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A SIMPLE DISCRETE APPROACH TO THE MECHANISM OF COMMENSURATE-INCOMMENSURATE PHASE TRANSITIONS.

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INTRODUCTION

This study arose from a detailed investigation by one of us (F.V.) of the magnetic behaviour of cubic rare earth intermetallics ($ReBe_{13}$) for heavy rare earths[1,2] : RE = Gd, Tb, Dy, Ho, Er. These compounds exhibit an antiferromagnetic structure below a given T_N. A careful study of the powder neutron diffraction spectrum reveals the existence of a distorted helicoïdal structure, the moments lying in the (xy) plane, with a propagation vector $\vec{\tau}$. A strong ferromagnetic coupling is apparent within each plane. There is no evidence for a modulation of the magnitude of the average moment per plane, which will be denoted by M(T).

There exists a temperature T_N' below which $\vec{\tau}$ locks in at a commensurate value $\vec{c}^*/3$. Between T_N' and T_N $\vec{\tau} = \frac{\vec{c}^*}{3}\,[1 - \varepsilon(T)]$ and varies continuously. Moreover, the spectrum above T_N' is consistent with a remaining modulation in the incommensurate regime. The results are summarized in Table 1.

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TABLE I

R_E^{3+}	T_N(°K)	T_N'(°K)	structure	C.E.F. splitting (°K)
Gd	27	0	helix	0
Tb	16.5	$8.5=T_N$	IC → C	10
Dy	10	10	C	20
Ho	6	4.5	IC → C	30
Er	3	$3.5=T_N$	C	40

There is in this problem a competition between exchange interactions and crystal field induced anisotropy (the rôle of which increases with decreasing temperature). As seen from Table I, the overall crystal field splitting is of the same order as exchange energy, except for Gd where there is no crystal field. For non Kramers ions (Tb, Ho; J = n) the crystal field ground state levels are isotropic and anisotropy arises only through the mixing with excited states where $T < T_N$ and when exchange cannot be considered as a small perturbation. In the case of Kramers ions (Dy, Er; J = n+1/2), the crystal field ground state is already anisotropic, which is the reason for the structure to be commensurate at T_N.

The basic purpose of this work has been to understand the locking at $\vec{c}^*/3$ in terms of a competition between exchange between first and second neighbouring sheets with a periodic potential, commensurate with the lattice (four-fold in this particular case).

The theoretical problem is of course much more general than this particular experimental situation that was considered. Most structural problems are described in terms of a harmonic chain perturbed by a periodic potential[3,4,5]. This implies the validity of the harmonic description,

and therefore only small distortions are allowed. Here, owing to the difference in magnitude between magnetic and cohesive energies, the amplitude of the modulation of the direction of a moment is very large : moreover the orientation occurs only through trigonometric functions and is defined modulo 2π. We expect the continuous approach[3,4] to be much less valid than in the structural case.

This work has been already presented at a conference on rare-earths[6]. We do not pretend in this short paper to be exhaustive but we aim to explain what, from our view point, is the essential reason for the occurrence of a C/CI transition. We think that the discreteness of the lattice is crucial in order to feel the transition. Our approach will be that of a crystallographer faced with the understanding of diffraction by modulated structures[7]. A much more complete theory will be published elsewhere.

THE MODEL

Ⓐ We denote the magnetization of each plane by $M_j(T)$. As stated in the introduction, we assume the exchange interactions within a plane to be so strongly ferromagnetic that $\vec{M}_j$ lies in the plane and has a constant magnitude $M(T)$. The only degree of freedom in each plane is the angle θ_j of $\vec{M}_j$ with a given direction. The average free energy per plane will be :

$$F = \langle f(M) \rangle - J_1 \langle \vec{M}_j \cdot \vec{M}_{j+1} \rangle - J_2 \langle \vec{M}_j \cdot \vec{M}_{j+2} \rangle + \langle V(M_j) \rangle \qquad (1)$$

in which $f(M)$ is the free energy of a sheet, J_1 and J_2 are the exchange integrals between first and second neighbouring sheets and V is the magnetocrystalline periodic

potential. It can be quite generally represented by :

