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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 ($T_N \cong 23,8$ 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 ($T_N \cong 23.8$ 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 Fe_{1-x}M_xCl₂ vary with x , that is with the concentration of the metallic ion M⁺² which replaces Fe⁺². The pure compound FeCl₂ is antiferromagnetic ($T_N \cong 23.8$ 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 Fe_{1-x}M_xCl₂ 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 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

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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].

FeCl_2 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 FeCl_2 is $R\bar{3}m$, n° 166. We have determined by X-ray diffraction ($\lambda = 2.28970 \text{ \AA}$) 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 uncer-

Fig. 1. — Thermal variation of the (hexagonal super cell) parameters a and c of FeCl_2 . From the relative variations of c we obtain 26.1 K for T_N , the Néel temperature of this antiferromagnetic compound.

tainties 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 $v = a^2 c \sqrt{3}/2$ is displayed in figure 2 and it appears to be monotonic. To investigate this behaviour, we assume that the classical law $v^{-1}(dv/dT) \sim T^3$ can be applied ⁽²⁾. The statistical fitting of the data between 4.2 and 30 K leads to $v = 193.783 (1 + 1.64 \times 10^{-9} T^4)$, 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 T_N .

Table I. — Values of the crystalline parameters a and c of FeCl_2 in a hexagonal super cell. Two standard deviations in brackets are given.

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

⁽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 T^3 law at very low temperatures only [15].

Fig. 2. — Thermal variation of the (hexagonal super cell) volume of FeCl_2 . 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

$$a' = a'_0 + a'_1 T^4 \quad \text{and} \quad c' = c'_0 + c'_1 T^4 \quad (\text{see Fig. 3}) :$$

$$\begin{aligned} a'_0 &= 3.5850, & c'_0 &= 17.4301, \\ a'_1 &= 4.65 \times 10^{-11}, & c'_1 &= 2.67 \times 10^{-10}, \end{aligned}$$

thus $a'_{4.2} = 3.5850 \cong a_{30}$ and $c'_{4.2} = 17.4301 \cong c_{30}$.

Fig. 3. — Thermal variations of the (hexagonal super cell) parameters a and c . Points : experimental data; dotted lines a' , a'' , c' , c'' : phenomenological curves (see text).

The global variations of a and c between the paramagnetic and antiferromagnetic phases can be evaluated by the relative variations of these parameters at 4.2 and 30 K :

$$\left. \begin{aligned} \left(\frac{a_{30} - a_{4.2}}{a_{4.2}} \right)_{\text{exp}} &= (1.1 \pm 0.4) \times 10^{-3} \\ \left(\frac{c_{30} - c_{4.2}}{c_{4.2}} \right)_{\text{exp}} &= - (7.2 \pm 0.6) \times 10^{-4} \end{aligned} \right\} \quad (\text{R1})$$

We recall that absolute uncertainties are calculated from the measurement uncertainties on line position of the two reflections (11.0), and (00.15).

Finally, below the transition (25 $\rightarrow$ 4.2 K), the actual behaviour can be phenomenologically account-

ed for with the form $a'' = \sum_0^3 a''_i T^{2i}$ (idem for c). The fittings give (see Fig. 3) :

$$\begin{aligned} a''_0 &= 3.5816, & c''_0 &= 17.4430, \\ a''_1 &= 3.53 \times 10^{-7}, & c''_1 &= -2.78 \times 10^{-7}, \\ a''_2 &= 6.81 \times 10^{-10}, & c''_2 &= -3.65 \times 10^{-9}, \\ a''_3 &= 9.06 \times 10^{-12}, & c''_3 &= -3.65 \times 10^{-11}. \end{aligned}$$

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 [24].

3. Theoretical interpretation.

Below T_N the thermal expansion of FeCl_2 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 :

$$\alpha_{ii} = \frac{C_v}{V} \sum_{k,l=1}^3 s_{iikl} \gamma_{kl} \quad i = 1 \text{ or } 3 \quad k, l = 1, 2, 3 \quad (1)$$

