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On Ferrites. Theory and Practise

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Prologue: I feel rather proud to talk here for two reasons, first to comment on Professor Néel's message and second because I got my diploma of chemical engineering and of master in math, physics, chemistry, here in Bordeaux.

Néel's message : Néel published his famous paper "Propriétés Magnétiques des Ferrites : Ferrimagnétisme et Antiferromagnétisme" in *Les Annales de Physique* (1948).

It is true that he has coined there in 1948 the definition of ferrimagnetism. However, Néel's formula, alluded to in his message, was born much earlier, in fact in 1932 where it appears as formula (83) in his thesis work. In view of its historical importance, it is printed here with the original notations and with the proof, given in the thesis.

Néel considers two magnetic species A and B of magnetic moments μ_A and μ_B , Curie constants C_A and C_B , and in proportions P and Q (1). The total moment is μ (2). Néel postulates the existence of two local molecular fields h_A (3) and h_B (4) depending linearly on μ_A and μ_B . Here n_{AA} , $n_{AB} = n_{BA}$, n_{BB} are interaction coefficients which Néel abridges a, b, c, respectively (5). One has not the Curie law $\mu = C H/T$ where H is the applied field but the relations (6) (7) where the local molecular fields h_A and h_B are added to the applied field. The result of the elimination of h_A , h_B , μ_A and μ_B in the equations written here is the famous formula (8) which relates the total moment μ to the applied field H.

The magnetic susceptibility χ is the ratio M/H . It is easily seen that the inverse susceptibility has the form (9) where the last term is Néel's hyperbola.

$$P + Q = 1 \tag{1}$$

$$\mu = \mu_A + \mu_B \tag{2}$$

$$h_A = n_{AA} \mu_A + n_{AB} \mu_B \tag{3}$$

$$h_B = n_{BA} \mu_A + n_{BB} \mu_B \tag{4}$$

$$a = n_{AA}, \quad b = n_{AB} = n_{BA}, \quad c = n_{BB} \tag{5}$$

$$\mu_A = PC_A (H + h_A) / T \tag{6}$$

$$\mu_B = QC_B (H + h_B) / T \tag{7}$$

Neel's formula (83) (1932)

$$\mu = \frac{T (PC_A + QC_B) - PQC_A C_B (a + c - 2b)}{T^2 - T(PC_A a + QC_B c) + PQC_A C_B (ac - b^2)} H \tag{8}$$

$$\frac{1}{\chi} = \frac{H}{\mu} = \frac{T}{C'} + \frac{1}{\chi_0} - \frac{\sigma}{T - \Theta} \quad (9)$$

$$C' = PC_A + QC_B \quad (10)$$

Although Néel knew about Kramer's work (1934) on negative super-exchange interactions ($n_{AB} < 0$) he remained silent because at that time the linearity of the $1/\chi$ plot versus T was a dogma and it was a heresy to fight against the unique molecular field (1906) of P. Weiss who was the Director of the laboratory. Verwey and Heilmann in (1947) gave Néel the key for his theory of ferrimagnetism. They found $\text{Cd Fe}_2 \text{O}_4$ to be a "normal" spinel with Cd^{2+} in a tetrahedral and Fe^{3+} in an octahedral oxygen environment. They called $\text{Mg Fe}_2 \text{O}_4$ an "inverse" spinel with Mg^{2+} being in an octahedron. In the usual notation the formulae would be written $(\text{Cd}^{2+}) [\text{Fe}_2^{3+}] \text{O}_4$ and $(\text{Fe}^{3+}) [\text{Mg}^{2+} \text{Fe}^{3+}] \text{O}_4$. Note that Verwey is also the father of the "Verwey transition" in magnetite $\text{Fe}_3 \text{O}_4$ where Fe^{2+} and Fe^{3+} order in the octahedral positions at 113°K with a discontinuity in the conductivity.

I shall now show you the similarity of formula (83) of Néel's thesis and the formula (13) mentioned in his message.

Call λ and μ the proportions of Fe^{3+} on A- and B- sites respectively $\text{Mg Fe}_2 \text{O}_4$ for instance ; λ and μ will replace P and Q respectively. One has here $C_A = C_B = C$. The total magnetisation is written J instead of μ ; also in the demonstration of (13) λJ_A and μJ_B stand for μ_A and μ_B (11). The interaction coefficients n_{AA} , n_{BB} and n_{AB} are denoted by $n \alpha$, $n \beta$ and $n \varepsilon$ (12).

Thus except for minor differences in the notations the equations (83) and (13) of the message are identical.

$$\mu_A = \lambda J_A, \mu_B = \mu J_B \quad (11)$$

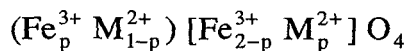
$$n_{AA} = n \alpha ; n_{BB} = n \beta ; n_{AB} = n \varepsilon \quad (12)$$

$$\text{with } n > 0, \varepsilon = -1$$

Néel's formula (13) Annales (1948) is

$$J = C \frac{T - n C \lambda \mu (2 + \alpha \beta)}{T^2 - n C T (\lambda \alpha + \mu \beta) + n^2 C^2 \lambda \mu (\alpha \beta - 1)} H \quad (13)$$

Néel's hyperbola (9) is characterized by a set of three constants χ_0, σ, Θ wherefrom one can deduce the three interaction-coefficients n_{AA} , n_{AB} , n_{BB} (see Néel 1948 and textbooks). In fact, normal and inverse spinels are limiting cases of the general formula



for $p=0$ and for $p=1$ respectively, so that one has to do with a fourth variate, the "degree of inversion", represented by p . Néel knew already in 1948 that p depended on temperature and thus on the thermal history of the sample.

To measure p versus T in copper ferrite, for instance, from X ray intensities seems to be a difficult task because Fe^{3+} and Cu^{2+} have nearly the same diffusing power. I could show that by using "anomalous dispersion", say a radiation near to the absorption edge $K\alpha$ of Fe one can increase the contrast between Fe and Cu and get reliable values of p (Bertaut 1950). Nowadays one can certainly do better by approaching the absorption edge at will with the continuous spectrum of synchrotron radiation.

