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Elastic properties, lattice dynamics and structural transitions in molybdenum at high pressures

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ABSTRACT

The structural phase transitions in molybdenum under pressures are investigated on the basis of first principle analysis of elastic constants behavior and phonon dispersions. The definition of the effective elastic constants of nth order ($n \geqslant 2$), governing the elastic properties of a loaded crystal, is given. The effective elastic constants of second and third order and the phonon dispersions are calculated by DFT methods in the pressure range of $P = 0 - 1400$ GPa, $T = 0$ K. The calculation results at $P = 0$ are in good agreement with the available experimental data. On the basis of the obtained results the stability of the *bcc* phase of molybdenum under pressure and the possibility of the phase transition are investigated. It is shown that the effective elastic constant $\widetilde{C}'$ which corresponds to the tetragonal uniform strain of a loaded crystal undergoes significant softening at $P > 400$ GPa. In the same pressure range the frequencies of the transverse branch $T_{[1\bar{1}0]}[\zeta\,\zeta\,0]$ also begin to soften and already at $P \approx 1000$ GPa they become imaginary near the wave vector $\left[\frac{1}{4}\,\frac{1}{4}\,0\right]$. The *bcc* → *dhcp* phase transition associated with the softening of $\widetilde{C}'$ and the soft mode $T_{[1\bar{1}0]}\left[\frac{1}{4}\,\frac{1}{4}\,0\right]$ is discussed.

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1. Introduction

Investigation of the elastic properties of *bcc* transition metals of V and VI groups of the Periodic system under high pressures (the pressures comparable with the bulk modulus value) is currently a subject of great interest. In the first place, it is caused by the fact that lattice compression provides a very convenient way to probe the interatomic potentials, allowing one to study the nature of anharmonic contributions. In the second place, it is due to the recent discovery of the body centered cubic (*bcc*) → rhombohedral phase transition under the pressure of 69 GPa (at room temperature) in vanadium (V group) in the synchrotron X-ray diffraction experiments [1]. The peculiarity of this transition is that it contradicts to the general tendency of phase transitions under pressure i.e. transformation of a crystalline matter into the structures with a higher symmetry and atomic packing density under high pressure [2]. This transition is close to a second-order phase transition and it is associated with the loss of stability of the *bcc* lattice of vanadium to the uniform shear strain. The latter is shown by *ab initio* calculations [3,4], according to which the effective elastic constant $\widetilde{C}_{44}$ becomes negative in the vicinity of the transition (the effective elastic constants completely determine the response of a compressed crystal to an additional infinitesimal strain [5]). This conclusion is confirmed by the calculations of lattice dynamics of vanadium under high pressure [6,7]: the transverse acoustic modes in the directions [1 0 0] and [1 1 0] near the Brillouin zone center, associated with the elastic constant $\widetilde{C}_{44}$, undergo strong softening at the pressure $P \approx 70$ GPa. The structural transformations of this type are called elastic phase transitions [8]. Stability of a new high pressure phase is ensured by nonlinear elasticity of the crystal lattice, which is characterized by the elastic constants of third, fourth and higher orders.

The *ab initio* calculations of the second order elastic constants of other metals of V and VI groups (Nb, Ta, Mo and W) showed that under the pressure up to 400 GPa their *bcc* lattice remained stable with respect to uniform strain, since the softening of the elastic constants was not observed. However, in the case of molybdenum the calculation of the Gibbs free energy for typical metal structures (*bcc*, *fcc* and *hcp*) showed that the *bcc* molybdenum undergoes a phase transition under pressure in megabar range. Under normal conditions molybdenum has the *bcc* structure, which is preserved up to the highest experimentally achieved pressure of 560 GPa ($T = 300$ K) [9]. Authors of paper [10] predict the *bcc* → *hcp* phase transition under the pressure of about 420 GPa and the subsequent *hcp* → *fcc* transition under the pressure of approximately 620 GPa on the basis of first-principles total energy calculations. From the

