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EFFECT OF GRAIN-BOUNDARY CONDITIONS ON POLYTYPE TRANSFORMATIONS IN CLOSE-PACKED CRYSTALS

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Within the framework of a modified Ising model, the effect of the boundary conditions ("free ends" and periodic boundary conditions) on the polytype structure stability is studied in close-packed crystals. Using the ground state diagrams, feasible structures and transformation induced by an external field are identified. An analysis of the model system dimensions and long- and short-range many-body interaction on the shape of the ground state diagrams under different boundary conditions is made. The temperature effects on the polytype structure characteristics are discussed in detail. It is shown that both at the absolute zero and finite temperatures, the effects of the boundary conditions on certain properties could be predominant.

INTRODUCTION

Periodicity and boundary conditions do exert a significant influence on properties of a physical system. For one and the same chemical composition, single crystals and fine-grained crystals behave in a qualitatively different fashion. Single crystals are commonly modeled with periodic boundary conditions (PBCs). This approximation works generally well in the case of coarse grains too. The situation is, however, qualitatively different when the grain size or the characteristic size of heterogeneities approach nanometer scale. There is no translational asymmetry, and modeling of systems with PBCs may yield qualitatively erroneous results. In the case of fine grains and a large number of random defects or in a quasiamorphous case, the PBCs tend to become inadequate. It is, therefore, more practical to make use of the "free ends" or free surface boundary conditions. In the latter case, there is no translational asymmetry and the ends (or free surfaces) act as defects. In modeling, nevertheless, use is made of boundary conditions of one type only. It should be noted that it remains unclear whether the results obtained are due to the boundary conditions or the character of interactions in a model calculation. Hence, it makes sense to investigate the influence of boundary conditions on characteristics of a model system, compare the results for different types of conditions and, if the results substantially vary, then the choice of boundary conditions would become really critical. Below, within the framework of an axial Ising model reduced to that of a lattice gas, we present an investigation of such influence using a series of polytype structures being formed in close-packed crystals. The model disregards diffusion and the processes inside the close-packed layer, to say nothing of the electronic effects. The state of the system described by this model is, therefore, non-equilibrium in the general case.

1. GENERALIZED ISING MODEL

The Ising model is based on the concepts of the decisive role of exchange interactions between the first and further structural elements as basic units of crystal lattices in solids in the formation of polytype structures [2]. Its major postulates are as follows.

1. Polytypes are treated as series of different packing versions of structural layers.

2. Stability of polytypes is controlled by the effective energy of inter-layer interaction.

3. Effective interaction energy is a function of temperature, chemical composition, type of specimen preparation, etc. [2].

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In this paper we examine a model crystal within the framework of a generalized Ising model, which consists of close-packed atomic layers wherein the atoms form a regular triangular lattice. In this crystal, every layer may be in one of the following three positions only: *A*, *B* and *C*. The layer arrangement is singularly predetermined by a sequence of these symbols. The principle of close packing is assumed to be valid, and we look at the rearrangements of these layers with respect to each other, with every layer treated as a single whole. In this case, a three-dimensional crystal can be described within a one-dimensional model of lattice gas with the filling numbers $n_i = 1$ (displacement of the neighboring layers in the positive direction – sequences *AB*, *BC*, and *CA*) and $n_i = 0$ (displacement of the neighboring layers in the negative direction – sequences *BA*, *CB*, and *AC*) [3]. For instance, configurations 111111… and 000000… correspond to twinned modifications of 3*C*-lattice, configuration 101010…– hcp 2*H*-structure, 11001100…– 4*H*-lattice, etc. Unity in a configuration means a model lattice gas atom.

A block of $N + 1$ atomic planes corresponds to the lattice gas in N sites. The system possesses 2^N configurations. Each polytype corresponds to a certain type of plane arrangement in a real crystal with period λ measured in the interlayer spacings: $\lambda = 2$ – for 2*H*-lattice, $\lambda = 3$ – for 3*C*-lattice, $\lambda = 4$ – for 4*H*-lattice, etc.