Of course the difficulties of the degree of inversion do not exist in the YIG, the yttrium iron garnet which represents the case of "pure ferrimagnetism" with only Fe^{3+} ions present. Here the inverse susceptibility (9) is explicitly (Aléonard, Pauthenet, Barbier, 1956)

$$\frac{1}{\chi} = \frac{T}{50} + 30,5 - \frac{990}{T - 570}$$

The interaction coefficients are given there as

$$n_{aa} = -351,9, \quad n_{dd} = -210,5, \quad n_{ad} = -742$$

The lower indices a and d characterize the octahedral sites 16a) and tetrahedral sites 24d) respectively in $(\text{Fe})_3[\text{Fe}]_2\text{Y}_3\text{O}_{12}$ (YIG).

The exchange integrals, expressed in degrees K, are given in the same sequence as -8.3, -15.1 and -35.0 by Smart (1963), and -6.45, -12.05 and -30.4 according to Srivastava et al. (1981). Here, different temperature corrections have been used.

ON BINARY SULFIDES

I do not resist the temptation of citing our contribution to ferri- and antiferro-magnetism in the field of sulfides. Here, crystallography solved « the enigma posed by pyrrhotite Fe_7S_8 , a ferromagnetic compound which had long been studied by P. Weiss (1899, 1905 and 1929) which has a weak saturation moment of $3\mu\text{B}$ whereas on the basis of its formula a value almost ten times as large had been expected » (Néel, 1971).

Indeed Fe_7S_8 was the first structure in cristallography containing ordered vacancies (Bertaut 1952, 1953); its ferrimagnetism is due to the alternation along the c-axis of two kinds of iron planes of opposite spin directions, full iron planes and planes with ordered iron vacancies (fig. 1). The Néel temperature $T_N = 320^\circ\text{C}$ coincides with the vacancy disorder.

We continue with sulfides FeS. While there is only one oxide FeO, there are at least three FeS families.

Mackinawite is a mineral, but it is easily prepared by the action of H_2S on a suspension of iron powder in water. It is tetragonal: $a = 3.678 \text{ \AA}$, $c = 5.038 \text{ \AA}$, space group P4/nmm ; Fe is in the special position $2a:000; 1/2, 1/2, 0$. The distance Fe-S in the FeS_4 tetrahedron is 2.23 \AA , say shorter than the sum $\Sigma = 2.28 \text{ \AA}$ of the covalent radii $r_{\text{cov}}(\text{Fe}) = 1.22 \text{ \AA}$, $r_{\text{cov}}(\text{S}) = 1.04 \text{ \AA}$.

No magnetic ordering, no paramagnetic background, is detected by neutron diffraction down to 4.2 K . The unique line of the Mössbauer spectrum confirms the absence of magnetic order down to 1.7 K (Bertaut et al. (1965)). Thus we conclude that tetragonal FeS is a diamagnetic semiconductor with covalent bonding due probably to a d's hybridisation. Mackinawite is metastable and transforms irreversibly under heating to the hexagonal forms.

FeS blende, space group F43m , $a = 5.42 \text{ \AA}$ has been prepared by attacking a steel wire in a water solution of H_2S at room temperature. At the same time appear the impurity phases, wackinawite and troilite. The Néel temperature is $T_N = 234 \text{ K}$. The transition cubic \rightarrow orthorhombic is first order. This is seen by the discontinuity of the hyperfine field (Wintberger et al. (1978a)) which jumps from 100 kOe to zero at T_N , but also by the coexistence of the two phases: when cooling the sample from high temperature, an orthorhombic phase appears at 238 K and the cubic phase disappears at 230 K . The parameters of the orthorhombic phase, space group F22_2 , are $a = 5.54 \text{ \AA}$, $B = 5.48 \text{ \AA}$, $C = 5.195 \text{ \AA}$ at 81 K .

Mössbauer effect (Wintberger et al. (1978a)) and neutron diffraction (Wintberger et al. (1978b)) show that ferromagnetic planes are coupled antiferromagnetically along c, the spin direction being along a. The magnetic space group is $\text{F}22'2'$.

No transition blende \rightarrow warwickite, blende \rightarrow troilite has been reported.

The hexagonal form FeS, called troilite, has features which are suprising, at least for me (Bertaut, 1956, 1957).

In ionic structures, the cation generally occupies special positions. In troilite, Fe occupies a general position while S is distributed over three different special positions. The unit cell is rather large with $A = a\sqrt{3}$, $C = 2c$ where a and c are the parameters of the classical NiAs type. The space group in non centro-symmetric $\text{P6}_3\text{c}$. I had the pleasure to learn that my structure proposal was checked again and refined by H.T. Evans (1970) on a lunar sample of troilite. Between 138 and 150°C , FeS troilite transforms in a first order transition to an orthorhombic structure of MnP type Pnma (Putnis 1974, King et Prewit 1982, Töpel-Schadt et al. 1982). The heat of transformation, the so-called α -transition (Haraldsen, 1941) is rather high, about 550 cal/mol (Hirone 1954). A second order transition takes place above 220°C , giving rise to the nickel arsenide a,c-phase of space group $\text{P6}_3/\text{mmc}$ where $T_N = 600 \text{ K}$.

The reactions: troilite \rightarrow MnP type \rightarrow NiAs type are reversible (Töpel-Schadt et al. 1982) and I ask once more about the dielectric properties of FeS; the antiferromagnetic semi-conductor troilite, is it ferroelectric ?

It is remarkable that the magnetic interaction $\text{Fe}_{2+} - \text{S} - \text{Fe}_{2+}$ in blende and troilite is stronger than in $\text{Fe}^{2+} - \text{O} - \text{Fe}^{2+}$ ($T_N(\text{FeO}) = 190 \text{ K}$). However the interaction $\text{Fe}^{3+} - \text{S} - \text{Fe}^{3+}$ is much weaker than $\text{Fe}^{3+} - \text{O} - \text{Fe}^{3+}$.

The inverse spinel Fe_3S_4 exists, but no Verwey transition takes place (Coey et al. 1970). Goodenough has discussed in detail the electronic structure of troilite (1962) and more generally iron sulfides (1982) with respect to the nature, itinerant or localized, of their electrons.

