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Influence of Ferroelastic Phase Transitions on the Spatial Distribution of Point Defects in Real Solids

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The crystallographic sites available for the point defects in the unit cells of the Ti-Ni, Au-Cd, Heusler alloys and vanadium crystals have been considered. Two different effects have been analyzed: i) spatial redistribution of point defects during the ferroelastic phase transitions (such as martensitic transformations in the Ti-Ni, Au-Cd and Heusler alloys); ii) deformation of crystal lattice caused by the hydrogen ordering in the course of hydrogen absorption in vanadium. The configurational order parameters describing the spatial symmetry of defect or hydrogen system have been constructed from the probabilities of crystallographic sites occupation by the defects or hydrogen atoms, respectively.

Keywords: Crystal defects, Symmetry, Order parameter, Shape memory alloys, Hydrogen in metals.

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1. INTRODUCTION

It is of common knowledge that the existence of crystal defects and their spatial reconfiguration due to the diffusion process can drastically change the physical characteristics of crystalline solids. As so, the theory of phase transitions in the real crystalline solids should take into account the symmetry of crystal cells and positions of point defects in them. The physical effects caused by reconfiguration of defects system are especially pronounced in the case of ferroelastic phase transitions, which are the first-order phase transitions accompanied by the "spontaneous" deformation of crystal lattice and lowering of its symmetry. The martensitic transformations (MTs) of shape memory alloys (SMAs) are the most studied ferroelastic phase transitions [1, 2] and the Landau theory of phase transitions is used for theoretical description of MTs in the ideal crystals [3]. The MTs in the Heusler alloys attract special attention of researches because these alloys exhibit not only MTs, but different types of magnetic phase transitions as well [2]. The Ti-Ni alloys are widely known due to their medical applications [4]. Martensitic transformations of Au-Cd alloys are interesting in the academic aspect [5].

The SMAs undergo MTs from the high-symmetry (austenitic) phase to the low-symmetry (martensitic) phase [1]. The MTs of shape memory alloy are characterized by the “spontaneous” deformation of cubic crystal lattice, which arises on cooling of the alloy, or so-called “superelastic” deformation caused by the mechanical stressing. (These kinds of deformational behavior of SMAs are referred to as the temperature-induced and stress-induced MTs.) The spatial distribution of crystal defects in the high-temperature phase conforms with the cubic symmetry of crystal lattice and corresponds to zero value of configurational order parameter, while the deformation of crystal lattice during MT leads to the spatial reconfiguration of crystallographic defects [6-8] and appearance of non-zero value of this parameter. Numerous technical and medical applications of SMAs demands thorough theoretical analysis of defect influence on the characteristics of these alloys.

The Landau theory of ferroelastic phase transitions in the crystals with defects was developed in Refs. [7, 8]. This theory is referred to as the symmetry-conforming theory. The basic conception of this theory is the introduction of configurational order parameter, which is composed of the probabilities of occupation of certain crystallographic positions by crystal defects. This order parameter appeared to be transformationally equivalent to the multicomponent order parameter of ferroelastic phase transition, which, as commonly known, is composed of the strain tensor components.

In Refs. [7, 8] the cubic-tetragonal and cubic-rhombohedral phase transitions in SMAs were considered. The point defects were assumed to be located in the face centers and corners of cubic unit cell of the simple crystal lattice, respectively, to enable the construction of configurational order parameters, which are transformationally equivalent to the order parameters of phase transitions. It should be emphasized, however, that the atomic structure of the crystal cells of real SMAs and the types of point defects existing in these alloys were not specified.

Another kind of widely studied phase transitions of ferroelastic type are the phase transitions in the system of hydrogen atoms absorbed by metals [9, 10].

In the present article the general basis of symmetry-conforming theory is supplemented by consideration of real positions of point defects in the crystal cell of Ni-Mn-Ga Heusler alloy, Ti-Ni and Au-Cd alloys. The configurational order parameters corresponding to the diffusion of point defects between these positions are constructed. The order parameter, which describes the phase transition caused by the diffusion of hydrogen atoms in the body-centered cubic lattice of metal, is constructed.