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results of work [11] it follows that at $T = 0$ K the *bcc* structure of molybdenum transforms into the *hcp* phase at $P \approx 520$ GPa, which transforms into the *fcc* phase at $P \approx 740$ GPa. Further research [12,13] showed that the *hcp* Mo is not thermodynamically stable, and the *bcc* phase transforms directly into the *fcc* phase at 700 GPa. These results were later confirmed by the calculations of enthalpy difference among the *fcc*, *bcc*, *hcp* and A15 phases as a function of pressure, which revealed the only *bcc* → *fcc* transition at 720 GPa [14,15]. Later the *dhcp* phase was also considered [16] as a possible structure and a higher stability of this structure than both the *fcc* and *hcp* at low temperature and the pressure of 660 GPa was shown. In the recent research [17] the comparison of the *bcc*, *fcc*, *hcp* and *dhcp* structures' enthalpies confirmed the *bcc* → *dhcp* transition at 660 GPa.

Lattice dynamics and elastic constants of molybdenum under pressure were investigated in work [18]. Unfortunately the authors did not discuss observed pressure-induced softening of the phonon modes $T_{1\bar{1}0}[\zeta\,\zeta\,0]$ in the *bcc* at high pressure. Meanwhile this character of the phonon spectrum, together with the $\widetilde{C} = (\widetilde{C}_{11} - \widetilde{C}_{12})/2$ softening provides a transition path from the *bcc* to the *dhcp* structure [19]. Nevertheless peculiarities in the second order elastic constants behavior under pressure up to the $P = 420$ GPa were not observed, which is in agreement with the previous research [3]. However the pressure of the *bcc* transition to another phase is significantly higher than this value, thus a further investigation of the *bcc* phase elastic properties is an important problem.

In present work we continue the research of possible phase transitions in molybdenum at high pressure. For this purpose the elastic constants of second- and third-order, and the phonon dispersion of molybdenum in the pressure range of 0–1400 GPa ($T = 0$ K) were calculated in the framework of density functional theory (DFT) and density functional perturbation theory (DFPT) respectively. The stability of the *bcc* structure of molybdenum subjected to uniform strain was analyzed, and the possibility of a phase transition to the *dhcp* structure was considered. The definition of the effective elastic constants of various order, governing the elastic behavior of a loaded crystal is given before the discussion of the result.

2. Effective elastic constants

The elastic phase transitions are accompanied by small but finite strain of the crystal lattice. In order to include all nonlinear effects properly, it is convenient to use the finite strain theory. Therefore the Lagrangian strain parameters are used to describe the strained state of the crystal [20]:

$$\eta_{ij} = \frac{1}{2}(\alpha_{ki}\alpha_{kj} - \delta_{ij}), \tag{1}$$

where $\alpha_{ki} = \partial r_k/\partial R_i$ is the deformation gradient, r_k and R_i are the Cartesian coordinates of the chosen point of a crystal in the deformed and initial states, respectively; δ_{ij} is the Kronecker symbol. The summation over repeated indexes is implied. The tensor η_{ij} can be expressed in terms of the displacement gradient $u_{ij} = \partial u_i/\partial R_j$ ($u_i = r_i - R_i$), since

$$\alpha_{ij} = \delta_{ij} + u_{ij}, \tag{2}$$

thus $\eta_{ij} = \frac{1}{2}(u_{ij} + u_{ji} + u_{ki}u_{kj})$. Hereafter we consider the strain to be "pure" (rotation of a crystal is absent and $u_{ij} = u_{ji}$),

$$\eta_{ij} = u_{ij} + \frac{1}{2}u_{ki}u_{kj}. \tag{3}$$

Thermodynamic potential at a given temperature T and pressure P is the Gibbs potential G. The change in the Gibbs potential per unit volume in initial state V_0 due to an additional deformation superimposed on the initial state is expressed in the form [21]:

$$\frac{\Delta G}{V_0} = \frac{1}{2}\widetilde{C}_{ijkl}\eta_{ij}\eta_{kl} + \frac{1}{6}\widetilde{C}_{ijklmn}\eta_{ij}\eta_{kl}\eta_{mn} + \frac{1}{24}\widetilde{C}_{ijklmnpq}\eta_{ij}\eta_{kl}\eta_{mn}\eta_{pq} + \ldots \tag{4}$$