REPRESENTATION ANALYSIS

The magnetic energy is given by (14) in terms of interaction coefficients and magnetizations of the sublattices A and B or by the Van Vleck-Heisenberg hamiltonian of order two (15) in terms of exchange integrals and scalar spin products (Néel 1948, part IV). These expressions have proved useful in the many transition metal compounds where collinear structures are frequent. They are still applicable to helical situations.

$$\mathcal{H} = - \frac{1}{2} (n_{AA} \mu_A^2 + n_{BB} \mu_B^2 + 2n_{AB} \mu_A \mu_B) \quad (14)$$

$$\mathcal{H} = - 2 \sum_{ij} J_{ij} \bar{S}_i \bar{S}_j \quad (15)$$

The situation has changed with the advent of neutron scattering and with low temperature studies of compounds with f electrons, say with rare earths and actinides where the orbital moments play an important role. It is well known that in iron - rare earth compounds, iron orders first and the rare earth behaves like a paramagnetic ion in the molecular field of the iron lattice. Lowering the temperature the rare earth ion discovers its environment and the coupling rare earth-iron changes the structure to non collinear, say "canted" situations. The tool we have created for non collinear structures is called "Representation Analysis" and the essential role is played by "Basis Vectors of Irreducible Representations". This mathematical terminology sounds frightening. My intention is not to give a lecture on group theory, but to tell you in an every day language what representation analysis is for and how it works. No differential equations, no relativity theory come in ; no quantum mechanics is required. What you have to know is how a symmetry operation acts on a magnetic moment, say on an axial vector. As an example let us choose the compounds A B O₃ in the space group P b n m - D_{2h}¹⁶ where A stands for Fe and B for the rare earth in the deformed perovskite.

Basis vectors

The A-moments are in four symmetry centers, numbered from 1 to 4. I shall cite now some of the attractive properties of "basis vectors" of the A - moments.

"A basis vector is the portrait of a magnetic mode". The basis vector G_x

$$G_x = + S_{1x} - S_{2x} + S_{3x} - S_{4x}$$

represents an antiferromagnetic mode say a succession + - + - of the magnetic moments along the x - axis.

The basis vector F_z

$$F_z = + S_{1z} + S_{2z} + S_{3z} + S_{4z}$$

represents a ferromagnetic mode along the z - axis.

"A basis vector G_x under a symmetry operation transforms into itself, + G_x, or into its opposite - G_x"

The symmetry operations listed here (table 1) are the screw axes 2_{1x} and 2_{1y}, and the inversion center $\bar{1}$. I leave it up to the reader to explain while under the operation $\bar{1}$ one has always the + sign.

The basis vectors which we deal with are the x, y, z components of the vectors F, G, C, A, defined below :

$$F = + S_1 + S_2 + S_3 + S_4$$

$$G = + S_1 - S_2 + S_3 - S_4$$

$$C = + S_1 + S_2 - S_3 - S_4$$

$$A = + S_1 - S_2 - S_3 + S_4$$

G_x and F_z stay in the same line Γ_4 ; "they belong to the same representation Γ_4 " means that they transform in the same way.

A representation like Γ_4 is said "irreducible" when it cannot be made simpler anymore.

Coupling of magnetic modes

"The product $G_x F_z$ is invariant in any symmetry operation" means firstly that "an antiferromagnetism along x may be coupled with a ferromagnetism along z " and secondly that "the product $G_x F_z$ can figure in a hamiltonian".

Such a situation arises in many rare earth ferrites at room temperature : an antiferromagnetic mode G_x is seen by neutron diffraction and a weak ferromagnetic mode F_z appears from elementary magnetic measurements. A glance on table 1 suggests two questions, firstly why $G_x F_z$ in Γ_4 and not $F_x G_z$, allowed in Γ_2 and secondly can one provoke the situation $F_x G_z$? The answer is that much "spin reorientations" effectively take place either as a function of temperature or due to the application of an appropriate field. The theory is amply discussed by Yamaguchi (1974).

Representations	Symmetry operators			Basis vectors			Space group
	$\begin{matrix} 2 \\ 1x \end{matrix}$	$\begin{matrix} 2 \\ 1y \end{matrix}$	$\bar{1}$	x	y	z	
Γ_1	+	+	+	A	G	C	P b n m
Γ_2	+	-	+	F	C	G	b n' m'
Γ_3	-	+	+	C	F	A	b' n m'
Γ_4	-	-	+	G	A	F	b' n' m

Table 1: Basis vectors of irreducible representations. A-atoms are on the sites:

$$\frac{1}{2}00 \quad (1) ; \quad \frac{1}{2}0\frac{1}{2} \quad (2) ; \quad 0\frac{1}{2}\frac{1}{2} \quad (3) ; \quad 0\frac{1}{2}0 \quad (4). \quad (4b)$$

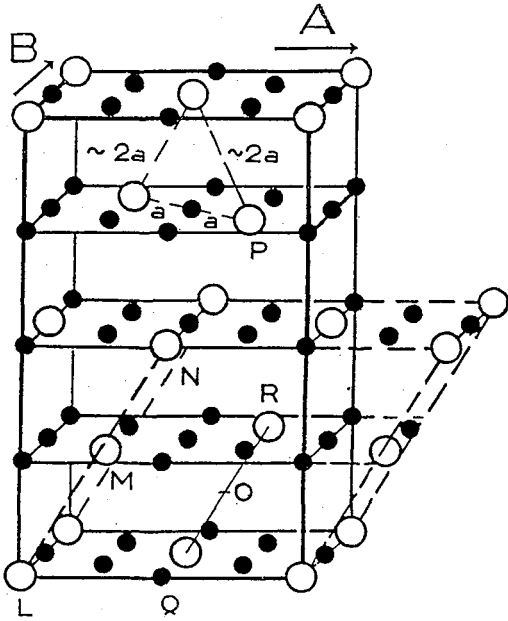


Fig. 1

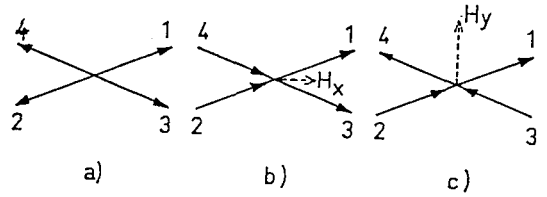


Fig. 2

Figure 1: Pyrrhotite Fe₇S₈. Planes of iron (full circles) with ordered vacancies (empty circles). Full planes of iron or sulfur are not shown.

