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## Microscopic mechanism of phase transition between bcc and hcp structures in zirconium

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In this work, the atomic mechanism of transformation between the bcc- ( $\beta$ ) and hcp- ( $\alpha$ ) phases of zirconium at low temperatures was studied using ab initio calculation methods. An exact two-parameter method is proposed for describing the Burger transformation mechanism, which takes into account the differences in the values of the equilibrium volumes of the phases, as well as the difference between the values of the degree of tetragonality  $c/a$  of real hexagonal crystals and the value of the ideal ratio. Using the proposed method for describing the transformation, a potential energy surface was calculated and the path of the minimum energy of the system during the  $\beta$ - $\alpha$  transition in zirconium was determined. The influence of pressure on the shape of the energy landscape and the path of transformation of the crystal lattice in the range from 0 GPa to 25 GPa was analyzed. It has been demonstrated that the use of single-parameter methods for describing the bcc-hcp transformation of the crystal structure may be incorrect.

**Keywords:** zirconium, phase transitions, atomic transformation mechanism, martensitic transformation, pressure.

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### 1. Introduction

Zirconium is a Group 4 metal, in solid state has three allotropic modifications. At normal pressure and low temperature, zirconium exists in hcp modification ( $\alpha$ ) that remains stable up to 1135 K [1], above which phase transition to bcc modification takes place ( $\beta$ ). Melting temperature of zirconium is 2128 K. As pressure rises,  $\beta$ - $\alpha$  transition temperature decreases [2], and at low temperature zirconium forms a hexagonal  $\omega$ -phase with three atoms in the lattice cell [2–6]. Zr has a high strength-weight ratio, outstanding corrosion and oxidation resistance, and low neutron capture cross-section. Owing to its properties, Zr plays an important role in aerospace, nuclear power and chemical industries [7–9].

In 1934 Burgers described a microscopic mechanism of phase transition from bcc to hcp using Zr as an example [10], analyzed orientational crystallographic relations between bcc- and hcp-lattices in phase transition and proposed a mechanism describing this transformation. According to Burgers, bcc and hcp lattices are related as  $(011)_{\text{bcc}} \parallel (0001)_{\text{hcp}}$  and  $[\bar{1}\bar{1}1]_{\text{bcc}} \parallel [1\bar{2}10]_{\text{hcp}}$ , while lattice rearrangement may be divided into two interconnected processes. The first process includes a long-wavelength shear in the cubic lattice along  $[\bar{1}\bar{1}1]$  direction in (112) plane that changes the angle between  $[\bar{1}\bar{1}1]$  and  $[\bar{1}1\bar{1}]$  from 109.5° to 120° and results in the appearance of regular hexagons in (011) planes. The second process is defined as shuffle of atomic layers parallel to (011) in opposite  $[0\bar{1}1]$  directions bringing the atoms in regular positions in the ideal hcp lattice. Hereinafter these processes are denoted as  $\eta$  (shear)

and  $\varepsilon$  (shuffle), respectively. The Burgers mechanism is a common  $\beta$ - $\alpha$  transformation model in Zr and has been supported by experimental and theoretical studies [11–13].

Simulating path for the Burgers mechanism may be described in various ways. For example, two parameters describing the shift and alternating atomic layer displacement in a lattice may be used for description. Studies [14–17] may serve as examples. For such description method of the Burgers mechanism, the system energy during transformation is described by the surface, while a particular lattice transformation path may be defined as a minimum energy path along this surface. Another description method of the Burgers mechanism involves one-parameter transformation paths where two transition parameters are replaced by one parameter [18–20]. Such approach reduces the problem dimensions, however, requires a particular path to be prescribed for the crystal system that, as will be shown herein, not always provides a correct representation of atomic transformation mechanisms. In addition, the transformation description not always considers a change in phase volume during transition and difference of  $c/a$  of the hcp phase from the ideal  $\sqrt{8/3}$ , which more often occurs in real systems. Moreover, this uncertainty is observed both for two-parameter and one-parameter methods [15,20].

This study investigates in detail the atomic mechanism of  $\beta$ - $\alpha$  transformation in Zr. The effect of pressure on the transformation path was analyzed in the range from 0 to 25 GPa. The incorrectness of using single-parameter methods for description of lattice transformation during bcc.hcp phase transitions is shown using the example of zirconium.

