

DEFINITION OF ELASTIC MODULES OF ORDERED HEXAGONAL CRYSTALS

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Abstract. Stability of crystal lattices of alloys with superstructures $D0_{19}$ and $D0_{24}$ at experimentally observable sizes of elementary cells was provided within the framework of model of pair not central interatomic interactions. The expressions for modules of elasticity C_{11} , C_{12} , C_{13} , C_{33} , C_{44} for HCP metals and alloys through interatomic potentials are received. Satisfactory coincidence of the experimental and calculated values C_{mn} are observed for HCP metals with axial ratio close to ideal – 1,633 – Co, Mg, Re, Ti. For alloys of above mentioned superstructures experimental values of modules are absent. Proportions between the calculated values of modules for alloys are approximately the same as for HCP of metals. However the absolute values C_{mn} for an alloy approximately in 1.5 – 2 times exceed those for HCP metal presenting in composition of an alloy. The attempt of explanation of such result was done and indirect confirmation is adduced.

Introduction

In modern engineering for manufacturing details of machines and devices a plenty of multi-component alloys is used. Details made of polycrystalline materials with enough small sizes included in their structure crystallites, are considered as isotropic bodies. For the description of elastic properties of these materials there are enough of two modules of elasticity – Young's module E and shift module G . However, at consideration the deformation in areas commensurable on the size to the sizes of crystallite it is necessary to know all set of elastic constants of this crystallite. The creation of new materials with application of nanotechnologies also requires the detailed description and forecasting of the elastic characteristics of crystals. Besides, the elastic properties of some alloys working at high temperatures change as a result of aging. For example, in constructional titanium alloy Ti-6-2222 (RMI Titanium Company) at aging the hardening phase $AlTi_3$ with superstructure $D0_{19}$ is allocated [1]. The basic hardening of martensite ageing steels containing titanium is reached as a result of allocation from martensite secondary HCP phase $TiNi_3$ with superstructure $D0_{24}$ [2]. The same phase is allocated in alloys of system Ni - Ti, with shape memory effect [3].

If the measurement of the Young's module and shift module for a polycrystal does not represent the difficult transactions, that in case of a monocrystal the experimental definition of elastic modules C_{mn} turns in hard-solvable task. It is connected, first of all, to necessity of preparing of enough large sample of the given stoichiometrical composition and superstructure. Therefore the experimental data about modules of elasticity are available only for small number of the ordered alloys, though for metals the elastic constants are measured. In this connection application of the theoretical methods in a combination to methods of computer simulations for definition of elastic modules of the ordered phases is represented as actual. The present work is devoted to definition of elasticity modules of the ordered phases with superstructures $D0_{19}$ and $D0_{24}$ on base of hexagonal lattice of knots.

Stability of crystal lattices with superstructures $D0_{19}$ and $D0_{24}$

For description at atomic level of the elastic characteristics of monocrystals near to their equilibrium state the construction of model is necessary, within the framework of which this state is reached. The stoichiometrical formula of superstructures $D0_{19}$ and $D0_{24}$ is AB_3 . Their construction can be presented as stacked in pile of identical layers of the hexagonal configuration. Each of layers is filled with atoms of sorts A and B in stoichiometrical ratio. The atoms of A sort also form a hexagonal grid with the size of a cell twice exceeding distance between the nearest atoms in a layer. The sequence of stacking of layers in superstructure $D0_{19}$ is ...abababab... that corresponds to stacking of layers in HCP metal lattice, and in superstructure $D0_{24}$ is ...abacabacabac..., what corresponds to stacking of layers in α lanthanums lattice. Thus, owing to affinity of crystal-geometrical

construction of the identical superstructures, the application of the uniform approach to their consideration is meaningful.

The internal energy of the ordered alloys with superstructures D0₁₉ and D0₂₄ in account on structural unit AB₃ was represented as the sum of energies of pair interatomic interactions

$$U_{all} = \frac{1}{2} \sum_i \sum_j \varphi_{(p_i),(q_j)}(\vec{r}_i - \vec{r}_j) \quad (1)$$

where i is number of knot of structural unit, and j is number of lattice knot from an environment i-th; p_i and q_j - sorts of atoms located on i-th and j-th knots. That is, pair of indexes i and j determines a sort of interatomic potential A-A, A-B or B-B.

