Possibility of an exchange-induced latent paramagnetism in a system of equivalent ions

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It is predicted on the basis of a symmetry analysis of magnetic structures in the exchange approximation that a system of ions of a three-dimensional, three-sublattice magnetic material, which are equivalent in the paramagnetic phase, may acquire an order in which the magnetization of one of the sublattices is zero. The conclusion that there is the possibility of a latent paramagnetism in the exchange approximation remains in force for a greater number of sublattices.

Magnetic ions which are arranged in a crystal in such a way that they are equivalent in the paramagnetic phase may be rendered nonequivalent by a magnetic ordering even in the exchange approximation. This process produces structures in which the magnetizations of ions which are equivalent in the paramagnetic phase are different.

Such "unequal-module" structures with different sublattice magnetizations are not described by the approaches of Refs. 1 and 2, since the symmetry space group of the crystal is lowered by the appearance of such structures. Nevertheless, unequal-module structures exist and may even arise through second-order transitions.[3]

In the present letter we show that among unequal-module structures there are some for which the effective exchange field is identically zero at some of the ions which are equivalent in the paramagnetic phase by virtue of the symmetry of the magnetically ordered configuration. This result is unrelated to a low dimensionality of the magnetic material, as has been suggested in the derivation of a theory of a partially ordered $CsCoCl_3$ phase.[4] In particular, we would like to call attention to the circumstance that the equivalence of magnetic ions in the paramagnetic phase makes the structures predicted in the present letter fundamentally different from those in a situation with fluctuationally interacting sublattices, which were studied in Ref. 5 in the example of $Ca_3Fe_2Ge_3O_{12}$, where the magnetic ions are in nonequivalent sublattices.

As an example we consider a three-sublattice magnetic material in which all three of the sublattices occupied by magnetic ions belong to a common regular system of points in the paramagentic phase. We introduce some vectors: the ferromagnetic moment $\overline{\mathbf{M}} = (1/\sqrt{3})(\overline{\mathbf{S}}_1 + \overline{\mathbf{S}}_2 + \overline{\mathbf{S}}_3)$ and the antiferromagnetic moments $\overline{\mathbf{U}} = 1/\sqrt{6}(2\overline{\mathbf{S}}_1 - \overline{\mathbf{S}}_2 - \overline{\mathbf{S}}_3)$ and $\mathbf{V} = (1/\sqrt{2})(\overline{\mathbf{S}}_2 - \overline{\mathbf{S}}_3)$. The exchange symmetry group of the three-sublattice magnetic material is $C_{3v} \otimes O_3$. The complete basis of invariants made up of components of the vectors $\overline{\mathbf{U}},\overline{\mathbf{V}},\overline{\mathbf{M}}$. (or $\overline{\mathbf{S}}_1,\overline{\mathbf{S}}_2,\overline{\mathbf{S}}_3$) consists of nine invariants.[6] In order to list the antiferromagnetically ordered phases and to determine their regions of stability on the phase diagram, however, it is sufficient to use only three invariants:

$$J_1 = \bar{\mathbf{U}}^2 + \bar{\mathbf{V}}^2, \qquad J_2 = (\bar{\mathbf{U}}^2 - \bar{\mathbf{V}}^2)^2 + 4(\bar{\mathbf{U}}\bar{\mathbf{V}})^2,$$
$$J_3 = (\bar{\mathbf{U}}^2 - \bar{\mathbf{V}}^2)^3 - 12(\bar{\mathbf{U}}^2 - \bar{\mathbf{V}}^2)(\bar{\mathbf{U}}\bar{\mathbf{V}})^2. \qquad (1)$$

