ELASTIC PHASE TRANSITION IN METALS: THE PRESSURE EFFECT

ДЕФОРМАЦИОННЫЕ ФАЗОВЫЕ ПЕРЕХОДЫ В МЕТАЛЛАХ: ЭФФЕКТ ДАВЛЕНИЯ

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Abstract: *At high pressures (the pressure is comparable with the bulk modulus) the crystalline lattice may become unstable relative to the uniform shear deformations, and as a result the low symmetric crystalline structures will appear (the so called "elastic phase transitions"). The order parameters at these transitions are the components of the finite deformations tensor. The stability of the high-pressure phases is defined by the nonlinear elasticity of the lattice (the third, fourth etc. order elastic constants). Here the different cases of stability loss at hydrostatic pressure of the cubic and hexagonal structures are considered. The relation between the second, third and fourth order elastic constants is given, which defines the possibility of the first order deformation phase transition. The jump of the order parameter and the height of the potential barrier are defined by the third and fourth order elastic constants. As an example, the experimentally observed elastic phase transition in vanadium at $P \approx 69$ GPa from bcc to the rhombohedral phase is analyzed, and the possible structural transitions in bcc Mo and W at $P \geq 700$ GPa are considered. The stability of the Ru in the pressure interval $0 \div 600$ GPa is also analyzed. The necessary values of the different order elastic constants for Mo, W and Ru are calculated in the framework of the density functional theory using VASP (Vienna Ab initio Simulation Package).*

1.Intoduction

The experimental data show that in metals at the pressures usually the phase transitions in the closed packed structure take place [1]. But the high pressure phases (the pressure is comparable with the bulk modulus) frequently become less symmetrical, with a lower packing density [2]. It is occured because with the pressure increasing the crystalline lattice becomes unstable relative to the small uniform shear deformations. As a result, the phase transition takes place in the spontaneously deformed state with a lower symmetry. Almost the all phase transitions in solids are accompanied by the elastic deformations. In most cases, the deformation is not the order parameter, and is connected with it only by the striction interaction. In our case the deformation is the order parameter, and such transitions were called "the elastic phase transitions". At these transitions the number of atoms in the unit cell is conserved, the point group symmetry of the new phase is subgroup of the point group of the parent structure, the translation symmetry is conserved. The critical phenomena at the elastic phase transitions are suppressed [3], and the Landau theory of the phase transitions can be used with the finite deformation tensor components as the order parameters.

2.Lattice stability and the elastic phase transitions.

According to the Landau theory of the phase transitions, the thermodynamical potential can be decomposed in to power series over the order parameter components. The Gibbs free energy G is the thermodynamic potential at given T and P. The structural transitions are accompanied by small, but finite deformations of the crystalline lattice, for taking into account the nonlinear effects it is convenient to choose the finite strain tensor components η_{ij} as the order parameters. Decompose G near the equilibrium state at given T and P over η_{ij} (Lagrangian strain tensor). Let us the spontaneous deformations η_{ij} are isothermal. Then, the change $\Delta G = G(P,T,\eta) - G(P,T,0)$ on the unit volume will be

$$\Delta G / V_0 = (1/2)\widetilde{C}_{ijkl}\eta_{ij}\eta_{kl} + (1/6)\widetilde{C}_{ijklmn}\eta_{ij}\eta_{kl}\eta_{mn} + (1/24)\widetilde{C}_{ijklmnpq}\eta_{ij}\eta_{kl}\eta_{mn}\eta_{pq} + ... \tag{1}$$

(the summation is from 1 to 3). In the expression (1) the linear contribution is absent because the system is in equilibrium state. Here

$$\widetilde{C}_{ijkl....} = (1/V_0)(\partial^n G / \partial \eta_{ij} \partial \eta_{kl})_0 \tag{2}$$

are the n-order isothermal effective elastic constants (EC) (n =2, 3, 4) at the given load and temperature T, which characterize the elastic properties of a loaded crystal [4]. In the absence of a load, $\widetilde{C}_{ijkl..}$ coincide with the usual elastic constants $C_{ijkl..}$. The all equations of the elasticity theory with $\widetilde{C}_{ijkl..}$ are the same as with the load as in the unloaded state. In particular, the stability conditions coincide with the Born conditions for unloaded crystal.