$$V = - \sum H_K(T) \cos (n_K \theta_j + \alpha_K)$$

In the case of $REBe_{13}$, $n_K = 4$. For metallic rare earths, $n_K = 6$. We could also apply a magnetic field ($n_K = 1$). We shall here limit the expansion to one term. If M_o represents the saturated value of M when $T \to 0$, we assume the usual behaviour :

$$H = K\left(\frac{M}{M_o}\right)^{\frac{n(n+1)}{2}} \tag{2}$$

for magnetocrystalline anisotropy. We modify (1) into :

$$\begin{aligned} F &= f(M) + M^2\Phi \\ \Phi &= - J_1 < \cos(\theta_{j+1} - \theta_j) > \\ &\quad - J_2 < \cos(\theta_{j+2} - \theta_j) > \\ &\quad - H(M) < \cos(n\theta_j) > \end{aligned} \tag{3}$$

The ground state is obtained by minimisation of (3) with respect to all θ_j.

$$\partial F/\partial M = 0 \tag{4a}$$

$$\partial \Phi/\partial \theta_j = 0 \tag{4b}$$

We are essentially interested here in the equilibrium arrangement of moments, dictated by (4b). Then the determination of M through (4a) is straightforward. In the case we look for an approximate variational solution, each $\partial\phi/\partial\theta_j$ is different from zero and represents a local torque, the magnitude of which controls the accuracy of the model.

In the absence of the potential V, the ground state is easily shown to be an helix of angular step θ_o [8,9] such that

$$\cos \theta_o = - J_1/4J_2 \tag{5a}$$

provided $J_1 + 4J_2 < 0, \qquad J_2 < 0$

The structure is thus

$$\theta_j = j\theta_o \tag{5b}$$

We will assume $J_1 > 0$ ($\theta_o < \pi/2$). We renormalize the energy in units of $|J_2|$, and get :

$$\Phi_o = -[1 + 2\cos^2\theta_o] \tag{6}$$

in the absence of the potential, and

$$\Phi = -4\cos\theta_o < \cos(\theta_{j+1} - \theta_j) > + < \cos(\theta_{j+2} - \theta_j) > - h < \cos(n\theta_j) > \qquad (h = H/|J_2|) \tag{7}$$

The two parameters in describing the phase diagram are θ_o and h. When h increases, we expect a growing competition between the original period θ_o and the period $(2\pi/n)$ of the potential. The two major effects will be a variation of the mean angular step bewteen neighbouring planes and a modulated distortion from an helix.

(B) The case of an harmonic chain has been extensively studied, either by continuous methods[3,4] or by discrete numerical iterative solution[5,10,11]. It is shown that the solution is of the type

$$\theta_j = j\theta + \alpha + g_n(j\theta + \alpha) \tag{8}$$

where g_n is a periodic function of period $2\pi/n$, which can become nonanalytic in strong potentials. g_n can always be expanded in a Fourier series.

In the magnetic case we are facing, and in the case of an external applied field (n = 1), the magnetic structure tends

towards a ferromagnet ($\theta = 0$) but exhibits in an extended range of fields a modulation around the ferromagnetic order[9,10] [fan structure], represented by

$$\theta_j = g_1(j\theta_o + \alpha) \tag{9}$$

Therefore, if we look for a variational trial solution, one may assess more generally :

$$\theta_j = j\theta + \alpha + g_n (j\theta' + \alpha') \tag{10}$$

In what follows, we will restrict ourselves to a sinusoïdal approximation to g_n. This excludes the occurrence of discontinuity in g_n, only obtainable from an infinite expansion. We cannot either get a very precise description of the evolution of the structure at the vicinity of a transition point. However, it is quite sufficient to point out the essential features of the phase diagram. We thus assume :

$$\theta_j = j\theta + \alpha + A \sin [n(j\theta' + \alpha')] \tag{11}$$

A being by symmetry an odd function of h.

