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X-ray investigation of magnetostriction in FeCl₂

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Résumé. — Les paramètres cristallins a et c de la maille hexagonale de FeCl₂ ont été mesurés sur une poudre par diffraction de rayons X. On rapporte ici les valeurs de ces paramètres à 77 et 300 K, ainsi que leur évolution entre 4,2 et 30 K. Les variations globales \( \frac{a_{30} - a_{4,2}}{a_{4,2}} \) et \( \frac{c_{30} - c_{4,2}}{c_{4,2}} \) ont pour valeurs respectives \( (1,1 \pm 0,4) \times 10^{-3} \) et \( -(7,2 \pm 0,6) \times 10^{-4} \). De part et d’autre de la température de Néel \((T_N \approx 23,8 \text{~K})\) de ce composé antiferromagnétique, les paramètres a et c présentent des comportements différents. Attribuant ce fait au couplage magnéto-élastique, nous déterminons — en utilisant des résultats antérieurs obtenus sur FeCl₂ soumis à des contraintes mécaniques — les dérivées des interactions magnétiques (qui comprennent le champ cristallin) en fonction des composantes diagonales du tenseur de déformation du cristal. Nous en estimons à 1,6 erg/cm³ la valeur de la constante élastique \( C_{13} \), qui n’a pas été mesurée jusqu’à présent. De plus, nous disposons de suffisamment de données expérimentales pour tester la qualité des résultats obtenus sur FeCl₂ soumis à des contraintes mécaniques.

Abstract. — The crystalline parameters a and c of the FeCl₂ hexagonal cell have been measured by X-ray diffraction on a powdered specimen. Here we report the values of these parameters at 77 and 300 K, and also their thermal variations between 4.2 and 30 K. The relative variations \( \frac{a_{30} - a_{4,2}}{a_{4,2}} \) and \( \frac{c_{30} - c_{4,2}}{c_{4,2}} \) are \( (1.1 \pm 0.4) \times 10^{-3} \) and \( -(7.2 \pm 0.6) \times 10^{-4} \) respectively. When the temperature goes below the Néel temperature \((T_N \approx 23.8 \text{~K})\), the parameters a and c display different kinds of variations. This change is attributed to the magneto-elastic coupling and by using previous experimental data obtained on FeCl₂ submitted to mechanical stresses, we determine the derivatives of the magnetic interactions (including crystalline field) versus the diagonal crystal strain tensor components. We estimate the value of the elastic constant \( C_{13} \) to be 1.6 erg/cm³. Moreover the experimental results at our disposal are sufficient for checking the magnetic studies of FeCl₂ submitted to mechanical stresses.

1. Introduction

The crystal cell parameters of the diluted compounds \( \text{Fe}_{1-x} \text{M}_x \text{Cl}_2 \) vary with \( x \), that is with the concentration of the metallic ion \( \text{M}^{+2} \) which replaces \( \text{Fe}^{+2} \). The pure compound FeCl₂ is antiferromagnetic \((T_N \approx 23.8 \text{~K})[24]\). This substitution induces variations of the magnetic interaction relative to those present in FeCl₂ because of the changes in inter-atomic distances. However, the various magnetic phenomena which are actually observed in \( \text{Fe}_{1-x} \text{M}_x \text{Cl}_2 \) are due both to the dilution of the iron ions and to the above mentioned magnetic interaction variations [1]. Therefore, in order to isolate phenomena due to dilution alone, it is necessary to evaluate the contribution of the magnetic interaction variations. This can only be done by knowing the magnetic interactions derivatives of the pure compound versus the diagonal components of its strain tensor.

Some years ago, a number of experimental studies [2 to 9] were made on the magnetic properties variations in FeCl₂ submitted to mechanical stresses which preserve the crystal symmetry \((D_{3d}^5 \text{~or~} R\bar{3}m)\). The magnetic interaction derivatives can be deduced from these studies if the elastic constants \( C_{33}, C_{13} \) and the sum \( C_{11} + C_{12} \) are known; however, until now, no value has been proposed for \( C_{13} \) [10-12].

In this article we report the results obtained from the X-ray investigation of the hexagonal super cell parameters a and c of FeCl₂. We have measured the values of these parameters at 294 and 77 K, and their thermal variations between 4.2 and 30 K. Attributing the low
temperature thermal variations to the magneto-elastic coupling, we deduced results which, combined with previous data, allow us i) to determine the magnetic interactions derivatives versus the crystal strain tensor diagonal components, ii) to check the validity of these derivatives values and hence iii) to obtain a quantitative control of previous experimental studies [2 to 9].

FeCl₂ displays a structural transition when mechanical stresses are applied [2]. Here we are only interested in the low pressure crystalline structure.

In the second section, the experimental results are presented and the third section is concerned with the theoretical interpretation.