The necessary conditions of the stability of crystal lattices of superstructures D0₁₉ and D0₂₄ at their experimentally observable sizes of elementary cells a₀ and η₀, bond energy E_{cell} and bulk module B can be written as

$$\left. \begin{aligned} U_{all}(a_0, \eta_0) &= -E_{cell} \\ \frac{dU_{all}}{da} \Big|_{a_0, \eta_0} &= 0 \\ \frac{dU_{all}}{d\eta} \Big|_{a_0, \eta_0} &= 0 \\ V_0 \left(\frac{d^2 U_{all}}{dV^2} \right) \Big|_{a_0, \eta_0} &= B \end{aligned} \right\} \quad (2),$$

Where η=c/a – is axial ratio; a – lattice parameter; c – distance between basic “a” layers. a₀, η₀ - are appropriate experimental values for a considered alloy; - V₀ = $\frac{\sqrt{3}}{4} \eta_0 a_0^3$ volume of the elementary cell.

The stability of hexagonal lattice at given axial ratio η₀, generally speaking, can not be explained within the framework of model of central isotropic pair potentials. The decision of this problem was offered in works [4-6], in which the interatomic interactions were described with the help of anisotropic not central pair potentials.

$$\varphi(r) = (1 + \xi \cdot \cos^2 \theta) \cdot \varphi_M(r) \quad (3),$$

where θ - angle between a vector of interatomic bond and main axis of a crystal,

$$\varphi_M(r) = D \beta \exp(-\alpha r) (\beta \exp(-\alpha r) - 2) \quad (4)$$

– Morse potential function traditionally used for simulation defects of cubic crystals; ξ, α, β, D – parameters. That is the potential (3) is four-parametrical. It is obvious, that at ξ=0 potentials (3) transform in isotropic Morse potential. Therefore parameter ξ as a matter of fact is parameter of anisotropy. For the description of two-component alloy (AB₃) the presence of three interatomic potentials is necessary: A-A, A-B, B-B. It is usually supposed, that the potentials connecting atoms of an identical sorts in an alloy, completely correspond to the same potentials in metal. At construction of potentials the interactions in six coordination spheres were taken into account, that for a hexagonal lattice makes 38 interatomic bonds of each atom with the neighbours of the nearest environment. The parameter values of potentials such as A-A and B-B were determined from stability conditions of lattice of the appropriate metal at experimentally observable sizes of elementary

cell, sublimation energy and bulk module. The potentials connecting atoms of a different sorts were determined from stability conditions (2) lattice of an alloy. Thus was considered, that

$$E_{\text{cell}} = n_A E_A + n_B E_B + H_{\text{all}} \quad (5),$$

where E_A and E_B - energies of sublimation of metals A and B accordingly; H_{all} - heat of an alloyage, which for different alloys equal approximately 3 - 6 % from bond energy; n_A and n_B - numbers of atoms of A and B sorts in elementary cell.

Table 1. Initial experimental data and parameters of interatomic potentials (3) for alloys with superstructures $D0_{19}$ and $D0_{24}$