Figure 2 : spin-flip in TbAlO₃. a) G_xA_y; b) F_xC_y; c) C_xF_y.

The hamiltonian for the A-atoms has the form (16) where i and j design the numbers 1 to 4, α and β stand for x,y,z so that one has to discuss 144 terms under the summation. I hope that the reader will appreciate our approach by the basis vectors.

$$\mathcal{H} = \sum_{i,j} \sum_{\alpha,\beta} A_{i,j}^{\alpha,\beta} S_{\alpha}^i S_{\beta}^j \tag{16}$$

The B atoms.- For the construction of Table 2 we use the same designations F,G,C,A as before. There are 8 representations Γ_j. Our first application will be the metamagnetism in TbAlO₃ (Holmes et al. (1968)) which orders at T_N=3.8 K, in a configuration G_xA_y (Γ₅). The local anisotropy is supposed so high that the angle α of the spins with the axis Ox does not change. Thus when a field H_x is applied along the x-axis, the moments 1 and 3 will be conserved whilst those of 2 and 4 shall get inverted if the field H_x exceeds a critical value H_{xcrit} (fig.2). The energy balance is given by

$$W_1 = W_{12} + W_{34} = 2W_{12} \quad \text{before switching}$$

and

$$W_2 = -2W_{12} - 4MH_x \cos \alpha \quad \text{after switching}$$

where M is the magnetic moment of the (Ising-like) spins.
The critical field is given by

$$W_1 = W_2 \quad \text{say } W_{12} = -MH_{x \text{ crit}} \cos \alpha$$

Consulting the figure 2 and table 2 one has switched the configuration G_xA_y(Γ₅) to F_xC_y(Γ₂)

Applying the field along Oy one finds by the same procedure

$$W_{12} = -MH_{ycrit} \sin \alpha$$

where H_{ycrit} is the critical field along Oy which switches $G_x A_y (\Gamma_5)$ to $C_x F_y (\Gamma_3)$ (table 2).

One has

$$\frac{H_{xcrit}}{H_{ycrit}} = \text{tg } \alpha$$

From the plots of Holmes et al. (1968) one extrapolates

$$H_{xcrit} = 8.5 \text{ K}\alpha \quad \text{and} \quad H_{ycrit} = 12.5 \text{ K}\alpha \quad \text{so that}$$

$\text{tg } \alpha = 0.68$ and $\alpha = 34.2^\circ$, which is near to $\alpha = 34^\circ$ as determined directly by neutron diffraction at 1.5 K on TbAlO_3 (Maréchal et al. (1968)).

	2_{1x}	2_{1y}	$\bar{1}$		x	y	z	
Γ_1	+	+	+		.	.	C	P b n m
Γ_2	+	-	+		F	C	.	b n' m'
Γ_3	-	+	+		C	F	.	b' n m'
Γ_4	-	-	+		.	.	F	b' n' m
Γ_5	+	+	-		G	A	.	b' n' m
Γ_6	+	-	-		.	.	A	b' n m
Γ_7	-	+	-		.	.	G	b n' m
Γ_8	-	-	-		A	G	.	b n m'

Table 2: Basis vectors of irreducible representations. B-atoms are on the sites:

$$\begin{aligned}
 & xy \frac{1}{4} \quad (1) ; \quad \bar{xy} \frac{3}{4} \quad (2) ; \quad \frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{4} \quad (3) ; \quad \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{4} \quad (4) \\
 & x = -.18 \quad ; \quad y = .060
 \end{aligned}
 \tag{4c}$$

The simultaneous use of tables 1 and 2 is most rewarding for coupling magnetic modes of A with B atoms.

In HoCrO_3 at $T_{N1} = 141.3$ K, the Cr - moments order in the $F_x G_z (\Gamma_2)$ - configuration, the ferromagnetic component being weak, table 1, and at $T_{N2} = 12$ K the rare earth orders to $F_x C_y$ in the same representation Γ_2 , table 2 (Bertaut et al. 1963). It is remarkable that the same structure has been reported for HoFeO_3 (Koehler et al. 1960, cf. Fig. 3). Here we can infer a scalar coupling for the ferromagnetic components $F_x(\text{Cr})$ and $F_x(\text{Ho})$, by classical superexchange. Our tabulation tells us that the orthogonality of the components $G_z(\text{Cr})$ and $C_y(\text{Ho})$, coupled in Γ_2 is justified by symmetry, but does not tell us the physical reason. For the time being we put forward the hypothesis of the Dzyaloshinskii-Moriya coupling $\mathbf{D} \cdot [\mathbf{S} \times \mathbf{M}]$ where \mathbf{S} stands for $G_z(\text{Cr})$ and \mathbf{M} for $C_y(\text{Ho})$. The vector \mathbf{D} would be along Ox .

