# Neutron-diffraction studies of magnetic structures of crystals

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The contemporary state of neutron diffraction of magnetic structures is analyzed from the standpoint of the theory of symmetry of crystals. It is shown that the varied and numerous structures determined in neutrondiffraction studies can be classified and described by the theory of representations of space groups of crystals. This approach is based on expanding the spin density of the crystal in terms of basis functions of the irreducible representations of its space group. Thus the magnetic structure can be specified by the mixing coefficients of the basis functions. Analysis of a large number of different kinds of magnetic structures shows that they arise in the overwhelming majority of cases, in accord with Landau's hypothesis, from a phase transition that follows a single irreducible representation. This means that the number of parameters that fully fix the magnetic structure of an arbitrarily complex crystal is small and equal to the dimensionality of the responsible irreducible representation. This offers great advantages in employing the symmetry approach in deciphering neutron-diffraction patterns of a crystal under study. This is because it reduces the problem of determining a large number of magnetic-moment vectors of the crystal to finding a small number of mixing coefficients. This review presents the fundamentals of such a symmetry analysis of magnetic structures and methods of determining them from neutron-diffraction data. The described method, which is closely allied to Landau's general theory of phase transitions, is illustrated by the most recent neutron-diffraction studies of magnetic structures. They included the so-called multi-k-structures, which are characterized simultaneously by several wave vectors, and structures described simultaneously by several irreducible representations of the space group of the crystal. The article gives a physical explanation of the existence of such structures. The experimental studies of crystal-lattice distortions accompanying the onset of magnetic ordering are reviewed. It is shown how symmetry arguments allow one to determine these distortions as well as the unknown magnetic structure. This review presents in condensed but accessible form the symmetry approach to describing the magnetic structures of crystals and analyzes on this basis the feasibility and degree of reliability of deciphering them by employing the scattering of unpolarized and polarized neutrons.

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#### **1. INTRODUCTION**

Thus far the magnetic structures of more than a thousand magnetic materials have been studied by neutron diffraction. The results of these studies have been presented most fully in a handbook on magnetic structures<sup>1</sup> published in Poland in 1976 in the English language. The book, which consists of more than 700 pages of text, gives the fundamental information on the magnetic structure of crystals studied by neutron diffraction in the past 25 years.

We can trace in the bibliography given in this handbook how neutron-diffraction studies have developed



FIG. 1. Yearly numbers of neutron-diffraction studies of magnetic structures in the 25 years of studies using reactors.

during this time (Fig. 1). Their peak lies in the period from 1960 to 1970 (the golden decade of magnetic neutron diffraction). This is explained by the establishment of a large number of neutron-diffraction laboratories throughout the world and by the interest aroused by the discovery at the beginning of this period of helicoidal and other exotic magnetic structures. In recent years the flood of neutron-diffraction studies has ebbed, but is still very high.

Two problems arise in studying and correlating the material given in the handbook<sup>1</sup>: first, one can systematize in some way this "zoo" of magnetic structures; second, how reliably have the magnetic structures themselves been determined? The latter question is especially topical since, as we know, usually a small number of magnetic reflections (Bragg peaks) are well marked on a neutron-diffraction pattern, and the magnetic structure cannot always be deciphered unambiguously from them. This uncertainty in the interpretation of the magnetic neutron-scattering pattern becomes greater with increase in complexity of the crystal and in the number of magnetic atoms per unit cell.

This article aims to show how a systematic account taken of the symmetry of the crystal helps to solve both these problems. Here a method proves fruitful that rests not on the symmetry of the magnetically ordered structure, but on the symmetry of the initial paramagnetic phase of the crystal, which is described by its space group G. This is based on the fact that the magnetic structure usually arises from the paramagnetic phase of the crystal, and as a rule, the distortions of the crystal structure itself in this phase transition are negligibly small, and the problem reduces solely to the orientation of the atomic magnetic moments.

In practive the problems of classifying magnetic structures and of devising effective methods of deciphering them from experimental neutron-diffraction data can be solved by using the ideas of Landau's<sup>2</sup> symmetry theory of phase transitions. Here the density of a parameter that characterizes the low-temperature phase (in this case the spin density of the magnetically ordered crystal) is expanded in terms of basis functions of the irreducible representations of the symmetry group of the initial phase. Dzyaloshinskii<sup>3,4</sup> first successfully employed this approach for describing magnetic structures of crystals; a systematic method that constitutes the working apparatus for applying symmetry in neutron-diffraction studies of magnetic structures has been recently developed in a series of studies by Izyumov, Naish, Petrov, and Syromyatnikov.<sup>5-10</sup>

An analysis of the results of neutron-diffraction studies of crystals performed in recent years in the highflux reactors at Brookhaven, Oak Ridge, Grenoble, and in other laboratories of the world shows that the study of magnetic structures has progressed to a qualitatively new level. Here the aim is not the standard (crude) determination of the magnetic structure of a crystal, but the discovery of its subtle characteristics or concomitant phenomena, e.g., adjustment of the crystal structure accompanying magnetic ordering. In this situation it is important to be guided in an experimental study by theoretical ideas that are often based on symmetry theory or on the general concepts of the theory of phase transitions.

This review will present the major results of neutrondiffraction studies of magnetic structures based on the above-cited ideas of symmetry theory and concepts of phase transitions. Examples will be given of recent "subtle" neutron-diffraction studies performed with account taken of these ideas. Apparently the latter define the level of character of the neutron-diffraction studies of the coming decade.

# 2. METHODS OF DESCRIBING MAGNETIC STRUCTURES OF CRYSTALS

### a) Magnetic symmetry

The first fruitful attempts to systematize the magnetic structures of crystals have involved studying their intrinsic symmetry as systems of spatially ordered axial vectors (atomic magnetic moments). This approach constitutes a natural development of the theory of symmetry of crystal structures as spatially ordered systems of points (atoms). As we know, the entire variety of crystal structures can be described by the 230 Fedorov (space) groups. To describe fully any crystal structure means to specify its space group and the positions of the multiple points occupied by atoms in it, i.e., in essence, the positions of the atoms in the unit cell.

The space group G of a crystal is the group of symmetry operations, consisting of translations, rotations, inversions, etc., that leave this crystal invariant. In order to describe magnetic structures, it has been proposed to add one additional operation R of spin inversion, i.e., change of the direction of a spin to the opposite, to the listed, purely crystallographic symmetry elements. The groups constructed by using the elements of the space groups and the operation R are called the Shubnikov groups. There are 1651 Shubnikov groups in total that are called on to describe the symmetry of magnetically ordered crystals (including also the 230 Fedorov groups, which describe the symmetry of paramagnetic crystals).<sup>11</sup> To state the magnetic structure of a crystal means to specify its Shubnikov group and the positions of the multiple points in it, i.e., in essence, to specify the orientations of the atomic spins in the unit cell.



FIG. 2. Magnetic lattices arising from the simple tetragonal lattice  $\Gamma_{a}$ .

Up to a certain time, this approach described all the known magnetic structures and seemed quite satisfactory. Before the discovery of helicoidal and other socalled incommensurable magnetic structures, all magnetic structures could be characterized by a magnetic unit cell. The neutron-diffraction studies of the first decade (the fifties) led to the discovery of a multitude of magnetic structures having a magnetic cell enlarged by a factor of two, four, or eight over the chemical cell of the crystal. This type of magnetic structures is excellently described by the apparatus of Shubnikov symmetry. An important point here proves to be the concept of the magnetic lattice.

As is well known, crystal structures are characterized by Bravais lattices constructed from the fundamental translation vectors  $t_1$ ,  $t_2$ , and  $t_3$ . Each of the 230 Fedorov groups is described by one of the 14 Bravais lattices. A magnetic lattice constructed from the fundamental translation vectors  $t_1^m$ ,  $t_2^m$ , and  $t_3^m$  of the magnetically ordered crystal belongs to one of the 36 magnetic (black-white) Bravais lattices. The concept of a magnetic lattice incorporates the concept of antitranslation, i.e., the operation tR, which consists of an ordinary translation and a spin inversion. Figure 2 shows as an example some magnetic lattices that can arise from the simple tetragonal crystal lattice  $\Gamma_{q}$ . The translations of the original lattice joining modes of different color in the magnetic lattice correspond to antitranslations. The cases a) and b) correspond to doubling of the magnetic cell in one direction, case c) in two directions, and d) corresponds to a twofold increase in the volume of the magnetic cell. If we ascribe a different orientation of atomic spins to the black and white dots, the stated lattices describe collinear magnetic structures. In cases a) - c), these are antiferromagnetic, and ferromagnetic<sup>1</sup>) in d).

Any Shubnikov symmetry lattice describes a collinear magnetic structure. Yet we should not suppose that the Shubnikov groups cannot describe noncollinear magnetic



FIG. 3. One of the proposed magnetic structures in  $UO_2$ . The black dots indicate the uranium atoms, which lie on the body diagonals of the cube. Oxygen occupies positions at the vertices and center of the cube, at the center of each face, and at the midpoint of each edge. The oxygen atoms are drawn in full only in a single octant of the unit cell.

structures. Just as any arbitrarily complex crystal structure can be treated as a set of a certain number of identical Bravais lattices interpenetrating one another, many noncollinear magnetic structures can be treated as interpenetrating magnetic Bravais lattices. Each of these lattices is formed of collinear spins. However, the relative orientation of the spins belonging to the different lattices can be arbitrary and can lead to a noncollinear antiferromagnetic structure. An example can be the antiferromagnetic structure of  $UO_2$  (Fig. 3), which consists of four collinear ferromagnetic Bravais lattices.<sup>12</sup>

Shubnikov symmetry does not suffice for describing magnetic structures for which a magnetic cell does not exist. Examples of these are the structures: simple spiral (SS) and longitudinal spin wave (LSW) (Fig. 4). The first of these contains ferromagnetic layers in which the orientation of the spins varies by a certain angle in going from one layer to another along the direction of the hexagonal axis. This type of structures, which have been called spiral, helicoidal, or screw structures, has been found in many tens of different crystals. The second structure in Fig. 4 is an example of the magnetic structures. This structure is collinear, but the projections of the atomic spin vary by a harmonic law along a certain direction. If the conserved pro-



FIG. 4. Incommensurable magnetic structures observed in the rare-earth metals: (a) simple spiral (Dy, Tb, Ho); (b) longitudinal spin wave (Er, Tm).

<sup>&</sup>lt;sup>1)</sup>Transl. ed. note: The Russian original does read "ferromagnetic," but the translator correctly queried the appropriateness of this term applied to Fig. 2d.

jection of the spin is oriented along the direction of modulation (as in Fig. 4b), the structure is called a longitudinal spin wave (LSW), while if it is perpendicular to this direction, it is a transverse spin wave (TSW).

Magnetic structures of this type (they are often called modulated) are not rare cases, but are observed in different variations in a multitude of crystals of different types (see, e.g., the handbook of Ref. 1). Since the phase change between two adjacent spins can be arbitrary, one speaks of the incommensurability of the period of this structure with respect to the crystal period. Hence they cannot be characterized by a finite magnetic unit cell. In order to describe their symmetry, as well as that of a number of other structures not describable by the apparatus of Shubnikov groups, various generalizations of these groups have been developed that have generally been termed color symmetry.<sup>13-15</sup> However, from the physical standpoint this method of describing magnetic structures is not very constructive. Success in describing the most general type of magnetic structures involves the use of the theory of representations of the space groups of crystals. Before we proceed to present the fundamental ideas of this method, let us study the problem of the wave vectors of a magnetic structure.

#### b) Wave vectors of a structure

The information of the translational properties of the magnetic structure of a crystal can be conveniently expressed by using the concept of the wave vector. By definition, the wave vector k of a magnetic structure relates the spin  $S_{ni}$  of the *i*th atom in the *n*th primitive cell<sup>\*2</sup> of the crystal of the spin  $S_{0i}$  of the *i*th atom in the zero cell by the relationship

$$\mathbf{S}_{nt} = e^{\mathbf{i}\mathbf{k}t_n}\mathbf{S}_{0i}.\tag{2.1}$$

Here  $t_n$  is the translation vector from the zero cell to the *n*th cell. The wave vector of the structure is always one of the wave vectors of the first Brillouin zone, and can be represented in the form

$$\mathbf{k} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3. \tag{2.2}$$

Here  $b_1$ ,  $b_2$ , and  $b_3$  are the basic vectors of the reciprocal lattice of the crystal, while h, k, and l are certain numbers chosen so that the vector of (2.2) always lies in the first zone.

We can easily verify that the magnetic lattices shown in Fig. 2 have the following wave vectors:

a) 
$$\mathbf{k} = \frac{1}{2} \mathbf{b}_{33}$$
 b)  $\mathbf{k} = \frac{1}{2} \mathbf{b}_{1}$ ,  
d)  $\mathbf{k} = \frac{1}{2} \mathbf{b}_{1} + \frac{1}{2} \mathbf{b}_{2}$ . (2.3)

Lattice c) cannot be derived by using a single wave vec-



FIG. 5. Two wave-vector stars  $\{\frac{1}{2}b_3\}$  and  $\{\frac{1}{2}b_1, \frac{1}{2}b_2\}$  of a simple tetragonal lattice.

# tor, but is described by the wave-vector star $\{k\}$ .

We recall that a wave-vector star is the term applied to the set of nonequivalent arms obtained from a given wave vector (the arm  $\mathbf{k}_1$ ) by the action of all the symmetry elements h of the point group of the crystal. If we denote the elements that generate the nonequivalent arms  $\mathbf{k}_L$  as  $h_L$ , then the entire star can be derived by using the relationship

$$\mathbf{k}_L = h_L \mathbf{k}_1. \tag{2.4}$$

Here  $L = 1, 2, ..., l_k$  is the number of arms of the star.

