

ON THE THEORY OF STRUCTURE PHASE TRANSITIONS IN CRYSTALS
WITH INTERNAL DEGREES OF FREEDOM

V. A. Koptsik

Moscow University Dept. of Physics
11 7234, Moscow, USSR

(received: March 1980)

The theory of structure phase transitions in crystals with internal degrees of freedom may be developed as the generalization of the Landau theory of the second order phase transitions. As it is known [1] the second order phase transitions may not be connected obligatory with the changing of Fedorov-Schönflies space symmetry group \mathbb{D}_p , which describes the atom configurations in crystal structure. They may be connected with some other symmetry changing. The well-known example are the spin reorientation phase transitions in magnetic crystals which change the order properties in the spin substructure of the crystal structure.

This kind of symmetry is known as magnetic symmetry. It is defined by the specific group of the proper symmetry $\infty/m'm' = \infty 2'2' \bar{1}$ of the stationary magnetic moment and by the way how the component of the combined operators $p\phi$ act on the coordinates of the external (geometric) R and the internal (spin) S subspaces of the magnetic crystal space.

All the known kinds of magnetic symmetry P , Q , Wp and Wq may be embedded in the construction of the wreath product of two groups [2,3]

$$\mathbb{W}^{(h)} \subseteq P \wr \mathbb{W}_{\text{mod}N} = (\tilde{P}^{\phi_1} \otimes \tilde{P}^{\phi_2} \otimes \dots \otimes \tilde{P}^{\phi_N}) \circledast \mathbb{W}_{\text{mod}N} = \overset{N}{\tilde{P}} \circledast \mathbb{W}_{\text{mod}N} ,$$

\wr , \otimes and \circledast being the symbols of the wreath, direct and semidirect products. The crystal space group $\mathbb{W}_{\rho_0} = \mathbb{W}_{\text{mod}N}$ is restricted there by modulo N , N being a big figure.

$\tilde{P} = \infty \otimes 1'$ is the permutation group of states possible for the spin coordinates $\hat{s} \in S$, ∞ being the proper part of the orthogonal group of $O^+(3)$ and $1'$ the time inversion operator which acts at the spins s of the point $\hat{s}(\vec{r}) = (\hat{s}, \vec{r})$ as follows: $1' \hat{s}(\vec{r}) = -\hat{s}(\vec{r})$.

In the cases of P - and Q - symmetry the composite space of a crystal $(S,R) = \{(\hat{s}, \vec{r})\}$ is homogeneous in a sense that operators $\phi^{(P)} = p\phi$ and $\phi^{(Q)} = q\phi$ of the generalized groups $\mathbb{W}^{(P)}$ and $\mathbb{W}^{(Q)}$ act globally on the every point $(\hat{s}, \vec{r}) \in (S,R)$ as rigid motions:

$$p\phi(\hat{s}, \vec{r}) = (p\hat{s}, \phi\vec{r}), \quad p\phi \in \mathbb{W}^{(P)} = P\mathbb{W} \subseteq \tilde{P}\mathbb{W}_{\rho_0}, \quad P \subseteq \tilde{P}, \quad p \in P, \phi \in \mathbb{W}_{\rho_0}$$

$$q\phi(\hat{s}, \vec{r}) = (q[\phi]\hat{s}, \phi\vec{r}), \quad q\phi \in \mathbb{W}^{(Q)} = Q\mathbb{W} \subseteq \tilde{Q} \circledast \mathbb{W}_{\rho_0}, \quad Q \subseteq \tilde{Q} \equiv \tilde{P}, \quad q \in Q$$

For the non-magnetic atoms $(\hat{s}, \vec{r}) = (o, \vec{r})$, $[\phi]$ being the proper part of the operator $\phi \in \mathbb{W}_{\rho_0}$.

