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First-principles study of the third-order elastic constants and related anharmonic properties in refractory high-entropy alloys

Xiaoqing Li

Applied Materials Physics, Department of Materials Science and Engineering, KTH - Royal Institute of Technology, Stockholm, SE-10044, Sweden

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ABSTRACT

The third-order elastic constants (TOECs) and elastic anharmonic behavior in four body-centered cubic refractory high-entropy alloys (HEAs) based on elements of the fourth, fifth, and sixth groups are investigated using density-functional simulations. We find that the values of the TOECs C_{111} are the largest in magnitude among the studied six independent TOECs and strongly increase with increasing average valence electron concentration (VEC). Interestingly, the TOEC C_{456} undergos a sign change as a function of the VEC. Using the obtained TOECs, we investigate the mode Grüneisen constants γ_i as well as the low temperature limit $\overline{\gamma}$, derive the long-wavelength acoustic nonlinearity parameters β, and reveal the pressure derivatives of effective elastic constants and polycrystalline moduli as a function of the VEC. Our results show that β displays a different directional order along the pure mode [100], [110], and [111] directions for the four considered refractory HEAs. Furthermore, we show that the directional order of β is not correlated to the crystal symmetry. With the help of the obtained pressure derivatives of polycrystalline moduli, we predict the low temperature volume expansion coefficient.

1. Introduction

High-entropy alloys (HEAs) have attracted great attention in the scientific community due to their outstanding properties [1–10], e.g., a dual-phase HEA that exhibits both high strength and high ductility was reported by Li et al. [6]. A recently proposed class of refractory HEAs is composed of refractory elements, e.g., Zr, V, Nb, Cr, and W, and mostly forms a solid solution with single body-centered cubic (bcc) phase. These alloys usually have excellent high-temperature strength, high melting point, and are synthesized from comparably cheap constituents [11–18]. These features render them uniquely suited for high-temperature applications making them a strong potential competitor to expensive Ni-based super alloys. Some refractory HEAs, such as ZrHfNb, have shown to exhibit a high resistance to irradiation damage and therefore are considered as a candidate structure material for nuclear energy systems [19–21]. In addition, refractory elements or alloys are potential materials for ambient temperature applications, such as fabrication materials for micro- or nanodevices, electrical resistors, and medical implants [10,22,23].

Elastic properties of materials play an important role in describing their mechanical deformation and structural stability under external loading condition. The second-order elastic constants (SOECs) characterize the linear elastic properties. Beyond the linear regime, the third-order elastic constants (TOECs) are the most important parameters for understanding the nonlinear response of materials [24–26]. The knowledge of the TOECs allows the evaluation of the anharmonicity of the crystal lattice and therefore is important in investigating the properties of lattice defects, such as dislocations and interfaces [27,28], the order of a martensitic phase transition [29], and the Invar behavior of alloys [30]. Furthermore, the TOECs have been used to develop empirical interatomic potentials [31] suitable for applications that involve relatively large displacements of atoms from equilibrium. In recent years, nondestructive testing techniques employing nonlinear ultrasound have been developed, which enable characterizing microstructural changes caused by fatigue or irradiation damage [32–34]. Specifically, the monitored nonlinear ultrasonic waves are connected to the TOECs of the material and strain fields created by defects such as dislocations or precipitates.

To our best knowledge, today, there is no information available on the TOECs of refractory HEAs. Since HEAs have many potential applications that involve different loading and working conditions, such as highly nonuniform applied stress or neutron irradiation in future nuclear power reactors, and often show surprising

E-mail address: xiaoqli@kth.se.

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properties compared to traditional alloys, it is fundamentally interesting to explore their TOECs and related anharmonic properties. In the present paper, we employ *ab initio* simulations to investigate the TOECs of four refractory HEAs, TiZrHfVNb, TiZrVNb, TiVNbMo, and NbTaMoW, and analyze other anharmonic properties, namely mode Grüneisen constants, pressure derivatives of effective elastic constants and polycrystalline moduli, and nonlinearity parameters. The present results are expected to be useful in studying and understanding other nonlinear phenomena in refractory HEAs and provide a theoretical guideline for further optimizing them.

2. Computational method

2.1. Continuum elasticity theory and methodological details

First, we present a short overview of finite-strain elasticity theory [25,35]. Let the initial coordinates of a material point be a_i and let $x_i = x_i(a_j)$ be its new position after applying strain. This deformation can be measured by the deformation gradients,

$$J_{ij} = \frac{\partial x_i}{\partial a_j}, \qquad i,j = \{1,2,3\}, \tag{1}$$

from which we may define the symmetric Lagrangian strain tensors as

$$\eta_{ij} = \frac{1}{2}\sum_k \left(J_{ki}J_{kj} - \delta_{ij}\right), \tag{2}$$

where $\delta_{ij} = 0$ for $i \neq j$ and 1 for $i = j$. The free energy $E(\eta_{ij})$ per unit mass at 0 K may be expanded as a Taylor series in terms of the strains around the equilibrium state, viz.,

$$\rho_0 E\left(\eta_{ij}\right) = \rho_0 E(0) + \frac{1}{2}\sum_{ijkl} C_{ijkl}\eta_{ij}\eta_{kl} + \frac{1}{6}\sum_{ijklmn} C_{ijklmn}\eta_{ij}\eta_{kl}\eta_{mn} + \cdots, \tag{3}$$

where ρ_0 is the initial mass density of the material, $E(0)$ is the initial state energy, C_{ijkl} are the SOECs, and C_{ijklmn} are the TOECs.

