THEORY OF HELICOIDAL STRUCTURES IN ANTIFERROMAGNETS. I. NONMETALS

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Submitted to JETP editor October 30, 1963

J. Exptl. Theoret. Phys. (U.S.S.R.) 46, 1420-1437 (April, 1964)

A theory of magnetic superstructures in nonmetallic antiferromagnets, a particular case of which are the so-called helicoidal structures, is developed on the basis of the Landau theory of phase transitions of the second kind. The large superstructure period can be explained either by assuming that the structure is created by relativistic spin-lattice or spin-spin forces or by a sharp anisotropy in the exchange interaction.

1. INTRODUCTION

THERE have been discussions in the literature in recent years about the question of the formation in certain antiferromagnets of an unusual superstructure. Such a crystal is found to be inhomogeneous over its volume; on its basic structure, which, for example, is represented as a system of two sublattices with oppositely directed spins (Fig. 1a), there are superposed "beats" with a period many times greater than the interatomic spacings. In the simplest case the directions of the spins, while remaining the same for the ions of one layer, are turned through a small angle about the preferred axis as the transition is made from layer to layer, so that the ends of the spins trace out a helicoid in space (Fig. 1b, the so-called helicoidal structure).

The idea that such superstructures were possible was first expressed simultaneously by Villain[1], Kaplan,[2] and Yoshimori.[3] Subsequently the superstructures were experimentally observed in a whole series of antiferromagnetic substances. At present it can be stated with certainty that magnetic superstructures exist in all-antiferromagnetic metals and alloys; on the other hand, in nonmetals they are relatively rare.

In our opinion the current theory on this suffers from a number of deficiencies (more details at the end of Sec. 5). Below we give a theory of magnetic superstructures based on Landau's theory of phase transitions (see, e.g., [4]). The large period of the superstructure is attributed in the theory either to relativistic spin-lattice or spin-spin forces, or to a sharp anisotropy of the exchange interaction.

In Sec. 2, the necessary groundwork from Landau's theory is laid, and a general theory of the superstructure in the vicinity of the phase transi-
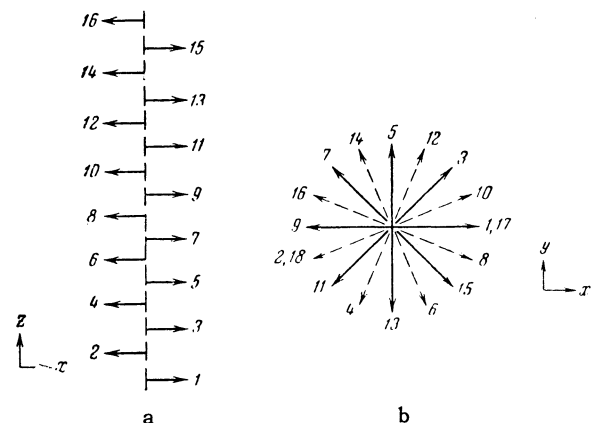

FIG. 1

tion point is given. In Secs. 3 and 4 the theory is applied to the case of nonmetallic antiferromagnets. In Sec. 5 the theory is generalized to the case of arbitrary temperature, and it is compared with the theories of Villain, Kaplan, and Yoshimori.

The theory of superstructures in metals differs in a number of particulars. It will be treated in a later publication.

2. PHASE TRANSITIONS OF THE SECOND KIND AND SUPERSTRUCTURES

The theory of phase transitions of the second kind of Landau enables one not only to determine the thermodynamic properties of the system near the transition point, but also to enumerate all the types of magnetic structures that can arise in a transition of the second kind. The number of such possible structures for each substance is in fact always found not to be very large, which is connected with the typical instability of most transitions (E. Lifshitz,[5] see also[4]).

The transition from the paramagnetic to the

ferro- or antiferromagnetic state consists of the appearance below the transition point—in the magnetic phase—of a non-zero average density of spin $s(r)$ [more exactly, in particular for the rare earths, it is necessary to speak of the average density of the magnetic moment $m(r)$]. The thermodynamic potential of the system Φ is then a function of $s(r)$, and the equilibrium value of the mean spin density is determined by minimizing the potential. Since in a transition of the second kind the change in $s(r)$ occurs continuously, such that at the very point of transition $s = 0$, then near the transition Φ can be expanded in a power series in s. In fact this expansion can be carried out by expanding $s(r)$ in terms of the basis functions of the irreducible representation of the symmetry group of the paramagnetic phase.

In what follows, it will be convenient for us to consider separately the dependence of $s^i(r)$ on the coordinates and its dependence on the vectorial index i. Hence we shall expand $s^i(r)$ in the functions $\varphi_{n\alpha}(r)$, which depend only on the coordinates and realize the n-th irreducible representation of the symmetry group of the paramagnetic phase (α is the number of the basis function):

$$s^i(r) = \sum_{n,\alpha} S^i_{n\alpha}\varphi_{n\alpha}(r). \qquad (2.1)$$

The coefficients $S^i_{n\alpha}$ in the expansion (2.1), in a transformation of the symmetry group, themselves transform like the components of a pseudovector. Actually, however, it makes no difference whether we consider that in a transformation of the coordinates x, y, z, the functions φ change and the coefficients S remain unchanged (except, of course, for the transformation over the index i), or that the functions φ are invariable and the coefficients $S_{n\alpha}$ transform with respect to the index α. In the latter case the quantities $S^i_{n\alpha}$ transform according to the representation that is the direct product of the representation n and the representation formed by the components of the pseudovector. This representation, generally speaking, is reducible. For example, in a uniaxial crystal the components $S^z_{n\alpha}$, and $S^x_{n\alpha}$, $S^y_{n\alpha}$ are known to transform according to different representations. In the general case one can construct from the quantities $S^i_{n\alpha}$ different linear combinations $c_{p\beta}$, $c_{q\gamma}, \ldots$, that transform now according to the irreducible representations p, q, $\ldots$.

Using the expansion (2.1), we can reduce the functional series in $s(r)$ for Φ to the usual series in powers of $S_{n\alpha}$ or of the quantities $c_{p\beta}$. The structure of the series is determined from the invariance requirement relative to the symmetry group of the paramagnetic phase. The latter consists of transformations of the usual crystallographic group of the substance and the transformation R, consisting of a change in sign of all spins, currents, and magnetic fields. The presence of R leads to the absence in the expansion of terms that are odd in S (and in c), since R changes the sign of all of them.

For each irreducible representation there exists only one invariant of the second order—a sum of squares; in general there are no invariants of the second order made up of terms that transform according to different irreducible representations. Thus, the expansion of the potential Φ has the form

$$\Phi(T) = \Phi_0(T) + \sum_p a_p(T) \sum_\beta c^2_{p\beta} + \ldots . \qquad (2.2)$$

Along with the expansion of Φ in c, it is convenient to use the expansion in $S_{n\alpha}$. The latter permits an estimate of the orders of magnitude of the coefficients in the expansion by separating out the invariants, the coefficients associated with exchange forces, and invariants connected with relativistic spin-spin and spin-lattice forces. In fact the magnitude of the exchange forces in the system does not change if all the spins are rotated by the same, but arbitrary angle. In this connection, the exchange invariants are only those made up of the $S_{n\alpha}$ which do not change under rotation by an arbitrary angle with respect to the index i for invariant α. It is clear that the exchange invariants are the products of a different number of combinations of two types:

$$S_{n\alpha}S_{n'\alpha'}, \qquad S_{n\alpha}[S_{n'\alpha}S_{n''\alpha''}].$$

In particular, for each representation n there exists only one exchange invariant of the second order $\sum_\alpha S^2_{n\alpha}$.

