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THEORY OF CRYSTAL ORDER IV. THE CASE OF HEXAGONAL CRYSTALS

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THEORY OF CRYSTAL ORDER IV. THE CASE OF HEXAGONAL CRYSTALS

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A b s t r a c t

Following the general ideas of the theory of crystal ordering, the case of the hexagonal symmetry of the local order parameter is studied. Unlike other point-symmetries, the hexagonal local order parameter is the sixth-rank-tensor. The variety of solutions of the MFA equations is studied. The temperature interval of an overheated (metastable) crystal is small: $\Delta T = 0.04$. The explanation of the non-existence of mesophase in simple hexagonal crystals is proposed.

1. Introduction

The statistical theory of crystal ordering, developed in [1,2], describes the liquid - crystal (melting) phase transition in terms of the local crystal order parameter field $\Lambda(\vec{x})$. The simplest case of the cubic symmetry of parameter $\Lambda(\vec{x})$ was studied in [1,2]. As shown in [3], in case of lower point-symmetry of parameter $\Lambda(\vec{x})$ a set of phase transitions in crystalline phase may exist. The general case of the lowest possible symmetry, the triclinic one, was studied in [4], where the nature of a polymorphic phase transition was examined and the appropriate mathematical apparatus introduced. Briefly, the interaction of various point-symmetries local order parameters results in the existence of the effective "external" field acting on one of the local order parameters. The "external" field is due to the global ordering of the other local order parameter.

The simple symmetry-considerations allow one to determine the symmetry of the low-temperature phase once the symmetry of the higher-temperature phase and the hamiltonian are known. In order to discuss such a problem, the cases of the highest point symmetries of the field $\Lambda(\vec{x})$ should be examined. In standard textbooks on crystallography (see, e.g. [5]) it is shown that any point group is a subgroup either of the cubic (m3m) or the hexagonal ($^{6}/_{mmm}$) group.

The aim of this paper is to introduce the local order parameter for the $^{6}/_{mmm}$ point-symmetry and to find the most important characteristics of the system described by this parameter.

2. The order parameter, hamiltonian and MFA equations

The local order parameter is the smallest-rank irreducible tensor which reflects the characteristic anisotropy of atoms' arrangement. Unlike the other point-symmetries, in the case of $^{6}/_{mmm}$ symmetry it is necessary to introduce the sixth-rank tensors. It can be easily seen that the fourth-rank tensor of $^{6}/_{mmm}$ symmetry is uniaxial (see Herman theorem in [5]).

In order to construct the local order parameter consider the simple geometric figure S of Fig. 1. Note that figure S does not give rise to simple hexagonal Bravais lattice. Nevertheless, figure S reflects properly the characteristic arrangement of atoms in a 6/mmm-symmetry crystal. One can hope that the analogous treatment using more refined figure S will result in the existence of small (numerical) corrections to our present results. Our choice of figure S is due to computational simplifications.

The choice of numerical values of α and B is not a trivial one. In the theory of crystal order only the point-symmetry, of a cluster is fixed; its numerical characteristics are, a priori, undetermined. The most general treatment would be to leave one free parameter, α/B, and then extremizing the final results.

In this article it is supposed that the geometric characteristics of cluster (and figure S) are that of the elementary cell. Such a preposition seems natural and is supported by the following theorem: the number of independent invariants of the local order parameter of a given point-symmetry is equal to the number of parameters describing the corresponding Bravais lattice. In what follows, we take $\alpha = \frac{16}{3}$, $B = 3.16$.

Let' construct tensor $H^{(0)}_{\alpha\beta\gamma\delta\mu\rho}$:

$$H^{(0)}_{\alpha\beta\gamma\delta\mu\rho} = \sum_i n^{(i)}_\alpha n^{(i)}_\beta n^{(i)}_\gamma n^{(i)}_\delta n^{(i)}_\mu n^{(i)}_\rho \,, \qquad (1)$$

where $\vec{n}^{(i)}$ is the radius-vector of the i-th atom of figure S, and the summation extends over all such atoms. In the rigid form approximation [1,2] one has

$$H(\vec{x}) = \hat{g}(\vec{x})\,\tilde{H}^{(0)}, \qquad (2)$$

where tilda denotes the irreducible part of a given tensor and $\hat{g}(\vec{x})$ describes rotation in point $\vec{x}$. Tensor $\tilde{H}^{(0)}_{\alpha\beta\gamma\delta\mu\rho}$ has 10 components in cartesian coordinate system of Fig. 1, two of them linearly independent. For example, for $\tilde{H}^{(0)}_{111111}$ and $\tilde{H}^{(0)}_{333333}$ one has

$$\tilde{H}^{(0)}_{111111} = \frac{1}{231}(281-5B);\quad \tilde{H}^{(0)}_{333333} = \frac{16}{231}(-10+B). \qquad (3)$$