There are three independent SOECs (C_{11}, C_{12}, and C_{44}) and six independent TOECs (C_{111}, C_{112}, C_{123}, C_{144}, C_{166}, and C_{456}) for a cubic crystal structure. Here, the Voigt notation [25] ($C_{\alpha\beta}$ and $C_{\alpha\beta\gamma}$, where $\alpha,\beta,\gamma = 1-6$) and the full index notation are used interchangeably as needed. These elastic constants can be obtained by applying appropriate homogeneous Lagrangian strains [36]. In this work, six Lagrangian strain matrixes $\boldsymbol{\eta}$ shown in Table 1 were employed, where the nonzero components of each strain matrix are expressed in terms of a single parameter ξ. The elastic energy change Eq. (3) can then be written as an expansion in the strain parameter ξ, viz.,

$$\rho_0[E(\xi) - E(0)] = \frac{1}{2}\lambda_2\xi^2 + \frac{1}{6}\lambda_3\xi^3 + \mathscr{O}\left(\xi^4\right). \tag{4}$$

Here, the coefficients λ_2 and λ_3 are a combination of SOECs and a combination of TOECs, respectively. Table 1 displays the relationship between these coefficients and the SOECs and TOECs for the specific strain matrices $\boldsymbol{\eta}$. The coefficients λ_2 and λ_3 may be obtained by fitting Eq. (4) to the computed energy-strain data for each $\boldsymbol{\eta}$. In this work, for each $\boldsymbol{\eta}$, ξ was varied between −0.10 and 0.10 with step 0.01 after careful convergence tests.

The crystal lattice is distorted by applying homogeneous strains. To construct the deformed crystal structure spanned by a basis lattice vector $\boldsymbol{r}'$ from the unstrained configuration, the deformation gradients J_{ij} are applied to an unstrained basis lattice vector $\boldsymbol{r}$ as in Ref. [36], viz.,

$$r_i' = \sum_j J_{ij} r_j. \tag{5}$$

The deformation gradients J_{ij} may be obtained from the Lagrangian strain η_{ij} by inverting Eq. (2), viz.,

$$J_{ij} = \delta_{ij} + \eta_{ij} - \frac{1}{2}\sum_l \eta_{li}\eta_{lj} + \frac{1}{2}\sum_{lm}\eta_{li}\eta_{ml}\eta_{mj} + \mathscr{O}\left(\eta_{ij}^4\right). \tag{6}$$

Table 1
The relations between the coefficients λ_2 and λ_3 in Eq. (4) and the second- and third-order elastic constants for the Lagrangian strain matrix $\boldsymbol{\eta}$.

$\boldsymbol{\eta}$	λ_2	λ_3
$\boldsymbol{\eta}^A = (\xi,0,0,0,0,0)$	C_{11}	C_{111}
$\boldsymbol{\eta}^B = (\xi,\xi,0,0,0,0)$	$2C_{11} + 2C_{12}$	$2C_{111} + 6C_{112}$
$\boldsymbol{\eta}^C = (\xi,\xi,\xi,0,0,0)$	$3C_{11} + 6C_{12}$	$3C_{111} + 18C_{112} + 6C_{123}$
$\boldsymbol{\eta}^D = (\xi,0,0,0,0,2\xi)$	$C_{11} + 4C_{44}$	$C_{111} + 12C_{166}$
$\boldsymbol{\eta}^E = (0,0,0,2\xi,2\xi,2\xi)$	$12C_{44}$	$48C_{456}$
$\boldsymbol{\eta}^F = (\xi,\xi,0,2\xi,0,0)$	$2C_{11} + 2C_{12} + 4C_{44}$	$2C_{111} + 6C_{112} + 12C_{144} + 12C_{166}$

2.2. Mode Grüneisen constants

The Grüneisen constant is an important parameter for characterizing the anharmonic properties of crystals. This parameter is often used to test atomic theories and describe thermodynamical properties of materials [37,38]. Within the quasiharmonic approximation, the mode Grüneisen constants γ_i can be described by the volume dependence of the phonon frequencies ν_i, viz [39],

$$\gamma_i = -\frac{\partial \ln \nu_i}{\partial \ln V}. \tag{7}$$

For a cubic crystal and in the continuum limit, the long-wavelength acoustic modes γ_i may be expressed in terms of the SOECs and TOECs [39],

$$\gamma_i = -\frac{3K + 2w + k}{6w}, \tag{8}$$

where

$$w = C_{11}D_1 + C_{44}D_2 + C_{12}D_3 \tag{9a}$$

$$k = C_1D_1 + C_2D_2 + C_3D_3 \tag{9b}$$

with

$$D_1 = q_1u_1 + q_2u_2 + q_3u_3 \tag{10a}$$

$$D_2 = (q_2u_3 + q_3u_2)^2 + (q_3u_1 + q_1u_3)^2 + (q_1u_2 + q_2u_1)^2 \tag{10b}$$

$$D_3 = 2(q_2q_3u_2u_3 + q_3q_1u_3u_1 + q_1q_2u_1u_2) \tag{10c}$$

and