Description of Polymorphic Transformations in Metals Relying on the Cluster Model of Structure Formation

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Abstract

Structure formation processes were considered during polymorphic transformations in metals. A model of polymorphic transitions in metals with face-centered cubic (fcc), hexagonal closed-packed (hcp), and body-centered cubic (bcc) lattices was proposed from the standpoint of the cluster approach. The model is based on the idea of preserving the volume of octahedral cluster elements of the corresponding lattices. It was found that calculation data were in good agreement with the model representations proposed in the paper.

Key words: polymorphous transition, crystal clusters, fcc, hcp, and bcc lattices

INTRODUCTION

Peculiarities of polymorphic transitions in metals have already been attracting the attention of researchers for centuries. Understanding and predicting peculiarities of these processes are of great practical importance, as the latter are carried out in more than a dozen of metals [1–3]. The list of metals able to undergo polymorphic transformations under non-equilibrium conditions is being expanded [4]. Upon research on polymorphic transitions, particular attention is paid to so-called martensite transformation that plays a determining part in the quenching phenomenon [5, 6].

Currently, models of relative shifts of planar grids are generally being attracted to describe changing the type of crystal lattices upon polymeric transitions [7–9]. Similarly to authors of a number of publications on peculiarities of amorphic transformations, we ran into the difficulty to describe structure evolution due to the diversity of designations of atomic planes and vectors of the direct and reverse lattices for structures with different symmetries.

In parallel with a model of plane grids, there was the approach of geometric volumes [10]. The simulation method of cooperative atom movement in symmetric systems with the preservation of their coherency based upon representing each structural state as a combination of elementary crystal clusters is known [11–21]. Let us consider the description of the most common crystal lattices in metals within the cluster model.

Pierson [11] describes the structure of the body-centered cubic (bcc) lattice as a system consisting of six irregular octahedra (Fig. 1, *a*). This octahedron has a height equal to the edge of the cube of the bcc lattice (a) and two other heights equal to $a\sqrt{2}$. Six irregular octahedra make up a dodecahedron with twelve faces with a shape of rhombs (rhombidodecahedron). One height of the diamond is equal to the edge of the body-centered cubic (bcc) lattice, a, whereas another one is $a\sqrt{2}$. Therefore, the described irregular octahedron may be represented as an elementary cluster of the bcc lattice.

According to [13], the face-centered cubic (fcc) lattice may be presented as a combination of one

regular octahedron surrounded by regular tetrahedra linked by common triangle faces (see Fig. 1, *b*). The hexagonal closed-packed (hcp) lattice may be represented as a combination of interconnected pairs of regular octahedra alternating with pairs of regular tetrahedra (see Fig. 1, *c*). Thus, elementary clusters of fcc and hcp lattices are a regular octahedron (all faces of which are equal to cube edge *a*, edges are $a/\sqrt{2}$) and a regular tetrahedron (all heights of which are $a/\sqrt{3}$, edges $a/\sqrt{2}$) [13].

The fcc and hcp lattices are notable for the arrangement of tetrahedra and octahedra. Thus, the interplanar distance, d_{200} of the hcp lattice is equal to d_{111} of the fcc lattice. Therefore one lattice may readily move to another one with minor displacements of individual atoms. Their maximum value is $a/\sqrt{6}$, as demonstrated, for example, in [22].

Let us emphasize that faces of octahedral and tetrahedral clusters making up the fcc or hcp lattice are equal within a crystal lattice of one type (see Fig. 1, *b*, *c*). A great number of transitions from hcp into fcc when increasing temperature are known in the literature; they are easily explainable [13].

Let us emphasize that faces of octahedral and tetrahedral clusters making up the fcc or hcp lattice are equal within a crystal lattice of one type (see Fig. 1, *b*, *c*). A great number of transitions from hcp into fcc when increasing temperature are known in the literature; they are easily explainable [13]. It is known that the space fill density in hcp and fcc lattices is identical and amounts to 0.74. The grid model of crystal structures assumes the location of triangular grids in the fcc lattice according to the system *ABCABC*, whereas in the hcp lattice − in accordance with *ABABAB*. Thus, in order to pass to the fcc lattice from the hcp one, it is sufficient to transfer one planar triangular grid from the ABC series by a value of $a/\sqrt{6}$. Nevertheless, in reality, this operation is impossible, whereas shifting separate atoms is quite likely.

The bcc−hcp transition is explained ambiguously [11]. In our view [22], upon phase transformation, atoms of the bcc lattice may become shifted onto a distance of $0.15 \times a$ of the fcc lattice (this distance is shown by the arrows in Fig. 2).