To the paramagnetic state correspond all $c_{p\beta}$ in (2.2) that are equal to zero. This can take place only in case all $a_p(T) > 0$. Non-zero $c_{p\beta}$ appear if one of the a_p changes sign. By determining $c_{p\beta}$ from the condition of minimum Φ, we can then calculate the thermodynamic properties of the system near the transition point and by means of (2.1) find the distribution of spin density, i.e., the magnetic structure of the crystal. Here the basic features of the structure, as in the Bravais lattice, are the angles between the spins at the different lattice points, which are determined by the exchange invariants, and the relativistic invariants determine the orientation of the "vectors" $S_{n\alpha}$ relative to the crystallographic axes. The theory of representations of the space groups is well

known (see, e.g., [4,6]). A representation is realized by a set of functions of the form

$$\varphi_f(\mathbf{r}) = u_f(\mathbf{r}) e^{i\mathbf{f}\mathbf{r}}, \qquad (2.3)$$

where $\mathbf{f}$ is a vector whose range of variation is confined to the cell of the reciprocal lattice, and u_f is a function that is periodic in the lattice. Besides the functions (2.3), there also enter into the irreducible representation given by the vector $\mathbf{f}$ other functions as well, based on vectors $\mathbf{f}'$, $\mathbf{f}''$, ..., which are obtained from $\mathbf{f}$ by operating on it with the rotating elements of the symmetry group.

If the vector $\mathbf{f}$ takes an arbitrary (non-symmetrical) position in the reciprocal lattice, then all the vectors $\mathbf{f}$, $\mathbf{f}'$, $\mathbf{f}''$, ... will be different.[1] The number of functions φ_f, $\varphi_{f'}$, $\varphi_{f''}$, ... that form the representation then agrees simply with the number of effective rotating elements of the space group, which, as is well known, equals the number of elements of the point group that determines the crystallographic class of the substance. Another situation arises when $\mathbf{f}$ lies along one of the axes or planes of symmetry. In this case there always exists a set of rotating elements that leave the vector $\mathbf{f}$ invariant or change it into $\mathbf{f} + 2\pi\mathbf{b}$, where $\mathbf{b}$ is any of the periods of the reciprocal lattice. In the application of such an element to the function φ_f the factor $e^{i\mathbf{f}\cdot\mathbf{r}}$ does not change and the representation will be determined by the transformation properties of the function u_f. In particular, "degenerate" representations are possible, in which several functions u_f belong to each vector $\mathbf{f}$.

The coefficients $\mathbf{S}_f$ that correspond to a representation with given $\mathbf{f}$'s [see (2.1)] transform like $\sigma e^{i\mathbf{f}\cdot\mathbf{r}}u_f(\mathbf{r})$, where σ is the usual pseudovector conveying the dependence on the variables that determine the spin direction.

These considerations do not impose any limitations on the magnitude of $\mathbf{f}$. It might be shown that a magnetic structure with an arbitrary Bravais lattice can arise as a result of a phase transition of the second kind. However, as E. Lifshitz[5] first showed, there is a reason that essentially limits the possible types of phase transitions of the second kind.

In fact, we shall return to our representation to see how a phase transition takes place. As was mentioned above, above the transition point all a_p in the expansion (2.2) are greater than zero, and the transition proceeds at a temperature at which

the first one of the coefficients a_{p_0} vanishes, and the rest of them remain positive. Is such a situation possible for each of the representations of the space group? To answer this question we must know how the coefficients a_p depend on the only continuous parameter that numbers the representation, the vector $\mathbf{f}$. If it turns out that in the close vicinity of the considered transition (representation p_0) the coefficients vary linearly with $\mathbf{f}$, then, as is known, some of the coefficients a_p will go to zero earlier than a_{p_0} and the transition of the type considered will not be able to proceed.

The dependence of the coefficients a_p on the "quasi-momentum" $\mathbf{f}$ can be investigated in a general way on the basis of symmetry considerations, as is done in the theory of the electronic spectra of metals. We begin with the case of a transition of "nondegenerate" type, when [see (2.3)] the vector $\mathbf{f}$ belongs to only one function φ_f (i.e., one u_f). Consider the transition, also "non-degenerate," with the vector $\mathbf{f} + \mathbf{k}$, $\mathbf{k} \ll 1/d$, where d is the interatomic spacing. To this corresponds a single function $\varphi_{f+k} = e^{i(\mathbf{f}+\mathbf{k})\mathbf{r}}u_{f+k}(\mathbf{r})$ and a single term of second order in the expansion (2.2):

$$a_{f+k}|c_{f+k}|^2.$$

Thus, in the "nondegenerate case" it is sufficient to expand a_{f+k} in a power series in $\mathbf{k}$. The form of the expansion is determined from the requirement of invariance relative to the rotational transformations that leave the vector $\mathbf{f}$ invariant. It is obviously possible here to replace all screw axes and glide planes with ordinary axes and planes, i.e., to consider the symmetry of the vector $\mathbf{f}$ in a crystal that does not have real screw axes and glide planes. The set of transformations so obtained always forms a group, the so-called group of the vector $\mathbf{f}$.

Now it is easy to imagine that the linear terms in the expansion a_{f+k} are always present, if the group of the vector $\mathbf{f}$ does not contain intersecting axes and planes of symmetry, i.e., for the groups C_1, C_s, C_n, C_{nv} and in the nondegenerate case not for any other groups. In particular,

$$a_{f+k} \approx a_f + \alpha k_x + \beta k_y + \gamma k_z \text{ for } C_1,$$

$$a_{f+k} \approx a_f + \alpha k_x + \beta k_y \qquad \text{for } C_s,$$

$$a_{f+k} \approx a_f + \gamma k_z \qquad \text{for } C_n, C_{nv}$$

(the z axis in the corresponding cases is perpendicular to the plane of symmetry or directed along the axis of rotation).

If the representation is "degenerate" the vector $\mathbf{f}$ corresponds to several functions φ_f: $\varphi_{f\alpha}$

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[1] Naturally, two vectors that differ by the period of the reciprocal lattice $\mathbf{b}$ are considered to be identical.

$= e^{i\mathbf{f}\mathbf{r}} u_{\mathbf{f}\alpha}(\mathbf{r})$, $\alpha = 1, 2, \ldots$. For the representation with the vector $\mathbf{f} + \mathbf{k}$ the "degeneracy" can be completely or partially removed. In this case it is necessary to do something like the quantum-mechanical perturbation theory for a degenerate state. Namely, let there be several representations for the vector $\mathbf{f} + \mathbf{k}$:

$$\varphi_{\mathbf{f}+\mathbf{k},n\beta} = e^{i(\mathbf{f}+\mathbf{k})\mathbf{r}} u_{\mathbf{f}+\mathbf{k},n\beta},$$

where n numbers the representation and β its basis functions. Then, in the first approximation

$$\varphi_{\mathbf{f}+\mathbf{k},n\beta} = e^{i\mathbf{k}\mathbf{r}} \sum_{\alpha} L^{\alpha}_{n\beta}(\mathbf{k}) \varphi_{\mathbf{f}\alpha},$$

whereby, as in quantum mechanics, the coefficients $L^{\alpha}_{n\beta}$ are determined simultaneously with the form of the expansion of $a_{\mathbf{f}+\mathbf{k}}$ in $\mathbf{k}$.

