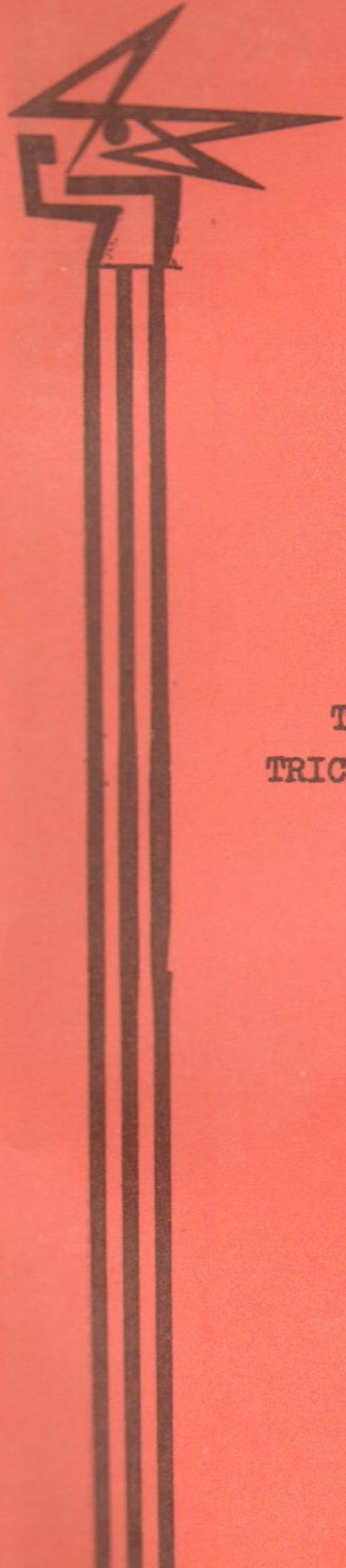


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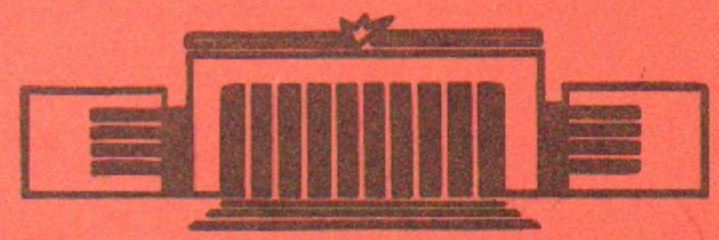
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A.C.Mitus' and A.Z.Patashinskii

THEORY OF CRYSTAL ORDER III.
THE POINT-SYMMETRY OF CRYSTALS WITH
TRICLINIC-SYMMETRY LOCAL ORDER-PARAMETER

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THEORY OF CRYSTAL ORDER III.
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A b s t r a c t

The case of the lowest possible symmetry of the local ordering in the theory of crystal order developed in [1] - [3] is studied. The associated crystal order parameter is a triclinic rank-4 irreducible tensor $\Lambda_{\circ}^{(4)}$. The decomposition of $\Lambda_{\circ}^{(4)}$ into the point-symmetries is given; its geometrical interpretation is proposed. The role of the liquid-crystal order parameter in phase transitions in crystals is investigated. The algorithm of calculations necessary to determine the point symmetry-change at the phase transition is presented.

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1. Introduction

The crystals and the liquids in the vicinity of the crystallization temperature T_c are dense systems with mean distances between the atoms of order of the atom's size. As the result of strong repulsive forces, the thermal kinetic energy can't be the origin of the strong fluctuations of interatomic distances. In such a system, the location of atoms in a volume with the radius of a few interatomic distances, exhibits strong correlations. In other words, in systems considered there exists the local order. The correlations of local order at distances large as compared to the mean nearest-neighbour distance are connected with much smaller energies. The discontinuous changes of the properties of the system associated with the symmetry-change are the phase transitions (melting-crystallization, the lattice-symmetry changes). The statistical mechanics of the homogeneous changes of atoms' ordering plays the principal role in the theory of the crystal's order, proposed in [1]-[3]. The idea that the local structure of the liquid near its crystallization temperature resembles that of the crystal was put forward in Frenkel's kinetic theory of fluids [4]. The articles [1]-[3] give, to some degree, the realization of Frenkel's ideas. In our theory, the local order is described by the set $\Lambda(x)$ of tensor fields. The field $\Lambda(x)$ is described, in point x , by the multiple moments of the density of the components of the system. The multipole moments are calculated in a small volume δV centered in x , with the radius of a few interatomic distances. The experimental data show that at normal temperatures and pressures ($T < 10^3$ °K, $p < 10^2$ atm) the physical point (cluster) contains $\sim 10^2$ atoms. Consequently, the fields $\Lambda(x)$ have the semi-macroscopic character.