A similar approach may be suggested for a transition of the bcc lattice into fcc. To that end, it is similarly required to transfer the irregular octahedron of the bcc lattice into the regular octahedron of the bcc one.

Upon great stresses, lengths of all interatomic bonds tend to "align", which is easily explained by the repulsion energy, which is usually described by B/r^n potentials where r is the interatomic distance; n is a natural series of numbers; B is a constant [23].

As demonstrated by the author of [23], repulsion in symmetric structures, such as fcc lattice clusters, is of a much smaller role. Upon high pressures, when system energy is mainly determined by repulsion forces, structures with almost the same bond length turn out to be most stable [23].

As demonstrated in Fig. 2, the green octahedral cluster of bcc is significantly inferior to the
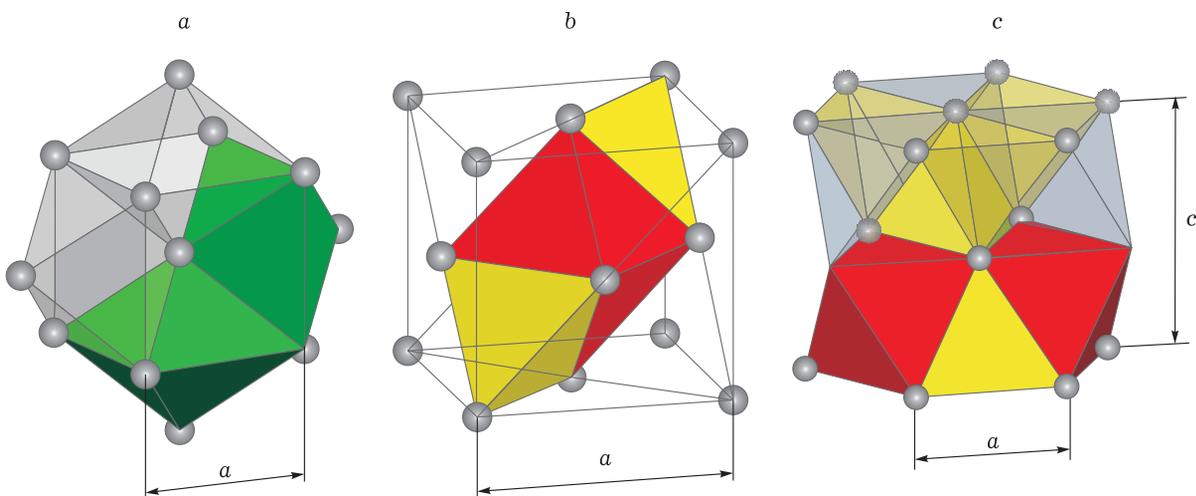
Fig. 1. Cluster representation of crystal structures: *a* − octahedral clusters of the body-centered cubic (bcc) lattice [11], *b* − rhombohedral cluster unit of the face-centered cubic (fcc) lattice [13] consisting of tetrahedral clusters, and *c* − cluster unit of the face-centered close-packed (fcp) lattice
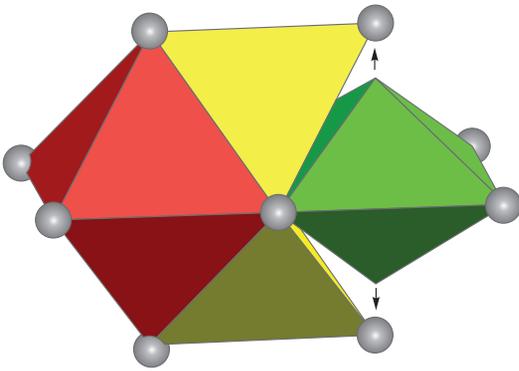
Fig. 2. Formation of the face-centered cubic (fcc) lattice based on the octahedral cluster of the body-centered cubic (bcc) one (errors indicate a shift of bcc atoms and the position of fcc species) [22].

red octahedral fcc one according to its volume. Nevertheless, *according to our hypothesis, the volumes of these two cluster elements should be similar*. This may be reached by small displacements of cluster atoms from their idealised positions (see Fig. 2).

In order to analyse an opportunity for this transition, the calculation of geometric parameters for the regular octahedron of the fcc or hcp

lattice and for the irregular octahedron was made. Figure 3 gives the volume of the regular and irregular octahedra of the bcc lattice *vs* edge length, and also a parameter of irregular octahedron of the fcc lattice made of regular octahedra with a given edge length.

