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Peculiarities of the Low-Symmetry Phase Structure Near the Phase-Transition Point

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Abstract

The structure of the low-symmetry phase near the transition point depends on the number of arbitrary parameters, which is smaller than that determined by the space group G_D of this phase. Such a feature gives rise to some nontrivial structural effects in the vicinity of the transition point: there are numerical relationships among the displacements of the atoms belonging to different orbits of the G_D group. In some cases, atoms may be displaced in a direction not singled out by symmetry in any of the 230 space groups. These effects are revealed by group-theoretical methods and the Landau concept of one irreducible representation.

1. Group-theoretical methods for studying the structure of low-symmetry phases

The method of the complete condensate of order parameters (hereafter referred to as the COP method) has already been proposed for obtaining the structure of low-symmetry phases (Sakhnenko, Talanov & Chechin, 1986; Chechin, Ivanova & Sakhnenko, 1989). Let G be the space group of the original (high-symmetry) phase and G_D that of the low-symmetry phase that arises from the continuous structural transition $G \rightarrow G_D$ ($G_D \subset G$). The COP method allows one to obtain, for the given phase transition, the explicit form of the density function that describes the G_D phase structure in the Landau theory (Landau & Lifshitz, 1980).

The change of the density function $\delta\rho(\mathbf{r})$ for the transition $G \rightarrow G_D$ can be written as a sum of the contributions Δ_j that correspond to the different irreducible representations (IRs) Γ_j of dimension n_j

of the original group G :

$$\delta\rho(\mathbf{r}) = \sum_{j=0}^p \Delta_j = \sum_{j=0}^p [\mathbf{C}_j, \Phi_j(\mathbf{r})], \quad (1.1)$$

where p is the total number of these representations. Each of the contributions Δ_j is a formal scalar product of the stationary (invariant) vector $\mathbf{C}_j = (C_j^1, C_j^2, \dots, C_j^{n_j})$, which is a multicomponent order parameter, and the vector $\Phi_j = [\varphi_j^1(\mathbf{r}), \varphi_j^2(\mathbf{r}), \dots, \varphi_j^{n_j}(\mathbf{r})]$, which determines a set of the basis functions $\varphi_j^i(\mathbf{r})$ of the IR Γ_j . The stationary vector may be found from the equation

$$(\Gamma_j \downarrow G_D) \mathbf{C}_j = \mathbf{C}_j, \quad (1.2)$$

where $\Gamma_j \downarrow G_D$ is the restriction* of the IR Γ_j of the group G to its subgroup G_D . Thus, the vector \mathbf{C}_j is the common eigenvector with the eigenvalue of unity of those matrices of the IR Γ_j that correspond to all $g \in G_D$. Being the general solution to a system of homogeneous linear equations, the stationary vector depends on a certain number of arbitrary parameters, which we denote a, b, c, \dots ; hence, it singles out a certain subspace in the space of the representation, whose dimension equals the number of these arbitrary parameters. The general algorithm for constructing all the stationary vectors for the Γ_j of different IRs corresponding to a given G_D phase, which constitute the complete condensate of order parameters, is given by Sakhnenko, Talanov & Chechin (1986) and Chechin, Ivanova & Sakhnenko (1989). The basis functions $\varphi_j(\mathbf{r})$ are not only determined by the IR Γ_j but also depend on the transition type (ordering, displacement *etc.*) and on

* The set of matrices of the IR Γ_j of group G corresponding to the elements of its subgroup G_D only.

the distribution of the crystal's atoms in the original phase over the orbits of the group G . These functions may be constructed either by the standard method of projection operators (see, for example, Izyumov, Naish & Syromyatnikov, 1979) or by the 'direct' method described by Sakhnenko, Talanov, Chechin & Ulyanova (1983). The knowledge of the stationary vector C_j and of the basis functions of the IR Γ_j fully determines the contribution Δ_j by this representation to the function $\delta\rho(\mathbf{r})$. Thus, the COP method allows one to construct the $\delta\rho(\mathbf{r})$ function for a given low-symmetry phase and, consequently, to describe its structure.

Another group-theoretical method for obtaining the low-symmetry phase structure has been suggested by Chechin (1989) (see also Ipatova, Krivtsova & Chechin, 1989 and Chechin & Krivtsova, 1989, 1990). The atoms of the crystal occupy, in the original phase, a certain set of orbits (regular systems of points) of the space group G . All sites of each orbit of the group G are equivalent, being linked by certain symmetry operations $g \in G$. However, owing to the symmetry lowering occurring because of the phase transition $G \rightarrow G_D$, a given orbit R of the group G may split into a certain set of independent orbits R_D^i of its subgroup G_D . Every R_D^i is characterized by its stabilizer S_D^i (i.e. a group of site symmetry), which is a subgroup of the stabilizer S of the original orbit R .*

In practice, the splitting of the orbit R may be performed in the following manner. Take an arbitrary point $\mathbf{r}_1 \in R$ and act on it with all elements of the group G_D . The set of the different points obtained forms the first orbit, R_D^1 , and those elements of the symmetry under whose action the point \mathbf{r}_1 does not change its position enter into the stabilizer S_D^1 . Cross all the points of the set R_D^1 off the points of the orbit R and act upon the first of the remaining points with all elements of the group G_D , thereby singling out the second orbit R_D^2 and its stabilizer S_D^2 ; continue thus until all the points of R are crossed off. This method of space-group-orbit splitting is hereafter referred to as the SOS method.