2. X-Ray investigation results (1).

The space group of FeCl₂ is R3m, n° 166. We have determined by X-ray diffraction (λ = 2.28970 Å) on a powdered specimen the values of its hexagonal super cell parameters a and c for different temperatures comprised between 4.2 and 30 K, and also at 77 and 294 K. The specimen was prepared in a controlled atmosphere to avoid any hydration.

We cannot directly measure the sample temperature, but rather that of the copper sample holder. Because of the absence of exchange gas, the sample and the sample holder are at slightly different temperatures between 4.2 and 30 K. Near 20 K both temperatures are equal.

In table I we report the values of a and c at 4.2, 77 and 294 K. These results, obtained by means of eight reflections, are in agreement with the previous results of Ferrari et al. [13] and Birgeneau et al. [14], given in table I.

The thermal variations of a and c have been followed from 4.2 K to 30 K with the (11.0) and (00.15) reflections. The values of a and c, obtained at 4.2 K with these two reflections only, are respectively equal to 3.581 and 17.443 Å, in agreement with the values obtained with the eight reflections. Figure 1 shows these thermal variations.

The errors bars, which correspond to relative uncertainties equal to 2 × 10⁻⁴ and 3 × 10⁻⁵ for a and c respectively, are evaluated by taking into account only measurement uncertainties on the line positions. No hysteresis was observed.

The variation of the volume v = a²c√3/2 is displayed in figure 2 and it appears to be monotonic. To investigate this behaviour, we assume that the classical law v⁻¹(dv/dT) = T³ can be applied (2). The statistical fitting of the data between 4.2 and 30 K leads to v = 193.783 (1 + 1.64 × 10⁻⁹ T⁴), which is drawn in figure 2 and shows no evidence of any discontinuity at the transition. This fact, together with the absence of hysteresis mentioned above, is consistent with a second order transition at Tₙ.

Table I. — Values of the crystalline parameters a and c of FeCl₂ in a hexagonal super cell. Two standard deviations in brackets are given.

<table>
<thead>
<tr>
<th></th>
<th>present work</th>
<th>Ferrari et al. [13]</th>
<th>Birgeneau et al. [14]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>294 K</td>
<td>77 K</td>
<td>4.2 K</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.600(3)</td>
<td>3.586(4)</td>
<td>3.581(4)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>17.539(2)</td>
<td>17.439(2)</td>
<td>17.442(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.593 ± 3</td>
<td>3.583 ± 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.58 ± 9</td>
<td>17.45 ± 3</td>
</tr>
</tbody>
</table>

(1) This experimental work has been done in collaboration with the late Doctor R. Kleinberger.

(2) In fact, the specific heat for laminar crystals obeys the T³ law at very low temperatures only [15].
Fig. 2. — Thermal variation of the (hexagonal super cell) volume of FeCl₂. Points : from experimental data; dashed line : « theoretical » curve (see text). \( T_N \) : Néel temperature.

The background lattice expansion can be estimated in the same way. From the paramagnetic values measured at 28, 30 and 77 K, we get for

\[
\begin{align*}
\alpha' &= \alpha_0' + \alpha_1' T^4 \\
\beta' &= \beta_0' + \beta_1' T^4
\end{align*}
\]

(see Fig. 3):

\[
\begin{align*}
\alpha_0' &= 3.5850, \\
\alpha_1' &= 4.65 \times 10^{-11}, \\
\beta_0' &= 17.4301, \\
\beta_1' &= 2.67 \times 10^{-10},
\end{align*}
\]

thus \( \alpha'_{4,2} = 3.5850 \approx \alpha_{30} \) and \( \beta'_{4,2} = 17.4301 \approx \beta_{30} \).

By extrapolating the relative thermal variations of \( c \) in the paramagnetic and antiferromagnetic phases, a Néel temperature near 26.1 K is obtained, which is in reasonable agreement with the established value of 23.8 K [24].

3. Theoretical interpretation.

Below \( T_N \) the thermal expansion of FeCl₂ is due to i) the anharmonicity of the potential energy of the crystal and ii) the magneto-elastic coupling. The cubic symmetry part of Fe⁺² crystalline fields is included in the potential energy while the trigonal symmetry part is included in the magneto-elastic coupling [16]. We shall first estimate the thermal expansion of the cell parameters related to the anharmonicity of the crystal potential energy (background lattice expansion).