At the given T and P the system state will be stable if the quadratic form in (1) will be positively defined. As a result, for the usual *bcc*, *fcc* and *hcp* metallic structures we obtain the following stability conditions of relatively uniform shear deformation. For cubical symmetry are:

$$\widetilde{C}_{11} - \widetilde{C}_{12} \rangle 0 \text{ (a)}; \quad \widetilde{C}_{44} \rangle 0 \text{ (b)} \tag{3}$$

For *hcp* structure they are following:

$$\widetilde{C}_{11} - \widetilde{C}_{12} \rangle 0, \text{ (a)}; \quad \widetilde{C}_{44} \rangle 0, \text{ (b)}; \quad \widetilde{C}_{66} = (\widetilde{C}_{11} - \widetilde{C}_{12})/2 \rangle 0 \text{ (c)}. \tag{4}$$

Here $\widetilde{C}_{\alpha\beta}$ are the second order effective elastic constants in Voigt notation.

With the pressure and temperature changes these conditions may be distorted, and as a result the structural transition will take place in spontaneously deformed state, which stability is defined by the nonlinear elasticity of the material (by anharmonic contributions of the third, fourth ets. order). In Table 1 the different cases of spontaneous deformation are given, when the lattice instability of crystals with the cubical and hexagonal symmetry is possible. In the present cases the decomposition of the thermodynamic potential (1) is following:

$$\Delta G(P,\eta,T)/V_0 = (1/2)q\eta^2 + (1/3)v\eta^3 + (1/4)w\eta^4 + ... \tag{5}$$

The values of q, v и w are given in Table 1, where $\widetilde{C}_{\alpha\beta..}$ are the isothermal elastic constants at the pressure P.

Table 1. *Elastic phase transitions under pressure in crystals with cubical (1, 2, 3) and hexagonal (4, 5, 6) structures*

№	Spontaneous deformation	q	v	w	The change of symmetry after transition
1	$-\eta_{11} = -\eta_{22} = 0.5\eta_{33} = \eta$	$6(\tilde{C}_{11} - \tilde{C}_{12})$	$3(\tilde{C}_{111} - 3\tilde{C}_{112} + 2\tilde{C}_{123})$	$3(\tilde{C}_{1111} - 4\tilde{C}_{1112} + 3\tilde{C}_{1122})$	$\Gamma_c \to \Gamma_q$ $\Gamma_c^f, \Gamma_c^v \to \Gamma_q^v$
2	$\eta_{11} = -\eta_{22} = \eta$	$2(\tilde{C}_{11} - \tilde{C}_{12})$	$v\eta^3 = 0^{1)}$	$(\tilde{C}_{1111} - 4\tilde{C}_{1112} + 3\tilde{C}_{1122})/3$	$\Gamma_c \to \Gamma_0$ $\Gamma_c^f, \Gamma_c^v \to \Gamma_0^v$
3	$\eta_{12} = \eta_{13} = \eta_{23} = \eta/2$	$3\tilde{C}_{44}$	$3\tilde{C}_{456}$	$(\tilde{C}_{4444} + 6\tilde{C}_{4455})/2$	$\Gamma_c, \Gamma_c^f, \Gamma_c^v \to \Gamma_{rh}$
4	$\eta_{11} = -\eta_{22} = \eta$	$\tilde{C}_{11} - \tilde{C}_{12}$	$2(\tilde{C}_{111} - \tilde{C}_{222})/3$	$2\tilde{C}_{6666}/3$	$\Gamma_h \to \Gamma_o^b$
5	$\eta_{23}(\eta_{13}) = \eta$	$\tilde{C}_{44}$	0	$2\tilde{C}_{4444}/3$	$\Gamma_h \to \Gamma_m$
6	$\eta_{12} = \eta$	$\tilde{C}_{11} - \tilde{C}_{12}$	0	$2\tilde{C}_{6666}/3$	$\Gamma_h \to \Gamma_o^b$