Here $\Delta G = G(P,T,\eta) - G(P,T,0)$ is the change in the Gibbs potential caused by the deformation η,

$$\widetilde{C}_{ijkl..} = \frac{1}{V_0}\left(\frac{\partial^n G}{\partial\eta_{ij}\partial\eta_{kl..}}\right)_T, \tag{5}$$

are the isothermal effective elastic constants of nth order ($n = 2,3,4$) at a given stress and temperature T. The linear term of the expansion is absent because the system is in the equilibrium state. The strain-induced change in G is

$$\frac{\Delta G}{V_0} = \frac{\Delta F}{V_0} - \int_0^{\eta} t_{ij}d\eta_{ij}. \tag{6}$$

Here ΔF is the change in the Helmholz free energy caused by the deformation η_{ij}, $t_{ij} = J\sigma_{ij}\gamma_{ik}\gamma_{jl}$ is the Cauchy strain tensor, where $J = det|\alpha_{ij}|$, γ_{ik} is the inverse of α_{ki} [20]. The tensor t_{ij} considers the change in the strain value due to deformation, i.e. it depends on η_{ij}, thus the term $\sigma_{ij}u_{ij}$ in the expression of the Gibbs energy [22] has to be replaced by $\int_0^{\eta} t_{ij}d\eta_{ij}$. For the isothermal and adiabatic deformations of a crystal, the value of the integral in Eq. (6) does not depend on the path of integration [23]. In case of hydrostatic pressure the expression for $\frac{\Delta G}{V_0}$ is simplified and we have

$$\frac{\Delta G}{V_0} = \frac{\Delta F}{V_0} + P\frac{\Delta V}{V_0}, \tag{7}$$

where $\Delta V = V - V_0$ is the change in the volume of a crystal caused by the deformation, determined by the tensor component η_{ij}.

The value $\frac{\Delta F}{V_0}$ can be written in the form [20]:

$$\frac{\Delta F}{V_0} = -P\eta_{ii} + \frac{1}{2}C_{ijkl}\eta_{ij}\eta_{kl} + \frac{1}{6}C_{ijklmn}\eta_{ij}\eta_{kl}\eta_{mn} + \frac{1}{24}C_{ijklmnpq}\eta_{ij}\eta_{kl}\eta_{mn}\eta_{pq} + \ldots, \tag{8}$$

here

$$C_{ijkl..} = \frac{1}{V_0}\left(\frac{\partial^n F}{\partial\eta_{ij}\partial\eta_{kl..}}\right)_T. \tag{9}$$

The constants $C_{ijkl..}$ are the generalization of the elastic constants of nth order introduced by Bragger [24] for the zero-stress case to the case of the loaded condition.

Unlike the elastic constants expressed by Eq. (9), the effective elastic constants in Eq. (5) include both the change in the free energy F in the presence of deformation near the initial stressed state, and the work against external stress by the forces caused by the deformation itself. Therefore, according to works [25,26], $\widetilde{C}_{ijkl..}$ completely characterize the elastic properties of the loaded crystal. Unlike the Bragger type elastic constants (9), $\widetilde{C}_{ijkl..}$ posses full Voigt symmetry to indexes permutation only in case of the hydrostatic loading [20,26]. Since these constants take into account external stress, the Cauchy relations cannot be fulfilled for them.

If the effective elastic constants are used, all relations of theory of elasticity have the same form for both loaded and unloaded states. Particularly Born's stability conditions of a material to a uniform strain which are obtained from the requirement of a positively defined quadratic form of the thermodynamic potential (for a loaded crystal it is G). For a cubic crystal under hydrostatic pressure, the conditions violation of which leads to the loss of stability of the crystal to a uniform strain, are obtained from Eq. (4):

$$\widetilde{C}_{11} + 2\widetilde{C}_{12} > 0, \tag{10a}$$

$$\widetilde{C}_{11} - \widetilde{C}_{12} > 0, \tag{10b}$$

$$\widetilde{C}_{44} > 0, \tag{10c}$$

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