3.1 Background lattice expansion between 0 and 30 K. — Within the quasi-harmonic approximation (Grüneisen’s theory) [17] the thermal expansion coefficients \( \alpha_{11} = \frac{1}{a} \frac{da}{dT} \) and \( \alpha_{33} = \frac{1}{c} \frac{dc}{dT} \) are related to the lattice (non magnetic) specific heat at constant volume \( C_v \) by the relations:

\[
x_{il} = \frac{C_v}{V} \sum_{k,l=1}^{3} s_{ijkl} \gamma_{kl}
\]

\[
i = 1 \text{ or } 3 \quad k, l = 1, 2, 3
\]

(1)

where : \( V \) is the volume of the crystal; \( s_{ijkl} (i, j, k, l = 1, 2, 3) \) are the components of the fourth-order elastic compliance tensor of the crystal in an orthogonal frame \( \{ O_x(i = 1, 2, 3) \} \) such that \( O_x_3 \) is parallel to the \( 3 \) axis and \( O_x_2 \) is contained in the mirror, \( m \), of the iron point group \( 3 m \); and \( \gamma_{kl} \) are \( \gamma \)-like Grüneisen constants. For many crystals the Grüneisen constant \( \gamma \) is approximately constant at high temperatures with a numerical value of about 2. At very low temperatures (\( T \ll \theta_D \), the Debye temperature) \( \gamma \) approaches a lower limiting value.

Integrating between 0 and 30 K at constant pressure both sides of relations (1) gives the \( a \) and \( c \) global variations related to crystal potential energy anharmonicity. To do this one neglects volume thermal
variations and considers as constants the parameters $s_{11kl} \gamma_{kl}$ and $s_{33kl} \gamma_{kl}$ ($\theta_0$ for FeCl$_2$ is significantly higher than 30 K. Three values have been proposed: 297 K [11], 290 K [11], 290 K [18, 19], 200 K [18]).

So

$$\frac{(a_{30} - a_0)}{a_0} = \frac{K_{11}^0}{V_0} \int_0^{30} C_v \, dT$$  (2a)

$$\frac{(c_{30} - c_0)}{c_0} = \frac{K_{33}^0}{V_0} \int_0^{30} C_v \, dT$$  (2b)

where $V_0$, $K_{11}^0$, and $K_{33}^0$ are the values at 0 K of the volume and the sums $\sum_{k,l=1}^{3} s_{11kl} \gamma_{kl}$ and $\sum_{k,l=1}^{3} s_{33kl} \gamma_{kl}$ respectively.

The lattice specific heat at constant pressure $C_p$ and volume $C_v$ are related by

$$C_p - C_v = \frac{\alpha^2 V T}{\kappa_T}$$  (3)

where $\alpha = \frac{1}{V} \frac{dV}{dT}$ is the volume lattice expansion coefficient and $\kappa_T = -\frac{1}{V} \frac{dV}{dP}$ is the lattice isothermal compressibility. An average value of $3.4 \times 10^{-4}$ K$^{-1}$ can be obtained for $\alpha$ by using values of $a$ and $c$ at 30 and 77 K (see Table I). For $\kappa_T$ the experimental value obtained by Stevenson [20] at 300 K is $1.1 \times 10^{-3}$ kbar$^{-1}$. As mentioned by Kostryukova [21] the molar lattice specific heat of FeCl$_2$ at constant pressure is close to that of the isomorphous non-magnetic compound CdCl$_2$. By using data obtained by Itskevich et al. [15] for CdCl$_2$, we obtain $\frac{\alpha^2 V T}{\kappa_T} \approx 0.1$ at 30 and 77 K (for lower temperatures this value is certainly lower). So we can use the approximation $C_v(\text{FeCl}_2) \approx C_v(\text{FeCl}_2) \approx C_v(\text{CdCl}_2)$.

Using the data of Itskevich et al. [15] the definite integral $\int_V^{30} \frac{1}{V_0} C_p(\text{CdCl}_2) \, dT$ takes the values $4 \times 10^{-3}$, $1.4 \times 10^{-1}$, $5.1 \times 10^{-1}$, 1.8 and 4.1 J/cm$^3$ for the temperatures 4.9, 10.9, 15.2, 22.5 and 30 K respectively. Hence relations (2a) and (2b) can be written:

$$\frac{(a_{30} - a_0)}{a_0} \approx 4.1 K_{11}^0$$  (3a)

$$\frac{(c_{30} - c_0)}{c_0} \approx 4.1 K_{33}^0$$  (3b)

One can obtain an estimation of $K_{11}^0$ and $K_{33}^0$ by integrating the relations (1) between 30 and 77 K with the same approximation as above. This leads to:

$$\frac{a_{37} - a_{30}}{a_{30}} = \frac{K_{11}^0}{V} \int_{30}^{77} C_p(\text{CdCl}_2) \, dT$$  (4a)

$$\frac{c_{37} - c_{30}}{c_{30}} = \frac{K_{33}^0}{V} \int_{30}^{77} C_p(\text{CdCl}_2) \, dT.$$  (4b)

Using the data of Itskevich et al. [15] and the values of $a$ and $c$ at 30 and 77 K (see Table I), we find

$$K_{11} = K_{33} \approx 1.7 \times 10^{-5} \text{ cm}^3 \text{ J}^{-1}.$$  (5)

Assuming for $K_{11}^0$ and $K_{33}^0$ the value $1.7 \times 10^{-5} \text{ cm}^3 \text{ J}^{-1}$, we deduce from relations (3a) and (3b):

$$\frac{(a_{30} - a_0)}{a_0} \approx 4.1 \frac{(c_{30} - c_0)}{c_0} \approx 7 \times 10^{-5}.$$  (6)

Comparing results (6) to results (1) we can conclude that the observed variations of the parameters $a$ and $c$ between 0 and 30 K are not due to the background lattice thermal expansion but are essentially due to the magneto-elastic coupling.