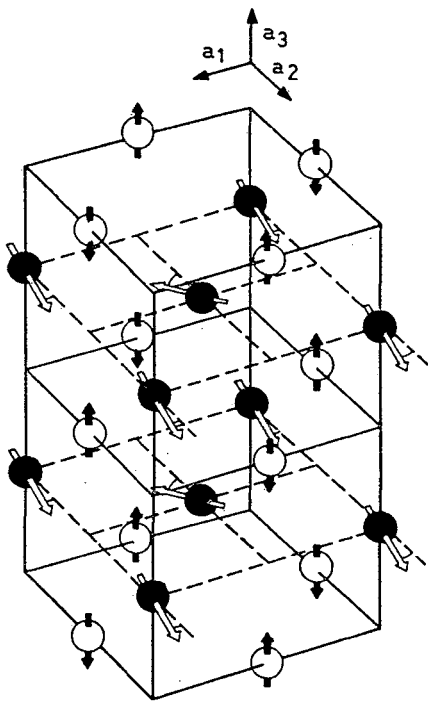


Fig. 3

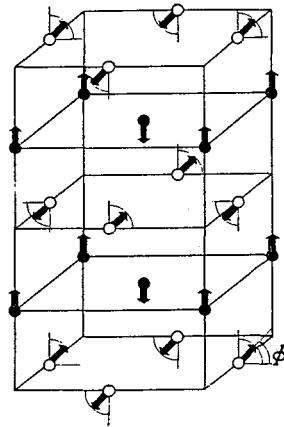


Fig. 4

Figure 3: Magnetic structure at low temperature : rare earth (full circle) : Fe,Cr (empty circle). 3) Phase Γ_2 HoFeO_3 ; HoCrO_3 ; the rare earth moment is in the plane a_1, a_2

Figure 4: Magnetic structure at low temperature: 3b) Phase $\Gamma_1 + \Gamma_4$ ErFeO_3 ; the rare earth moment is along a_3 .

Our second example for A-B coupling is ErCrO_3 where at $T_{N1} = 133.2$ K the Cr-moments order in the $G_x F_z (\Gamma_4)$ mode. Below $T_{N2} = 9.8$ K, neutron diffraction on powders established the existence of a C_z mode of Er coupled to a G_y mode of Cr in Γ_1 (Bertaut et al. 1963). Single crystal studies by magnetization, specific heat measurements (Eibschütz et al. 1970) and optical spectroscopy (Courths et al. 1970) prove the nature of first order transition at $T_{N2} = 9.8$ K and also that below T_{N2} the magnetization F_z of Γ_4 has disappeared. Here too we infer a D-M coupling with \mathbf{S} for $G_y(\text{Cr})$, \mathbf{M} for $C_z(\text{Er})$ and \mathbf{D} along Ox .

The argument I put forward is that vector \mathbf{D} depends on spin-orbit coupling and therefore on the existence of orbital moments L which have the high values $L = 6$ for Ho and for Er. ErCrO_3 and HoCrO_3 have rather high temperatures for rare earth ordering $T_{N2} = 9.8$ K and 12 K respectively. In GdFeO_3 the orbital moment of Gd is zero and we expect a low temperature transition for the Gd-Fe ordering which indeed takes place at $T_{N2} = 1.47$ K (Cashion et al. 1970).

Comparison with ErFeO_3 .- The Fe spins which just below T_N are in the $G_x F_z (\Gamma_4)$ mode reorient to $F_x G_z (\Gamma_2)$ mode (Gorodetsky et al. 1973) continuously in the temperature interval

100-90 K. The low temperature configuration of ErFeO_3 comprises the $F_x G_z$ mode of iron in the representation Γ_2 plus the modes G_y of iron coupled to the mode C_z of erbium in the representation Γ_1 (cf. Fig 4). The magnetic space group is the intersection of Γ_1 and Γ_2 , say $2_1'x/m$ (Cracknell 1974).

Our last example is TbFeO_3 where Fe^{3+} orders again in the $G_x F_z$ mode of Γ_4 at $T_{N1}=681$ K. Below and at $T_{N2}=8.4$ K one observes the same magnetic structure as described above for HoCrO_3 and HoFeO_3 , say a $F_x G_z$ mode on Fe coupled with $F_x C_y$ on Tb. Lowering the temperature once more below $T_{N3}=3.1$ K one finds a $A_x G_y$ configuration in Tb, but cannot decide between G_x or G_z mode on the Fe site (Bertaut et al. 1967).

Actually in TbCoO_3 where Co^{3+} is in the low spin state, Tb orders in the $A_x G_y$ configuration at $T_N=3.31$ K (Maréchal et al. 1968). The conclusion was then that in TbFeO_3 the magnetic orders of Fe^{3+} and Tb^{3+} were “decoupled”. In fact one must be more prudent. If Fe is in the G_x mode of Γ_4 and Tb in the Γ_8 mode, the magnetic space group, common to Γ_4 and Γ_8 is the non centrosymmetric group $P2_1'2_1'2_1$ in which Fe and Tb would remain coupled, provided that by a small displacement, Fe loses its inversion centre.

Representation analysis is not restricted to magnetism and can be applied to ferroelectricity with the only difference that the basis vectors are *polar* (Bertaut 1968b).

A final application of interest is the field of magnetoelectricity, abridged ME. The phenomenon was foreseen by P. Curie one century ago, predicted by Dzyaloshinskii (1960) to occur in Cr_2O_3 and measured first by Astrov (1960). The example considered here is $\text{Fe}_{1.15}\text{Ga}_{0.85}\text{O}_3$, space group $\text{Pc}2_1'n$. ME was seen there first by Rado (1964). The crystallographic structure was solved by Abrahams et al. (1965). The Grenoble team added the knowledge of the magnetic structure and space group $\text{Pc}'2_1'n$ (Bertaut et al. 1965,1966). Delapalme (1968), using polarized neutrons, measured with a good precision the percentages of iron on the three octahedral sites and also on the tetrahedral site where Ga predominates.

	$\text{Pc}'2_1'n$			$\text{Pc}2_1'n$		
	AXIAL			POLAR		
	VECTORS					
	x	y	z	x	y	z
Γ_1 (++)	C	G	F	A	F	G
Γ_2 (+-)	F	A	C	G	C	A
Γ_3 (-+)	A	F	G	C	G	F
Γ_4 (--)	G	C	A	F	A	C

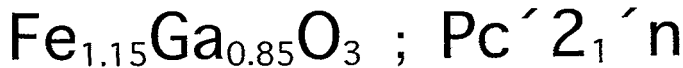


Table 3 : Axial and polar basis vectors.

In table 3, under the headings $Pc'2_1n$ and $Pc2_1n$, one finds respectively the axial and the polar basis vectors. The product F_z (axial) F_y (polar) in the identity representation Γ_1 corresponds to the ME observed by Rado: a magnetic field H applied in the direction Oz induces a magnetic moment F_z and one measures an electric moment F_y in the direction Oy . Reciprocally one may also apply an electric field E in the direction Oy , induce an electric moment F_y and measure the magnetic moment F_z . The two methods are abridged $(ME)_H$ and $(ME)_E$.