In the cases of W_p - and W_q - symmetry the space (S, R) is inhomogeneous and splits into the set of homogeneous subspaces of (S, R) . The single component $p_i^{\phi_k}$ of the combined operator $\langle p_i^{\phi_1} \dots p_i^{\phi_k} \dots p_i^{\phi_N} | \phi_i \rangle$ acts locally on the spin of the point $(\vec{s}, \vec{r}_k) \in (S, R)$ according to the ordering $\vec{r}_k = \phi_k \vec{r}_i$ which is defined on R :

$$\langle \dots p_i^{\phi_k} \dots | \phi_i \rangle (\vec{s}, \vec{r}_k) = (p_i^{\phi_k} s_{\phi_i \vec{r}_k}, \langle \dots | \phi_i \rangle \in \mathbb{O}^{(W_p)} \subseteq \tilde{P} \setminus \mathbb{O}_{\text{mod} N}$$

$$\langle \dots q_i^{\phi_k} \dots | \phi_i \rangle (\vec{s}, \vec{r}_k) = (q_i^{\phi_k} [\phi_i] s_{\phi_i \vec{r}_k}, \langle \dots | \phi_i \rangle \in \mathbb{O}^{(W_q)} \subseteq \tilde{Q} \setminus \mathbb{O}_{\text{mod} N}$$

From the physical point of view the P - symmetry corresponds to the spin to spin interactions and the Q -symmetry to the spin to lattice ones [4].

It is important to note that the phase transition of the second order from the paramagnetic phase $1^{(\infty 1')}$ $\otimes \mathbb{O}_{\rho^0}$ into the magnetic ordered phase $\mathbb{O}_{\rho^0}^{(P)}$ is connected with the decreasing $\mathbb{O}^* \subseteq \mathbb{O}_{\rho^0}$ of the space symmetry group $\mathbb{O}_{\rho^0} = \mathbb{O}^* \phi_1 \cup \mathbb{O}^* \phi_2 \cup \dots \cup \mathbb{O}^* \phi_j$ into the subgroup \mathbb{O}^* of the index j at the classical level only. This decreasing is compensated by the appearance of the new symmetry properties in the physical system on the level of the magnetic group $\mathbb{O}_{\rho^0}^{(P)} = \mathbb{O}^* \phi_1 \cup \mathbb{O}^* \phi_2^{(P_2)} \cup \dots \cup \mathbb{O}^* \phi_j^{(P_j)}$ which is isomorphic to $\mathbb{O}; \mathbb{O}^{(P)} \leftrightarrow \mathbb{O}$. At the same time the factor $1^{(\infty 1')}$ is changed by the factors $1^{(1)}$, $1^{(2')}$ or $1^{(\infty 2' 2')}$ which preserve the function $\mathbb{S}(P, T)$ of the temperature-pressure dependence of the spin s at the fixed point \vec{r} for the 3-dimensional, coplanar and collinear ordered magnetic crystals [5]. All the

restrictions on the space modulation of the crystal lattice parameters are removed in the theory of the magnetic symmetry [4]. The reason is that the group $\phi_{\rho^{\circ}}$ may always be multiplied by the local symmetry group $\Omega_{\text{helix}}^{(W)}$ of the magnetic helix in the direct way.

The abovementioned theory deals with the magnetic interpretation of the P-, Q- and W-colour symmetry groups. It may be generalized on the case of crystals with internal degrees of freedom which correspond to other coordinates than spin ones. The generalized coordinates describe the internal motions of substructures of the crystal structure, for instance the space modulation of the crystal lattice parameters connected with the charge density wave, the occupation wave or with the wave of the atom deviations from the equilibrium positions.

Let us define now the electron density function of an "imperfect" crystal with the internal degrees of freedom in the composite form $\rho(\vec{r}) = \rho^{\circ}(\vec{r}) + \delta\rho(\vec{r})$. The function $\delta\rho(\vec{r})$ describes there the deviation of the electron density distribution of the actual crystal from some "perfect" distribution $\rho^{\circ}(\vec{r})$ which one accepts as a basic one. In the zero approach one neglects the weak perturbation of a system $\rho^{\circ}(\vec{r})$ connected with the function $\delta\rho(\vec{r})$ and identifies the functions $\rho(\vec{r}) \equiv \rho^{\circ}(\vec{r})$ and their symmetry groups $\mathbb{W}_{\rho} \equiv \mathbb{W}_{\rho^{\circ}}$:

$$\mathbb{W}_{\rho} \cdot \rho(\vec{r}) = \rho(\vec{r}) \equiv \rho^{\circ}(\vec{r}) = \mathbb{W}_{\rho^{\circ}} \cdot \rho^{\circ}(\vec{r}).$$