2. ORDER PARAMETERS OF FERROELASTIC PHASE TRANSITIONS

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The free energy of the deformed ideal crystal can be expressed in terms of the multicomponent order parameter of ferroelastic phase transition. The ferroelastic phase transitions in different solids are always the first-order phase transitions because the Landau expansion of the free energy in terms of the multicomponent order parameter u_α contains the third-power terms u_α^3 and $u_\alpha u_\beta^2$. The order parameter components of cubic-tetragonal and cubic-rhombohedral phase transitions are the linear combinations of strain tensor components ε_{ik} $(i,k = x,y,z)$. The value

$$u_1 = (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})/3, \quad (1)$$

describes the isotropic expansion or contraction of the crystal lattice,

$$u_2 = \sqrt{3}(\varepsilon_{xx} - \varepsilon_{yy}), \qquad u_3 = 2\varepsilon_{zz} - \varepsilon_{yy} - \varepsilon_{xx}, \quad (2)$$

and

$$u_4 = \varepsilon_{yz}, \quad u_5 = \varepsilon_{xz}, \quad u_6 = \varepsilon_{xy} \quad (3)$$

are the order parameter components of the cubic-tetragonal and cubic-rhombohedral phase transitions, respectively. From the mathematical point of view, the values (2) and (3) are the basic functions of two- and three-dimensional irreducible representations of the cubic group, respectively.

To describe the spatial redistribution (diffusion) of point defects between the different crystallographic positions, the configurational order parameter must be introduced in consideration. As it was shown in Refs. [7, 8], the multicomponent configurational order parameters η_α, which are transformationally equivalent to the order parameters of cubic-tetragonal and cubic-rhombohedral ferroelastic phase transitions, can be presented as the linear combinations of probabilities of occupation of certain crystallographic sites by point defects. The procedure of "construction" of these order parameters is explained below for the intensively studied crystalline solids.

3. CONFIGURATIONAL ORDER PARAMETERS COMPOSED FOR REAL SHAPE MEMORY ALLOYS

3.1 Heusler Alloy

The Ni-Mn-Ga alloy, which undergoes cubic-tetragonal MT, is probably the most widely studied Heusler SMA. The crystallographic cell of Ni_2MnGa alloy is shown in the Figure 1(a). Four types of symmetric crystallographic positions can be marked out in this cell: Mn1, located in cubic face centres, Mn2, located in cubic cell corners, Ga, located in centres of cubic edges, and positions of Ni atoms, which form the cube of smaller size, with the center situated at the center of crystallographic cell.

After MT the cubic lattice appears to be tetragonal, so let us consider how tetragonal deformation will change the symmetry of spatial distribution of defects (probabilities of their location at the certain crystallographic sites).

For the sake of simplicity let's consider the point defects (vacancies, substitutional atoms or antisite defects) located in the crystallographic positions of one type, for example Mn1. Figure 1(b) shows the symmetric Mn1 positions and probabilities P_x, P_y and P_z of occupation of these positions by point defects. It is easy to conclude, that the nonzero values of deformations Eq. (2) appeared after MT mandatory induce the nonzero values of two-component order parameter

$$\eta_2 = \sqrt{3}r_A(P_x - P_y), \ \eta_3 = r_A(2P_z - P_y - P_x), \quad (4)$$

where r_A is the defect concentration, the value η_1 is defined as $\eta_1 = r_A(P_x + P_y + P_z) = r_A$. This conclusion follows from the Table 1, which shows the transformation of probabilities and strain tensor components by the generating elements of the cubic symmetry group ($\hat{1}$ is the inversion operation, 4_y and 4_z are the fourth-fold rotations around *y*- and *z*-axes, respectively). The generating elements of the cubic symmetry group interchange the atomic sites shown in Figure 1(b), and therefore, renumber the probabilities as it is shown in Table 1. As it is seen, the transformational properties of probabilities P_i are similar to those of strain tensor components ε_{ii}, and therefore, not only u_2, u_3, but η_2, η_3 as well, are the basic functions of two-dimensional irreducible representation of cubic symmetry group. According to the Curie principle, the transformationally equivalent physical values are linearly interrelated with each other. In the given case it means that the deformation described by the nonzero value u_2 or u_3, immediately leads to the appearance of nonzero component η_2 or η_3 (respectively), and vise versa, spatial redistribution of point defects, which result in the nonzero values η_2 or η_3, must be accompanied by the deformation of crystal lattice characterized by the nonzero value u_2 or u_3, (respectively).

Table 1 – Transformation of probabilities and strain tensor components by the generating symmetry operations of the cubic group.

