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Arithmetic extraction of elastic constants of cubic crystals from first-principles calculations of stress

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ABSTRACT

In the extraction of elastic constants of cubic crystals from first-principles calculations of energy or stress, the relative deviation of the adopted lattice-constants from true values ($\Delta a/a_0$) is inevitably added to the diagonal components of the applied elastic strains, which might lead to sizeable inaccuracy of bulk modulus B and tetragonal shear modulus C'. This paper suggests an arithmetic scheme that dramatically decrease the error transfer from $\Delta a/a_0$ in the extraction of B and C' from first-principles calculations of stress. By using this scheme, we compute the elastic constants of α-Fe, which are all in good agreement with those extracted by least-squares scheme from the same level first-principles calculations of energy and stress. The computed Young's modulus E and polycrystalline shear modulus G of Fe-base binary alloys at alloy concentration of 0.78 at.% are both satisfactorily consistent with the data at 0 K deduced from the available experimental measurements. Theoretical basis and tests both indicate that the suggested scheme is accurate and efficient in extracting elastic constants of cubic crystals at equilibrium.

1. Introduction

To date, first-principles quantum mechanical calculations have well developed to such an extent that quantitatively accurate predictions of the physical and chemical properties of materials are possible. Particularly, the calculation of elastic constants, which requires high numerical and methodological precision, can be performed by first-principles [1]. For a newly developed first-principles method, the comparisons of the calculated elastic constants with experimental measurements, or with other results of more precise, well-established first-principles methods often provide a critical feasibility test [2,3]. Due to continued developments, first-principles technique is able to explore the effects of temperature, pressure, and additives as well as impurities on elastic properties of materials, and such applications have appeared in a comprehensive range of physics, materials, geophysics, and mineralogy journals [4–12]. The standard method to compute elastic constants (either at equilibrium or under pressure) through first-principles modeling is to calculate second derivatives of the total energy $E(\varepsilon)$ per volume as a function of properly chosen strain ε [1,3,11]. The procedure is usually as follows (see also Ref. [13]). The modeling system is first fully relaxed so that minimum-energy cell data are derived. Then ionic relaxation is performed on the strained system with fixed volume and shape. Several elastic strains with different distortions δ are applied for each strain type, giving an energy parabola as a quadratic function of δ. The coefficients of δ in each quadratic function are then derived, and consequently, elastic constants are obtained since they are linear combinations of these coefficients. In practice, strains are often specially chosen so that the elastic constants directly act as the coefficients of δ [3,9,11,14]. As regards this procedure, one underlying problem is that small deviation of the minimum-energy cell data from the true ones leads to the inaccuracy of strain values for calculating elastic constants. Le Page and Saxe recognized the importance of this problem and put forward a symmetry-general least-squares solution [13]. In their paper, a small unknown initial strain is introduced by $\mathbf{S} = \varepsilon - \mathbf{e}$, where ε is the true strain and $\mathbf{e}$ is the nominal strain applied on the modeling system with minimum-energy. Adequate first-principles simulations are performed on the modeling system applied with different nominal strains and then a set of redundant quasilinear equations is constructed. Fairly accurate values of $\mathbf{S}$ components and single-crystal elastic con-

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stants C_{ij} can be obtained by least-squares solution for this set of equations by iterative procedure.

Besides the abovementioned "energy-strain" method, the elastic constants of materials can be extracted from first-principles calculations of stress according to the generalized Hooke's law [15]. In the elastic deformation regime, stress is in linear response to the applied strain while the total energy is a quadratic function of the strain. Therefore, from the viewpoint of first-principles calculation, the resulted stress is more sensitive to elastic strain, compared with the resulted total energy, which offers big advantage for the stress–strain method in computing elastic constants [15]. This "stress–strain" method originates from Nielsen and Martin's work of an explicit, practical expression for the stress tensor of an arbitrary periodic solid within the local-density-functional and its application to calculations of second-, third-, and fourth-order elastic constants of silicon [16]. This method is also commonly used for computing elastic constants either at equilibrium or under pressure [3,5,7,8,10,12]. Kiefer et al. calculated the three elastic constants C_{11}, C_{12} and C_{44} of cubic Mg_2SiO_4 spinel under different pressures by an arithmetic scheme with a single monoclinic strain tensor [5]. By using the concepts and methods for extracting elastic data and initial strain from total energy calculations [13], Le Page and Saxe developed a symmetry-general least-squares scheme for extracting elastic data and initial stress from first-principles calculations of stress [15].