3.2 MAGNETO-ELASTIC COUPLING. — At all temperatures FeCl$_2$ has a crystal structure of the CdCl$_2$ type, the ferrous ions being contained in sheets perpendicular to the three-fold axis, $c$ axis of the hexagonal super cell. The magnetic properties of this compound can be described by using an effective spin $s \,(s = 1)$ and by introducing three parameters [22]: 1) $D$, the crystalline anisotropy parameter which confines the spins to the $3$ axis; 2) $(2 n_1 J_1)$, the ferromagnetic parameter related to the exchange interaction between a ferrous ion and its neighbours contained in the same sheet; and 3) $(2 n_2 J_2)$, the antiferromagnetic parameter related to the exchange interaction between a ferrous ion and its neighbours contained in both adjacent sheets. The parameter $D$ is the product of $|\lambda|$ and a function of the ratio $\alpha = D/|\lambda|$, where $|\lambda|$ is the absolute value of the spin-orbit coupling constant of the 3d electrons of Fe$^{2+}$ in the crystal, and $\Delta$ is a parameter which characterizes the trigonal part of the crystalline field of Fe$^{2+}$. Hence the four independent parameters of the magnetic system are $|\lambda|$, $D$, $(2 n_1 J_1)$ and $(2 n_2 J_2)$.

Ono et al. [22, 23] first suggested acceptable values for those parameters. Subsequently other sets of values have been proposed [24, 25]. The model of Ono et al. is characterized by [22]:

$$\Delta = 1.25, (2 n_1, J_1) = 6.6 \text{ cm}^{-1}, (2 n_2, J_2) = -0.73 \text{ cm}^{-1}, |\lambda| = 95 \text{ cm}^{-1}$$

In this model $D = 0.133, |\lambda| = 12.6 \text{ cm}^{-1}$.

These four parameters are taken to be constant when the magnetoelastic coupling is neglected. If not, they are considered as functions of the strain tensor components of the crystal. By symmetry considerations it can be shown that in the frame $\{Ox_i\}$ the four parameters only depend on the components $\varepsilon_{ij}$.
and the sum \( e_i + e_j \) (we use matrix notations for the strain components). In this article we consider the parameters \( \bar{a}, 2 n_1 J_1 \) and \( 2 n_2 J_2 \) to be linear functions of \( e_3 \) and \( e_1 + e_2 \), and \( \bar{a} \) to be a constant (the spin-orbit coupling is an intra-atomic interaction). Thus, if \( w \) represents any function of the three independent parameters \( \bar{a}, (2 n_1 J_1) \) and \( (2 n_2 J_2) \) we have:

\[
w = w_0 + \frac{\partial w}{\partial e_1}(e_1 + e_2) + \frac{\partial w}{\partial e_3} e_3
\]  

(7)

with \( \frac{\partial w}{\partial e_1} = \frac{\partial w}{\partial e_2} \) by symmetry considerations.

For the constant \( w_0 \) one can take the value deduced from the studies of Ono et al. [22, 23].

In a molecular field approximation the variational free-energy at temperature \( T \), \( G(T, \eta, \mu, e_i) \), can be written [16, 24] :

\[
G = N(u - Ts) + \frac{1}{2} C_{ij} e_i e_j + NE + t_1 e_1
\]

(8)

with \( i, j = 1, 2, 3 \)

\( e_1 = e_2 \) and \( t_1 = t_2 \)

\[
n = \frac{1}{2} B \eta^2
\]

\[
s = \frac{-k}{2} \left[ 2 \log \mu + (1 - \mu + \eta) \log \frac{1}{2} (1 - \mu + \eta) + (1 - \mu - \eta) \log \frac{1}{2} (1 - \mu - \eta) \right]
\]

\[
B = g^2 \left[ 2 (n_1 J_1) - (2 n_2 J_2) \right].
\]

