ANON-AA 70-1376

LOCALIZED MAGNETISM AND HIGH PRESSURES

In the following lectures we :

1 - give a brief account on magnetism, with emphasis on volume effect.

2 - discuss about thermodynamical properties of magnetic solids

3 - discuss about magnetostriction in magnetic solids with negligible magnetocrystalline anisotropy (Gd, MnO,...) and high pressure or stress experiments

4 - discuss about magnetostriction in magnetic solids with magnetocrystalline anisotropy (Tb, Dy,...)

If some time remains, we will :

a - discuss about apparatus for high pressure magnetic measurements.

b - discuss about first order magnetic transitions and high pressure informations (FeRh, CrN, Mn_3GaC, $HoCr_2$, $ErCo_2$,...)

1 - Basic magnetism

Ref. : S. CHIKAZUMI - Physics of magnetism, J. Wiley (1964),

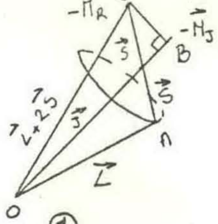
A. HERPIN - Théorie du magnétisme, Institut National des Sciences et Techniques Nucléaires, et P U F (1968),

C. KITTEL - Introduction to Solid State Physics, J. Wiley (1968),

T. KASUYA - Magnetism, Rado and Suhl IIB, Academic Press, (1966).

a - Bohr magneton and Landé factor

Two fundamental problems of magnetism are the origin of the magnetic moments and the existence of magnetic ordering. The vector model allows for a simple understanding of the magnetic properties of free atoms. If one considers an incomplete electronic shell, after coupling each individual electronic orbital moment $\vec{L} = \sum_i \vec{l}_i$ and spin vectors $\vec{S} = \sum_i \vec{s}_i$, we consider that $\vec{L}$ and $\vec{S}$ are coupled through spin-orbit interaction to form the resultant angular momentum $\vec{J} = \vec{L} + \vec{S}$ Russel Saunders rule) $\vec{L}$ and $\vec{S}$ precess around their resultant $\vec{J}$ (fig. 1). Hund's rules are used to determine the most stable configuration. The magnetic moment of a classical circular



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orbit is $M_L = - \frac{e}{2mc} L$ which holds in quantum mechanics. Projection along the applied H direction gives $M_{L,z} = - \frac{e\hbar}{2mc} L_z$; $\mu_B = \frac{e\hbar}{2mc}$ is called the Bohr magneton. An electron with spin $s = 1/2$ possesses a 1 μ_B moment so $M_{S,z} = - 2 \mu_B S_z$ and the resultant magnetic moment is $\vec{M}_R = - \mu_D [\vec{L} + 2\vec{S}]$.

$\vec{M}_R$ precesses around J so

$$\vec{M}_J = - g_J \mu_B \vec{J}$$

with $g_J^J = |\vec{L} + 2\vec{S}| \cos \widehat{BOC}$

$= J + S \cos \widehat{ABO}$

As $L^2 = J^2 + S^2 - 2SJ \cos \widehat{ABO}$

$$g_J = 1 + \frac{J^2 + S^2 - L^2}{2J^2}$$

In an exact treatment $(J^2)_{op}$ has $J(J + 1)$ as eigen value... so

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

g_J is the Landé factor.

b - crystalline field

If one locates magnetic ions in a crystal, two points of view can be used in order to discribe its physical properties. One can find its properties from those of the insulated atom, with some modifications due to interactions between electronic shells. That is the Heitler-London approach. Alternatively one can find these properties by considering the properties of collective electrons in the crystal. These electrons are not free. They are submitted to the crystalline potential, to interactions with other electrons which give rise to some localization. This is the Hund-Mulliken type approach.

These two approaches are used in magnetism. The first one is frequently used for insulating materials whereas the second one is frequently used for metals. On the basis of the simplest point-charge ionic model the electrostatic potential $V(r, \theta, \varphi)$ due to the surrounding point charges at a point (r, θ, φ) near the origin is :

$$V(r, \theta, \varphi) = \sum_j \frac{q_j}{|\vec{R}_j - \vec{r}|}$$

where q_j is the charge at the j^{th} neighboring ion, at distance $\vec{R}_j$ from the origin. If the magnetic ion has a charge q_i at $(r_i, \theta_i, \varphi_i)$ then the perturbing crystalline potential energy will be

$$W_c = \sum_i q_i V_i = \sum_i \frac{q_i\ q_j}{|\vec{R}_j - \vec{r}_i|}$$

where V should satisfy the Laplace equation. Symmetry considerations provide some help to study cristalline potential since this potential possesses the symmetry of the crystalline charge distribution.

Crystalline fields affects often iron group ions and rare earth group ions on a different way, since major energy, is in the first case crystalline field energy, and in the second case spin orbit-coupling.

Consider a single electron with $L = 1$ in an orthorombic $(a \neq b \neq c\ ;\ \alpha = \beta = \gamma = \pi/2)$ crystalline potential. The crystalline energy is then

$$W_c = Ax^2 + By^2 - (A + B)\ z^2$$

Where A and B are functions of interatomic distances.

The ground state consists of 3 magnetic sub-levels. The three wave functions

$$U_x = z\ f\ r)$$
$$U_y = y\ f(r)$$
$$U_z = z\ f(r)$$

are orthogonal. We suppose they are normalized. They have the property

$$(\ell^2)_{op}\ U_i = l(l + 1)U_i = 2\ U_i$$

(non diagonal elements vanish). These levels do not lead to arbital moments (See for instance $\langle U_x | L_z | U_x \rangle = - i \int x \frac{\partial}{\partial \varphi} U_x\ d_x\ d_y\ d_z$ = imaginary number). We have $\langle U_x | L_x | U_x \rangle = \langle U_x | L_y | U_x \rangle = 0$, too. This is known as <u>quenching</u>. Time average of the magnetic orbital moment is zero. Suppose U_x is the ground state orbital wave function. For $S = 1/2$ there are 2 possible spin state $S_z = \pm 1/2$ (→ spin functions α and β).

Application of a field orients the spin moments which slightly unquench the orbital moment through spin-orbit coupling $\lambda L.S$. Perturbation theories give as a first approximation $\Psi = U_{x,\alpha} - \frac{i\lambda}{2\Delta_1} U_{y,\alpha}$ ... Then $\langle\Psi|L_z|\Psi\rangle = - \frac{\lambda}{\Delta_1}$, and the magnetic moment in the z direction is :

$$\langle\Psi|L + 2S|\Psi\rangle \mu_B = (1 - \frac{\lambda}{\Delta_1}) \mu_B,$$

giving $g = 2(1 - \frac{\lambda_1}{\Delta_1})$,;

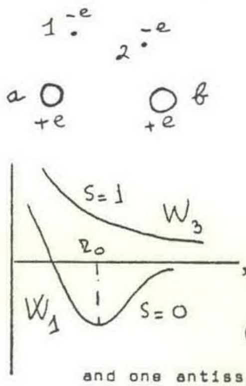
g value and magnetization are anisotropic ; they depend on Δ, which is largely volume dependent. Paramagnetic resonance or optical absorbtion allows for the discussion of these crystalline field effects. They are of a large importance for magnetism since magnetization processus depends on magnetocrystalline anisotropy where crystalline fields play a fundamental role. Due to spin-orbit interactions the charge distribution is less symmetric. This lack of symmetry is tied to the direction of magnetization. Thus changing the spin direction changes the overlap energy. For an uniaxial crystal the anisotropic part of energy is $W_a \simeq \frac{\lambda^2}{\Delta} \cos^2\theta$ for instance in transition metal ions, where θ is the angle between the crystallographic axis and the direction of the magnetization. The case of rare earths is simplier. J is then a good quantum number and the transitions to be considered are $|L\ S\ J\ J_z\rangle \rightarrow |L\ S\ J\ J'_z\rangle$. In the case of rare earth metals, of hexagonal compact symmetry, the anisotropy is then simply proportionnal to $(1,63 - \frac{c}{a})$ where 1,63 is the ideal compact c/a ratio. Uniaxial stress will modify this anisotropy in a large extend.

c - exchange interactions

Dipolar effects are usually negligible. Interactions between magnetic moments have an electrostatic origin. The interaction mechanisms are numerous. The direct exchange mechanism usually plays a minor role in magnetic solids though it has a fundamental importance for simple molecules. If one considers a hydrogen molecule, one can built molecular functions from individual ones. Due to Pauli principle, there are 3 symmetric wave functions, with total spin S = 1 (++), (--), (+-)+ (-+) and one antissymmetric with S = 0 (+-)-(-+) . If we take into account Coulomb interactions and evaluate the energy of the singulet (W_1) and triplet (W_3) states as a function of interatomic distances, one obtains the result that the non magnetic S = 0 state is the stable one, with interatomic distance r_0. The type of discussion is quite different in magnetic solids since as a first approximation distances are given independently of the magnetic state of ions. In this case, however, as well as for hydrogen molecule, exchange interactions between spins S_a and S_b of ions a and b can be written as :

a $$H = - 2J_{ab} \vec{S}_a.\vec{S}_b .$$

J_{ab} is a function of interatomic distances which is very difficult to evaluate <u>ab-initio</u>