THE EFFECT OF COMMENSURABILITY

We will make use of the expansion* :

$$e^{iz \sin \xi} = \sum_{m=-\infty}^{+\infty} J_m(z) e^{im\xi} \tag{12}$$

It is quite clear that the exchange energy will be less negative than for a pure helix. We therefore have to first minimize the contribution from the potential h. We write

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* $J_m(z)$ is the m^{th} order Bessel function.

$$\varphi_a = \langle \cos(n\,\theta_j) \rangle$$

$$= \sum_{m=-\infty}^{+\infty} J_m(nA)\, \mathcal{R}e \left\{ e^{in(\alpha+m\alpha')} \langle e^{inj(\theta+m\theta')} \rangle \right\} \quad (13)$$

It is clear that the chain average $\langle \quad \rangle$ vanishes unless

$$(\theta + m\theta') = \frac{2p\pi}{n} \quad (14)$$

Owing to the structure of Bessel functions, we want (14) to be satisfied with m as small as possible. In the general case of variational θ and θ' we get :

(i) : $\theta = \theta' \qquad \alpha = \alpha'$

(ii) : $\theta = \frac{2p\pi}{m} \qquad \theta' = \ldots \qquad \alpha = 0$

case (ii) corresponds to an average alignment towards the axes of easy magnetization (similar to fan structure). It could only occur asymptotically for large h.

We thus have to consider essentially case (i), which goes back to the assumption (8). We write φ_a as :

$$\varphi_a = \sum_{m=-\infty}^{+\infty} J_{m-1}(nA) \langle e^{imnj\theta} \rangle \cos mn\alpha \quad (15)$$

The crucial point in the discussion is easily apparent from the expansion (15).

1. If $\theta \neq \frac{2\pi}{n} \frac{p}{q}$ (i.e. the two periods θ and $\frac{2\pi}{n}$ are incommensurate) only the term (m = 0) contribute to (15) and we simply get :

$$\varphi_a^{IC} = - J_1(nA) \quad (16)$$

for which we expect A to be negative. The phase α is irrelevant.

2. However, if $\theta = \frac{2\pi}{n}\frac{p}{q}$ (p,q mutual primes) there are additional terms in the energy, corresponding to m = r.q. Therefore, any time θ and $2\pi/n$ become commensurate, the energy becomes discontinuous. We write, limiting the expansion to the major term (r = 1)

$$\varphi_a^C = \varphi_a^{IC} + \Delta\varphi_a$$

$$\Delta\varphi_a = J_{q-1}(nA)\cos[qn\alpha] \qquad (17)$$

The phase becomes locked at the value which maximises (17):

$$\begin{aligned} q = 2k &\rightarrow \alpha = \pi/nq \quad (\mathrm{mod}\ 2\pi/nq) \\ q = 2k+1 &\rightarrow \alpha = 0 \quad (\mathrm{mod}\ 2\pi/nq) \end{aligned} \qquad (17')$$

The discontinuity in energy is thus of order q in h and tends to give a stabilisation. Commensurability is therefore favorable. We notice here the similarity with the occurrence of constructive interference within a lattice sum, leading to the celebrated diffraction condition.

3. In order to "feel" for the difference between commensurate and incommensurate structures, let us consider commensurability with increasing q. There is a superlattice of period q. The contribution φ_a can be written exactly as:

$$\varphi_a = \frac{1}{q}\sum_{j=0}^{q-1}\cos\left\{\frac{2\pi j}{q} + n\alpha + nA\sin\left[\frac{2\pi j}{q} + n\alpha\right]\right\} \qquad (18)$$

Now take any value of θ. It can be approached by a series of rationals $\frac{2\pi}{n}\,p/q$ with increasing q. When $q \to \infty$, $n\alpha$ can be represented by a given $\frac{2\pi j_0}{q}$ and choosing the phase becomes equivalent to choosing an origin in the supercell. That is why it becomes irrelevant. Then the sum (18)

becomes a close representation of the integral :

$$\lim_{q\to\infty} \varphi_a = \frac{1}{2\pi}\int_o^{2\pi} \cos\left[x + nA \sin x\right]\, dx$$

$$= - J_1(nA) = \varphi_a^{IC} \qquad (19)$$

The degree of commensurability is therefore estimated by the difference between (19) and (18). In our case, we estimated $\left|\frac{\varphi_a - \varphi_a^{IC}}{\varphi_a^{IC}}\right|$ to be smaller than 10^{-4} when $q \geqslant 10$.