The splitting of high-symmetry space-group orbits provides full symmetry-related information on the structure of the low-symmetry G_D phase. For example, let us consider a commensurate phase transition $Fd\bar{3}m \rightarrow C2/m$ with quadrupling of the primitive-cell volume (the low-symmetry phase $C2/m$ is induced by the six-dimensional irreducible representation X_3 or X_4 of the group $Fd\bar{3}m$).† As a result

of this transition, the orbit $R = 16(d)$ with the stabilizer $S = \bar{3}m$ is split as follows:

$$2(1):2/m + 1(2):\bar{1} + 1(2):m + 1(2):2 + 2(4):1. \quad (1.3)$$

Addition in this formula signifies union of the sets R_D^i . The number before the round bracket indicates the number of the orbits R_D^i of the same type. The brackets enclose multiplicity of the orbit R_D^i referring to the primitive cell of the $C2/m$ phase. After the brackets, the stabilizers S_D of the orbits are given.

Thus, the atoms occupying the position $16(d)$ of the group $Fd\bar{3}m$ become, as a result of the phase transition, physically unequivalent – they divide into seven different types. Such information may be useful when the electron spin resonance and nuclear magnetic resonance experimental data are examined and also when the low-symmetry structure is refined with the aid of X-ray, neutron and other methods. The splitting of the orbits of the group G as the result of the phase transition $G \rightarrow G_D$ also permits one to obtain a symmetry-allowed set of atomic displacements that characterizes the structure of the low-symmetry G_D phase (see § 3).

The SOS method and the COP method are equivalent in the geometrical sense and, broadly speaking, correspond to each other as methods of examining a periodic function in coordinate space and in Fourier space, respectively. However, near the transition point, the situation changes radically: the COP method permits some additional information on the structure of a low-symmetry phase to be obtained. Indeed, the Landau theory proves that, in the second-order phase transition, the loss of stability of a crystal structure is associated with the appearance of an order parameter C_o corresponding to a single (critical) irreducible representation Γ_o . There is full accord between this result and the concept of the soft mode. The Γ_o provides the main contribution to the function $\delta\rho(\mathbf{r})$ and, therefore, to the alteration in the crystal structure.

The physical nature of the emergence of the non-critical (secondary) order parameter $C_j (j \neq 0)$ connected with the critical (primary) parameter C_o is related to the nonlinear interactions between various degrees of freedom in a crystal. For this reason, near the phase transition point, the noncritical parameters are of a higher order of smallness in comparison with the critical ones. It may be deduced from the general principles of the Landau theory that, in such a case, the values of the critical and noncritical order parameters ($C_o = |C_o|$, $C_j = |c_j|$) are proportional to different powers of $\theta = |(T - T_c)/T_c|$:

$$C_o \approx \theta^{1/2}, \quad C_j \approx \theta^{m/2} \quad (j \neq 0). \quad (1.4)$$

Here, m is the least direct symmetrized power of the critical IR Γ_o that contains the noncritical IR Γ_j and T_c is the temperature of the phase transition (in K)

* Different points of an orbit generally have different stabilizers. However, these are conjugate and, consequently, isomorphic groups, therefore, we denote them by the same symbol (S or S_D^i).

† Note that we use one distinct subgroup of type $C2/m$ out of the set of the several different subgroups of this type (see Appendix).

(Sakhnenko, Talanov & Chechin, 1986; Chechin, Ivanova & Sakhnenko, 1989). Thus, in the vicinity of the phase-transition point, there are essential and nonessential atomic displacements and this feature of the crystal structure leads to a variety of interesting crystallographic effects that show up in low-symmetry phases (Chechin, Ipatova & Sakhnenko, 1989; Veligonenko, Krivtsova & Chechin, 1989).

2. A simplest example of specific features that characterize the low-symmetry phase near the phase-transition point

In the present work, we consider the low-symmetry structure for the phase transition of the displacement type only. The occurrence of specific structural features near the transition point may be illustrated by the simplest example of a phase transition, $P\bar{1} \rightarrow P1$, between the crystal phases $G = P\bar{1}$ and $G_D = P1$, without enlargement of the primitive cell. Such transitions are induced by irreducible representations with the wave vector $\mathbf{K} = 0$. The group $G = P\bar{1}$ has two IRs with $\mathbf{K} = 0$: Γ_1 and Γ_2 , both of which are one-dimensional; Γ_1 being even and Γ_2 odd with respect to inversion. The representation Γ_2 is a critical IR that induces the transition $P\bar{1} \rightarrow P1$ and the change of the density function $\delta\rho_2(\mathbf{r}) = a\varphi_2(\mathbf{r})$ corresponds to it. This function is odd with respect to the inversion vanishing as a result of the phase transition. Evidently, this expression does not provide the most general form of the density function but it may be supplemented with the contribution $\delta\rho_1(\mathbf{r}) = b\varphi_1(\mathbf{r})$, corresponding to the identical IR Γ_1 , which, in this case, is noncritical. Thus, we have

$$\delta\rho(\mathbf{r}) = \delta\rho_2(\mathbf{r}) + \delta\rho_1(\mathbf{r}) = a\varphi_2(\mathbf{r}) + b\varphi_1(\mathbf{r}), \quad (2.1)$$

where φ_1 and φ_2 are the basis functions of the representations Γ_1 and Γ_2 , respectively. This expression for $\delta\rho(\mathbf{r})$ that corresponds to the complete condensate [see (1.1)] is, in this case, nothing other than a representation of an arbitrary function in the form of symmetric and antisymmetric parts, each of which is transformed according to one of the IRs of the group that consists of the identity element and the inversion:

$$\delta\rho(\mathbf{r}) = [\delta\rho(\mathbf{r}) - \delta\rho(-\mathbf{r})]/2 + [\delta\rho(\mathbf{r}) + \delta\rho(-\mathbf{r})]/2. \quad (2.2)$$