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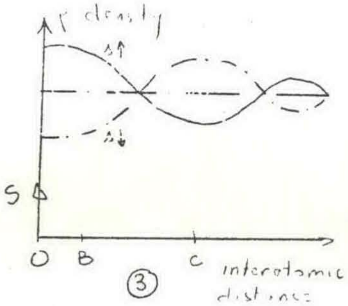
Many criticisms can be done concerning this hamiltonian, due to the non-orthogonality of the wave functions in the atomic orbital model. As previously mentionned many indirect exchange mechanisms are important in solids. Interactions through conduction electrons can be understood as indicated fig. 3. Consider a magnetic ion with a spin S in O. It polarizes on a different footing ↑ or ↓ electrons, giving rise to a dissymmetric electronic density ρ. A magnetic ion, located in B will be ferromagnetically aligned with $\vec{S}$ in O. Whereas this magnetic atom, when located in C will be antiferromagnetically aligned.



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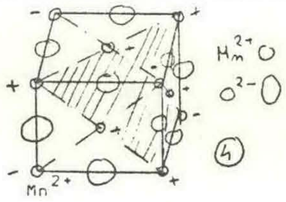
Superexchange mechanisms play the major role in insulating substances. Consider for instance MnO (fig. 4) which is antiferromagnetic. The magnetic arrangement can be described as ferromagnetic plans antiferromagnetically stacked along one of the body diagonal.



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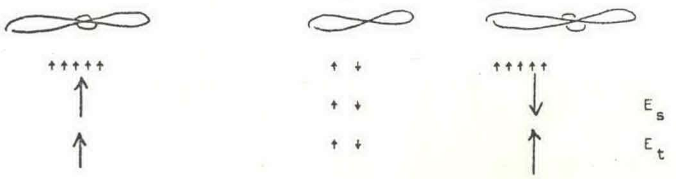
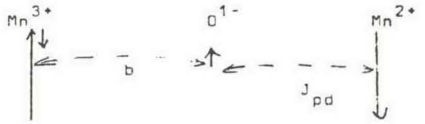


In the fundamental state the singulet and triplet states possess the same energy. These two states are degenerated. Coupling results from the hybridation of fundamental and excited states, described as below.

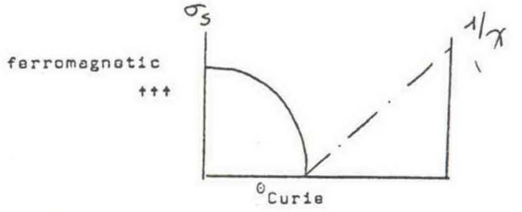


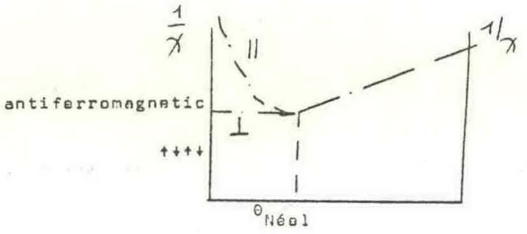
According to J_{pd} sign, exchange interaction is ferro- or antiferromagnetic. Magnetic energy depends on J_{pd} exchange interaction, b transfer and excited energies of Mn^{2+} ions. A priori considerations are difficult in order to give the sign of the variation of these exchange interactions with interatomic distances, since exchange interactions, affinity considerations and energy levels are to be considered. In many oxides the situation is even more complicated, due to the possible variation with pressure of the angle of superexchange interaction.

All cases discussed above can be treated, as a first approximation with the Heisenberg isotropic exchange hamiltonian

$$H = -2 \sum_{(i,j)} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

Approximation, such as molecular field theory will be used in order to facilitate the description of the energy states. Main properties encountered are summarized in the figure below, where σ_s is the magnetization within an elementary domain





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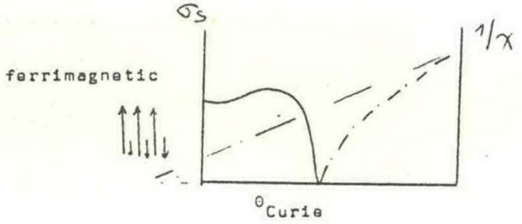


Non colinear configurations will be discussed when necessary.

2 - Thermodynamics

Ref. : D. BLOCH - Ann. de Phys. I, 93, (1966),
A. HERPIN - Théorie du magnétisme, (op. cit.).

a - Gibbs function and volume magnetostriction

We consider an isotropic magnetic sample of 1 g at temperature T, pressure p, under magnetic field H (intensive variables). It has a volume V, a magnetic moment σ and an entropy S (extensive variables). The energy used to modify adiabatically its magnetic moment by $d\sigma$ is $dU = H.d\sigma$.

According to first law of thermodynamics, in an infinetesimal transformation, the variation of internal energy for the closed system is

$$dU = dQ + Hd\sigma - pdV = TdS + Hd\sigma - pdV.$$

We can introduce a Gibbs magnetic function,

$$G = U - TS + pV - H\sigma ,$$

such as the minimum of G gives the equilibrium situation.

In an elementary reversible transformation :

$$dG = - SdT + Vdp - \sigma dH.$$

Then

$$\left(\frac{\partial V}{\partial H}\right)_{T,p} = - \left(\frac{\partial \sigma}{\partial p}\right)_{H,T}.$$

The variation of magnetization with pressure is equal to that of volume with applied field.

b - Molecular field theory

Molecular field theory allows for a simple treatment of exchange interaction.

$$H = -2 \sum_{(i,j)} J_{ij} S_i S_j .$$

J_{ij} is often a rapidly decreasing function of interatomic distances R_{ij}. We will, for simplicity, take in account exchange interactions J_{ij} between identical first neighbours only $J_{ij} = J$.

If we suppose that spin S alone contributes to magnetic moment μ, then

$$\vec{\mu} = 2 \mu_B \vec{S}$$

and

$$H = - \frac{J}{4\mu_B^2} \sum_i \vec{\mu}_i \sum_j \vec{\mu}_j .$$

We can define

$$\vec{H}_m = \sum_j \frac{J}{4\mu_B} \vec{\mu}_j = \sum_j n_j \vec{\mu}_j .$$

The hypothesis of molecular field is to consider $\vec{H}_m$ as time independent. Then :

$$<H> = - \sum_i <\vec{\mu}_i . \vec{H}_m> = - \sum_i <\vec{\mu}_i><\vec{H}_m>$$

$<\vec{H}_m>$ is called the molecular field.

$$<\vec{H}_m> = \sum_j n_j <\vec{\mu}_j> = z \, n_j \frac{\sigma_s}{N} = \frac{z \, J \, \sigma_s}{4\mu_B^2 \, N} = N \sigma_s$$

Where σ_s is the spontaneous magnetization of the system of N atoms.

N is the molecular field coefficient.

When the orbital moment contributes to the magnetic moment,

$$<\vec{\mu}_j> = g \mu_B <\vec{J}> = \vec{\mu}_B <\vec{J}+\vec{S}> = \mu_B <\vec{J}> + \mu_B <\vec{S}>$$

Then

$$<\vec{J}> = \frac{<\vec{S}>}{g-1}$$

$$<\mu> = \frac{g}{g-1} \mu_B <\vec{S}>$$

The internal energy of the system is

$$U_M = - \frac{N}{2} \sum_i <\vec{\mu}_i> \sum_j <\vec{\mu}_j> = - \frac{1}{2} N \sigma_s^2$$

The associated magnetic specific heat is :

$$C_m = \frac{\partial U_M}{\partial T} .$$

c - First order magnetic transition

Let us consider a system with a first order magnetic transition at temperature θ_t, when submitted to p_t and H_t. This transition is characterized by a discontinuity in the derivatives of the thermodynamical potential G as a function of T, p or H, that is by a discontinuity in S, V or σ. We call A and B the two phases. At equilibrium $G_A = G_B$, under θ_t, p_t, H_t. This transition can be modified with temperature, pressure or field.

At the new transition $G'_A = G'_B$, so

$dG_A = dG_B$.