The simplest cases with cubic-symmetry local order were studied in [1]-[2]. The global symmetry of the system changes from the isotropic symmetry (liquid) to the cubic one (crystal). The case of the rhombic symmetry of local order was studied in [3]. Such a system exhibits the following phases: liquid, mesophase (the liquid crystal), the cubic, tetragonal and rhombic crystal. For the special values of the interaction constants

the mesophase or the cubic phase don't exist.

In general the local order has the lowest possible symmetry. The aim of this paper is to study the types and properties of the local order parameter $\Lambda(x)$ and the associated phase transitions in the system.

2. The crystal-order hamiltonian

The local order parameter $\Lambda(x)$ characterizes the local order in a small volume δV containing $n_0 \gg 1$ atoms. In order to fix a few first multipole moments a relatively small number of all $3n_0$ cluster's degrees of freedom (DOF) should be fixed. The rest of DOF describe the short-wavelength fluctuations in a cluster itself. The integration of Gibbs distribution over this DOF gives the probability distribution of the configurations $\{\Lambda(x)\}$ of field $\Lambda(x)$

$$w\{\Lambda(x)\} = \exp\left(\frac{\Phi - H\{\Lambda(x)\}}{T}\right) = \sum_{\{\Lambda(x)\}} \exp\left(\frac{F - \hat{H}}{T}\right), \quad (1)$$

where $\sum_{\{\Lambda(x)\}}$ means the summ over all configurations with fixed $\{\Lambda(x)\}$ and \hat{H} is the microscopic hamiltonian of the system. $H\{\Lambda(x)\}$ is the effective hamiltonian of the local order parameter. Note that the description of the cluster in terms of all the multipole moments is one of the versions of the microscopic theory. The number of the multipole moments included and the highest rank of the tensor used in our semi-macroscopic description follow from simple requirements. Namely, these tensors should describe properly the atoms' ordering in any of the phases. In order to distinguish between the crystal and the liquid the tensor with rank $\gamma \gg 4$ are necessary [1]-[3].

The irreducible rank-4 tensor with cubic symmetry was as well applied in the description of the kinetics of the cubic crystal melting in Hess work [5]. The thermodynamic potential and the relaxation equation in [5] were introduced in analogy with the liquid-crystal case.

In statistical theory of crystal order [1]-[3] the essential role is played by the effective hamiltonian $H\{\Lambda(x)\}$. The

multipole corresponding to the higher - rank tensors describe the small-scale characteristics. One expects that the summation over these short-wavelength DOF (see eq. 1) doesn't produce the long-range interactions in $H\{\Lambda\}$. The treatment of the simple models $H\{\Lambda\}$ carried out in papers [1]-[3] shows that at temperatures where the crystal is absolutely stable the crystal order doesn't deviate strongly from an ideal one (i.e. at $T = 0$). Hence, (1) the molecular field approximation can be used and (2) the behaviour of the system near its melting point is practically model-independent.

The general form of the effective hamiltonian of crystal order with two-body interactions only is [1]

$$H = \int \mathcal{H}(x, y) dx dy,$$

$$\mathcal{H}(x, y) = \sum_{k, l} f_{kl}(\Lambda^{(k)}(x); \Lambda^{(l)}(y)) J(|x-y|), \quad (2)$$

where f_{kl} is a scalar function and $\Lambda^{(s)}(x)$ denotes the field of the irreducible rank - s tensor. The function $J(|r|)$, playing the role of the exchange integral, tends quickly to 0 at $|r| > r_0$. The formulas (1) and (2) give the statistical-mechanic description of the semi-macroscopic (cluster) structure of the crystal and the associated phase transitions: liquid-crystal and crystal PT.

The character of the approximation depends on the class of configurations accounted for in the partition function $Z = \int dW\{\Lambda\} \mathcal{D}\Lambda(x)$. For most of the crystals (the crystal is the exception) the rigid-form approximation

$$\Lambda(x) = \hat{g}(x) \Lambda_0; \quad \mathcal{D}\Lambda(x) \equiv d\hat{g}(x), \quad (3)$$

can be applied [1]. Here $\hat{g}(x)$ is the rotation in point x ; Λ_0 is a set of tensor fields that characterize the fixed local order in a given coordinate-frame.