In recent years, some new methods for extracting elastic constants from first-principles calculations of stress or energy have been developed [17–19]. Among the algorithms for improving the accuracy of the calculated elastic constants, one crucial is that very precise structure optimizations be performed to obtain the "equilibrium" lattice parameters in both energy-strain and stress–strain methods [7,18]. However, there has been no detailed discussion about the effects of the imprecision of adopted lattice parameters in extracting elastic constants from first-principles calculations of energy or stress. Noticeably, as regards the mathematical technique for extracting elastic constants, the least-squares fitting is very popular while the straight arithmetic scheme is sparsely used. The reason is that the least-squares scheme usually provides valuable improvement in the precision of the extracted elastic constants over the straight arithmetic scheme. Nonetheless, since arithmetic scheme is obviously more cost-saving than least-squares scheme, it is attractive once the same accuracy as least-squares scheme is realized in computing elastic constants. In this paper, we make a detailed analysis on the error transfer from the relative deviation of the adopted lattice-constants from true values $(\Delta a/a_0)$ in extracting the elastic constants of cubic crystals from first-principles calculations of energy and stress. We suggest a new arithmetic scheme that can dramatically decrease the error transfer in computing bulk modulus B and tetragonal shear modulus C' by using two special equations and three simple strain tensors. By using this scheme, we compute the elastic constants of α-Fe, and compare with other theoretical results extracted from the same-level first-principles calculations of stress and energy by least-squares fitting. In addition, we compute the Young's modulus E and polycrystalline shear modulus G of a series of dilute Fe-base binary alloys, and compare with the extrapolated values at 0 K based on experimental measurements. There is satisfactory coincidence in either of the above two comparisons. The later parts of this paper are organized as follows. Section 2 describes computational methods, including the first-principles settings and this arithmetic scheme. In Section 3, we first present explanations on the strain magnitudes and k-point mesh settings. Then we make a detailed analysis on the error transfer from $\Delta a/a_0$ in computing elastic constants of cubic crystals. Herein, we show clearly that there is very small error transfer from $\Delta a/a_0$ in computing elastic constants by this scheme. Finally the elastic constants of α-Fe and Fe-base binary alloys are computed and compared with other theoretic results as well as experimental measurements in this section. A short summary is given in Section 4.

2. Methodology

In this paper the structure optimizations of all systems, i.e., α-Fe and Fe-base binary alloys, are performed within spin-polarized density functional theory as implemented in Vienna *ab initio* simulation package (VASP) [20]. The interaction between ions and electrons is described by projector augmented wave (PAW) method [21]. Exchange and correlation functions are taken in a form proposed by Perdew and Wang (PW91) within generalized gradient approximation (GGA) [22], while the correlation energy interpolation is done by Vosko–Wilk–Nusair method [23]. The pseudopotential with suffix "pv" that treat outmost p electrons as valence is used for Mo, Mn, Nb, Pd, Rh and Ru, while the standard is used for all other elements. The energy cutoff for plane-wave expansion of wave functions is 350 eV. The minimum-energy lattice constants of all systems are firstly optimized by using conjugate gradient algorithm with changing volume and shape. In structure optimizations of the strained models, the conjugate gradient algorithm is used with constant volume and shape. The first order Methfessel–Paxton broadening scheme is selected for Brillouin-zone integration, and force convergence criterion is less than 0.002 eV/Å in all structure optimizations. This force convergence criterion is necessary for obtaining reliable elastic constants since the internal ions should be fully relaxed. For all Fe-base binary alloy systems, the $4\times4\times4$ bcc (body-centered cubic) supercell with periodic boundary conditions is used, along with the Γ-centered $5*5*5$ k-point mesh adopted for Brillouin zone sampling according to Monkhorst–Pack scheme. In each of the $4\times4\times4$ bcc supercells there are 127 Fe atoms and one alloying atom. In k-point mesh convergence testing, the two-atom $(1\times1\times1)$ bcc supercell of pure α-Fe is used, with which all k-point meshes are Γ-centered and generated by Monkhorst–Pack scheme. The projection operator integration for the non-local part of pseudopotential is done in reciprocal space for the $1\times1\times1$ bcc supercell, but in real space for the $4\times4\times4$ bcc supercell.

In this paper, the model system is described in Cartesian frame with coordinate axis 1, 2 and 3 being chosen along [100], [010] and [001] directions of a perfect cubic crystal, respectively. The cubic model with minimum energy is specified by three lattice vectors along the three orthogonal coordinate axes, i.e., $\boldsymbol{R}_1=(r,0,0), \boldsymbol{R}_2=(0,r,0)$ and $\boldsymbol{R}_3=(0,0,r)$, where r is the length. For convenience, the three lattice vectors can be arranged in a matrix form, denoted by $\mathbf{R}$,

$$\mathbf{R}=\begin{pmatrix}\boldsymbol{R}_1\\ \boldsymbol{R}_2\\ \boldsymbol{R}_3\end{pmatrix}. \tag{1}$$

Strain tensor is also described in this Cartesian frame, denoted by $\mathbf{e}$,

$$\mathbf{e}=\begin{pmatrix}e_{11} & e_{12} & e_{13}\\ e_{21} & e_{22} & e_{23}\\ e_{31} & e_{32} & e_{33}\end{pmatrix}, \tag{2}$$

where $e_{21}=e_{12}, e_{31}=e_{13}$ and $e_{32}=e_{23}$. We define $\overline{R}=\mathbf{R}(\mathbf{e}+\mathbf{I})$, where $\mathbf{I}$ is unit matrix. The three elements in each row of Matrix $\overline{R}$ composes a lattice vector, so that $\overline{R}$ can be expressed by

$$\overline{R}=\begin{pmatrix}\overline{\boldsymbol{R}}_1\\ \overline{\boldsymbol{R}}_2\\ \overline{\boldsymbol{R}}_3\end{pmatrix}. \tag{3}$$