1) due to the deformation symmetry

Here also the possible variants of the structural transitions in *bcc*, *fcc* and *hcp* lattices due to the stability loss relative to the shear deformations are given, which were obtained by the theoretical group analyses of the Brave lattices symmetry. If the third order contribution in (5) is equal zero (cases 2, 5 and 6), then the second order phase transition can take place when the appropriate stability condition is distorted.

$$f(a, x) = a \cdot \frac{x^2}{2} - \frac{x^3}{3} + \frac{x^4}{4}, \quad (6)$$

where $f(a, x) = \Delta G/(V_0 G_0)$, $x = (w/v)\eta$, $a = qw/v^2$ (7)

The coefficient a takes into account the 2, 3 and 4 order ECs changes with *P* and *T*. The equation (6) has the different maximums and minimums depending on its value (see Fig 1). The value of a for the first order transition is found from the solution of the system of equations $f(a, x) = 0$ and $\partial f/\partial x = 0$. As a result, $a = 2/9$. For this value the function (6) has the two minimums corresponding $x = 0$ and $x = 2/3$ and the maximum at $x = 1/3$ (see Fig 1, curve 3). The value of the potential barrier and the jump of the order parameter in this transition can be estimated from the relations (6) and (7). The result, we will get

$$\Delta G/V_0 = (1/324)(v^4/w^3); \quad \eta = 2v/(3w) \quad (8)$$

Now we'll define the entropy change $\Delta S = -(1/V_0)(\partial \Delta G/\partial T)_P$ at the elastic phase transition between the two states connected by the deformation $\eta = (2v/3w)$. Substituting η into the formula (5) for Gibbs potential and taking the derivative over the temperature, we'll find ΔS till the fourth order degree over the order parameter. With the

Now will consider the equation (5) when the third order contribution is not zero (the cases 1, 3 and 4). The calculations of EC show that usually far from the loss of stability point, q and w are positive, but v is negative. The equation (5) contains the three parameters, which depend on *P* and *T*, but dividing the both parts of the equation on $G_0 = v^4/w^3$, we will get the dimensionless equation with one coefficient [4]

known ΔS, we'll find the latent transition heat $\Delta Q = T\Delta S$. So, the height of the potential barrier, the order parameter jump, the entropy change and the latent heat of transition are defined by the relations between the third and fourth order elastic constants, e.g. by the nonlinear elasticity of the crystalline lattice. It is seen from the expression for the parameter a (see (7)), that the first order phase transition can take place at rather big values of q (corresponding second order EC), if the value of v is approximately equal to w (the third order anharmonism contribution is comparable with the fourth order contribution).

If $0 \langle a \langle (2/9)$, then $f(a, x)$ has besides the metastable minimum has the stable minimum at $x \rangle 2/3$ with the maximum $f(a, x) \rangle 0$ for x between these minima (Fig 1, curve 4). As a result, the first order phase transition close to the second order will take place, because the potential barrier height is decreased with decreasing of a.
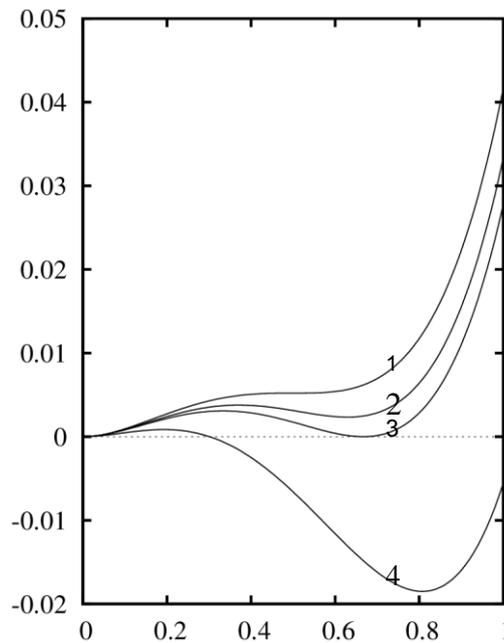
Fig 1.The dimentionless Gibbs potential (6) at different values of a : 1. $a =1/4$, 2. $a = 2.1/9$ 3. $a = 2/9$ .4. $a = 1.4/9$.