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 $\{\text{Ox}_i (i = 1, 2, 3)\}$ such that Ox_3 is parallel to the $\bar{3}$ axis and Ox_2 is contained in the mirror, m , of the iron point group ($\bar{3}m$); and γ_{kl} are γ -like Grüneisen constants. For many crystals the Grüneisen constant γ is approximately constant at high temperatures with a numerical value of about 2. At very low temperatures ($T \ll \theta_D$, the Debye temperature) γ 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 $\sum_{k,l=1}^3 s_{11kl} \gamma_{kl}$ and $\sum_{k,l=1}^3 s_{33kl} \gamma_{kl}$ (θ_D 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

$$\left(\frac{a_{30} - a_0}{a_0} \right)_{\text{anh.}} = \frac{K_{11}^0}{V_0} \int_0^{30} C_v dT \quad (2a)$$

$$\left(\frac{c_{30} - c_0}{c_0} \right)_{\text{anh.}} = \frac{K_{33}^0}{V_0} \int_0^{30} C_v dT \quad (2b)$$

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

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

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 $3.4 \times 10^{-4} \text{ K}^{-1}$ can be obtained for α by using values of a and c at 30 and 77 K (see Table I). For κ_T the experimental value obtained by Stevenson [20] at 300 K is $11 \times 10^{-3} \text{ kbar}^{-1}$. As mentioned by Kostyukova [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 $\frac{\alpha^2 VT}{\kappa_T C_p} \cong 0.1$ at 30 and 77 K (for lower temperatures this value is certainly lower). So we can use the approximation $C_v(\text{FeCl}_2) \cong C_p(\text{FeCl}_2) \cong C_p(\text{CdCl}_2)$. Using the data of Itskevich *et al.* [15] the definite integral $\int_0^T \frac{1}{V_0} C_p(\text{CdCl}_2) dT$ takes the values 4×10^{-3} , 1.4×10^{-1} , 5.1×10^{-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 :

$$\left(\frac{a_{30} - a_0}{a_0} \right)_{\text{anh.}} \cong 4.1 K_{11}^0 \quad (3a)$$

$$\left(\frac{c_{30} - c_0}{c_0} \right)_{\text{anh.}} \cong 4.1 K_{33}^0 \quad (3b)$$

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 :

$$\frac{a_{77} - a_{30}}{a_{30}} = \frac{\tilde{K}_{11}}{V} \int_{30}^{77} C_p(\text{CdCl}_2) dT \quad (4a)$$

$$\frac{c_{77} - c_{30}}{c_{30}} = \frac{\tilde{K}_{33}}{V} \int_{30}^{77} C_p(\text{CdCl}_2) dT \quad (4b)$$

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

$$\tilde{K}_{11} \cong \tilde{K}_{33} \cong 1.7 \times 10^{-5} \text{ cm}^3 \text{ J}^{-1}. \quad (5)$$

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) :

$$\left(\frac{a_{30} - a_0}{a_0} \right)_{\text{anh.}} \cong \left(\frac{c_{30} - c_0}{c_0} \right)_{\text{anh.}} \cong 7 \times 10^{-5}. \quad (6)$$

Comparing results (6) to results (R1) 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) $(2n_1 J_1)$, the ferromagnetic parameter related to the exchange interaction between a ferrous ion and its neighbours contained in the same sheet; and 3) $(2n_2 J_2)$, 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 $\tilde{a} = \Delta/|\lambda|$, where $|\lambda|$ is the absolute value of the spin-orbit coupling constant of the 3d electrons of Fe^{+2} in the crystal, and Δ 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 $|\lambda|$, Δ , $(2n_1 J_1)$ and $(2n_2 J_2)$.

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] :

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

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 $\{\text{Ox}_i\}$ the four parameters only depend on the components ε_3

and the sum $\varepsilon_1 + \varepsilon_2$ (we use matrix notations for the strain components). In this article we consider the parameters $\tilde{a}$, $2n_1 J_1$ and $2n_2 J_2$ to be linear functions of ε_3 and $\varepsilon_1 + \varepsilon_2$, and $|\lambda|$ to be a constant (the spin-orbit coupling is an intra-atomic interaction). Thus, if w represents any function of the three independent parameters $\tilde{a}$, $(2n_1 J_1)$ and $(2n_2 J_2)$ we have :

$$w = w_0 + \frac{\partial w}{\partial \varepsilon_1}(\varepsilon_1 + \varepsilon_2) + \frac{\partial w}{\partial \varepsilon_3} \varepsilon_3 \quad (7)$$

with $\partial w / \partial \varepsilon_1 = \partial w / \partial \varepsilon_2$ 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 , $G(T, \eta, \mu, \varepsilon_i)$, can be written [16, 24] :

$$G = N(u - Ts) + \frac{1}{2} C_{ij} \varepsilon_i \varepsilon_j + NE + t_i \varepsilon_i \quad (8)$$