In the broken symmetry approach which is usual in the theory of imperfect crystals [6-8] and in the theory of the second order phase transitions [1] the perturbation $\delta\rho(\vec{r})$ is taken into account at the level of classical space groups only. In this approach the symmetry group \mathbb{O}_ρ reduces to the intersection (or the common part) of the group \mathbb{O}_{ρ_0} and the symmetry group $\Omega_{\delta\rho}$ of the perturbation function, $\mathbb{O}_\rho = \mathbb{O}_{\rho_0} \cap \Omega_{\delta\rho} \subset \mathbb{O}_{\rho_0}$. The group \mathbb{O}_ρ will be a nontrivial subgroup of \mathbb{O}_{ρ_0} if the group $\Omega_{\delta\rho}$ has the classical subgroup $\mathbb{O}_{\delta\rho} \subset \Omega_{\delta\rho}$ which is an usual assumption.

The broken symmetry approach is useful for the investigation of the local properties of the lattices connected with the local deviations of crystal structures. For the system properties depending on the structure of imperfect crystal as a whole this approach turns out to be too rough. In the latter case a more adequate approach will be the one which is based on the laws of conservation or extension of the abstract symmetry group of a system under consideration [2,9]. In this approach the symmetry group of imperfect crystal in the initial state or after the second order phase transition is a subgroup Ω_ρ of the wreath product $\tilde{P}\{\mathbb{O}_{\text{mod}N}$ which maps onto the initial basic space group $\mathbb{O}_{\rho_0} = \mathbb{O}_{\text{mod}N}$ isomorphically ($\Omega_\rho \leftrightarrow \mathbb{O}_{\rho_0}$) or homomorphically ($\Omega_\rho \rightarrow \mathbb{O}_{\rho_0}$). In this sense the symmetry of a crystal in the full correspondence with magnetic analogy is not decreased but increased through the second order phase transition. Symbolically \mathbb{O}_{ρ_0} goes to Ω_ρ where

$$\Omega_{\rho} \cdot \rho = \Omega_{\delta\rho} \mathbb{O}_{\rho^{\circ}} (\delta\rho + \rho) = \Omega_{\delta\rho} \cdot \delta\rho + \mathbb{O}_{\rho^{\circ}} \cdot \rho^{\circ} = \rho, \Omega_{\rho} = \Omega_{\delta\rho} \mathbb{O}_{\rho^{\circ}} \subseteq \tilde{\Omega}_{\delta\rho} \setminus \mathbb{O}_{\rho^{\circ}}$$

The relations between the groups entering in this symbolic equation are illustrated in Fig. 1.

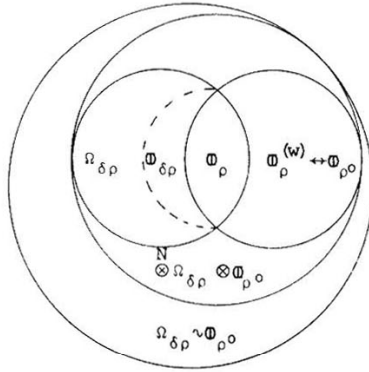


Fig.1

Euler diagrams show the relation between symmetry groups of imperfect crystals with electron density function $\rho(\vec{r}) = \rho^{\circ}(\vec{r}) + \delta\rho(\vec{r})$. In the broken symmetry approach $\tilde{\Omega}_{\rho}^{(q)} = \mathbb{O}_{\rho} = \mathbb{O}_{\delta\rho} \cap \mathbb{O}_{\rho^{\circ}} \subseteq \mathbb{O}_{\rho^{\circ}}$. In the approach of symmetry conservation $\tilde{\Omega}_{\rho}^{(h)} = \mathbb{O}_{\rho}^{(h)} \supseteq \mathbb{O}_{\rho^{\circ}}$ ($h=p, q, w_p, w_q$). In that of symmetry extension $\tilde{\Omega}_{\rho} = G^C \mathbb{O}_{\rho}^{(h)}$ where the proper symmetry of the function $\rho(\vec{r})$ at the fixed point \vec{r} is characterised by appropriate symmetrizer G^C [2,9]. In every case $\tilde{\Omega}_{\rho} \subseteq \tilde{\Omega}_{\delta\rho} \setminus \mathbb{O}_{\rho^{\circ}}$ or $\tilde{\Omega}_{\rho} \subseteq \tilde{\Omega}_{\delta\rho} \mathbb{O}_{\rho^{\circ}}$, $\tilde{\Omega}_{\delta\rho} \subseteq \tilde{\Omega}_{\delta\rho}$, $\mathbb{O}_{\rho^{\circ}} = \mathbb{O}_{\text{mod}N}$.