Let us give an example of the use of a nomograph. Cobalt undergoes the β-Co → α-Co transition at 450 °C (Table 1); β-Co has the crystal bcc lattice with parameter $a = 3.554$ Å, α-Co − the hcp lattice with parameter $a = 2.514$ Å. According to the cluster model of structure formation, the β-Co → α-Co transition is a small displacement of atoms of elementary crystal clusters at a distance less than the interatomic one in such a way that the order of the octahedra and tetrahedra in the initial hcc and finite hcp lattices is changed (see Fig. 1, *b* and *c*). An important point is that elementary octahedral and tetrahedral clusters should preserve their volume during transformation in accordance with our hypothesis.

In order to analyse this transition, let us use the nomograph in Fig. 3. Find a parameter of the crystal fcc lattice corresponding to β-Co and draw arrow *1* onto the line that describes the volume of the initial octahedron of the fcc phase. Knowing
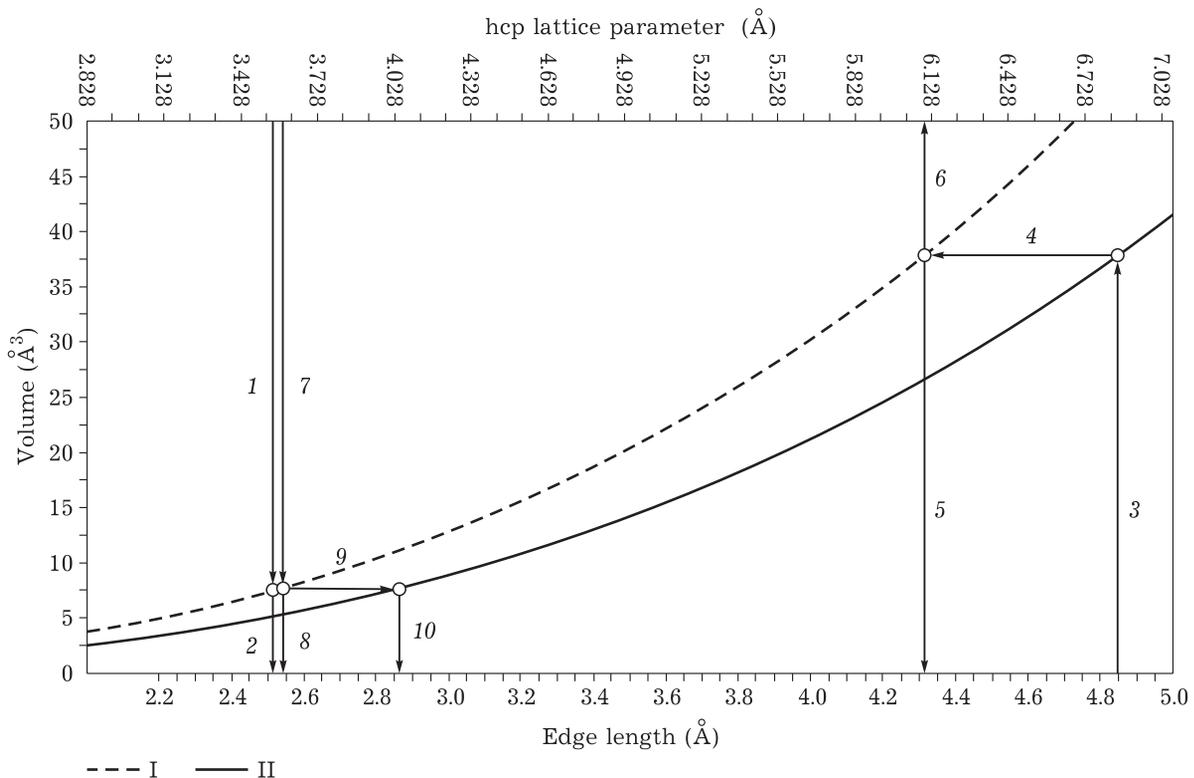
Fig. 3. Nomograph for determination of lattice parameters upon polymorphic transitions in metals, I and II are volumes of the regular octahedron of fcc or fcp lattice (I) and the irregular octahedron of the bcc lattice (II) with a given edge. *1−10* are auxiliary lines (see text).

TABLE 1

Experimental and calculated lattice parameters of phases experiencing polymorphic transformations