Near the phase-transition point $T = T_c$, the terms in (2.1) differ essentially in their orders of magnitude,

$$\delta\rho_2 \gg \delta\rho_1. \quad (2.3)$$

Indeed, from the phenomenological theory (Sakhnenko, Talanov & Chechin, 1986; Chechin, Ivanova & Sakhnenko, 1989), it follows that the emergence of the noncritical order parameter b is due to its interaction with the critical parameter a . This interaction is described in the Landau potential by a mixed

invariant of the type $I = a^2b$ (since in this case $\Gamma_2 \times \Gamma_2 = \Gamma_1$). Seeing that, according to the Landau theory, $a = |T - T_c|^{1/2}$, we have $b = a^2 = |T - T_c| \ll a$. Making use of the validity of (2.3) near the transition point, we obtain, from (2.1),

$$\delta\rho \approx \delta\rho_2. \quad (2.4)$$

In this approximation, the density function $\rho = \rho_0 + \delta\rho$ of the low-symmetry phase possesses additional symmetry: it is odd (antisymmetric) with respect to the inversion that has vanished in consequence of the phase transition. Inclusion of the second term in (2.1) gives rise to a quite insignificant contribution, which grows as the temperature changes away from the transition point, so that the function $\rho(\mathbf{r})$ is no longer definitely even with respect to the inversion.

We illustrate this with an example of a phase transition for a one-dimensional chain, whose primitive cell contains one 'heavy' atom of type M and two 'light' atoms of type m (see Fig. 1). Consider displacements of the light atoms, for which purpose corresponding basis functions of the Γ_2 and Γ_1 IR are constructed. It is easy to see that they have the form $\varphi_2 = \begin{bmatrix} \alpha \\ \alpha \end{bmatrix}$ and $\varphi_1 = \begin{bmatrix} \beta \\ -\beta \end{bmatrix}$, where α and β are the arbitrary parameters determining displacements of the atoms from their equilibrium positions in the $P\bar{1}$ phase. So as not to complicate the notation, these basis functions may conveniently be normalized as follows: $\varphi_2 = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$, $\varphi_1 = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$. Then, from (2.1), we have

$$\delta\rho = \delta\rho_2 + \delta\rho_1 = \begin{bmatrix} a \\ a \end{bmatrix} + \begin{bmatrix} b \\ -b \end{bmatrix} = \begin{bmatrix} a+b \\ a-b \end{bmatrix}. \quad (2.5)$$

As is evident from (2.5), the critical displacements of two light atoms located in the primitive cell of the low-symmetry phase are identical (Fig. 1*b*), whereas the noncritical ones are equal in value but opposite in direction (Fig. 1*c*). As regards the condensate, the displacements of the atoms in question, different in value, correspond to it. Thus, near the transition point, a pattern of atomic displacements will be observed that corresponds to Fig. 1*b*), while away from it a pattern as shown in Fig. 1*d*) will be observed.

Note that the two light atoms of the primitive cell of the one-dimensional crystal belong to one and the

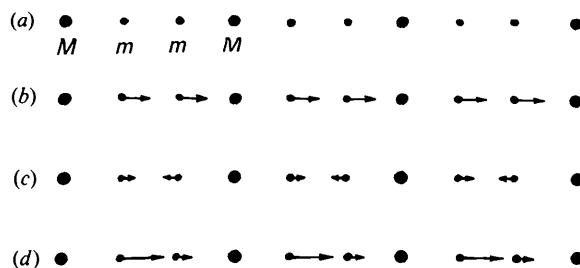


Fig. 1. Displacement structure corresponding to the phase transition $P\bar{1} \rightarrow P1$ in the one-dimensional crystal.

Table 1. Structure of the low-symmetry phase for the displacement-type transition $Fd\bar{3}m \rightarrow C2/m$ ($V'/V4$) induced by the IR X_3 or the IR X_4 of the $Fd\bar{3}m$ group for the orbit $16(d)$

The R_D^i orbits and their stabilizers S_D^i	$R_D^1:m$	R_D^2	$R_D^3:1$	$R_D^4:1$
Starting points of the R_D^i orbits	(1/8, 5/8, 5/8)	(1/8, 13/8, 5/8)	(5/8, 1/8, 5/8)	(13/8, 1/8, 5/8)
Symmetry-permitted atomic displacements	(X, Y, Y)	($0, -Z, Z$)	(X_1, Y_1, Z_1)	(X_2, Y_2, Z_2)
$\Delta(X_1)$	$(-2a_1, a_1 + a'_1, a_1 + a'_1)$	$(0, -a_1 + a'_1, a_1 - a'_1)$	$(a_1 + b'_1, -a_1 - b_1, a'_1 + b_1)$	$(-a_1 + b'_1, a_1 - b_1, -a'_1 + b_1)$
$\Delta(X_2)$	$(2a_2, a_2, a_2)$	$(0, -a_2, a_2)$	$(-a_2, -a_2, 0)$	$(a_2, a_2, 0)$
$\Delta(X_3)$	$(2a_3, a_3, a_3)$	$(0, -a_3, a_3)$	$(a_3, a_3 + b_3, b_3)$	$(-a_3, -a_3 + b_3, b_3)$
$\Delta(X_4)$	$(-2a_4, a_4 + b_4, a_4 + b_4)$	$(0, -a_4 + b_4, a_4 - b_4)$	$(-a_4, a_4, -b_4)$	$(a_4, -a_4, b_4)$

