	0	1
113 / 305	37	30
307	0	3
109	0	< 1
313	22	13
501	5	6
117	2	6
503 / 315	21	14

to 3.7 μ_B (this value normalizes calculated intensities to the observed ones).

As in the case of nuclear diffraction and for the same reasons the accordance between observed and calculated magnetic intensities is not excellent, but is good enough to show that the proposed magnetic structure is fundamentally correct.

† $I_M = \frac{jq^2 F_M^2 f^2}{\sin\theta \sin 2\theta} \left(\frac{e^2\gamma}{2mc^2}\right)^2 \cdot \mu^2$ (μ : magnetic moment of iron expressed in μ_B) in barn/nuclear cell. F_M is the structure factor of the magnetic configuration.

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L'étude des transitions de phase de FeI_2 en champ magnétique paralléle à l'axe d'anisotropie a montré que FeI_2 a une structure antiferromagnétique (en dessous de T_N = 9,3 K) plus complexe que la structure à deux sous-réseaux caractéristique de $FeCl_2$ et $FeBr_2$.

Nous avons effectué des expériences de diffraction de neutrons, à la température ambiante et à 4,2 K, sur un échantillon en poudre. Les résultats montrent que FeI_2 a une structure antiferromagnétique semblable à celle proposée par Koehler pour $MnBr_2$, mais avec les spins orientés le long de l'axe d'anisotropie cristalline perpendiculaire aux plans Fe^{++}. Cette orientation des spins est en accord avec les résultats de l'étude des susceptibilités paralléle et perpendiculaire.