4. Indeed, we have to consider also the exchange contributions. By similar arguments, we get, if θ and $2\pi/n$ are incommensurate :

$$\varphi_1^{IC} = \langle \cos(\theta_{j+1} - \theta_j) \rangle$$
$$= \cos\theta\ J_p\left(2A \sin\frac{n\theta}{2}\right) \qquad (20)$$
$$\varphi_2^{IC} = \langle \cos(\theta_{j+2} - \theta_j) \rangle$$
$$= \cos 2\theta\ J_o(2A \sin n\theta).$$

As said earlier, since $J_o(z) < 1$, the effect of the external potential is some kind of screening of exchange interactions.

If θ and $2\pi/n$ are commensurate

$$\varphi_{1,2} = \varphi_{1,2}^{IC} + \Delta\varphi_{1,2} \qquad (21)$$

with a discontinuity which depends on the parity of q.

$$\begin{aligned} q = 2k \qquad & \Delta\varphi_1 = -2(-1)^{k+p} \cos\theta\ J_q(2A \sin\frac{n\theta}{2}) \\ & \Delta\varphi_2 = -2(-1)^{k} \cos 2\theta\ J_q(2A \sin n\theta) \\ q = 2k+1 \qquad & \Delta\varphi_1 = -2(-1)^{k+p} \sin\theta\ J_q(2A \sin n\theta/2) \\ & \Delta\varphi_2 = -2(-1)^{k} \sin 2\theta\ J_q(2A \sin n\theta) \end{aligned} \qquad (21')$$

The correction is again of order q in h, but can be shown to be in general smaller than the effect on φ_a, that drives the behaviour of the system. Of course, an exact expression is

$$i = 1,2; \varphi_i^C = \frac{1}{q} \sum_{j=0}^{q-1} \cos\left\{ i\theta + 2A \sin\left(\frac{ni\theta}{2}\right) \cos\left[\frac{2\pi j}{q} + \frac{ni\theta}{2} + n\alpha \right] \right\} \tag{22}$$

Finally, we notice for q = 2k+1, and from (17) that a change of origin by π/n is not possible, which breaks the symmetry of A which existed only for the continuous case. It is also clear that inclusion of harmonics should be necessary to have a truly consistent description. However one can show that the qualitative behaviour would not change. The basic message remains that commensurability condition leads to a stabilizing discontinuity in the energy, which will be the most pronounced for small values of q.

TOWARDS THE PHASE DIAGRAM

We recall that the energy is given by

$$\Phi = -4 \cos\theta_o \varphi_1 + \varphi_2 - h\varphi_a \tag{23}$$

For given θ_o and h, we have the choice between the continuous incommensurate structure Φ^{IC} and the set of $\phi_{p,q}$ for commensurate (p,q) structures. The ground state corresponds to the minimum of these functions. In practice we limited ourselves to $q < 10$. The helix step angle θ_o lies in the range 50-55 degrees for $REBe_{13}$ but we considered the whole range $[0, \pi/2]$. The resulting phase diagram is shown in Fig. 1, obtained by using a grid of 0.05 in h, and limiting the accuracy in ϕ to 10^{-4}. Similar diagrams have been obtained for n = 6.

1. Only very few domains exist with an appreciable range of stability. The leading conclusion is the locking of the structure at (2,3) with an average period of $\pi/3$ for large h values (~ 1) for $REBe_{13}$. So this simple model