The energy of polytype modifications is calculated using the formula

$$E = \frac{E_0}{\omega_1} = -\sigma \sum_i n_i - \sum_i n_i n_{i+1} - A_2 \sum_i n_i n_{i+2} - A_3 \sum_i n_i n_{i+3} - V n_{4H}, \quad (1)$$

where E_0 is the polytype energy, ω_k is the energy parameter of interaction of model lattice gas atoms in the k-th neighborhood, σ is the characteristic of the external stress field, $n_i = 0(1)$ are the filling numbers for the i-th site, $A_k = \omega_k/\omega_1$ is the relative energy parameter of interaction of the k-th neighbors (it might be obtained from the crystal geometry of a hcp lattice that the energy parameter A_2 characterizes the interaction of atoms of a real crystal in six coordination spheres, while A_3 – does so in ten [1]).

2. GROUND STATE DIAGRAMS

The model used permits us to construct ground state diagrams (GSDs) – the phase stability diagrams in the space of energy parameters at the absolute zero temperature. In the proposed finite size model all possible polytype modifications are taken into account within limits of a block of planes considered. We assume the main state to be a structure whose energy in this range of energy parameter measurement has the largest value compared to the other possible structures. It is useful to consider a plane of energy parameters wherein along one axis there is an external field characteristic σ, and along the other – certain parameters A_2, A_3, and V. This plane is broken into regions where either one polytype or a mixture of polytypes are stable at absolute zero. When the external field is changed, the model undergoes polytype transitions since the image point in the GSD crosses the phase stability boundary line. Transitions are also possible when the alloy component concentration is changed. Under alloying/doping or changing the cooling regime, there is a displacement of the image point across the phase diagram. This corresponds to a change of one of the parameters A_2, A_3, or V.

From the crystal geometry of a hcp lattice it can be obtained that the energy parameter A_2 characterizes interactions of a real crystal atoms in six and A_3 – in ten coordination spheres [1, 2].

Based on the GSD, an analysis is made of the structure stability in a model with PBCs compared to the case with free ends ($N = 4, 5, 6, \ldots, 10$, N is the number of sites in one-dimensional model lattice gas). These results correspond to the case of low temperatures (strictly speaking, the temperature of absolute zero).

To begin with, let us analyze a GSD including interactions of the nearest and next nearest neighbors only in a lattice gas (for $\omega > 0$ and $\omega < 0$, where $\omega \equiv \omega_1$). Primes denote the twinning modifications of the structure (Fig. 1). An analysis of the results demonstrates that in the case of PBCs there is a general decrease in the number of possible polytypes, compared to the boundary conditions where the ends are free. The most common polytypes are those with rhombohedral symmetry (Table 1).

Let us refer to the structures that occur only for one of the boundary conditions as characteristic structures. Their number depends on the value of parameters A_3, relative energy parameter of interactions in the third neighborhood in a model lattice gas, and parameter V influencing stability of 4*H*-structure. Note that for certain values of these parameters

TABLE 1. Number of Rhombohedral Polytypes for Different Interactions

ω	A_3	V	Number of rhombohedral polytypes, %	
			Free ends	PBCs
ω > 0	0	0	60.0	61.5
ω < 0			57.6	74.2
ω > 0	1	0	58.3	66.7
	–1	0	65.4	76.9
ω < 0	1	0	67.6	71.4
	–1	0	71.4	57.9
ω > 0	0	1	65.0	66.7
	0	–1	65.5	71.4
	1	1	58.8	66.7
	1	–1	64.7	62.5
ω < 0	0	1	67.4	73.9
	0	–1	64.5	65.0
	1	1	65.9	69.7
	1	–1	71.4	65.4
Average over the cases considered			64.5	67.9

Note. At $A_2 = A_3 = V = 0$, there are only rhombohedral polytypes for any type of boundary conditions.