The mean-field approximation (MFA) equations are

$$\frac{1}{\nu} h_{\alpha\beta\gamma\delta\mu\rho} = Z^{-1}\int D\hat{g}\, H_{\alpha\beta\gamma\delta\mu\rho}(\hat{g})\, e^{-\frac{1}{T}H_{MFA}}, \qquad (4)$$

where the MFA hamiltonian is

$$-H_{MFA}(\hat{g}) = H_{\alpha\beta\gamma\delta\mu\rho}(\hat{g})\, h_{\alpha\beta\gamma\delta\mu\rho}, \qquad (5)$$

and the self-consistence condition is

$$h_{\alpha\beta\gamma\delta\mu\rho} = \nu \langle H_{\alpha\beta\gamma\delta\mu\rho} \rangle_{e^{-\frac{1}{T}H_{MFA}}}. \qquad (6)$$

ν is the coordination number, $Z = \int D\hat{g}\, e^{-\frac{1}{T}H_{MFA}}$.

At T = 0 the global ordering in the system is described by formula (3). From here it follows the natural parametrisation for the mean-field tensor $h_{\alpha\beta\gamma\delta\mu\rho}$. One obtains

$$h_{111111}(T) = \frac{\nu}{231}(281a(T) - 5b(T)) \qquad (7a)$$

$$h_{333333}(T) = \frac{16\nu}{231}(-10a(T) + b(T)), \qquad (7b)$$

with a(T), b(T) satysfying obvious conditions

$$a(0) = 1, \quad b(0) = B. \qquad (8)$$

The choice of h_{111111} and h_{333333} as independent components was due to computational simplifications only. Numerical analysis showed that the system of 10 equations, eq. 4, is equivalent to the system of two equations for a(T) and b(T).

The mean-field hamiltonian H_{MFA} (eq. 5) is

$$-H_{MFA} = a(T)(6H_{111111} - 26H_{222222} - 5H_{333333} - 30H_{222233}) + b(T)H_{333333}. \qquad (9)$$

In formula (9) we put $\nu = 1$.

The system of two integral MFA equations was solved numerically. The minimal domain of integration over three Euler angles was determined from the symmetry arguments. The integration was carried out using the Gauss method, with 32 points on each of the axes.

3. The solutions of MFA equations

At high temperatures the only solution of MFA equations (4) is $a(T) = b(T) = 0$ (an isotopic irreducible tensor vanishes).

At $T = 0$ one finds the obvious solution (8) and a non-trivial one

$$a(0)=0 \quad , \quad b(0)=B-10 \tag{10}$$

The physical meaning of solution (10) will be discussed in Sect. 4.

In Fig. 2 the plot of functions $a(T)$, $b(T)$ is given. Curve 1 satisfies conditions (8) at $T = 0$.

In order to examine the physical meaning of these solutions it is necessary to find the thermodynamical potential $\Phi(a,b,T)$ corresponding to MFA equations (4). One finds

$$\Phi(a,b,T)=\frac{8}{231}\left(b^2+562a^2-20ab\right)-T\ln Z. \tag{11}$$

The system of two equations, $\partial\Phi/\partial a=0$ and $\partial\Phi/\partial b=0$ is equivalent to MFA equations (4). With the help of Φ one finds that curve 1 of Fig. 2 describes the solution which is stable for temperatures $T < T_c$, and metastable for $T_c < T < T_c^*$. Here T_c, T_c^* denote the melting temperature and the temperature of crystals absolute instability, respectively. The solution given by curve 2 in Fig. 2 is metastable.

Both for curve 1 and 2, the "negative" and "positive" (i.e. under or over T axis) solution, corresponding to the same temperature are characterized by the same value of Φ, which implies they are equivalent. Consider, for an example the positive and negative solutions, given by curve 1, at $T = 0$. The former describes figure S of Fig. 1, the latter -

- the same figure S in the coordinate system rotated round the $\hat{z}$ axis by $\pi/2$.

The temperature interval of the metastable (overheated) crystal, found with help of Φ is

$$\Xi \equiv \frac{T_c^* - T_c}{T_c^*} = 0.04 \tag{12}$$

Note that this value is twice as much as it is in the cubic-symmetry case [1,2].