For this we write out the general form of the expansion of the thermodynamic-potential terms quadratic in $c_{\mathbf{f}\alpha}$ in a power series in $\mathbf{k}$, a series permitted by the symmetry:

$$\Phi \approx (a_{\mathbf{f}} + \alpha k_x + \beta k_y + \gamma k_z) \sum_{\alpha} |c_{\mathbf{f}\alpha}|^2$$
$$+ k_x J_x (c_{\mathbf{f}\alpha}) + k_y J_y (c_{\mathbf{f}\alpha}) + k_z J_z (c_{\mathbf{f}\alpha}), \qquad (2.4)$$

where $J_{x,y,z}$ are quadratic combinations of the quantities $c_{\mathbf{f}\alpha}$ different from the scalar $\sum |c_{\mathbf{f}\alpha}|^2$ and transforming as the corresponding component of a vector under all transformations that leave the vector $\mathbf{f}$ invariant. Transforming now this quadratic form to a diagonal form, we obtain

$$\Phi \approx \sum_{n} a_{\mathbf{f}+\mathbf{k},n} \sum_{\beta} |c_{\mathbf{f}+\mathbf{k},n\beta}|^2,$$

where

$$c_{\mathbf{f}+\mathbf{k},n\beta} = \sum_{\alpha} L^{\alpha}_{n\beta}(\mathbf{k}) c_{\mathbf{f}\alpha},$$

and $a_{\mathbf{f}+\mathbf{k},n\beta} \approx a_{\mathbf{f}} + $ terms of order $\mathbf{k}$.

Thus, in the case of "degenerate" representations the linear terms in $\mathbf{k}$ in the expansion of $a_{\mathbf{f}+\mathbf{k}}$ can in principle arise not only for vectors $\mathbf{f}$ having the group C_1, C_s, C_n, or C_{nv} when the quantities α, β, γ in (2.4) are different from zero. At this point the investigation must be carried out concretely for each "degenerate" representation. We note, however, that the linear terms are surely absent if the group of the vector $\mathbf{f}$ contains the inversion. Actually, in this case the coefficients $c_{\mathbf{f}\alpha}$ are either all even with respect to inversion, or odd. Therefore any quadratic combination of $c_{\mathbf{f}\alpha}$ is even, whence follows the assertion just made. Consequently, only vectors $\mathbf{f}$ with the following eleven groups require a special treatment:

$$D_2, D_{2d}, C_{3h}, D_3, D_{3h}, S_4, D_4, D_6, T, T_d, O. \qquad (2.5)$$

These considerations very strongly limit the number of possible types of phase transitions and, in particular, the change in the Bravais lattice described by the vector $\mathbf{f}$. If it is considered that only transitions with the vector $\mathbf{f}$ whose symmetry group is one of the set C_1, C_s, C_n, C_{nv} are forbidden, while vectors with symmetry of the type (2.5) are in general allowed, then analysis shows that the following types of transition are possible (see Lifshitz [5]). In the majority of cases either the Bravais lattice is generally unchanged, or one or the other of its periods is doubled. In body-centered lattices (rhomdohedral, tetragonal, and cubic) and in the cubic face-centered lattice, transitions are possible in which some periods are quadrupled. In the hexagonal lattice there is a case when one of the periods is tripled. [2]

There are, however, cases in which exceptions to the rules formulated above become possible. Namely, it can turn out that the coefficients for the terms linear in $\mathbf{k}$ in the expansion of the quantity $a_{\mathbf{f}+\mathbf{k}}$ for some physical reason are anomalously small; for example, associated in their structure with forces of relativistic nature. Then, in addition to the linear terms in the expansion of $a_{\mathbf{f}+\mathbf{k}}$ in $\mathbf{k}$, it is necessary to take into account also terms of the second order, the coefficients of which, as we shall see, are always large. Let, for example,

$$a_{\mathbf{f}+\mathbf{k}} \approx a_{\mathbf{f}} + \gamma k_z + A\mathbf{k}^2, \qquad A > 0,$$

where, by assumption, $\gamma/A \ll 1/d$ (d is of the order of the interatomic spacing). But this means that the coefficient $a_{\mathbf{f}+\mathbf{k}}$ for $k_z = k_0 = -\gamma/2A \ll 1/d$ has a minimum:

$$a_{\mathbf{f}+\mathbf{k}} \approx a_{\mathbf{f}} - \gamma^2/4A + A (k_z - k_0)^2 + A (k_x^2 + k_y^2).$$

Thus the presence of terms linear in $\mathbf{k}$ with small coefficients leads to a phase transition that proceeds in fact not to a state described by a representation with vector $\mathbf{f}$, but to a state with vector $\mathbf{f} + \mathbf{k}_0$.

We emphasize in connection with this that these considerations are applicable principally only when $\gamma/A \ll 1/d$, since writing terms quadratic in $\mathbf{k}$ itself loses meaning already when $\gamma/A \sim 1/d$. In the latter case the quadratic terms are comparable in order of magnitude with the linear ones only for $k_0 \sim \gamma/A \sim 1/d$, when the expansion in powers of $\mathbf{k}$ is generally invalid.

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[2] In a recent paper by Dimmock,[7] these results were doubted in connection with an inaccuracy in the discussions in the original communication of Lifshitz.[5] It seems to us that the deviation presented above completely removes Dimmock's objections.

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It can be shown in various concrete examples that the coefficients of the linear terms are in practice small only for transitions corresponding to a small number of vectors f with high symmetry. In general these will again be transitions with 1-, 2-, 3-, or 4-fold change of the periods of the Bravais lattice. This circumstance leads to the following pattern of possible phase transitions.

Besides the types of transitions listed by Lifshitz, there are possible phase transitions accompanied by the appearance of structures with a period many times greater than the period of the original lattice. In the majority of cases (and to all appearances in all of them, although we have no proof in the general case), the crystal has a unique superstructure after the transition. On the fine scale of distances of the interatomic spacings, the structure of the crystal does not differ from those postulated by Lifshitz, i.e., it corresponds to a change of the periods of the Bravais lattice by 1, 2, 3, or 4 times. On this structure is superposed a superstructure, which appears as unique "beats" with the basic structure and has a period always many times greater than the interatomic spacings.

The above expansion of the coefficients a_f in a power series in the vector f can be given another ("coordinate") form. In this formulation, instead of "beats" of the form $e^{ik \cdot r} S_{f\varphi f}(r)$, which correspond to one irreducible representation, we consider "beats" of a more general form: $S_f(r) \varphi_f(r)$, where the $S_f(r)$ are arbitrary, slowly varying functions of the coordinates. Since $\varphi_f(r)$ oscillates in the interatomic spacings and $S_f(r)$ is practically invariant over them, the function Φ for these "beats" can be brought to the form $\int \Phi(r) dr$, where the density of thermodynamic potential $\Phi(r)$ is represented as a series in powers of $S_f(r)$ and their derivatives over the coordinates.