same orbit of the group $G = P\bar{1}$ of the original phase (they are interconnected *via* inversion), but to different orbits R_D^1 and R_D^2 of the low-symmetry phase with $G_D = P1$. Therefore, between the displacements of the atoms that belong to different orbits of a low-symmetry phase, some numerical relationships can exist, which in this, the simplest, case are reduced to equality of atomic displacements for two orbits R_D^1 and R_D^2 . These relationships cannot be accounted for by purely crystallographic (symmetry-related) considerations,* rather they follow from the applicability, near the phase-transition point, of Landau's concept of one irreducible representation. In the general case, this concept may give rise to an interesting picture of atomic displacements, in which a non-symmetry-related relationship would be observed in both the magnitudes and the directions of these.

3. Structure of the low-symmetry phase near the transition point

Let us now consider an example that would allow all geometry effects to be illustrated following from the concept of one critical irreducible representation. The phase transition $G = Fd\bar{3}m \rightarrow G_D = C2/m$ ($V'/V = 4$), which is considered in detail in the Appendix, is induced by one of two six-dimensional IRs X_3 or X_4 belonging to the star of the vector $\mathbf{K}_{10} = \frac{1}{2}(\mathbf{b}_1 + \mathbf{b}_2)$ of the original space group, where \mathbf{b}_1 and \mathbf{b}_2 are the basis vectors of the reciprocal lattice. Consider displacements of the atoms that correspond to the orbit $16(d)$ of the group $Fd\bar{3}m$ (such a regular system of points is occupied by ions in, for instance, spinel-type crystals).

A scheme to split the orbit $16(d)$ for the $Fd\bar{3}m \rightarrow C2/m$ phase transition was given earlier [(1.3)]. It follows from this scheme that the orbit in question is split into seven orbits R_D^i of the group $C2/m$. Note that, in this case, the list of stabilizers S_D^i of those orbits ($2/m, \bar{1}, m, 2, 1$) comprises all subgroups of the crystal class of the group $C2/m$. The atoms that correspond to the first three orbits in (1.3) cannot be

* In the example under consideration, the atoms in the low-symmetry phase with the space group $G_D = P1$ will have different displacements regardless of the difference between the phase-transition temperature and the temperature at which the structure of this phase is observed.

displaced from their equilibrium positions in the original $Fd\bar{3}m$ phase, since their stabilizers contain inversions. Nonzero atomic displacements for four other orbits are given in Table 1, which presents all necessary information on the structure of the low-symmetry $C2/m$ phase (see Appendix). Row 1 shows the symbols for stabilizers S_D^i of the orbits R_D^i . Row 2 shows the coordinates of the starting points of these orbits referred to an oblique-angle basis of the primitive cell of group $Fd\bar{3}m$. Row 3 shows the most general pattern of atomic displacements obtained by means of the SOS method, determined by their Cartesian coordinates. Rows 4, 5, 6 and 7 show the displacements $\Delta(X_i)$ corresponding to the IRs X_1, X_2, X_3 and X_4 , respectively.

The atomic displacements in Table 1 correspond to a quite definite domain of the low-symmetry $C2/m$ phase (see Appendix). This domain is singled out by the stationary vector (a, a, a, a, b, b) of the critical IR X_3 or by the stationary vector $(a, a, a, a, 0, 0)$ of the critical IR X_4 and its twofold axis is in the direction $[0\bar{1}1]$. Therefore, the displacements obtained by the SOS method of the starting atoms that correspond to the orbits with the stabilizers 2 and m and to two orbits with $S_D^i = 1$ have the forms $(0, -Z, Z)$, (X, Y, Y) , (X_1, Y_1, Z_1) , and (X_2, Y_2, Z_2) , respectively. Hence, the structure of the atomic displacements associated with the $16(d)$ orbit depends, in the most general case, on nine arbitrary parameters:

$$X, Y, Z, X_1, Y_1, Z_1, X_2, Y_2, Z_2. \quad (3.1)$$

According to Sakhnenko, Talanov & Chechin, (1986) and Chechin, Ivanova & Sakhnenko (1989), the complete condensate for the phase of the space group $G_D = C2/m$ ($V'/V = 4$) (see Appendix) contains the following IRs corresponding to the points Γ and X only of the Brillouin zone: $\Gamma_1, \Gamma_5, \Gamma_7, \Gamma_9, X_1, X_2, X_3, X_4$. A contribution to the displacements of the atom occupying the orbit $R = 16(d)$ of the group $G = Fd\bar{3}m$ is made only by those IRs that enter into the mechanical representation corresponding to this orbit. For the case in hand, it is the four IRs of the star of the vector X , *i.e.* X_1, X_2, X_3, X_4 . The contribution $\Delta(X_i)$ made by the IR X_i to $\delta\rho(\mathbf{r})$ is a particular linear combination of its basis functions with coefficients determined for this IR by the stationary vector corresponding to the given G_D phase.

