Elastic properties and lattice dynamics of ruthenium at high pressures

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Abstract. The elastic properties and structural stability in ruthenium under pressure are investigated. The analysis is performed in the framework of Landau theory and nonlinear elasticity. For this purpose the definition of effective elastic constants (EC) of n-th (n≥2) order characterizing elastic properties of loaded crystal and the relations between effective EC and corresponding EC of Bragger type for hcp crystals is given. The conditions of hcp lattice stability to the uniform shear strain under the pressure P are expressed in terms of the second order effective EC. The method of effective EC calculations for hcp crystals under hydrostatic pressure is presented. The equation of state and EC of second and third order and phonon dispersion relations in high-symmetry directions in the pressure range of 0 – 600 GPa are calculated in the framework of the density functional theory (DFT) and the density functional perturbation theory (DFPT) respectively. EC are in the good agreement with available experimental data and increase monotonically with pressure, no softening or stability condition violation are observed. Softening of phonon frequencies near the Brillouin zone center is also not observed.

1. Introduction
Ruthenium is a transitional 4d metal with the hexagonal closed packed (hcp) structure at normal conditions. A sequence of the bcc metals (V, Mo, W) demonstrates a possibility of structural transitions at high pressure associated with the EC and phonon frequencies softening. Hexagonal closed packed structure is common for transitional metals, however the most calculations were performed for metals with cubic lattice. To our knowledge data on elastic constants and phonon dispersion of Ru at pressure are poor. Elastic constants of second order for the number of metals with hcp structure (including ruthenium) were calculated ab initio [1] at \( T = 0 \) K and the single \( C_{44} \) EC was determined from the Raman frequencies up to 60 GPa [2]. In work [3] the elastic constants of second and third order of Os and Ru were calculated at \( P = 0 \) \( (T = 0 \) K) using Lennard-Jones potential. The phonon dispersion in high-symmetry directions at ambient pressure were measured by the neutron scattering and calculated using the DFT in work [4]. The purpose of these research is to investigate the elastic properties and phonon stability of the hcp ruthenium at high pressure. The elastic constants of second and third order of hcp ruthenium in the wide pressure range (0 – 600 GPa) are calculated by the DFT from the energy – strain relation. The phonon dispersions in high-symmetry directions in the same pressure range are determined by the DFPT.

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2. Elastic constants of loaded crystal and stability conditions

Thermodynamic definition of the elastic constants of $n$-th order ($n \geq 2$) for the unloaded crystal is presented in work [5]. For the isothermal constants we have:

$$C_{ijkl} = \frac{1}{V_0} \left( \frac{\partial^n F}{\partial \eta_{ij} \partial \eta_{kl}} \right)_0$$  \hspace{2cm} (1)

Here $F$ is the Helmholtz free energy, $V_0$ is the volume in the initial state, $\eta_{ij}$ is the components of the Lagrangian finite strain tensor [6]. The isothermal elastic constants of the loaded crystal (effective elastic constants [7]) can be defined the same way as it is done in work [8]

$$\bar{C}_{ijkl} = \frac{1}{V_0} \left( \frac{\partial^n G}{\partial \eta_{ij} \partial \eta_{kl}} \right)_0,$$  \hspace{2cm} (2)

where $G$ is the Gibbs free energy (thermodynamic potential at given temperature and external loading). The change of $G$ at the hydrostatic pressure $P$ caused by the deformation $\eta$, $\Delta G = G(P,T,\eta) - G(P,T,0)$ can be presented in form $\Delta G = \frac{\Delta F}{V_0} + P \frac{\Delta V}{V_0}$; here $\Delta F$ and $\Delta V$ are the change in free energy and volume at this strain respectively. The effective elastic constants (2) in contrast to (1) include both the change in free energy $F$ in presence of small strain near the initial loaded state and the work against external stress by the forces caused by the strain itself. If strain isn’t applied, definitions (1) and (2) are identical. When the effective constants $\bar{C}_{ijkl}$ are used all the relations of the theory of elasticity can be applied including Born's stability conditions which are identical in both loaded and unloaded states.

From the requirements of a positively defined quadratic form of the thermodynamic potential we obtain the stability conditions of a crystal to a uniform strain. For crystals with hexagonal symmetry we have $\bar{C}_{33}(\bar{C}_{11} + \bar{C}_{12}) - 2\bar{C}_{13}^2 > 0$, $\bar{C}_{11} - \bar{C}_{12} > 0$, $\bar{C}_{44} > 0$; here $\bar{C}_{\alpha\beta}$ are the elastic constants of second order in the Voigt’s notation. These conditions can be violated if temperature or pressure are changed. This violation can cause the structural transformation into spontaneously deformed state, stability of which is ensured by the nonlinear elasticity of the lattice (elastic constants of 3, 4 and further orders).