More generally if α_{ij} represents the ME tensor, one has in conventional notations

$$\alpha_{ij} \cdot \delta H_j = \delta P_i \quad \text{and} \quad \alpha_{ij} \cdot \delta E_i = \delta M_j$$

Here, M_j and P_i are the magnetic and electric moments. M stands for F (axial) and P for F (polar).

In $Fe_xGa_{2-x}O_3$, α_{yz} is observed. One easily checks from table 3 that only α_{yz} and α_{zy} differ from zero. The main conclusion is that *the knowledge of the magnetic and of the crystallographic structure allows the construction of the magneto-electric tensor α_{ij} with the only help of the basis vectors, axial and polar.*

Recently the crystallographic structure of $FeAlO_3$ has been investigated and described in space group $Pna2_1$ which is equivalent to $Pc2_1n$. It is isomorphous to $FeGaO_3$ piezo-electric, ferrimagnetic and magnetoelectric (cf. Bourée et al. 1966 and references there in).

I have predicted magnetoelectricity to occur in $FeNaO_2\beta$ (Bertaut 1968b), also crystallising in $Pna2_1$, but having the magnetic space group $Pn'a2_1$ (Bertaut et al. 1963); here α_{zy} and α_{xz} differ from zero. The Néel temperature is exceptionally high $T_N=723$ K, compared to $T_N \approx 310$ K in Cr_2O_3 and in $Fe_{1.15}Ga_{0.85}O_3$.

The Néel temperatures are much lower in compounds with bivalent transition metal compounds like the olivine type structure $LiCoPO_4$, $T_N=23$ K, space group $Pnma$ which again is ME (Mercier et al. 1967).

In rare earth compounds like $TbAlO_3$, the Néel temperature is very low ($T_N = 3.9$ K) but one has the satisfaction of an ME-effect ten times stronger than in Cr_2O_3 (Mercier et al. 1968). It is interesting to note that the ME-effect in $TbAlO_3$ disappears when the applied magnetic field is high enough to provoke a spin-flip. RA shows indeed that F (axial) and F (polar) are no longer found in the same representation. Similarly, there is no ME on Fe in the rare-earth iron oxides. Here, the *axial* vectors are in the representation Γ_1 to Γ_4 and the *polar* vectors in those from Γ_5 to Γ_8 so that they have no representation in common. More generally there is no ME on centres of symmetry. An application of RA to ME is found in the paper "ME in theory and experiment" (Bertaut et Mercier 1971) which also summarizes Mercier's thesis work.

REPRESENTATION ANALYSIS AND GARNETS

Representation analysis has been summarized and commented with favour by Cracknell (1974). My own opinion is that RA is not so widely used as it should be in magnetic structure research (Sivardière 1970). What are the objections?

"Basis vectors of irreducible representations form an essential part of RA" - which is true - "and they are not always easy to find". I have proposed a formula (Bertaut 1981) for creating the b.v.i.r. which is easier to handle than those found in text books on group theory. Another more serious objection is that "RA lacks a thermodynamical basis and neglects Landau's theory of second order transitions". I have considered this objection more explicitly in the reference cited (Bertaut 1981). Here, I must say that RA is not a thermodynamic, but geometrical construction, that we are not yet able to predict a magnetic structure and its thermal evolution and also that the principal use of Landau's theory is to show that most phase transitions must be first order.

I shall consider here RA in the thermal evolution of the structures of terbium and erbium iron garnets.

TbIG

It is well known that in all rare earth-iron garnet *above* the compensation temperature T_c , all magnetic moments are along *one* axis [111] in a given domain, so that from the start there is a magnetic anisotropy in the structure. Still let us use representation theory in the cubic paramagnetic group $Ia3d$ ($N^\circ 230$).

The research team is composed of Tch  ou, Bertaut, Delapalme, Sayetat, Fuess. Tch  ou is preparing his thesis, Delapalme is the specialist of polarized neutrons, Sayetat measures lattice distortions by X-rays, Fuess is interested in garnets. Neutron diffraction *below* T_C shows the presence of two modes on Tb, denoted S_{\parallel} and S_{\perp} , respectively parallel and orthogonal to [111]. RA in the cubic group gets an acceptable agreement with observed intensities, but needs two different three-dimensional representations of the cubic group, Γ_{4g} for S_{\parallel} and Γ_{5g} for S_{\perp} , the direction of S_{\perp} being $[1\bar{1}0]$ plus permutations. However Sayetat finds a rhombohedral splitting in the X-ray pattern of the high angle reflections $\{8,6,4\}$ and $\{10,4,0\}$. Thus RA continues in the rhombohedral space group $R\bar{3}c$ for two reasons. Firstly, S_{\parallel} and S_{\perp} are found there in the same representation, and secondly S_{\perp} is along $[\bar{1}\bar{1}2]$ and $[2\bar{1}\bar{1}]$ $[\bar{1}2\bar{1}]$ with an improved agreement of experimental and theoretical intensities.

The main conclusion is that the observed magnetic order does not belong to an irreducible representation of the paramagnetic group $Ia\bar{3}d$, but to the magnetic group $R\bar{3}c'$. Landau's theory of second order transitions does not apply to TbIG. The team cited above presented his results at the Rare Earth Conference, mai 1969 wich took place in Paris for the chemical part, in Grenoble for the physical part (cf. references cited Tch  ou, Congress, and Solid State Comm. 1970). Their findings were confirmed and refined by Lahoubi et al. (1984).