The form of this series is determined by the requirements of symmetry. In particular, the first derivatives can enter in the expansion only in the form of the antisymmetric combinations

$$S_f^i \partial S_{f'}^j / \partial x - S_f^j \partial S_{f'}^i / \partial x, \qquad (2.6)$$

since the symmetric ones are total derivatives and describe surface effects, which are unimportant for our present purposes.

Expanding $s(r)$ in terms of the irreducible representations, which corresponds to the substitution in the expansion of $S_f(r)$ in the form $e^{ik \cdot r}$, we obtain the expansion of the coefficients a_{f+k} in k that we investigated earlier. We therefore arrive

at the original formulation of the criterion of Lifshitz,[5] which says that the possibility of a given phase transition depends on the presence or absence of terms of the type (2.6).

The large size of the period of the superstructure in this formulation corresponds to the smallness of the coefficient of terms linear in the derivatives compared to the coefficient of terms involving their squares. This situation is perfectly real in magnetic transitions. In this case it can happen that, for example, the coefficient of the first derivatives has a relativistic origin (connected with forces of the spin-lattice and spin-spin type) and is consequently small compared to the coefficient of the second derivatives, which is always determined by the exchange interactions (e.g., there is always a term of the type $(\partial S_f / \partial x)^2$). Other reasons for the smallness of this coefficient in the magnetic case will be discussed in Sec. 4.

A number of questions concerning the order of magnitude of the coefficients of the first derivatives in magnetic transitions can be explained by using the aforementioned results of E. Lifshitz. We have seen that an invariant of type (2.6) surely exists for all those representations in which the group of vector f does not have intersecting axes or planes of symmetry or inversion, i.e., it is a group of the type C_1, C_s, C_n, or C_{nv}. Consequently in a magnetic transition an invariant of this type can be composed only of coordinate functions in the expansion (2.1):

$$\varphi_f \partial \varphi_{f'} / \partial x - \varphi_{f'} \partial \varphi_f / \partial x.$$

But then the expression

$$S_f \partial S_{f'} / \partial x - S_{f'} \partial S_f / \partial x \qquad (2.7)$$

with the functions S_f corresponding to these φ_f will be invariant: the exchange nature of (2.7) is obvious. Therefore, transitions of this type are in general certainly non-existent only if there are no special reasons for the coefficients of the first derivatives to be small. Thus, magnetic superstructures can in principle arise on account of relativistic interactions only for transitions corresponding to representations in which the group of the vector is one of the eleven groups in (2.5).

3. MAGNETIC SUPERSTRUCTURES IN NON-METALS

The magnetic structure of a nonmetallic crystal is completely determined by the values of the average spins of its magnetic ions s_a at each lattice site. The corresponding spin density in this case has the form

$$s(\mathbf{r}) = \sum_a' s_a \delta(\mathbf{r} - \mathbf{r}_a).$$

In practice it would be necessary to use in place of $\delta(\mathbf{r} - \mathbf{r}_a)$ in this relation a function $f(\mathbf{r} - \mathbf{r}_a)$ having a sharp maximum at $\mathbf{r} = \mathbf{r}_a$, the form factor of the ion. For us, however, only the presence of this sharp maximum is important, and the δ-function is eminently suitable for this.

This form of the spin density essentially limits the number of possible irreducible representations according to which $s(\mathbf{r})$ should be expanded. In particular, "little" representations are determined by it for crystals whose symmetry group has no real screw axes or glide planes. There is a simple recipe for finding them. Namely, let us symbolize all the magnetic ions within the limits of one elementary cell by the different numbers A_1, A_2, ..., and the magnetic ions in other cells in a corresponding manner by $A_1 e^{i\mathbf{f}\cdot\mathbf{R}_1}$, ..., where $\mathbf{R}$ is the number of the cell. Then in the transformations of the little group, the magnetic ions go into one another, and the quantities A_1, A_2, ... go into one another or into $A_1 e^{i\mathbf{f}\cdot\mathbf{R}_1}$, ... All the little representations of interest to us are contained in the representation that arises in this way (see, e.g., [5]).

In case the crystallographic group contains real screw axes and glide planes, the task of finding irreducible representations is more difficult. We shall not give the general procedure, but shall when necessary find the representations by using specific group properties.

As an example we shall consider a crystal having a cubic body-centered lattice and symmetry group O_h^9 (close-packed), in which the magnetic ions are on the points of its Bravais lattice, and find out for which second-order transitions in it we can expect a magnetic superstructure.

The reciprocal lattice of this crystal has a cubic face-centered Bravais lattice and symmetry group O_h^5. Using the International Tables, [8] we readily verify that besides the vectors $\mathbf{f}$ having the symmetry of the type C_1, C_s, C_n, C_{nv}, which describe absolutely unstable transitions [in the sense of the appearance of exchange invariants of the type (2.7)], there is only one vector $\mathbf{f}$ whose symmetry group is included among the eleven groups (2.5). This is a vector with coordinates $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$; $\overline{\frac{1}{4}}$, $\overline{\frac{1}{4}}$, $\overline{\frac{1}{4}}$ and symmetry T_d. Corresponding to this the functions $e^{i\mathbf{f}\cdot\mathbf{r}}$ have the form [3]

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[3] It should be taken into account that the period of the reciprocal lattice for the face-centered cube is twice as great as the period of the lattice itself.

$$e^{i\pi(x+y+z)/a}, \qquad e^{-i\pi(x+y+z)/a}.$$

Furthermore, since there is only one ion per unit cell, and this is immobile under all the transformations of the group of the vector $\mathbf{f}$, i.e., there is always one quantity A, then it is necessary to take the unit representation as the little representation for the function $\varphi_{\mathbf{f}}$ from (2.1). Thus, as $\varphi_{\mathbf{f}}$ we may take the function transforming like

$$e^{i\pi(x+y+z)/a} + e^{i\pi(x-y-z)/a} + e^{i\pi(-x+y-z)/a} + e^{i\pi(-x-y+z)/a},$$

and the complex conjugate function or its real and imaginary parts:

$$\varphi^+ \sim \cos\frac{\pi x}{a}\cos\frac{\pi y}{a}\cos\frac{\pi z}{a}, \qquad \varphi^- \sim \sin\frac{\pi x}{a}\sin\frac{\pi y}{a}\sin\frac{\pi z}{a}.$$

The corresponding vectors $\mathbf{S}^+$ and $\mathbf{S}^-$ [see (2.1)] transform like

$$\mathbf{S}^+ \sim \boldsymbol{\sigma}\cos\frac{\pi x}{a}\cos\frac{\pi y}{a}\cos\frac{\pi z}{a},$$

$$\mathbf{S}^- \sim \boldsymbol{\sigma}\sin\frac{\pi x}{a}\sin\frac{\pi y}{a}\sin\frac{\pi z}{a}. \qquad (3.1)$$

We emphasize that the functions on the right hand sides of (3.1) are not equal to the real spin density in the crystal, which is given by a δ-type function. The sign $\sim$ means only that the quantities that describe the real spin density transform like the right sides of (3.1). However, knowing to which representation of the symmetry group the real spin density of the crystal corresponds, i.e., knowing $\mathbf{S}^+$ and $\mathbf{S}^-$, it is possible to construct, if necessary, also the density itself $s(\mathbf{r})$. For this we note that from the transformation properties of the vectors $\mathbf{S}^+$ and $\mathbf{S}^-$ it follows that the spin density corresponding to $\mathbf{S}^+$ goes to zero at the center of the cube, and the density corresponding to $\mathbf{S}^-$ goes to zero at its vertices. Thus, in a non-metallic crystal $\mathbf{S}^+$ represents simply the average spin of the ions located on the vertices of the cube and $\mathbf{S}^-$ the average spin at its center.

