APPENDIX I. CALCULATIONS OF ELASTIC PARAMETERS

On the basis of the Hooke's law, the stress σ_{ij} is proportional to the elastic strain ε_{kl} by $\sigma_{ij} = \sum_{kl} C_{ijkl} \varepsilon_{kl}$, where i, j, k and l are indies running from 1 to 3. The elastic constants C_{ijkl} form a fourth-order tensor, which, in general, can be arranged in a 6×6 matrix with maximum 21 independent elements.[127, 128] The number of independent elastic constants can be reduced by crystal symmetry. For instance, there are only three independent parameters (C_{11}, C_{12}, and C_{44}) for cubic crystal, and five independent parameters ($C_{11}, C_{12}, C_{13}, C_{33}$, and C_{44}) for hexagonal crystal. For ab initio calculated elastic constants, one of available approaches is based on the energy-strain relations. Here, the elastic constants of cubic and hexagonal lattices obtained from equation of state and structural deformation are briefly introduced.

A. Single-crystal elastic constants

The adiabatic elastic constants are the second order derivatives of the internal energy E with respect to the strain tensor e. At volume V, the elastic constants are obtained by straining the lattice and evaluating the total energy changes due to the strain as a function of its magnitude. Since the total energy depends on the volume much more strongly than on the strain, one may choose the applied strains to be volume conserving (except for the bulk modulus). The energy change upon strain can be written as

$$E(e_1, e_2, \dots, e_6) = E(0) + \frac{1}{2} V \sum_{i,j=1} C_{ij} e_i e_j + \mathcal{O}(e^3), \tag{1.1}$$

where $E(0)$ is the energy of undistorted lattice, and $\mathcal{O}(e^3)$ represents the terms proportional to e^k with $k \geq 3$. The strain matrix as follows

$$D(e) = \begin{pmatrix} e_1 & \frac{1}{2} e_6 & \frac{1}{2} e_5 \\ \frac{1}{2} e_6 & e_2 & \frac{1}{2} e_4 \\ \frac{1}{2} e_5 & \frac{1}{2} e_4 & e_3 \end{pmatrix}. \tag{1.2}$$

Mathematically, isochoric strain corresponds to a strain matrix with $det(D + I) = 1$, where I is the 3×3 identity matrix. As a consequence, the distortion matrix can be formulated as function of single parameter, and results in a particular combination of the elastic constants.[55]

In a cubic lattice, two of the independent elastic constants can be derived from the bulk modulus $B = (C_{11} + 2C_{12})/3$ and the tetragonal shear modulus $C' = (C_{11} - C_{12})/2$. Usually, B corresponds to isotropic lattice expansion and can be obtained from the equation of state fitted to the ab initio total energies calculated for a series of different volumes. C' and C_{44} can be determined from the volume-conserving orthorhombic and monoclinic deformations

$$\begin{pmatrix} 1 + \delta_o & 0 & 0 \\ 0 & 1 - \delta_o & 0 \\ 0 & 0 & \frac{1}{1-\delta_o^2} \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 1 & \delta_m & 0 \\ \delta_m & 1 & 0 \\ 0 & 0 & \frac{1}{1-\delta_m^2} \end{pmatrix}, \tag{1.3}$$

which lead to the energy change $\Delta E(\delta_o) = 2VC'\delta_o^2 + \mathcal{O}(\delta_o^4)$ and $\Delta E(\delta_m) = 2VC_{44}\delta_m^2 + \mathcal{O}(\delta_m^4)$, where $\mathcal{O}$ stands for the neglected terms.[55]

In a hexagonal lattice, the bulk modulus can be calculated from the equation of state as $B = C^2/C_S$, where $C^2 \equiv C_{33}(C_{11} + C_{12}) - 2C_{13}^2$ and $C_S \equiv C_{11} + C_{12} - 4C_{13} + 2C_{33}$.[129] The volume dependent hexagonal axial ratio $(c/a)_0(V)$ is related to the difference in the linear compressibilities along the a and c axes, viz., $R = -d\ln(c/a)_0(V)/d\ln V$, which in terms of hexagonal elastic constants becomes $R = (C_{13} + C_{33} - C_{11} - C_{12})/C_S$. In general, C_S gives the second order energy variation with c/a around the equilibrium value. C_S and C_{44} can be obtained from the isochoric and monoclinic deformations