	P_x	P_y	P_z	ε_{xx}	ε_{yy}	ε_{zz}
$\hat{1}$	P_x	P_y	P_z	ε_{xx}	ε_{yy}	ε_{zz}
4_y	P_z	P_y	P_x	ε_{zz}	ε_{yy}	ε_{xx}
4_z	P_y	P_x	P_z	ε_{yy}	ε_{xx}	ε_{zz}

The formal conclusion about the strict interrelationship between the deformation of crystal lattice and redistribution of crystal defects can be explained physically. Indeed, it is obvious that all faces of the cubic cell are physically equivalent, and therefore, the probabilities P_x, P_y and P_z are equal to each other. The rectangular side faces of tetragonal cell are not physically equivalent to its square bases, and therefore, for the tetragonal crystallographic cell with the principal axis || Oz the relationships $P_x = P_y \neq P_z$ must take place.

It is easy to see that the considerations presented above for Mn1 spatial positions are true also for the point defects located at Ga sites. This statement is illustrated by the Figure 1(c), which shows the Ga positions located in the centres of the edges of cubic cell.

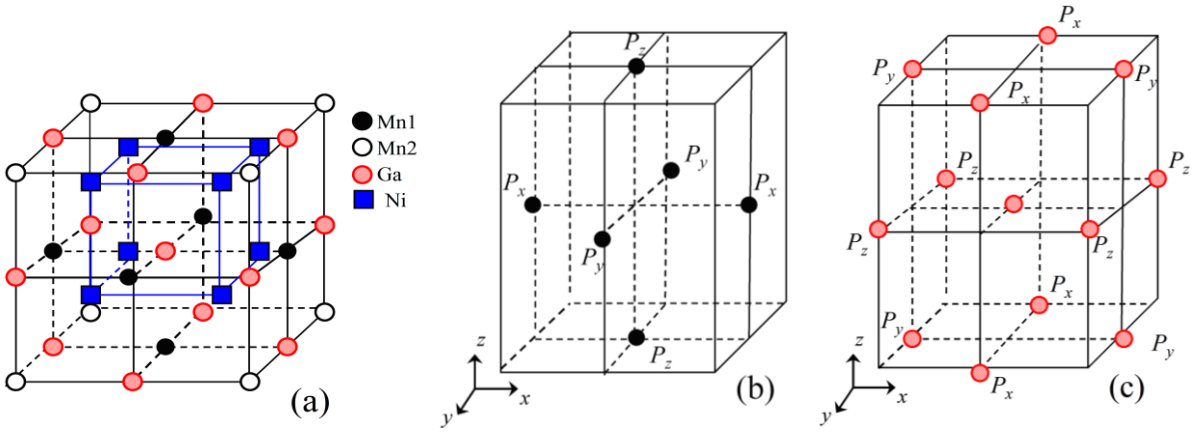

Fig. 1 – The Heusler lattice of Ni_2MnGa alloy (a). The Mn1 positions in the tetragonal crystallographic cell received after MT (b). The Ga positions in the tetragonal crystallographic cell (c)

After MT, the cubic cell appears to be tetragonal, and so, the probabilities of occupation of long and short edges of the cell by point defect must be different, while in cubic phase these probabilities were equal. There are four atoms in one of the symmetric positions and P_x, P_y, P_z are the probabilities of occupation of these positions (see Fig. 1(c)). Like in Mn1 case, the configurational order parameter is composed from the probabilities of defects occupation of Ga crystallographic sites and is described by Eq. (4). It can be concluded, therefore, that the cubic-tetragonal MT characterized by the tetragonal deformation of crystal lattice u_2, u_3, is followed by the spatial reconfiguration of crystal defects located in Ga positions, and this reconfiguration is described by the configurational order parameter components but η_2, η_3.

As it was shown in Ref. [11], the reconfiguration of point defects located in the corners of cubic crystallographic cell is interrelated with cubic-rhombohedral MTs. The Mn2 and Ni positions coincide with the corners of big and small cubes depicted in Fig. 1(a), but the cubic-rhombohedral MT was never observed in Ni_2MnGa alloy. However, this kind of MTs is peculiar to Au-Cd and Ti-Ni alloys considered below.

3.2 Au-Cd and Ti-Ni Alloys

The cubic-rhombohedral martensitic transformation in Au-Cd and Ti-Ni alloys are very similar from the crystallographic point of view [12]. In both alloys the cubic (so-called B2 phase) austenitic phase is transformed to the rhombohedral (so-called R phase) martensitic phase. The crystal lattice of Au-Cd or Ti-Ni is shown in Figure 2. This lattice is similar to the body-centered cubic, but the centered atoms and cornered atoms are not identical. As so, it is so-called simple lattice.