The magnetic structure described by the vectors $\mathbf{S}^+$ and $\mathbf{S}^-$ can be represented in the form of two interlacing antiferromagnetic sublattices, the first of which is formed by the ions on the cube vertices and the second by the ions at the centers. Inside each of the sublattices the spins of the ions differ only in sign; however, the spins of the different sublattices are oriented arbitrarily with respect to one another. In Fig. 2 is shown the order of the alternation of sign of the spins for the sublattice formed by the spins on the corners of the cubes.

The representation based on the vectors $\mathbf{S}^+$ and $\mathbf{S}^-$ is irreducible. Hence in the expansion of the potential Φ in powers of $\mathbf{S}^+$ and $\mathbf{S}^-$ there is only
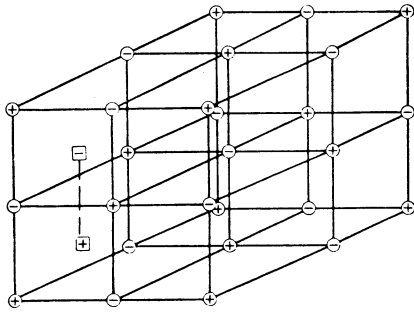
FIG. 2

one second-order invariant that does not contain derivatives:

$$\tfrac{1}{2}A\,[(S^+)^2 + (S^-)^2].\tag{3.2}$$

In its structure this invariant has an exchange character. It is not difficult to show that for the transition we are considering there is one invariant containing first derivatives with respect to the coordinates:

$$b\left(S_x^+\frac{\partial S_y^-}{\partial z} - S_y^-\frac{\partial S_x^+}{\partial z} + S_y^+\frac{\partial S_x^-}{\partial z} - S_x^-\frac{\partial S_y^+}{\partial z} + \ldots\right).\tag{3.3}$$

To the terms written out here there should be added terms obtained from them by cyclic permutation $x \to y \to z$. The structure of Eq. (3.3) shows that its origin can only be relativistic spin-spin and spin-lattice interactions. To it should be added a single exchange invariant of the second order containing second derivatives:

$$\tfrac{1}{2}B\left[\left(\frac{\partial S^+}{\partial x}\right)^2 + \left(\frac{\partial S^+}{\partial y}\right)^2 + \left(\frac{\partial S^+}{\partial z}\right)^2 + \left(\frac{\partial S^-}{\partial x}\right)^2\right.$$

$$\left. + \left(\frac{\partial S^-}{\partial y}\right)^2 + \left(\frac{\partial S^-}{\partial z}\right)^2\right].\tag{3.4}$$

We do not write out the non-exchange invariants quadratic in the derivatives, since they give a small contribution.

Near the transition temperature ($\Theta - T \ll \Theta$, Θ the transition temperature) it is necessary to add to these invariants, which are quadratic in S^+ and S^-, exchange invariants of the fourth order (more will be said about the effect of non-exchange invariants of this type below). These have the form

$$\tfrac{1}{4}C\,[(S^+)^2 + (S^-)^2]^2 + \tfrac{1}{2}D\,(S^+)^2(S^-)^2 + \tfrac{1}{2}E\,(S^+S^-)^2.\tag{3.5}$$

In the immediate vicinity of the transition point the magnetic structure is determined from the condition of absolute minimum of the sum of the expressions (3.2)–(3.5). In general, a very complex structure arises from this. The mean spins of the ions can change in space from point to point,

generally speaking both in magnitude and direction, even though the "rate" of change will undoubtedly be small. The determination of the magnetic structure in this case requires the solution of a cubic algebraic equation and cannot be carried out in general form. At temperatures not too close to the transition point the task of determining the magnetic structure is greatly simplified. At these temperatures the invariant (3.5) will already be many times greater than the sum of the invariants (3.3) and (3.4), so that the minimization of the free energy can be carried out in stages.[4] Namely, first it is necessary to minimize the exchange invariant (3.5) under the condition of constant magnitude of $(S^+)^2 + (S^-)^2 = 2s^2$, where s is the mean spin of an ion at the considered temperature. From this is determined the "coarse" magnetic structure, i.e., the average ion spins and the angles between them (but not relative to the lattice!). After this, the sum of the terms (3.3) and (3.4) is minimized, now for the given "coarse" structure.

Three types of "coarse" structure correspond to a minimum of Eq. (3.5):

$$\text{I. } S^+ = \sqrt{2}s, \quad S^- = 0 \text{ or } S^- = \sqrt{2}s, \quad S^+ = 0;$$
$$\text{II. } S^+ = S^- = s, \quad S^+ \perp S^-;$$
$$\text{III. } S^+ = \pm S^-.$$

Structure I exists for $D > 0$ and $D + E > 0$, structure II for $D < 0$ and $E > 0$, and structure III for $D + E < 0$ and $E < 0$. In cases I and III, the invariants linear in the derivatives go to zero and the superstructure does not arise. Superstructure appears only in case II, when the ion spins on the corners and in the centers of the elementary cube are perpendicular to each other.

The dependence of S^+ and S^- on the coordinates is determined by a linear second-order differential equation obtained by variation of the sum of the functions (3.3) and (3.4) under the condition of constancy of the exchange invariants (3.2) and (3.5). The real solution of the equation has the form

$$S^+ = 2^{-1/2}\,(l e^{ikr} + l^* e^{-ikr}), \quad S^- = i2^{-1/2}\,(l e^{ikr} - l^* e^{-ikr});$$
$$l^2 = 0,\ ll^* = s^2.\tag{3.6}$$

Substituting (3.6) in (3.3) and (3.4), we obtain an expression for the addition to the thermodynamic potential, associated with the superstructure:

$$\Phi' = -4b\,\mathrm{Re}\,(k_z l_x l_y^* + k_y l_x l_z^* + k_x l_y l_z^*) + Bk^2 s^2.\tag{3.7}$$

The wave vector of the superstructure $\mathbf{k}$ and the

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[4]A more exact estimate for this temperature region will be given below.

vector l are determined by the variation of (3.7) over k and l with the additional conditions $l^2 = 0$, $l \cdot l^* = s^2$. It is found that k is directed along one of the three-fold axes and has the magnitude $k = |b|/B(3)^{1/2}$. The components of the vector l then lie in a plane perpendicular to k, and the addition $\Phi' = -b^2 s^2 / 3B$.