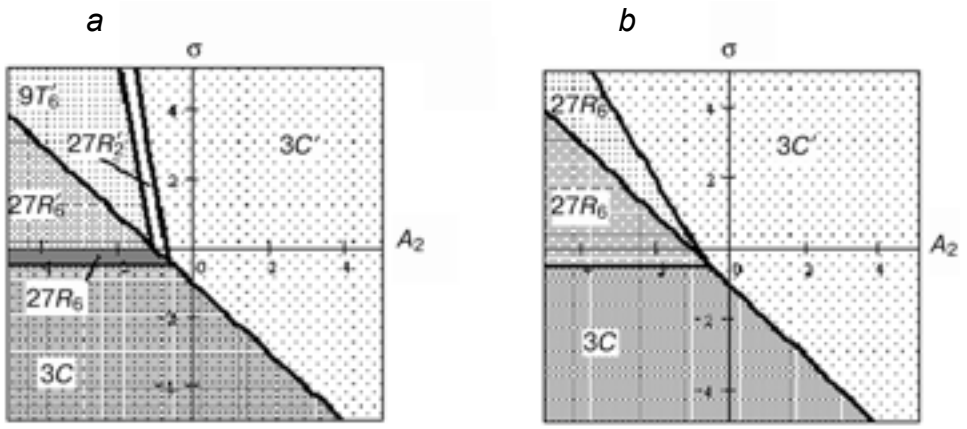

Fig. 1. Ground state diagrams: $N = 9$, $A_3 = V = 0$, ω > 0: free ends (*a*) and PBCs (*b*).

there is an equal number of characteristic structures for a certain type of boundary conditions, while under another boundary condition their number differs by several times if the sign of ω is changed. In particular, at $A_3 = 1$, $V = 0$ and $A_3 = 0$, $V = 1$ (ω > 0, ω < 0), the number of characteristic structures is equal for PBCs, while for the free-ends case they are four and six times as numerous as in the previous case, respectively; at $A_3 = –1$, $V = 0$ and $A_3 = 0$, $V = –1$ (ω > 0, ω < 0), the number of structures coincides in the case of free ends, while for PBCs it differs by a factor of three; at $|A_3| = 1, 2$ and $|V| = 1, 2$ (ω > 0, ω < 0), the number of characteristic structures for PBCs is smaller. Thus, a change in the boundary conditions for a certain type of interactions considerably affects the number of structures being formed.

We calculated the dependence of the average polytype period on the values A_3 and V (Fig. 2). A switch to another type of boundary conditions sometimes results in a qualitative change of this dependence.

The energy parameters are selected on the basis of the analysis of polytype structures for a particular system. From the experimental data on the effects of doping on the number of polytypes and their average length we may find relationship

TABLE 2. Average Period of Polytypes for Different Interactions

Boundary conditions	Average polytype period	
	Free ends	PBCs
$A_2 = A_3 = V = 0$	12.0	12.0
$A_3 = V = 0$	18.5	15.6
$A_3 = 1$, $V = 0$	18.5	19.6
$A_3 = -1$, $V = 0$	18.6	18.5
$A_3 = 0$, $V = 1$	18.6	17.9
$A_3 = 0$, $V = -1$	16.1	19.6
$A_3 = 1$, $V = 1$	18.3	17.9
$A_3 = 1$, $V = -1$	19.6	17.4
Average over the cases considered	17.5	17.3

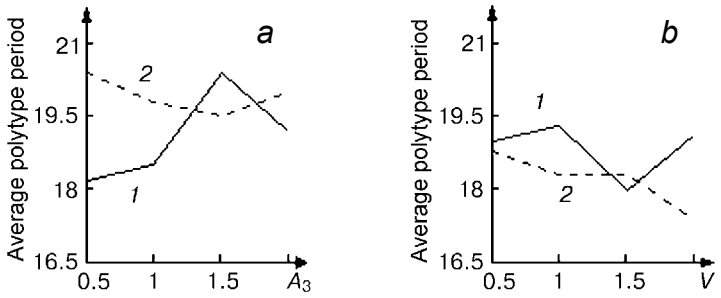

Fig. 2. Dependence of the average polytype period on interaction: free ends (curve *1*) and PBCs (curve *2*); $V = 0$ (*a*) and $A_3 = 0$ (*b*).

between doping by a single component and a change in a certain energy parameter, and select the type of boundary conditions. This would allow us to predict doping by which particular element would give us the required number and how this would affect the average length of the structure period.

Listed in Table 2 are the values of the average polytype period for the boundary conditions considered in this paper. The smallest period is observed in the absence of many-body and long-range interactions, the largest – in the presence of either of these. For the case of free-ends boundary conditions, the average period of polytypes is somewhat larger than for PBCs.