Small form-fluctuations $\delta\Lambda(x)$ can be described in terms of the interaction of $\Lambda(x)$ with a strain field $u_{\alpha\beta}(x)$. The partition function Z can be evaluated in a standard way [6]. In paper [1] this problem was treated in a phenomenological way.

In this paper we apply rigid-form approximation (3) and the corrections aren't taken into account. Consequently, the phase transition is determined by 1) formulas (1) - (7), 2) the measure $d\hat{g}(x)$ and 3) the parameter Λ_0 .

3. The properties of the local order parameter Λ_0

The number n in formula (2) is the smallest rank of the tensor describing fully the orientation in space of the system of crystallographic axes of a given crystal. For all the crystals but the hexagonal ones it is necessary and sufficient to put $n = 4$ ($n = 6$ for hexagonal symmetry). The higher-rank tensors describe the details of the locations of the atoms in a cluster and play the second role in a cluster description of a PT. The symmetry of the even rank tensor physical characteristics of the crystal is uniquely determined by a rank-6 tensor. The symmetry of the physical properties of the crystal is given in terms of point-groups. It can be fully classified with the help of a rank-6 tensor. In this case the "universality class" is the Laue class; the point-groups within a given Laue class can be distinguished by the odd-rank tensors only. Analogously, the rank-4 tensors give rise to the universality classes which are crystallographic syngonies. The details of the classification scheme of the point-symmetries with respect to the crystal order parameter will be published elsewhere.

In this paper the $n = 4$ case is studied ($n = 6$ case can be worked out in a similar way). The local crystal order parameter $\Lambda(x)$ is, in approximation (3), a set of fields $\Lambda^{(k)}(x)$ ($k = 1, \dots, 4$), given by the fixed tensors $\Lambda_0^{(k)}$. $\Lambda_0^{(k)}$ have, in general, the lowest possible point-symmetry, i.e. the triclinic one. The local-order symmetry is given by a "mixture" of all the point symmetries, with coefficients depending on numerical values of the components of $\Lambda_0^{(k)}$. At low temperatures the system's symmetry is the triclinic one; however at elevated temperatures the PT to phases with higher symmetries may occur. Let us decompose the tensors $\Lambda_0^{(k)}$ into point-group invariant tensors. Consider the case $k = 4$, important in the present theory. Denote by P the set of point-symmetry groups that form a basis

for the decomposition of $\Lambda_0^{(4)}$. The rank-4 tensors characterize, as stated before, the crystallographic systems (syngonies), so the set P should be chosen starting from a scheme they obey. Such a scheme is given in Fig. 1 (see, e.g. [7]). Let us study, for definiteness, the set P formed by the following point-symmetries: $m3m, 4/mmm, mmm, 2/m, \bar{1}$. The decomposition of $\Lambda_0^{(4)}$ can be obtained as follows. A G -invariant tensor can be obtained by taking the average of a general tensor A over group G :

$$\langle A \rangle_G = \frac{1}{N} \sum_{g \in G} gA \quad (4)$$

To write down the irreducible rank-4 tensor it is convenient to use the table with the minimal number of components necessary to restore the tensor (see, e.g. [8]). For the triclinic-symmetry tensor one has

$$\Lambda_0^{(4)} = \begin{array}{cccccc} & 11 & 22 & 33 & 23 & 13 & 12 \\ \begin{array}{c} b+c \\ c+a \\ a+b \end{array} & -c & -b & e & g & k \\ & -a & f & h & l \\ & & a+b & -e-f & -g-h & -k-l \end{array} \begin{array}{c} 11 \\ 22 \\ 33 \end{array} ; \quad (5)$$

the other components follow from the internal-symmetry arguments. The coordinate system K , where $\Lambda_0^{(4)}$ is given by (5) forms the crystallophysical coordinate system of a cube. The 48 symmetry-elements of the $m3m$ group (the symmetry group of a cube) are associated with K . One obtains from (4), where $G = m3m, N = 48$ and $A = \Lambda_0^{(4)}$, the $m3m$ -invariant tensor D_{m3m} in this coordinate system. It is useful to extract D_{m3m} from $\Lambda_0^{(4)}$:

$$\Lambda_0^{(4)} \equiv D_{m3m} + (\Lambda_0^{(4)} - D_{m3m}) \equiv D_{m3m} + \Lambda_0^{(4)'} \quad (6)$$