The coordinate dependence of the spins at the vertices S^+ and centers S^- of the cubes for the case $k \parallel [111]$ has the form

$$S^+ = s\,[\mu \cos k\,(x + y + z) - \nu \sin k\,(x + y + z)]$$
$$\times \cos \frac{\pi x}{a} \cos \frac{\pi y}{a} \cos \frac{\pi z}{a} ,$$

$$S^- = s\,[-\mu \sin k\,(x + y + z) - \nu \cos k\,(x + y + z)]$$
$$\times \sin \frac{\pi x}{a} \sin \frac{\pi y}{a} \sin \frac{\pi z}{a} ;$$

$$k = |b|/B\sqrt{3}, \qquad (3.8)$$

where μ, ν are mutually perpendicular unit vectors lying in the (111) plane.

The smallness of the vector k is guaranteed by the smallness of the coefficient b relative to B. The coefficient b, being related to interactions of relativistic nature, is of order $bs_0^2 \sim v^2 \epsilon_0^2 d / c^2 \Theta$, where v is of the order of the velocity of the atomic electrons, ϵ_0 is of the order of atomic energies, d is the interatomic spacing, s_0 is the average spin of an ion far from the transition point, and Θ is the order of the exchange energy, i.e., the transition temperature in energy units. The coefficient B has exchange origin: $Bs_0^2 \sim \Theta d^2$. Thus, $k \sim (v^2 \epsilon_0^2 / c^2 \Theta^2)d^{-1}$; the ratio $v^2 \epsilon_0^2 / c^2 \Theta^2$ is small for magnetic substances, as a rule never exceeding 0.1.

The results finally obtained can be formulated in the following way. The "coarse" magnetic structure was described above (see p. 965). To this it is necessary only to add the possibility of three different relative orientations of the spins of the ions located on the vertices S^+ and at the centers S^- of the cubes. That is, S^+ and S^- can be either perpendicular or parallel, or one of them can go to zero. In the two latter cases, no kind of superstructure results; but in the first one gets a magnetic superstructure of the "helicoidal" type. The axis of the helicoid is directed along one of the [111] axes and the rotation of the spins occurs in the corresponding planes of the (111) type. The pitch of the helicoid is great in comparison with the period of the "coarse" structure. The directions of the spins at each point are given by Eq. (3.8).

As has already been mentioned, this picture must undergo strong changes very close to the transition point. The closeness to the transition point is determined from the condition that the contribution to the thermodynamic potential from terms associated with derivatives with respect to the coordinates should not surpass the contribution of the exchange invariant:

$$b^2 s^2 / B \ll Cs^4,$$

or, considering that at $\Theta - T \ll \Theta$ we have from Landau's theory of phase transitions the formula $s^2 = s_0^2(\Theta - T)/\Theta$,

$$\Theta - T \gg \Theta\,(v^4 \epsilon_0^4 / c^4 \Theta^4).$$

At $\Theta - T \lesssim \Theta(v^4 \epsilon_0^4 / c^4 \Theta^4)$, the magnetic structure can turn out to be immensely more complicated. We also note that if the ratio between the coefficients in the exchange invariant (3.5) are such that the states type I and II are energetically favorable, then the superstructure that must arise at the transition point must subsequently disappear at temperatures such that $\Theta - T \sim \Theta(v^4 \epsilon_0^4 / c^4 \Theta^4)$.

It should be noted further that at temperatures far from the transition point, relativistic invariants of higher order can become important. In the case considered, when the rotation of the spins takes place in (111) planes (anisotropy of sixth order), they are of order $v^6 \epsilon_0^6 / c^6 \Theta^5$. Considering that the contribution of the terms with derivatives has the order $v^4 \epsilon_0^4 / c^4 \Theta^3$, we conclude that the anisotropy can be neglected at all temperatures.

4. MAGNETIC SUPERSTRUCTURE OF MnO₂

We now turn to the case when the magnetic structure that arises as a result of a phase transition of the second kind is such that the thermodynamic potential has exchange terms linear in the derivatives. Such a situation leads, as a rule, to the impossibility of the transition. There are, however, substances in which for one reason or another associated with their structure and not with symmetry, as before, the exchange invariant linear in the derivatives turns out to be small compared with the invariant quadratic in the derivatives. Then a superstructure arises, the large period of which is due to this smallness. The investigation in this case should be carried through separately for each concrete substance.

As an example we consider antiferromagnetic MnO_2. The crystal has a simple tetragonal lattice with two Mn atoms in a unit cell (positions 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$); the space group of the lattice is D_{4h}^{14}. The group has essential screw axes and glide planes; hence, in using the results given in Sec. 2, it is necessary to assign to the vector f that de-

termines the representation the symmetry it would have if the screw axes and glide planes were replaced by simple axes and planes. Such a lattice for MnO_2 is a body-centered tetragonal lattice (group D_{4h}^{17}). By consulting the International Tables,[8] we find at once that only one vector, namely $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ (symmetry D_{2d}), has a group that belongs to the set of eleven (2.5). In all the other cases exchange invariants arise.

We begin with the representation based on the vector $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ when there is only the relativistic invariant. To the vector $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ corresponds the function $e^{i\pi(x+y)/a + i\pi z/c}$, in place of which we can also take $\cos(\pi x/a)\cos(\pi y/a)\cos(\pi z/c)$, which has the same translational properties. The latter remains invariant under all symmetry transformations that leave in place the Mn ions arranged on the lattice sites and transforms to the function $\sin(\pi x/a)\sin(\pi y/a)\sin(\pi z/c)$ under transformations that carry the corners of a cell to its center. It immediately follows that as functions φ_f in (2.1) we can select the functions

$$\varphi^+ \sim \cos\frac{\pi x}{a}\cos\frac{\pi y}{a}\cos\frac{\pi z}{c}, \qquad \varphi^- \sim \sin\frac{\pi x}{a}\sin\frac{\pi y}{a}\sin\frac{\pi z}{c}.$$

It is not difficult to verify that the representation realized by φ^+ and φ^- is irreducible. To it correspond the vectors

$$S^+ \sim \sigma \cos\frac{\pi x}{a}\cos\frac{\pi y}{a}\cos\frac{\pi z}{c}, \qquad S^- \sim \sigma \sin\frac{\pi x}{a}\sin\frac{\pi y}{a}\sin\frac{\pi z}{c}.$$

The structure described by the vectors S^+ and S^- coincides precisely with the structure we considered in the preceding section for a cubic body-centered crystal; for MnO_2 (for $S^+ \perp S^-$) it had been assumed in early work by Erickson.[9]

The representation realized by the vectors S^+ and S^- is reducible; it breaks down to three irreducible representations based on different combinations of their components

$$S_z^+, S_z^-; \qquad S_x^+ + S_y^+, S_x^- - S_y^-; \qquad S_x^+ - S_y^+, S_x^- + S_y^-. \quad (4.1)$$

It is not difficult to show that terms of the second order in S^+, S^- in the expansion of the thermodynamic potential have the following form:

$$\Phi = \tfrac{1}{2}A\left[(S^+)^2 + (S^-)^2\right] + \tfrac{1}{2}a_1\left[(S_x^+ + S_y^+)^2 + (S_x^- - S_y^-)^2\right]$$

$$+ \tfrac{1}{2}a_2\left[(S^+ - S_y^+)^2 + (S_x^- + S_y^-)^2\right] + b\left(S_x^+\frac{\partial S_y^-}{\partial z} + S_y^+\frac{\partial S_x^-}{\partial z}\right.$$

$$\left. - S_y^-\frac{\partial S_x^+}{\partial z} - S_x^-\frac{\partial S_y^+}{\partial z}\right) + \tfrac{1}{2}B\left[\left(\frac{\partial S^+}{\partial z}\right)^2 + \left(\frac{\partial S^-}{\partial z}\right)^2\right].$$

The presence, however, of an invariant linear with respect to the derivatives in this case does not indicate any instability. This is due to the terms with derivatives being much smaller in order of

magnitude than the terms connected with anisotropy. In fact the contribution of the first is, to within a factor, equal to b^2s^2/B, and the ratio of it to the anisotropy energy $b^2/a_{1/2}B$ is of the order $v^2\epsilon_0^2/c^2\Theta^2$; this quantity, which is merely the ratio of the anisotropy energy to the exchange energy, is always small, attaining order unity only for very heavy ions. For Mn ions, then, there is no basis for not considering it to be small.