## 2. Methods

This study used a two-parameter method for description of bcc–hcp lattice transformation. The transformation described by this method follows the Burgers mechanism [10]. The transformation is explicitly described by a cell with lattice vectors

$$\left[ \frac{\sqrt{3}}{2} a_{\text{bcc}}, 0, 0 \right], \left[ \frac{\sqrt{3}}{2} a_{\text{bcc}} \cos(\theta), \frac{\sqrt{3}}{2} a_{\text{bcc}} \sin(\theta), 0 \right],$$

$$[0, 0, \sqrt{2} a_{\text{bcc}}],$$

where [001] direction corresponds to [011] direction in the bcc cell, and by the atomic basis consisting of two atoms in (0,0,0) and (1/2, 1/2, 1/2) positions. The shuffle  $\eta$  in  $[\bar{1}\bar{1}1]$  direction is parametrized by the angle  $\theta$  between vectors

$$\left[ -\frac{\sqrt{3}}{2} a_{\text{bcc}}, \frac{\sqrt{3}}{2} a_{\text{bcc}}, -\frac{\sqrt{3}}{2} a_{\text{bcc}} \right]$$

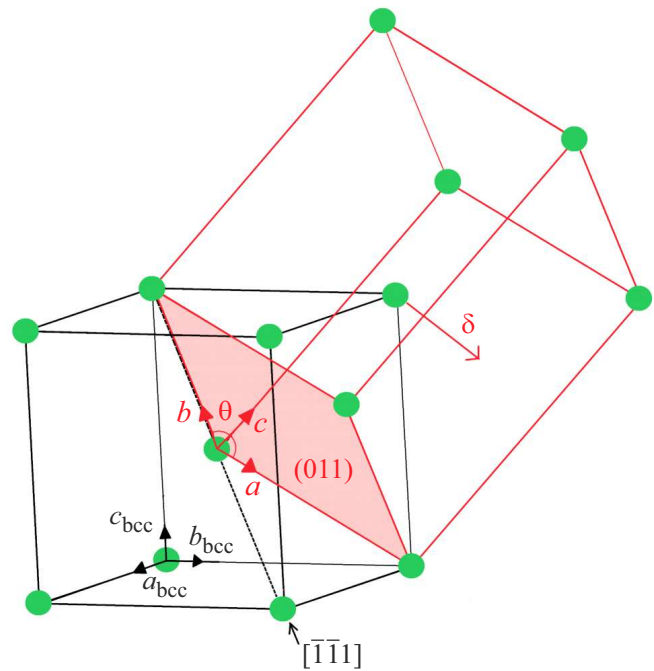
and

$$\left[ -\frac{\sqrt{3}}{2} a_{\text{bcc}}, -\frac{\sqrt{3}}{2} a_{\text{bcc}}, \frac{\sqrt{3}}{2} a_{\text{bcc}} \right],$$

and shuffle  $\varepsilon$  of (011) atomic planes is parametrized by relative displacement  $\delta$  of atom (1/2 +  $\delta$ , 1/2 –  $\delta$ , 1/2) in position corresponding to the hcp cell.  $\theta$  varies from 109.47 to 120° and  $\delta$  varies from 0 to 1/6, that corresponds to the variation of  $\eta$  and  $\varepsilon$  from 0 to 1, respectively. To consider the variation of volume per atom and obtain correct  $c/a$ , the lattice parameters were linearly scaled from the values corresponding to bcc to hcp. This study correlates the volume variation with shear  $\eta$ , therefore scaling of lattice constants was performed only in the direction of variation of this parameter. The method is schematically illustrated in Figure 1.

To calculate a particular transformation path at various pressures, total energies of all possible intermediate structures between bcc and hcp shall be known. All these structures and their energies are unambiguously defined by  $\eta$  and  $\varepsilon$ . The total energies of these structures were calculated by *ab initio* methods in terms of the electronic density functional theory implemented using VASP package [21–23] and plane wave basis for representation of the electron wave function and PAW-potentials [24,25] to set the crystal ion core potential. The criterion for exiting the electronic self-consistent cycle is the difference in energy between the last two iterations of  $10^{-5}$  eV. Exchange and correlation in the electronic gas were described in the generalized gradients approximation in PBE parametrization [26]. The plane wave basis cutoff energy was equal to 500 eV. To build a grid of  $k$ -points, the study used automatic generation provided in VASP using the Monkhorst–Pack method [27] with the density of integrating grid by the Brillouin zones  $18 \times 18 \times 10$ .