Figure 5 shows two stars for the  $\Gamma_{q}$  lattice. One of them is single-armed with  $k = \frac{1}{2}b_{3}$ , and the other is two-armed with

$$\mathbf{k}_1 = \frac{1}{2} \mathbf{b}_1$$
 and  $\mathbf{k}_2 = \frac{1}{2} \mathbf{b}_2$ . (2.5)

Evidently, many-armed stars arise whenever the wave vector lies in a direction for which crystallographically equivalent directions exist. If the wave vector belongs to a many-armed star, then a superposition of the states described by single arms is possible. Thus, in the case of the star of (2.5), a magnetic lattice can occur having the following relationship between  $S_{ni}$  and  $S_{oi}$ :

$$\mathbf{S}_{ni} = e^{\mathbf{j} \cdot \frac{1}{2} \cdot \mathbf{b}_{i} \mathbf{i} \mathbf{n}} \mathbf{S}_{0i}^{1} + e^{\mathbf{j} \cdot \frac{1}{2} \cdot \mathbf{b}_{i} \mathbf{n}} \mathbf{S}_{0i}^{2}.$$
 (2.6)

Here  $S_{0i}^{1}$  and  $S_{0i}^{2}$  are certain vectors that are specified in the zero cell of the crystal. Upon testing all the translation vectors  $\mathbf{t}_{n}$  of the original lattice, we see that certain of them are translations, and certain are antitranslations of the magnetic lattice. Thus one derives lattice c) of Fig. 2. The nodes of the original lattice marked by crosses in the diagram correspond neither to translations nor antitranslations. The spins of the atoms corresponding to them are not collinear with the spins of the magnetic lattice marked with black and white dots, and must form *per se* the same type of lattice.

We see from the discussed example that the magnetic structure in the case of a many-armed star must be characterized by all the arms of this star. Instead of (2.1), we must have the following relationship<sup>7</sup>:

$$\mathbf{S}_{ni} = \sum_{L} e^{i\mathbf{k}_{L} i \mathbf{n}} \mathbf{S}_{0i}^{L}.$$
(2.7)

We shall call the vectors  $S_{ol}^{L}$ , which can be complex, the *arm contributions* to the magnetic structure.

The fundamental relationship (2.7) defines the translational properties of an arbitrary magnetic structure when the wave-vector star is defined. However, these properties depend not only on the star, but also on the set of arm contributions  $\{S_{of}^{L}\}$ , that differ from zero. Let us call the set of arms of the star for which the arm

<sup>&</sup>lt;sup>2)</sup>Henceforth we shall be referring to the primitive cell of the crystal, since the concept of the unit cell is not identical to that of the primitive cell for all centered lattices. The concept of the unit cell, which is convenient and generally accepted in problems of diffraction and structural analysis, gives way to the concept of the primitive cell in group-theoretical analysis. The identification of these two different concepts can be the source of serious errors.

contributions differ from zero the *transition channel*.<sup>7,16</sup> We can easily see that the transition channel fixes unambiguously the translational properties of the magnetic structure. Thus the following theoretical problem arises: to indicate all the magnetic lattices that can be derived from a given crystal lattice by magnetic ordering.

To solve it, we should take the wave-vector stars differing in symmetry for each of the 14 Bravais lattices (the list of all such stars is finite and is contained in handbooks, e.g., in Kovalev's book<sup>17</sup>). For all channels of each star (by combining its arms in different ways), we should find the lattices corresponding to them by Eq. (2.7). For all the Lifshits stars<sup>18</sup> (whose wave vectors end at symmetry points of the Brillouin zone). this task has been accomplished in Refs. 5 and 7. The results are reduced to a table which can be used to specify the magnetic lattice for a given transition channel in the original lattice. It has turned out that one of the 36 magnetic Shubnikov symmetry lattices arises in all the channels of the Lifshits stars. Thus the specification of the magnetic lattice and the concept of the magnetic unit cell prove unnecessary if one specifies the wave vectors of the magnetic structure, or more exactly, the transition channel.

In the case of non-Lifshits stars, the relationship (2.7) gives rise to modulated magnetic structures. Actually, in crystals having an inversion center, any non-Lifshits star contains also the arm -k as well as the arm k, so that a two-arm channel always exists in which Eq. (2.7) acquires the form:

$$\mathbf{S}_{nt} = e^{iktn} \mathbf{S}_{0t}^{k} + e^{-iktn} \mathbf{S}_{0i}^{k}.$$
(2.8)

This relationship describes a structure of the spin-wave type (LSW or TSW) if the arm contribution  $S_{0i}^{k}$  is real, and some spiral structure if  $S_{0i}^{k}$  is complex. In particular, if  $S_{0i}^{k} = S(m_{1i} + im_{2i})$ , where  $m_{1i}$  and  $m_{2i}$  are two orthogonal vectors perpendicular to the wave vector k, the magnetic structure corresponding to (2.8) amounts to a simple spiral (SS).

Thus we conclude that a full specification of any magnetic structure of a crystal does not require specifying individually the spin vector at each magnetic atom of the crystal. To do this, it suffices to fix the transition channel (i.e., the participating arms of the star) and the set of arm contributions—the vectors  $S_{ol}^L$  to be fixed in the zero primitive cell of the crystal. If the channel and the arm contributions are known, Eq. (2.7) enables us to find the spin vectors of the atoms in any cell of the crystal. The maximum number of vector parameters  $S_{ol}^L$  is  $l_k \sigma$ , where  $\sigma$  is the number of magnetic atoms in the primitive cell of the crystal.

The fundamental relationship (2.7) is based on the hypothesis that the magnetic structure is described by a single wave-vector star. This statement is a generalization of an enormous amount of experimental material on magnetic structures. It also has a theoretical justification within the framework of the Landau theory of phase transitions<sup>2</sup> (see below). There are several exceptions in which the structure is characterized at the same time by two stars. Each of them usually characterizes the ordering of mutually orthogonal projections of the atomic magnetic moment. An example might be the ferromagnetic spiral (FS) found in Ho and Er. In this case the helicoidal ordering of the spin projections on the basis plane is characterized by a non-Lifshits star, while the ferromagnetic component of the spins on the hexagonal axis is characterized by the star k = 0.

#### c) Expansion in basis functions

We can attain a deeper description of a magnetic structure by expanding the arm contributions in terms of the basis functions of the irreducible representations of the group of the wave vector  $k_L$ . We can write this expansion in the form<sup>9</sup>

$$\mathbf{S}_{0i}^{L} = \sum_{\mathbf{v}} \sum_{\lambda} C_{\lambda}^{L \mathbf{v}} \mathbf{S} \left( \frac{\mathbf{k}_{L} \mathbf{v}}{\lambda} \middle| i \right).$$
(2.9)

Here  $S_{\lambda}^{(\mu\nu)}|i\rangle$  is the atomic component of the basis function of the  $\nu$ th irreducible representation of the group  $G_k$  (we shall denote the irreducible representations of the group  $G_k$  by  $d^{\mu\nu}$ , while the index  $\lambda$  enumerates the basis functions of this representation). The basis function itself amounts to a multidimensional column consisting of all the atomic components  $S_{\lambda}^{(\mu\nu)}|i\rangle$  of the crystal. However, owing to the relationship<sup>6</sup>

$$\mathbf{S}\begin{pmatrix} \mathbf{k}\mathbf{v} \\ \lambda \end{pmatrix} = e^{i\mathbf{k}\mathbf{l}\mathbf{n}\mathbf{S}}\begin{pmatrix} \mathbf{k}\mathbf{v} \\ \lambda \end{pmatrix} \mathbf{0}_{i}, \qquad (2.10)$$

it is fully fixed by the atomic components  $S_{\lambda}^{(\nu)}|0i\rangle$  of the zero primitive cell, which we shall denote by  $S_{\lambda}^{(\nu)}|i\rangle$ .

If we denote the multicomponent column of the atomic spin vectors  $S_{nf}$  by  $S^{(k)}$ , then, owing to Eqs. (2.7), (2.9), and (2.10), we obtain the following representation of the magnetic structure  $S^{(k)}$  in terms of the basis functions  $\psi_{k}^{(k)}$  of the wave-vector group:

$$S^{(k)} = \sum_{L^{N}} \sum_{\lambda} C_{\lambda}^{L^{N}} \psi_{\lambda}^{k_{L}^{V}}.$$
(2.11)

The set of basis functions for all the arms of the star realizes an irreducible representation of the space group G of the crystal. Thus the relationship (2.11) expresses an expansion of the magnetic structure in terms of the basis functions of an irreducible representation of the space group. The Landau theory of phase transitions is based on this type of relationships. The relationship (2.9) and the equivalent (2.11) are exact. If we employ the constructive idea of Landau that a phase transition (in this case from a paramagnetic to a magnetically ordered phase) follows a single irreducible representation (say,  $d^{\mu\nu}$ ), then we can omit the summation over  $\nu$ in Eqs. (2.11) and (2.9). Then (2.9) is written in the form

$$\mathbf{S}_{0i}^{L} = \sum_{\lambda} C_{\lambda}^{L\nu} \mathbf{S} \left( \frac{\mathbf{k}_{L}\nu}{\lambda} \middle| i \right).$$
(2.12)

The hypothesis of a single irreducible representation finds a microscopical substantiation in structural transitions of the distortion type that occur via the mechanism of a soft mode. As applied to magnetic phase transitions, its validity is not so evident, since the paramagnetic phase of the crystal possesses no soft magnetic modes that might "freeze in" in the crystal below the magnetic transition temperature  $T_k$  to form a magnetic structure. However, magnetic order fluctuations arise in the system near  $T_k$  that can be classified in terms of the irreducible representations of the space group of the crystal. Those whose characteristic energy vanishes first (at higher temperature) freeze in in the crystal, as it were, thus giving rise to the magnetic structure. Let us call the corresponding irreducible representation the *responsible* or relevant one.

These arguments offer certain grounds for expecting that a magnetic phase transition will follow a single irreducible representation of the group G. Consequently the magnetic structure should be described by a single irreducible representation. In Sec. 5 we shall analyze the manner in which this hypothesis is fulfilled, while for the present, anticipating later discussion, we merely note that it is fulfilled satisfactorily. What we have said makes it understandable why the magnetic structure is described by a single wave-vector star: the irreducible representation of the space group is specified primarily by the wave-vector star (and in addition by the index  $\nu$ ).

We now summarize. The magnetic structure can be described by two relationships—(2.7) and (2.12). The former defines the translational properties and reduces the magnetic structure of the entire crystal to the magnetic structure of its primitive cell. The latter relationship expresses the magnetic structure of the primitive cell in terms of the mixing coefficient of the basis functions of the responsible representation.

Further, let us discuss the following problems: 1) how does one determine from neutron-diffraction data the required characteristics of the magnetic structure; 2) to what extent are the employed assumptions about the magnetic structure fulfilled, in particular, the hypothesis of a single irreducible representation; 3) how does one calculate the basis vectors  $S(\lambda^{\mu\nu}|i)$  in terms of which the unknown magnetic structure is expanded.

# 3. DECIPHERMENT OF THE MAGNETIC STRUCTURE FROM EXPERIMENTAL NEUTRON-DIFFRACTION DATA

# a) Diffraction of neutrons by a magnetically ordered crystal

Diffraction is governed by the well-known expression for the elastic magnetic scattering cross-section<sup>19</sup>

$$\frac{\mathrm{d}\sigma_{\mathbf{x}}^{m}}{\mathrm{d}\Omega} = (r_{0}\gamma)^{2} | \mathbf{F}(\mathbf{x}) |^{2}.$$
(3.1)

Here  $r_0 = e^2/mc^2$  is the electromagnetic radius of an electron,  $\gamma = -1.99$  is the magnetic moment of the neutron in nuclear magnetons, and we have

$$\mathbf{F}(\mathbf{x}) = \sum e^{-i\mathbf{x}\mathbf{R}_l} F_l(\mathbf{x}) \left(\mathbf{S}_l - (\mathbf{e}\mathbf{S}_l) \mathbf{e}\right).$$
(3.2)

Here  $S_i$  and  $F_i(n)$  are the spin and the magnetic form factor of the *l*th atom situated at the lattice node  $R_i$ , and e = n/n is the unit scattering vector.

Whenever the crystal has a magnetic structure characterized by the wave-vector star  $\{\mathbf{k}_L\}$ , the spin of the atom  $l(\mathbf{R}_i = \mathbf{t}_n + \mathbf{x}_i)$  of an arbitrary cell of the crystal is expressed in terms of the arm contributions  $\mathbf{S}_{0i}^L$  by Eq. (2.7). Upon substituting it into (3.2) and summing over all the translations  $\mathbf{t}_n$ , we represent the cross-section  $d\sigma_{\mathbf{x}}^{\mathbf{x}}/d\Omega$  in the following form:

$$\frac{1}{N} \frac{\mathrm{d}\sigma_{\mathbf{x}}^{m}}{\mathrm{d}\Omega} = (r_{0}\gamma)^{2} \sum_{L} \left( \overset{\bullet}{\mathbf{M}}_{\mathbf{x}}^{L} \mathbf{M}_{\mathbf{x}}^{L} \right) N \sum_{\mathbf{b}} \delta_{\mathbf{x}-\mathbf{k}_{L},\mathbf{b}}.$$
(3.3)

Here we have

$$\begin{aligned} \mathbf{M}_{\mathbf{x}}^{L} &= \mathbf{f}_{\mathbf{x}}^{L} - (\mathbf{e}_{\mathbf{x}}^{L}) \, \mathbf{e}_{\mathbf{s}} \end{aligned} \tag{3.4} \\ \mathbf{f}_{\mathbf{x}}^{L} &= \sum_{i} e^{-i\mathbf{x}\mathbf{x}_{i}} F_{\mathbf{t}} \left( \mathbf{x} \right) \mathbf{S}_{0\mathbf{t}}^{L}. \end{aligned} \tag{3.5}$$

The summation over b is performed over the reciprocal-lattice vectors of the original crystal.