Let us express the effective elastic constants $\bar{C}_{\alpha\beta}$ and $\bar{C}_{\alpha\beta\gamma}$ in terms of the corresponding Bragger type elastic constants, calculated in loaded state as it is done in [8] for cubic crystals. The crystals of hexagonal symmetry (622, 6/mmm, 6m2, 6mm) have five elastic constants of second and ten elastic constants of third order [6]. The obtained results are presented in Table 1. Thus for the calculation of the effective elastic constants $\bar{C}_{\alpha\beta}$ it is required to find pressure and elastic constants $C_{\alpha\beta}$ from the expansion of free energy $F$ in components $\eta_{ij}$ (see [8], formula (6)).

| Table 1. Relations between $\bar{C}_{\alpha\beta}$ and $C_{\alpha\beta}$. |
|---------------------------------------------------------------|
| $\bar{C}_{11} = C_{11} - P$ | $\bar{C}_{111} = C_{111} + 3P$ | $\bar{C}_{144} = C_{144} - P$ |
| $\bar{C}_{12} = C_{12} + P$ | $\bar{C}_{112} = C_{112} - P$ | $\bar{C}_{155} = C_{155} + P$ |
| $\bar{C}_{13} = C_{13} + P$ | $\bar{C}_{113} = C_{113} - P$ | $\bar{C}_{222} = C_{222} + 3P$ |
\[ \tilde{C}_{44} = C_{44} - P \]
\[ \tilde{C}_{123} = C_{123} + P \]
\[ \tilde{C}_{333} = C_{333} + 3P \]
\[ \tilde{C}_{66} = (\tilde{C}_{11} - \tilde{C}_{12})/2 = (c_{11} - c_{12} - 2P)/2 \]
\[ \tilde{C}_{133} = C_{133} - P \]
\[ \tilde{C}_{344} = C_{344} + P \]

3. Calculation details and results discussion

To calculate all five second order and ten third order elastic constants ten various deformation schemes were applied for each of the initial configurations. The initial loaded state was defined by the volume \( V_0 \). Deformed lattice vectors were expressed by relation \( r_i = a_j R_j \), where strain gradient \( a_{ij} \) is expressed in terms \( \eta_{ij} \) (see [8], formula (7)), \( r \) and \( R \) are the lattice vectors components in stressed and initial states respectively. For the calculation of the full energy of hcp Ru (\( T = 0 \text{ K} \)) at various values of \( V_0 \) and the deformation \( \eta_{ij} \) VASP [9] package was used. The pressure and the elastic constants \( C_{\alpha\beta\gamma} \) were determined as the coefficients of the expansion of free energy \( F \) in components \( \eta_{ij} \) or their combinations (see [8], formula (6)) by the mean square method (30 points with step 0.003 in the range of \( \eta = \pm 0.045 \)).

The phonon dispersions at the studied pressure range were calculated by DFPT through QuantumESPRESSO code (QE) [10]. Exchange-correlation effects were treated by the generalized gradient approximation with PW91 parameterization [11]. To describe ion-electron interactions the projector augmented wave method was applied [12] in VASP and Vanderbilt ultrasoft pseudopotential in QE.

For the integration of Brillouin zone the \( \Gamma \)-centered Monkhorst-Pack grids [13] were used with 28x28x18 and 16x16x10 meshes in VASP and QE respectively to take into account the symmetry of the studied crystal. The plane wave cutoff energy equaled to 600 eV in VASP and 50 Ry in QE.

All the initial loaded states of crystal in the range \( V_0/V(0) = 1 \pm 0.59 \) were fully relaxed. In the VASP calculations the Methfessel-Paxton smearing [14] with broadening of 0.2 eV was used for relaxation. For total energy calculations the tetrahedron method with Blochl [15] corrections was applied. In all QE calculations the Marzari-Vanderbilt cold-smearing scheme [16] was used.

The obtained lattice parameters are in good agreement with both experimental and theoretical results of other authors.

The results of second order EC calculations are given in table 2. As it follows from the table all three stability conditions, mentioned in section 2 are satisfied throughout the whole pressure range studied.