In expression (8), \( N \) is the number of ferrous ions per unit volume; \( N_u \) and \( N_s \) are the internal energy and the entropy per unit volume respectively; \( 1/2 C_{ij} e_i e_j \) is the elastic-free energy per unit volume; the \( t_i \) parameters describe the background thermal expansion related to the anharmonicity of the potential energy of the crystal (the \( t_i \) parameters depend on \( T \) with \( t(T = 0) = 0 \) and \( t_1 \sim T^3 \) when the specific heat obeys the Debye cubic law); \( E \) is the fundamental energy level of the ferrous ion when the spin-orbit coupling and the trigonal part of crystalline field are taken into account; \( \eta \) is the order parameter of the antiferromagnetic phase and \( \mu \) the occupation probability of the \( s_z \) eigenstate corresponding to the eigenvalue \( m_s = 0 \); \( k \) is the Boltzmann constant and \( g^2 \) is a spectroscopic term which depends only on the parameter \( \bar{a} \). The sums \( 1/2 C_{ij} e_i e_j \) and \( e_i e_i \) are written with the Einstein convention. The strain tensor components, \( e_i \), describe the crystal deformations from the equilibrium configuration which minimises its potential energy (adiabatic approximation). The spin-orbit coupling, the trigonal part of the Fe \(^{2+} \) crystalline field, the exchange interactions are not included in this crystal potential energy [16].

At thermodynamic equilibrium, at temperature \( T \), the parameters \( \eta, \mu, e_i \) take values which minimise the variational free-energy \( G \). An approximate solution of the free-energy minimization equations is given by the following relations:

\[
\eta_0 = \mu_0 e_i e_j 2 \sinh \beta B_0 \eta_0
\]

(9)

\[
\mu_0 = (1 + 2 e_i e_j \cosh \beta B_0 \eta_0)^{-1}
\]

(10)

\[
(C_{11} + C_{12}) e_1 + C_{13} e_3 + N \left( \frac{\partial E}{\partial e_1} - \frac{1}{2} \frac{\partial B}{\partial e_1} \eta_0 - \frac{1}{2} \frac{\partial D}{\partial e_1} \mu_0 \right) + t_1 = 0
\]

(11)

\[
2 C_{13} e_1 + C_{33} e_3 + N \left( \frac{\partial E}{\partial e_3} - \frac{1}{2} \frac{\partial B}{\partial e_3} \eta_0 + \frac{1}{2} \frac{\partial D}{\partial e_3} \mu_0 \right) + t_3 = 0
\]

(12)

\( \eta_0 \) and \( \mu_0 \) are the values of \( \eta \) and \( \mu \) when neglecting magneto-elastic coupling.

At 0 K, \( \eta_0 = 1 \) and \( \mu_0 = 0 \). So \( e_1 \) and \( e_3 \) become \( e_1^0 \) and \( e_3^0 \) respectively, which verify the following equations:

\[
(C_{11} + C_{12}) e_1^0 + C_{13} e_3^0 + N \left( \frac{\partial E}{\partial e_1} - \frac{1}{2} \frac{\partial B}{\partial e_1} \right) = 0
\]

\[
2 C_{13} e_1^0 + C_{33} e_3^0 + N \left( \frac{\partial E}{\partial e_3} - \frac{1}{2} \frac{\partial B}{\partial e_3} \right) = 0.
\]

The deformations \( e_1^0 \) and \( e_3^0 \) cannot be observed; the deformation parameters which can be directly deduced from our X-ray study are \( e_1 = e_1 - e_1^0 \) and \( e_3 = e_3 - e_3^0 \). Neglecting the terms \( t_1 \) and \( t_3 \) we find:

\[
(C_{11} + C_{12}) e_1 + C_{13} e_3 + N \left( \frac{\partial E}{\partial e_1} - \frac{1}{2} \frac{\partial B}{\partial e_1} \eta_0 - 1 + \frac{\partial D}{\partial e_1} \mu_0 \right) = 0
\]

(13)

\[
2 C_{13} e_1 + C_{33} e_3 + N \left( \frac{\partial E}{\partial e_3} - \frac{1}{2} \frac{\partial B}{\partial e_3} \eta_0 - 1 + \frac{\partial D}{\partial e_3} \mu_0 \right) = 0.
\]

(14)

Solving the molecular field equations (9) gives \( \eta_0 \) and \( \mu_0 \) as functions of the temperature. From (13) and (14) we can then obtain \( e_1 \) and \( e_3 \) as functions of the temperature provided that the following nine parameters are known:

\[
C_{13}, C_{33} \quad \text{and} \quad C_{11} + C_{12}, \quad \frac{\partial (2 n_1 J_1)}{\partial e_1} \quad \text{and} \quad \frac{\partial (2 n_1 J_1)}{\partial e_3}, \quad \frac{\partial (2 n_2 J_2)}{\partial e_1} \quad \text{and} \quad \frac{\partial (2 n_2 J_2)}{\partial e_3}. \]

3.2.1 Values of the model parameters.

3.2.1.1 Parameters : \( C_{11} + C_{12}, C_{33} \). — From acoustic phonon spectra determined at room temperature using inelastic neutron scattering, Vettier deduced the value of all the elastic constants of FeCl₂.
except $C_{13}$ [10, 11]. For $C_{11}$, $C_{12}$ and $C_{33}$ Vettier gives the respective values (66.3 ± 3.0, 26.9 ± 4.0 and 16.9 ± 1.3) × 10^{10} dyne/cm². This value of $C_{33}$, which has been confirmed by Vettier and Lefebvre [10, 11] by sound velocity measurement in the c-direction, is quite different from the value 27 × 10^{10} dynes/cm² obtained by Gorodetsky et al. [12] from ultrasonic studies. In this article we take for $C_{11}$, $C_{12}$ and $C_{33}$ the values proposed by Vettier.