At constant magnetic field :

$$S_A\, d\theta_t + V_A dp_t = S_B\, d\theta_t + V_B dp_t$$

$$\frac{\partial \theta_t}{\partial p_t} = - \frac{\sigma_B - \sigma_A}{S_B - S_A} = \frac{V_B - V_A}{L}\ \theta_t$$

Where L is the latent heat for the transition. That is the Clapeyron equation.

At constant pressure

$$\frac{\partial \theta_t}{\partial H_t} = - \frac{\sigma_B - \sigma_A}{S_B - S_A} = - \frac{\sigma_B - \sigma_A}{L}\ \theta_t$$

At constant temperature

$$\frac{\partial p_t}{\partial H_t} = \frac{\sigma_B - \sigma_A}{V_B - V_A}.$$

d - Second order magnetic transition

When second derivatives of G are discontinuous at temperature θ_m, under p_m and H_m, then entropy, volume and magnetization are continuous

$dV_A = dV_B$,

$dS_A = dS_B$,

$d\sigma_A = d\sigma_B$.

At constant field for instance

$$\left(\frac{\partial V_A}{\partial T}\right)_H d\theta_m + \left(\frac{\partial V_A}{\partial p}\right)_H dp_m = \left(\frac{\partial V_B}{\partial T}\right)_H d\theta_m + \left(\frac{\partial V_B}{\partial p}\right)_H dp_m$$

Thus

$$\frac{d\theta_m}{dp_m} = \frac{K_A - K_B}{\beta_A - \beta_B}$$

where β is the volume expansion coefficient.

One could obtain 8 other relations for $\frac{d\theta_m}{dp_m}$, $\frac{d\theta_m}{dH_m}$, $\frac{dH_m}{dp_m}$ But considerable care should be taken in magnetism since the application of field leads to a magnetization at all temperatures and theory of second order transition cannot be applied.

If we take the molecular field as :

$$H_m = N(V)\ \sigma_s$$

Where σ_s is the spontaneous magnetization, and N a function of the volume alone, then

$$U(T) = U_L(T) - \frac{1}{2} N(V)\ \sigma_s^2(T)$$

where U_L is the internal energy of the lattice.

Then for H = 0

$$dU = \left(\frac{\partial U_L}{\partial T} - \frac{N}{2}\frac{\partial \sigma_s^2}{\partial T}\right) dT + \left(\frac{\partial U_L}{\partial V} - \frac{1}{2}\frac{dN}{dV}\ \sigma_s^2 - \frac{N}{2}\frac{\partial \sigma_s^2}{\partial V}\right)\frac{dV}{T}$$

The entropy change is : $dS = \frac{dQ}{T} = \frac{1}{T}\left[dU + pdV\right]$.

$$= \left(\frac{\partial U_L}{\partial T} - \frac{N}{2}\frac{\partial \sigma_s^2}{\partial T}\right)\frac{dT}{T} + \left(\frac{\partial U_L}{\partial V} - \frac{1}{2}\frac{dN}{dV}\ \sigma_s^2 - \frac{N}{2}\frac{\partial \sigma_s^2}{\partial V} + p\right)\frac{dV}{T}$$

dS is a perfect differential, then :

$$\frac{\partial}{\partial V}\left[\frac{\partial U_L}{T\partial T} - \frac{N}{2T}\ \frac{\partial \sigma_s^2}{\partial T}\right] = \frac{\partial}{\partial T}\left(\frac{1}{T}\right)\left(\frac{\partial U_L}{\partial V} - \frac{1}{2}\frac{dN}{dV}\sigma_s^2 - \frac{N}{2}\frac{\partial \sigma_s^2}{\partial V} + p\right)$$

$$\frac{\partial}{\partial T}\left(\frac{P}{T}\right) = \frac{1}{T^2}\ \frac{\partial U_o}{\partial V} - \frac{1}{2T^2}\left(\frac{dN}{dV}\sigma^2 + N\frac{\partial \sigma^2}{\partial V}\right)$$

The pressure p consists of two terms, a classical pressure p_o, given by

$$\& \quad \frac{\partial}{\partial T}\ \frac{p_o(T,V)}{T} = \frac{1}{T^2}\frac{\partial U_o}{\partial V}$$

and a magnetic pressure

$$\frac{\partial}{\partial T}\frac{p_m(T,V)}{T} = -\frac{1}{2T^2}\left(\frac{dN}{dV}\ \sigma^2 + N\frac{\partial \sigma^2}{\partial V}\right)$$

Below the Curie temperature :

$$\sigma_s = \sigma_s^o\, B_J\left(\frac{H_m}{T}\right) = \sigma_s\, B_J\left(\frac{N\sigma_s}{T}\right)$$

which can be expressed as

$$\sigma_s^2 = f\left(\frac{N}{T}\right)$$

Then

$$\frac{\partial \sigma_s^2}{\partial T} = -\frac{N}{T^2}\, f'\left(\frac{N}{T}\right)$$

$$\frac{d\sigma^2}{dV} = \frac{1}{T}\frac{dN}{dV}\, f'\left(\frac{N}{T}\right)$$

$$= -\frac{1}{T}\frac{dN}{dV}\frac{T^2}{N}\frac{\partial \sigma_s^2}{\partial T} = -T.\ \frac{d\log N}{dV}\ .\ \frac{\partial V}{\partial T}\ .$$

$$\frac{\partial}{\partial T}\left(\frac{p_m(T,V)}{T}\right) = -\frac{1}{2T^2}\ \frac{dN}{dV}.\left[\sigma^2 - T\frac{\partial N}{\partial T}\right]$$

$$= \frac{1}{2}\ \frac{dN}{dV}\ \frac{\partial}{\partial T}\left(\frac{\sigma_s^2}{T}\right)$$

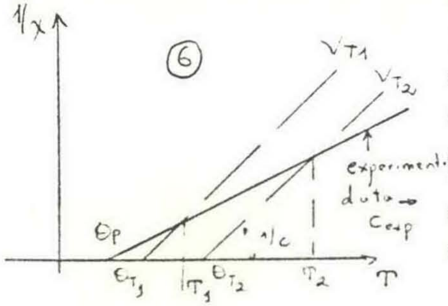
so

$$p_m = \frac{\sigma_s^2}{2}\ \frac{dN}{dV}$$

this additional pressure is responsible of the anomalous dependence of thermal expansion coefficient of magnetically ordered system.

e - Secondary effects

Variation with thermal expansion (and lattice vibrations) of exchange interaction coefficients can lead to unexpected behavior of magnetic systems. It is often important to think about these effects in order to understand the thermal variation of magnetization, magnetic susceptibility, magneto-crystalline anisotropy coefficients, or nature of the magnetic phase transition. We will discuss only about paramagnetic data. We consider the high temperature behavior of a ferro-magnetic substance, with a thermal expansion coefficient β.



If the volume of the sample is constant, equal to that observed at temperature T_1, we have the

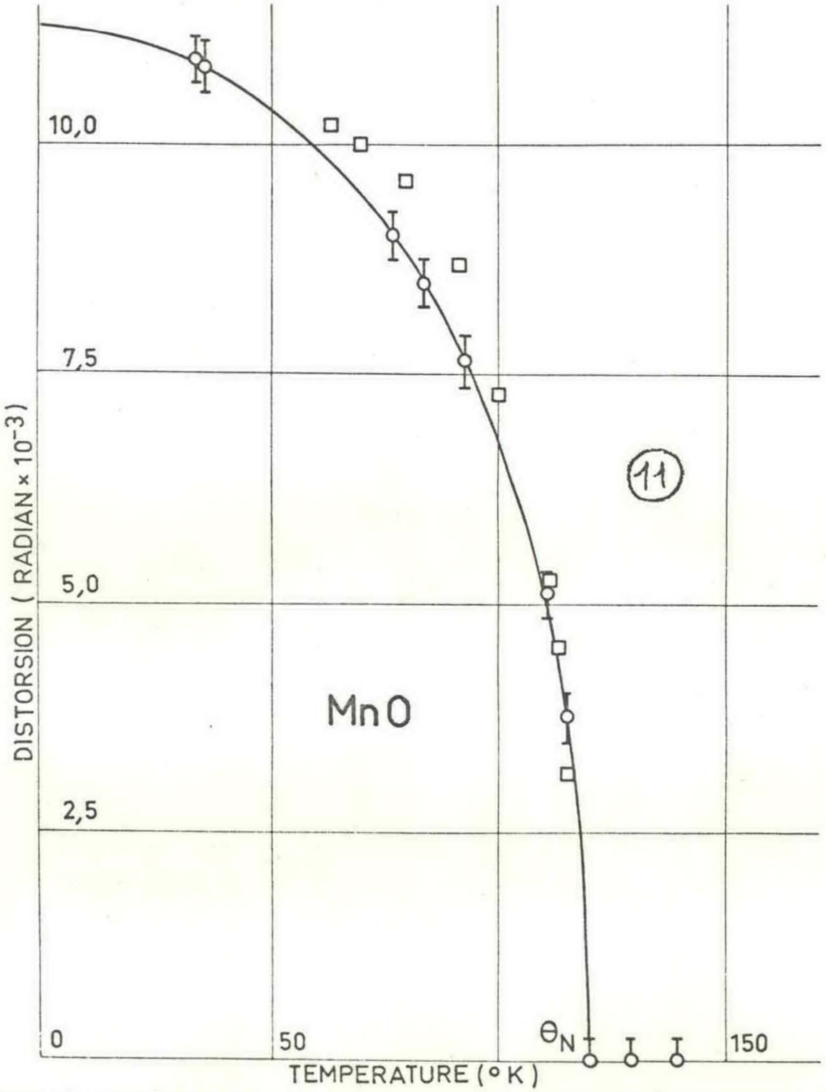
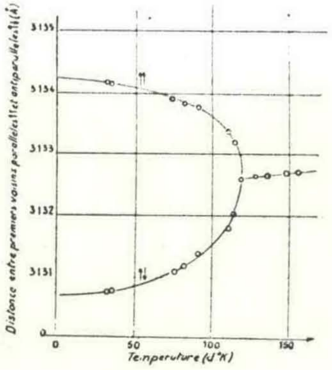