For potential energy surface analysis by the second-order spline method, an interpolation function was built using the *ab initio* calculation data. The minimum energy



**Figure 1.** Illustration to the proposed Burgers transformation description method Green spheres — Zr atoms. Black lines show the bcc lattice cell, red lines show the cell used in this work.

paths along the energy surfaces at different pressures were found by the gradient descent method. Interpolation and search for paths were implemented in Mathematica software package [28].

## 3. Results

To describe the transformation using the method described in the present study, at first, *ab initio* calculations of bcc and hcp phase relaxation at 0 K were performed and equilibrium specific (per atom) volumes and axial parameter ratios  $c/a$  at 0, 5 and 25 GPa were determined. These results together with some literature data are shown in the table. The volume and  $c/a$  of Zr hcp obtained herein differ by less than one percent from the theoretical results obtained by Wang et al. [31]. Deviation from the experimental data for  $\alpha$ -Zr is about 2% and 1% for specific volumes and  $c/a$ , respectively. The table shows the difference in Zr bcc phase volumes at 0 GPa calculated herein at zero temperature and measured experimentally by Zhao et al. [32] at  $T = 973$  K. However, the deviation is 5%, it lies on the boundary of predictions acceptable for theoretical calculations. In addition, the deviation from the experimental data may be explained by considering the temperature expansion effect. In addition, the discrepancy between the data and experiment can be explained if we take into account the effect of thermal expansion. Taking into account the effect of thermal expansion in an explicit form requires the use of the molecular dynamics method,

Comparison of specific volumes of Zr phases and  $c/a$  of Zr hcp phase at different pressures (given in brackets) calculated in the present study and in some previous studies

bcc Zr	Low-temperature <i>ab initio</i> calculations				Experiment at 973 K	
	This study	Anzellini et al. [29]	Stavrou et al. [30]	Wang et al. [31]	Zhao et al. [32]	
$V, \text{\AA}^3/\text{atom}$	22.6 (0 GPa)	22.65 (0 GPa)		22.83 (0 GPa)	23.87 (0 GPa)	
	21.65 (5 GPa)		21.87 (3.96 GPa)	21.62 (5.35 GPa)	21.93 (6.38 GPa)	
	18.53 (25 GPa)	18.48 (25 GPa)	18.48 (25 GPa)	18.63 (24.61 GPa)		
hcp Zr	Low-temperature <i>ab initio</i> calculations		Experimental studies at 300 K			
	This study	Wang et al. [31]	Stavrou et al. [30]	Akahama et al. [33]	Anzellini et al. [29]	Zhao et al. [32]
$V, \text{\AA}^3/\text{atom}$	23.26 (0 GPa)	23.43 (0 GPa)	23.33 (0.74 GPa)	23.37 (0 GPa)	23.13 (0.69 GPa)	23.29 (0 GPa)
	22.23 (5 GPa)	22.27 (5.35 GPa)	22.28 (5.57 GPa)	22.41 (4.33 GPa)	22.08 (5.71 GPa)	22.11 (4.93 GPa)
	19.18 (25 GPa)				19.59 (21.97 GPa)	
$c/a$	1.602 (0 GPa)	1.597 (0 GPa)				1.592 (0 GPa)
	1.615 (5 GPa)	1.603 (5.35 GPa)				1.594 (4.93 GPa)
	1.656 (25 GPa)					

which in the framework of *ab initio* calculations is quite resource-intensive and was not carried out in this work.