3.2.1.2 Parameters : $\frac{\partial}{\partial \varepsilon_3} (2 n_1 J_1), \frac{\partial}{\partial \varepsilon_3} (2 n_2 J_2), \frac{\partial \varepsilon_1}{\partial \varepsilon_3}$

Hammann and Nasser studied at helium-temperature the variation with applied mechanical stresses of two FeCl₂ magnetic parameters : $h_0$, the critical value of the magnetic field which produces the metamagnetic phase transition [14] and $x_\perp$, the magnetic susceptibility in the plane perpendicular to the c-axis [3]. They did not measure the crystal deformations created by the applied mechanical stresses, but assuming that the strain tensor is well described by the following components values :

$\varepsilon_1 = \varepsilon_2 \equiv 0$, $C_{33} \varepsilon_3 = -1$ kbar, $\varepsilon_4 = \varepsilon_5 = \varepsilon_6 = 0$. (R2)

$\varepsilon_4$, $\varepsilon_5$ and $\varepsilon_6$ correspond to the shear strain components.

Assuming that the ferromagnetic parameter $(2 n_1 J_1)$ is due essentially to a direct exchange mechanism they deduce from their studies the following results :

$$\frac{\partial}{\partial \varepsilon_3} (2 n_1 J_1) = 0 \quad \text{(hypothesis)}$$

$$\frac{\partial \varepsilon_1}{\partial \varepsilon_3} = (-4.5 \pm 0.6) \times 10^{-2} \text{ kbar}^{-1}$$

$$\frac{\delta(2 n_2 J_2)}{(2 n_2 J_2)} = (2.2 \pm 0.3) \times 10^{-2} \text{ kbar}^{-1}$$

Using (R2), (R3) and the $C_{33}$ value obtained by Vettier we find :

$$\frac{\partial \varepsilon_1}{\partial \varepsilon_3} = 9.5 \pm 2$$

$$\frac{\partial(2 n_2 J_2)}{\partial \varepsilon_3} = (2.7 \pm 0.6) \text{ cm}^{-1}.$$ (15)

The uncertainties are calculated by supposing that the values of the four parameters $\varepsilon_1$, $(2 n_1 J_1)$, $(2 n_2 J_2)$ and $| \lambda |$ are free of error.

3.2.1.3 Parameter : $C_{13}$. — At 30 K, $\eta_0$ is equal to zero and $\mu_0$ to 0.215. If we call $e_1(30)$ and $e_3(30)$ the values of the parameters $e_1$ and $e_3$ at 30 K, equation (14) can be written :

$$2 \frac{C_{13}}{C_{33}} e_1(30) + e_3(30) +$$

$$+ \frac{N}{C_{33}} \left[ \frac{1}{2} \frac{\partial B}{\partial e_3} + 0.215 \frac{\partial D}{\partial e_3} \right] = 0. \quad (17)$$

Using the experimental results (R2) and (R3) we can calculate $\delta B/\delta e_3$ and $\delta D/\delta e_3$. Hence, taking the value $1.5 \times 10^{22}$ Fe²⁺/cm³ for $N$, we obtain the value $5.22 \pm 0.94 \times 10^{-4}$ for the term

$$\frac{N}{C_{33}} \left[ \frac{1}{2} \frac{\partial B}{\partial e_3} + 0.215 \frac{\partial D}{\partial e_3} \right].$$

The absolute uncertainty is calculated from the experimental error on $\delta a$ and $\delta (2 n_2 J_2)$ (see (R3)) and in the case of $\mu_0$ by assuming, a temperature uncertainty equal to 1.5 K.

Using our X-ray results (R1) for $e_1(30)$ and $e_3(30)$, we deduce that equation (17) is satisfied if the ratio $C_{13}/C_{33}$ is near 0.1. This value is only an estimate for the ratio $C_{13}/C_{33}$ because the second and the third terms of the left hand side of equation (17) are opposite and nearly equal. No experimental value exists for either $C_{13}$ or $C_{13}/C_{33}$.