The first order phase transition can take place at $0\langle a \leq \dfrac{2}{9}$, or

for the elastic constants $0\langle qw \leq \dfrac{2}{9}v^2$

Thus, the data for the second-forth order EC at the different pressures are needed to analyze the elastic phase transitions. The experimental data for the different order elastic constants at the high pressures are practically absent. But the second and higher order EC at the different pressures can be obtained from the "first principles" calculations in the framework of DFT. We have described the calculation method of the second-forth order EC for cubical and hexagonal crystals in the papers [5,6].

3. The EC of the refractory metals at high pressures.

Vanadium. The structural phase transition under pressure from *bcc* to rhombohedral structure was found at $P = 69$ *GPa* and the room temperature [7]. The authors of [7] explain it by softening of EC $\tilde{C}_{44}$ ($\tilde{C}_{44}$ becomes negative in the investigated pressure range) and connect the absence of the volume jump with the second order transition. The softening of $\tilde{C}_{44}$ (it becomes negative) was found also in framework of the first principles calculations (see, for example [9]). It is possible to estimate from [9] the value of a (see (6) and (7)) at the different pressures (*T=OK*) near the phase transition point (50 - 70 *GPa*), using the results of the second - forth order ECs calculations. In a result, we have: at $P \approx 68$ *GPa*, the a becomes equal to the critical value 2/9, and the *bcc* structure (Γ_c^v) can experience the structural transition to the rhombohedral phase (Γ_{rh}), (see Table 1, line 3).From (8) it is possible to obtain the jump of the order parameter

$\eta_{12} = \eta_{13} = \eta_{23} = \eta / 2 = (1/3)(|v| / w) = 0.0075$ at this

transition. The small value of the order parameter means that it is the first order transition, close to the second order. The calculation results are in a good agreement with the experimental data [7].

Molybdenum. The effective EC of Mo in the pressure interval 0-1400 *GPa* (*T=0K*), which were obtained in our work

[9], are given on Fig 2-4. It is seen on Fig 2, that $\tilde{C}'$ at P> 500 *GPa* is strongly softened (this is the precursor of the phase transition) and passes the zero at P= 1400 *GPa* ($V / V_0 \approx 0.42$).The *bcc* lattice at these experiences the phase transition to a tetragonal or orthorhombic structure (the stability condition (2b) is distorted). But according to [10, 11] the *bcc* molybdenum structure at $P \approx 700$ *GPa* (*T=0K*) becomes thermodynamically unstable and should transform in *fcc* or hexagonal phase. The estimations of the coefficient a (see (6)) show, that at these pressures its exceeds the critical value 2/9, when the first order phase transition can take place. The results of the stability criteria (3) and (4) calculations for *f*cc and *hcp* structures of molybdenum are given on Fig 3 and 4. It is seen that at the normal (atmospherically) pressure these structures are unstable relative to the shear deformations ($\tilde{C}_{44}\langle 0$ и $\tilde{C}'\langle 0$)). They are stabilized only at the high pressures: *hcp* at $P \geq 150$ *GPa*, *fcc* at $P \geq 300$. As can be seen from Fig. 3 and 4, from the point of view of resistance to homogeneous deformation of the hexagonal structure is more preferable. The small $\tilde{C}'$ value creates the small energetic barrier for this structural transformation. The transition will be of the first kind and occurs before a phonon mode in the original lattice becomes unstable. Thus, the structural transition in Mo in the *hcp* phase must occur before the EC $\tilde{C}'$ will become zero.