Figure 16 : Variation thermique de la distorsion rhomboédrique dans MnO : ○
comparaison avec l'aimantation des sous-réseaux : □



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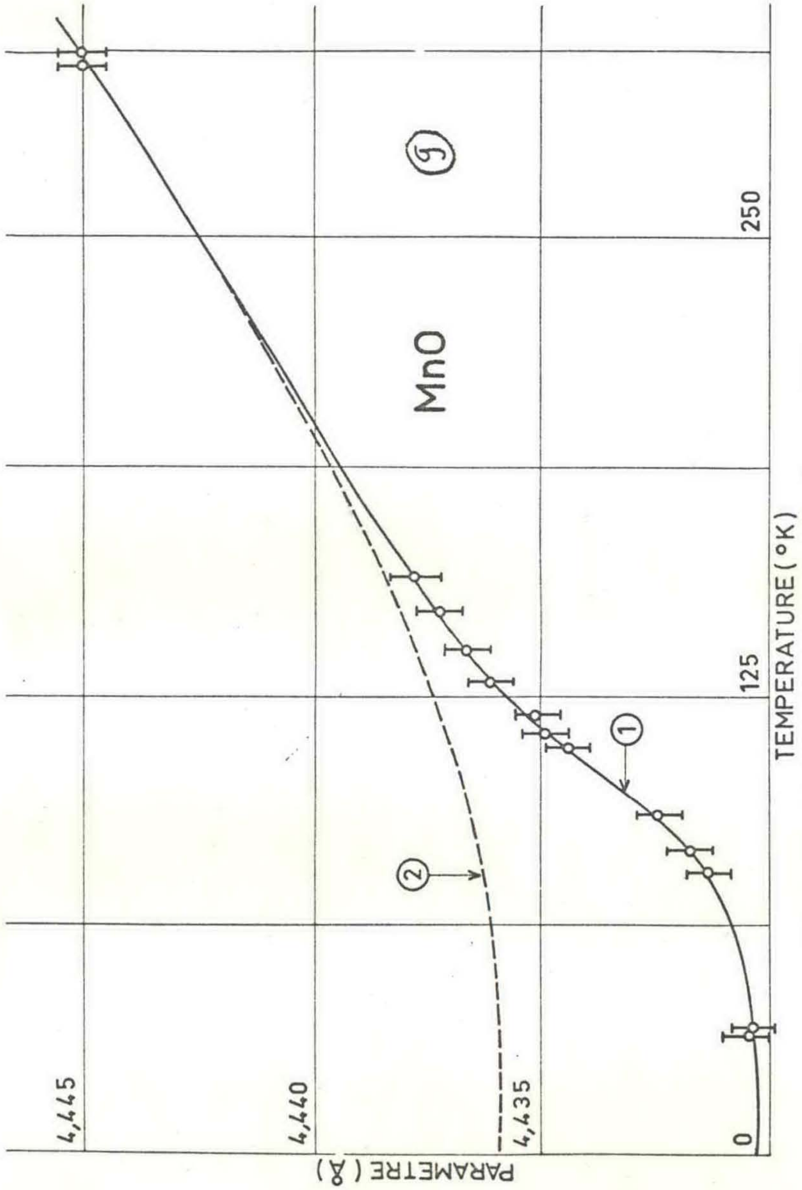


Figure 15 : Variation thermique du paramètre de MnO
1) variation expérimentale; 2) variation calculée en l'absence de magnétostriction.

Curie-Weiss law $\frac{1}{\chi} = \frac{T - N_1C}{C}$, where C is the Curie constant , and N_1C the Curie temperature. If the volume of the sample is that at T_2, then $\frac{1}{\chi} = \frac{T - N_2C}{C}$.

Experimental data can be analysed as

$$\frac{1}{\chi} = \frac{T - \Theta_p}{C_{exp}}$$

but experimental C_{exp} can be quite different from spectroscopic C (fig.6).

We can write

$$\Theta_p = N \, |1 + \lambda T| \, C$$

so

$$\frac{1}{\chi} = \frac{T - N\,[1 + \lambda T]\,C}{C} = \frac{T\,[1 - \lambda CN] - NC}{C}$$

$$= \frac{T - N/1 -. \lambda CN}{\frac{C}{1-\lambda CN}}$$

and

$$\Theta_p = \frac{NC}{1-\lambda NC} \qquad C_{exp} = \frac{C}{1 - \lambda CN}$$

$$\approx \frac{C}{1 - \lambda\Theta_p}$$

Value of λ is necessary in order to get C from C_{exp}. From the variation of Curie temperature with volume we have

$$\gamma = \frac{d \log r}{d \log} = \frac{d \log \Theta_p}{d \log V} \simeq - \frac{1}{K} \frac{d\Theta_p}{\Theta_p}$$

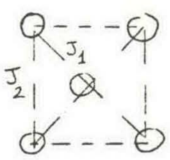
as $\lambda = \frac{1}{\theta_p} \frac{d\theta_p}{dT} = \frac{V}{\theta_p} \frac{d\theta_p}{dV} \frac{1}{V} \frac{dV}{dT}$

$$\lambda = - \frac{1}{K} \frac{d\theta_p}{\theta_p} \cdot \beta.$$

λ can be then experimentally determined.

3 - Magnetostriction in MnO - R. GEORGES, Thesis, Grenoble (1969)

a - Pressure



Magnetic properties of NaCl type MnO can be explained using two types of exchange interactions: J_1 between first neighbours and J_2 between second neighbours. A Mn^{2+} ion has 6↑↑ and 6↑↓ first neighbours and 6↑↓ second neighbours.

Spontaneous variations of interatomic distances due to magnetostriction are weak, so we can use :

$j_1 = \frac{d \log |J_1|}{d \log r_1}$, and $j_2 = \frac{d \log |J_2|}{d \log r_2}$.

to describe the observed phenomena, r_1 is the distance between nearest neighbours (nn) and r_2 the distance between next nearest neighbours (nnn).

Variation of Néel temperature with pressure allows for the determination of j_2, since, according to the molecular field theory

$\theta_N = - 12J_2 \frac{S(S+1)}{3}$ (θ_N = 118 K at Rp)

In principle, variation of paramagnetic Curie temperature with pressure allows then the determination of j_1, since :

$\theta_p = + (12J_1 + 6J_2) \frac{2S(S+1)}{3}$ (θ_p = - 610 K at Rp).

Values of J_1 and J_2 as given by molecular field theory and other theory (green function) are :

J_1 = - 7,2 K (MF) or - 5 K (GF)

J_2 = - 3,5 K (MF) or - 5,5 K (GF)

For example :

$$\frac{\delta V}{V} = - K\delta p$$

$$\frac{\delta r_2}{r_2} = - \frac{1}{3} K\delta p$$

$$J_2 = - \frac{3}{K} \frac{1}{\Theta_N} \frac{\delta\Theta_N}{\delta p}$$

We have not taken there in account the effect of thermal expansion of the lattice, which is usually negligible.

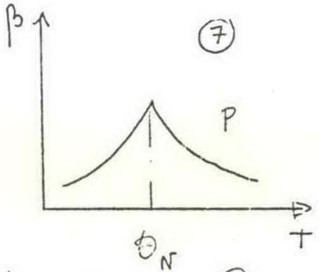
Variation of Θ_N with p can be determined using the thermal variation of the thermal expansion coefficient β measured at various constant pressures.