Alloy, super-structure	Initial data, source		Sort of the bond	Parameters of a potential			
	$a_0, \text{\AA}$	η_0		ξ	$\alpha, \text{\AA}^{-1}$	β	D, eV
1	2	3	4	5	6	7	8
WCo ₃ , D0 ₁₉	5.13 [7]	1.61014 [7]	Co-Co	-0.25480	1.41228	45.8561	0.53795
			Co-W	-0.30481	1.77388	115.6713	0.93372
			W-W	0.0	1.40873	62.6848	1.13016
MoCo ₃ , D0 ₁₉	5.13 [8]	1.60624 [8]	Co-Co	-0.25480	1.41228	45.8561	0.53795
			Co-Mo	-0.36151	1.84795	137.4457	0.84389
			Mo-Mo	0.0	1.45763	69.7440	0.90043
AlTi ₃ , D0 ₁₉	5.793 [9]	1.60711 [9]	Ti-Ti	-0.46777	1.04914	30.1143	0.58133
			Ti-Al	-0.09798	1.82980	212.2137	0.58968
			Al-Al	0.0	1.02635	27.4642	0.31789
TiNi ₃ , D0 ₂₄	5.101 [7]	1.62845 [7]	Ni-Ni	0.0	1.36720	41.2911	0.47119
			Ni-Ti	-0.28935	1.02725	21.3633	0.53333
			Ti-Ti	-0.46777	1.04914	30.1143	0.58133
HfPd ₃ , D0 ₂₄	5.595 [8]	1.64290 [8]	Pd-Pd	0.0	1.54072	86.0102	0.48587
			Pd-Hf	-0.13945	1.28686	48.5459	0.71841
			Hf-Hf	-0.48839	0.97173	30.3060	0.76712
TiPd ₃ , D0 ₂₄	5.489 [8]	1.63308 [8]	Pd-Pd	0.0	1.54072	86.0102	0.48587
			Pd-Ti	-0.41789	1.25706	40.8011	0.61751
			Ti-Ti	-0.46777	1.04914	30.1143	0.58133
ZrPd ₃ , D0 ₂₄	5.612 [8]	1.64558 [8]	Pd-Pd	0.0	1.54072	86.0102	0.48587
			Pd-Zr	0.00859	1.31860	54.2784	0.62937
			Zr-Zr	-0.44977	0.83723	21.4452	0.68484
HfPt ₃ , D0 ₂₄	5.636 [8]	1.63378 [8]	Pt-Pt	0.0	1.57871	97.7855	0.73741
			Pt-Hf	-0.25095	1.26331	47.0464	0.89364
			Hf-Hf	-0.48839	0.97173	30.3060	0.76711
ZrPt ₃ , D0 ₂₄	5.644 [8]	1.63448 [8]	Pt-Pt	0.0	1.57871	97.7855	0.73741
			Pt-Zr	-0.11256	1.45287	77.2155	0.83368
			Zr-Zr	-0.44977	0.83723	21.4452	0.68484

Last condition of system (2) describing stability of a crystal can be useful only in a case, when the appropriate experimental value of the bulk module is known. For the overwhelming majority of the ordered alloys in view of the above marked reasons these modules are not measured. As an alternative of conformity of the alloy bulk module to its experimental value the stability criterion of a crystal of considered superstructure relatively its transition in disordered state or in a state with other ordered arrangement of atoms can be used. In the present work such criterion was expressed in an acceptability of values of formation energies of antiphase boundaries oriented in basic planes. The parameters of potentials of some alloys with superstructures $D0_{19}$ and $D0_{24}$ determined in according with described scheme and initial experimental data are listed in the table 1.

Modules of elasticity

Elasticity modules of of an alloy, according to their definition [10] can be obtained from a ratio

$$C_{mn} = \frac{d^2 U_{all}}{de_m de_n} \quad (6),$$

where U_{all} is density of internal energy of an alloy; e_m, e_n - components of deformation tensor; $m, n=1,2\dots 6$. Let's designate through

$$\vec{r}_{ij} = (x_{ij}, y_{ij}, z_{ij}) = (\vec{r}_i - \vec{r}_j) = ((x_i - x_j), (y_i - y_j), (z_i - z_j)) \quad (7)$$

- is vector, linking i-th and j-th knots in a deformed crystal, and through

$$\vec{r}_{0ij} = (x_{0ij}, y_{0ij}, z_{0ij}) \quad (8)$$

- is vector, linking the same knots in undeformed crystal. In further, for simplification of records, it is meaningful to remove indexes " i, j " both near a sign of a sum, and in summarizing expressions. That is, we shall write \vec{r} in exchange \vec{r}_{ij} , \vec{r}_0 in exchange \vec{r}_{0ij} , Σ in exchange \sum_{ij} and φ_{pq} in exchange $\varphi_{(p_i),(q_j)}$. The coordinates of vectors of interatomic bonds in elastic deformed and undeformed crystals are connected between themselves by ratio

$$\left. \begin{aligned} x &= (1 + e_1)x_o + \frac{e_6}{2}y_o + \frac{e_5}{2}z_o \\ y &= \frac{e_6}{2}x_o + (1 + e_2)y_o + \frac{e_4}{2}z_o \\ z &= \frac{e_5}{2}x_o + \frac{e_4}{2}y_o + (1 + e_3)z_o \end{aligned} \right\} \quad (9).$$