We now consider the representation determined by the vector $0\,0\,\frac{1}{2}$. In the reciprocal lattice of group D_{4h}^{17} the vector corresponding to it has C_{4v} symmetry, from which it follows that an exchange invariant should appear in the thermodynamic potential. It is not difficult to show that to the vector $0\,0\,\frac{1}{2}$ there belongs a representation given by two vectors S^+ and S^- transforming like

$$S^+ \sim \sigma \cos(\pi z/c), \qquad S^- \sim \sigma \sin(\pi z/c).$$

The corresponding structure is shown in Fig. 3. It is made up of two interpenetrating antiferromagnetic lattices, the first of which is formed by Mn ions on the points of the Bravais lattice and the second by ions in the centers of the unit cells. The orientation of the spins in the two lattices relative to one another is arbitrary. Here S^+ and S^- represent the mean spins in the corresponding lattices (circles and squares in Fig. 3).
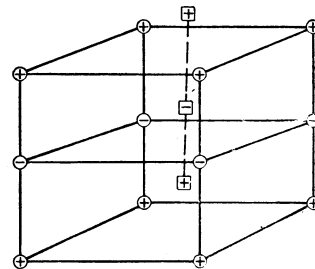

FIG. 3

The representation realized by S^+ and S^- is again reducible; the irreducible representations are given by the same combinations of components as in (4.1). The second-order terms in the thermodynamic potential have the following form:

$$\Phi = \tfrac{1}{2}A\left[(S^+)^2 + (S^-)^2\right] + \tfrac{1}{2}a_1\left[(S_x^+ + S_y^+)^2 + (S_x^- - S_y^-)^2\right]$$

$$+ \tfrac{1}{2}a_2\left[(S_x^+ - S_y^+)^2 + (S_x^- + S_y^-)^2\right]$$

$$+ b\,(S^+\partial S^-/\partial z - S^-\partial S^+/\partial z) + \tfrac{1}{2}B\left[(\partial S^+/\partial z)^2 + (\partial S^-/\partial z)^2\right]. \quad (4.2)$$

In (4.2) we have dropped terms quadratic in S^+ and S^- that contain higher derivatives. Such neglect is justified if the derivatives themselves are small; for this it is required that the coefficient b

be small in comparison with B. This is just the case in MnO_2. In fact, from the structure of the linear invariant it is seen that it is due exclusively to the interaction of the ions located on the points of the unit cell with the ions at the cell centers (in particular, this invariant goes to zero when the average spin at the centers goes to zero). On the other hand the quadratic terms in the derivatives are connected mainly with interactions between themselves of the ions situated at the corners (or at the centers) of the cell. We might remark at this point that the distance between the ions of different type is 20% greater than the minimum distance between ions of one type (a = 4.44 Å, c = 2.89 Å). Because of the exponential fall-off in the exchange forces this should lead to the inequality b ≪ B. In later estimates we shall use the relation b ~ λB, where λ is a small quantity. According to Erickson,[3] $\lambda \approx 0.1$.

If, as in the preceding section, we do not interest ourselves in the special region very close to the transition point, then at first it is necessary to minimize the exchange terms of the fourth order. For MnO_2 they have exactly the same form as in (3.5). Again, we can show that for structures I and III (see p. 966) the linear invariant goes to zero. For structure II, however, we shall seek $\mathbf{S^+}$ and $\mathbf{S^-}$ in the form

$$S_x^+ = s\cos\varphi, \qquad S_y^+ = s\sin\varphi, \qquad S_x^- = -s\sin\varphi,$$

$$S_y^- = s\cos\varphi, \qquad S_z^+ = S_z^- = 0.$$

(We can, without losing generality consider that the spins lie in a (001) plane, which corresponds to $a_1 < 0$, $a_2 < 0$. Similar results are obtained for other relations between a_1 and a_2.)

The terms in (4.2) that depend on the angle φ take the form

$$\Phi' = (a_1 - a_2) s^2 \sin 2\varphi - 2bs^2 d\varphi/dz$$

$$+ Bs^2 (d\varphi/dz)^2. \tag{4.3}$$

For $|a_1 - a_2| \ll b^2/B$ we can neglect the effect of the first term. By varying the remaining expression with respect to φ, we obtain $\varphi = kz$. The value of k is obtained by the minimization of the expression $-2bs^2k + Bs^2k^2$, whence $k = |b|/B$.

Thus we can have in MnO_2 a helicoidal structure of large period (k = b/B ~ $\lambda \ll 1$). The axis of the helicoid is along [001], and the rotation of the spins takes place, depending on the relation between a_1 and a_2 either in the (001) plane, or in planes of the type (100) and (110). For the case of rotation in the (001) plane, the spins of the ions at the corners and at the centers of the lattice are described by the formulas

$$S_x^+ + iS_y^+ = se^{ibz/B} \cos (\pi z/c),$$

$$S_x^- + iS_y^- = ise^{ibz/B}\sin (\pi z/c). \tag{4.4}$$

For a_1, $a_2 \gtrsim b^2/B$, the anisotropy should be considered more carefully. This will be done in a later publication.

5. SUPERSTRUCTURES FAR FROM THE TRANSITION POINT

The theory of superstructures presented above rests heavily on the possibility of expanding the thermodynamic potential in a power series in the spin density $\mathbf{s(r)}$. At temperatures far from the transition point, the series expansion is already unsuitable. In this case, however, it is possible to put the question about the stability of the magnetic structure found from some theory or approximately fitting neutron diffraction data.

One can try to explain on the basis of symmetry considerations whether any other magnetic structure exists [i.e., another spin density $\mathbf{s(r)}$] that would give a minimum value to the thermodynamic potential. As before, we may treat the potential Φ as a function of $\mathbf{s(r)}$ and assume that the form of the function and its apparent temperature dependence are determined by the properties of the paramagnetic phase. The latter is associated with the smallness of the magnetic interaction energy (of the order of the Curie temperature Θ for one atom) with respect to the change in the coupling energy of the atoms in the crystal ϵ_0. We may assume in the zeroth approximation that the arrangement of the atoms and the interaction between them remains the same as in the paramagnetic phase and take their small magnetostrictive changes into account via the functional dependence of Φ on $\mathbf{s}$.