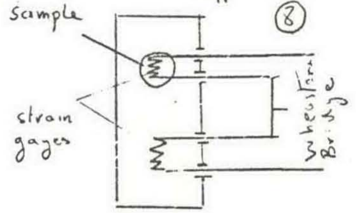
β is determined for instance with strain gages (fig.). The result (up 3000 bar) i

$$\frac{d\Theta_N}{dp} = (0.30 \pm 0.02) \times 10^{-3} \text{ K/bar}^{-1},$$

then J_2 = - 10.8 (MF).

(RT compressibility is 0.70×10^{-6} bar^{-1}).





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b - X-Rays

X-Rays studies have been undertaken on MnO, between 30 K and RT. Results thus obtained are given (fig. 9, 10). The parameter a is the distance between nnn. First neighbours (nn) ↑↑ or ↑↓ behave on a different manner giving rise to a lattice distorsion.↑↑ go apart, whereas ↑↓ come closer. Volume anomaly at absolute zero is $\left(\frac{\Delta V}{V}\right)_0 = - (3.8 \pm 0.4) \times 10^{-3}$, value which can be obtained from a careful extrapolation of the non-magnetic high temperature a - T relation. Distorsion of the lattice (fig. 11) is easily determined from X-rays data.

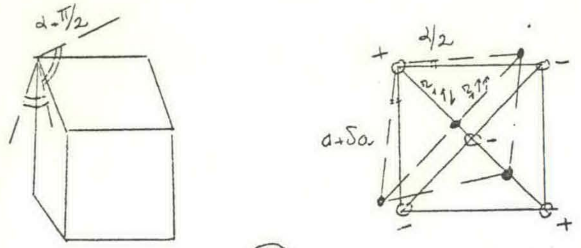
c - Magnetostriction

Magnetic energy as well as elastic energy are functions of interatomic distances.

Crystalline anisotropy of MnO is weak, so, at low temperature we can consider the equilibrium conditions as given by :

$$\frac{\partial W_{elast}}{\partial u} + 2 \sum_{(i,j)} \overline{\vec{S}_i . \vec{S}_j} \frac{\partial J_{ij}}{\partial u} = 0,$$

where u, v,... are the crystallographic parameters. The crystal obtained, after deformation, possesses the common symmetries of $W_{elast.}$ and $W_{magn.}$. When the magnetic system does not possess all the symmetry elements of the lattice, in the absence of magneto-elastic interactions, then the crystal distorts, keeping only the common symmetry elements. (in fact in ferromagnetic substances, there is a slight magnetostriction due to domains arrangments).



(12)

α is a measure of the distorsion, and

$$r_1\uparrow\downarrow = \frac{a\sqrt{2}}{2}\left(1+\frac{\delta a}{a}+\frac{\alpha}{2}\right)$$

$$r_1\downarrow\uparrow = \frac{a\sqrt{2}}{2}\left(1+\frac{\delta a}{a}-\frac{\alpha}{2}\right)$$

$$r_2\uparrow\downarrow = a\left(1+\frac{\delta a}{a}\right)$$

where $r_1\uparrow\downarrow$ is the distance between antiparallel nn and $r_1\uparrow\uparrow$ the distance between parallel nn.

In the molecular field approximation (MF), then for a mole, of volume V_m :

$$\delta W_m = N\bar{S}_Z^2\left(6J_1(r_1\uparrow\uparrow) - 6J_1(r_1\uparrow\downarrow) - 6J_2(r_2)\right)$$

and, variation of W_m, due to magnetostriction is

$$\delta W_m = 6N\bar{S}_Z^2\left(J_1J_1\ \alpha - J_2J_2\ \frac{\delta a}{a}\right)$$

and

$$W_{elast} = V_m\left[\frac{c_{11}}{2}(e_{xx}^2+e_{yy}^2+e_{zz}^2) + c_{12}(e_{yy}e_{zz}+e_{zz}e_{xx}+e_{xx}e_{yy}) + \frac{1}{2}c_{44}(e_{yz}^2+e_{zx}^2+e_{xy}^2)\right]$$

As $e_{xx} = e_{yy} = e_{zz} = \frac{\delta a}{a}$

$e_{yz} = e_{zx} = e_{xy} = -\alpha$

$$\delta W_{el} = \frac{3}{2}V_m\left[(c_{11}+2c_{12})\left(\frac{\delta a}{a}\right)^2 + c_{44}\alpha^2\right]$$

δW_m and δW_{el} can be expressed as a function of the two modes of deformation : isotropic contraction $\frac{\delta a}{a}$ and rhomboedral distorsion α.

Equilibrium considerations (parameters $\frac{\delta a}{a}$, and α) give :

$$\alpha = -\frac{2N}{V_m}\frac{J_1\ J_1\ S_2^2}{c_{44}}$$

$$\frac{\delta a}{a} = \frac{2N}{3V_m}K\ J_2\ J_2\ S_2^2 = +\frac{1}{3}\frac{\delta V}{V}$$

with $K = \frac{3}{c_{11}+2c_{12}}$

isotropic $\frac{\delta a}{a}$ depends only on J_2 and its variation, whereas α depends only on J_1 and its variation. For MnO

$c_{11} = 2.2 \times 10^{12}$ dyne.cm^{-2}

$c_{12} = 1.1 \times 10^{12}$ - -

$c_{44} = 0.87\times 10^{12}$ - -

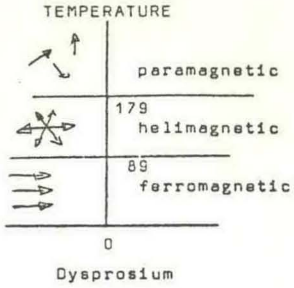
From J_1 and J_2 as given by MF, and $\frac{\delta a}{a}$, α, given by RX measurements $J_1 = -21$, $J_2 = -18$. From J_1 and J_2 as given by GF : $J_1 = -26$, $J_2 = -12$, to be compared with -10.8 ± 0.6 given by pressure experiments. GF values for J_1 and J_2 are thus better than those given by MF approximation. Further experiments are needed to discuss on j_1 and J_1, such as pressure, or stress effects measurements.

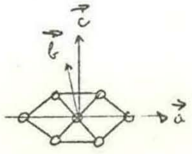
4 - Magnetostriction in Dysprosium

Ref. : - COOPER, Solid State Phys. N° 21, 393 (1968)
- BARTHOLIN, Thesis, Grenoble, (1970).

Our next example is Dysprosium (Dy) which has a large magnetocrystalline anisotropy. We will show how high pressure or stress experiments can lead to a quantitative understanding of the magnetostriction phenomena of Dy. These are of peculiar importance in this type of magnetic substance since the magnetic ordering itself is largely dependent on magnetostriction phenomena.

Rare earth metals can be describe as an assembly of ions, generally trivalent with incomplete 4f shells, immersed in a sea of conduction electrons. The 4f electrons, which occupy a deep shell, play a secondary role in their chemical and mechanical properties. On the other hand, they are at the origin of the magnetic moment. The magnetic moment of the ions R^{3+} in the metal is that of the free ions. Thus, if we neglect the induced magnetization of the conduction electrons, the magnetic moment at absolute saturation does not depend upon T or p. The arrangement of the spins in preferential planes or along preferential directions results from the magneto-crystalline anisotropy, magnetoelastic and exchange energies.





a - Experimental data

At atmospheric pressure the Néel temperature Θ_N of dysprosium is 179 K. Hydrostatic pressure experiments show that Θ_N decreases with pressure at the rate of $(-0.41 \pm 0.01)\ 10^{-3}$ K bar^{-1}. Uniaxial stress applied along the orthogonal $\vec{a}$ (100), $\vec{b}$ (110), $\vec{c}$ (001) axes leads to the results given fig.14,16 The $\vec{c}$ axis is the hexagona axis, whereas $\vec{a}$ axis joins first neighbours in the basal plane and is perpendicular to the c-axis. Experimental configuration is given fig. 13.

The Néel temperature of Dy can be written as

$$k\Theta_N = \frac{2}{3}(g_J - 1)^2 J(J+1) I(q) + \frac{2}{5} \tilde{V}_0^2 (J - \frac{1}{2})(J + \frac{3}{2})$$

where q is the magnetic helical pitch, I(q) an exchange coefficient, $\tilde{V}_0^2$ is the first uniaxial anisotropy coefficient.