Transformation	Lattice type		Lattice parameter a, Å			
	Initial	Final	Initial	Final		
				Experimental	Calculated	Difference, %
β-Co → α-Co	fcc	fcp	3.554	2.514	2.513	0.04
δ-Fe → γ-Fe	bcc	fcc	2.93	3.671	3.692	−0.56
γ-Fe → α-Fe	fcc	bcc	3.65	2.89	2.897	−0.24
δ-Mn → γ-Mn	bcc	fcc	3.08	3.862	3.881	−0.48
β-Ca → α-Ca	fcp	fcc	3.94	5.56	5.572	−0.22
β-Li → α-Li	bcc	fcp	3.5093	3.086	3.126	−1.31
β-Th → α-Th	bcc	fcc	4.12	5.0843	5.191	−2.10
γ-Sr → β-Sr	bcc	fcp	4.85	4.32	4.321	−0.02
β-Sr → α-Sr	fcp	fcc	4.32	6.085	6.109	−0.40
γ-La → β-La	bcc	fcc	4.26	5.296	5.367	−1.35
β-La → α-La	fcc	fcp	5.296	3.754	3.745	0.24
β-Tl → α-Tl	bcc	fcp	3.882	3.456	3.458	−0.07
β-Ti → α-Ti	bcc	fcp	3.28	2.951	2.922	0.98
β-Zr → α-Zr	bcc	fcp	3.62	3.232	3.225	0.21
β-Hf → α-Hf	bcc	fcp	3.615	3.195	3.221	−0.80
δ-Ce → γ-Ce	bcc	fcc	4.12	5.143	5.191	−0.93
γ-Ce → β-Ce	fcc	fcp	5.143	3.65	3.637	0.37

Note. Data of the first five columns are given according to [24].

that the volumes of octahedra of the initial and final phases should match, and therefore their verges have to coincide, too, we draw an arrow that describes the verge length of the hcp phase octahedron. Parameter a of this phase is equal to the edge length of the regular octahedron (and tetrahedron) of the hcp lattice (see Fig. 1, *c*), therefore arrow *2* is likely to indicate its value. In fact, this characteristic is 2.514 Å (see Fig. 3 and Table 1 data).

Consider another example of work with a nomogram. It is known that upon cooling, strontium undergoes two equilibrium phase transitions: γ-Sr → β-Sr and β-Sr → α-Sr at 605 and 215 °C, respectively. Table 1 presents characteristics of the corresponding phases. Let us explore lattice parameters of strontium upon phase transitions. The γ-Sr (bcc) → β-Sr (hcp) transition may be monitored on the basis of the hypothesis regarding the equality of the volumes of the initial irregular octahedron of bcc and the final, regular octahedron of hcp. To that end, let us find the parameter that corresponds to the verge length of the irregular octahedron of the bcc lattice (is in agreement with parameter a of the crystal bcc lattice, see Fig. 1, *a*). Let us determine the volume of the irregular octahedron of the bcc lattice according to arrow *3* in Fig. 3. According to

arrow *4*, define the volume of the regular octahedron of the hcp lattice corresponding to the initial irregular bcc octahedron by volume, whereas in accordance to arrow *5* − the verge length of the regular octahedron of the hcp lattice (coinciding with parameter a). Again, as in case with cobalt, there is a close agreement of parameters of the actual phase transition and the description made on the basis of the cluster model. The β-Sr (hcp) → α-Sr (fcc) transition is monitored according to arrow *6* and demonstrates a close agreement with the experiment (see Fig. 3 and Table 1).

Based upon this model, calculations of crystal lattices parameters for elements that undergo phase transitions in the equilibrium state were made (see Table 1). Experimental data regarding types and parameters of crystal lattices taken from [24] are listed here, too.

It can be seen that the proposed method makes it possible to model lattice parameters for phases formed upon polymorphic transformations for most pure metals with an error not exceeding 1 %.

Satisfactory results were acquired upon analysis of not only pure metals but also some alloys. Let us consider the phase transition in iron-manganese alloys with a manganese content of 15 %. According to the data of [25], there may be solid solutions of manganese in crystal lattices based

on α-(bcc), γ-(fcc), and и ε-(hcp) of iron present therein with a parameters of 2.868, 3.586, and 2.535 Å, respectively. One may monitor the fcc $\rightarrow$ hcp $\rightarrow$ bcc transition in this alloy according to lines $7-10$ (see Fig. 3).

When decoding the electronic diffraction pattern obtained from the neck of the titanium nickelide sample stretched until the fracture, paper [26] determined the following phases with a parameters: austenite with the bcc-structure, B2, 3.28 Å; martensite with the hcp structure, B19′, 2.89 Å, and the phase with the fcc structure, 4.10 Å. Paper [22] proved an opportunity to carry out the martensitic transition in titanium nickelide *via* an intermediate phase of the fcc structure with a parameter of 4.10 Å. Mutual transitions of the indicated phases may be monitored according to the nomograph presented in Fig. 3.

CONCLUSION

It has been demonstrated that within the cluster structure formation approach originally outlined in papers by Laves and Pierson and continued in those by Bulienkov, Kraposhnin, *etc.*, it is possible to elaborate cluster schemes. The latter make it possible to adequately simulate crystal lattice parameters of phases upon polymorphic transformations in both metals and some metal alloys.

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