In deriving Eq. (3.3), we have employed the known identity

$$\frac{1}{N}\sum_{n}e^{-iqt_{n}}=\sum_{\mathbf{b}}\delta_{\mathbf{q},\mathbf{b}}$$
(3.6)

(N is the number of cells in the crystal, and  $\delta_{q,b}$  is the Kronecker delta symbol). We have also used the fact that two arms  $k_L$  and  $k_L$ , of the star cannot differ by an integral reciprocal-lattice vector. Owing to the latter situation, the scattering by the magnetic structure is additive with respect to the arm contributions and is grouped into Bragg peaks whose angular arrangement is defined by the conditions

$$\kappa = \mathbf{b} + \mathbf{k}_L. \tag{3.7}$$

The nuclear scattering cross-section is described by the expression  $^{19}$ 

$$\frac{1}{N} \frac{d\sigma_{\mathbf{x}}^{\text{nucl}}}{d\Omega} = |f_{\mathbf{x}}^{\text{nucl}}| N \sum_{\mathbf{b}} \delta_{\mathbf{x}, \mathbf{b}}.$$
(3.8)

This implies the appearance of a nuclear peak under the condition

 $\kappa = b$ ,

i.e., at every reciprocal-lattice node of the crystal. The quantity  $f_x^{\text{nucl}}$  is called the nuclear-scattering structure amplitude, while the quantity  $f_x^L$  in (3.5) should be called the magnetic-scattering structure amplitude.

Thus, in the general case the magnetic-scattering peaks do not coincide with the nuclear-scattering peaks. Only when the magnetic structure is characterized by the wave vector  $\mathbf{k} = 0$  (as happens in a ferromagnetic structure or antiferromagnetic structure if the magnetic and crystal cells coincide) are they superimposed on one another. Observation of a system of magnetic reflections allows one to determine from (3.7) the wave vectors of the magnetic structure. This constitutes the first stage in the neutron-diffraction study of the magnetic structure. In virtue of the relationships (3.3) -(3.5), measurement of the intensities of the peaks enables one to determine the atomic spin vectors  $S_{ni}$ . This constitutes the second, final stage in the neutrondiffraction study. Now let us examine both these stages in greater detail.

#### b) Determination of the wave vectors

The relationship (3.7) implies that each arm of the star gives rise to a system of magnetic reflection replicated from a given one by all the translations of the reciprocal lattice of the original crystal. Each magnetic reflection, which is characterized by the scattering vector  $\varkappa$  ( $\varkappa = hb_1 + kb_2 + lb_3$ ), can be symbolized by a triplet of numbers (h kl) called the Miller indices. If we subtract the indices of the nuclear reflections from the



FIG. 6. Magnetic lattices derivable according to three different channels of the star  $\{k_{10}\}$  of a fcc crystal, and the corresponding pattern of magnetic and nuclear reflections. In the right-hand side of the diagram, the open circles denote the nuclear reflections lying at the reciprocal-lattice nodes, and the black dots denote the magnetic reflections.

Miller indices of the magnetic reflections, we get the Miller indices  $(h_L k_L l_L)$  of the arm  $k_L$  of the magnetic structure under study. This is how one must determine the wave vectors of the magnetic structure that constitute the transition channel.

As an example, let us examine the magnetic structures that arise in the fcc lattice from a magnetic transition following the three-arm star having the arms

$$\mathbf{k}_1 = \frac{1}{2} (\mathbf{b}_1 + \mathbf{b}_2), \quad \mathbf{k}_2 = \frac{1}{2} (\mathbf{b}_1 + \mathbf{b}_3), \quad \mathbf{k}_3 = \frac{1}{2} (\mathbf{b}_2 + \mathbf{b}_3)$$
 (3.9)

(the star  $\{k_{10}\}$  in the nomenclature of Ref. 17). The fundamental reciprocal-lattice vectors of

$$\mathbf{b}_1 = \frac{2\pi}{a} (\overline{1}11), \quad \mathbf{b}_2 = \frac{2\pi}{a} (1\overline{1}1), \quad \mathbf{b}_3 = \frac{2\pi}{a} (1\overline{1}\overline{1}).$$
 (3.10)

Here a is the length of the edge of the cubic unit cell of the crystal, which is characterized by the shortest translations:

$$\mathbf{t}_1 = \left(0 \frac{a}{2} \frac{a}{2}\right), \quad \mathbf{t}_2 = \left(\frac{a}{2} 0 \frac{a}{2}\right), \quad \mathbf{t}_3 = \left(\frac{a}{2} \frac{a}{2} 0\right). \tag{3.11}$$

We can easily verify by Eq. (2.7) that we obtain the magnetic lattices shown in Fig. 6 in the three channels: one-arm (with the wave vector  $\mathbf{k}_1$ ), two-arm ( $\mathbf{k}_2$  and  $\mathbf{k}_3$ ), and three-arm ( $\mathbf{k}_1, \mathbf{k}_2$ , and  $\mathbf{k}_3$ ). Magnetic reflections distinguish each of these lattices: (001) for the one-arm channel; (010) and (100) for the two-arm channel; and (001), (010), and (100) for the three-arm channel. The Miller indices of these reflections coincide with the notation of the arms in (3.9) with use of the expressions (3.10):

$$\mathbf{k}_{t} = \frac{2\pi}{a} (001), \quad \mathbf{k}_{2} = \frac{2\pi}{a} (010), \quad \mathbf{k}_{3} = \frac{2\pi}{a} (100).$$
 (3.12)

We see clearly from this example how the transition

channel must be determined from the system of magnetic reflections. A table is given in Refs. 5 and 7 from which one can determine the transition channel and the magnetic lattice (its unit cell and Shubnikov-group symbol) from the observed system of magnetic reflections for all the Lifshits stars of all 14 original Bravais lattices. By using this table, an experimenter can translate the information on the translational properties of magnetic structures from diffraction language into group-theoretical language, i.e., determine the wavevector star and the transition channel.

Evidently, in principle one can determine the transition channel from the system of magnetic reflections (i.e., without treating the intensities) only by neutron diffraction using single crystals. In neutron diffraction using powders, one must bear in mind, e.g., that the reflections (100), (010), and (001) are indistinguishable for a cubic crystal. Then to establish the transition channel, i.e., the magnetic lattice, we must compare the intensities of the magnetic reflections. Thus the study of powders enables one to establish from the system of magnetic reflections only the wave-vector star, so that the magnetic structure must be represented in the form of the superposition of (2,7) of spin functions of individual arms. The inter-arm mixing coefficients (or the arm contributions  $S_{ot}^{L}$ ) are chosen by best agreement with experiment.

However, the described situation pertains only to the case in which no domain (antiferromagnetic) structure exists in the studied single crystal. The existence of domains substantially complicates the possibility of determining the transition channel from the system of magnetic reflections. One domain differs from another (when they differ arbitrarily in volume and shape) only in the overall orientation of the magnetic structure. The orientations of the atomic spins in two domains are related by the rotational transformation  $h_{e}$ , which does not depend on the number l of the atom. That is, we have

$$\mathbf{S}_l^a = h_a \mathbf{S}_l^1. \tag{3.13}$$

Here  $S_i^l$  is the spin of the *l*th atom in the first domain, and  $S_i^a$  is the spin of the same atom when it belongs to the domain *a*.

Now let us study the neutron-diffraction pattern in a multidomain specimen. To do this, let us write the structural magnetic amplitude F(k) by subdividing the summation in (3.2) over all the atoms of the single crystal into a summation over the domains and a summation within an individual domain. Since the domains are of macroscopic dimensions, coherent scattering arises in each of them. Then in calculating the amplitudes in (3.2) we can take the limit as the number of cells  $N_a$  per individual domain approaches infinity. The coherent nature of the scattering allows us to transform to the averaged magnetic amplitude  $\langle F(\varkappa) \rangle$ :

$$\langle \mathbf{F}(\mathbf{x}) \rangle = \frac{1}{N} \sum_{ni} e^{-i\mathbf{x} \cdot (\mathbf{i}_n + \mathbf{x}_i)} F_i(\mathbf{x}) \sum_a p_a h_a | \mathbf{S}_{ni}^1 - (\mathbf{c}\mathbf{S}_{ni}^1) \mathbf{e} ].$$
(3.14)

Here  $p_a$  is the relative fraction of domains of type a.

The calculation of Eq. (3.14) depends on the type of domains. Let us assume that a magnetic structure is realized in an individual domain that has a single wave

vector (a one-arm channel). In this case domains having crystallographically equivalent directions of the wave vector must exist. All such wave vectors are arms of the star and can be derived from the first arm by Eq. (2.4). Upon comparing this relationship with (3.13), we see that the rotation operation  $h_a$  that superposes the magnetic structures in the two domains is the operation  $h_L$ .

In the single-arm channel, Eq. (2.7) reduces to the following relationship:  $\mathbf{S}_{\pi i}^{1} = e^{i \mathbf{k}_{1} \cdot \mathbf{t}_{\pi}} \mathbf{S}_{0i}$ . Upon operating on it on the left and on the right by the operation  $h_{L}$ , we get

$$h_a \mathbf{S}_{ni}^1 = e^{i\mathbf{k}_L t_n} h_L \mathbf{S}_{0i}. \tag{3.15}$$

Upon substituting this relationship into (3.14) and summing over the integral translations by using (3.6), we can represent the magnetic amplitude for a multidomain specimen in the following form:

$$\langle \mathbf{F} (\mathbf{x}) \rangle = \sum_{L} p_L \sum_{i} F_i (\mathbf{x}) e^{-i\mathbf{x}\mathbf{x}} i h_L \mathbf{S}_{0i}^4 \sum_{\mathbf{b}} \delta \mathbf{x} - \mathbf{k}_L, \mathbf{b}.$$
(3.16)

Thus, a calculation of the cross-section in (3.1) by using this amplitude gives rise to the same structure as in (3.3), namely: magnetic-scattering peaks arise at the scattering vectors  $\mathbf{k} = \mathbf{k}_{L} + \mathbf{b}$  that are the same as in scattering by a magnetic structure characterized by all the arms of the star (all-arm channel). Hence the systems of magnetic reflections for a one-arm structure in a multidomain specimen and for an all-arm structure in a one-domain specimen are indistinguishable. This introduces difficulties in establishing the transition channel in neutron diffraction by a single crystal. We have treated the simplest case of a domain magnetic structure. In the general case the diffraction pattern becomes more complicated. In some cases one can distinguish the effects of the domain structure in deciphering neutron-diffraction patterns from differences in the intensities of the Bragg peaks in the case of one-domain and multidomain structures.<sup>20</sup> The problem of how experimenters establish the transition channel will be discussed in greater detail in Sec. 5.

### c) Determination of the atomic spin vectors

After the wave-vector star and the transition channel have been revealed, one must determine the atomic spin vectors in the primitive cell. To do this, one should employ the expression for the intensity of the magnetic reflections:

$$I_{\mathbf{x}}^{L} \sim (\mathbf{\tilde{M}}_{\mathbf{x}}^{L} \mathbf{M}_{\mathbf{x}}^{L}). \tag{3.17}$$

Each reflection among the entire series of magnetic reflections generated by a single arm  $k_L$  contains  $\sigma$  complex vectors  $S_{oi}^L$ , which can be found by a variational procedure by best fit with the measured intensities. An analogous procedure for the series of reflections corresponding to another arm enables one to find the vectors of the corresponding arm contribution, etc. Each time one varies  $\sigma$  complex vectors when studying a single crystal (one-domain), and  $l_k \sigma$  vectors when studying a powder neutron-diffraction pattern.

This corresponds to the traditional way of deciphering a magnetic structure, in which one seeks directly the atomic spin vectors (or the arm contributions in the case of a many-arm magnetic structure). By employing the theory of representations of the space groups, one can sharply reduce the number of parameters to be varied. Actually, let us substitute the expression (2.12) for the arm contribution in terms of the basis functions of some irreducible representation of the wave-vector group  $G_k$  into the formula (3.5) for the magnetic structure amplitude. We see that it decomposes into the sum of the normal amplitudes  $f_{kk}^{L\nu}$ :

$$\mathbf{f}_{\mathbf{x}}^{L} = \sum_{\lambda} C_{\lambda}^{L\nu} \sum_{i} e^{-i\mathbf{x}\mathbf{x}_{i}} F_{i} \left( \mathbf{x} \right) \mathbf{S} \left( \mathbf{x}_{\lambda}^{L\nu} \middle| i \right) \equiv \sum_{\lambda} C_{\lambda}^{L\nu} \mathbf{f}_{\mathbf{x}\lambda}^{L\nu}.$$
(3.18)

The normal amplitudes can be calculated in advance and hence are considered to be known. Thus, in employing the expression (3.18) in the formula (3.17) for the intensity of the Bragg peak, it is not the  $\sigma$  unknown complex vectors  $S_{0l}^{L}$  that are to be varied, but the  $l_{\nu}$  mixing coefficients  $C_{\lambda}^{L\nu}$ . Here  $l_{\nu}$  is the dimensionality of the responsible irreducible representation. For the space groups, the  $l_{\nu}$  are small numbers (1, 2, 3, and rarely 6). Reduction of the variables to be varied in the adjustment procedure is especially effective when there is a large number  $\sigma$  of magnetic atoms in the primitive cell of the crystal.

In the magnetic structure under study, the responsible irreducible representation is not known in advance. Hence one should run one by one through all the irreducible representations of the space group having the given star (the number of them is small, and the irreducible representations themselves are taken from the handbooks). Each time here one must deal with a small number of parameters to be varied, or mixing coefficients. The representation that yields the best fit of the calculated and observed intensities determines the responsible representation. If it turns out that none of the irreducible representations gives a satisfactory fit, one must combine them, assuming that the magnetic structure is described by a reducible representation of the space group (see Sec. 5).

### d) Potentialities of using polarized neutrons

We have been treating the decipherment of magnetic structures employing unpolarized neutrons. Evidently, part of the information on the magnetic structure that is contained in the scattered beam is lost here in averaging over the spin of the neutrons. Use of polarized neutrons allows one in principle to obtain more reliable information on the magnetic structure with a substantially smaller number of measured magnetic reflections. Here one can treat two types of effects: the relationship of the scattering cross-section in the Bragg peaks to the polarization vector of the incident neutron beam and the change in the polarization vector of the beam upon scattering.

