Toward an accurate ab initio estimation of compressibility and thermal expansion of diamond in the \([0, 3000 \text{ K}]\) temperature and \([0, 30 \text{ GPa}]\) pressures ranges, at the hybrid HF/DFT theoretical level

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ABSTRACT

The isothermal bulk modulus, together with its temperature dependence, and the thermal expansion of diamond at various pressures were calculated from first principles in the \([0, 30 \text{ GPa}]\) and \([0, 3000 \text{ K}]\) pressure and temperature ranges, within the limits of the quasi-harmonic approximation (QHA). The hybrid HF/DFT functional employed (WC1LYP) proved to be particularly effective in providing a very close agreement between the calculated and the available experimental data. In particular, the bulk modulus at 300 K was estimated to be 444.6 GPa (\(K' = 3.60\)); at the same temperature, the (volume) thermal expansion coefficient was \(3.19 \times 10^{-6} \text{ K}^{-1}\). To the authors' knowledge, among the theoretical papers devoted to the subject, the present one provides the most accurate thermo-elastic data in high-pressure and temperature ranges. Such data can confidently be used in the determination of the pressure of formation using the “elastic method” for minerals found as inclusions in diamonds (recently applied on different minerals included in diamonds), thus shedding light upon the genesis of diamonds in the Earth’s upper mantle.

Keywords: Diamond, thermo-elastic properties, thermal expansion, ab initio calculations

INTRODUCTION

This work is part of a wider project devoted to the study of diamond formation in the upper mantle and its growth relationships with those minerals that are commonly found as inclusions in diamonds. In particular, subcratonic diamonds can contain inclusions of other minerals like olivine, garnet, spinel, pyroxenes, and sulfides (Nestola et al. 2011; Shirey et al. 2013). Diamonds and their inclusions are among the deepest materials originating from the Earth’s interior and reaching the planet surface. Their study plays a key role in understanding and interpreting the geodynamics, geophysics, petrology, geochemistry, and mineralogy of the Earth’s mantle (Stachel and Harris 2008, and references therein). By the study of such inclusions, in situ, by means of diffractionmetric or spectroscopic techniques, it is possible to determine the pressure (and the corresponding depth in the Earth’s mantle) at which the inclusions were formed (Nestola et al. 2011; Izraeli et al. 1999) using the so-called “elastic method” (see Shirey et al. 2013 for a review). However, to this end, very accurate data concerning the pressure-volume equation of state, the thermal expansion and the bulk modulus temperature dependence of both diamond and its inclusions are absolutely crucial to obtain low error in the pressure of formation.

As concerns diamond, previous experimental and theoretical determinations of the elastic parameters and thermal expansion existed. In particular, from the experimental side, the elastic constant measurements from Brillouin scattering, at room or higher temperatures, allowed the estimation of the bulk modulus and its temperature dependence (Grimsditch and Ramdas 1975; McSkimin and Andreatch 1972; Vogelgesang et al. 1996; Zouboulis et al. 1998). Experimental thermal expansion data (from low to high temperature up to 3000 K) at room pressure are available from Stoupin and Shvyd’ko (2011) and from Reeber and Wang (1996). Due to technical difficulties in the experimental determinations of accurate bulk moduli and thermal expansion at simultaneous high pressure and temperature, a number of theoretical works were devoted to the subject, both at the ab initio level (Hebbache 1999; Kune et al. 2003; Ivanova and Mavrin 2013; Maezono et al. 2007; Moutet and Marzari 2005; Valdez et al. 2012; Xie et al. 1999; Zhi-Jian et al. 2009) or the empirical one (force fields and other techniques based on some specific models; Agudo and Baonza 2006; Gao et al. 2006). Strongly depending upon the specific method employed, the calculated bulk moduli could be overestimated or underestimated by more than 10 GPa with respect to the experimental datum at 300 K, so that a more reliable ab initio methodology is required to get values that could parallel the experimental techniques in accuracy and under very extreme conditions of \(P\) and \(T\). To this end, the equation of state and the thermal expansion of diamond in the \([0, 3000 \text{ K}]\) and \([0, 30 \text{ GPa}]\) temperature and pressure ranges, respectively, have been determined by using the most recent ab initio techniques so far developed. In particular, an hybrid Hartree-Fock/density

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