3. INFLUENCE OF TEMPERATURE ON PHASE STABILITY

Let us consider the effects of temperature on stability of polytypes and their average period for different boundary conditions.

When interactions of the atoms in a real crystal are taken into account in a few coordination spheres ($\omega > 0$, $\sigma = A_2 = A_3 = V = 0$), at the absolute zero temperature only fcc-structure is stable. It has been shown via determination of the phase composition at finite temperatures using the Metropolis algorithm [4] that twinning process in an fcc-structure is of a complicated multi-stage character. In the initial stage, considerably large patches of 4*H*, 9*R*, and 2*H* structures are formed, with 4*H* and 9*R* structures predominating (especially at PBCs), the next dominating structure is an fcc structure (3*C*). This is qualitatively supported by the experimental data. In [5], the influence of high-amplitude ultrasonic impact treatment on the structure of austenite steel (Russian standard 45Г17ю3) was investigated experimentally. This treatment results in structural changes: interlayers of hcp 2*H*-martensite and 3*C*-twins are formed. A conclusion is made in [5] that 2*H*-martensite is

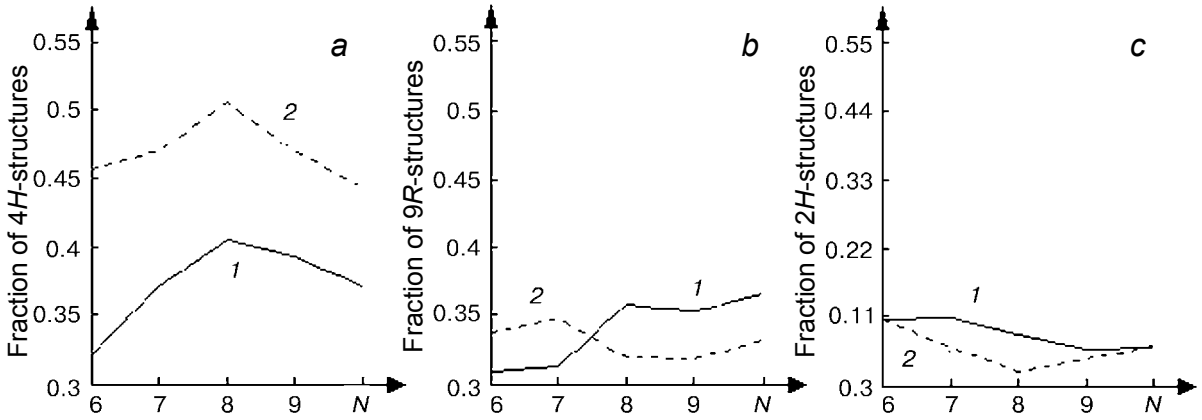

Fig. 3. Dependence of the fraction γ of 4*H*-, 9*R*-, and 2*H*-structures on the number of sites *N* at θ = 0.1: 4*H* (*a*), 9*R* (*b*), and 2*H* (*c*) structures. Free-ends boundary conditions (curve *1*) and PBCs (curve *2*), $\sigma = A_2 = A_3 = V = 0$; $\omega > 0$.

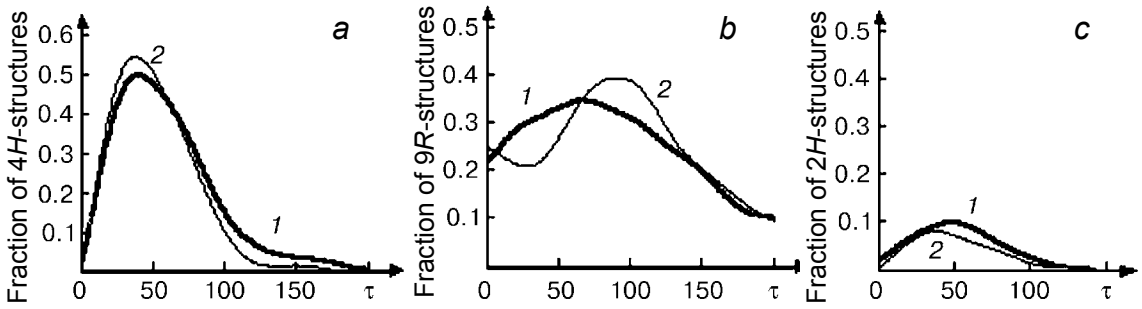

Fig. 4. Dependence of the fraction γ of 4*H*- (*a*), 9*R*- (*b*), and 2*H*-(*c*) structures on time τ (time of the process is measured in Monte Carlo steps per site). Free-ends boundary conditions (curve *1*) and PBCs (curve *2*), $N = 7$; $\sigma = A_2 = A_3 = V = 0$; $\omega > 0$; $\theta = 0.1$.