4. The mesophase-like solutions

In this paragraph the problem of the existence of stable mesophase-like solutions of eqs. (4) is shortly discussed. Mesophase is characterized by the orientation in space of its order parameter, the director. In our parametrisation (7) such a phase is described by a solution of the following type: $a = 0$, $b \neq 0$. As seen from Fig. 2, and formula (10), such a solution exists. It is, nevertheless, metastable. It explains the well-known experimental fact that for systems which crystallize into h.c.p. lattice the liquid-cuptal mesophase doesn't exist.

In what follows it is shown that this result is of purely geometric origin. Namely, the real hexagonal crystals have h.c.p. lattice built from two simple hexagonal Bravais lattices. The simple hexagonal Bravais lattice is characterized by ratio C/A (C,A - standard parameters of hexagonal-lattice elementary cell, [6]). In case of ideal crystals $C/A = \sqrt{8/3} \approx 1.63$. For real crystal this number varies from 1.56 (Be) to 1.89 (Cd) [6].

We examined the case when $C/A = 2\sqrt{8/3}$. The character of ordering in the system changes drastically as compared to that of Sect. 3. Namely, the liquid phase transforms into the mesophase, which is thermodynamically stable. At still lower temperatures the hexagonal crystal appears.

As it was shown in [4], the effective hamiltonian of space arrangement can be split into two parts, the self-srys-

talline and the liquid-crystal one. The interaction constants depend on geometrical characteristics of the cluster.

In case of hexagonal crystals these coefficients depend on ratio C/A. When $C/A \gtrsim 2\sqrt{8/3}$, the liquid-crystal term in the effective hamiltonian plays the central role at temperatures not too small. For real crystals, with C/A having nearly the ideal value, the self-crystalline part in the hamiltonian is dominant.

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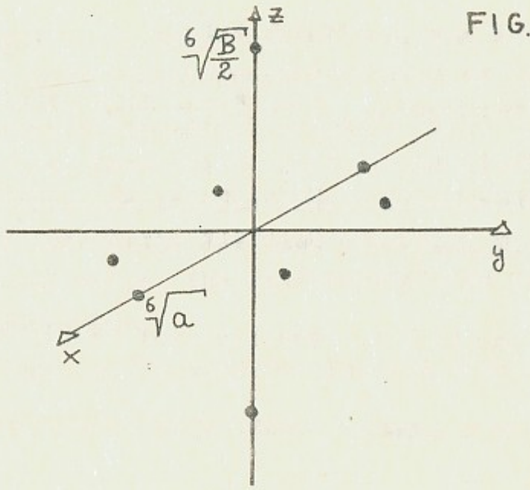