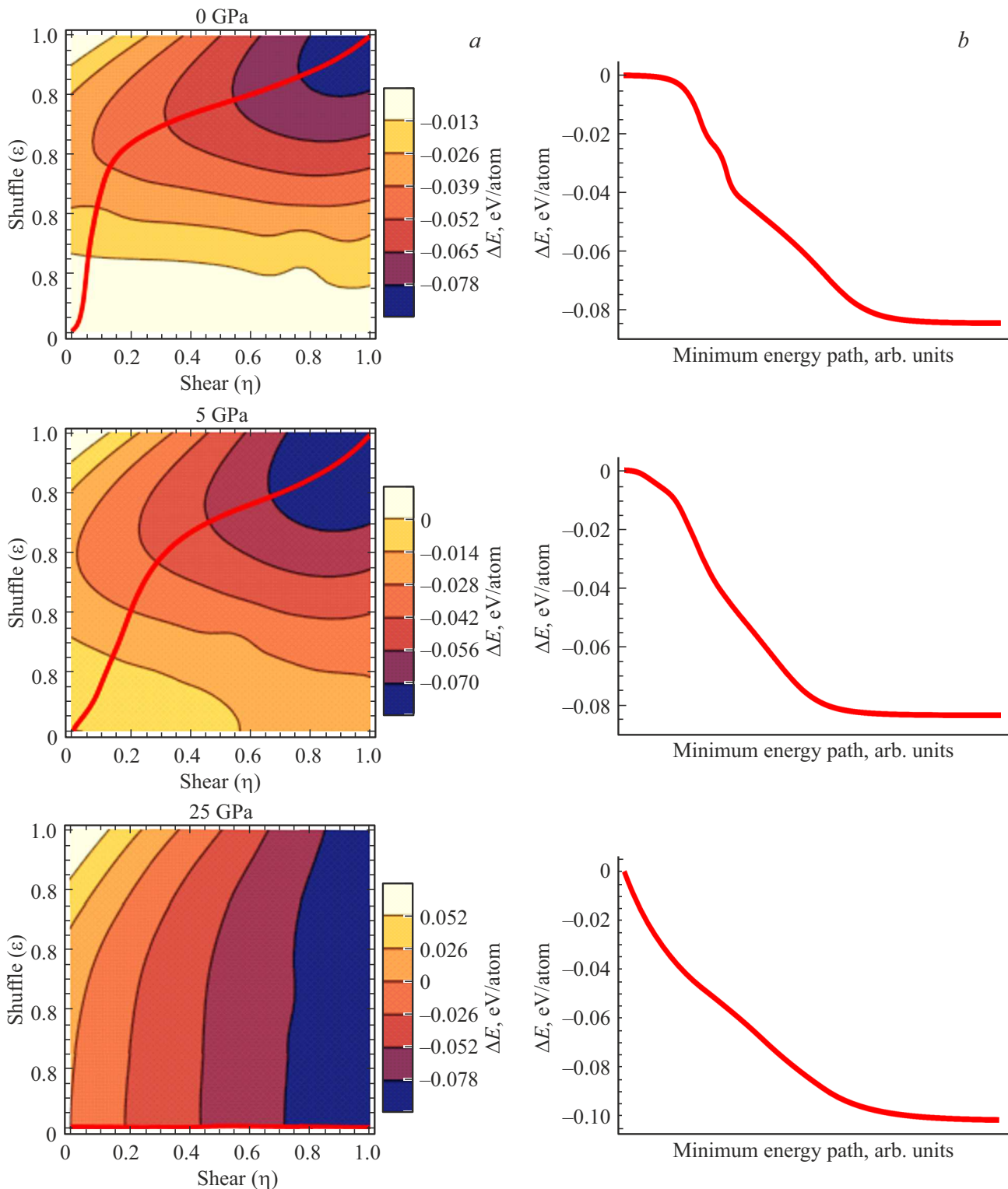
Then, using the obtained equilibrium lattice parameters at various pressures, *ab initio* calculation methods were used to determine the dependence of the total energy of Zr crystal with varying parameters ( $\eta, \varepsilon$ ) on the  $10 \times 10$  grid. Using these data, energy variation surface  $\Delta E$  Zr in transformation from  $\alpha$  to  $\beta$  modification, its contour map and minimum energy path at 0, 5 GPa and 25 GPa were built, all results are shown in Figure 2.

Foremost it may be noted that the results in Figure 2 show instability of  $\beta$  Zr modification to shear  $\eta$  and shuffle  $\varepsilon$  fluctuations, which fully corresponds the fact that  $\beta$  Zr is dynamically unstable at low temperatures because its phonon spectrum contains imaginary frequencies [34]. The shown data demonstrate high energy asymmetry in ( $\eta, \varepsilon$ ) at each pressure. It is shown that the shear  $\eta$  and the related lattice cell volume variations at low pressures have a low effect on the energy in the bottom halfplane  $\varepsilon < 0.5$ . At low pressure, the system energy varies most of all in the shuffle direction  $\varepsilon$ , and  $\Delta E(\varepsilon)$  at any  $\eta$  has its valley that moves towards hcp as  $\eta$  increases. In addition, the minimum energy path at low pressure goes primarily in  $\varepsilon$  direction at the start of transformation and then, when the system is no longer able to reduce its energy by means of shuffle, changes its direction towards  $\eta$ . The change in enthalpy during a phase transition at zero pressure is equal to the energy difference between the bcc and hcp phases, which in this work is equal to the value of the function  $\Delta E$  at the point (1,1) of the surface shown in Figure 2,  $a$  and is  $\Delta E(1, 1) = 85 \text{ meV/atom}$ . This agrees well with the *ab initio* values calculated in the previous studies:  $84 \text{ meV/atom}$