The contribution Θ_N^a of magnetocrystalline anisotropy to the Néel temperature is 19.3 K. This value can be deduced from the anisotropy of the paramagnetic Curie temperature $\Theta_{p//} - \Theta_{p\perp} = -58$ K. Θ_N^a is simply proportionnal to

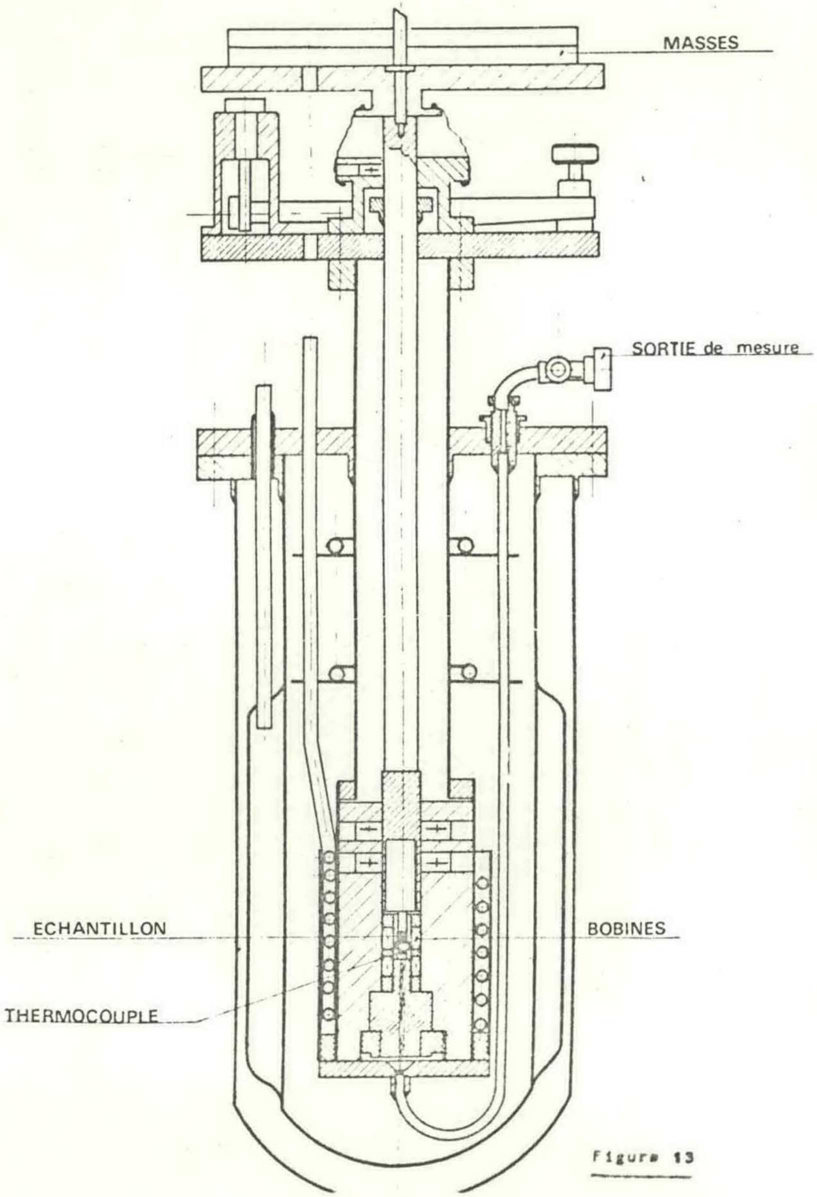


Figure 13

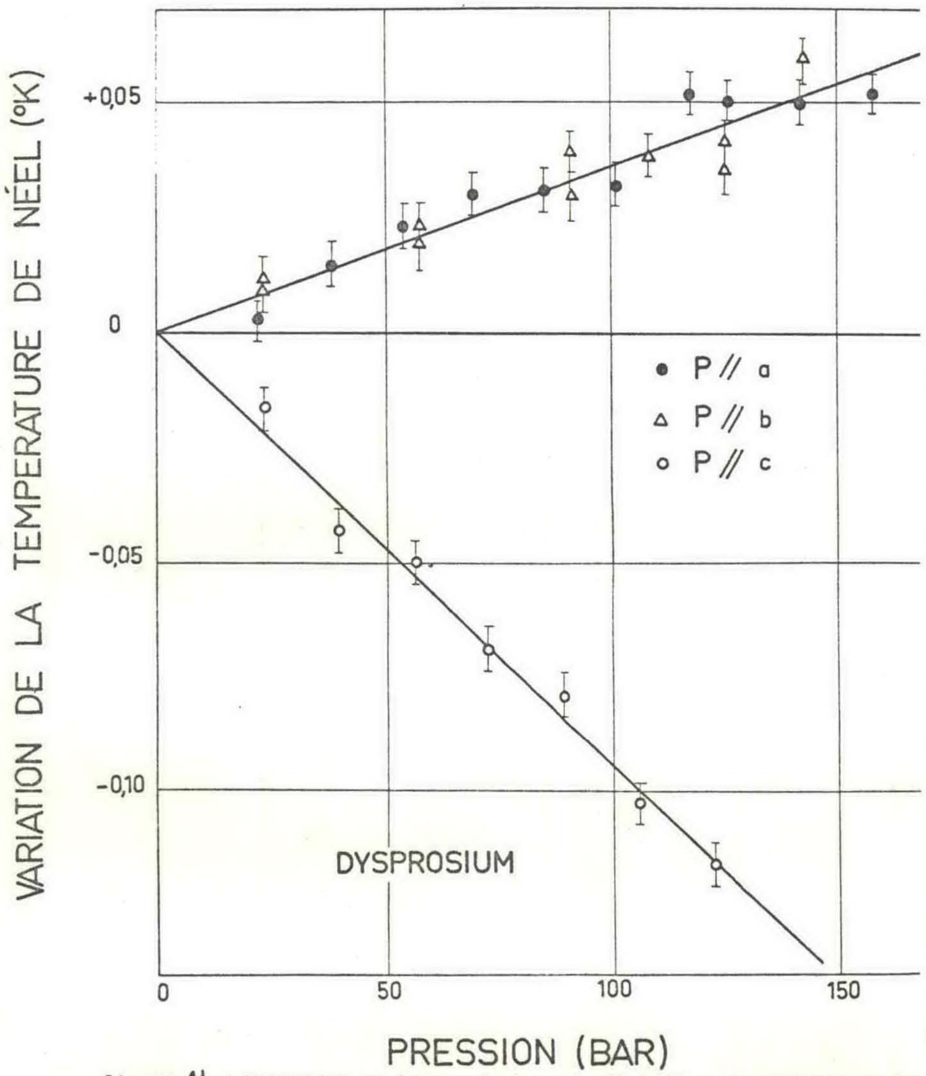
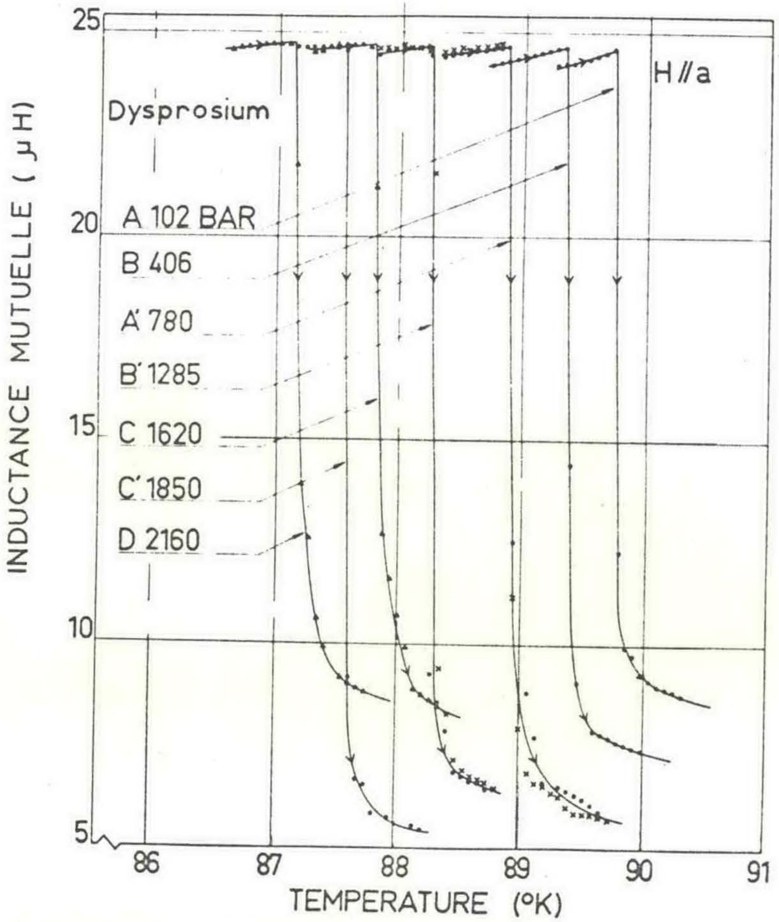


