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Elastic constants of cubic crystals

M. Jamal [a], S. Jalali Asadabadi [b], Iftikhar Ahmad [c,d,*], H.A. Rahnamaye Aliabad [e]

[a] Department of Physics, Islamic Azad University, Shahr-e-Qods Branch, Tehran, Iran
[b] Department of Physics, Faculty of Science, University of Isfahan (UI), Hezar Gerib Avenue, Isfahan 81746-73441, Iran
[c] Center for Computational Materials Science, University of Malakand, Chakdara, Pakistan
[d] Department of Physics, University of Malakand, Chakdara, Pakistan
[e] Department of Physics, Hakim Sabzevari University, Sabzevar, Iran

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ABSTRACT

In this paper we present details of our developed open source software, *cubic-elastic*, for the calculation of the elastic constants (ECs) of cubic crystals. The comparison of the calculated ECs for various types of cubic systems by this software with those from the other available softwares as well as experimentally measured results confirms that our code can predict reliable results. The success of our code originates from its use of single deformation. The other codes usually use rhombohedral strain (RS). RS leads to $3B_0 + 4C_{44}$ expression. Hence, RS systematically adds error to the C_{44} through the bulk modulus calculations, and thereby may not be mathematically an appropriate approach. The total energy is accurately calculated by the WIEN2k within the highly accurate full-potential (linearized) augmented plane-waves plus local orbitals method. The ECs are calculated by the second-order derivatives of the fitted polynomials to the calculated total energies with respect to the elements of strain tensors at zero strains. We have presented the theoretical background and methodology of the *cubic-elastic*. We have validated the software by taking a variety of cubic samples into consideration and calculated their ECs. The *zero bulk error* calculations show that the results obtained from the *cubic-elastic* are in good agreement with the available experimental data and the previous theoretical results and predicts the sign of elastic constants correctly. The calculated Cauchy's pressure (C'') and Poisson's ratio (v) of LaS predict that it is an ionic compound. This prediction is in agreement (disagreement) with the previous ionic (covalent) bonds prediction deduced from previous v (C'').

1. Introduction

Materials modelling and simulations have attracted great attention in the last decade because of the substantial growth in the processing speed of computers and progressive algorithms. Density functional theory based calculations are extensively used in the study of various physical and chemical properties of solids with great accuracy. One of these properties of solids is elastic compliance constants or simply elastic constants (ECs). Elastic constants is a response function to the external forces and are of significant importance in the materials properties [1–4]. The ECs have a relationship with the dynamical matrix [5] within the theory of elasticity [6] based on the continuum assumption or macroscopic nature of materials. On the other hand, the dynamical matrix can be related to the phonon frequencies which in turn have a connection with the atomic force constants through the discrete or microscopic nature of materials [5,7]. Consequently, the ECs provide a bridge between the atomic and the large-scale worlds. Therefore, the ECs can be used to evaluate the validity and accuracy of the microscopic and macroscopic theories by comparing the results with the corresponding experimental data. The ECs relate stress tensor to strain tensor [8,6] and can be used to distinguish elastic from plastic regimes by the elastic stability criteria [9]. For small deformations, the strain (stress) components can be linearly expanded in terms of the stress (strain) components whose expansion coefficients are elastic constants (elastic stiffness) [10]. The ECs provide a tool to obtain technological and mechanical important properties such as strength, hardness, wear, Voigt's modulus, Reuss's modulus, Hill's modulus, shear modulus, Young's modulus, bulk modulus, elastic stiffness coefficients, Poisson's ratio, and melting temperature [11]. Phonon density of states, phonon dispersion spectrum, and thereby phonon heat capacity, entropy, thermal expansion coefficient, and other thermodynamic properties are related to the ECs as well [12–14]. The sound velocities

* Corresponding author at: Center for Computational Materials Science, University of Malakand, Chakdara, Pakistan.
E-mail address: ahma5532@gmail.com (I. Ahmad).