$$\begin{pmatrix} 1 + \delta_h & 0 & 0 \\ 0 & 1 + \delta_h & 0 \\ 0 & 0 & \frac{1}{(1+\delta_h)^2} \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 1 & 0 & \delta_m \\ 0 & \frac{1}{1-\delta_m^2} & 0 \\ \delta_m & 0 & 1 \end{pmatrix}, \tag{1.4}$$

which lead to the energy change $\Delta E(\delta_\text{h}) = VC_S\delta_h^2 + \mathcal{O}(\delta_h^3)$ and $\Delta E(\delta_\text{m}) = 2VC_{44}\delta_\text{m}^2 + \mathcal{O}(\delta_\text{m}^4)$. The elastic constant $C_{66} = (C_{11} - C_{12})/2$ can be obtained from the orthorhombic strain as shown in Eq. 1.3, leading to a change in total energy $\Delta E(\delta_\text{o}) = 2VC_{66}\delta_o^2 + \mathcal{O}(\delta_o^4)$.[55]

The mechanical stability condition implies that the energy change $\Delta E \sim VC_{ij}e_ie_j$ upon any small deformation is positive, which can be formulated in terms of elastic constants.[128] For a cubic lattice the stability conditions are $C_{11} > 0$, $C_{44} > 0$, $C_{11} - C_{12} > 0$ and $C_{11} + 2C_{12} > 0$. The stability criteria for hexagonal crystal requires that $C_{11} > |C_{12}|$, $C_{44} > 0$, $C_{11}C_{33} > C_{13}^2$ and $C_{33}(C_{11} + C_{12}) > 2C_{13}^2$.

B. Polycrystalline elastic moduli

Using the single-crystal elastic constants, one can estimate the related properties of polycrystalline alloys. Two approximations are widely used to calculate the elastic modulus: a uniform strain for Voigt method and a uniform stress for Reuss method.[128] For cubic crystals,

$$B_\text{V} = \frac{C_{11}+2C_{12}}{3} \quad \text{and} \quad B_\text{R} = B_V, \tag{1.5}$$

$$G_\text{V} = \frac{(C_{11}-C_{12}+3C_{44})}{5} \quad \text{and} \quad G_\text{R} = \frac{5(C_{11}-C_{12})C_{44}}{4C_{44}+3(C_{11}-C_{12})}, \tag{1.6}$$

where B_V (G_V) and B_R (G_R) are the Voigt and Reuss bounds for the bulk (shear) modulus, respectively. For hexagonal crystals,

$$B_\text{V} = \frac{2(C_{11}+C_{12})+4C_{13}+C_{33}}{9} \quad \text{and} \quad B_\text{R} = \frac{C^2}{C_S}, \tag{1.7}$$

$$G_\text{V} = \frac{12C_{44}+12C_{66}+C_S}{30} \quad \text{and} \quad G_\text{R} = \frac{5}{2}\frac{C_{44}C_{66}C^2}{(C_{44}+C_{66})C^2+3B_VC_{44}C_{66}}. \tag{1.8}$$

The Voigt and Reuss bounds can be used to characterize the polycrystalline solids formed by randomly oriented anisotropic single-crystal grains. In these quasi-isotopic materials, one can measure the Voigt-Ruess anisotropy by the relation $A_\text{VR} =$

$(G_V - G_R)/(G_V + G_R)$. For isotropic crystal A_{VR} is zero, and for anisotropic crystal it is a single-valued measure of the elastic anisotropy, and it gives a relative magnitude of the actual elastic anisotropy. Additionally, based on the Hill method,[130] the arithmetic average for the bulk and shear modulus can be estimated form the Voigt and Reuss bounds, e.g., as $B = (B_V + B_R)/2$ and $G = (G_V + G_R)/2$.

The Young's modulus Y and Poisson ratio v can be derived from the bulk modulus B and shear modulus G by the relations

$$Y = \frac{9BG}{(3B+G)} \quad \text{and} \quad v = \frac{3B-2G}{2(3B+G)},$$ (1.9)

The Debye temperature obtained from elastic modulus is close to that determined form specific heat measurements at cryogenic conditions. One of the standard methods to calculate the Debye temperature θ_D is from the average sound velocity v_m according to

$$\theta_D = \frac{h}{k_B}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{1/3} v_m,$$ (1.10)

where h is the Planck's constant, k_B is the Boltzmann constant, N_A is the Avogadro number, n is the number of atoms in the unit cell, ρ is the density, M is the molecular weight, and v_m is expressed as

$$v_m = \left[\frac{1}{3}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right)\right]^{-1/3},$$ (1.11)

where v_L and v_T are the longitudinal and transverse sound velocities, respectively, which can be obtained from the polycrystalline elastic moduli and density, viz., $v_L = \sqrt{(B + 4G/3)/\rho}$ and $v_T = \sqrt{G/\rho}$.