Liu et al. [13] and  $80 \text{ meV/atom}$  Wang et al. [31]. The literature data on the experimentally measured thermal effect of the bcc–hcp phase transition in zirconium is very scarce. Study [35] reports a transition enthalpy of  $40 \text{ meV/atom}$  that is twice as low as the theoretically calculated value.

The energy surface shape and minimum energy path vary greatly as the pressure increases. It can be seen that as the pressure grow from 0 to 5 GPa, the system energy starts responding more actively to the shear in  $\eta$  direction, that is shown by the change in the minimum energy path slope at the beginning of the transformation. When pressure increase to 25 GPa, the system energy surface changes critically. The valley on  $\Delta E(\varepsilon)$  disappears at any  $\eta$ , moreover, as shown in Figure 2, the contour lines are almost perpendicular to the  $\eta$  axis at  $\varepsilon < 0.5$  and only when  $\varepsilon$  approaches 1, the energy variation in shear becomes obvious. All this suggests that the system energy changes at high pressure during transformation is mainly associated with the lattice volume and shape variations. At 25 GPa, a structure with energy lower by  $10.5 \text{ meV}$  than that of hcp occurs in (1,0) point, therefore the minimum energy path is parallel to the  $\eta$  axis. The  $\omega$  phase of Zr is known to become energy-favorable at high pressure. This suggests that atomic configuration in (1,0) point is some intermediate structure on the transformation path to the omega phase. More detailed investigation of this problem requires an individual transformation mechanism to be built.

It should be pointed out that to describe the transformation by one-parameter methods as, for example, by Friak et al. [20], the minimum energy path shall be a simple straight line on the contour map — (0,0)–(1,1) diagonal.



**Figure 2.** (a) The contour maps of the energy surface  $\Delta E$  Zr in shear and shuffle coordinates in the bcc–hcp transformation at different pressures.  $\Delta E = E_{(\eta,\epsilon)} - E_{(0,0)}$  — structure energy variation in  $(\eta, \epsilon)$  point with respect to bcc. (0,0) point — bcc, (1,1) point — hcp. Red line shows the minimum energy path. (b) Crystal structure energy variation  $\Delta E$  in transformation from bcc to hcp via the minimum energy paths along the corresponding surfaces.

However, the data in Figure 2 show that the minimum energy path is not a straight line from bcc to hcp at any pressure. When using one-parameter methods, one can try to take into account the features of the potential energy surface of the given system in the wxplicit formulation of the transformation path, but the search for such an atomic mechanism is far from a trivial task for most real systems, even without taking pressure into account. Pressure consideration may make the problem much more complicated. The foregoing allows us to argue that the one-parameter transformation description methods are incorrect and give wrong representation of the atomic mechanisms of phase transitions.

#### 4. Conclusion

This study uses the electronic density functional theory to investigate the atomic mechanism of Zr bcc–hcp phase transformation under pressure by the modified Burgers mechanism. For this, crystal structure relaxation was calculated and the equilibrium parameters of bcc and hcp phases were determined at low temperature with pressures from 0 to 25 GPa. Zr phase energy surface was calculated for the bcc–hcp transformation in  $(\epsilon, \eta)$  coordinates and the minimum energy path was determined. Using the findings, analysis of the pressure effect on the atomic mechanism of transformation was performed. It was shown that pressure greatly changes the energy surface landscape, which leads to a change in the sequence of intermediate crystalline structures along the minimum energy path. It is shown that the transformation path is not a simple straight line on the contour map of the energy surface, which, together with discovered strong dependence of the surface shape on pressure, makes the one-parameter description of the bcc–hcp crystal structure transformation incorrect.

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#### Conflict of interest

The authors declare that they have no conflict of interest.

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