Making use of the basis functions of the IRs X_i for the group $G = Fd\bar{3}m$ obtained in the paper by Sakhnenko, Talanov, Chechin & Ulyanova (1983) and of the stationary vectors obtained by Sakhnenko, Talanov & Chechin (1986), one may readily arrive at the explicit forms of the contributions $\Delta(X_i)$ to the set of displacements of atoms occupying the orbit $16(d)$ that are listed in Table 1. The complete set of atomic displacements is a sum of all four contributions; it depends on nine arbitrary parameters ($a_1, b_1, a'_1, b'_1, a_2, a_3, b_3, a_4, b_4$) with the representations X_1, X_2, X_3 and X_4 providing, respectively, 4, 1, 2 and 2 parameters.

As already noted, in the case of the $Fd\bar{3}m \rightarrow C2/m$ transition, there may, in principle, be two different critical IRs, *i.e.* either X_3 or X_4 . On the other hand, Table 1 shows that these critical IRs give rise to different types of atomic displacements. Since, near the phase-transition point, the critical displacements are those of the greatest order of magnitude [see (1.4)], there exists a possibility of determining from the X-ray and neutron diffraction experiments the true critical (primary) parameter for a particular phase transition in a given substance.

For both variants of the critical IR, the corresponding set $\Delta(X_i)$ of atomic displacements in a low-symmetry phase is determined by two arbitrary parameters. This means that, near the transition point, among the nine parameters [(3.1)] determined from purely crystallographic considerations, seven additional relationships exist. If the IR X_3 is critical, the following temperature dependences of the different contributions $\Delta(X_i)$ to the structure under consideration can be obtained from (1.4):

$$\Delta(X_3) \approx \theta^{1/2}; \quad \Delta(X_1) \approx \theta^1; \quad \Delta(X_2), \Delta(X_4) \approx \theta^{3/2}. \quad (3.2)$$

For $\theta \ll 1$, *i.e.* in the vicinity of the phase-transition point, critical displacements (corresponding to IR X_3) are the greatest in magnitude; they make the main contribution to the crystal structure of the low-symmetry phase emerging upon the transition. When the contribution from noncritical displacement is entirely disregarded (*i.e.* setting $a_1 = b_1 = a'_1 = b'_1 = a_2 = a_4 = b_4 = 0$), we obtain quite definite relationships between the Cartesian coordinates of the atomic displacements ($X, Y, Z, X_1, Y_1, Z_1, X_2, Y_2, Z_2$). For example, comparison of the form of the symmetry-allowed displacement of the starting atom of the orbit $R_D^4(X, Y, Y)$ with the critical displacement of that atom ($2a_3, a_3, a_3$) listed in Table 1 clearly leads to $X = 2Y$. The full list of such relationships for the case when the IR X_3 is critical can be found in this way:

$$\begin{aligned} X &= 2Y; & Y_1 &= X_1 + Z_1; & Y_2 &= X_2 + Z_2; \\ Z &= Y = X_1 = -X_2; & Z_1 &= Z_2. \end{aligned} \quad (3.3)$$

Analogously, with the IR X_4 being critical, we have

$$\begin{aligned} Y_1 &= -X_1; & Y_2 &= -X_2; & X_1 &= -X_2; & Z_1 &= -Z_2; \\ X_2 + Z_2 &= Y; & Y_1 + Z_1 &= Z; & X &= 2X_1. \end{aligned} \quad (3.4)$$

Among these relationships, there are some that limit the directions of possible atomic displacements, and also some that give rise to additional numerical relationships between displacements of the atoms belonging to different orbits of the low-symmetry $C2/m$ phase. Let us examine this question in greater detail for critical displacements $\Delta(X_3)$ corresponding to the IR X_3 . The atom corresponding to the orbit R_D^4 with the stabilizer m has two degrees of freedom [its Cartesian coordinates are (X, Y, Y)] and is thus displaced in the plane defined by the stabilizer. On the other hand, its critical displacements $\Delta(X_3)$ have the form $(2a_3, a_3, a_3)$, depending solely on one arbitrary parameter a_3 . Evidently, this displacement occurs in the plane m , but corresponds to the quite definite direction [211]. Crucial here is the fact that this direction is not symmetry determined either in the group $Fd\bar{3}m$ or in any of the 230 space groups. (In the original cubic lattice, this is the direction from a vertex of the cube to the center of the opposite face.) Consequently, a displacement in such a direction cannot, in principle, be obtained from symmetry considerations.