Expressions for elastic modules can be receive by differentiating (1) and using expressions (9).

$$\begin{aligned} C_{11} &= \frac{1}{2V_o} \sum \left(x^2 \frac{d^2 \varphi_{pq}}{dx^2} \right); \\ C_{12} &= \frac{1}{2V_o} \sum \left(xy \frac{d^2 \varphi_{pq}}{dxdy} \right); \\ C_{13} &= \frac{1}{2V_o} \sum \left(xz \frac{d^2 \varphi_{pq}}{dxdz} \right); \\ C_{33} &= \frac{1}{2V_o} \sum \left(z^2 \frac{d^2 \varphi_{pq}}{dz^2} \right); \\ C_{44} &= \frac{1}{8V_o} \sum \left(z^2 \frac{d^2 \varphi_{pq}}{dy^2} + 2yz \frac{d^2 \varphi_{pq}}{dydz} + y^2 \frac{d^2 \varphi_{pq}}{dz^2} \right) \end{aligned} \quad (10),$$

where V_o – is volume of one structural unit of an alloy - AB_3 . The calculation of elasticity modules for HCP metals was carried out in according with the similar scheme. The calculated and experimental values of elasticity modules (C_{mn}) for HCP metals are listed in table 2, and calculated values C_{mn} for a set of alloys - in table 3.

Table 2. Values of elasticity modulus C_{mn} (10^{11} Pa) of HCP metals. Numerator - is experimental value [11], denominator – is calculated one.

Metal	$\eta=c_0/a_0$	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}
Be Beryllium	1.5799	$\frac{2.923}{2.0996}$	$\frac{0.267}{0.6999}$	$\frac{0.140}{0.3553}$	$\frac{3.364}{2.0067}$	$\frac{1.625}{0.3678}$
Cd Cadmium	1.8859	$\frac{1.152}{0.6156}$	$\frac{0.397}{0.2052}$	$\frac{0.405}{0.2337}$	$\frac{0.512}{1.7321}$	$\frac{0.203}{0.2390}$
Co Cobalt	1.6329	$\frac{3.07}{3.8703}$	$\frac{1.65}{1.2901}$	$\frac{1.03}{0.7243}$	$\frac{3.581}{4.0085}$	$\frac{0.753}{0.7263}$
Hf Hafnium	1.5830	$\frac{1.811}{2.2804}$	$\frac{0.661}{0.7602}$	$\frac{0.772}{0.3758}$	$\frac{1.969}{2.2253}$	$\frac{0.557}{0.3824}$
Mg Magnesium	1.6240	$\frac{0.585}{0.7177}$	$\frac{0.250}{0.2392}$	$\frac{0.208}{0.1349}$	$\frac{0.610}{0.7284}$	$\frac{0.166}{0.1354}$
Re Rhenium	1.6148	$\frac{6.126}{7.5393}$	$\frac{2.700}{2.5131}$	$\frac{2.060}{1.4618}$	$\frac{6.827}{7.5275}$	$\frac{1.625}{1.4649}$
Ru Ruthenium	1.5824	$\frac{6.6957}{6.6957}$	$\frac{2.2319}{2.2319}$	$\frac{1.1866}{1.1866}$	$\frac{6.2707}{6.2707}$	$\frac{1.1943}{1.1943}$
Sc Scandium	1.5935	$\frac{0.9067}{0.9067}$	$\frac{0.3023}{0.3023}$	$\frac{0.1532}{0.1532}$	$\frac{0.8841}{0.8841}$	$\frac{0.1570}{0.1570}$
Tl Tallium	1.6002	$\frac{0.408}{0.7399}$	$\frac{0.356}{0.2467}$	$\frac{0.290}{0.2933}$	$\frac{0.528}{0.7257}$	$\frac{0.073}{0.1338}$
Ti Titanium	1.5885	$\frac{1.624}{2.1930}$	$\frac{0.920}{0.7310}$	$\frac{0.690}{0.3651}$	$\frac{1.807}{2.1508}$	$\frac{0.467}{0.3710}$
Zn Zinc	1.8563	$\frac{1.610}{0.9183}$	$\frac{0.342}{0.3061}$	$\frac{0.501}{0.2714}$	$\frac{0.610}{2.0174}$	$\frac{0.383}{0.2714}$
Zr Zirconium	1.5925	$\frac{1.434}{1.7372}$	$\frac{0.728}{0.5791}$	$\frac{0.653}{0.2901}$	$\frac{1.648}{1.7039}$	$\frac{0.320}{0.2965}$