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can also be obtained in different directions in a variety of materials by the ECs and as a result Debye temperature [15,16]. Moreover, based on the calculated elastic constants, we are able to define the elastic anisotropy ratio which is an important physical quantity for the structural phase stability of crystal structures [17]. All these evidences indicate that ECs can play crucial role in the derivation of many important physical quantities and evaluate the validity and accuracy of the associated theories.

In practice there are other codes available for the ECs calculation, even together with the WIEN2k, but one of the issues of these softwares is the systematic errors which is accumulated when one EC is calculated by others, discussed in details in the next sections. The other reason which also motivated us to develop new software was the use of the self-inconsistent softwares for the prediction of the nature of bond for cubic systems by Cauchy's pressure and Poisson's ratio [18–20]. Hence, we developed "*cubic-elastic*" using our previous experience of "*ortho-elastic*" [21] software, to overcome issues of the existing softwares for cubic systems and calculate ECs efficiently in order to predict experimental data accurately. In this work, we extend the *zero bulk error* EC calculations to ECs of cubic (or isometric) crystal systems which involve a large family of important compounds ranging from 195 to 230 space group numbers which is freely available at the WIEN2k website [22]. The underlying concepts and methodology in arriving at the current version of the *cubic-elastic* is presented here. We utilize the fact that the ECs can be calculated by the second-order derivative of a fitted polynomial of energy, $E(\epsilon)$, with respect to the strains, ϵ, at zero strains, i.e., $\frac{\partial^2 E(\epsilon)}{\partial \epsilon^2}|_{\epsilon=0}$ [23]. *Cubic-elastic* is interfaced to the WIEN2k code [24] which accurately solves the set of single particle Kohn–Sham equations within a self-consistent procedure based on the full-potential (linearized) augmented plane-waves plus local orbital, FP-(L) APW+lo, method [25]. We examine the accuracy of the *cubic-elastic* software by calculating the ECs for several cubic compounds. The results show that our calculated ECs are in good agreement with the experimental and previous theoretical data.

2. Theoretical background and computational details

2.1. Theoretical Background

ECs can be derived either from the calculated total ground state energy $E(x, \epsilon_{ij})$, known as the *energy approach* discussed by Stadler et al. [23], or from the relation between σ_{ij} and ϵ_{ij} ($\sigma_{ij} \leftrightarrow \epsilon_{ij}$), known as the *stress theorem* proposed by Nielsen and Martin [26]. Here, x stands for $V(P)$, the volume of (the exerted pressure on) the compound in question, and ϵ_{ij} (σ_{ij}) are the elements of strain (stress) tensor [11]. In this work we utilize the *energy approach* [23] in implementing *cubic-elastic*. We then calculate the ECs of the cubic systems by means of the *cubic-elastic* as interfaced to the WIEN2k code [24] within the *ab initio* FP-(L) APW+lo method [25]. To this end, we need to apply three different kind of appropriate strains. However, the *energy approach* does not tell us what kinds of strains are to be used to estimate the ECs. What we do in practice is to introduce some suitable strains to derive the ECs of cubic systems in better agreement with the experiments. Naturally, the question arises how well these strains can imitate the true ECs. We answer this question qualitatively after we complete the methodology discussion in this section. The validation of the introduced strains will be discussed in the later sections, where we show the accuracy of our results within the *cubic-elastic*.

We proceed with the idea of the *energy approach*. The internal energy of an elastic solid can be changed by a *volumetric* or *dilation* strain (change in volume and/or in shape) and by *distortional* or *isochoric* strain (change in shape but not in volume, i.e., volume-conserving). The energy can be expanded in a Taylor series up to the second-order about the unstrained situation for small deformations in the regime of Hooke's law:

$$E(V,\{\epsilon_k\}) = E_0 + V_0\left(\sum_{i=1}^{6}\sigma_i\epsilon_i + \frac{1}{2}\sum_{i,j=1}^{6}C_{ij}\epsilon_i\epsilon_j\right) \tag{1}$$