If one takes into account that the imperfect crystal in the initial state has non-classical space symmetry group Ω_{ρ_1} then the symmetry changing (\Rightarrow) into the state of Ω_{ρ_2} may be performed through the structure phase transitions in three ways:

- 1°. $\mathbb{W}_{\rho_1^o} \Rightarrow \mathbb{W}_{\rho_2^o}, \Omega_{\delta\rho_1} = \Omega_{\delta\rho_2}, \Omega_{\rho_1} = \Omega_{\delta\rho_1} \mathbb{W}_{\rho_1^o} \Rightarrow \Omega_{\delta\rho_1} \mathbb{W}_{\rho_2^o} = \Omega_{\rho_2}$
- 2°. $\mathbb{W}_{\rho_1^o} = \mathbb{W}_{\rho_2^o}, \Omega_{\delta\rho_1} \Rightarrow \Omega_{\delta\rho_2}, \Omega_{\rho_1} = \Omega_{\delta\rho_1} \mathbb{W}_{\rho_1^o} \Rightarrow \Omega_{\delta\rho_2} \mathbb{W}_{\rho_1^o} = \Omega_{\rho_2}$
- 3°. $\mathbb{W}_{\rho_1^o} \Rightarrow \mathbb{W}_{\rho_2^o}, \Omega_{\delta\rho_1} \Rightarrow \Omega_{\delta\rho_2}, \Omega_{\rho_1} = \Omega_{\delta\rho_1} \mathbb{W}_{\rho_1^o} \Rightarrow \Omega_{\delta\rho_2} \mathbb{W}_{\rho_2^o} = \Omega_{\rho_2}$

The case 2° may be realized for instance as the remodulation phase transition $\delta_{\rho_1} \Rightarrow \delta_{\rho_2}$ which doesn't affect (in the adopted approximation) the basic structure $\rho^o(\vec{r})$ and acts in the separate space of internal degrees of freedom of a crystal. As an example of such transitions let us consider the physical behavior of Na_2CO_3 crystal [10].

Figure 2 taken from [10] gives the temperature dependence $\vec{q}_O(T)$ of the stationary space modulation wave vector of Na_2CO_3 crystal between 620° and $4,2^\circ\text{K}$. Above 620°K the crystal has a normal β -phase with the symmetry group $\mathbb{W}_{\rho^o} = C_m^2 = P_{(\vec{a} + \vec{c})/2} \frac{2}{m}$. Below 130°K it has the superstructure δ -phase with the constant wave vector of the commensurate space modulation $\vec{q}_O = \frac{1}{6} \vec{a}^* + \frac{1}{3} \vec{c}^*$ and the generalized W_p -symmetry group $\Omega_{\vec{q}}^{(w)} = P_{(\vec{a} + \vec{c})^*} \frac{2(2z2y)}{m}$ in the phase space $(\Psi, R) = \{(\vec{\psi}, \vec{r})\}$ quite analogous to the spin space $(S, R) = \{(\vec{s}, \vec{r})\}$ of the magnetic crystals. Between 620°K and 130°K according to [10] the crystal has the incommensurate γ -phase with the property of the wave vector of the deformation wave $\vec{q}_O(T_1) \neq \vec{q}_O(T_2)$ if $T_1 \neq T_2$.