The intensity  $I_x^L$  of the Bragg peak  $\varkappa = b + k_L$  of the polarized beam having the polarization vector  $p_0$  is determined by the relationship<sup>10,21</sup>

$$I_{\mathbf{x}}^{L} \sim \{(\mathbf{\tilde{M}}_{\mathbf{x}}^{L}\mathbf{M}_{\mathbf{x}}^{L}) + i [\mathbf{\tilde{M}}_{\mathbf{x}}^{L}\mathbf{M}_{\mathbf{x}}^{L}] \mathbf{p}_{0}\}.$$
(3.19)

(This expression holds only when  $k_L \neq 0$ , since the magnetic and nuclear scattering are superimposed in the case of magnetic scattering with  $k_L = 0$ , and the formula

for the intensity is altered.) The polarization vector p of the beam scattered into this Bragg peak is given by the expression<sup>10,21</sup>

$$\mathbf{p} = \frac{-i \left[\mathbf{\tilde{M}}_{\mathbf{x}}^{L} \times \mathbf{M}_{\mathbf{x}}^{L}\right] + \left(\mathbf{p}_{0}\mathbf{M}_{\mathbf{x}}^{L}\right) \mathbf{\tilde{M}}_{\mathbf{x}}^{L} + \left(\mathbf{p}_{0}\mathbf{\tilde{M}}_{\mathbf{x}}^{L}\right)\mathbf{M}_{\mathbf{x}}^{L} - \mathbf{p}_{0}\left(\mathbf{\tilde{M}}_{\mathbf{x}}^{L}\mathbf{M}_{\mathbf{x}}^{L}\right)}{\left(\mathbf{\tilde{M}}_{\mathbf{x}}^{L}\mathbf{M}_{\mathbf{x}}^{L}\right) + i \left[\mathbf{\tilde{M}}_{\mathbf{x}}^{L}\mathbf{M}_{\mathbf{x}}^{L}\right]\mathbf{p}_{0}}$$

As we see from Eqs. (3.17), (3.19), and (3.20), all the effects of Bragg scattering on the magnetic structure are governed by the same axial vector  $\mathbf{M}_{\mathbf{x}}^{L}$ , which depends on the arm-contribution vectors  $\mathbf{S}_{d}^{L}$ .

If one measures the intensity of the Bragg peak for three mutually perpendicular positions of the initial polarization vector po, then, owing to the second term in (3.19), we get three equations for determining  $M_x^L$ . If one derives the magnetic structure from a representation of dimensionality no higher than three (higher dimensionalities are seldom encountered), these equations prove sufficient to determine the mixing coefficients  $C_{\lambda}^{L\nu}$  of one arm contribution. Then, for a complete determination of the magnetic structure, it suffices to study one reflection each among the system of reflections produced by an individual arm. Analogously we can determine the arm contribution to the magnetic structure by measuring the polarization vector of the scattered beam of polarized neutrons or the spontaneous-polarization vector that arises in scattering of an unpolarized beam. Thus, if the magnetic structure is characterized by a single-arm star or a single-arm channel of some star, often it would suffice to have only one magnetic reflection to determine it completely. if we measure the polarization effects and use symmetry analysis. The maximum number of necessary reflections for an arbitrary magnetic structure is evidently no greater than the number of arms of the star.

Of course, these unique potentialities of polarized neutrons work only in the case of a single-domain specimen. In the presence of magnetic domains with an equally probable orientation distribution, the stated effects disappear owing to averaging over these orientations.

# 4. CALCULATION OF THE BASIS FUNCTIONS

# a) Irreducible representations of the space groups

The preceding sections have shown that the problem of describing and deciphering the magnetic structure of a crystal reduces to calculating the basis functions of the irreducible representations of its space group, i.e., the vector quantities  $S(\frac{w}{\lambda}|i)$ . Now we shall show how they should be calculated. First we shall provide the necessary information from the theory of irreducible representations of the space groups.

A representation of the space group  $D^{(k)\nu}$  is constructed from the representations  $d^{k\nu}$  of the wave-vector group  $G_k$ . The wave-vector group is a subgroup of the space group G consisting of the elements g that leave the wave vector k invariant. That is, the element g is contained in  $G_k$  if

$$g\mathbf{k} = \mathbf{k} + \mathbf{b}. \tag{4.1}$$

Here b is an arbitrary reciprocal-lattice vector.

A representation of the group  $G_k$  is a set of matrices  $d_{\lambda\mu}^{b\nu}$  correlated with each element  $g \in G_k$  that satisfies the same multiplication rules as do the elements of the group themselves. The matrices of the irreducible representations are tabulated for the elements  $g = \{h | \tau_h\}$  of the so-called zero block of the group  $G_k$ , i.e., for the set of elements that do not contain integral translations  $t(\tau_h \text{ is some fractional part of the translation accompanying the rotation <math>h$ ).<sup>17</sup> Arbitrary elements of the group  $G_k$  satisfy the relationship

$$d_{\lambda\mu}^{k\nu}(\{h \mid \tau_h + \mathbf{t}\}) = e^{-i\mathbf{k}\mathbf{t}_n} d_{\lambda\mu}^{k\nu}(\{h \mid \tau_h\}), \qquad (4.2)$$

that reduces all elements to elements of the zero block. The matrix  $d_{\lambda\mu}^{\mu\nu}(g)$  is defined on some basis of functions  $\psi_{\lambda}^{\mu\nu}$  that are transformed in terms of one another by the action of an element  $g \in G_{k}$  by the relationship<sup>22</sup>

$$\Gamma(g) \psi_{\lambda}^{k\nu} = \sum d_{\mu\lambda}^{k\nu}(g) \psi_{\mu}^{k\nu}.$$
(4.3)

If an element g of the space group G that doesn't belong to  $G_k$  acts on the function  $\psi_{\lambda}^{\mu\nu}$ , linear combinations will arise that are composed of functions  $\psi_{\lambda}^{kL\nu}$  that belong to other arms of the star  $\{k\}$ . Thus the set of functions  $\psi_{\lambda}^{kL\nu}$  having the indices  $L = 1, 2, \ldots, l_k$ ;  $\lambda = 1, 2, \ldots, l_{\nu}$  is transformed in terms of one another to create an irreducible representation of the group G having the same index  $\nu$  as the irreducible representation of the group  $G_k$ . Evidently the dimensionality of the representation is  $l_k \times l_{\nu}$ . Henceforth all the final formulas will contain only the matrices of the irreducible representations of the group  $G_k$ . Therefore we shall not explain the structure of the matrices of the representations of the large group G.

#### b) Reducible representations of the space groups

In calculating the basis functions of the irreducible representations of the groups G and  $G_k$  in which one can expand the spin density of the crystal in the form of (2.9) or (2.11) (as well as other quantities, e.g., the charge density, the dipole-moment density, etc.) it is useful to employ reducible representations of these groups constructed of localized atomic functions, thus including information on the properties of the crystal of interest to us. The idea of constructing these representations consists of the following.

Let the state of each atom be characterized by some atomic function localized near its equilibrium position in the crystal. The state of the crystal as a whole is characterized by the set of these functions defined for the individual atoms and forming some multidimensional vector in atomic-function space. When acted on by the elements of the space group, this set will be transformed into another set of atomic functions from the same space. Thus it realizes some representation of this group, which in the general case should be reducible. The properties of this representation depend not only on the structure of the crystal, i.e., on the arrangement of the atoms in space, but also on the physical content of the chosen atomic functions.

An atomic function may describe no specific characteristic of an atom other than its definite number in the crystal. Thus, when the elements of the space group act on this type of state vector of the crystal, everything is reduced to a permutation of the numbers of the atoms. In another case, a characteristic can be associated with each atom that is described by a polar vector (e.g., its displacement from its equilibrium position) or an axial vector (pseudovector), which might be the magnetic moment of the atom. When acted on by the elements of the group G, along with the change in the number of the atom, the vector ascribed to it will be transformed. The representations of the space group that are generated on the basis of scalar, vector, and pseudovector atomic functions are respectively called permutational, mechanical, and magnetic. A mechanical representation is employed to describe phonons in a crystal and atomic displacements in structural phase transitions,<sup>22</sup> and a magnetic representation is used to describe the magnetic structures of crystals.6,23,24 The permutational representation is auxiliary in nature, and we shall use it to analyze the exchange Hamiltonian in the crystal.9

We shall present the final form of the matrices of these three representations, whose derivation in such a convenient form was given in Refs. 5 and 6. The permutational, mechanical, and magnetic representations of the wave-vector group  $G_k$  for a given crystal will be denoted respectively as  $d_p^k$ ,  $d_m^k$ , and  $d_M^k$ . Their matrices have the following form:

$$\{d_p^{k}(g)\}_{ij} = e^{-ika_p(g,j)}\delta_{i,gj},$$
(4.4)

$$\{d_m^{\mathbf{k}}(g)\}_{i\alpha,\ \boldsymbol{\beta}\boldsymbol{\beta}} = e^{-i\mathbf{k}\boldsymbol{a}_p(g,\ \boldsymbol{\beta})}\delta_{i,\ gj}R_h^{\alpha\beta},\tag{4.5}$$

$$\{d_M^{\mathbf{k}}(g)\}_{i\alpha,\ j\beta} = e^{-i\mathbf{k}\mathbf{a}_p(g,\ j)}\delta_{i,\ gj}\delta_h R_h^{\alpha\beta}.$$
(4.6)

Here *i* and *j* are the numbers of the atoms in the primitive cell of the crystal, and  $\alpha$  and  $\beta$  are the vector indices of *x*, *y*, *z*. Thus the matrices of a permutational representation have the dimensionality  $\sigma \times \sigma$ , while those of vector representations have  $3\sigma \times 3\sigma$ .  $R_h^{\alpha\beta}$  is the rotation matrix of the position vector under the action of the rotational component *n* of the element  $g = \{h \mid \tau_h\}$ , while we have  $\delta_h = \pm 1$ , depending on whether the element *h* is an element of the first type (ordinary rotations) or of the second type (inversion, reflection). The vector  $a_p(g, j)$ , which is called the *returning translation*, indicates the cell into which the atom of number *j* is transferred from the zero cell by the action of the element *g* (it has the number *i* in the new cell). This vector is defined by the relationship

$$\mathbf{g}\mathbf{x}_{j} = h\mathbf{x}_{i} + \mathbf{\tau}_{h} \equiv \mathbf{x}_{i} + \mathbf{a}_{p} (g, j). \tag{4.7}$$

Thus we can easily calculate the matrices of all three representations by compiling a table of the permutations of the atoms of the primitive cell under the action of the elements of the group  $G_{k}$ .

The representations that have been introduced can be decomposed into irreducible representations of the group  $G_k$ . For example, for a permutational representation this decomposition has the form

$$d_p^{\mathbf{k}} = \sum_{\mathbf{v}} n_p^{\mathbf{v}} d^{\mathbf{k}\mathbf{v}}.$$
 (4.8)

Here we have

$$n_{\rho}^{v} = \frac{1}{n(G_{k}^{\theta})} \sum_{h \in G_{k}^{\theta}} \chi_{\rho}^{k}(g) \, \chi^{kv}(g).$$
(4.9)

Further  $\chi^{\mu}(g)$  is the character of the irreducible representation  $d^{\mu\nu}$ , while  $\chi^{k}_{\rho}$  is the character of the permu-

tational representation; and we have

χ

$$\chi_{p}^{k}(g) = \sum_{j} e^{-i k a_{p}(g, j)} \delta_{j, gj}.$$
(4.10)

The summation in (4.9) is performed over the elements of the zero block of the group  $G_k$ , and  $n(G_k^0)$  is the number of these elements (which coincides with the number of elements of the point group  $G_k^0$  corresponding to the group  $G_k$ ). For the mechanical and magnetic representations one can derive formulas analogous to (4.8) and (4.9), while their characters are given by the formulas

$$\chi_m^k(g) = \chi_p^k(g) \operatorname{Sp} R_h, \qquad (4.11)$$

$$\chi_M^k(g) = \chi_p^k(g) \left( \delta_h \operatorname{Sp} R_h \right).$$
(4.12)

We can treat Sp  $R_h$  as being the character of the representation V that a vector follows while being transformed by the action of the rotational component of an element of the space group. Then  $\delta_h \operatorname{Sp} R_h$  is the character of the representation V' that a pseudovector follows while being transformed. Therefore the relationships (4.11) and (4.12) imply that the vector representations  $d_m^k$  and  $d_M^k$ are the direct products of the permutational representation  $d_p^k$  by the representations V or V'. That is, we have

$$d_m^{\mathbf{k}} = d_\mu^{\mathbf{k}} \times V, \quad d_M^{\mathbf{k}} = d_\mu^{\mathbf{k}} \times V'. \tag{4.13}$$

#### c) Formulas for the basis functions

In order to construct the basis functions  $\psi_{\lambda}^{\mu\nu}$  of the irreducible representations of the group  $G_{k}$ , we can employ the general formula for the projection operator (see, e.g., Ref. 22):

$$\psi_{\lambda}^{\mathbf{k}v} = \frac{1}{N} \sum_{\boldsymbol{\mu} \in G_{\mathbf{k}}} \hat{d}_{\lambda\boldsymbol{\mu}}^{\mathbf{k}v}(g) T(g) \psi.$$
(4.14)

Here  $d_{\lambda\mu}^{b\nu}$  is the matrix of the chosen representation, and  $\psi$  is some starting function. If we fix the index  $\mu$ , Eq. (4.14) determines the  $l_{\nu}$  basis functions of the irreducible representation  $d^{b\nu}$ . Upon choosing as the starting function the state vector in the space of localized atomic functions, we obtain one of the three types of basis functions, scalar, vector, or pseudovector.