These considerations apply to tungsten. Elastic constants of 2 – 4 order in *bcc* – W and their analysis is given in [12]. EC $\tilde{C}'$ also demonstrates a tendency to soften, although at higher pressures.

Ruthenium. Elastic constants $\tilde{C}'$ and $\tilde{C}_{44}$ *hcp* Ru grow monotonically in the range of 0-600 *GPa* [6]. Thus, the *hcp* structure of ruthenium remains mechanically stable in the investigated pressure interval.
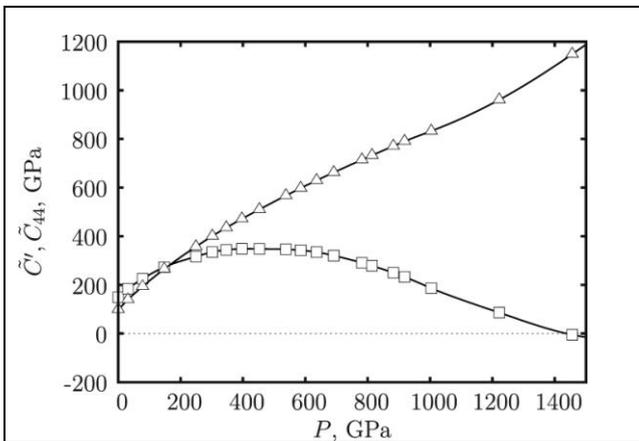
Fig.2 *The pressure dependence of the shear ECs of bcc Mo:*
$$\widetilde{C}' = (\widetilde{C}_{11} - \widetilde{C}_{12})/2 \text{ -square}, \quad \widetilde{C}_{44} \text{ - triangular}$$
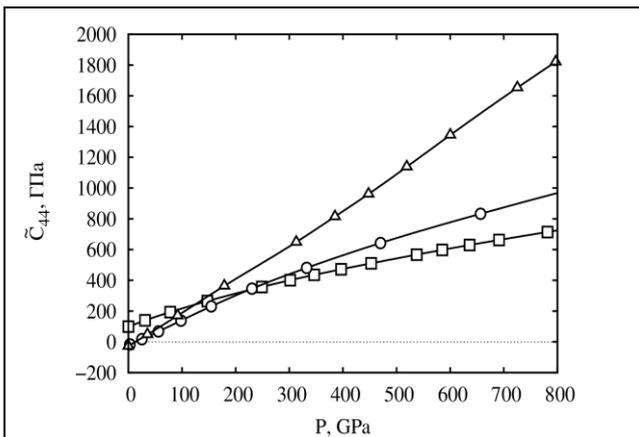
Fig.3. *The change of the EC $\widetilde{C}_{44}$ under pressure in bcc, fcc and hcp molybdenum. The square – fcc, circle – fcc, triangular - hcp*
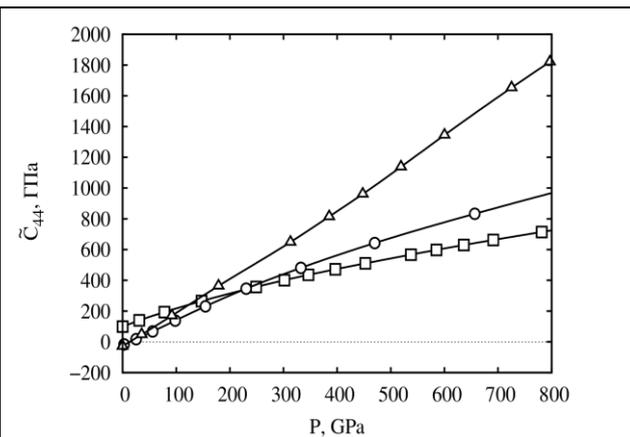
Fig.4. *The change of the EC $\widetilde{C}'$ under pressure for bcc, fcc and hcp molybdenum. Square-bcc, circle - fcc, triangle – hcp structures.*

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