APPENDIX II. ASSESSING THE EXCHANGE-CORRELATION FUNCTIONAL

To learn about the impact of exchange-correlation approximation on the elastic properties of multi-component alloys, in the EMTO-CPA calculations, the exchange-correlation effects treated within GGA in the form of PBE[58] and PBE for solid (PBEsol)[131] are considered here. Figure 9 shows the theoretical single-crystal elastic constants of the equiatomic CrMoW, CrMoWMn, CrMoWNi, and CrMoWNiFe in the bcc and fcc structures, respectively.[132] As one can see, PBEsol gives larger elastic constants than PBE for all considered alloys. In the case of the bcc CrMoW, for example, the PBEsol predicted C_{11}, C_{12}, and C_{44} are 504.4 GPa, 144.6 GPa, 133.6 GPa, respectively, which are ~7.7%, ~6.8%, and ~8.7 % larger than the PBE values. One possible reason is that the PBEsol produce smaller equilibrium volume when compared to the PBE data for the present alloys.[132] The somewhat large scattering in the elastic constants from PBEsol and PBE are still acceptable, especially if one consider the trends of the late $3d$ elements alloying additions.

Based on the PBEsol and PBE results, all bcc lattices are found to fulfill the mechanical stability criteria. The tetragonal shear modulus C' of CrMoW decreases with the increase of the late $3d$ elements, while the cubic shear modulus C_{44} almost has no changes. On the other hand, the fcc phase is mechanically unstable. For instance, $C_{44} < 0$, $C_{11} - C_{12} < 0$ for CrMoW, and $C_{44} < 0$ for CrMoWMn, CrMoWNi, and CrMoWNiFe. Thus, the bcc phase is predicted to be more stable than the fcc phase for all alloys considered here.

The bulk modulus, shear modulus, and Young's modulus given by PBEsol and PBE are shown in Fig. 10, together with the average values obtained from the rule of mixture based on the corresponding experimental data of the alloy components.[83, 132] To further examine the distribution of the calculated properties with respect to the average values, the changes of the corresponding properties in percentage are also presented. In the case of Young's modulus,