Analogously, the atoms of the orbits R_D^6 and R_D^7 with the stabilizer 1 have not three but only two critical degrees of freedom, thus shifting in the fixed plane $(1\bar{1}1)$. Restrictions leading to these effects arise from the numerical relationships between the degrees of freedom that correspond to one and the same atom. For the critical IR X_3 , these restrictions are:

$$X = 2Y, \quad Y_1 = X_1 + Z_1, \quad Y_2 = X_2 + Z_2; \quad (3.5)$$

while, for the critical IR X_4 , they have the form

$$Y_1 = -X_1, \quad Y_2 = -X_2. \quad (3.6)$$

The remaining relationships between free parameters lead to certain numerical relationships between displacements of the atoms of different orbits of the low-symmetry $C2/m$ group. For the IR X_3 they have the form

$$Z = Y = X_1 = -X_2, \quad Z_1 = Z_2; \quad (3.7)$$

for the IR X_4 they have the form

$$\begin{aligned} X_1 &= -X_2, & Z_1 &= -Z_2, & X_2 + Z_2 &= Y, \\ Y_1 + Z_1 &= Z, & X &= 2X_1. \end{aligned} \quad (3.8)$$

As the temperature is changed away from the phase-transition point, the role of noncritical displacements gradually increases and some of the above-mentioned additional relationships are no longer valid (see § 1 of the present work). According to (3.2), first to appear in the experiment after the

Table 2. Displacements of the atoms that occupy the 3(c) orbit of the $Pm\bar{3}m$ group as a result of the phase transition $Pm\bar{3}m \rightarrow Amm2$

	Type of basis	$mm2$	Stabilizers	m
Atomic coordinates	$\left\{ \begin{array}{l} a \\ A \end{array} \right.$	$(1/2, 1/2, 0)$ $(0, 0, 1/2)$		$(0, 1/2, 1/2)$ $(1/2, 3/4, 1/4)$
Atomic displacements obtained by the SOS method	$\left\{ \begin{array}{l} a \\ A \end{array} \right.$	$(x_1, x_1, 0)$ $(0, 0, Z_1)$		$(x_2, y_2, 0)$ $(0, Y_2, Z_2)$
Atomic displacements obtained by the COP method	$\left\{ \begin{array}{l} a \\ A \end{array} \right.$	$(a + a', a + a', 0)$ $(0, 0, A + A')$		$(b, a - a', 0)$ $[0, (A - B - A')/2, (A + B - A')/2]$
Experimentally determined displacements of the atoms in $BaTiO_3$ (Å)	A	$(0, 0, 0.06)$		$(0, 0.02, 0.07)$
Experimentally determined displacements of the atoms in $KNbO_3$ (Å)	A	$(0, 0, 0.120)^*$		$(0, 0.022, 0.200)^*$
	A	$(0, 0, 0.208)^\dagger$		$(0, 0.014, 0.196)^\dagger$

* Katz & Megaw (1967).

† Hewat (1973).

critical parameters IR X_3) will be those noncritical parameters that correspond to IR X_1 . (In Table 1, the free parameters that correspond to different IRs are designated by different letters with an index which is the ordinal number of the IR of the star of the vector \mathbf{K}_{10}).

The complete condensate $\Delta = \Delta(X_1) + \Delta(X_2) + \Delta(X_3) + \Delta(X_4)$ of critical and noncritical displacements is like the set of the displacements obtained by the orbit-splitting method (row 3 of Table 1), determined by nine arbitrary parameters a_1, b_1, \dots . Note that this condensate does not depend on which IR - X_3 or X_4 - is critical. One may easily see that Δ contains the same displacements as row 3, the only difference being that they are represented as a sum of contributions from individual IRs of the symmetry group of the original phase (expanded in the basis functions of those IRs). As already noted, such a representation of atomic displacements is analogous to the representation of a periodic function as a Fourier series. The use of the concept of one irreducible representation is equivalent in this case to taking into account, in the Fourier series of several harmonics, only those of which the amplitudes are the largest and are determinative for the physical phenomenon under consideration. Note that all the above-described specificities in the structure of a low-symmetry phase can be observed experimentally near the phase-transition point.

4. Comparison of the theoretical results with experimental data

The temperature vicinity of the transition point is of special interest for an investigation of the physical nature of a transition. However, little experimental data can be found in the literature on the low-symmetry phase structure in this region. The displacement-type transition $Pm\bar{3}m \rightarrow Amm2$ without enlargement of the primitive unit cell in $KNbO_3$ and $BaTiO_3$ crystals is an example for which such data are available. This transition is induced by the

critical IR τ_{10} , which is the vectorial representation of the group $Pm\bar{3}m$ (Kovalev, 1961). In a $KNbO_3$ crystal, the atoms of potassium, niobium and oxygen occupy in this perovskite crystal the orbits 1(a), 1(b) and 3(c), respectively, of the original space group. Let us analyze the structure of the low-symmetry $Amm2$ phase that arises from the orbit 3(c). The primitive cell of this phase, like the cell of the original phase, contains three O atoms with coordinates (in fractions of the cubic-cell edges) $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$. In addition to the identity element, the group $G_D = Amm2$ contains two sets of mirror planes normal to the directions [001] and [1 $\bar{1}$ 0], respectively, and twofold axes parallel to [110]. The periods $\mathbf{A}_1, \mathbf{A}_2$ and \mathbf{A}_3 of the face-centered cell of the low-symmetry phase (whose volume is twice as large as that of the primitive cell) are connected with the periods $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ of the cubic cell of the original $Pm\bar{3}m$ phase, in the following manner:

$$\mathbf{A}_1 = \mathbf{a}_3; \quad \mathbf{A}_2 = +\mathbf{a}_1 - \mathbf{a}_2; \quad \mathbf{A}_3 = \mathbf{a}_1 + \mathbf{a}_2.$$

Hereafter, we differentiate between the atomic coordinates in the a basis and those in the A basis, depending on whether they are expressed in the basis of the original $Pm\bar{3}m$ phase or in that of the low-symmetry $Amm2$ phase. For example, the coordinates of the oxygen atoms have, in the A basis, the form $(0, 0, \frac{1}{2})$; $(\frac{1}{2}, \frac{1}{4}, \frac{1}{4})$; $(\frac{1}{2}, -\frac{1}{4}, \frac{1}{4}) \equiv (\frac{1}{2}, \frac{3}{4}, \frac{1}{4})$.

