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MAGNETIC PHASE DIAGRAM OF FeI_2

A. WIEDENMANN[1], L.P. REGNAULT[2], P. BURLET[2], J. ROSSAT-MIGNOD[2], O. KOUNDÉ[3] and D. BILLEREY[3]
[1]*Hahn-Meitner-Institut, Glienicker Str. 100, D-1000 Berlin 39, Fed. Rep. Germany*
[2]*CEN6 – DRF/MDN, 85X, F-38041 Grenoble Cedex, France*
[3]*Université de Nancy, F-54037 Nancy Cedex, France*

Neutron diffraction experiments and magnetization measurements have revealed first order transitions between the paramagnetic (P), a commensurate (C), and four ferrimagnetic phases F1 to F4, moments being aligned along the ***c***-axis. F1 and F2 are multi-***k*** structures, F4 is a single-***k*** structure and F3 is an "amorphous-like" phase. Five exchange integrals showing competing interactions are derived.

1. Introduction

FeI_2 belongs to the ferrous halides which crystallize in a hexagonal layered structure of space group P$\bar{3}$ml. The unit cell ($a = 4.05$ Å, $c = 6.75$ Å) contains one Fe^{2+} ion located on the trigonal axis at the origin (000) and two I^--ions at the positions (1/3 2/3 z) and (2/3 1/3 $\bar{z}$) with $z \simeq 1/4$. At the Néel temperature, $T_N = 9.3$ K [1], a commensurate magnetic structure is built up in zero field [2]. The magnetic phase diagram (H, T) and the nature of the various intermediate magnetic phases were studied by means of neutron scattering and magnetization measurements [4]. A single crystal of FeI_2 grown by a Bridgman technique was oriented with the ***c***-axis parallel to the external field.

2. Results

Magnetization isotherms $M(H)$ below $T_N = 9.3$ K exhibit several magnetization steps at the critical values H_{c_i} which (accompanied by hysteresis effects) are characteristic for first order phase transitions (fig. 1). The corresponding H–T phase diagram is shown in fig. 2. In zero applied field a commensurate magnetic ordering is defined by the wave vector $\boldsymbol{k} = [1/4\ 0\ 1/4]$. It consists of a stacking of ferromagnetic (101) layers in a $++--$ sequence with moments ($m_0 = 4.1\ \mu_B$) aligned along the ***c***-axis. At a

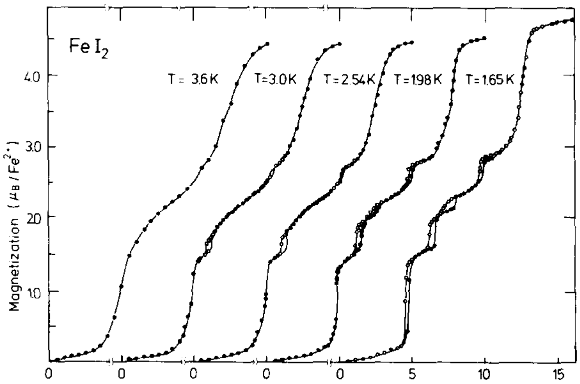

Fig. 1. Magnetization as a function of a magnetic field applied along the ***c***-axis.

critical field H_{c_1} a first order transition to a ferrimagnetic phase F1 takes place for temperatures below the tricritical point $T_{c_1} = 3.8$ K. The F1 phase is a multi-***k*** structure involving the three fundamental components with $\boldsymbol{k}_1 = [1/6\ 1/6\ 0]$, $\boldsymbol{k}_2 = [1/3\ \overline{1/6}\ 0]$ and $\boldsymbol{k}_3 = [1/6\ \overline{1/3}\ 0]$ and the second and sixth harmonics. Good agreement between observed and calculated intensities ($R = 6\%$) is found for the inplane ordering shown in fig. 3(a). It consists of blocks of four magnetic neighbour moments aligned along the ***c***-axis and antiparallel to the applied field surrounded by parallel aligned moments, yielding a net magnetization $\sigma(\mathrm{F1}) = m_0/3$. Nearest neighbouring moments in adjacent (001) layers are aligned parallel to each other.

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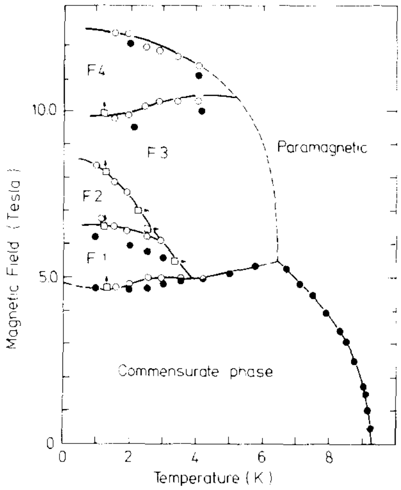

Fig. 2. Magnetic phase diagram of FeI_2 determined from magnetization (circles) and neutron diffraction experiments (squares) (full circles: [3]).