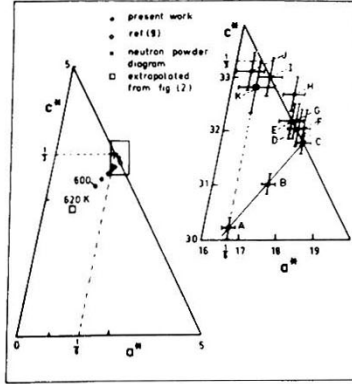
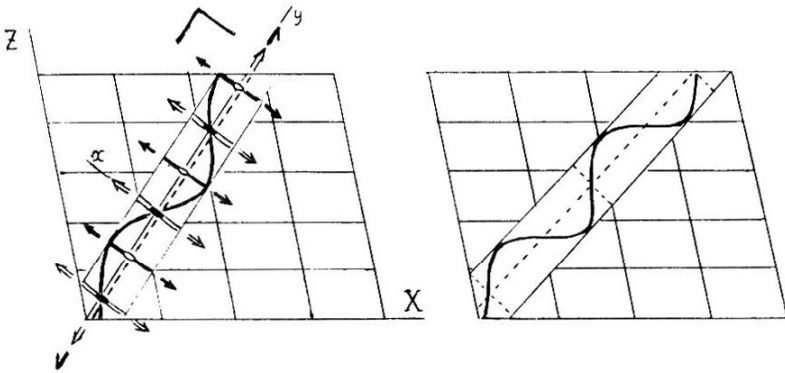


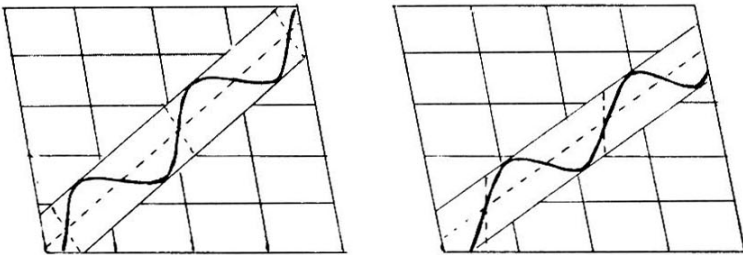
Fig.2 The temperature dependence of the wave vector of the modulated wave for the incommensurate γ_1 (from A to C), γ_2 (C to G), γ_3 (G to I) and commensurate (I to K) δ -phases of Na_2CO_3 crystal in the plane \vec{a}^* , \vec{c}^* of the reciprocal lattice. A: 470°K , B: 370°K , C: 300°K , D: 295°K , E: 275°K , F: 235°K , G: 200°K , H: 175°K , I: 120°K , J: 20°K and K: $4,2^\circ\text{K}$ (according to [10])

But Fig. 2 shows that actually the γ -phase splits at least into two incommensurate phases γ_1 and γ_2 . Let us suppose that the temperature dependence $q_{\vec{a}^*}(T) + \alpha q_{\vec{c}^*}(T) = 0$ of the wave vector between 620° and 300°K corresponds to the homogeneous deformation of the compression of the modulation wave in the direction of \vec{q} . The remodulation phase transition at approximately 300°K may be connected with a shear deformation of the modulation wave. Accordingly the slope of the curve $\vec{q}_0(T)$ changes into $q_{\vec{a}^*}(T) + q_{\vec{c}^*}(T) = \frac{1}{2}$ within the interval 300° to 200°K .

Then follows the complicate remodulation process of the continuous transformation of the modulation wave to the commensurate state which ends at the point 130° K of the lock-in phase transition. The outlined hypothetical scheme is present at Fig. 3.