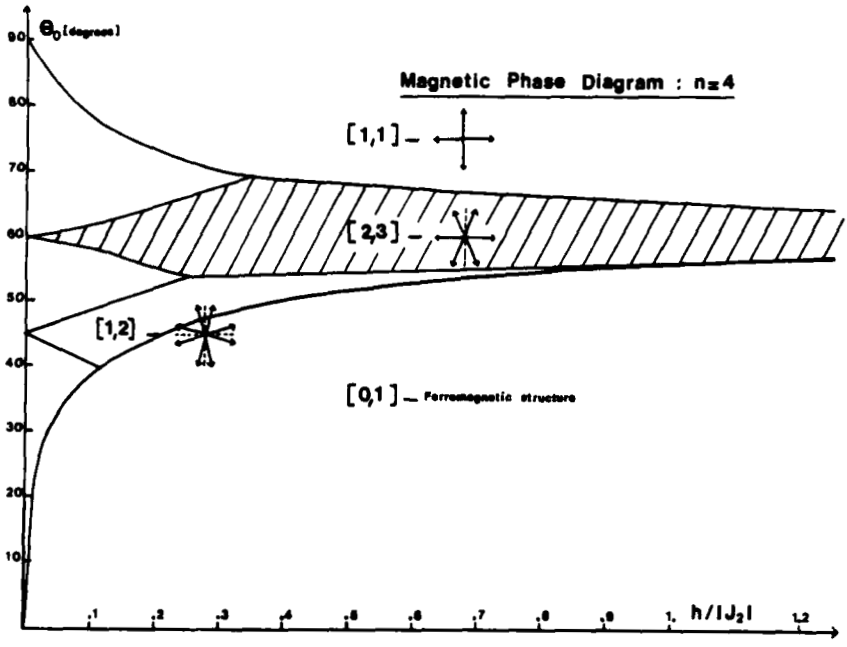


Fig. 1

Phase diagram together with the spin arrangement in each phase.

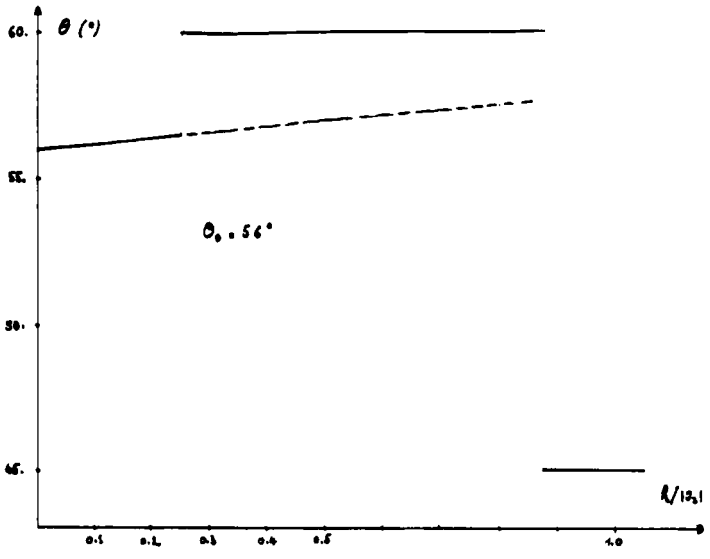


Fig. 2a

Average period as a function of h in the case n = 4 - the 45° period is not found experimentally, because h is limited.

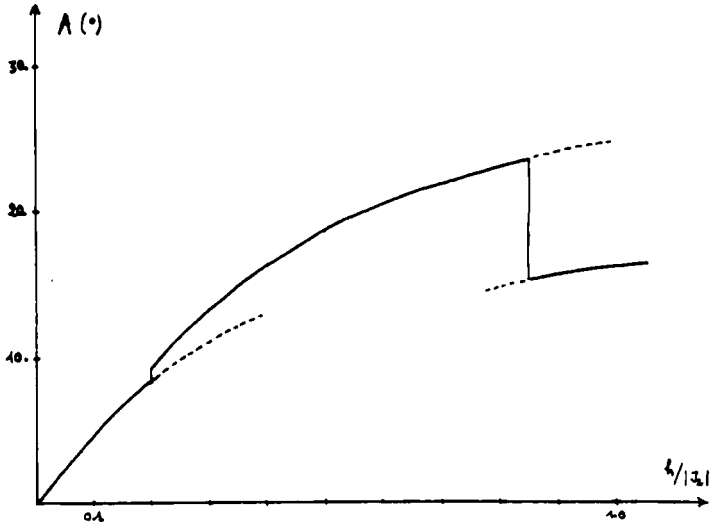


Fig. 2b

Modulation amplitude in the same conditions as Fig. 2a. For θ = 45°, the phase α = 22.5°.

is capable of explaining unambiguously the observed situation in these compounds. Making a $h \to T$ correspondence through the observed M(T) the transition temperature in the case of H_o and Tb is predicted to within 50 %.

