Incommensurate structures induced by an external field

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An external field can produce in a crystal a phase transition accompanied by formation of an incommensurate magnetic structure. A situation is analyzed wherein the onset of the incommensurate structure is inevitable by virtue of general symmetry consideration; the magnetic ordering in the absence of a field is assumed homogeneous.

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1. INTRODUCTION

We consider a crystal in which a certain homogeneous magnetic structure is realized in the absence of external fields. If such a sample is now placed in a magnetic field, it is not excluded in principle that long-period beats, whose period depends essentially on the applied action, will be superimposed on the initial magnetic structure. We are dealing thus with an effect that is the inverse of the destruction of a modulated structure by a magnetic field.[1]

We analyze in this paper a situation wherein the appearance of a modulated structure is inevitable by virtue of general symmetry considerations. We name actual compounds in which such an effect should take place, and determine the character of the magnetic structure as a function of the magnitude and direction of the external field.

Assume that a homogeneous magnetic structure is produced at the Curie point T_C via a second-order phase transition. The microscopic density of the magnetic moment $\mathbf{S}(\mathbf{r})$ in the magnetically ordered phase corresponds to an active irreducible representation (IR) of the symmetry group τ of the paramagnetic phase G; the IR τ is assumed to be not one-dimensional. We consider next the same phase transition, but now in the presence of a sufficiently weak external magnetic field $\mathbf{H}$. At $T > T_C$ the presence of the field H lowers the symmetry group of the paramagnetic state to $G(\mathbf{H}) \subset G$. Obviously, the matrices of the Ir τ of group G realize also a certain representation of the group $G(\mathbf{H})$, which we shall designate by the symbol τ' [according to standard terminology, τ' is the restriction of the IR τ of the group G on the subgroup $G(H) \subset G$]. We are interested in the case when the representation τ' is also irreducible, but is now passive by virtue of the presence of Lifshitz invariants. In thermodynamic language this means that it is possible to group the order parameters $\{c_i\}$ a combination of the type

$$c_i \frac{\partial c_j}{\partial x} - c_j \frac{\partial c_i}{\partial x}, \tag{1}$$

which is invariant to all the operations from $G(\mathbf{H})$, but is not invariant to certain transformations of the group G (since the IR τ is assumed to be active). It is clear that the coefficient at the invariant (1) will effectively depend on the magnitude and direction of the external field, and in particular, will vanish as $\mathbf{H} \to 0$.

Repeating now Dzyaloshinskiĭ's reasoning (given on pp. 1425–1426 of Ref. 2), it is easily understood that in the case described above it is always possible to induce in the vicinity of T_C a modulated magnetic structure with arbitrarily large modulation. (The modulation period tends to infinity in the immediate vicinity of T_C as $\mathbf{H} \to 0$). With increasing field $\mathbf{H}$, just as with increasing deviation from T_C, the modulated structure may turn out to be unstable.

The situation considered is distinguished by the fact that the large modulation (as, e.g., in Ref. 2) period is not connected with the assumption that certain interactions in the crystal are weak, and can always be obtained by a suitable choice of the value of the external field $\mathbf{H}$.

Of course, the field-induced inhomogeneous magnetic structure may turn out to be stable in a more extensive region on the T–H phase diagram, and not only in the vicinity of T_C as $\mathbf{H} \to 0$. It is impossible, however, to discuss this question within the framework of a pure symmetry analysis.

2. MAGNETIC ORDERING IN CaV_2O_4 IN AN EXTERNAL FIELD

In the paramagnetic state, CaV_2O_2 belongs to the Fedorov group *Pnma* (the choice of the coordinate axes corresponds to that assumed in Ref. 3), and the vanadium ions occupy 4*c*-positions. It has been reliably established that below T_N a collinear antiferromagnetic ordering is realized, corresponding to a wave vector $\mathbf{k} = [0\frac{1}{2}\frac{1}{2}]$, and the magnetic moments are parallel to the z axis.[4–6] The magnetic ordering corresponds to one of the two active IR whose matrices are given in Table I. The fact that the mutual orientation of the spins is not uniquely determined is of no significance to us: all that matters is that the magnetic structure corresponds to one of the IR (τ_1 or τ_2) of the single-ray star of the

TABLE I. Matrices of irreducible representations of the *Pnma* group, corresponding to elements of a null block.*

	e	r_x	r_y	r_z	I	m_x	m_y	m_z
τ_1	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & \bar{1} \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \bar{1} \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & \bar{1} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & \bar{1} \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
τ_2	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \bar{1} \\ 1 & 0 \end{pmatrix}$

*The (single-ray) star of the wave vector $\mathbf{k} = [0, \frac{1}{2}, \frac{1}{2}]$; the description of the *Pnma* group is taken from the handbook.[3]

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wave vector $\mathbf{k}=[0\frac{1}{2}\frac{1}{2}]$. All the conclusions that follow are valid to equal degree for the irreducible IR τ_1 as well as τ_2. We shall therefore simply refer to an IR τ, bearing in mind either of these possibilities.