The spin density of a real crystal is a periodic function of the coordinates; the corresponding magnetic Bravais lattice is determined by three vectors $\mathbf{f_1}$, $\mathbf{f_2}$, $\mathbf{f_3}$. Therefore only integral degrees will enter in the decomposition of $\mathbf{s(r)}$ into the irreducible representations (2.1), and all possible products of the representations based on the vectors $\mathbf{f_1}$, $\mathbf{f_2}$, $\mathbf{f_3}$, and consequently the potential Φ will be a function of the maximum of three continuous parameters. There are fewer of them if all $\mathbf{f}$ or any two of them transform into one another under rotations.

Thus the question of the stability of the magnetic structure comes down to a determination of the form of the expansion of Φ in degrees of the vectors $\mathbf{f_1}$, $\mathbf{f_2}$, $\mathbf{f_3}$, i.e., the very same problem we took up in Sec. 2. At temperatures far from the

transition point, however, complications arise in connection with the necessity of considering invariants formed from arbitrary powers of the representations entering into $s(r)$. Still, some highly important conclusions can be drawn without getting into the complications [5]:

1) If at least one of the vectors f_1, f_2, f_3 has symmetry of the type C_1, C_s, C_n or C_{nv}, then in the expansion of Φ there are always terms linear in f with coefficients of an exchange nature. Such structures, consequently, are absolutely unstable, except in special cases (see Sec. 4).

2) The spin density, whether even or odd with respect to inversion $[s(-r) = \pm s(r)]$, is always stable.

We note that the criterion of stability can be given, as before, in the coordinate form of Lifshitz. It appears as the absence of invariants of arbitrary order that are linear in the derivatives.

The theory given above of superstructures that occur if the coefficients of the linear terms are small remains completely valid also for arbitrary temperatures. The reason for this is the smallness of the energy of formation of the superstructure in comparison to the energy of the basic structure. Actually, the basic features of the original structure are determined by the strong exchange interactions. The latter, in particular, set the angles between the spins of the ions at neighboring points and their absolute values. Hence the only result of the effect of relativistic forces or especially weak exchange forces that lead to the emergence of a superstructure can only be a rotation of the spin system of the basic structure as a whole relative to the crystal axes, but differing now at different points in the lattice. The angle of rotation between close neighbors will of course be small on account of the large period of the superstructure.

Thus the superstructure can be represented as a twisting of the basic structure. We remark, however, that in real substances, particularly in the case of transition temperatures close to zero or with large atomic numbers, the difference between the relativistic and exchange forces is often quite small. As a result there can appear a greater wealth of superstructures; in particular the magnitudes of the spins will change. A concrete theory can scarcely be constructed in these cases, however.

The orientation of the system of spins relative to the lattice at each point can be given by the

three Eulerian angles or by a single unit complex vector γ ($\gamma \cdot \gamma^* = 1$, $\gamma^2 = 0$); this can be a vector directed along any of the parameters $S_{n\alpha}$. Since all remaining $S_{n\alpha}$ are firmly tied to the first, they are also expressed through γ. Carrying through this orientation it is not difficult to see, for example, that the exchange invariants linear in the derivatives (if, of course, all their coefficients are small), reduce to $\gamma \cdot \partial\gamma^*/\partial z - \gamma^* \cdot \partial\gamma/\partial z$. And if all such invariants are relativistic, then it is sufficient to be limited by the invariant of the lowest order in γ.

In particular, at arbitrary temperatures the theory of superstructures considered in Secs. 3 and 4 is still valid. In the first case it can be shown that from the coordinate functions φ^+ and φ^- [see (3.1)] and arbitrary powers of them it is in general impossible to make up an invariant linear in the derivatives. Therefore, it is sufficient at arbitrary temperatures to limit ourselves to only two invariants (3.3) and (3.4), replacing S^+ and S^- in them by $\mathrm{Re}\,\gamma$ and $\mathrm{Im}\,\gamma$, respectively. In this it is necessary, of course, to treat b and B as arbitrary functions of the temperature. In the case of MnO_2 any exchange invariant will be small, since it must certainly contain as a factor the quantity $S^+ \cdot \partial S^-/\partial z$ ($S^+ \cdot S^- = 0$), which gives a large period to the superstructure. As has been pointed out, it is sufficient in the theory to take into account the single exchange invariant

$$\gamma \partial\gamma^*/\partial z - \gamma^* \partial\gamma/\partial z, \qquad \gamma = (S^+ + iS^-)/|S^+ + iS^-|.$$

In conclusion, we pause to compare the results of this theory with the theories of magnetic structures given by Kaplan[2] and Yoshimori.[3] They are based on an investigation of the classical analog of the Heisenberg Hamiltonian:

$$\mathcal{H} = \tfrac{1}{2}\sum_{i,j} J_{ij} S_i S_j, \tag{5.1}$$

where S_i is the average value of the spin on the i-th lattice site, and the J_{ik} are the corresponding exchange integrals. The exchange integrals for the interaction between 1, 2, and 3 —the nearest neighbors —were considered here, generally speaking, to be quantities of the same order ($J_1 \sim J_2 \sim J_3$).

It was found that the smallest eigenvalue of the quadratic form (5.1) for certain relations among J_1, J_2, J_3 corresponds to a distribution of the average spins of the form $S(r) = S_0 e^{if \cdot r}$ with the vector f having type C_{nv} symmetry. This result can agree with the criterion of stability providing it is assumed that because of the specific properties of the model not connected with symmetry the

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[5]We present these without proofs, since they completely duplicate the corresponding items in Sec. 2.

coefficients of the linear term in the expansion of the energy of the system in powers of f goes to zero.

This property is none other than having an energy quadratic in the average spins. But this is found to be in our problem a completely artificial circumstance. In fact, the quadratic form (5.1) emerges as the classical limit of the usual Heisenberg spin Hamiltonian, the transition to which has meaning only for very large spins ($S \gg 1$). On the other hand, for a spin not equal to $\frac{1}{2}$, the quantum spin Hamiltonian will by no means be quadratic in the spins; it may contain powers of the scalar products $\hat{S}_1 \cdot \hat{S}_2$, different from unity, and in the classical limit $S \to \infty$ also as many greater ones as desired. Then all the exchange integrals will be a priori of a single order of magnitude. Besides, because of the use in the theory of the assumption $J_1 \sim J_2 \sim J_3$ there is no basis whatsoever for neglecting third-order, fourth-order, etc., interactions of the form $(\hat{S}_1 \cdot \hat{S}_2)(\hat{S}_1 \cdot \hat{S}_3)$, and so forth.

Thus, in the classical limit the problem of finding the magnetic structures at absolute zero comes down to an investigation of the general form of the function of the spin density $s(r) = \sum_i S_i \delta(r - r_i)$, which is precisely the approach described at the beginning of this section. The solution of the question about the possibility of a given spin density as the ground state of the system can be found only with the aid of symmetry considerations. The results obtained with the model of the Hamiltonian (5.1) have therefore hardly any connection with reality.

Finally, we shall mention the results of the investigation of magnetic structures, based on the molecular field theory.[1,10,11] In essence, in these papers one finds the dependence of the coefficients a_f in (2.2) on the temperature and the vectors f. It is frequently found then, that in the absence of some physically small parameter a_f has minima at those points of the reciprocal lattice where its symmetry does not demand it. This circumstance, as in the preceding case, indicates probably that the simplifications on which the molecular field theory is founded render it inadequate for the present problem.

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