As a result of the phase transition $Pm\bar{3}m \rightarrow Amm2$, the orbit 3(c) of the group $G = Pm\bar{3}m$ splits into two orbits R_D^1 and R_D^2 of the group $G_D = Amm2$ by the scheme

$$1(1): mm2 + 1(2): m \quad (4.1)$$

It may be seen from this scheme that the low-symmetry phase structure found by the SOS method is characterized by three degrees of freedom, of which one corresponds to the orbit R_D^1 and the other two to the orbit R_D^2 . In Table 2, the arbitrary parameters for the orbit R_D^1 are designated x_1 in the a basis and by Z_1 in the A basis, while those for the orbit R_D^2 are designated (x_2, y_2) and (Y_2, Z_2) , respectively.

The low-symmetry $Amm2$ phase structure can also be found by the COP method. Besides the critical IR τ_{10} , its complete condensate contains the representations τ_1 , τ_5 , τ_7 and τ_8 (Ivanova, Kesoretskikh, Sakhnenko & Chechin, 1986). Only two of these IRs enter into the mechanical representation associated with the $3(c)$ orbit, namely, the critical IR τ_{10} (twice) and the noncritical IR τ_8 (once). It is these IRs that make a contribution to the low-symmetry phase structure for the displacement-type transition $Pm\bar{3}m \rightarrow Amm2$. By calculating the basis functions of these two three-dimensional representations and taking into account the form of the corresponding stationary vectors – (a, a, o) for the IR τ_{10} and $(a', -a', o)$ for the IR τ_8 – the critical and noncritical displacements of the atoms are found for the orbit $3(c)$. The complete condensate of these displacements, obtained by the COP method, is given in row 4 of Table 2. The parameters a and b are critical, while the parameter a' is noncritical. In the case where only the critical atomic displacements are considered (setting $a' = o$), one connection is revealed between the displacements of the atoms of the two different orbits of the $Amm2$ group, to which the stabilizers $mm2$ and m correspond; namely, $Y_2 + Z_2 = Z_1$.

It should be noted that the transitions in $KNbO_3$ and $BaTiO_3$ are of the first order. Therefore, estimation of the smallness of the noncritical parameters using the formula $a' \approx |(T - T_c)/T_c|^{m/2}$ is not a correct procedure, since this formula was obtained for the second-order phase transitions. Let us analyze the experimental data on $BaTiO_3$ (Shirane, Danner & Pepinsky, 1957) and $KNbO_3$ (Katz & Megaw, 1967) listed in Table 2. These data show that the value of the displacement (Y) of the O atom of the orbit R_D^2 along the axis Y is much smaller than the displacements of O atoms along the axis Z ($Y_2 \ll Z_1, Z_2$); it lies near the limits of experimental accuracy given in the above-mentioned references. Hence, the relationship $Y_2 + Z_2 = Z_1$ derived above may be reduced to the form $Z_1 \approx Z_2$. As can be seen from Table 2, the latter relationship is fulfilled rather well for $BaTiO_3$ and also in regard to $KNbO_3$ (Hewat, 1973); it is, however, in marked disagreement with the results obtained for the latter compound in an earlier work (Katz & Megaw, 1967). Note that the relationship $Z_1 \approx Z_2$ for the displacements of O atoms reflects a weak distortion of the oxygen octahedron upon a phase transition in the crystals under consideration.

In conclusion, we wish to emphasize that the relationships of the (3.3), (3.4) type between the displacements of the atoms belonging to different orbits of the space group of the low-symmetry phase are of a general character and must be fulfilled near T_c for most crystals, even though they cannot be deduced from purely crystallographic considerations.

The study of the structures of low-symmetry phases in the immediate vicinity of the phase-transition point is of particular importance for the verification of the above relationships containing valuable information as to the mechanism and character of a given phase transition.

APPENDIX

Second-order phase transitions in crystals of the space group $G = Fd\bar{3}m$ may generate many different low-symmetry phases belonging to the group $G_D = C2/m$. They differ in the multiplicity of the primitive-cell volume as well as in the way they are positioned in the parent group $G = Fd\bar{3}m$. The Bravais lattice of the group $G = Fd\bar{3}m$ is defined by three basis vectors $\mathbf{a}_1 = (0, \frac{1}{2}, \frac{1}{2})$, $\mathbf{a}_2 = (\frac{1}{2}, 0, \frac{1}{2})$, $\mathbf{a}_3 = (\frac{1}{2}, \frac{1}{2}, 0)$, determined by their Cartesian coordinates. These vectors determine the primitive cell of volume V of the original group G . According to Sakhnenko, Talanov & Chechin, (1986) and Chechin, Ivanova & Sakhnenko (1989), the phase transition $G = Fd\bar{3}m \rightarrow G_D = C2/m$ ($V'/V = 4$) may be induced either by the IR X_3 – stationary vector (a, a, a, a, b, b) – or by the IR X_4 – stationary vector (a, a, a, a, o, o) . Let us consider the former case. By singling out the matrices M_i of this representation that leave the vector $\mathbf{C} = (a, a, a, a, b, b)$ invariant, *i.e.* satisfy the condition $M_i\mathbf{C} = \mathbf{C}$, and then the elements of the original group $G = Fd\bar{3}m$ that correspond to those matrices, we obtain all the symmetry elements surviving the phase transition. The set of these elements comprises