However, there are no limits to progress. The famous powder instrument D2b of I.L.L. (which was conceived at the neutron diffraction laboratory of the CEN-G and constructed there (Roudaut)) had a higher resolution and a much lower background, divided by 40 in the $\{110\}$ region, and a new study was started by Hock, Fuess, Vogt, and Bonnet. Here Hock is the thesis student, Fuess the team leader, Vogt the I.L.L. representative, and Bonnet (CEN-G) is programming the RA according to the version Bertaut (1972). The reflections $\{200\}\{600\}\{422\}$ (in cubic notation) which are forbidden in $R\bar{3}c'$ appear in the powder diagram. The space group is finally $R\bar{3}$ where a full refinement is made (Hock et al. 1990) whith significant changes in the atomic positions. More particularly one has $m_{\perp}(Tb_1) \neq m_{\perp}(Tb_2)$.

ErIG

The erbium iron garnet at low temperature (4.2 K) was refined in space group $R\bar{3}c'$ (Tch  ou et al. 1970) with results which seemed to be satisfactory ; the two erbium moments turned out to be $m(Er_1)=6.7\pm 0.2\mu_B$ and $m(Er_2)=4.4\pm 0.2$. About ten years later, Guillot et al. (1981a) had an unambiguous proof from magnetic measurements that at 4.2 K the easy direction of magnetization was [001]. A particularly elegant experiment is due to Antonini et al. 1981 : A[110] disc of ErIG, allowed to rotate freely in a magnetic field, underwent an abrupt rotation at $73 K \pm 1.5 K$ by an angle of 54.7° which is the angle between [111] and [001]. A specific heat anomaly was seen by Guillot et al. (1981b) at $T=77\pm 4 K$.

Finally, a new neutron diffraction study was launched by the same team as under TbIG (Hock et al.), and RA was applied to space group $I4_1/acd$, maximal subgroup of $Ia\bar{3}d$. Among the 10 possible irreducible representations of $I4_1/acd$, listed in the book of Bradley and Cracknell (1972) only two, Γ_{2g} and Γ_{5g} , couple Er and Fe moments. Γ_{2g} alone is convenient and corresponds to the magnetic group $I4_1/ac'd'$. Once more Γ_{2g} does not belong to an irreducible representation of the paramagnetic group $Ia\bar{3}d$ and Landau's theory of second order transitions does not apply. The basis vectors of Γ_{2g} are tabulated in the paper by Hock et al. 1991. Those of Fe in 8a are collinear and opposite along [001] with $S_{\parallel}(Er)=7\mu_B$. Those of Er in 16e and Fe in 16c and 16d participate in the ferri-magnetism along Oz, but are allowed to have m_{\perp} components, forming anti-ferromagnetic arrays.

The refinement from the powder diagram resulted in $m_{\parallel}(Er)=4\mu_B$ $m_{\perp}=1.7\mu_B$ for Er(16e) ; for the iron moments only m_{\parallel} could be refined with m_{\parallel} nearer to 4 than to $5\mu_B$.

The most spectacular and direct proof for the first order transition of the spin reorientation from [111] to [001] was established by Hock et al. (1992) using X-ray and neutron topography and vidualising the coexistence of the rhombohedral and tetragonal phases of ErIG in the temperature interval $73 < T < 79$.

In the garnet case, I conclude that the moments m_{\parallel} follow from the superexchange mechanism of ferrimagnetism. The moments m_{\perp} are mainly due to the antisymmetric D-M interaction. I hope that studies with single crystals will continue.

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THE STORY OF THE GARNETS

The story starts with the perovskites MRO_3 , where M is a transition metal and R a rare earth. In 1953 I got a Fulbright fellowship and spent the major part of the year at State College, Pa., USA (now University Park) in the laboratory of Prof. Ray PEPINSKY, engaged in a project on ferroelectricity.

There I met his coworkers Franco JONA and Gen SHIRANE, specialists of ferroelectricity (1962). At this period, Chalmers FRAZER, another coworker of R. Pepinsky did neutron work at the Brookhaven National Laboratories on the ferroelectric transitions of the famous perovskite $BaTiO_3$ in order to determine the oxygen displacements. After returning from the States, I launched a rather ambitious program for preparing MRO_3 compounds with $M = Ti, V, Cr, Mn, Fe, Co$ and for R those rare earths which were available, say the lighter ones called « ceric », Ce, Pr, Nd, Sm, Gd. My thesis student Francis FORRAT prepared them with the help of our chemist, Claudine MOESCH, by the method usual in our laboratory: dissolution of the oxides separately in nitric acid, mixture, evaporation of the nitric acid followed by heating the powder to temperature between 1100 and 1400 °C. We had the secret hope to find new structures with interesting dielectric properties.

We knew about magnetic measurements on compounds labelled « $RFeO_3$ », which has the strange property of showing two Curie-temperatures (FORESTIER and GUIOT-GUILLAIN (1950-1954)) and even a third critical temperature where the magnetisation changed its sign (FORESTIER, PAUTHENET and GUIOT-GUILLAIN (1954), PAUTHENET and BLUM (1954)).

To interpret these results, NEEL (1954) made the hypothesis of a ferrimagnetism acting on the rare earth.

On our side some powder diagrams like that already known of $LaCoO_3$ were easily indexed in the rhombohedral system. But in most cases, we were unable to find the unit cell and cumulated lists of $\sin^2\Theta$ of MRO_3 compounds.

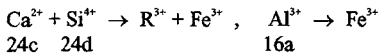
One day, end of 1954, Néel got the visit of Bernd MATTHIAS, well known specialist in ferroelectricity and superconductivity of alloys, then at the Bell Laboratories; Matthias learnt about the rare earth-ferrites problems and promised to send a single crystal of $GdFeO_3$, convinced that J.P. REMEIKKA, specialist of crystal growth could solve the problem. After a long while, Professor Néel got such a crystal and in a short time we could determine the unit cell, the space group $P6mm$, the positions of the four Fe atoms, located at symmetry centres and a good approximation for the Gd locations in the deformed perovskite type.

We summarized the unit cells and space groups of about forty compounds MRO_3 in a paper by Bertaut and Forrat (1956b) « Sur les déformations dans les pérovskites à base de terres rares et d'éléments de transition trivalents ». We also learnt that the structure of $GdFeO_3$ had been already solved at Bell Labs (Geller 1955, 1956) and included this information in our paper, published in february 1956.