The other invariants describe the appearance of a latent antiferromagnetism[3] or of a phase with an intrinsic, rather than stimulated, ferromagnetism. Using (1), we can easily list all the various antiferromagnetic structures.[6] In addition to the paramagnetic phase ($\mathbf{I}, \overline{\mathbf{U}} = \overline{\mathbf{V}} = \overline{\mathbf{M}} = 0$), they are as follows:

$$\text{II.}\ \bar{\mathbf{U}} \perp \bar{\mathbf{V}},\ \bar{\mathbf{U}}^2 = \bar{\mathbf{V}}^2,\ \bar{\mathbf{M}} = 0\ (\bar{\mathbf{S}}_1^2 = \bar{\mathbf{S}}_2^2 = \bar{\mathbf{S}}_3^2,\ (\bar{\mathbf{S}}_i\mathbf{S}_k) = -\frac{1}{2}S^2);$$
$$\text{III.}\ \bar{\mathbf{U}} \perp \bar{\mathbf{V}},\ \bar{\mathbf{U}}^2 > \bar{\mathbf{V}}^2,\ \bar{\mathbf{M}} \neq 0\ (\bar{\mathbf{S}}_1 \perp (\bar{\mathbf{S}}_2 - \bar{\mathbf{S}}_3),\ |\bar{\mathbf{S}}_1| > |\bar{\mathbf{S}}_2| = |\bar{\mathbf{S}}_3|); \qquad (2)$$
$$\text{IV.}\ \bar{\mathbf{U}} \perp \bar{\mathbf{V}},\ \bar{\mathbf{U}}^2 < \bar{\mathbf{V}}^2,\ \mathbf{M} \neq 0\ (\bar{\mathbf{S}}_1 \perp (\bar{\mathbf{S}}_2 - \bar{\mathbf{S}}_3),\ |\bar{\mathbf{S}}_1| < |\bar{\mathbf{S}}_2| = |\bar{\mathbf{S}}_3|);$$
$$\text{V.}\ \bar{\mathbf{U}} \neq 0,\ \bar{\mathbf{V}} = 0,\ \bar{\mathbf{M}} \neq 0\ (\bar{\mathbf{S}}_1 \neq \bar{\mathbf{S}}_3;\ \bar{\mathbf{S}}_2 = \bar{\mathbf{S}}_3);$$
$$\text{VI.}\ \bar{\mathbf{U}} = 0,\ \bar{\mathbf{V}} \neq 0,\ \bar{\mathbf{M}} = 0\ (\bar{\mathbf{S}}_1 = 0;\ \bar{\mathbf{S}}_2 = -\bar{\mathbf{S}}_3);$$
$$\text{VII.}\ \bar{\mathbf{U}} \parallel \bar{\mathbf{V}},\ \bar{\mathbf{M}} \neq 0\ (\bar{\mathbf{S}}_1 \parallel \bar{\mathbf{S}}_2 \parallel \bar{\mathbf{S}}_3);$$
$$\text{VIII.}\ \bar{\mathbf{U}} \neq 0,\ \bar{\mathbf{V}} \neq 0,\ \bar{\mathbf{M}} \neq 0\ (\bar{\mathbf{S}}_1 \neq 0,\ \bar{\mathbf{S}}_2 \neq 0,\ \bar{\mathbf{S}}_3 \neq 0).$$

It can be seen from (2) that in phase VI we have $\overline{\mathbf{S}}_1 = 0$, $\overline{\mathbf{S}}_2 = -\overline{\mathbf{S}}_3$; i.e., the effective

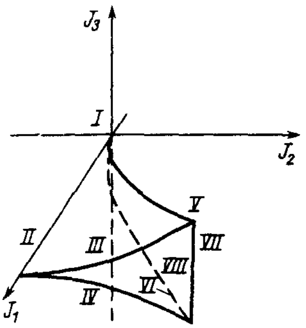

FIG. 1. Subsets in the space of invariants corresponding to different magnetically ordered structures.

exchange field at one of the sublattices has canceled out completely. The problem is to determine the existence domain of this phase on the phase diagram, i.e., to prove its stability and to determine the conditions for its appearance. To construct a phase diagram of a three-sublattice exchange antiferromagnetic which does not depend on the theoretical model, we find subsets of the space of invariants which correspond to various antiferromagnetic structures. For this purpose we substitute (2) into (1). We find Fig. 1, from which we can see unambiguously which of the phases border each other on the phase diagram. Lines II, V, and VI correspond to single-parameter phases in Fig. 1; surfaces III, IV, and VII correspond to two-parameter phases. The lowest-symmetry phase corresponds to the volume (phase VIII) bounded by surfaces III, IV, and VII. There is an interesting fact here: Magnetic materials also have anti-isostruc-