where $\{\epsilon_k\}$ denotes $\epsilon_1, \epsilon_2, \ldots, \epsilon_6$, $V_0(V)$ is the volume, $E_0(E)$ is the energy of the unstrained (strained) cubic system in question, and C_{ij} are the ECs. For simplicity, the elements of the two indexed strain (stress) ϵ_{ij} (σ_{ij}) tensor in Eq. (1) are transformed to those of the single indexed ϵ_i (σ_i) tensor by means of Voigt notation which uses the well-known transformations of $11 \rightarrow 1, 22 \rightarrow 2, 33 \rightarrow 3, 32\ \&\ 23 \rightarrow 4, 13\ \&\ 31 \rightarrow 5$, and $12\ \&\ 21 \rightarrow 6$. For the *distortional* strain the volume is not changed, viz. $\Delta V = 0$. In this case, the first sum of Eq. (1) involves stress tensors multiplied by strain tensors. The ECs can be calculated by taking the second-order partial derivatives of Eq. (1) for both *volumetric* and *distortional* deformations with respect to strains, at zero strains:

$$C_{ij} = \frac{1}{V_0}\left[\frac{\partial^2 E}{\partial\epsilon_i\partial\epsilon_j}\right]_{\{\epsilon_k\}=0} \tag{2}$$

We calculate the total energy for the unstrained system, namely, E_0 in Eq. (1), by using the full-potential APW+lo method. The original cubic system can be deformed by applying the following deformation matrix **D**:

$$\mathbf{D} = \boldsymbol{\epsilon} + \mathbf{I} = \frac{1}{2}\begin{pmatrix} 2+2\epsilon_1 & \epsilon_6 & \epsilon_5 \\ \epsilon_6 & 2+2\epsilon_2 & \epsilon_4 \\ \epsilon_5 & \epsilon_4 & 2+2\epsilon_3 \end{pmatrix} \tag{3}$$

where $\boldsymbol{\epsilon}$ is the matrix representation of the symmetric strain tensor in Voigt notation. After a small uniform deformation of the system, the lattice vectors can be distorted in orientation and in length. The distorted lattice vectors in their matrix representation, $\mathbf{R}'$ (see Appendix A), can be obtained by multiplying the matrix representation of the lattice vectors of an unstrained cubic structure, **R**, by **D**, viz. $\mathbf{R}' = \mathbf{RD}$. The elastic tensor of a cubic system can be determined by three independent C_{11}, C_{12}, and C_{44} ECs. The following deformations are used in the *Cubic-elastic* software to determine the C_{11}, and C_{12}:

$$\mathbf{D}_{ortho} = \begin{pmatrix} 1+\epsilon & 0 & 0 \\ 0 & 1-\epsilon & 0 \\ 0 & 0 & \frac{1}{1-\epsilon^2} \end{pmatrix} \tag{4}$$

$$\mathbf{D}_{cubic} = \begin{pmatrix} 1+\epsilon & 0 & 0 \\ 0 & 1+\epsilon & 0 \\ 0 & 0 & 1+\epsilon \end{pmatrix} \tag{5}$$

where $\mathbf{D}_{ortho}$ is a *distortional* orthorhombic deformation, and $\mathbf{D}_{cubic}$ is a *volumetric* cubic deformation. The C_{44} is determined in *Cubic-elastic* by:

$$\mathbf{D}_{monoc} = \begin{pmatrix} 1 & \epsilon & 0 \\ \epsilon & 1 & 0 \\ 0 & 0 & \frac{1}{1-\epsilon^2} \end{pmatrix} \tag{6}$$

where $\mathbf{D}_{monoc}$ is a *distortional* monoclinic deformation.

The energy for these three distortions can be obtain as (see Appendix B):

$$E(V,\epsilon) = E_0 + V_0\{(C_{11}-C_{12})\epsilon^2 + O(\epsilon^4)\} \tag{7}$$

$$E(V,\epsilon) = E_0 + V_0\epsilon(\sigma_1+\sigma_2+\sigma_3) + V_0\left\{\frac{3}{2}(C_{11}+2C_{12})\epsilon^2 + O(\epsilon^3)\right\} \tag{8}$$

and

$$E(V,\epsilon) = E_0 + V_0\{(2C_{44})\epsilon^2 + O(\epsilon^4)\} \tag{9}$$