Let us give the final formulas for the atomic components of the functions of the scalar, vector, and pseudovector bases, which are respectively<sup>6</sup>:

$$\varphi\left(\begin{smallmatrix}\mathbf{k}_{\lambda}\\ \lambda\end{smallmatrix}\right) = \sum_{h\in G_{\lambda}^{*}} \overset{\mathbf{k}_{\lambda}}{d_{\lambda}(\mu)}(g) e^{-i\mathbf{k}\mathbf{a}_{p}(g, j)} \delta_{i, g(j)}, \qquad (4.15)$$

$$u^{\alpha}\left(\frac{\mathbf{k}v}{\lambda}\middle|i\right) = \sum_{h\in G_{\mathbf{k}}^{\mathbf{k}}} \overset{\dagger v_{\alpha}}{\partial_{\lambda[\mu]}}(g) e^{-i\mathbf{k}\mathbf{a}_{p}(g,j)} \delta_{i,g[j]} R_{h}^{\alpha[\beta]}, \qquad (4.16)$$

$$S^{\alpha} \begin{pmatrix} \mathbf{k} \mathbf{v} \\ \lambda \end{pmatrix} = \sum_{h \in G_{\mathbf{k}}^{\mathbf{k}}} \hat{d}_{\lambda[\mu]}^{\mathbf{k}\mathbf{v}}(g) e^{-i\mathbf{k}\mathbf{a}_{p}(S, J)} \delta_{i, g[J]} \delta_{h} R_{h}^{\alpha[\beta]}.$$
(4.17).

The vectors  $S_{\lambda}^{(\mu)}[i)$  are precisely the quantities that figured in the expansions of the spin density of the crystal of (2.9) and (2.12). The indices  $\mu$ , j, and  $\beta$  enclosed in square brackets must be fixed in the calculations. A shift to another set of indices implies a change of starting function in Eq. (4.14), and it can lead either to an identical zero or yield a new set of functions that transform according to the given representation, provided that it enters more than once into the makeup of the corresponding reducible representation  $d_{P}^{k}$ ,  $d_{m}^{k}$ , or  $d_{M}^{k}$ .

One can obtain the basis functions for another arm  $k_L$ 

of the wave-vector star by the action of the corresponding element  $g_L = \{h_L | \tau_{h_L}\}$  on the basis function of the first arm k. For a pseudovector basis, for example, the corresponding formula has the form<sup>6</sup>

$$S^{\alpha} \begin{pmatrix} \mathbf{k}_{L} \mathbf{v} \\ \lambda \end{pmatrix} = e^{-i\mathbf{k}_{L} \mathbf{e}_{p} \left( s_{L}, i \right)} \delta_{h_{L}} \sum_{\beta} R_{h}^{\alpha\beta} S^{\beta} \begin{pmatrix} k \mathbf{v} \\ \lambda \end{pmatrix} \left( i \right).$$
(4.18)

The change of the numbers i and i' of the atoms follows the rule

$$g_L \mathbf{x}_i = h_L \mathbf{x}_i + \tau_{h_L} \equiv \mathbf{x}_{i'} + \mathbf{a}_p (g_L, i).$$
(4.19)

It suffices to employ Eqs. (4.17) and (4.18) for actual calculation of the pseudovector basis functions. We note that one must calculate the basis functions of only those irreducible representations that enter into the makeup of the magnetic representation  $d_{\mathbf{M}}^{\mathbf{k}}$  (for the other irreducible representations, Eqs. (4.17) and (4.18) should identically give zero).

# d) An example

Let us describe the magnetic structures of the heavy rare-earth elements shown in Fig. 4 in terms of basis functions of the irreducible representations. Their crystal structure is characterized by the space group  $D_{6A}^4$ , with atoms occupying the position 2 (c) with the following coordinates (in the hexagonal system) (Fig. 7):

$$1\left(\frac{1}{3}\frac{2}{3}\frac{1}{4}\right), \quad 2\left(\frac{2}{3}\frac{1}{3}\frac{3}{4}\right).$$
 (4.20)

The group  $D_{6h}^4$  contains 24 symmetry elements in the zero block. In agreement with the handbook,<sup>17</sup> we shall denote their rotational components h as  $h_1, h_2, \ldots, h_{24}$ . Here  $h_1$  is the unit element,  $h_2 - h_6$  are the  $C_6^n$  rotations about the hexagonal axis,  $h_7 - h_{12}$  are the  $C_2$  rotations about the twofold axes perpendicular to the major axis,  $h_{13}$  is an inversion, and all the rest are products of the stated rotations by the inversion, so that  $h_{12+i} = h_i h_{13}$ . In the group  $D_{6h}^4$ , the rotational elements with even indices contain the accompanying translation  $\tau = \{00\frac{11}{2}\}$  of a half-period along the hexagonal axis.<sup>17</sup> The atoms 1 and 2 are permuted by the action of the stated elements of the group. Their permutations are calculated by Eq. (4.7) are shown in Table I along with the returning translations ap.

We see directly from Fig. 4 that the wave vectors of the SS and LSW structures lie along the hexagonal axis. Therefore in both cases we have  $k = \mu b_3$ , where  $\mu$  is a numerical factor that defines the phase change of the magnetic structure in going from one crystal plane to another. According to the handbook,<sup>17</sup> this wave vector belongs to a two-arm star whose second arm is  $k_2 = -k_1$ 



FIG. 7. Crystal structure of the heavy rare-earth metals.

TABLE I. Permutations of atoms for the group  $D_{6h}^4$ .

	Positio	on 2 (c)	1	Position 2 (c)		
Elements	1, a <sub>p</sub>	2, a <sub>p</sub>	Elements	1, a <sub>p</sub>	2. a <sub>p</sub>	
λ <sub>1</sub> λ <sub>2</sub> λ <sub>3</sub> λ <sub>5</sub> λ <sub>5</sub> λ <sub>5</sub> λ <sub>5</sub> λ <sub>10</sub> λ <sub>11</sub> λ <sub>12</sub>	$\begin{array}{c} 1\\ 1\\ -t_1\\ -t_1-t_2\\ 2\\ -t_1-t_2\\ 2\\ 2\\ -t_1-t_2\\ 2\\ -t_1-t_2\\ 2\\ -t_1-t_2-t_3\\ 1\\ -t_3\\ 1\end{array}$	$\begin{array}{c} 2 \\ 1 \\ 2 \\ -t_1 \\ -t_1 \\ -t_2 \\ -t_3 \\ +t_2 \\ +t_3 \\ -t_1 \\ -t_1 \\ -t_1 \\ -t_1 \\ -t_1 \\ -t_3 \\ -t_1 \\ -t_3 \\ -t_3$	$h_{13}$ $h_{14}$ $h_{15}$ $h_{16}$ $h_{17}$ $h_{10}$ $h_{20}$ $h_{21}$ $h_{22}$ $h_{23}$ $h_{23}$	$\begin{array}{c} 2t_1 - t_2 - t_3 \\ 1t_2 \\ 2t_3 \\ 1t_1 - t_3 \\ 1t_1 - t_2 \\ 1t_1 - t_2 \\ 2t_1 \\ 1t_1 - t_2 \\ 2t_1 \\ 1t_1 - t_2 \\ 2t_1 - t_3 \end{array}$	$\begin{array}{c} 1t_1 - t_2 - t_1 \\ 2t_1 - t_2 - t_1 \\ 1t_2 - t_3 \\ 2t_3 \\ 4t_5 \\ 2t_1 - t_3 \\ 1t_5 \\ 1t_1 - t_2 + t_1 \\ 1t_1 - t_2 + t_1 \\ 1t_2 + t_3 \end{array}$	

=  $h_{13}k_1$ . Consequently the wave-vector group  $G_k$  contains 12 elements in the zero block and has six irreducible representations<sup>17</sup>:  $\tau_1, \ldots, \tau_4$  are one-dimensional, and  $\tau_5$  and  $\tau_6$  are two-dimensional. One can find their matrices in the handbook.<sup>17</sup> Here it is obvious that they must contain the parameter  $e^{-ik_1\cdot\tau} = e^{-i\tau\mu}$ , so that the basis functions calculated by Eqs. (4.17) and (4.18) will also contain phase factors of this type (Table II). The basis functions are written out in Table II of those irreducible representations of the group  $G_k$  that enter into the magnetic representation  $d_M^k$ . According to Eqs. (4.8) - (4.12), we have

$$d_M^{k} = \tau_2 + \tau_4 + \tau_5 + \tau_{\theta}, \qquad (4.21)$$

Here we have indicated the atomic components of the basis functions only for the atoms of the primitive cell of the crystal. They can be expressed in terms of these for an arbitrary atom by using Eq. (2.10). Each triplet of numbers indicated in Table II gives the three components of the vector  $S(^{k\nu}_{\lambda}|i)$  written in the Cartesian system of coordinates.

Now let us examine the structure of the LSW shown in Fig. 4b. It can be written analytically as follows:

$$\mathbf{S}_{\mu i} = \mathbf{S}_{0i} \cos (2\pi \mu n_3), \ \mathbf{S}_{02} = \mathbf{S}_{01} \cos \pi \mu, \ \mathbf{S}_{01} = (00W).$$
 (4.22)

Here  $R_{\varphi}$  is fixed by the manner of writing the arbitrary translation  $\mathbf{t}_n = n_1 \mathbf{t}_1 + n_2 \mathbf{t}_2 + n_3 \mathbf{t}_3$ . We can easily verify by using Table II and Eqs. (2.10) that this structure corresponds to a two-arm superposition of the basis func-

TABLE II. Basic functions of the irreducible representations having  $\mathbf{k} = \mu \mathbf{b}_3$  for the group  $D_{6h}^4$ .

Representa-		Atoms				
ion	Arms	1	2			
τs	<b>k</b> 1	(001)	(001) e <sup>inµ</sup>			
-	k <sub>2</sub>	(001) $e^{-i\pi\mu}$	(001) $e^{-i2\pi\mu}$			
τ.	k <sub>1</sub>	(001)	$(001) e^{i\pi\mu}$			
	k2	$(00\bar{1}) e^{-i\pi\mu}$	$(001) e^{-i2\pi\mu}$			
		(1~ <i>i</i> 0)	$(1-i0) e^{i\pi\mu}$			
τ,	<b>k</b> 1	$(\bar{1} - i0)$	$(\overline{1} - i0) e^{i\pi\mu}$			
		$(1 - i0) e^{-i\pi\mu}$	$(1-t0) e^{-i2\pi\mu}$			
	k2	$(\overline{1}-i0)e^{-i\pi\mu}$	$(\overline{t}-i0)e^{-i2\pi\mu}$			
		( <b>1</b> – <i>i</i> 0)	$(\bar{1}i0) e^{i\pi\mu}$			
τ <sub>e</sub>	<b>k</b> 1	(1- <i>i</i> 0)	(110) e <sup>iπμ</sup>			
		$(\bar{1}i0) e^{-i\pi\mu}$	$(1 - i0) e^{-i2\pi\mu}$			
	k.	$(1i) e^{-i\pi\mu}$	$(\bar{1} - i0) e^{-i2\pi\mu}$			

tions of the one-dimensional representation  $\tau_2$ :

LSW: 
$$\psi^{k_1\tau_1} + e^{i\pi\mu}\psi^{k_1\tau_2}$$
. (4.23)

Evidently the structure of the SS shown in Fig. 4a is given by the analytic relationships:

$$\mathbf{S}_{n1} = R_{\phi}^{2n} \mathbf{S}_{01}, \quad \mathbf{S}_{02} = R_{\phi} \mathbf{S}_{01}, \quad \mathbf{S}_{01} = (\mathbf{UVO}).$$
 (4.24)

Here  $R_{\varphi}$  is a rotation through the angle  $\varphi$  about the principal axis of the crystal. This structure corresponds to the following superposition of the basis functions of the two-dimensional representation  $\tau_5$ :

SS: 
$$\psi_1^{k_1 \tau_5} - e^{i\pi\mu} \psi_2^{k_2 \tau_6}$$
. (4.25)

Here we have  $\varphi = \pi \mu$ .

Thus the incommensurable magnetic structures of the rare-earth metals are described by a superposition of the basis functions for the two arms k and - k of the wave-vector star, which can always yield a real combination. Analogously we can show that the other magnetic structures observed in the heavy rare-earth metals: ferromagnetic helix, complex helix, can be described by the basis functions of the irreducible representations of the space group  $D_{gh}^4$ . In the cascades of magnetic phase transitions observed in a number of rare-earth elements as the temperature is varied, each magnetic phase is described by basis functions of the site functions of the space group  $D_{gh}^4$ .

# 5. ANALYSIS OF MAGNETIC STRUCTURES BASED ON THE THEORY OF PHASE TRANSITIONS

# a) The concept of a single irreducible representation

The fundamental relationships (2.7) and (2.12) on which the symmetry analysis of magnetic structures is based are a consequence of Landau's hypothesis that a phase transition follows a single irreducible representation of the original phase. One can verify the fulfillment of this hypothesis by trying to represent a known magnetic structure with a given wave vector as a superposition of the basis functions of some irreducible representation of the wave-vector group.

Such an analysis of numerous magnetic structures, as performed in Refs. 5-9, 1, and also in Refs. 50-52, shows that in the overwhelming majority of cases the magnetic structures are described by the basis functions of a single irreducible representation. At the same time, a certain number of exceptions exists.

For example, among the 40 rare-earth orthoferrites described in the handbook of Ref. 1 several (LuCrO<sub>3</sub>, NdMnO<sub>3</sub>, ErFeO<sub>3</sub>, and TmCrO<sub>3</sub>) are simultaneously described by two irreducible representations (all irreducible representations of their space group *Pnma* for  $\mathbf{k} = 0$ are one-dimensional). The magnetic structures of the antiferromagnetics DySb and HoSb, which are characterized by the wave vector  $\mathbf{k} = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$ , are described by a combination of one- and two-dimensional irreducible representations of the wave-vector group (the space group *Fm3m*).

The umbrella-shaped structures of the garnets

 $ReFe_5O_{12}$  (Re = Dy, Ho, Er, Tb, Yb) are described by a combination of three- and one-dimensional irreducible representations of the space group *Ia3d*, etc. However, these exceptions are relatively rare.