Fixing at 0.1 the value of $C_{13}/C_{33}$ and from the data of Vettier [10, 11] for the strain components under hydrostatic pressure we find $e_1 = e_1^H = (-9.7 \pm 0.7) \times 10^{-4}$ kbar⁻¹ and $e_3 = e_3^H = (-5.7 \pm 0.4) \times 10^{-3}$ kbar⁻¹. When the ratio $C_{13}/C_{33}$ runs from 0.05 to 0.15, $e_1^H$ and $e_3^H$ are found to change monotonically. A $5 \times 10^{-1}$ relative variation for $C_{13}/C_{33}$ implies for $e_1^H$ and $e_3^H$ relative variations of $5 \times 10^{-2}$ and $1.5 \times 10^{-2}$ respectively. We can conclude that $e_1^H$ and $e_3^H$ are not very sensitive to the variations of $C_{13}/C_{33}$ around 0.1. Thus we adopt for this ratio the value 0.1.

With the estimated values $e_1^H$ and $e_3^H$ we find $(-7.6 \pm 0.5) \times 10^{-3}$ kbar⁻¹ for the crystal compressibility. This value is situated between the experimental values of Stevenson [20], $-11 \times 10^{-3}$ kbar⁻¹ and those of Vettier [26], $-4 \times 10^{-3}$ kbar⁻¹.

3.2.1.4 Parameters Using neutron scattering, Vettier et al. [9] studied the magnetic properties of FeCl₂ at low temperatures when it was submitted to hydrostatic pressure. From the variations versus pressure of the energy gap and of the shape of the magnon dispersion curve, they deduced :

$$\frac{\delta(2 n_1 J_1)}{(2 n_1 J_1)} \simeq 0 \quad \text{(R4)}$$

$$\frac{\delta D}{D} = (9.0 \pm 0.1) \times 10^{-2} \text{ kbar}^{-1}. \quad (R5)$$

As $\frac{\delta(2 n_1 J_1)}{\delta e_1} = 0$ (see (R3)), the result (R4) leads to :

$$2 e_1 \frac{\delta(2 n_1 J_1)}{\delta e_1} \simeq 0.$$
We interpret this relation by assuming that
\[ \frac{\partial (2n_1 J_1)}{\partial \varepsilon_1} \approx 0. \] (18)

The nearly zero value occurs as \((2n_1 J_1)\) is in fact the sum of two exchange parameters \([14]\), the derivatives of which have opposite signs and nearly equal magnitudes.

From (R5) using the model of Ono et al. we deduce
\[ \frac{\partial \tilde{a}}{\partial \varepsilon_1} = (9.82 \pm 0.1) \times 10^{-2} \text{ kbar}^{-1}. \] (19)

Using relations (7) and (15) and the calculated values \(\varepsilon_1^H\) and \(\varepsilon_3^H\) we deduce from (19)
\[ \frac{\partial \tilde{a}}{\partial \varepsilon_1} = -84.8 \pm 14.7. \] (20)

3.2.1.5 Parameter \(\frac{\partial}{\partial \varepsilon_1} (2n_2 J_2)\) — The variations

versus a hydrostatic pressure of \(h_s\) have been studied by Narath et al. [2] who found:
\[ \frac{\partial h_s}{h_s} = (8.7 \pm 0.5) \times 10^{-2} \text{ kbar}^{-1}. \] (R6)

This result has been confirmed by Vettier et al. [7, 8] who found \((7.0 \pm 0.1) \times 10^{-2} \text{ kbar}^{-1}\).

In the model of Ono et al. we can write [4]:
\[ \frac{\partial h_s}{h_s} = \frac{d(2n_2 J_2)}{(2n_2 J_2)} + 0.07 \frac{\partial \tilde{a}}{\partial \varepsilon_1}. \] (21)

Putting (R6) and (19) in (21) we obtain
\[ \frac{d(2n_2 J_2)}{(2n_2 J_2)} = (8.08 \pm 0.5) \times 10^{-2} \text{ kbar}^{-1}. \] (22)

Using relations (7), (16) and the calculated values \(\varepsilon_1^H\) and \(\varepsilon_3^H\) we obtain:
\[ \frac{\partial (2n_2 J_2)}{\partial \varepsilon_1} = (22.5 \pm 5.9) \text{ cm}^{-1}. \] (23)

At the present time we have determined all the nine parameters of the model. To obtain them we used previous experimental results and equation (14) at 30 K. To obtain a quantitative check on the obtained parameters we use equation (13) at 30 K.

3.2.2 Quantitative check of the parameters values.

3.2.2.1. At 30 K, equation (13) can be written
\[ (C_{11} + C_{12}) \epsilon_1(30) + C_{13} \epsilon_3(30) + \]
\[ + N \left[ \frac{1}{2} \frac{\partial B}{\partial \varepsilon_1} + 0.215 \frac{\partial D}{\partial \varepsilon_1} \right] = 0. \] (24)

The sum \(A_1 = (C_{11} + C_{12}) \epsilon_1(30) + C_{13} \epsilon_3(30)\) contains parameters which have been measured on crystals at atmospheric pressure, while the sum \(A_2 = \frac{1}{2} \frac{\partial B}{\partial \varepsilon_1} + 0.215 \frac{\partial D}{\partial \varepsilon_1}\) contains parameters deduced from experiments under mechanical stresses. \(A_2\) and \(A_1\) are found to be equal to \((3.4 \pm 1.5) \times 10^2 \text{ cm}^{-1}\) and \((-3.29 \pm 0.60) \times 10^2 \text{ cm}^{-1}\) respectively, thus verifying equation (24). This result suggests that all the experimental data under pressure we have used are reliable.