Using the table, it is easy to show that the restrictions of the representations τ_1 and τ_2 on the subgroup $G(H)$ have the following properties:

$$F=F_{un}+F_{amb}, \tag{2}$$

$$F_{un}=A(c_1^2+c_2^2)/2+B(c_1^2+c_2^2)^2/4+B_1[(c_1^2-c_2^2)^2/4-4c_1^2c_2^2] -DH_yH_z(c_1^2-c_2^2), \tag{3}$$

$$F_{amb}=\alpha_1H_xH_y\left(c_1\frac{\partial c_2}{\partial z}-c_2\frac{\partial c_1}{\partial z}\right)+\alpha_2H_xH_z\left(c_1\frac{\partial c_2}{\partial y}-c_2\frac{\partial c_1}{\partial y}\right) +\alpha_3H_yH_z\left(c_1\frac{\partial c_2}{\partial x}-c_2\frac{\partial c_1}{\partial x}\right)+\frac{1}{2}\delta_x\left[\left(\frac{\partial c_1}{\partial x}\right)^2+\left(\frac{\partial c_2}{\partial x}\right)^2\right] +\frac{1}{2}\delta_y\left[\left(\frac{\partial c_1}{\partial y}\right)^2+\left(\frac{\partial c_2}{\partial y}\right)^2\right]+\frac{1}{2}\delta_z\left[\left(\frac{\partial c_1}{\partial z}\right)^2+\left(\frac{\partial c_2}{\partial z}\right)^2\right] +\delta_{yz}\left(\frac{\partial c_1}{\partial y}\frac{\partial c_1}{\partial z}-\frac{\partial c_2}{\partial y}\frac{\partial c_2}{\partial z}\right). \tag{4}$$

a) they are irreducible and active if **H** is parallel to one of the twofold axes (x, y, or z);

b) they are irreducible and possible (according to E. M. Lifshitz) if $H_xH_y\neq 0$ and $H_z=0$ or if $H_xH_z\neq 0$ and $H_y=0$;

c) they are reducible if $H_yH_z\neq 0$.

Thus, if the field **H** is directed in the xy or xz plane (case b), at sufficiently low **H**, at any rate, the modulated structure will be stable in the immediate vicinity of T_N ($T\lesssim T_N$). In case a) no modulated structure is produced, and in case c) the answer to this question depends on the ratio of the different interactions (and, of course, on the direction of the field **H**).

Assuming the magnetic field to be sufficiently weak, we write down the expansion of the free energy in powers of the order parameter $\{c_i\}$ ($i=1,2$) in the vicinity of T_C (the form of the expansion does not depend on whether the phase transition proceeds according to τ_1 or τ_2). The coefficients A, B, and B_1 in (3) must be assumed dependent on the field:

$$A=A_0+\sum_{\alpha=x,y,z}a_\alpha H_\alpha^2,\quad B=B_0+\sum_{\alpha=x,y,z}b_\alpha H_\alpha^2, \qquad B_1=B_0^{(1)}+\sum_{\alpha=x,y,z}b_\alpha^{(1)}H_\alpha^2. \tag{5}$$

At **H** = 0, all the terms in (4) that are linear in the derivatives vanish, this being a consequence of the activity of the IR τ of the *Pnma* group.

We consider now the case $H_z=0$. Making the standard change of variables

$$c_1=\rho\sin\varphi,\quad c_2=\rho\cos\varphi,$$

in (3) and (4), we obtain for the free energy

$$F=\frac{1}{2}A\rho^2+\frac{1}{4}B\rho^4+\frac{1}{4}B_1\rho^4\cos 4\varphi-\alpha_1H_xH_y\rho^2\frac{\partial\varphi}{\partial z} +\frac{1}{2}\delta_z\left[\left(\frac{\partial\rho}{\partial z}\right)^2+\rho^2\left(\frac{\partial\varphi}{\partial z}\right)^2\right]. \tag{6}$$