Figure 2 shows the symmetric crystal sites in the corners of cubic cell of Au-Cd or Ti-Ni lattice (P_{1-4} are the probabilities of occupation of these sites by defects). These probabilities form the basic functions of three-dimensional irreducible representation of the cubic symmetry group

$$\begin{aligned}\eta_4 &= r_A(P_1 - P_2 - P_3 + P_4)\\ \eta_5 &= r_A(P_1 - P_2 + P_3 - P_4)\\ \eta_6 &= r_A(P_1 + P_2 - P_3 - P_4)\end{aligned}. \qquad (5)$$

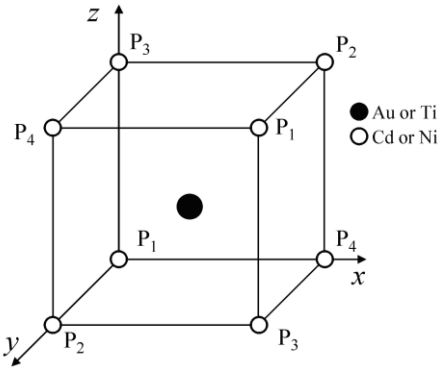

Fig. 2 – The symmetric crystal sites in cubic crystallographic cell of Au-Cd or Ti-Ni alloy

The Table 2 shows the transformation rules for the probabilities P_{1-4} and non-diagonal strain tensor components ε_{ik}. As it follows from the Table 2, and analogy between the Equations (3), and (5), the transformational rules for P_{1-4} and ε_{ik} are the same, and therefore, the order parameters $\eta_{4,5,6}$ and $u_{4,5,6}$ are transformationally equivalent.

Table 2 – Transformation of probabilities and strain tensor components by the generating symmetry operations of the cubic group

	P_1	P_2	P_3	P_4	ε_{yz}	ε_{xz}	ε_{xy}
$\hat{1}$	P_1	P_2	P_3	P_4	ε_{yz}	ε_{xz}	ε_{xy}
4_y	P_4	P_3	P_1	P_2	$-\varepsilon_{xz}$	ε_{yz}	$-\varepsilon_{yx}$
4_z	P_2	P_3	P_4	P_1	ε_{yx}	$-\varepsilon_{zx}$	$-\varepsilon_{zy}$

It can be concluded that the configurational order parameter, which characterizes the symmetry of spatial distribution of the crystal defects, can be composed of the probabilities of occupation of the crystallographic positions by defects [7, 11]. The deformation of crystal lattice during MT initiates the diffusion of crystal defects, which conforms the spatial distribution of defects to the symmetry of crystal cells. The opposite situation, where the diffusion of point defects causes the deformation of crystal lattice, is considered below for the metal-hydrogen system.

4. HYDROGEN ABSORPTION AND DIFFUSION IN METALS

The hydrogen absorption in metals is an example of interstitial point defects in the crystal lattice. It is interesting that the hydrogen system undergoes the order-disorder phase transition in the vanadium crystal lattice [9, 10]. In this case the hydrogen atoms firstly occupy tetrahedral sites in the vanadium crystal cells, and after that hydrogen atoms start ordering at octahedral sites. The hydrogen ordering in the octahedral sites results in the tetragonal deformation of crystal lattice [10]. It means that the phase transition in the system of absorbed hydrogen atoms causes the deformation of crystal lattice. This case is opposite to the case of shape memory alloys, where the deformation of crystal lattice results in the spatial reconfiguration of crystal defects.

The tetrahedral sites, which hydrogen can occupy in the base-centered crystal cell of metal, are shown in Figure 3(a). As it is seen from this figure the fourth-fold rotations around x-, y- and z-axes (the elements 4_x, 4_y and 4_z of cubic symmetry group, respectively) render the defect system in the state, which is equivalent to the initial state. It means that the defects/hydrogen atoms appeared in the tetrahedral sites do not reduce the crystal symmetry. As so, the strains induced by the hydrogen atoms are equal to each other $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz}$. Therefore, the configurational order parameter components are equal to zero, and only the scalar value η_1, which corresponds to the trivial group representation, arises. This value is equal to the defect/hydrogen concentration.