with $i, j = 1, 2, 3$

$$\varepsilon_1 = \varepsilon_2 \quad \text{and} \quad t_1 = t_2$$

$$u = D\mu - \frac{1}{2} B \eta^2$$

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

$$B = g_z'^2 [(2n_1 J_1) - (2n_2 J_2)].$$

In expression (8), N is the number of ferrous ions per unit volume; Nu and Ns are the internal energy and the entropy per unit volume respectively; $1/2 C_{ij} \varepsilon_i \varepsilon_j$ 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 $t_i(T=0) = 0$ and $t_i \sim T^3$ 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; η is the order parameter of the antiferromagnetic phase and μ the occupation probability of the s_z eigenstate corresponding to the eigenvalue $m_s = 0$; k is the Boltzmann constant and g_z' is a spectroscopic term which depends only on the parameter $\tilde{a}$. The sums $1/2 C_{ij} \varepsilon_i \varepsilon_j$ and $t_i \varepsilon_i$ are written with the Einstein convention. The strain tensor components, ε_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 η , μ , ε_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 :

$$\eta_0 = \mu_0 e^{\beta D_0} 2 \sinh \beta B_0 \eta_0 \quad (9)$$

$$\mu_0 = [1 + 2 e^{\beta D_0} \cosh \beta B_0 \eta_0]^{-1} \quad (10)$$

$$(C_{11} + C_{12}) \varepsilon_1 + C_{13} \varepsilon_3 + N \left[\frac{\partial E}{\partial \varepsilon_1} - \frac{1}{2} \frac{\partial B}{\partial \varepsilon_1} \eta_0^2 + \frac{\partial D}{\partial \varepsilon_1} \mu_0 \right] + t_1 = 0 \quad (11)$$

$$2 C_{13} \varepsilon_1 + C_{33} \varepsilon_3 + N \left[\frac{\partial E}{\partial \varepsilon_3} - \frac{1}{2} \frac{\partial B}{\partial \varepsilon_3} \eta_0^2 + \frac{\partial D}{\partial \varepsilon_3} \mu_0 \right] + t_3 = 0 \quad (12)$$

η_0 and μ_0 are the values of η and μ when neglecting magneto-elastic coupling.

At 0 K, $\eta_0 = 1$ and $\mu_0 = 0$. So ε_1 and ε_3 become ε_1^0 and ε_3^0 respectively, which verify the following equations :

$$(C_{11} + C_{12}) \varepsilon_1^0 + C_{13} \varepsilon_3^0 + N \left[\frac{\partial E}{\partial \varepsilon_1} - \frac{1}{2} \frac{\partial B}{\partial \varepsilon_1} \right] = 0$$

$$2 C_{13} \varepsilon_1^0 + C_{33} \varepsilon_3^0 + N \left[\frac{\partial E}{\partial \varepsilon_3} - \frac{1}{2} \frac{\partial B}{\partial \varepsilon_3} \right] = 0.$$

The deformations ε_1^0 and ε_3^0 cannot be observed; the deformation parameters which can be directly deduced from our X-ray study are $e_1 = \varepsilon_1 - \varepsilon_1^0$ and $e_3 = \varepsilon_3 - \varepsilon_3^0$. Neglecting the terms t_1 and t_3 we find :

$$(C_{11} + C_{12}) e_1 + C_{13} e_3 + N \left[-\frac{1}{2} \frac{\partial B}{\partial \varepsilon_1} (\eta_0^2 - 1) + \frac{\partial D}{\partial \varepsilon_1} \mu_0 \right] = 0 \quad (13)$$

$$2 C_{13} e_1 + C_{33} e_3 + N \left[-\frac{1}{2} \frac{\partial B}{\partial \varepsilon_3} (\eta_0^2 - 1) + \frac{\partial D}{\partial \varepsilon_3} \mu_0 \right] = 0. \quad (14)$$

Solving the molecular field equations (9) gives η_0 and μ_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 :

$$\begin{array}{cc} C_{13}, C_{33} & \text{and} & C_{11} + C_{12} \\ \frac{\partial \tilde{a}}{\partial \varepsilon_1} & \text{and} & \frac{\partial \tilde{a}}{\partial \varepsilon_3} \\ \frac{\partial(2n_1 J_1)}{\partial \varepsilon_1} & \text{and} & \frac{\partial(2n_1 J_1)}{\partial \varepsilon_3} \\ \frac{\partial(2n_2 J_2)}{\partial \varepsilon_1} & \text{and} & \frac{\partial(2n_2 J_2)}{\partial \varepsilon_3}. \end{array}$$