This is precisely the equation investigated earlier.[7,8] The only difference is that instead of one parameter (temperature) we already have two (temperature and field). The following magnetic states are therefore possible in the system:

I. $\rho=0$;
II. $\rho\neq 0$; $\partial c_{1,2}/\partial z\neq 0$;
III. $\rho\neq 0$; $\partial c_{1,2}/\partial z=0$.

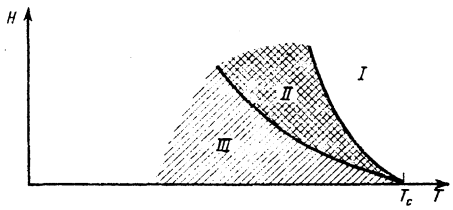

FIG. 1. Possible form of the phase diagram of CaV_2O_4 in the region of small $\mathbf{H}\perp z$ and $T\sim T_C$. The direction of H is fixed in the x-y plane. The cross-hatched region corresponds to the incommensurate magnetic structure (phase II).

The actual form of the phase diagram plotted in coordinates T and **H** depends on the ratio of the phenomenological parameters in (5) and (6). One possible phase-transition type is shown in Fig. 1, which represents the region of small **H** in the vicinity of T_C. Unfortunately, it is impossible to obtain analytic expressions for the lines of the phase diagram,[1)] but this is not our problem. It is important to us only to ascertain that the presence of a stability region of phase II (of the modulated phase) is mandatory. The period λ of the "beats" in the immediate vicinity of the magnetic-ordering temperature is determined by the relation

$$\lambda=2\pi\delta_z/|\alpha_1H_xH_y| \tag{7}$$

and is thus inversely proportional to H^2.

If $H_y=0$ we obtain a similar picture except that the magnetic structure is modulated along the y axis.

Finally, in the case $H_yH_z\neq 0$ a modulated structure is not obligatory in principle at any T and H: everything is determined in this case by the competition between the parameter D in (3) and the constants of the gradient invariants in (4) and depends, naturally, on the direction cosines of the vector **H** relative to the crystallographic axes. No corresponding mathematical analysis can be carried out (at $H_yH_z\neq 0$ the value of ρ depends significantly on the coordinates even in the vicinity of T_N).

It can be shown that all the phenomenological coefficients in (3)–(5) are of exchange origin. Cases are possible in principle, in which the coefficients α, D, or C_1 are of relativistic origin, i.e., they vanish in the exchange approximation.

3. OTHER POSSIBILITIES OF OBTAINING MODULATED STRUCTURES

A situation analogous to those considered above can arise not only in the vicinity of the magnetic-ordering temperature, but also near some other second-order phase transition, either magnetic or structural. In the latter case we deal with a modulated crystal structure. We, however, did not search for concrete examples of this kind.

We note further that, besides a magnetic field, an external action can be a homogeneous deformation or else an electric field. Indeed, since the product $H_\alpha H_\beta$ transforms just as the component $u_{\alpha\beta}$ of the strain tensor, it can be shown that everything considered in the preceding section holds also for the case of a phase transition in a deformed CaV_2O_4 sample [it suffices to replace $H_\alpha H_\beta$ in Eqs. (3)–(7) by $u_{\alpha\beta}$].

Finally, as an example in which the appearance of the modulated structure in the vicinity of T_C can be due to an external electric field E, we point out the ferrimagnet $NiMnO_3$ and the antiferromagnetic $CoTiO_3$ and $FeTiO_3$ (all beong to the Fedorov group $R\bar{3}$). In all these compounds, a modulated structure is induced in the vicinity of T_C by a field $\mathbf{E} \| z$ (z is the trigonal axis). Indeed, it is easy to verify that in all these compounds the magnetic structure corresponds to an active two-dimensional IR of the group $R\bar{3}$, but the restriction of this IR on the subgroup $G(E_z)$ [the analog of $G(\mathbf{H})$] is physically irreducible but is already passive. Thus, the situation is perfectly analogous to that considered in Sec. 1. The gradient invariant is of the form

$$\alpha E_z\left(c_1\frac{\partial c_2}{\partial z}-c_2\frac{\partial c_1}{\partial z}\right),$$

where c_1 and c_2 are the x and y components of the ferromagnetism vector in the case of $NiMnO_3$ and of the antiferromagnetism vector in the case of $CoTiO_3$ and $FeTiO_3$. The constant α is in this case of relativistic origin.

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[1)] Some of the difficulties encountered in this case are analyzed in Ref. 8.

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