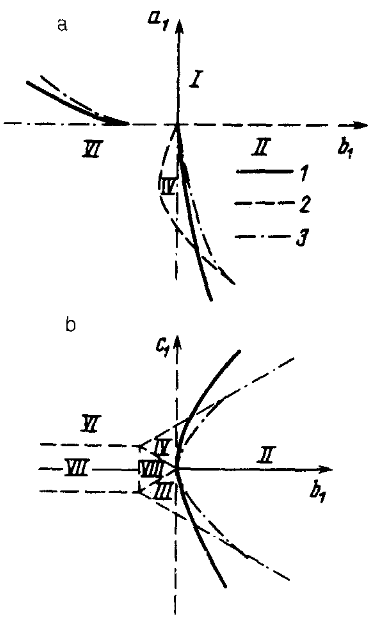

FIG. 2. Phase diagram in the space of phenomenological parameters. 1—Lines of first-order transitions; 2—lines of second-order transitions; 3—lines of a loss of phase stability. a) Near the transition to the paramagnetic phase; b) at low temperatures.

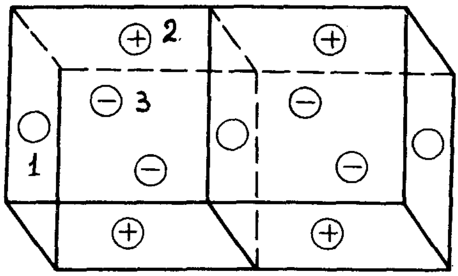

FIG. 3. Perovskite magnetic structure in a phase with a latent paramagnetism. ⊗, ⊖—Two antiparallel sublattices; O—third sublattice, at which the exchange fields cancel out exactly.

tural phases.[6] In the system under consideration here, these are phases III and IV. It follows from (1) that a description of all phases requires a Landau potential of at least the 12th degree, and it must include the square of the invariant of the highest degree.[6] We choose it in the structurally stable form

$$\phi = a_1 J_1 + a_2 J_1^2 + b_1 J_2 + b_2 J_2^2 + c_1 J_3 + c_2 J_3^2 \qquad (3)$$

The phase diagram corresponding to (3) has all the features determined by the symmetry of the problem. The incorporation of other interactions in (3) leads to features associated with the choice of a specific model (a distortion of lines, a change in the nature of the transition from second to first order upon the appearance of a tricritical point, etc.). For the purposes of this discusison, therefore, the interactions which are ignored in (3) are unimportant. It can be seen from the phase diagram corresponding to potential (3) (Fig. 2) that near the four-phase point the transition from phase VI to the paramagnetic phase may occur as a second-order phase transition. Figure 2b shows possible boundaries between the magnetically ordered phases of different symmetry in the case $a_1 < 0$. In other words, this diagram characterizes exchange orientation transitions in this system at low temperatures, e.g., from the phase $\overline{U}\perp\overline{V}$(IV) to the phase $\overline{U}\|\overline{V}$(VII) [see (2)].

Examples of three-dimensional magnetic structures in which phase VI can be observed are magnetic perovskites, in which the arrangement of magnetic ions is as shown in Fig. 3. It can be seen from this figure how the oppositely directed effective exchange fields of ions 2 and 3 cancel out at the position of ion 1. The same clear picture of a magnetic structure with a complete cancellation of effective exchange fields at the position of one of a number of equivalent ions in a paramagnetic phase is presented by structures of the RCo_3Ga_2 type and derivatives of intermetallic compounds of the RCo_5 type. This result is also very interesting for reaching an understanding of the properties of $CsCoCl_3$, since it indicates that the choice of magnetic structure which was made in Ref. 4 is not unambiguous: The R factor also allows structure V.

Corresponding results have been derived for a larger number of magnetic sublattice. In particular, for four sublattices which are equivalent in the paramagnetic phase there exist 22 antiferromagnetic structures which differ in symmetry, three of which have a latent paramagnetism.

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