Figure 14 : Variation de la température de Néel d'un monocristal de Dy soumis à des contraintes uniaxiales suivant l'axe *a*, l'axe *b* ou l'axe



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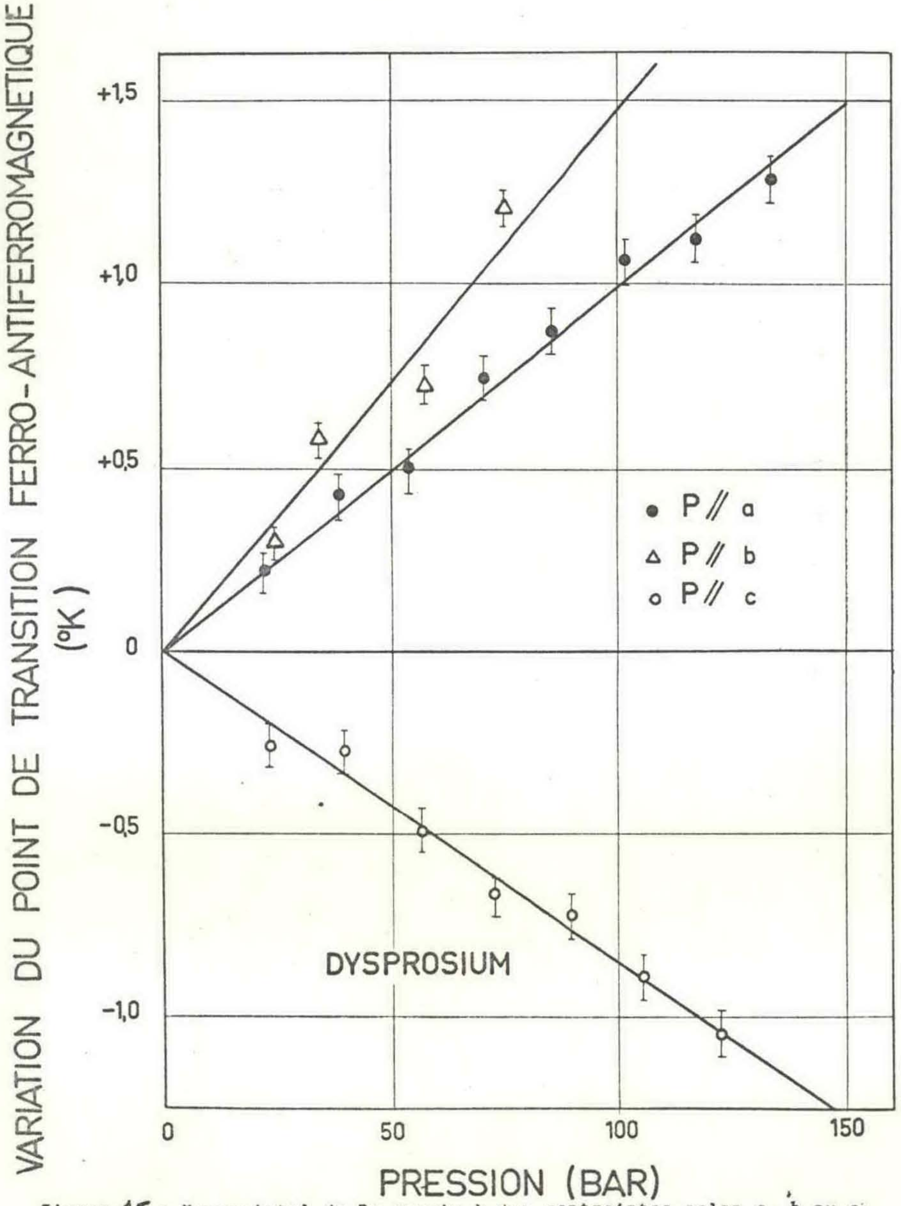

Figure 16 : Monocristal de Dy soumis à des contraintes selon *a*, *b* ou *c*

$\frac{1}{a^3}$ (1.636 - c/a) in the crystalline field model. Thus pressure modifies θ_N^a by 0.07×10^{-3} K bar^{-1}, whereas uniaxial stress, applied along the c axis, modifies θ_N^a by 0.84×10^{-3} K bar^{-1}.

The variation of θ_F^{AF} with uniaxial stress is quite large, and of opposite sign when stress is applied along a or b axes and c axis (fig. 16).

From data on θ_N, we deduce :

$$\left(\frac{\partial(I/k)}{\partial \log a}\right)_{b,c} = \left(\frac{\partial(I/k)}{\partial \log b}\right)_{a,c} = -57.4 \text{ K/bar}$$

$$\left(\frac{\partial(I/k)}{\partial \log c}\right)_{a,b} = 230 \text{ K/bar.}$$

b - Spontaneous magnetostriction

The free energy can be written as

$$F = H_{elast} + \langle H_{me} \rangle + \langle V \rangle + F^0_{magn}$$

for homogeneous lattice deformations

where $\langle H_{me} \rangle$ and $\langle V \rangle$ are mean values of magnetoelastic and magnetocrystalline energies. We will consider that magnetic energy is due to isotropic exchange and that magnetocrystalline coefficients come from a crystalline field model as discussed above. In the hexagonal structure of Dy we can describe the lattice deformations by independent "modes" as described fig. 17.

Then :

$$F = \frac{1}{2} c_{11}(e_{aa}^2 + e_{bb}^2) + \frac{1}{2} c_{33} e_{cc}^2 + c_{12} e_{aa} e_{bb}$$

$$+ c_{13}(e_{aa} e_{cc} + e_{bb} e_{cc}) + V + I(\vec{q})\, M^2 S^2$$

$$- kT \log \left[\sum_{m-J}^{J} \exp \frac{m}{kT} \left[g_J\, \mu_B\, H + 2\, I(\vec{q})\, M(g_J - 1)\, S \right] \right]$$

Where M is the relative magnetization M(T)/M(0).

In order that $<H_{me}>$ appears, we develop at first order exchange and magnetocristalline anisotropy energy

$$I(q) = I(a_o, b_o, c_o) + \left(\frac{\partial I}{\partial \log a}\right)_{bc} e_{aa} + \left(\frac{\partial I}{\partial \log b}\right)_{ac} e_{bb}$$

$$+ \left(\frac{\partial I}{\partial \log c}\right)_{ab} e_{cc}, \text{ with } \left(\frac{\partial I}{\partial \log a}\right)_{bc} = \left(\frac{\partial I}{\partial \log b}\right)_{ac}$$

$$V = V(a_o\ b_o\ c_o) + \left(\frac{\partial V}{\partial \log a}\right)_{bc} e_{aa} + \left(\frac{\partial V}{\partial \log b}\right)_{ac} e_{bb}$$

$$+ \left(\frac{\partial V}{\partial \log c}\right)_{ab} e_{cc}.$$

Then, when H = 0, we get the spontaneous magnetostriction, by minimization of F versus e_{aa}, e_{bb} and e_{cc},

$$e_{aa} = \frac{A(c_{11}c_{33} - c_{13}^2) - B(c_{12}c_{33} - c_{13}^2) - C(c_{13})(c_{11} - c_{12})}{(c_{11} - c_{12}) \left[c_{33}(c_{12} + c_{11}) - 2c_{13}^2\right]}$$

$$e_{bb} = \frac{A(c_{12}c_{33} - c_{13}^2) + B(c_{11}c_{33} - c_{13}^2) - C(c_{13})(c_{11} - c_{12})}{(c_{11} - c_{12}) \left[c_{33}(c_{12} + c_{11}) - 2c_{13}^2\right]}$$

$$e_{cc} = \frac{-(A + B)\, c_{13} + C(c_{12} + c_{11})}{c_{33}\,(c_{12} + c_{11}) - 2c_{13}^2}$$

with

$$A = M^2\, S^2\, k \left[\left(\frac{\partial (I/k)}{\partial \log a}\right)_{b,c} - \left(\frac{\partial V}{\partial \log a}\right)_{b,c}\right]$$

$$B = M^2\, S^2\, k \left[\left(\frac{\partial (I/k)}{\partial \log b}\right)_{a,c} - \left(\frac{\partial V}{\partial \log b}\right)_{a,c}\right]$$

$$C = M^2\, S^2\, k \left[\left(\frac{\partial (I/k)}{\partial \log c}\right)_{a,b} - \left(\frac{\partial V}{\partial \log c}\right)_{a,b}\right]$$

a - in the helimagnetic range, the hexagonal symmetry remains and $V = \frac{1}{2} \bar{V}_0^2 \sim \frac{1}{a^3} \left(1.636 - \frac{c}{a}\right)$

$\frac{\partial \log V}{\partial \log i}$ can be determined by a simple calculation as the elastic coefficients of Dy are known