The next step is to extract from $\Lambda_0^{(4)'}$ its tetragonal ($4/mmm$) part. The proper crystallophysical coordinate-system is, of course, the cube's coordinate system K . One can not select, a priori, one of the axes of K along which there lays the long edge of the tetragonal parallelepiped, so the three decompositions are to be constructed. The one that corresponds to the proper orientation of the 4-fold symmetry axis maximizes the tetrago-

nal part $D_{4/mmm}$ of $\Lambda_o^{(4)}$. $D_{4/mmm}$ depends on one parameter only (see below, (8)) so the choice is unique. Subtracting $D_{4/mmm}$ from $\Lambda_o^{(4)}$ one obtains (analogously to (6)) the tensor $\Lambda_o^{(4)11}$. Its rhombic component D_{mmm} can be easily obtained; the crystallophysical coordinate system coincides with K. The tensor $\Lambda_o^{(4)111} = \Lambda_o^{(4)11} - D_{mmm}$ has the triclinic symmetry. $\Lambda_o^{(4)111}$ is the superposition of three monoclinic-symmetry tensors, with the two-fold symmetry axes laying along the axes of the coordinate system K. Note that the superposition of two monoclinic-symmetry tensors has the triclinic symmetry. Hence, it is convenient to split $\Lambda_o^{(4)111}$ into two parts, one ($D_{2/m}$) with a monoclinic (2/m), the other (D_1) with the triclinic symmetry. The decomposition of $\Lambda_o^{(4)}$ into the point-symmetry groups of P is

$$\Lambda_o^{(4)} = \sum_{\alpha \in P} c_\alpha D_\alpha, \quad (7)$$

where D_α is the α -invariant nonor. The decomposition coefficients c_α are introduced to make possible to use the standard form of the tensors D_α . For the symmetries discussed above the standard forms D_α are as follows:

$$\begin{array}{l}
 D_{m3m} = \begin{array}{|c|c|c|} \hline 2 & -1 & -1 \\ \hline & 2 & -1 \\ \hline & & 2 \\ \hline & & & 0 \\ \hline \end{array}; \quad D_{4/mmm} = \begin{array}{|c|c|c|} \hline 1 & -2 & 1 \\ \hline & 1 & 1 \\ \hline & & -2 \\ \hline & & & 0 \\ \hline \end{array} \\
 \\
 D_{mmm} = \begin{array}{|c|c|c|} \hline 1 & 0 & -1 \\ \hline & -1 & 1 \\ \hline & & 0 \\ \hline & & & 0 \\ \hline \end{array}; \quad D_{2/m} = \begin{array}{|c|c|c|c|c|c|} \hline 0 & 0 & 0 & 0 & g & 0 \\ \hline & 0 & 0 & 0 & h & 0 \\ \hline & & 0 & 0 & -g-h & 0 \\ \hline \end{array} \\
 \\
 D_1 = \begin{array}{|c|c|c|c|c|c|} \hline 0 & 0 & 0 & e & 0 & k \\ \hline & 0 & 0 & f & 0 & l \\ \hline & & 0 & -e-f & 0 & -k-l \\ \hline \end{array}
 \end{array} \quad (8)$$

The decomposition coefficients depend on a, b, c:

$$\begin{aligned}
 c_{m3m} &= \frac{1}{3}(a+b+c); \quad c_{4/mmm} = \frac{1}{6}(2c-a-b); \quad c_{mmm} = \frac{1}{2}(b-a) \\
 c_{2/m} &= c_1 = 1
 \end{aligned} \quad (9)$$

Let us make a few comments on the decomposition (7). Firstly, it is only D_{m3m} that has the general form allowed by symmetry requirements. It follows from the procedure described above (formula (6)) that D_α ($\alpha \neq m3m$) does not contain parts more symmetric than α :