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 $(66.3 \pm 3.0, 26.9 \pm 4.0$ and $16.9 \pm 1.3) \times 10^{10}$ 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 : $\frac{\partial}{\partial \varepsilon_3} (2n_1 J_1), \frac{\partial}{\partial \varepsilon_3} (2n_2 J_2),$

$\frac{\partial \tilde{a}}{\partial \varepsilon_3}$. — Hammann and Nasser studied at helium-temperature the variation with applied mechanical stresses of two FeCl₂ magnetic parameters : h_s , the critical value of the magnetic field which produces the metamagnetic phase transition [14] and $\chi_{\perp}$, 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 assume that the strain tensor is well described by the following components values :

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

$\varepsilon_4, \varepsilon_5$ and ε_6 correspond to the shear strain components.

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

$$\left. \begin{aligned} \frac{\partial}{\partial \varepsilon_3} (2n_1 J_1) &= 0 \quad (\text{hypothesis}) \\ \frac{\delta \tilde{a}}{\tilde{a}} &= (-4.5 \pm 0.6) \cdot 10^{-2} \text{ kbar}^{-1} \\ \frac{\delta(2n_2 J_2)}{(2n_2 J_2)} &= (2.2 \pm 0.3) \cdot 10^{-2} \text{ kbar}^{-1} \end{aligned} \right\} \quad (R3)$$

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

$$\frac{\partial \tilde{a}}{\partial \varepsilon_3} = 9.5 \pm 2 \quad (15)$$

$$\frac{\partial(2n_2 J_2)}{\partial \varepsilon_3} = (2.7 \pm 0.6) \text{ cm}^{-1}. \quad (16)$$

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

3.2.1.3 Parameter : C_{13} . — At 30 K, η_0 is equal to zero and μ_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 :

$$2 \frac{C_{13}}{C_{33}} e_1(30) + e_3(30) + \frac{N}{C_{33}} \left[\frac{1}{2} \frac{\partial B}{\partial \varepsilon_3} + 0.215 \frac{\partial D}{\partial \varepsilon_3} \right] = 0. \quad (17)$$

Using the experimental results (R2) and (R3) we can calculate $\partial B / \partial \varepsilon_3$ and $\partial D / \partial \varepsilon_3$. Hence, taking the value 1.5×10^{22} Fe²⁺/cm³ for N , we obtain the value $5.22 \pm 0.94 \times 10^{-4}$ for the term

$$\frac{N}{C_{33}} \left[\frac{1}{2} \frac{\partial B}{\partial \varepsilon_3} + 0.215 \frac{\partial D}{\partial \varepsilon_3} \right].$$

The absolute uncertainty is calculated from the experimental error on $\delta \tilde{a}$ and $\delta(2n_2 J_2)$ (see (R3)) and in the case of μ_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 $\varepsilon_1 = \varepsilon_1^H = (-9.7 \pm 0.7) \times 10^{-4} \text{ kbar}^{-1}$ and $\varepsilon_3 = \varepsilon_3^H = (-5.7 \pm 0.4) \times 10^{-3} \text{ kbar}^{-1}$. When the ratio C_{13}/C_{33} runs from 0.05 to 0.15, ε_1^H and ε_3^H are found to change monotonically. A 5×10^{-1} relative variation for C_{13}/C_{33} implies for ε_1^H and ε_3^H relative variations of 5×10^{-2} and 1.5×10^{-2} respectively. We can conclude that ε_1^H and ε_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 ε_1^H and ε_3^H we find $(-7.6 \pm 0.5) \cdot 10^{-3} \text{ kbar}^{-1}$ for the crystal compressibility. This value is situated between the experimental values of Stevenson [20], $-11 \times 10^{-3} \text{ kbar}^{-1}$ and those of Vettier [26], $-4 \times 10^{-3} \text{ kbar}^{-1}$.