For us, the important point was the following one: we realized at once that iron in equivalent symmetry centres could not give rise to ferrimagnetism, but at most to a weak ferromagnetism comparable to that of $\alpha-Fe_2O_3$, which was soon confirmed by Pauthenet's measurements given in his thesis (1957, 1958).

Thus we looked systematically for the « ferrimagnetic impurity ». Increasing the proportion of Fe_2O_3 , we saw in our Debye-Scherrer diagram the progressive fading of the many perovskite reflections and the appearance of a very simple pattern of Debye-Scherrer lines which could be indexed in the body-centered cubic system and started with the relatively high indices 1,1,2. The many extinctions clearly indicated the last space group of the International Tables N° 230, $Ia\bar{3}d$ which assigns the parameterless positions 16a, 24c and 24d to the cation's positions which are compatible with the proportions of iron and rare earth in the sample. The corresponding site symmetries are 3, 222 and 4.

As for each distance $d(ac)$ one finds an equal distance $d(ad)$, we hesitated between two models, model I with Fe in 24d) and R in 24c) and model II with the 24 fold positions interchanged, until we discovered that we had to do with garnets like $Al_3(CaSiO_3)_4$ (MENZER, 1928) realizing the substitutions



To summarize, Fe^{3+} is in the octohedral positions 16a and the tetrahedral positions 24d while R is in the positions 24c, centres of highly deformed cubes.

From Felix TROMBE, famous specialist of rare earth chemistry - discoverer of the ferromagnetism of Gd and EuO - and also father of the solar furnace of ODEILLO, we had got very pure oxides of Gd and in decreasing order of weight of Sm, Dy, Er and also of Y.

A detail, amusing today, but rather deceiving in 1956, was that the first rare earth-iron garnet synthesised, $3Gd_2O_3 \cdot 5Fe_2O_3$, was only weakly ferimagnetic at room temperature, its compensation temperature being 290 K as we learnt later on. Our generator of magnetic fields was a little magnet of five grammes.

However the strong action of the YIG sample confirmed our hopes. Our first paper on the iron garnets of the rare earths was written in november 1955. After some criticism and additional remarks of Professor Néel, a second draft was ready in december 1955. The final note was presented by Prof. Charles MAUGUIN to the French Academy of Sciences, and appeared in print january 1956 (BERTAUT and FORRAT (1956 a)).

I got an enthusiastic letter of congratulation from Dr J.S. SMART, then « Liaison Officer of the U.S. Navy » in London, U.K., who propagated the news to the USA. I recall here that J.S. Smart is coauthor with C.G. SHULL of the first neutron diffraction study of MnO (1949) and that with Mrs GREENWALD he did pioneering work on the crystallographic deformations of transition metal oxides at the Néel temperature.

R. PAUTHENET chose at once the rare earth-iron garnets - and our samples - as principal subject of his doctor thesis. With his colleagues ALEONARD and BARBIER (1956) *CR. Acad. sci.* (195, 242, 2531), he used Néel's formula (13) to represent the inverse susceptibility of YIG, the ideal ferrimagnet, and to obtain reliable interaction coefficients.

Francis PERRIN, head of the French Atomic Energy Commission (CEA), Néel's colleague at the Institut de France, allowed us the use of the Research Reactor EL2 in Saclay during two days and two nights for recording the first neutron diffraction diagrams in France, those of YIG, which definitely established its ferrimagnetic nature (BERTAUT, FORRAT, HERPIN, MERIEL (1956), *C.R. Acad. Sci.* 243 (1956) 898-901).

In fact, two powder diagrams were recorded at room temperature.

The first one reproduced the nuclear and magnetic contributions. In the second diagram, a permanent magnet created a magnetic field parallel to the scattering vector, eliminating the magnetic contributions. The difference diagram showed only magnetic intensities in good agreement with the theoretical prediction of the ten measured intensities.

Finally we completed our papers on cell dimensions of rare earth orthoferrites $RFeO_3$ and iron garnets $3R_2O_3 \cdot 5Fe_2O_3$ (Bertaut and Forrat 1956 a,b) by those of gallates and aluminates (Bertaut and Forrat 1956 c, *C.R. Acad. Sci.* 243 (1956) 1219-1220) and showed that the parameter values of garnets are reproduced by linear relation (Bertaut and Forrat, *C.R. Acad. Sci.* 246 (1957) 96-98).

Pauthenet on his side examined the whole series of rare earth iron garnets from the experimental (1956 a) and theoretical (1956 b) point of view. These two papers summarize so to speak his thesis defended in January 1957 and printed in 1958. There he lists the inverse susceptibilities and the measured magnetisations and deals with the case of three sublattices.

As far as international meetings are concerned, there has been a presentation at the Magnetic Materials Conference, 23-31 March 1956, Moscow, by L. NEEL, F. BERTAUT, F. FORRAT and R. PAUTHENET with the title: « A new type of ferromagnetic substances, rare earth ferrites having the garnet type structure ». The paper appeared in *Izvest. Akad. Nauk. SSSR MOSCOW* (1957) 21 904.

Pauthenet and myself got an invitation to the « Convention on Ferrites of the I.E.E. London 1956 ». On 31 October, I talked there about the crystallographic properties of the ferrimagnetic garnets followed by Pauthenet, who treated their magnetic properties. Our contributions appeared in *Proc. IEE* (1957) 104B suppl. N°5, 261-264. This paper had the privilege of being reprinted in the volume I of « Selected Papers in Physics (1950-1957) » of the Physical Society of Japan.

These lines are written to recall that the rare earth- and yttrium-iron garnets have been described and characterized crystallographically and magnetically in one year, from January 1956 to January 1957, and there was no need to rediscover them in other countries.

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Structure des ferrites ferrimagnétiques des terres rares.

1956 b, *J. de Physique et du Radium*, 17, 129-131

Sur les déformations dans les pérovskites à base de terres rares et d'éléments de transition trivalents.

1956 c, *C.R. Acad. Sci.* 243, 1219-1222

Etude des combinaisons des oxydes des terres rares avec l'alumine et la galline.

1957, *C.R. Acad. Sci.* 244, 96-98

Etude des paramètres des grenats.

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