#### b) Exchange multiplets

One of the reasons why magnetic structures can arise simultaneously according to several irreducible representations of the group G is degeneracy of the exchange energy. As we know, the symmetry of the exchange Hamiltonian is higher than the symmetry of the crystal as described by its space group G, owing to the invariance of rotation of all the spins by an arbitrary angle. We can see this directly by writing the exchange Hamiltonian:

$$\mathscr{H}_{ex} = -\sum_{ij} \sum_{nm'} J_{ij} \left( \mathbf{t}_n - \mathbf{t}_{n'} \right) \mathbf{S}_{n\,i} \mathbf{S}_{n'j}.$$
(5.1)

The symmetry group of the Hamiltonian of (5.1) (the exchange group)  $G_{e_x}$  can be written in the form  $G_{e_x} = G_a \times G_s$ , where  $G_a$  is the space group (acting only on the atoms of the crystal), and  $G_s$  is the rotation group in spin space.<sup>26</sup>

This implies that its irreducible representations are  $d^{\mathbf{k}\nu} \times V'$ , where V' is the representation in accordance with which a pseudovector transforms. One can write down in these same terms the magnetic representation  $d^{\mathbf{k}}_{4'}$  (see the second relationship in (4.13) as the direct product of the permutational representation  $d^{\mathbf{k}}_{p}$  by the representation V'. If we substitute into (4.13) the expansion (4.8) for  $d^{\mathbf{k}}_{p}$  in terms of irreducible representation an expansion of the group  $G_{\mathbf{k}}$ , then we in fact obtain an expansion of the irreducible representations of the exchange group:

$$d_{\rm M}^{\rm k} = \sum n_{\rm p}^{\rm v} (d^{\rm kv} \times V'). \tag{5.2}$$

The representation  $d^{k\nu} \times V'$  is irreducible for the exchange group, although its restriction to the space group G is reducible; the reduction is performed by using the obvious relationships:

$$d^{kv} \times V' = \sum_{\mu} r^{\nu}_{\mu} d^{k\mu}, \qquad (5.3)$$

$$r_{\mu}^{\nu} = \frac{1}{n(G_{k}^{0})} \sum_{h \in G_{k}^{0}} \chi^{k\nu}(g) \chi^{k\mu}(g) (1 + 2\cos\varphi_{n}).$$
 (5.4)

Here  $\varphi_h$  is the rotation angle corresponding to the element  $g = \{h | \tau_h\}$  (the factor  $(1 + 2\cos\varphi_h)$  is the character of the representation V'). A rigorous derivation of these formulas has been given in Refs. 5 and 9.

The physical meaning of Eq. (5.3) is clarified if we recall Wigner's theorem on the relation of the energy terms to the irreducible representations of the symmetry group of the Hamiltonian. The right-hand side of Eq. (5.3) defines the set of states of the magnetically ordered crystal having the same exchange energy. Let us call this set the exchange multiplet. The exchange multiplet is generated by the irreducible representation of the group  $G_k$  that enters into the permutational representation. Thus, Eq. (5.2) gives an expansion of the magnetic representation into exchange multiplets, while (4.3) determines the composition of these exchange multiplets. The dimensionality of the representation  $d^{k\nu} \times V'$  that corresponds to an individual multiplet is  $3l_{\nu}$ , and determines the multiplicity of degeneracy of the states of the crystal having the corresponding exchange energy. When a crystal characterized by the space group  $G_k$  has an anisotropic interaction, this level can split in agreement with the right-hand side of Eq. (5.3). If the anisotropic interactions are small in comparison with the exchange energy, these splittings are also small, and the magnetic structure can be characterized by a set of irreducible representations of the space group that form an exchange multiplet.

The situation that arises here is fully analogous to that which occurs in the theory of strong interactions. The strong interaction between hadrons is invariant with respect to rotation in isotopic-spin space, and is characterized by the group SU(2). The charge multiplets corresponding to the irreducible representations of this group are partially split under the influence of the electromagnetic interaction, which has a lower symmetry. Thus, from the standpoint of the ideology of phase transitions, the magnetic structure arises also in this case from a single irreducible representation, but a representation of the symmetry group of the Hamiltonian rather than of the symmetry group of the system.

We have seen that one can actually get a classification of the energy levels of the exchange Hamiltonian by listing the irreducible representations of the space group  $G_k$  that enter into the permutational representation. Let us examine now what information on the magnetic structure can be given by the basis functions of the permutational representation of the group  $G_k$ . As early as 1961, Bertaut<sup>29</sup> proposed a method of studying a magnetic structure in which it is treated as being an eigenfunction of the exchange Hamiltonian. From this standpoint, to find the possible magnetic structures in a given crystal (if the exchange interactions in it are dominant) means to solve the problem of diagonalizing the exchange Hamiltonian. Then each eigenfunction corresponds to a possible magnetic structure.<sup>29,30</sup>

On the other hand, the eigenvectors of the exchange matrix have a direct relationship to the basis functions of the permutational representation. If some irreducible representation  $d^{b\nu}$  of the group  $G_k$  enters once into  $d_{\rho}^k$ , then the basis function (4.15) of this representation is an eigenfunction of the exchange matrix.<sup>9</sup> If  $d^{b\nu}$  enters several times into  $d_{\rho}^k$ , the eigenfunction of the exchange matrix is a superposition of the corresponding sets of basis functions of the permutational represen-



FIG. 8. Type III ordering in a fcc lattice.

tation.<sup>9</sup> The basis functions  $\varphi({}^{\boldsymbol{\nu}}_{\lambda}|i)$  of the permutational representation are scalar (rather than vector) functions and cannot in the literal sense define a magnetic structure. The atomic component of some function  $\varphi({}^{\boldsymbol{\nu}}_{\lambda}|i)$  determines only the cosine of the angle between the spin vector at a given atom and some other vector. Hence they define only the relative orientation of the spin vectors of the individual atoms. This is a direct consequence of the above-cited invariance of the exchange Hamiltonian with respect to rotation of all the spins.

#### c) Multi-k-structures

Analysis of the magnetic structures determined by neutron diffraction that are described in the handbooks<sup>1,25</sup> shows that they are practically all characterized by only one wave vector. At the same time, often the stated wave vector belongs to a many-arm star. Thus the question arises: has one assumed a singlearm channel from the outset in deciphering neutrondiffraction patterns, or has one sorted out all the possibilities of many-arm channels, and obtained best agreement of the calculated with the observed intensities precisely for a single-arm channel? It is very difficult to gain a definite answer from reading the original literature, since usually the articles do not discuss this question.

Most of the neutron-diffraction studies have been performed on powders, in which the reflections arising from the individual arms of the wave-vector star are superimposed on one another and hence are not at all distinguishable. As we have seen, the determination of the transition channel when one is studying single crystals is complicated by the domain structure. If one finds magnetic reflections in different directions in the reciprocal lattice, then one cannot infer from their presence that the magnetic structure arises in an all-arm channel, since the same effect arises from scattering by differently oriented domains. These arguments lead to the conclusion that one must review the results of deciphering magnetic structures having a wave vector that belongs to a many-arm star.

As an example of magnetic structures characterized simultaneously by several wave vectors belonging to a single star (we shall call them multi-k-structures), we can cite the so-called Type III ordering a a fcc crystal<sup>32</sup> (Fig. 8). This magnetic lattice is defined by the two arms:

$$\mathbf{k}_1 = \frac{1}{4} (\mathbf{b}_1 + \mathbf{b}_2) + \frac{1}{2} (\mathbf{b}_2 + \mathbf{b}_3), \quad \mathbf{k}_2 = -\mathbf{k}_1$$
 (5.5)

of the six-arm Lifshits star  $\{k_g\}$ ,<sup>33</sup> as can be verified by using the fundamental relationship (2.7). Upon substituting into (5.5) the expression (3.10) for the fundamental reciprocal-lattice vectors, we find that they correspond to the magnetic reflections  $(10\frac{1}{2})$  and  $(\overline{10\frac{1}{2}})$  (and others differing by any reciprocal-lattice vector). In a neutron-diffraction study of a single crystal of K<sub>2</sub>IrCl<sub>8</sub> [space group  $O_h^s$ , with the magnetic Ir atoms occupying the positions 4(a)], the authors of Ref. 34 observed the magnetic reflections  $(1\frac{1}{2}0)$ ,  $(1\frac{3}{2}0)$ ,  $(3\frac{1}{2}0)$ , and  $(3\frac{3}{2}0)$ . In this system, two progenitors  $(1\frac{1}{2}0)$  and  $(1\frac{3}{2}0)$ are singled out, which are not reducible to one another, and which indicate the star  $\{k_{a}\}$ . They correspond to the rays  $k_4$  and  $k_3$  (with  $k_4 = -k_3$ ), which lead directly to the lattice depicted in Fig. 8.

Another example of a multi-k-structure, which now corresponds to a non-Lifshits star, is the recently studied magnetic structure of CeAl<sub>2</sub>. The study of this structure is highly instructive, so that we shall describe it in some detail. This substance belongs to the Laves phases and has the space group  $O_k^7$  (fcc lattice). The first neutron-diffraction studies on powders<sup>35</sup> showed the existence of a satellite having  $\mathbf{k} = (2\pi/a) (\frac{1}{2} + \mu, \frac{1}{2} - \mu, \frac{1}{2})$ , with  $\mu = 0.112$ . This wave vector can be represented as a slight deviation by  $\delta \mathbf{k}$  from the Lifshits point  $\mathbf{k}_n$ :

$$\mathbf{k} = \mathbf{k}_0 + \delta \mathbf{k}_0, \quad \mathbf{k}_0 = \frac{2\pi}{a} \left( \frac{1}{2} \frac{1}{2} \frac{1}{2} \right), \quad \delta \mathbf{k} = \frac{2\pi}{a} \, \mu \, (1\overline{10}). \tag{5.6}$$

Initially<sup>35</sup> the magnetic structure was interpreted as a sinusoidal modulation in the direction [110] perpendicular to the (110) plane. This plane contains the spins of the two Ce atoms belonging to the primitive cell that have the coordinates 1 (000), 2  $(\frac{1}{4}\frac{1}{44})$  [positions 8(a)]. They are oriented in antiparallel fashion along the direction of the body diagonal of the cube, i.e.,  $S_{01} \sim$  [111],  $S_{02} \sim [111]$ . Thus an antiferromagnetic ordering of the spins exists that is characterized by the wave vector  $k_0$  and an additional modulation described by the vector  $\delta k$ .

Such a structure can be described by basis functions of irreducible representations of the group  $G_k$ . The star of the vector k is 24-armed. Its three arms:

$$\mathbf{k}_{1} = \frac{2\pi}{a} \left( \frac{1}{2} + \mu, \frac{1}{2} - \mu, 0 \right), \quad \mathbf{k}_{2} = \frac{2\pi}{a} \left( \frac{1}{2} - \mu, \frac{1}{2}, \frac{1}{2} + \mu \right),$$
$$\mathbf{k}_{3} = \frac{2\pi}{a} \left( \frac{1}{2}, \frac{1}{2} + \mu, \frac{1}{2} - \mu \right), \quad (5.7)$$

which are grouped around the vector  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  are replicated around the directions  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ ,  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ , etc.

After Ref. 35 had appeared, the problem of the magnetic structure of  $CeAl_2$  could have been considered to be settled if the neutron-diffraction studies performed later on a single crystal<sup>36</sup> had not shown a more complex diffraction pattern. They found that there is not one satellite around  $k_0$  but three, having the wave vectors  $k_1$ ,  $k_2$ , and  $k_3$  of (5.7). If the specimen is a single domain, the extra satellites can indicate a 3k-structure (a six-arm channel, since whenever the ordering follows a non-Lifshits star, the arm -k must always exist as well as the arm k in order to ensure that the structure is real). Otherwise they can result from scattering by a 1k-structure divided into domains.

Since it is hard to choose between these two possibilities, various details in the diffraction pattern have been studied. Thus it has been found that a weak satellite with the wave vector  $\mathbf{k}_0 = (2\pi/a)(\frac{j}{2}\frac{1}{2}\frac{1}{2})$ , accompanies the three satellites corresponding to the wave vectors  $\mathbf{k}_1$ ,  $\mathbf{k}_2$ , and  $\mathbf{k}_3$ . Here the temperature-dependence of its intensity differs from that of the rest of the satellites. While the intensity of the main satellites varies near  $T_N = 3.85 \mathrm{K}$  as  $(T_M - T)^{2\beta}$ , the intensity of the extra satellite varies as  $(T_N - T)^{\alpha\beta}$ . One can explain the appearance of this satellite and its special temperature-dependence by assuming that the free energy of the magnetically ordered CeAl<sub>2</sub> crystal contains a quaternary term of the following form:  $S^{\mathbf{k}_1}S^{\mathbf{k}_2}S^{\mathbf{k}_3}S^{\mathbf{k}_0}$ , composed of the magnetic order parameters  $S^{\mathbf{k}}$ . Certain symmetrized combinations of the arm-contribution vectors  $S_{of}^{L}$  serve as the magnetic-order parameters. In our discussion, the vector indices of the order parameter are inessential. Therefore we shall employ an abbreviated notation and have indicated only the arm indices.

From the standpoint of translational symmetry, such a term in the energy is allowed because the following coupling exists between the wave vectors:  $\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ =  $k_0$ , while the sum of all the wave vectors in the quaternary term under discussion is  $2k_0$ , which is equal to a reciprocal-lattice vector. Minimization of the energy with account taken of the guadratic term leads to the following coupling between the order parameters:  $S^{k_0}$  $\sim S^{k_1}S^{k_2}S^{k_3} \sim (T_N - T)^{3\beta}$ , if  $S^{k_L} \sim (T_N - T)^{\beta}$ . This explains the observed difference in the temperature-dependence of the main and extra satellites. Since a quaternary term of this type can exist only for a structure characterized simultaneously by three wave vectors (a 3kstructure), the observation of the extra peak can be viewed as a well grounded argument in favor of a multik-structure in CeAl,.