$\frac{\partial I/k}{\partial \log i}$ are given from the experiments in which the Néel temperature of Dy is studied under stress

$$\left(\frac{\partial(I/k)}{\partial \log c}\right) = 315 \cos \alpha(T) \ (K/at), \quad \left(\frac{\partial I/k}{\partial \log a}\right)_{b,c} = -57 (K/at)$$

We observed, fig 18 and 19 a good agreement between calculated and experimental values.

b - In the ferromagnetic range, the moments are directed along the a-axis, which is a direction of easy magnetization. There occurs an orthorombic distorsion along this direction, and

$$V = -\frac{1}{2}\bar{V}_2^0 + \bar{V}_2^{2c},$$

where $\bar{V}_2^{2c}$ gives account of the anisotropy associated to this distorsion

$$\left(\frac{\partial V}{\partial \log a}\right)_{b,c} = -\frac{1}{2}\bar{V}_2^0\left(\frac{\partial \log \bar{V}_2^0}{\partial \log a}\right)_{b,c} + \bar{V}_2^{2c}\left(\frac{\partial \log \bar{V}_2^{2c}}{\partial \log a}\right)_{b,c}$$

$$\left(\frac{\partial V}{\partial \log b}\right)_{a,c} = \quad 0 \quad - \bar{V}_2^{2c}\left(\frac{\partial \log \bar{V}_2^{2c}}{\partial \log b}\right)_{a,c}$$

$$\left(\frac{\partial V}{\partial \log c}\right)_{a,b} = -\frac{1}{2}\bar{V}_2^0\left(\frac{\partial \log \bar{V}_2^0}{\partial \log c}\right)_{a,b}.$$

$\frac{\partial V}{\partial \log a}$ can be determined from experiments of magnetostriction, and spontaneous magnetostriction derived (fig. 18 and 19) on the same manner as in the helimagnetic domain.

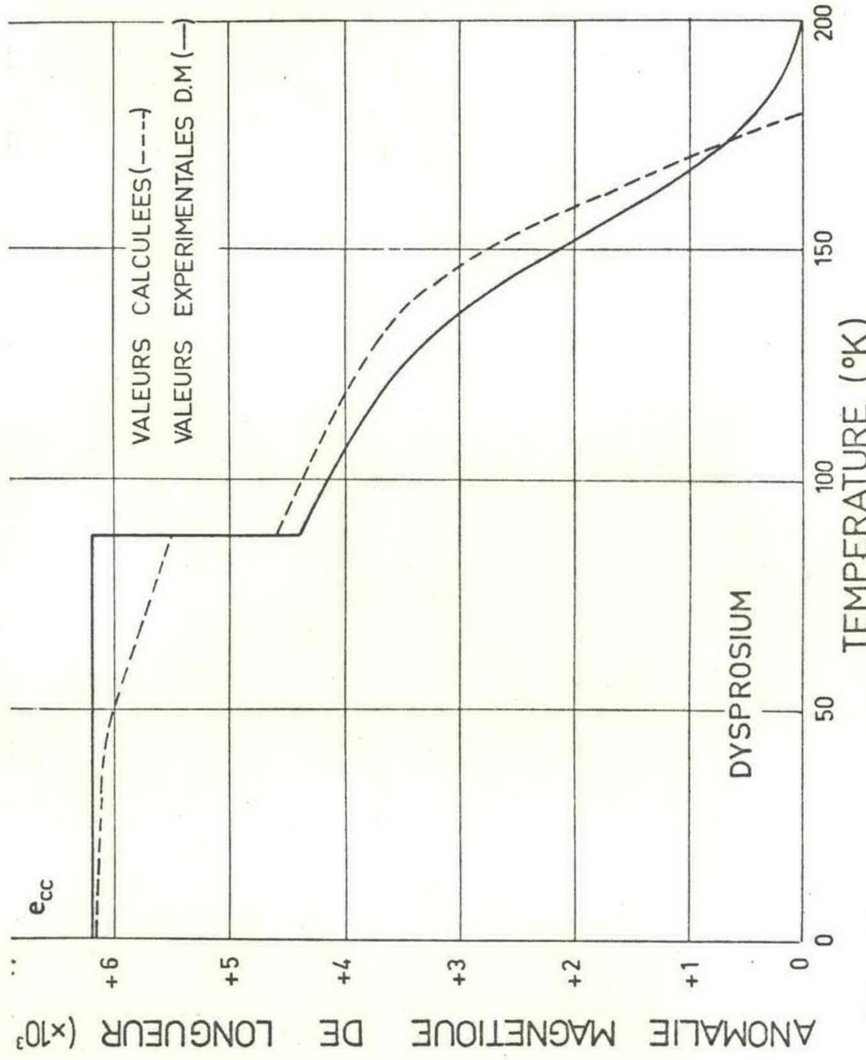

Figure 18 : Anomalie magnétique de longueur suivant l'axe $\vec{a}$ du dysprosium. Valeurs calculées (- - - -)((V-14) à (V-16), (V-47) à (V-52)). Valeurs expérimentales (——) déterminées à partir de, mesures de Darnell et Moore (DM), (DA 63).

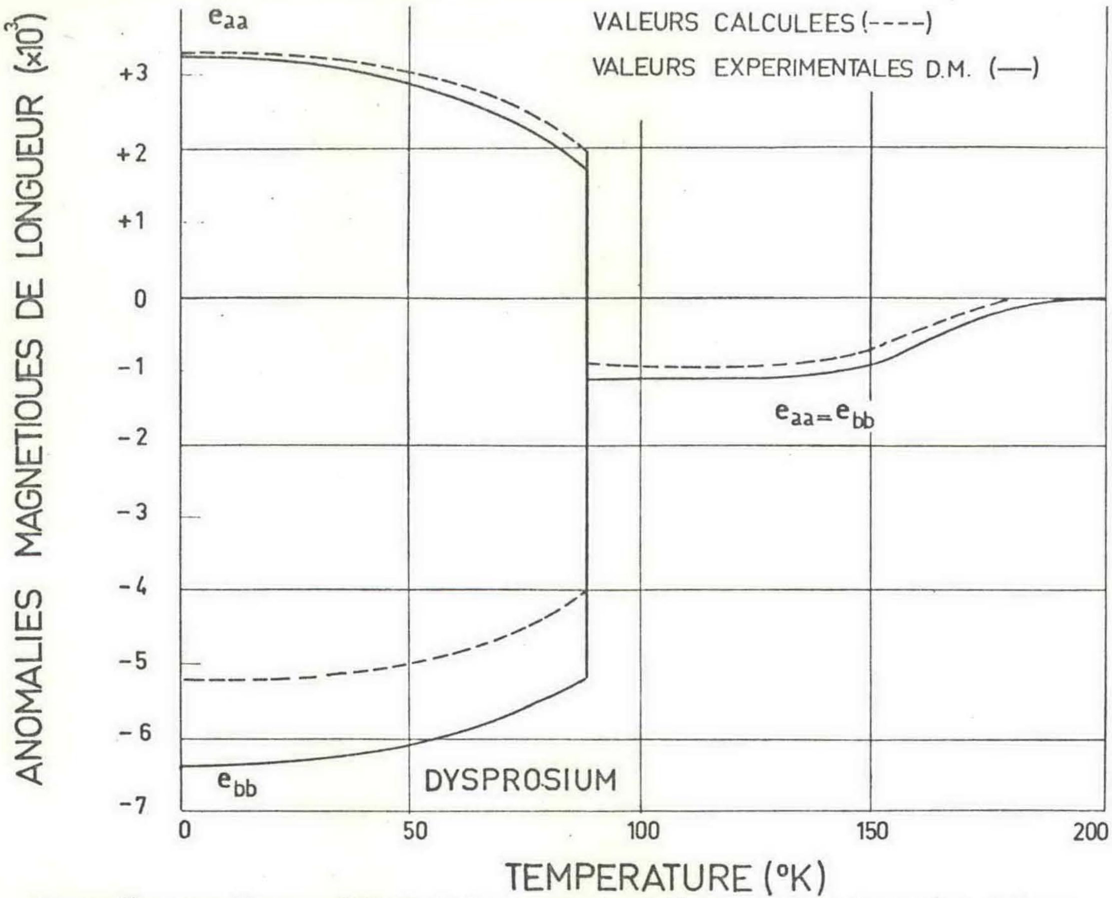

Figure 19 : Anomalies magnétiques de longueur suivant l'axe *a* et *b* du dysprosium. Valeurs calculées (- - -) ((V-14) à (V-16), (V-47) à (V-52)) . Valeurs expérimentales (——) déterminées à partir des mesures de Darnell et Moore (DM). (DA 63).