3.2.1.4 Parameters : $\frac{\partial}{\partial \varepsilon_1} (2n_1 J_1), \frac{\partial}{\partial \varepsilon_1} \tilde{a}$. — 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 :

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

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

As $\frac{\partial(2n_1 J_1)}{\partial \varepsilon_3} = 0$ (see (R3)), the result (R4) leads to :

$$2 \varepsilon_1^H \frac{\partial(2n_1 J_1)}{\partial \varepsilon_1} \simeq 0.$$

We interpret this relation by assuming that

$$\frac{\partial(2n_1 J_1)}{\partial \varepsilon_1} \simeq 0. \quad (18)$$

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

$$\frac{\delta \tilde{a}}{\tilde{a}} = (9.82 \pm 0.1) \cdot 10^{-2} \text{ kbar}^{-1}. \quad (19)$$

Using relations (7) and (15) and the calculated values ε_1^H and ε_3^H we deduce from (19)

$$\frac{\partial \tilde{a}}{\partial \varepsilon_1} = -84.8 \pm 14.7. \quad (20)$$

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 :

$$\frac{\delta h_s}{h_s} = (8.7 \pm 0.5) \cdot 10^{-2} \text{ kbar}^{-1}. \quad (R6)$$

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

In the model of Ono *et al.* we can write [4] :

$$\frac{dh_s}{h_s} = \frac{d(2n_2 J_2)}{(2n_2 J_2)} + 0.07 \frac{d\tilde{a}}{\tilde{a}}. \quad (21)$$

Putting (R6) and (19) in (21) we obtain

$$\frac{d(2n_2 J_2)}{(2n_2 J_2)} = (8.08 \pm 0.5) \cdot 10^{-2} \text{ kbar}^{-1}. \quad (22)$$

Using relations (7), (16) and the calculated values ε_1^H and ε_3^H we obtain :

$$\frac{\partial(2n_2 J_2)}{\partial \varepsilon_1} = (22.5 \pm 5.9) \text{ cm}^{-1}. \quad (23)$$

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

$$(C_{11} + C_{12}) e_1(30) + C_{13} e_3(30) + N \left[\frac{1}{2} \frac{\partial B}{\partial \varepsilon_1} + 0.215 \frac{\partial D}{\partial \varepsilon_1} \right] = 0. \quad (24)$$

The sum $A_1 = (C_{11} + C_{12}) e_1(30) + C_{13} e_3(30)$ con-

tains parameters which have been measured on crystals at atmospheric pressure, while the sum $A_2 = \frac{1}{2} \times$

$\frac{\partial B}{\partial \varepsilon_1} + 0.215 \frac{\partial D}{\partial \varepsilon_1}$ contains parameters deduced from experiments under mechanical stresses. NA_2 and A_1 are found to be equal to $(3.4 \pm 1.5) \cdot 10^2 \text{ cm}^{-1}$ and $(-3.29 \pm 0.60) \cdot 10^2 \text{ cm}^{-1}$ 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 $\chi_{\perp}$. They found :

$$\frac{\delta T_N}{T_N} = (1.1 \pm 0.1) \cdot 10^{-2} \text{ kbar}^{-1} \quad (R7)$$

$$\frac{\delta \chi_{\perp}}{\chi_{\perp}} = (-3.8 \pm 0.1) \cdot 10^{-2} \text{ kbar}^{-1}. \quad (R8)$$

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] :

$$1 + 0.5 e^{-\beta_N D} - \beta_N B = 0 \quad (25)$$

with $\beta_N = (kT_N)^{-1}$. In the model of Ono *et al.*, using (R4), equation (25) leads to :

$$1.423 \frac{dT_N}{T_N} = 0.124 \frac{d(2n_2 J_2)}{(2n_2 J_2)} + 0.311 \frac{d\tilde{a}}{\tilde{a}}. \quad (26)$$

From (R5) and (R6) obtained at 4.2 K we deduce :

$$\frac{dT_N}{T_N} = (2.6 \pm 0.1) \cdot 10^{-2} \text{ kbar}^{-1}. \quad (27)$$

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] :

$$\frac{d\chi_{\perp}}{\chi_{\perp}} = -1.1 \frac{d\tilde{a}}{\tilde{a}} - 0.16 \frac{d(2n_2 J_2)}{(2n_2 J_2)}. \quad (28)$$

Putting (19) and (22) in (28) we deduce :

$$\frac{d\chi_{\perp}}{\chi_{\perp}} = (-11.0 \pm 0.2) \cdot 10^{-2} \text{ kbar}^{-1}. \quad (29)$$

The discrepancy between this 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 η_0 and μ_0 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 μ_0 . For $T = T_N$ both curves show discontinuity of their derivatives.

Fig. 4. — Thermal variations of $(1 - \eta_0^2)$ and μ_0 calculated in the model of Ono *et al.* In this model $T_N = 23.8$ K. The parameter η_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 χ_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 χ_T versus hydrostatic pressure.

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