γ_1 -phase between 620° and 300° K



γ_2 -phase between 300° and 200° K

Fig.3

The hypothetical scheme of the remodulation phase transition $\gamma_1 \rightleftharpoons \gamma_2$ in Na_2CO_3 crystal. In the γ_1 -phase the harmonic atom displacement wave has the proper symmetry group $\hat{\Omega}_{\delta\rho}^{(p)} = 1 \begin{pmatrix} 2^* \\ 2 \end{pmatrix} \otimes P_{(b/2)^*}^{2^*} \frac{2^*(2)}{m^*(b)} \frac{2(2^*)}{m} \frac{2_1(2^*)}{m^*(m)}$ preserving under compressive deformation of the modulating wave in the direction of the local axis y , which lies in the plane XZ of the crystal. Shear deformation change it into centroaffine symmetry group $1 \begin{pmatrix} 2^* \\ 2^* \end{pmatrix} \otimes P_{(b/2)^*}^{2^*} \frac{2^*(2^*)}{m^*(b^*)} \frac{2(2^*)}{m} \frac{2_1(2^*)}{m^*(m^*)}$ of the phase γ_2 . The abstract symmetry group doesn't change through the phase transition $\gamma_1 \rightleftharpoons \gamma_2$ but complex antisymmetry group goes into the centroaffine ones A or A^* . At the fixed level the phase symmetry group $\hat{\Omega}_{\gamma_1}^{(p)}$ goes into subgroup $\hat{\Omega}_{\gamma_2}^{(p)} = 1 \begin{pmatrix} 2^* \\ 2 \end{pmatrix} p1 \frac{2}{m} 1$. The symmetry and complex antisymmetry elements are shown black or white respectively.

In order to receive the Wp-symmetry groups $\hat{\Omega}_\rho$ of the phase modulation of Na_2CO_3 let us take the complex coordinate $Q_{\vec{q}} = \eta e^{i\varphi}$ as the order parameter [8,10] and construct the phase space $\{(\vec{\varphi}, \vec{r})\}$ of the crystal. We shall describe the periodical perturbation of the threedimensional basic structure $\rho^0(\vec{r})$ of Na_2CO_3 in accordance with [11,12] as the phase modulation wave $\vec{r}_{1k} = \vec{r}_1 + \vec{r}_k + \vec{\lambda}_k \cdot \sin(\vec{q}_0 \cdot \vec{r}_1 + \varphi_k)$ where \vec{r}_{1k} is the coordinate of the atom k in the unit cell l . Then we combine each coordinate \vec{r}_{1k} with the appropriate phase vector $\vec{\varphi}_k = (\vec{n}_k, \varphi_k)$ which lies in the local Gaussian plane x, iy at the angle φ_k to the axis x . It is supposed that all the local systems of reference x, iy, z are parallel to each other, the unit vector of the phase normal \vec{n}_k being parallel to the local axis Z and axis Y of the crystal, $y \parallel Z, x \perp Z$ in the plane X, Z .

Symmetry groups which act in the phase space (φ, R) are called phase symmetry groups. They may be obtained from the known magnetic P - symmetry groups [2,3,5,13-15] by replacing the spin inversion operator $1'$ by the operator 1^* of complex conjugation, $1^* Q_{\vec{q}} = Q_{\vec{q}}^*$, i.e. the phase inversion operator $1^* \vec{\varphi}(\vec{r}) = -\vec{\varphi}(\vec{r})$, $1^* \varphi = \varphi + \pi$. Applying the phase equivalency condition $\hat{t} Q_{\vec{q}} = e^{-2\pi i \vec{q} \cdot \vec{c}} \cdot \eta e^{i\varphi} = \eta e^{i\varphi}$ [10] one may verify that Na_2CO_3 crystal has the superstructure parameters $\vec{A} = 2\vec{a} + 2\vec{c}$, $\vec{B} = \vec{b}$, $\vec{C} = 2\vec{a} + \vec{c}$ in the commensurate δ -phase with $\vec{q}_0 = \frac{1}{6} \vec{a}^* + \frac{1}{3} \vec{c}^*$. The nodes of the appropriate superstructure lattice have the phases $(\vec{\varphi}, \vec{r})$ equivalent on modulo 2π while two nodes \vec{r} and $\vec{r} + \frac{\vec{A}}{2}$ have the opposite phases $(\vec{\varphi}, \vec{r})$ and $(-\vec{\varphi}, \vec{r} + \vec{a} + \vec{c})$. Then the junior Wp-symmetry group of δ -phase will be $\Omega_{\vec{\varphi}}^{\text{jun}} = P_{(a+c)^*} \frac{2(2z, 2y)}{m}$ the sense of the color vector $(\vec{a} + \vec{c})^*$ being $(a+c)^* \cdot (\vec{\varphi}, \vec{r}) = (1^* \vec{\varphi}, \vec{r} + \vec{a} + \vec{c}) = (-\vec{\varphi}, \vec{r} + \vec{a} + \vec{c})$ and that of the positional rotation operator being

