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First principles investigation of the finite temperature dependence of the elastic constants of zirconium, magnesium and gold

Pär A.T. Olsson

Materials Science and Applied Mathematics, Malmö University, SE-205 06 Malmö, Sweden

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ABSTRACT

The purpose of this work is to investigate how well the temperature dependence of the elastic constants of single crystal zirconium, magnesium and gold are reproduced by *ab initio* density functional theory (DFT). The modelling was conducted via the quasi-harmonic approximation with the exchange–correlation functional based on the local density approximation. For gold and magnesium, the low and high temperature dependency agrees well with measurements, whereas the transition between low and high temperature ranges occurs over a wider range of temperature than observed experimentally. For zirconium, the simulations qualitatively predict the temperature dependence of the isentropic elastic constants, where C_{12} and C_{13} increase with increasing temperature. Because this behaviour is absent for the isothermal elastic constants, the increase can be attributed to the transformation from isothermal to isentropic elastic constants.

1. Introduction

The elastic constants of a material are important quantities that dictate many fundamental properties and characteristics that are essential in a wide range of applications. Their most fundamental use is to describe the strain energy and the relation between the elastic stress and strain fields of a body subjected to arbitrary triaxial loading through Hooke's Law [1]. However, they also play a central role in other contexts in solid state physics, for instance when describing the phonon frequencies in the long wave length limit [1] and predicting phase stability [2].

As with other fundamental physical properties, as a result of thermal vibrations the elastic constants vary with temperature and the variation is material specific. By surveying the literature on temperature dependent elastic properties of cubic metals it is seen that all elastic constants decrease with increasing temperature and that the magnitude is material specific [3]. For instance, for noble metals it has been observed that the elastic properties can decrease by 10% or more when the temperature is increased from about 0 K to 500 K [4–6]. For other more complex crystals, such as tetragonal (β-Sn) and orthorhombic (α-U, $BaSO_4$), the temperature dependent elastic constants do not behave as straightforward as for cubic materials and the elastic constants may increase or decrease with increasing temperature [3]. The same holds for hexagonal-closed-packed (HCP) materials for which it has been found that C_{12} and/or C_{13} may increase with increasing temperature [3]. Such examples include the group IVB transition metals (Zr, Ti and Hf [7]) for which C_{12} increases with increasing temperature, whereas for group IIA (Be [8,9] and Mg [10]) it is found that C_{12} and C_{13} are roughly constant. Meanwhile for group IIB materials (Zn [11,12] and Cd [13]) C_{12} does not vary significantly, but C_{13} decreases with increasing temperature. This demonstrates that despite the HCP materials have the same lattice structure, the elastic constants behave differently when increasing the temperature and to some accounts counterintuitively. It further implies that the electronic structure rather than the lattice geometry dictates its behaviour.

In order to find a unified description of the temperature dependent elastic properties, a great deal of experimental work has been performed in which some universal characteristics that are in common to most materials have been identified. For instance, the elastic tensor is constant in the low temperature limit and varies linearly at high temperatures. This has resulted in several empirical mathematical formulae, derived to reproduce these characteristics and to fit the experimental data [14–16]. Thus, for most formulations there is no theoretical justification for the analytical expressions other than their good fit and therefore they show limited success when applying them to materials other than those considered in the experiments. Two exceptions to this course of action, in which the analytical descriptions of temperature dependent elastic properties are based on a theoretically sound rationale, are the semi-empirical relations by Wachtman et al. [17] and

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E-mail address: Par.Olsson@mah.se

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Varshni [18]. To fit the elastic properties of oxides, Wachtman et al. [17] adopted an empirical relationship whose format was chosen only based on its good fit to experimental results. Although Wachtman et al. did not give any theoretical justification for its format, it was later proven that it could be derived from the Mie-Grüneisen equation of state [19], which explains its success in describing the experimental data. Varshni [18], on the other hand, assumed a completely theoretical approach for deriving a seminal equation, which is based on a simple Einstein oscillator model and the Leibfried–Ludwig assumption [20] that the temperature dependent elastic properties depend on the average thermal energy of an oscillator. This simple, yet powerful, relation has proven to predict the temperature dependent elastic properties of several materials with many different crystallographic symmetries with high accuracy. Despite the two analytical models have different functional formats and are derived from different rationales, they predict very similar temperature dependent elastic characteristics.

In order to supplement experimental work, quantum mechanical density functional theory (DFT) is a reliable numerical tool which has been used in numerous investigations to extract the elastic properties of metals, alloys and earth forming minerals. However, with only a few exceptions, such studies have been limited to modelling the elastic properties at low temperature. The reason for this is related to the significant numerical expense associated with calculating phonon densities of states required to describe the free energy within the quasi-harmonic approximation (QHA) [21]. Despite this, researchers have studied the temperature dependence of the calculated elastic constants of aluminium [22], tungsten [23], beryllium [24,25] and diamond [24], with varying degrees of success. In particular it has been shown that the elastic properties in the zero-temperature-limit and that the magnitude of the temperature dependence of the elastic constants do not necessarily correspond to those observed in experiments. These works demonstrate that the DFT/QHA approach predicts the general trends of the temperature dependent elastic constants, but yields a qualitative description at best.