$$\sum_{g \in \beta} g D_\alpha = 0, \quad (10)$$

where α is a subgroup of β . This property is to be taken into account while interpreting the symmetry-change at PT. The general and special form of D_α remaind of the general and special simple form of crystals (see, e.g. [8]). Secondly, the set $\{D_\alpha\}$ given by formulas (8) is independent on the initial choice of the coordinate system K. It is not true for the coefficients c_α . The triclinic-symmetry nonor has nine components (see (7)), but only six of them are associated with invariants (i.e. describe the shape of the corresponding volume δV of the system). The other three components fix the coordinate system only. Let's use the arbitrariness of the choice of K to lower the number of non-cubic components of $\Lambda_o^{(4)}$ from 8 to 5. For example, all the three monoclinic tensors can be reduced to the special form $D_{2/m}^{(sp)}$ with $g = -h$ etc (see (8)). On the other hand the number of the independent components of a triclinic-symmetry deviator $\Lambda_o^{(2)}$ (traceless symmetric rank-2 tensor) is 5. This fact makes possible to write down the decomposition (7) in the special coordinate system K_o as follows

$$\Lambda_o^{(4)} = c_{m3m} D_{m3m} + \widetilde{\Lambda_o^{(2)}} \Lambda_o^{(2)}, \quad (11)$$

where tilda " \sim " denotes the irreducible part. Formula (11) is the system of five equations for five unknown components of $\Lambda_o^{(2)}$. In this work it is assumed that the solutions of (11) exist for any of the studied point-symmetries. This assumption

was proved in the case of rhombic symmetry of $\Lambda_o^{(4)}$ and $\Lambda_o^{(2)}$. The scalar version of (11) is

$$L = 1 + m. \quad (12)$$

Here L denotes the number of invariants of $\Lambda_o^{(4)}$ and m is the number of independent components of $\Lambda_o^{(2)}$ for a given point symmetry. Eqs. (11) - (7) can be easily interpreted in geometric terms. $\Lambda_o^{(2)}$ is a liquid-crystal order parameter that is described by an ellipsoid. Using geometric language the cubic, tetragonal and rhombic symmetries correspond to the cube and the ellipsoid with common main axes and the ellipsoid reducing to spheroid, uniaxial and biaxial, respectively. The trigonal symmetry corresponds to the uniaxial ellipsoid laying along one of the main diagonals of the cube. The geometrical representation of $\Lambda_o^{(4)}$ for triclinic and monoclinic symmetries is given by a cube and a biaxial ellipsoid with one common axis for the monoclinic symmetry and no common axes in case of the triclinic symmetry. In the former case the number of DOF that characterize the mutual orientation of the cube and the ellipsoid is one; in the latter-three. The decomposition coefficients determine the dimensions and mutual orientation of the cube and the ellipsoid: C_{m3m} - the cube-side length, $C_{4/mmm}$ together with C_{mmm} - the ellipsoid-axes lengths, φ, ψ, θ (the parameters of the three special monoclinic tensors $D_{2/m}^{(sp)}$) fix the orientation of the ellipsoid's coordinate system with respect to the special crystallophysical coordinate system K_o of the cube.

In the special coordinate system K_o the cubic component $C_{m3m} D_{m3m}$ of $\Lambda_o^{(4)}$ has not, in general, the maximal possible value. In any coordinate system $C_{m3m} \sim \sum_{\alpha_1}^3 (\Lambda_o^{(4)})_{\alpha_1 \alpha_1 \alpha_1 \alpha_1}$. The "maximal-cubic" coordinate system requirement imposes some constraints on the Euler angles E_1, E_2, E_3 . These constraints are not, in general, fulfilled by the solution $E_1^{(o)}, E_2^{(o)}, E_3^{(o)}$ describing the special coordinate system K_o . The geometrical interpretation of the local order parameter $\Lambda_o^{(4)}$, based on formula (11), has the tensorial character. Hence, in any coordinate system the symmetry properties of the local order parameter are that of the system of two figures: the cube and the ellipsoid. It is important that there exists such a coordinate system

where the decomposition (7) does not contain tensors with symmetries lower than of $\Lambda_o^{(4)}$.

4. The symmetry-change at the phase transition

The local crystal-order parameter is given by the tensor fields $D_{m3m}(x)$ and $\Lambda_o^{(2)}(x)$ ($k = 4, n = 4$). The PT in the system studied should be described in terms of these fields. Suppose the crystal has the inversion center. Then the simplest form of hamiltonian (2) is, for $n = 4$ [3]

$$H = H_{cc} + H_{LC} + H_{int}. \quad (13)$$

H_{cc} is the self-crystalline interaction, H_{LC} - the liquid-crystal-type interaction and H_{int} describes the interaction of $D_{m3m}(x)$ with $\Lambda_o^{(2)}(x)$. For examples of the model hamiltonians of the Heisenberg model type see paper [3] where the special case of rhombic symmetry of $\Lambda_o^{(4)}$ was investigated. The spontaneous breakdown of α -symmetry takes place as a phase transition. The most general sequence of PT is given by P. For special values of C_α and φ, ψ, θ some of these phases and PT may disappear; the mesophase may exist. The simplest examples of the symmetry change at PT were examined analytically in paper [3]. In general, the problem of the symmetry change at PT can be solved, in this theory, at least numerically.