3.2.2.2. We can now check two more experimental results obtained by Vettier et al. [8]. They have measured the variations versus hydrostatic pressure of \(T_N\) and \(\chi_L\). They found:
\[ \frac{\delta T_N}{T_N} = (1.1 \pm 0.1) \times 10^{-2} \text{ kbar}^{-1}. \] (R7)
\[ \frac{\delta \chi_L}{\chi_L} = (-3.8 \pm 0.1) \times 10^{-2} \text{ kbar}^{-1}. \] (R8)

One can test the reliability of these results with the others obtained by Vettier et al. [8] and Narath et al. [2] ((R4), (R5) and (R6)).

3.2.2.2.1) Check of (R7). — In the molecular field approximation \(T_N\) is given by the relation [24]:
\[ 1 + 0.5 e^{-\beta_N D} - \beta_N B = 0 \] (25)
with \(\beta_N = (kT_N)^{-1}\). In the model of Ono et al., using (R4), equation (25) leads to:
\[ 1.423 \frac{d T_N}{T_N} = 0.124 \frac{d(2n_2 J_2)}{(2n_2 J_2)} + 0.311 \frac{d \tilde{a}}{\tilde{a}}. \] (26)

From (R5) and (R6) obtained at 4.2 K we deduce:
\[ \frac{d T_N}{T_N} = (2.6 \pm 0.1) \times 10^{-2} \text{ kbar}^{-1}. \] (27)

The discrepancy between this result and the experimental value (R7) is certainly due to the fact that the molecular field theory is a bad approximation near the transition.

3.2.2.2.2) Check of (R8). — In the molecular field approximation, at 0 K, using (R4) one obtains in the model of Ono et al. [3]:
\[ \frac{d \chi_L}{\chi_L} = -1.1 \frac{d \tilde{a}}{\tilde{a}} - 0.16 \frac{d(2n_2 J_2)}{(2n_2 J_2)}. \] (28)

Putting (19) and (22) in (28) we deduce:
\[ \frac{d \chi_L}{\chi_L} = (-11.0 \pm 0.2) \times 10^{-2} \text{ kbar}^{-1}. \] (29)

The discrepancy between this result and the experimental result (R8) cannot be explained in the frame of this article.
3.2.3. Theoretical interpretation of the thermal variations of the lattice parameters. — Numerical resolution of equations (9) and (10) gives the variation of $\eta_0$ and $\mu_o$ versus the temperature $T$. The Neel temperature calculated in the model of Ono et al. is equal to 23.8 K. In figure 4, we report the variations with reduced temperature $T/T_N$ of $(1 - \eta_0^2)$ and $\mu_o$. For $T = T_N$ both curves show discontinuity of their derivatives.

Fig. 4. — Thermal variations of $(1 - \eta_0^2)$ and $\mu_o$ calculated in the model of Ono et al. In this model $T_N = 23.8$ K. The parameter $\eta_0$ is the order parameter of the antiferromagnetic phase.

Putting in (13) and (14) central values for the different parameters and taking $C_{13} = 0.1 C_{33}$, we have calculated the thermal variations between 4.2 and 30 K of the crystalline parameters $a$ and $c$. Figure 5 displays the experimental and calculated values as function of the reduced temperature $T/T_N$ ($T_N$ is made equal to 26.1 K for the X-ray experimental data). The agreement between experimental and calculated results is satisfactory.

Fig. 5. — Crystalline parameters values as function of $T/T_N$. For the calculated values (points +) 23.8 K has been used for $T_N$ while for the experimental values (points o) $T_N$ has been taken equal to 26.1 K.

4. Conclusion.

This work has enabled us to estimate the magnetic interaction derivatives of FeCl$_2$ with respect to the diagonal components of its strain tensor, and to estimate the elastic constant $C_{13}$. Moreover we have also checked the magnetic experimental data obtained for FeCl$_2$ under mechanical stresses. We have shown the reliability of all these data except the relative variation versus hydrostatic pressure of $\chi_1$, the FeCl$_2$ magnetic susceptibility in the plane perpendicular to the easy magnetization axis.

It must be also noticed the role played by the Fe$^{+2}$ crystalline field in the magneto-elastic coupling. This situation is quite different from that in MnO for example.

Finally it will be interesting to have a direct determination of the elastic constant $C_{13}$ or the ratio $C_{13}/C_{33}$, and also to have a confirmation of the result of Vettier et al. for the variations of $\chi_T$ versus hydrostatic pressure.
References