Table 2. Equation of state and EC of second order of hcp Ru for various values of \( P \) (\( T = 0\text{K} \)). Pressure and \( C_{\alpha\beta\gamma} \) are given in GPa.

| \( V_0 \), \( \text{Å}^3 \) | \( P \)  | \( \tilde{B} \)  | \( \tilde{C}' \)  | \( \tilde{C}_{11} \)  | \( \tilde{C}_{12} \)  | \( \tilde{C}_{13} \)  | \( \tilde{C}_{33} \)  | \( \tilde{C}_{44} \) |
|----------------|--------|---------|-------------|----------------|----------------|----------------|----------------|----------------|
| 13.621         | 0.072  | 332.5   | 197.3       | 574.2          | 179.5          | 210.5          | 643.4          | 187.7          |
| 12.203         | 47.080 | 521.1   | 289.6       | 914.3          | 335.1          | 366.3          | 1008.0         | 267.1          |
| 10.880         | 127.300| 576.3   | 419.6       | 1416.0         | 576.5          | 605.2          | 1545.0         | 376.3          |
| 9.651          | 259.300| 1204.0  | 602.8       | 2149.0         | 943.3          | 969.2          | 2331.0         | 526.2          |
| 8.512          | 471.800| 1794.0  | 852.7       | 3203.0         | 1498.0         | 1526.0         | 3471.0         | 724.5          |
| 7.977          | 621.400| 2177.0  | 1005.0      | 3883.0         | 1873.0         | 1899.0         | 4216.0         | 841.5          |
The value of $C_{\alpha\beta\gamma}$ corresponding to $P=0$ are in good agreement with the experimental and theoretical data [1, 17].

We also calculated the phonon dispersions in the whole studied pressure range, however we present only date for $P=0$ and 600 GPa (see figure 1). Phonon dispersion at $P=0$ GPa is in good agreement with experimental data and reproduces peculiarities near the $M$-point, unique for Ru and described in [4]. These are essentially dispersionless acoustic branch of transverse vibrations for more than 1/3 of the $\Gamma$-$M$ direction and the presence of almost degenerate branches at $M$. The drop of the longitudinal modes discussed in [4] is pronounced weaker in present research which can be explained by a poorer consideration of Fermi-surface geometry (smaller k-points mesh size) in our calculation. Phonon modes become harder with increasing pressure while the mentioned peculiarities become less and less pronounced and quickly disappear which finally results in spectrum similar to the one shown for $P=600$ GPa on figure 1.

It is seen that hcp structure of ruthenium remains mechanically and dynamically stable at pressure range of 0 – 600 GPa. Moreover all the elastic constants of second order in this range increase monotonically (crystal lattice becomes more durable) with pressure.

The third order EC $\tilde{C}_{\alpha\beta\gamma}$ are the important parameters, characterizing nonlinear mechanical response of crystal at high pressures and finite strains. In work [3] elastic constants $\tilde{C}_{\alpha\beta\gamma}$ were calculated at $P=0$ using Lennard-Jones potential. It is obvious, that such a calculations produce only approximate values. Different values of $\tilde{C}_{\alpha\beta\gamma}$ calculated at various pressures in these research are given in table 3. All the obtained $\tilde{C}_{\alpha\beta\gamma}$ are negative and their absolute values increase monotonically with pressure in the studied pressure range. The only exception is the value of $\tilde{C}_{123}$.

**Table 3.** Third order elastic constants of hcp Ru at various pressures ($T=0$ K). All EC values are given in $10^{-2}$ GPa.

| $P$, GPa | $\tilde{C}_{111}$ | $\tilde{C}_{222}$ | $\tilde{C}_{333}$ | $\tilde{C}_{133}$ | $\tilde{C}_{113}$ | $\tilde{C}_{131}$ | $\tilde{C}_{123}$ | $\tilde{C}_{144}$ | $\tilde{C}_{155}$ | $\tilde{C}_{344}$ |
|----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 0.072    | 75.24          | 67.90          | 69.31          | 15.63          | 7.075          | 8.336          | 2.384          | 2.770          | 10.97          | 17.04          |
| 47.080   | 110.20         | 98.74          | 100.30         | 22.79          | 10.48          | 12.07          | 2.551          | 4.067          | 15.30          | 25.00          |
| 127.300  | 159.90         | 142.30         | 143.80         | 32.82          | 14.92          | 17.14          | 2.389          | 5.792          | 21.15          | 36.11          |
| 259.300  | 228.10         | 201.60         | 204.00         | 47.26          | 21.34          | 24.45          | 2.706          | 8.176          | 29.01          | 51.34          |
| 471.800  | 318.20         | 280.20         | 285.50         | 66.66          | 29.64          | 34.59          | 2.825          | 11.14          | 39.23          | 71.47          |
| 621.400  | 371.60         | 326.90         | 334.10         | 78.96          | 34.41          | 42.09          | 2.468          | 12.82          | 45.14          | 83.38          |
Conclusion
The technique of n-th (n\geq2) order elastic constants calculation based on nonlinear elasticity for the hcp lattice is briefly described. The elastic constants of second and third order and phonon dispersions for the hcp Ru were calculated in the wide pressure range. The analysis of the results indicates the mechanical and dynamical stability of hcp Ru throughout the whole pressure range studied. The results are in good agreement with the available experimental and theoretical data.

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