a transition structure in the course of twinning in 3*C*-structure. A more detailed analysis of this steel after ultrasonic treatment might reveal 4*H* and 9*R* –polytypes as transition structures in twinning.

At low temperatures (θ = 0.1–0.5), for PBCs there is an increase in the fraction of γ 4*H*- and 9*R*-structures, and a decrease in the fraction of 2*H*-polytype compared to the case of free ends (Fig. 3).

The fraction of 9*R* –structure as a function of time may have several extremums at $N = 6$ and 7 (Fig. 4).

The average period of intermediate structures is slightly increased with increasing *N*, its value being larger for PBCs than for the other boundary conditions (Tables 3 and 4), which is different from the case at $T = 0$ (Table 2).

SUMMARY

The investigation conducted permits us to make the following conclusions.

1. Under PBCs, rhombohedral polytype structures predominate compared to the case for free-ends boundary conditions.

2. Under PBCs, there is a decrease in the number of characteristic structures, i.e., those observed under one of the types of boundary conditions only.

TABLE 3. Average Period and Maximal Fractions of γ-Polytypes for Different Model Sizes at the Temperature θ = 0.1

Periodic boundary conditions				
N	γ_{4H}	γ_{9R}	γ_{2H}	$\langle\lambda\rangle$
6	0.347	0.281	0.101	4.932
7	0.411	0.347	0.100	5.393
8	0.398	0.363	0.082	5.494
9	0.366	0.370	0.063	5.523
10	0.372	0.342	0.084	5.340

TABLE 4. Average Period and Maximal Fractions of γ-Polytypes for Different Model Sizes at the Temperature θ = 0.1

Free-ends boundary conditions				
N	γ_{4H}	γ_{9R}	γ_{2H}	$\langle\lambda\rangle$
6	0.443	0.308	0.084	5.207
7	0.463	0.361	0.066	5.563
8	0.531	0.349	0.032	5.593
9	0.423	0.370	0.042	5.601
10	0.445	0.327	0.070	5.337

3. Under different types of boundary conditions, the dependence of the average period of polytypes on interaction may be of a qualitatively different character.

4. In the course of twinning in an fcc- structure under PBCs and finite temperatures, it is 4*H*, 9*R*, and 2*H*-structures that are stable, with the fraction of 4*H* being more than 0.5. Under the free-ends boundary conditions, the fraction of any of the structures in the course of twinning is always smaller than 0.5. Therefore, the kinetic factor under PBCs affects the stability of an intermediate 4*H*-structure in a much stronger way.

Thus, a change of the boundary conditions in the course of modeling polytype transformations qualitatively changes the results in a number of cases. This has to be taken into account when selecting the boundary conditions during investigations of polytype formation in a particular system. This circumstance is of principal importance in the studies of fine-grained materials, surface properties, quasi-onedimensional systems and systems with a large number of random defects or peculiarities in the nanometer size range.

REFERENCES

1. V. N. Udodov, Yu. I. Paskal, A. I. Potekaev, *et. al*., Metal. Fiz. Noveish. Tekhn. 16, No. 5, 43–51 (1994).
2. G. S. Oleinik, O. A. Shevchenko, and N. V. Danilenko, Plytypism in Non-Metal Crystals [in Russian], Kiev (1994), Preprint IMF 94.12.
3. B. N. Nikolin, Multi-Layer Structures and Polytypism in Metal Alloys [in Russian], Kiev, Naukova Dumka (1984).
4. Monte Carlo Methods in Statistical Physics, K.O. Binder (ed.) [Russian translation], Mir, Moscow (1982).
5. O. B. Perevalova, L. A. Kornienko, and V. P. Bezborodova, Fiz. Khim. Obr. Mater., 3, No. 82, 82–87 (1997).