$$2 \begin{pmatrix} 2z, 2y \\ 1/2, 1/2 \end{pmatrix} \hat{O}(000) = [2z \cdot \hat{O}] (\hat{2}_y(000)) = \pi(101)$$

$$2 \begin{pmatrix} 2z, 2y \\ 1/2, 1/2 \end{pmatrix} [\vec{n}, \frac{\pi}{3}] (100) = [\vec{n}, \hat{2}_y(\frac{\pi}{3})] \hat{O}_y(100) = [\vec{n}, \varphi + \frac{2\pi}{3}] (001) / \text{see Fig.4.}/$$

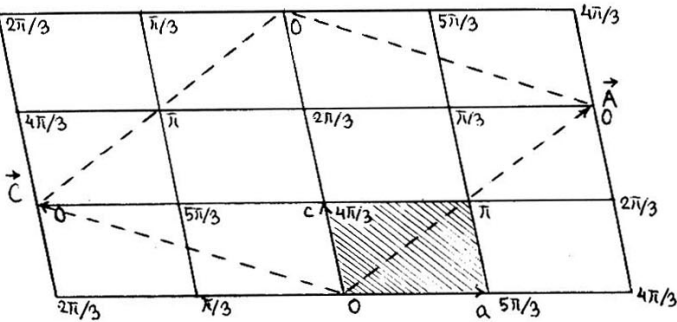


Fig.4 The enlarged unit cell of the superstructure commensurate δ -phase of Na_2CO_3 crystal with the parameters $\vec{A}=2\vec{a}+2\vec{c}$, $\vec{B}=\vec{b}$, $\vec{C}=2\vec{a}+\vec{c}$ according to [10]. The phases of the nodes are shown. Space symmetry group symbol $\Omega_{\delta}^{(w_p)} = 1 \frac{(2^*)}{2} \otimes P_{(a+c)^*} 1 \frac{2(2z, 2y)}{m} 1$ corresponds to the point group of the shaded unit cell.

The results of the full symmetry analysis of some of the modulated phases of Na_2CO_3 may be summarized as follows:

$$\Omega_{\rho} = \Omega_{\delta\rho}^{\text{point}} \otimes \Omega_{\delta\rho}^{\text{space}} \otimes \Omega_{\rho}^{\circ}$$

$$\Omega_{\gamma_1}^{(w_p)} = 1 \frac{(2^*)}{2} \otimes P_{(b/2)^*} \frac{2^*(2)}{m^*(b)} \frac{2(2^*)}{m} \frac{2_1(2^*)}{m^*(m)} \otimes P_{(\vec{a}+\vec{b})/2} 1 \frac{2}{m} 1, 620^{\circ} > T > 300^{\circ}\text{K}$$

$$\Omega_{\gamma_2}^{(w_p)} = 1 \frac{(2^*)}{2} \otimes P 1 \frac{2}{m} 1 \otimes P_{(\vec{a}+\vec{b})/2} 1 \frac{2}{m} 1, 300^{\circ} > T > 200^{\circ}\text{K}$$

$$\Omega_{\delta}^{(w_p)} = 1 \frac{(2^*)}{2} \otimes P_{(a+c)^*} 1 \frac{2(2z, 2y)}{m} 1, T < 130^{\circ}\text{K}$$

where $\Omega_{\delta\rho} \cdot \delta\rho(\vec{r}) = \delta\rho(\vec{r})$, $\Omega_{\delta\rho} = \Omega_{\delta\rho}^{\text{point}} \otimes \Omega_{\delta\rho}^{\text{space}}$. For the full symbol of the $\Omega_{\delta\rho}$ -space group see Fig.3.

One can see that those groups are in close relations with the symmetry group of the normal β -phase $\Omega_{\beta} = 1^* \otimes \Omega_{\beta} = 1^* \otimes P_{a+c} 1 \frac{2}{m} 1$ and that the phase transitions between γ_i and δ -phases are the ones of the phase remodulation types. The direct factor $1 \frac{(2^*)}{2}$ preserves the phase vector at every point of the complanar modulated crystals. $1 \frac{(2^*)}{2} \varphi(\vec{r}) = \varphi(\vec{r})$; the next one gives the proper symmetry groups of the one dimensional modulation wave.