2. The behaviour of $\theta(h)$ and A(h) is depicted on Fig. 2. We observe clearly the first order C/IC transitions. Advanced literature quotes transitions of second order[4,11] but this is not obvious. In particular, owing to the crudeness of our model, we should be cautious not to put too much emphasis on details. Notice that for well chosen values of θ_o, one may get more steps, but with a small range of stability only.

3. We notice in $REBe_{13}$ case the large amplitude of the modulation A. We observe that the resulting structure is twofold degenerate (the two equivalent structures being obtained by a $\pi/2$ phase shift) and the effective ground state should contain domains. The prediction of the direction of moments at low T is fairly accurate.

4. We observe two asymptotic regimes, depending on θ_o. If $\theta_o < \pi/3$ the limit structure is ferromagnetic ($\theta = 0$ mode 2π). If $\theta_o > \pi/3$ the limit structure is (1,1) with $\theta = \pi/2$. It is easily verified by comparing the limit energies

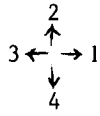
$$\phi_{0,1} = -4 \cos \theta_o + 1 - h$$

$$\phi_{1,1} = -1 - h$$

We tried to look for modulations around these structures, optimising A and θ'. We found $\theta' = \frac{\theta_o}{2n}$ and a domain of h where the distorted helix is more stable. This, for $n > 1$,

there should not be any "fan structure".

Notice that the (1,1) structure is degenerate :



equivalent to $3 \leftarrow\rightarrow 2$, $4 \leftarrow\rightarrow 1$

5. Finally, we would like to understand why so few steps are present, whereas we got the impression that commensurability is always favourable. We saw that the pinning energy is $\sim \frac{h^q}{(q-1)!}$ any time $\theta = \frac{2\pi}{h} p/q$. When h varies, θ goes through many (p,q) values with q large. If we consider two neighbouring values (p_1,q_1) and (p_2,q_2), if $q_1 < q_2$ the (p_1,q_1) structure may be stable over some range but (p_2,q_2) is unlikely to be stable. Moreover, if q_1 is large enough, the gain in pinning energy will not compensate the loss in Φ^{IC} due to the fact that we do not let θ vary in a commensurate structure. Therefore, in the range of small h, the commensurate structure will not have a significant stability range. Including harmonics will even lower this range. On the other hand, as soon as a commensurate structure occurs, the system can never go back to an incommensurate state. These arguments can be conforted by lengthy calculations.

CONCLUSIONS

We have seen how this simple discrete model enables us to understand the basic origin of the commensurate-incommensurate phase transition in a magnetic system. It is rather different from the usual Sine-Gordon continuous approach[3,4,5]. If we try such an approach in our case, it fails because the the fluctuation about the mean period from plane to plane is large and h is typically of order unity. A proper approach would certainly consist in deriving locally a Sine-Gordon

equation in a very small range of h and this would describe properly the occurring transitions.

The numerical approach of Aubry[11] is very interesting and leads to occurrence of chaotic behaviour for particular values of the parameters. Of course wo do not find such a situation here and we might be able to detect it by a divergence in the Fourier expansion of (8) in the incommensurate regime. However we must notice that Aubry finds a breaking of analyticity especially in chains with fixed or quasi-fixed ends - this looks quite normal since if we impose the average period to remain θ_o, which is not favourable for the energy, the system may prefer to vary its period to θ over a certain range and exhibit some distorted regions between these modulated domains, with a constraint of total fixed length. Here we have much more freedom and the system may always find a regular modulated arrangement.

We have recently considered the case where the order parameter is the length of the moment rather than its orientation (axial modulation, when $\vec{M}_j$ are along oz). Such a case is represented for example by cubic CeSb that exhibits many commensurate structures. By using the same kind of ideas, we found singularities in the entropy which plays a crucial rôle and were able to explain some peculiar features of the diagram of CeSb[12].

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