FIG. 1

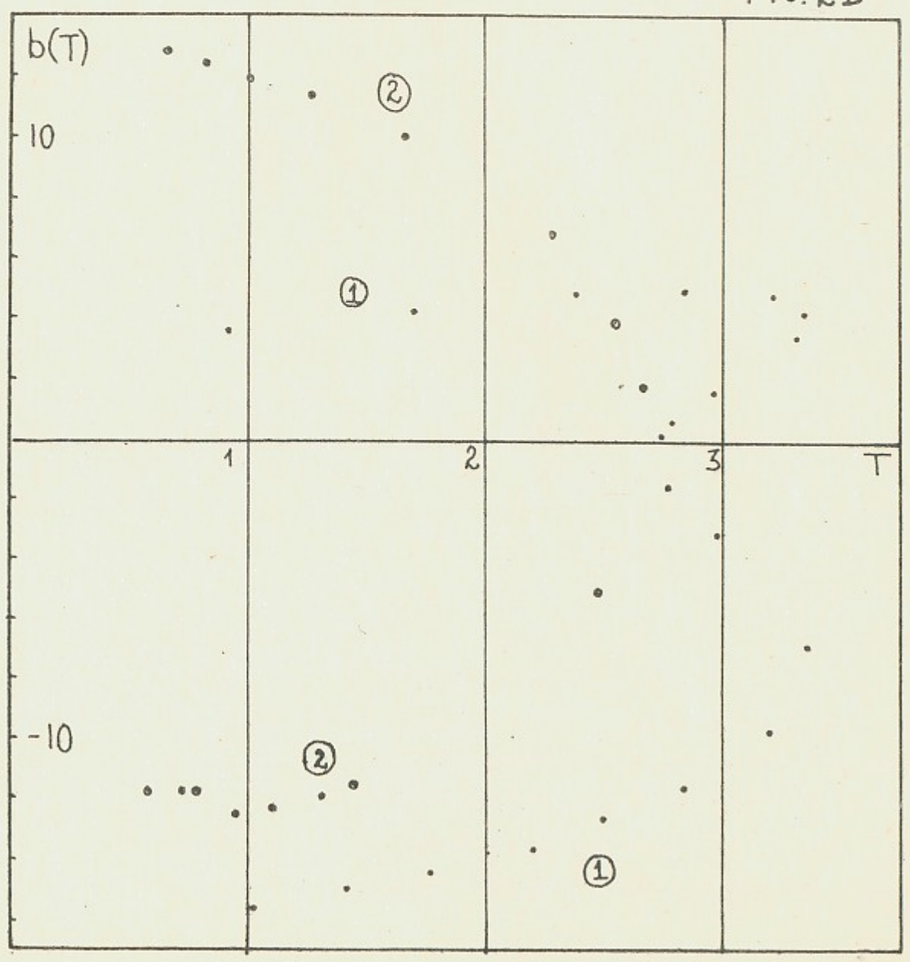

FIG. 2B

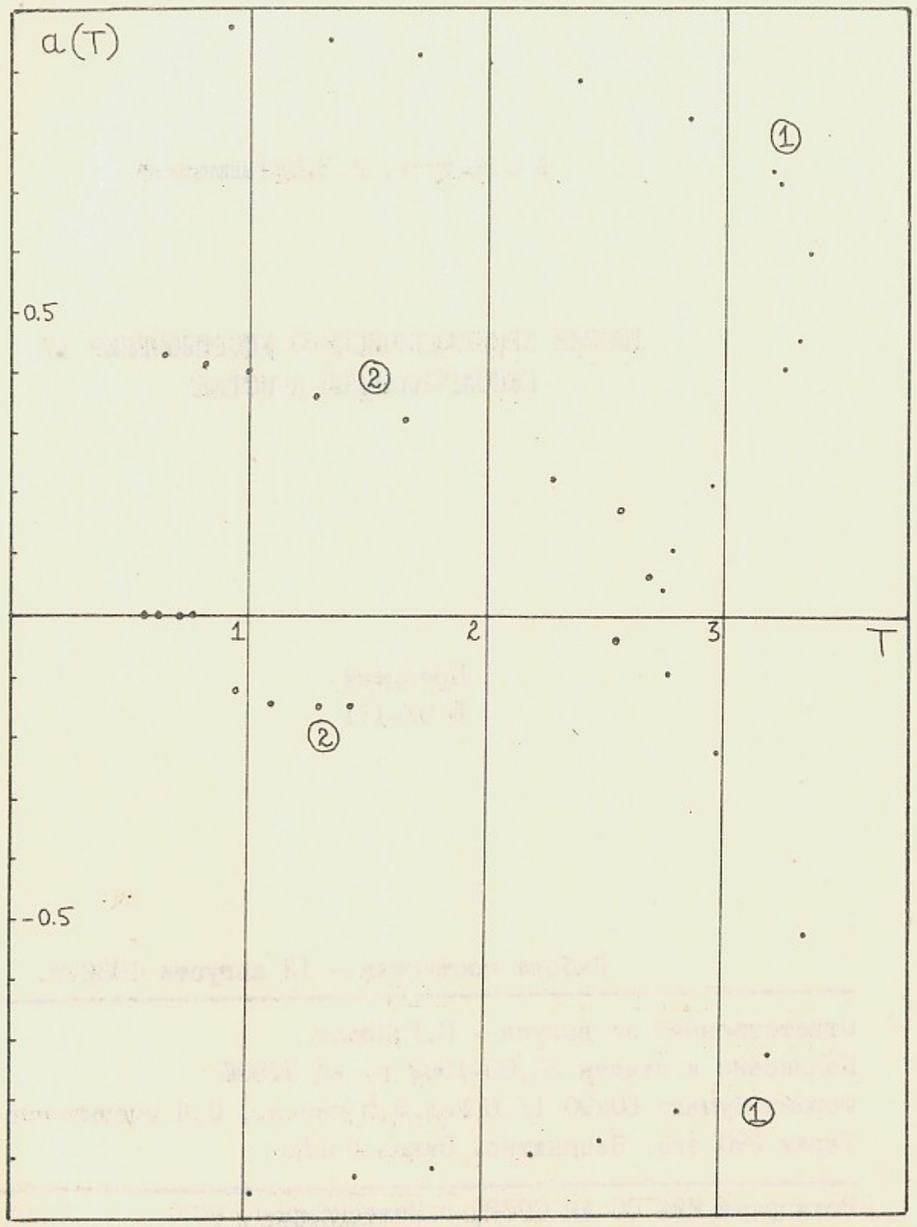

FIG. 2A

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