When the crystallization takes place into the cubic phase the PT is always the first order one (discontinuous) [1]-[3]. The order parameter for the lower-temperature PT is the rank-2 tensor. The character of the PT is studied, for that case, in works of E.M. Lifshic [9].

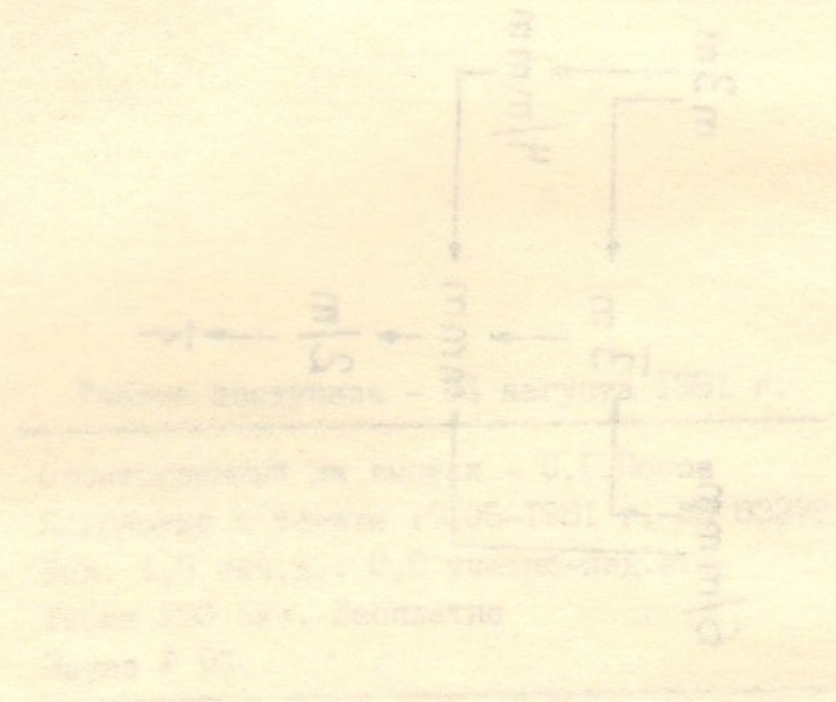
Formula (7) allows one to find the degree of deviation of a given crystal from the cubic one. The dimensions of the lattice elementary cells show that most of the crystals are nearly cubic. For example, in elements with rhombic symmetry (Br₂, Ga, P, S) the non-cubic part of $\Lambda_o^{(4)}$ constitutes less than 20 percents of the cubic part.

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Figure captions

Fig. 1. The relations between the crystallographic syngonies.



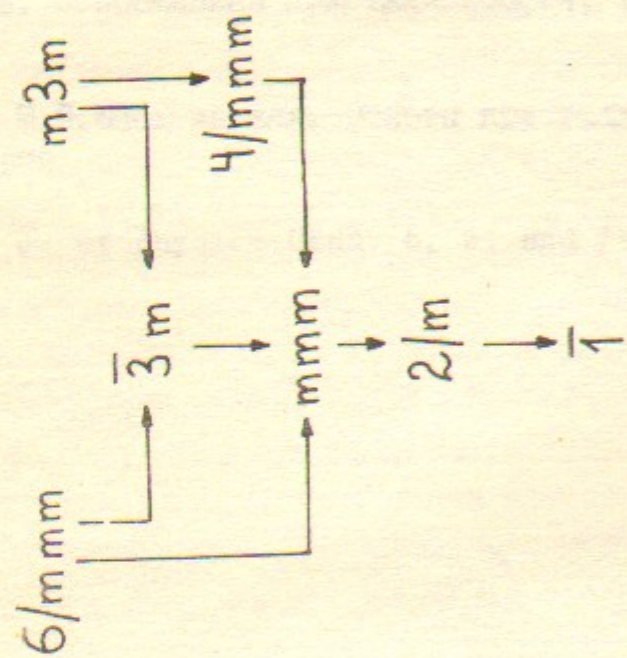


Fig. 1

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