The main purpose of this work is to investigate the temperature dependent elastic constants of zirconium and magnesium by DFT modelling within the QHA. The motive behind modelling zirconium is because the elastic properties of zirconium obtained from elastic wave velocity experiments have shown that C_{12} increases with increasing temperature [7] and it is of interest to investigate what causes such behaviour and if it can be captured by first principles modelling within the QHA. This is of importance because of the wide use of zirconium based alloys as fuel cladding in nuclear power reactors, for which the temperature dependent elastic properties play a central role in making lifetime predictions. Magnesium has the same lattice structure as zirconium and similar lattice parameters, but belongs to a different group in the periodic system and has a different electron structure than zirconium. From experiments it has been observed that the temperature dependent elastic constants of Mg behave differently from those in Zr. In particular it has been found that C_{12} and C_{13} do not vary with temperature, but rather remain constant throughout the measured temperature range. The differences and the counter-intuitive behaviour of these materials make it interesting to investigate the temperature dependence of the elastic constants using DFT/QHA, to see whether first principles modelling can give a qualitative explanation to what causes them to behave this way.

There are several reasons for why we choose to study gold in addition to the aforementioned HCP metals. Most theoretical works associated with the temperature dependent elastic constants have been limited to cubic or isotropic metals, which is why most of the analytical closed form expressions are not valid for HCP metals. Because gold is widely used as a calibration standard for high pressures and temperatures, there is a scientific value to study how well DFT predicts the elastic properties over a wide range of temperature. And finally, the experimentally measured temperature dependent elastic constants for gold are well-documented in the literature and there is little discrepancy between sources. For these reasons gold serves as a benchmark study for investigating the predictability of the adopted DFT/QHA approach, which is why it is included in this work.

The paper is organised as follows. In the following section we discuss elasticity theory, transformation from isothermal to adiabatic elastic constants and the Varshni relation and its implications for the temperature dependent elastic properties, which is followed by a thorough exposition of the modelling and numerical details. Thereafter we present the results: phonons, lattice parameters and thermal expansion for the considered materials, which are followed by discussions and analyses of the temperature dependent elastic properties of gold, zirconium and magnesium. The paper is concluded with a short summary and conclusions.

2. Elasticity

2.1. Elastic theory

The second order isothermal elastic tensor, C^T_{ijkl}, can be defined as the volume specific second derivative of the Helmholtz free energy, F, with respect to a homogeneous deformation of the body, i.e.,

$$C^T_{ijkl} = \frac{1}{V_0}\frac{\partial^2 F}{\partial\epsilon_{ij}\partial\epsilon_{kl}} \tag{1}$$

where ϵ_{ij} represents the strain tensor and V_0 is the reference volume. A suitable measure for the strain tensor is the Green–Lagrange strain tensor, whose components are related to the deformation gradient tensor, F_{ij}, via

$$\epsilon_{ij} = \frac{1}{2}(F_{ki}F_{kj} - \delta_{ij}) \tag{2}$$

where δ_{ij} is the Kronecker delta and the deformation gradient is a linear mapping relating the coordinates of the reference configuration, X_i, to the deformed configuration, x_i, i.e. $x_i = F_{ij}X_j$ [26].

At most a material has 21 independent elastic constants, but depending on the symmetry of the crystal lattice, the number of independent elastic constants can be significantly reduced. For materials with cubic symmetry, such as gold, they are reduced to three: C^T_{1111}, C^T_{1122} and C^T_{1212} (or C^T_{11}, C^T_{12} and C^T_{44}, respectively, in Voigt notation [27]). Depending on the conditions of the experiment or simulations performed, different types of elastic constants are extracted. Extracting the elastic constants from DFT calculations based on the Helmholtz free energy conducted within the QHA implies that they correspond to those obtained under isothermal conditions. However, resonance based experiments, such as elastic wave velocity measurements, resemble to a greater extent those of adiabatic conditions. Therefore, to make useful comparisons with experimental data it is necessary to transform isothermal elastic constants to isentropic. For cubic materials this can be achieved by using the conversions

$$C^S_{11} = C^T_{11} + \Delta, \quad C^S_{12} = C^T_{12} + \Delta, \quad C^S_{44} = C^T_{44} \tag{3}$$

where Δ is the conversion factor

$$\Delta = \frac{V_0 T\alpha^2 (C^T_{11} + 2C^T_{12})^2}{C_v} \tag{4}$$

in which α is the linear thermal expansion coefficient, C_v is the specific heat capacity and T is temperature [28]. Thus, C_{44} remains invariant when transforming from one thermodynamic condition to another. Likewise, by using the definition of isentropic and