Table 3. Calculated values of elasticity modulus C_{mn} (10^{11} Pa) of alloys with superstructures $D0_{19}$ and $D0_{24}$

Alloy, Superstructure	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}
WCo ₃ , D0 ₁₉	6.4062	2.1335	1.4118	6.5463	1.4152
MoCo ₃ , D0 ₁₉	6.1578	2.0526	1.3333	6.1651	1.3369
AlTi ₃ , D0 ₁₉	3.4881	1.1360	0.8040	3.7006	0.8060
TiNi ₃ , D0 ₂₄	2.9683	0.9884	0.6461	3.1700	0.6472
HfPd ₃ , D0 ₂₄	3.4151	1.1339	0.7478	3.6515	0.7574
TiPd ₃ , D0 ₂₄	3.3109	1.1025	0.6546	3.3480	0.6639
ZrPd ₃ , D0 ₂₄	3.5242	1.1893	0.8979	4.0529	0.8705
HfPt ₃ , D0 ₂₄	4.6061	1.5309	0.9878	4.8678	0.9982
ZrPt ₃ , D0 ₂₄	4.9801	1.6602	1.1773	5.4510	1.1759

It is visible from table 2, that for the majority of HCP metals the calculated proportions between elasticity modulus correspond to experimentally observable. Exceptions from this set are cadmium and zinc with the greatest values of an axial ratio. In cadmium and zinc the calculated values C_{33} appear more than three times exceed the experimental ones, while the values of remaining modulus C_{11} , C_{12} , C_{13} , C_{44} are underestimated. This circumstance is explained that at increase η the role of bonds close in the direction to the main axis of a crystal appears by more essential. Greatest deviations of values of elastic modulus from experimental ones are observed for beryllium. The most probable reason of this is that character of anisotropy of interatomic interactions in this metal appears much more complicated in contrast to included in considering model. Really, relation of experimental values $C_{11}/C_{12} > 10$ are not observe for any other of HCP metals.

Proportions between values of elasticity modulus of hexagonal crystals of alloys are close to the appropriate proportions in hexagonal metals. In particular, the modulus C_{11} and C_{33} , and also C_{13} and C_{44} are close on value. The ratio $C_{44} < C_{12} < C_{11}$, fair for HCP metals also appears fair and for the

ordered alloys. Calculated values C_{mn} for alloys with superstructure $D0_{19}$ in 1.5 - 2 times exceed the appropriate calculated values of modules of HCP metals included in composition of alloy. In superstructure $D0_{24}$ the given excess of modules makes 1.3 - 3 times. Reduction of modules in considered alloys do not occur in any one at all.

The reasons of this increase are as change of set of interatomic bonds in alloy in comparison with those in metals as presence in alloy composition the metal with higher elastic characteristics. As a rule, it is the metal with cubic (BCC, FCC) lattice (tungsten in WCo_3 , palladium in $ZrPd_3$ etc.).

On the other hand, increase of elastic modules of alloys in comparison with metals can be qualitatively explained and at atomic level. Really, in metals - components of alloys the quite certain "equilibrium" set of interatomic distances takes place. In ordered alloy the set of distances between atoms of identical sort appear different from such in pure metal. In result each sublattice of superstructure would appear as in a state of stress, what, in turn, lead to increase of modules. Apparently, that the greater mismatch of atomic diameters of component should result in to the greater mismatch of sets of lengths of interatomic bonds in metals and alloys. At greater distinction in atomic diameters it is necessary to expect greater increase of "pressure" between sublattices and, hence, increase of elastic modules of alloys. As an example can be an alloy $AlTi_3$ ($D0_{19}$), in which at rather low values of elastic modules of components were received high enough (in 1.5 - 2 times above, than for a titanium) values C_{mn} . Indirect experimental confirmation to this is the ratio between Young's modules for the given alloy and metals Al and Ti: $E_{Ti}=105$ GPa, $E_{Al}=60-70$ GPa, $E_{Ti3Al}=150$ GPa [12].

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