Another substance in which a multi-k-structure possibly exists is neodymium. A neutron-diffraction study<sup>37</sup> has been made of single crystal of Nd, and the magnetic structure was determined in two magnetically ordered phases having  $T_{N_1} = 19$ K and  $T_{N_2} = 7.5$ K. For  $T \le T_{N_1}$  six magnetic satellites were observed corresponding to the six-arm wave vector star  $\{k_s\}$  (the space group of Nd is  $D_{ab}^4$ ):

$$\begin{array}{ll} \mathbf{k}_1 = \mu \mathbf{b}_1, & \mathbf{k}_2 = \mu \mathbf{b}_2, & \mathbf{k}_3 = \mu \ (\mathbf{b}_2 - \mathbf{b}_1), \\ \mathbf{k} = -\mu \mathbf{b}_1, & \mathbf{k}_5 = -\mu \mathbf{b}_2, & \mathbf{k}_6 = -\mu \ (\mathbf{b}_2 - \mathbf{b}_1). \end{array}$$
 (5.8)

It was assumed that these satellites arise from three types of magnetic domains. Each of these possesses a magnetic structure characterized by a pair of conjugate wave vectors k and -k. Since the satellites have the same intensity, it was assumed that orientation of the domains in the three possible directions is equally probable. Each domain possesses an LSW structure with its wave vector along  $b_1$ ,  $b_2$ , or  $b_2 - b_1$ .<sup>37</sup>

As the authors of Ref. 37 themselves noted, the proposed model does not agree with all the details of the neutron-diffraction patterns. Therefore, recently new neutron-diffraction studies have been carried out on a single crystal<sup>38</sup> that have confirmed the neutron-diffraction patterns first observed in Ref. 37. As a supplement, careful measurements were made of the weak satellites that were not taken into account in the described model of the magnetic structure.<sup>37</sup> The intensity of one of them proved to have a different temperaturedependence than the intensity of the "main" satellites, which was proportional to  $\sim (T_{N_1} - T)^{2\beta}$ . (The temperature-dependence of the latter indicates a continuous variation of the order parameters near  $T_{N_1}$ , i.e., a second-order phase transition.) The intensity of the weak satellite varies according to a law close to  $(T_{\mu_1} - T)^{4\beta}$ .

These two new established facts – the second-order phase transition and the special temperature-dependence of the weak satellite – were utilized by the authors of Ref. 38 as a confirmation of the hypothesis of a multik-structure in Nd corresponding to a transition by a

#### six-arm channel of the star (5.8).

The essential arguments here proved to be those based on the Landau phenomenological theory of second-order phase transitions. Analysis of the expansion of the free energy in powers of the order parameter for the Nd crystal showed that a magnetic second-order phase transition is possible. Its occurrence depends on the relationship between the parameters in the quaternary terms in the expansion of the energy, both in the 1kstructure and in the 3k-structure, where all the components of the order parameter S<sup>k1</sup>, S<sup>k2</sup>, and S<sup>k3</sup> simultaneously differ from zero. An analysis of the phase transition taking account of the interaction of the fluctuations in the critical region has been based on the renormalization-group method.<sup>39</sup> However, it showed that only one stable fixed point exists that corresponds to a region of values of the parameters in the energy in which a 3k-structure must be realized. Since it was established experimentally that the transition to a magnetically ordered state in Nd is a second-order transition, this structure is unavoidably a 3k-structure. These arguments are an example of how one can gain information on the possible magnetic state of a crystal by adducing the ideas of the modern theory of secondorder phase transitions.

However, how can one discriminate between the 1kand 3k-structures? The special temperature-dependence of the weak satellite was taken into account to solve this problem. The authors of Ref. 38 proposed that this satellite is of nuclear, rather than magnetic origin, and that it arises from the adjustment of the crystal structure to the magnetic order characterized by the wave vectors of (5.8). The interaction of the magnetic order parameters  $S^k$  and the structural order parameters  $U^k$ is described by terms of the type  $S^{k_1}S^{-k_2}U^{k_3}$ , which differ from zero only in a multi-k-structure. This leads to a certain coupling between them:  $U^{k_3} \sim S^{k_1}S^{-k_2}$ , which gives rise to the special temperature-dependence of the structural satellite ~  $|U^k|^2 \sim (T_{N_1} - T)^{48}$  that is observed experimentally.

Thus the establishment of the nuclear nature of the weak satellite should have been a confirmation of the hypothesis of a multi-k-structure in Nd. However, a polarization analysis of this peak specially performed at Oak Ridge showed that it is purely magnetic in nature. Thus no experimental confirmation exists at present of the hypothesis of a 3k-structure in Nd. It is clear only that it is more complicated than the model proposed<sup>37</sup> in 1964.

# 6. MAGNETIC DIFFRACTION OF NEUTRONS BY STRUCTURALLY DISTORTED CRYSTALS

# a) Adjustment of the crystal structure to the magnetic structure

Thus far we have assumed that the onset of magnetic ordering does not distort the original crystal. Now we shall discuss the problem of how one must take into account possible distortions of the crystal structure in deciphering the magnetic structure and how one determines them simultaneously with the unknown magnetic structure from neutron-diffraction data. This problem is best discussed using the concrete example of the neutron-diffraction study of the antiferromagnetic  $UO_2$ .

The UO<sub>2</sub> crystal has a fcc lattice with space group  $O_{\lambda}^{5}$ , while the uranium and oxygen atoms occupy the positions: U-4(a), O-8(c) (see Fig. 3). Thus the primitive cell contains one U atom and two O atoms with the co-ordinates:

U: 1 (0 0 0), 0: 1 
$$\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$$
, 2  $\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$ 

Neutron-diffraction studies of  $UO_2$  have been carried out at various times, 40-42 and each experiment has revealed a system of magnetic reflections having progenitors of the (100) type. According to Fig. 6, this indicates the wave-vector star  $\{k_{10}\}$ . The arms of this three-arm star are given by the expressions (3.9). Though there are no contradictions between Refs. 40-42 with respect to determing the wave-vector star, yet each of them proposes a different magnetic structure. The first study<sup>40</sup> proposed a collinear magnetic structure corresponding to Type I ordering in the fcc lattice<sup>32</sup> with an orientation of the magnetic moment along the body diagonal of the cube. Reference 41 proposed a model that also corresponds to Type I, but with an orientation of the spins along the edge of the cube. One can easily show that Type I ordering in a fcc crystal described by doubling of the magnetic cell along one of the edges of the cube corresponds to a single-arm channel of the star  $\{k_{10}\}$ . The recent neutron-diffraction study,<sup>42</sup> which was carried out using a single crystal, detected all three types of magnetic reflections having the progenitors (100), (010), and (001). This indicates a three-arm channel of the star  $\{k_{10}\}$ , provided that it does not result from a domain structure. However, as we shall see below, this study revealed additional details in the diffraction pattern that allowed the authors to state that UO<sub>2</sub> can possess a noncollinear three-arm magnetic structure with an orientation of the magnetic moments at the uranium atoms along the body diagonals of the cube.

These additional details involve the discovery of a displacement of the oxygen atoms with the onset of magnetic ordering. Here the interpretation of the neutron-diffraction patterns requires one simultaneously to hypothesize a magnetic structure and a structural distortion. The hypothesis that atomic displacements arise in  $UO_2$ stemmed from the lack of agreement of the angular dependence of the intensities of the magnetic reflections as calculated from the magnetic form factor of uranium (calculated with high enough accuracy) with the observed values in the high-angle region. This discrepancy was attributed to the proposed distortion of the oxygen lattice, which is described by the same wave-vector star as the magnetic structure. In this case, nuclear superstructure peaks with an intensity proportional to the square of the displacements of the oxygen atoms from the sites occupied in the paramagnetic phase should be superimposed on the magnetic peaks. This hypothesis is favored by the fact that the difference between the observed intensity of the superstructure peak and that calculated under the assumption that this peak is purely magnetic in origin increases with increasing scattering angle. This cannot be explained as purely magnetic

large-angle scattering by the magnetic form factor.

As a result of the stated approach to the interpretation of the neutron-diffraction patterns, a four-sublattice model of a noncollinear magnetic structure with orientation of the magnetic moments of the uranium atoms along the body diagonals of the cube was proposed.<sup>42</sup> A certain model of collinear displacements of the oxygen atoms along one of the edges of the cube was proposed for the structural distortions of the oxygen sublattice. However, the proposed pattern of the oxygen displacements does not agree with the cubic symmetry of the  $UO_2$  crystal below the magnetic-ordering temperature, which was established with a high degree of accuracy in the x-ray structural study.<sup>43</sup>

This situation calls for an additional neutron-diffraction study of the  $UO_2$  crystal, which should be guided by the results of the symmetry analysis presented below.

The star  $\{\mathbf{k}_{10}\}$  has three arms, for each of which one should calculate the basis functions of the magnetic  $(d_M^k)$ and mechanical  $(d_M^k)$  representations. First we find by Eqs. (4.8)-(4.12) the composition of these representations for the wave-vector group  $G_k$ . This group has 10 irreducible representations<sup>17</sup>: 8 one-dimensional  $(\tau_1, \ldots, \tau_8)$  and 2 two-dimensional  $(\tau_9 \text{ and } \tau_{10})$ . The magnetic representation at the U atoms and the mechanical representation at the O atoms have the following expansions:

$$d_M^k = \tau_3 + \tau_9, \quad d_m^k = \tau_1 + \tau_4 + \tau_9 + \tau_{10}.$$
 (6.1)

(We do not need the mechanical representation for the U atoms, since the neutron-diffraction study<sup>42</sup> did not detect a shift of these atoms upon magnetic ordering.)

For the representations that entered into (5.1), let us calculate by Eqs. (4.16)—(4.18) the basis functions  $S(_{\lambda}^{kL\nu}|i)$  and  $U(_{\lambda}^{kL\nu}|i)$  for the U and O atoms, respectively, contained in the primitive cell of the crystal. Table III shows the results of the calculations for all three arms of the star. For the U and O atoms lying outside the boundaries of the chosen primitive cell, the components of the basis functions are found by using the relationships (2.10).

We see from Table III that the collinear magnetic structure proposed in Ref. 41 corresponds to a singlearm channel of the star, and is described by the basis

TABLE III. Basis functions of the magnetic and mechanical representations for the star  $\{k_{10}\}$  of the UO<sub>2</sub> crystal.

Arms Representation		k1 k2 k3					
		Uranium					
Magnetic	τ <sub>3</sub> τ,	001 110 110		010 101 101		100 011 011	
Representation				Oxy	/gen		
Mechanical	τ <sub>1</sub> τ <sub>3</sub> τ <sub>9</sub> τ <sub>10</sub>	001 001 110 110 110 110	001 001 110 110 110 110	010 010 101 101 101 101	010 010 101 101 101 101	100 100 011 011 011 011	100 100 011 011 011

TABLE IV. Allowable magnetic structures and structural distortions of the oxygen sublattice in  $UO_2$  that have cubic symmetry.

Magnetic structures					Atomic displacements				
Repre-	re-U atoms				Repre-	O atoms			
tions	1	2	3	4	tions	1	3	õ	7
τ <sub>s</sub> τ <sub>s</sub> τ <sub>s</sub>	111 111 111	111 111 111 111	717 771 171 177	111 111 111 111	$\tau_1, \tau_4$ $\tau_9, \tau_{10}$ $\tau_9, \tau_{10}$	111 111 111	111 711 711	111 111 111	111 111 111 111

functions of the two-dimensional representation  $\tau_9$ .

Now let us examine the three-arm channel. This implies that the magnetic structure must be described by a superposition of the basis functions for all three arms of the star. Let us construct a superposition having equal inter-arm mixing coefficients. Thus we can easily obtain several magnetic structures, which we can write out by fixing the spins of the four uranium atoms (Table IV). The atomic displacements of the oxygen sublattice for atoms 1, 3, 5, and 7 are also indicated in this table. The displacements u of the atoms 2, 4, 6, and 8 are determined by the relationships:

$$u_{1} = \pm u_{1}, \quad u_{4} = \pm u_{3}, \quad u_{6} = \pm u_{5}, \quad u_{8} = \pm u_{7}.$$
 (6.2)

Here the upper sign is taken in the case of the representations  $\tau_4$  and  $\tau_{10}$ , and the lower sign for  $\tau_1$  and  $\tau_9$ .

The possible types of magnetic ordering and concomitant displacement of the oxygen atoms in UO<sub>2</sub> have been studied theoretically<sup>44</sup> on the basis of minimizing the Landau free energy. They proved to be precisely the magnetic structures and displacements recorded in the individual rows of Table IV. In particular, the magnetic structure corresponding to the one-dimensional irreducible representation  $\tau_3$  (see Fig. 3) should be accompanied by structural distortions described by the representation  $\tau_4$  ( $\tau_1$  must be rejected, since it does not possess symmetry with respect to inversion) (Fig. 9). Thus, one of the noncollinear magnetic structures of cubic symmetry (with orientation of the spins of the uranium atoms along the body diagonals of the cube) should be realized in UO<sub>2</sub>.

The models of the magnetic structure that were proposed in Ref. 42, and which satisfy the diffraction pattern obtained, are described by one of the two rows in Table IV that correspond to the two-dimensional representation  $\tau_{g}$ . Apparently one can choose between them



FIG. 9. Displacements of the oxygen atoms in UO<sub>2</sub> according to the predictions based on the thermodynamic theory of Landau.<sup>44</sup> a) For the representation  $\tau_4$ ; b, c) for the representation  $\tau_{10}$ . Open circles: oxygen; black dots: uranium.

after recalculating the intensities with account taken of the adjustment of the oxygen sublattice that accompanies the magnetic structure. As we see from Table IV, this adjustment must also correspond to a three-arm channel, and it agrees with the cubic symmetry of the magnetically ordered UO<sub>2</sub> crystal. However, in Ref. 42 the adjustment was described by a single-arm channel. Thus, for a final solution of the problem of the magnetic structure of UO<sub>2</sub>, one should compare the calculated intensities for the two variants of magnetic structures corresponding to representation  $\tau_9$  and the rigidly coupled to them adjustments of the crystal lattice. Full grounds exist for expecting a confirmation of the conclusion that a three-arm magnetic structure is realized in UO<sub>2</sub>.

Just as in the cases described above (CeAl<sub>2</sub>, Nd), in which the existence of multi-k-structures was also proposed, in  $UO_2$  this conclusion has been drawn on the basis of the discovery of an additional property of the crystal, in this case the structural distortion accompanying the magnetic ordering. Every time, symmetry analysis has provided substantial arguments in favor of multi-k-structures.