The symmetric octahedral sites, which can be occupied by hydrogen with probabilities P_x, P_y and P_z, are presented in Figure 3(b). This figure shows the octahedral sites located in the centres of edges of cubic cell. The introduction of hydrogen atom in some of these symmetric positions results in the axial deformation (ε_{xx}, ε_{yy} or ε_{zz}) of crystal lattice. As an example, Figure 3(c) shows the case when the hydrogen location at the edges parallel to z-axis is favored, the small and big open circles show the "mostly empty" and "mostly occupied" sites. The two-side arrows show the direction of axial deformation of unit cell caused by the adsorbed hydrogen atoms. In this case the configurational order parameter is described by the functions $\eta_{2,3}$ (see Eq. (4)), similarly to the case of Mn1 positions in Ni-Mn-Ga alloy. The only difference is that the configurational order parameter is expressed through the value r_H, which is the relative number of octahedral sites occupied by hydrogen atoms, and c_H is the total hydrogen concentration [13]

$$\eta_1 = c_H\,,\ \eta_2 = \sqrt{3} r_H (P_x - P_y)\,,\ \eta_3 = r_H (2P_z - P_y - P_x)\,. \quad (6)$$

It can be concluded that the introduction of hydrogen atoms in the octahedral sites (Fig. 3(c)) leads to the symmetry lowering: symmetry operations 4_x, 4_y transform to the 2_x, 2_y, while 4_z remains in the symmetry group of the crystal cell. The symmetry lowering results in the appearance of configurational order parameter components η_2 and η_3, which originate the deformations u_2 and u_3. (As it was argued in Ref. [7], every deformation of the crystal triggers the reconfiguration of the point defects and, *vice versa*, the reconfiguration of defects results in the deformation of crystal lattice.) It means that the hydrogen diffusion from the tetrahedral to octahedral sites results in the change of local environment of hydrogen atoms and interacting forces of hydrogen atoms with metal atoms.

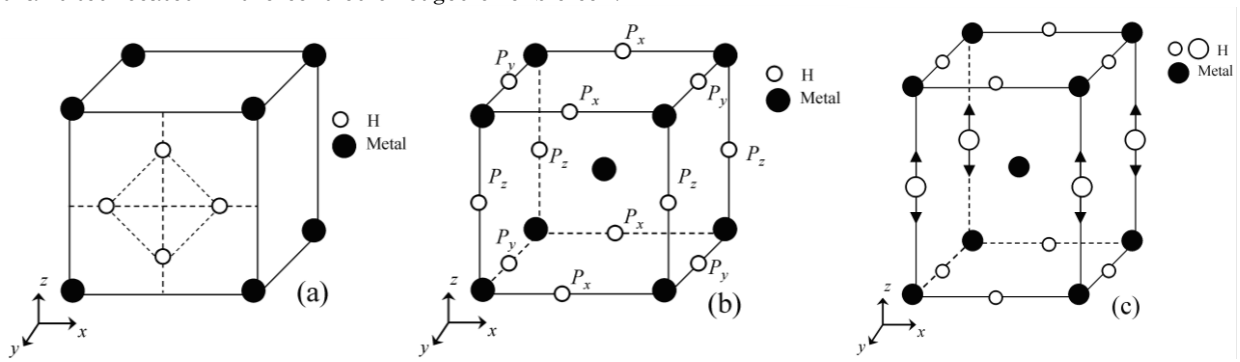

Fig. 3 – A unit cell of the cubic crystal lattice (closed circles) with the tetrahedral, (a), and octahedral, (b), interstitial sites. The tetragonal unit cell with the favorable (large open circles) and unfavorable sites for the hydrogen atoms (c). The favorable sites are "mostly occupied" by the hydrogen atoms while the unfavorable sites are "mostly empty". Two-side arrows show the direction of axial extension of unit cell caused by the adsorbed hydrogen atoms

Figures 3(b) and (c) also shows that the defects diffusion between the sites located at the physically equivalent edges of crystal cell does not induce the deformation of crystal lattice, while the defects diffusion between two differently oriented edges leads to the straining of crystal lattice. This statement is also valid for the defects diffusion between the physically equivalent/different face centers.

5. SUMMARY

In present article the different crystallographic sites available for i) point defects in the Heusler, Ti-Ni and Au-Cd alloys; ii) hydrogen atoms in vanadium are considered. The configurational order parameters describing the reduction of the spatial symmetry of defect system are constructed for all symmetric positions of point defects in the cubic crystal cell using the similari-

ty between the transformation of strain tensor components and permutation of crystallographic sites by the elements of cubic symmetry group. The interrelation between the ferroelastic phase transitions in the Heusler, Ti-Ni and Au-Cd alloys and spatial reconfiguration of point defects is described.

The system of hydrogen atoms adsorbed by vanadium is considered. The influence of the phase transition observed in the hydrogen system on the vanadium crystal lattice is described qualitatively using the configurational order parameter constructed for this system.

It is emphasized that the defects diffusion between the sites located at the physically equivalent faces/edges of crystal cell does not induce the deformation of crystal lattice, while the defects diffusion between two differently oriented faces/edges leads to the straining of crystal lattice.

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