Let us stress in the conclusion that in generalized theory of the structure phase transition one must expand Landau potential in powers of the composed order parameter $\eta_\rho = \eta_{\rho^0} + \eta_{\delta\rho}$ to construct the invariants of the generalized symmetry group $\Omega_\rho = \Omega_{\delta\rho} \Phi_{\rho^0}$ of a crystal with internal degrees of freedom.

The classification of those transitions may be obtained according to the irreducible representation of the group $\Omega_\rho \subseteq \tilde{\Omega}_{\delta\rho} \setminus \Phi_{\rho^0}$. This classification will be more extensive than the ordinary one because all the groups P- and Wp-symmetry Ω_ρ allow the gradient Lifschitz invariant $Q_{\vec{q}} \frac{\partial}{\partial z} Q_{\vec{q}}^* - Q_{\vec{q}}^* \frac{\partial}{\partial z} Q_{\vec{q}}$ without restrictions (compare the analogous result in [10]). In Q and Wq-symmetry approach there may be some restrictions on the space modulation. In any case one can assert that space modulation is not a rarity but a general phenomenon in the crystal world. Then the problem of the space modulation of crystals appears to be a problem of the physical model of the crystal and the choice of approximation. A lot of interesting physical properties of the space modulated crystals (such as the phase and amplitude fluctuations, the polarization waves in dielectrics, the proper and improper ferroelectricity, the lock-in phase transitions etc. [10,16-20]) may be predicted and explained in the frame of the symmetry generalization of the Landau second order phase transition theory.

REFERENCES

1. L. D. Landau, E. M. Lifschitz. Statistical Physics, "Science". Moscow 1976, 3-d Edition, v. 5, part 1, p. 488.
2. A. V. Shubnicov, B. A. Koptsik. Symmetry in Science and Art, Plenum Press, N. Y. 1974.
3. V. A. Koptsik, I. N. Kotzev. Comm. Joint. Inst. Nuclear Research. Dubna (1974) P4-8067, 8068.
4. I. E. Dzialoshinsky, J. Exp. Theor. Phys. (1964), 46, 1420, 47, 336, 992.
5. V. A. Koptsik. Ferroelectrics (1978), 21 499.
6. I. M. Lifschitz. J. Exp. Theor. Phys. (1942), 12, 117, 132, 156; (1947), 17, 1017, 1076.
7. A. M. Stoneham. Theory of defects in solids. Clazendon Press. Oxford, 1975.
8. J. L. Birman. Theory of crystal space groups and infra-red and Raman lattice processes of insulating crystals- Springer-Verlag. Berlin, N. Y. 1974.
9. V. A. Koptsik. In: "Problem of modern crystallography". Ed. by B. K. Vainshtain., "Science". Moscow, 1975, p. 42-60.
10. C. I. de Pater. An experimental study of the incommensurate phase transformations in Rb_2ZnBr_4 and Na_2CO_3 . Delft Univ. of Technology, 1978.
11. A. Janner, T. Janssen. Phys. Rev. (1977), 15, 643.
12. P. M. de Wollf. Acta Cryst. (1974), A30, 777; (1977), A33, 493.

13. V. A. Koptsik. Shubikov groups. Moscow University. 1966.
14. V. A. Koptsik, Zh. N. M. Kuzukeev. Sovjet Crystallography (1972), 17, 705.
15. V. A. Koptsik, I. N. Kotzev. Comm. Joint. Inst. Nuclear Research Dubna (1974) P4-8466; (1975), P4-9664, P4-9665.
16. W. L. McMillan. Phys. Rev. (1976) B14, 1496.
17. T. A. Aslanjan, A. P. Levanuk. Sovjet Physics of Solid State (1977), 19, 1399; (1978), 20, 804, 1259.
18. P. M. Zorky, V. A. Koptsik. In: "Modern problems of the physical chemistry". Moscow University, 1979, v. 14, p. 139-183.
19. V. A. Koptsik, R. A. Evarestov. Sovjet Crystallography (1980), 25, 1.
20. V. A. Koptsik. Reports of Academy of Science USSR (1980), 250, 353.