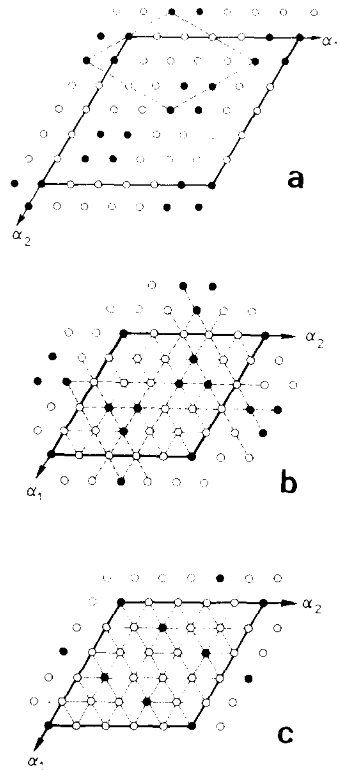

Fig. 3. Arrangement of moments of Fe ions in the (001) plane parallel (open circles) and antiparallel (closed circles) to the external field. (a) Ferromagnetic multi-k structure phase F1. The unit cell is $6a \times 6a \times c$ (full line) and the elementary unit cell $2\sqrt{3}a \times 2\sqrt{3}a \times c$, (dashed line). (b) Ferromagnetic multi-k structure F2. The magnetic unit cell is $5a \times 5a \times c$. (c) Ferromagnetic single-k structure F4 defined by the wave vector k (F4) = [1/5 $\overline{2/5}$ 0].

A transition to a second ferrimagnetic phase F2 occurs at H_{c_2} below a tricritical temperature $T_{c_2} = 2.9$ K. This phase has a net magnetization $\sigma(\mathrm{F2}) = 0.44m_0$ resulting from an in-plane moment arrangement reported in fig. 3(b), characterized by triangles and isolated "down" moments surrounded by "up" moments. This magnetic structure of a unit cell $5a \times 5a$ has a trigonal symmetry and hence has no k-domains.

Besides the observed commensurate wave vectors $\boldsymbol{k}_1 = [1/5\ 1/5\ 0]$, $\boldsymbol{k}_2 = [2/5\ \overline{1/5}\ 0]$, $\boldsymbol{k}_3 = [1/5\ \overline{2/5}\ 0]$ and $k_0 = 0$ for this ordering, the amplitude of the Fourier components associated with the second harmonics $2\boldsymbol{k}$ and with the wave vectors $\boldsymbol{k}' = [1/5\ 0\ 0]$, $\boldsymbol{k}'' = [0\ 1/5\ 0]$ and $\boldsymbol{k}''' = [1/5\ \overline{1/5}\ 0]$ and their second harmonics are non-zero, but they are too weak to be observed experimentally ($R = 25\%$).

Another ferrimagnetic phase F4 exists above a critical field H_{c_4} with a net magnetization $\sigma(\mathrm{F4}) = 0.6m_0$ with the same wave vectors as for phase F2. The ordering of the phase F4 corresponds to a single-$\boldsymbol{k}$ structure, i.e. a stacking of ferromagnetic (110) planes with a sequence + + + + − (fig. 3(c)). However, a squaring up of the sine-wave modulation would give rise to a second order harmonic $2\boldsymbol{k}$ which has not been observed experimentally.

The magnetic moments in the F3 phase must be ordered since the net magnetization $\sigma(\mathrm{F3}) = 0.5m_0$ is much lower than that expected for the paramagnetic state. The ordering is not long-range since no magnetic reflections but only a very broad peak was observed along the [110] direction. This type of incomplete long-range ordering is similar to that found in amorphous systems. A local ordering is present but the correlation length must be small due to the great variety of possible moment arrangements.

3. Discussion

The magnetic phase diagram of FeI_2 results from important frustration effects present in the triangular lattice due to the competition between various in-plane and inter-plane interactions. The most important in-plane couplings are the superexchange interactions via the iodide ions between first nearest neighbour (nn) Fe^{2+} ions (J_1) at $d_1 = 4.05$ Å second nn (J_2) at 7.01 Å, and third nn (J_3) at 8.1 Å. The couplings between adjacent layers J'_0 at $d'_0 = 6.75$ Å, J'_1 at $d'_1 = 7.78$ Å and J'_2 and $d'_2 = 9.73$ Å are expected to be much weaker. The energy of the various ferrimagnetic phases in an applied field can be written as

$$E_i(H) = E_{ex} - \sigma_f \cdot m_0 \cdot H \,. \qquad (1)$$

The exchange energy E_{ex} is calculated for the above determined structure F1, F2, F4, the commensurate and the paramagnetic phase according to

$$E_{ex} = -\sum_{ij} J_{ij} S^z_{i^2} \cdot S^z_{j^2} \qquad (2)$$

($S^z_{i^2} = \pm 1$). At the critical field H_c the energy of the corresponding phases must be equal i.e.

$$E_i - E_j = (\sigma_i - \sigma_j) m_0 \cdot H_c \,. \qquad (3)$$

Furthermore, the thermal energy at the Néel temperature T_N is equal to the ground state energy of the commensurate phase, i.e.

$$kT_N = \tfrac{2}{3} S(S+1)(E_c) \,. \qquad (4)$$

From eqs. (2) to (4) a set of five exchange integrals is derived. Using the observed values of H_{c_i}, $T_N = 9.3 \pm 0.2$ K and $m_0 = (4.1 \pm 0.1)\mu_B$, the following exchange integrals are obtained: $J_1/k = (1.65 \pm 0.3\text{ K})$, $J_2/k = -(0.29 \pm 0.01\text{ K})$, $J_3/k = -(1.55 \pm 0.04\text{ K})$, $J'_0/k = (0.47 \pm 0.08\text{ K})$ and $J'_1/k = -(1.36 \pm 0.03\text{ K})$. With this set a paramagnetic Curie temperature

$$k\theta_p = \tfrac{2}{3} S(S+1) E_p \,,$$

$20.6\text{ K} \leq \theta_p \leq 23.7$ K, is expected in good agreement with the experimental value of $\theta_p = 23.0$ K.

In summary, we conclude that in FeI_2 the coupling between first nn inside the (001) plane is ferromagnetic and is of comparable magnitude to that between third nn on the (001) plane and between second nn on adjacent layers.

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