# b) Magnetic-structure satellites

Another aspect of neutron diffraction in structurally distorted crystals involves the study of magnetic ordering in a crystal that has previously (in the temperature sense) undergone some structural phase transition of distortional type. Evidently, both these transitions, structural and magnetic, can be described in terms of the same initial phase. The neutron-diffraction pattern in the magnetically ordered phase is complicated by certain interference phenomena that arise from formation of superstructures in the crystal, and it requires special study.

First we shall examine pure nuclear neutron scattering in a crystal in which a structural modulation has arisen that is described by the wave-vector star  $\{q\}$ , whose arms will be denoted as  $q_{M}$  ( $M=1,2...,l_{q}$ ). Numerous examples of such structural transitions discovered in recent years are given in the review of Ref. 45. Most often the wave vectors of the superstructure are non-Lifshits in type. This means that a certain modulation arises in the positions of a fraction of the atoms of the original crystal, whereas another fraction of the atoms does not change in position. The new structure that arises after such a phase transition can be treated as a superstructure in the major phase. The superstructure gives rise to satellites in the diffraction pattern, whose regularities we shall now describe.

The displacement  $u_{ni}$  of atom number *i* in the *n*th cell associated with the spontaneous modulation is generally a superposition of the arm types  $u_{oi}^{W}$  as given in the zero cell:

$$\mathbf{u}_{nl} = \sum_{M=1}^{l_q} \mathbf{u}_{0l}^{M} e^{i\mathbf{q}_M t_{\mathbf{B}}}$$
(6.3)

[cf. Eq. (2.7)]. In the case of crystals having a center of inversion (and we shall restrict the treatment to these), the non-Lifshits star contains the arm -q as well as the

arm q. Hence we can rewrite Eq. (6.3) in the form

$$\mathbf{u}_{ni} = \sum_{M=1}^{l_0/2} [\mathbf{v}_i^M \cos{(\mathbf{q}_M \mathbf{t}_n)} - \mathbf{w}_i^M \sin{(\mathbf{q}_M \mathbf{t}_n)}].$$
(6.4)

We have resolved the arm contribution into real and imaginary parts:

$$\mathbf{u}_{0i}^{M} = \frac{1}{2} \left( \mathbf{v}_{i}^{M} + i \mathbf{w}_{i}^{M} \right).$$
 (6.5)

We shall employ this expression for calculating the nuclear-scattering structure factor of the modulated lattice:

$$F^{\text{nucl}}(\mathbf{x}) = \sum_{ni} b_i e^{-i\mathbf{x} \left( t_n + x_i + u_{ni} \right)} \,. \tag{6.6}$$

(Here  $b_i$  is the nuclear scattering amplitude of atoms of type *i*). The known expansion in Bessel functions is:

$$e^{iz\sin\varphi} = \sum_{p=-\infty}^{\infty} e^{ip\varphi} J_p(z) .$$
(6.7)

This enables us to transform the structure amplitude into the form

$$F^{\text{nucl}}(\mathbf{x}) = N \sum_{b \dots p_{M} \dots s_{M}} \sum_{i} \sum_{j} \sum_{i} b_{i} e^{-i\mathbf{x}\mathbf{x}_{i}}$$

$$\times \prod_{M=1}^{l_{q}/2} \left\{ \left(-i\right)^{s_{M}} J_{s_{M}}\left(\mathbf{x}\mathbf{v}_{i}^{M}\right) J_{p_{M}}\left(\mathbf{x}\mathbf{w}_{i}^{M}\right) \right\} \delta_{\mathbf{x}_{i},\mathbf{b}} + \sum_{M} \left(p_{M} + s_{M}\right) \mathbf{q}_{M}.$$
(6.8)

In deriving this expression, we have summed over the integral translations by using Eq. (3.6). We see that the lattice modulation is manifested in the appearance of a system of satellites separated from the fundamental reciprocal-lattice nodes of the original crystal by vectors that are multiples of  $q_{M}$ . The set of integers  $\{p_{M}, s_{M}\}$  defines the satellite characterized by the scattering vector

$$\mathbf{x} = \mathbf{b} + \frac{\nabla}{M} \left( p_M + s_M \right) \mathbf{q}_M. \tag{6.9}$$

First let us examine the case in which the modulation of the structure amounts to a simple wave described by a single term in (6.4), e.g., having  $\mathbf{v}_i^{t'} = 0$ . Then (6.8) gives rise to satellites having

$$\mathbf{x} = \mathbf{b} + \sum_{M} p_{M} \mathbf{q}_{M}. \tag{6.10}$$

They have the intensity

$$I_{\{p_{M}\}}(\mathbf{x}) \sim |\sum_{i} b_{i} e^{-i\mathbf{x}\mathbf{x}_{i}} \prod_{M=1}^{l_{q}/2} J_{p_{M}}(\mathbf{x}\mathbf{w}_{i}^{M})|^{2}.$$
(6.11)

As we know, for small arguments, the Bessel functions have the expansions

$$J_{0}(z) = 1 - \frac{z^{2}}{4} + \dots, J_{p}(z) = \frac{z^{p}}{2^{p}p!} + \dots$$
 (6.12)

These expressions enable us to estimate the intensities of the satellites. If all the  $p_{M} = 0$ , we get the fundamental reflection  $\varkappa = b$ . However, its intensity will be smaller than in the original unmodulated crystal, owing to the first of the relationships (6.12). If one of the numbers  $p_{M}$  equals unity, while the rest are zero, a first-order satellite arises with  $\varkappa = b + q_{M}$ . It has an intensity proportional to  $(\varkappa \cdot \mathfrak{w}_{i}^{M})^{2}$ . The number of such satellites equals the number of arms in the channel. That is, it is determined by the number of nonzero values of the amplitudes  $\mathfrak{w}_{i}^{M}$ . In the case of a single-arm channel (more exactly, a channel having q and -q), a pair of conjugate satellites exists with  $\varkappa = b + q(p = \pm 1)$ . They have the same intensity, owing to the property of the Bessel functions:  $J_{-p}(z) = (-1)^{p} J_{p}(z)$ .

If any  $p_M = 2$ , while the remaining  $p_M = 0$ , a secondorder satellite arises with  $\varkappa = b + 2q_M$ . It has a weaker intensity ~  $(\varkappa \cdot \mathbf{w}_M^i)^4$ , etc. The case is of especial interest in which the modulation is characterized by a manyarm channel. This includes, for example, the arms  $q_1$ and  $q_2$  of a single star. In this case one should observe special second-order satellites having  $\varkappa = b \pm q_1 \pm q_2$ . An observation of these is important in principle, since it aids in establishing the transition channel.

We have discussed the simple-wave type of modulation. If a helicoidal modulation exists for which both vectors  $v_i^{M}$  and  $w_i^{M}$  differ from zero, then according to (6.8), the first-order satellite having  $\varkappa = b + q$  is determined by the relationship

$$I(\mathbf{x}) \sim \left[\sum_{i} e^{-i\mathbf{x}\mathbf{x}_{i}} \left[J_{1}(\mathbf{x}\mathbf{w}_{i}^{M}) - iJ_{1}(\mathbf{x}\mathbf{v}_{i}^{M})\right]\right]^{2}.$$
(6.13)

Owing to the fact that the intensities of the first-order satellite with  $\mathbf{v}_i^{\mathbf{M}} = 0$  and with  $\mathbf{v}_i^{\mathbf{M}} \neq 0$  differ, the possibility exists of distinguishing the helicoidal and simple-wave types of modulation.

Now let us assume that a magnetic structure has arisen in the modulated crystal that is characterized by the wave-vector star  $\{k_L\}$ , with  $L = 1, 2, ..., l_k$ . If specifically the magnetic atoms have suffered a spontaneous modulation of their positions with the wave-vector star  $\{q\}$ , a phase modulation arises in the expression (3.2) for the magnetic scattering amplitude. Let us substitute Eq. (2.7) into (3.2) and take account of the fact that  $R_i = t_n + x_i + u_{ni}$  in the modulated crystal. Then we obtain by the above-described method the following expression for the magnetic scattering amplitude<sup>46</sup>:

$$\mathbf{F}(\mathbf{x}) = N \sum_{\mathbf{b}} \sum_{L, \dots, p_M} \sum_{\mathbf{x}, \mathbf{s}_M, \dots} \mathbf{f}_{(p_M, s_M)}^L(\mathbf{x}) \, \delta_{\mathbf{x}, \mathbf{b} + \mathbf{k}_L + \sum_M (p_M + s_M) \, \mathbf{q}_M}.$$
 (6.14)

Here we have

$$f_{\{p_{M},s_{M}\}}^{L}(\mathbf{x}) = \sum_{i} e^{-i\mathbf{x}\mathbf{x}_{i}} F_{i}(\mathbf{x}) \left[ \mathbf{S}_{0i}^{L} - (\mathbf{e}\mathbf{S}_{0i}^{L}) \mathbf{e} \right] \prod_{M=1}^{lq/2} \left\{ (-i)^{s_{M}} J_{s_{M}}(\mathbf{x}\mathbf{v}_{i}^{M}) J_{p_{M}}(\mathbf{x}\mathbf{w}_{i}^{M}) \right\}.$$
  
(6.15)

The formulas that we have derived show that satellites of different orders exist in the distorted lattice along with the magnetic Bragg peak  $\varkappa = b + k_L$ . The satellites have

$$\mathbf{x} = \mathbf{b} + \mathbf{k}_L + \sum_{m} \left( p_M + s_M \right) \mathbf{q}_M. \tag{6.16}$$

The zero-order magnetic reflection  $(p_{M} = 0, s_{M} = 0)$ proves to be weakened in proportion to the small deviation of the function  $J_{0}(z)$  from 1. The intensities of its satellites are determined by the corresponding powers of the parameters  $\varkappa \cdot \mathbf{w}_{i}^{M}$  and  $\varkappa \cdot \mathbf{w}_{i}^{M}$ . These satellites stem from interference: they are caused by magnetic scattering, but they exist only in a structurally distorted crystal owing to the modulation of the phase in the magnetic scattering amplitude.

A correct interpretation of the magnetic-structure satellites is necessary in deciphering the magnetic structure of the crystal. Detecting them would also indicate that the magnetic atoms of the crystal participate in the spontaneous modulation of the crystal structure.

We also note a possible case in which the magnetic structure corresponds to some Lifshits star, e.g., having the wave vector  $\mathbf{k} = \frac{1}{2}\mathbf{b}$ , where b is one of the fundamental reciprocal-lattice vectors. If an adjustment of the crystal lattice exists that has the same wave vector  $\mathbf{q} = \mathbf{k}$ , then the satellites of the first magnetic reflection with  $\mathbf{x} = \mathbf{k} \pm \mathbf{q}$  are superimposed on the nuclear reflections. Thus a magnetic (more exactly, magnetic-structural) component can arise at the nuclear-scattering peaks and can be falsely interpreted as a sign of a magnetic structure described by the vector  $\mathbf{k} = 0$  as well as the fundamental wave vector  $\mathbf{k} = \frac{1}{2}\mathbf{b}$ .

Apparently the described magnetic-structure satellites have been observed in BaMnF<sub>4</sub>.<sup>47</sup> This compound shows two phase transitions: a structural transition (at  $T_m = 247$  K) and a magnetic transition (at  $T_N = 26$  K). Satellites were found below  $T_m$  in a study of a single crystal that indicated the onset of some incommensurable superstructure having the wave vectors **q**, 2**q**, and 3**q**, where  $\mathbf{q} = (\mu, \pm \frac{1}{2}, \pm \frac{1}{2})$ . Below  $T_N$  they found magnetic Bragg peaks corresponding to the wave vector  $\mathbf{k}_0$  $= (0, \pm \frac{1}{2}, \pm \frac{1}{2})$  and a number of others whose positions were determined by the wave vectors  $\mathbf{k}_0 + \mathbf{q}$ , which indicates their magnetical-structure nature.

### 7. CONCLUSION

Now we shall return to discussing the two questions posed in the Introduction this review: how can one classify all the varied magnetic structures of crystals, and how reliably are they deciphered in neutron-diffraction studies?

The presented material, as well as the symmetry analysis of the numerous examples of magnetic structures performed in Refs. 1, 5-10, leads to the conclusion that they can be classified in terms of the irreducible representations of the space groups. The magnetic structure will be fully described if one specifies: its wave vectors belonging to a single star {k}, the number  $\nu$  of the irreducible representation, and the mixing coefficients  $\{c_{\lambda}^{L\nu}\}$  of the basis functions. Then it can be fully reconstructed by Eqs. (2.7) and (2.12) if one calculates the atomic components  $S(_{\lambda}^{L\nu}|i)$  of the basis functions of this representation.

This sort of information on the magnetic structure (specification of the irreducible representation) is physically much fuller of content than, for example, a specification of the magnetic symmetry group (Shubnikov or color group) and of the positions of the magnetic moments occupied by the magnetic atoms in this group. A knowledge of the irreducible representation for a magnetic structure can be employed to study a magnetic phase transition in the crystal, since it enables one to find by known methods the invariant expansions of the free energy in powers of the order parameters. The success of this approach has been recently demonstrated in Refs. 48-52 in a study of magnetic phase transitions employing the methods of renormalization groups and  $\varepsilon$ -expansion.

As a rule (but not always!), magnetic structures are actually described by a single irreducible representation of the space group of the crystal. (The reasons for the appearance of structures that simultaneously follow several irreducible representations have been discussed in Sec. 5). This situation offers an effective method of applying symmetry analysis in deciphering neutron-diffraction patterns; it has been rather fully described in Sec. 3. The reliability of this method enables one to extract more subtle information on the magnetic structure from the data of a neutron-diffraction experiment. At the same time, on the basis of the approach presented in this review, one can critically evaluate the degree of uniqueness of the decipherment of concrete structures from neutron-diffraction patterns. We should point out one general conclusion from this evaluation: it is not impossible that some experimenters have overlooked multi-k-structures in deciphering magnetic structures having wave vectors belonging to many-arm stars by assuming a priori that the magnetic structure under study is characterized by only one wave vector.

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