(a) the operations of point symmetry,

$$1, 2[0\bar{1}1], \bar{1}, m[0\bar{1}1]; \quad (A1)$$

(b) the translations, which determine the edges of the Bravais cell of the low-symmetry phase,

$$\mathbf{A}_1 = -\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3, \quad \mathbf{A}_2 = 2\mathbf{a}_1, \quad \mathbf{A}_3 = 2\mathbf{a}_2 - 2\mathbf{a}_3, \quad (A2)$$

and the translation $\frac{1}{2}(\mathbf{A}_2 + \mathbf{A}_3) = \mathbf{a}_1 + \mathbf{a}_2 - \mathbf{a}_3$ corresponding to the A -face center of this cell.

The operations 2 and $\bar{1}$ from (A1) are accompanied by the same translation part $\mathbf{a}_o = \frac{1}{4}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$. The shift of origin by the vector

$$\mathbf{R} = \frac{1}{8}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3) \quad (A3)$$

makes translation parts corresponding to all operations (A1) equal to zero. The formulae (A1)–(A3) define the subgroup $G_D = A2/m$ ($V'/V = 4$) $\subset G = Fd\bar{3}m$ precisely. All calculations in the present paper were made for such an A -centered type of group G_D . But instead of symbol $A2/m$, we prefer to use the standard symbol $C2/m$ for this space group.

Let us consider the splitting scheme of the orbit $R = 16(d)$ of the group $Fd\bar{3}m$ for this subgroup. This

orbit can be defined by the set of points

$$\begin{aligned}
 \mathbf{r}_1 &= (5/8, 5/8, 5/8), & \mathbf{r}_2 &= (13/8, 5/8, 5/8), \\
 \mathbf{r}_3 &= (5/8, 13/8, 5/8), & \mathbf{r}_4 &= (13/8, 13/8, 5/8), \\
 \mathbf{r}_5 &= (1/8, 5/8, 5/8), & \mathbf{r}_6 &= (9/8, 5/8, 5/8), \\
 \mathbf{r}_7 &= (1/8, 13/8, 5/8), & \mathbf{r}_8 &= (9/8, 13/8, 5/8), \\
 \mathbf{r}_9 &= (5/8, 1/8, 5/8), & \mathbf{r}_{10} &= (13/8, 1/8, 5/8), \\
 \mathbf{r}_{11} &= (5/8, 9/8, 5/8), & \mathbf{r}_{12} &= (13/8, 9/8, 5/8), \\
 \mathbf{r}_{13} &= (5/8, 5/8, 1/8), & \mathbf{r}_{14} &= (13/8, 5/8, 1/8), \\
 \mathbf{r}_{15} &= (5/8, 13/8, 1/8), & \mathbf{r}_{16} &= (13/8, 13/8, 1/8).
 \end{aligned} \tag{A4}$$

These points are given not by their Cartesian coordinates but rather by contravariant coordinates relative to the oblique-angle system of reference $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$, i.e. if $\mathbf{r} = \mu_1 \mathbf{a}_1 + \mu_2 \mathbf{a}_2 + \mu_3 \mathbf{a}_3$, then we indicate three numbers (μ_1, μ_2, μ_3) . Acting on the points (A4) with the operations of the group $G_D = C2/m$ ($V'/V = 4$), we obtain the following splitting:

$$\begin{aligned}
 R_D^1 &= \{1|2/m\}, & R_D^2 &= \{2|2/m\}, & R_D^3 &= \{3,4|\bar{1}\}, \\
 R_D^4 &= \{5,6|m\}, & R_D^5 &= \{7,8|2\}, \\
 R_D^6 &= \{9,16,11,13|1\}, & R_D^7 &= \{10,15,12,14|1\}.
 \end{aligned} \tag{A5}$$

The numbers of the points of the R_D^i orbit from the set (A4) and the stabilizer that corresponds to its starting point are given for each R_D^i in the braces.

The splitting (A5) generates the scheme (1.3). Note that, for conjugate subgroups $G'_D = g_o^{-1} G_D g_o$ ($g_o \in G$), which are the symmetry groups of different domains of the G_D phase, the same splitting scheme corresponds to them, in spite of the difference in

correspondence between the points of the orbit R and the orbits R_D^i .

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Determination of Composite Crystal Structures and Superspace Groups

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Abstract

Superspace groups introduced for usual modulated structures have recently been applied to the analysis of composite crystals. This review describes the method of composite-crystal analysis based on the superspace group. This method is efficient for the analysis of any (incommensurate or commensurate) composite crystals. The method is analogous to that for the modulated structure in many respects. The description of composite crystals in superspace,

determination of their superspace groups and unified setting of the unit vectors are mentioned. Two possible approximations and a relation between the superspace and space groups for commensurate composite crystals are discussed. Space groups of chimney-ladder structures with different periods are derived from a single superspace group by the application of this relation. Possible superspace groups for known composite structures are deduced from the space groups of average substructures. Finally, the refinement method is discussed.