for example, PBEsol (PBE) gives ~ 17.7 (8.6) % for CrMoW, ~ 16.5 (2.7) % for CrMoWMn, ~ 1.5 (-7.9) % for CrMoWNi, and ~ -0.3 (-10.0) % for CrMoWNiFe. One notices that the relative difference between PBEsol and PBE does not change significantly, i.e., the two schemes differ on the average by ~ 10 % for the polycrystalline elastic moduli of the present alloys. Figure 10 shows the Young's modulus along different crystallographic directions for CrMoW. The PBEsol (PBE) values are 440 (408) GPa, 343 (316) GPa, and 363 (335) GPa along the <001>, <111>, and <110> directions, respectively. The corresponding data of pure bcc Cr, Mo and W metals that obtained from the single-crystal elastic constants are shown for comparison.[126] In general, these data are close to each other, and further experimental work is required to make comparison with the present values.
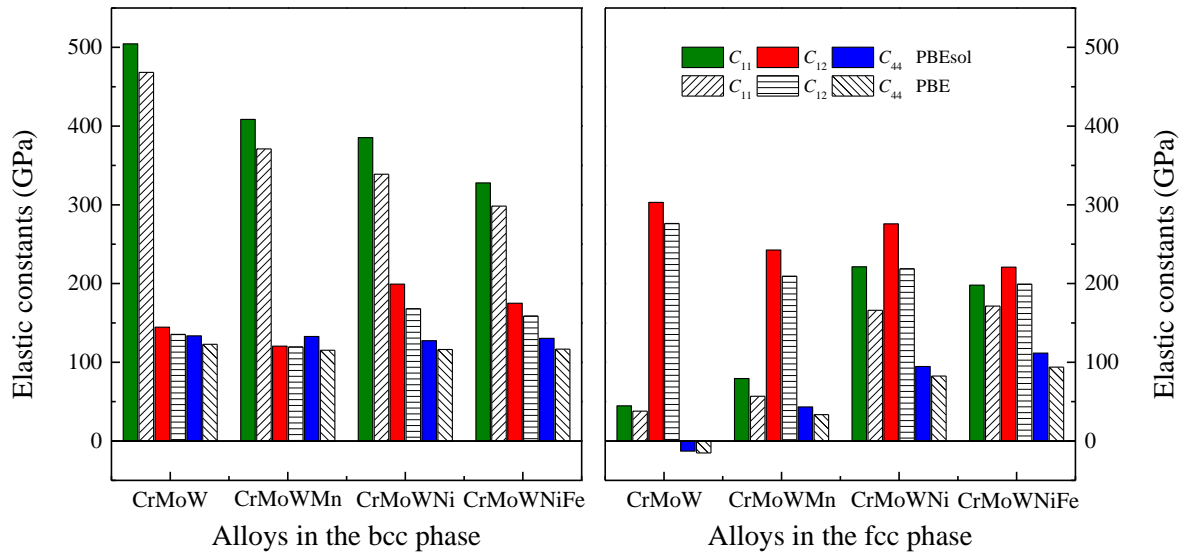
FIG. 9. Theoretical single-crystal elastic constants (C_{11}, C_{12}, and C_{44}) of CrMoW, CrMoWMn, CrMoWNi, and CrMoWNiFe in the bcc and fcc structures, respectively. Results are shown for two exchange-correlation functional (PBEsol and PBE). Data taken from Ref. 132.
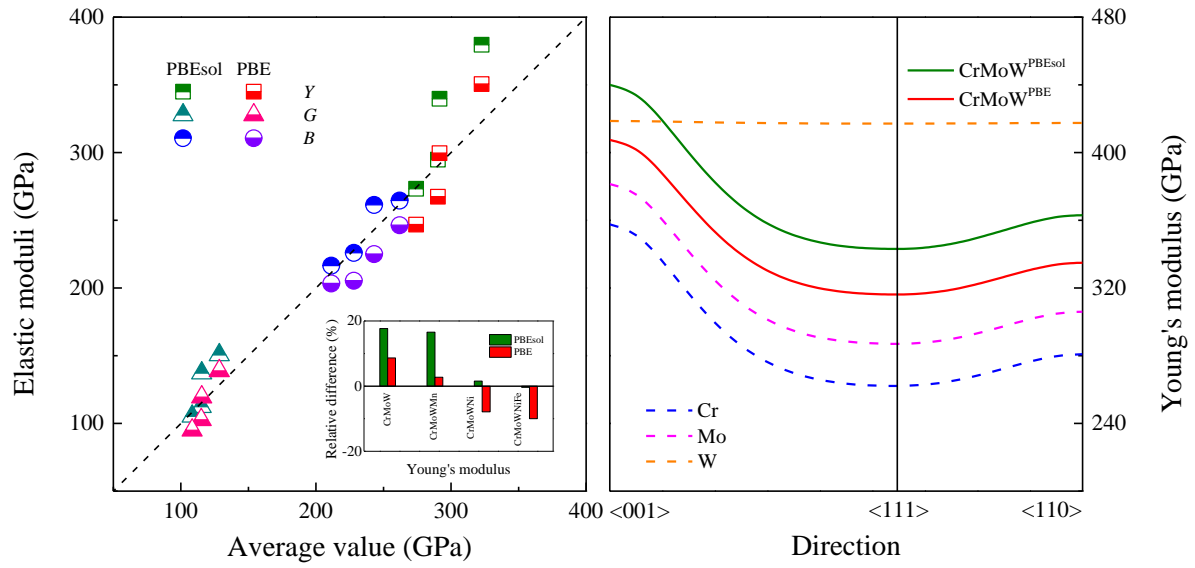
FIG. 10. Theoretical polycrystalline elastic moduli (B, G, and Y) of CrMoW, CrMoWMn, CrMoWNi, and CrMoWNiFe in the bcc structure. Results are shown for two exchange-correlation functional (PBEsol and PBE). The "average" values are obtained from the rule of mixture based on the corresponding experimental data of the alloy components. The "difference" values indicates the change of the calculated properties with respected to the corresponding "average" properties. Theoretical Young's modulus of CrMoW are shown as a function of direction, including the three main cubic directions. The corresponding data of pure bcc Cr, Mo, and W metals are plotted for comparison. Data taken from Refs. 126 and 132.