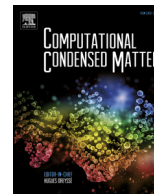




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journal homepage: <http://ees.elsevier.com/cocom/default.asp>Isotope effect on diamond's elastic-stiffness coefficients: An *ab initio* studyDaryl G. Clerc^{a,*}, Hassel Ledbetter^b^a ArTek Product Development, Inc., Red Bud, IL 62278, United States^b Mechanical Engineering, University of Colorado, Boulder, CO 80309, United States

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ABSTRACT

The effects of isotopic substitution on diamond's elastic-stiffness coefficients are studied theoretically by analyzing the zero-point motion and anharmonicity associated with lattice vibrations. Coefficients c_{11} , c_{12} , c_{44} , and bulk modulus B are reported as purely theoretical functions of x , where x denotes the atomic fraction of ^{13}C in $^{12}\text{C}_{(1-x)}^{13}\text{C}_x$. Second-order and third-order force constants are computed at the *ab initio* level and used as input to these expressions. As x increases, the predicted values of c_{11} , c_{12} , c_{44} , and B undergo essentially linear increases: $c_{11}(x) = c_{11}(0)(1 + 0.000049x)$, $c_{12}(x) = c_{12}(0)(1 + 0.00025x)$, $c_{44}(x) = c_{44}(0)(1 + 0.000021x)$ and $B(x) = B(0)(1 + 0.000088x)$. Thus, compared to the values at $x = 0$, the values of c_{11} , c_{12} , c_{44} , and B are predicted to change by only 0.0049%, 0.025%, 0.0021%, and 0.0088%, respectively, at $x = 1$. Our calculations also resolve a large discrepancy between two reported measurements of c_{12} , and provide a general method that can be used for arbitrary crystals having diamond's space group.

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1. Introduction

A material's elastic and anelastic properties enter quintessentially into a material's equation of state, which encompasses an enormous range of thermophysical properties. Diamond's elastic constants assume special importance because they relate directly to diamond's extreme properties: high hardness, high thermal conductivity, high resistance to extension and shear, low thermal expansivity. Less directly, elastic constants relate to diamond's other physical properties: low friction, wide optical transparency, low dielectric constant, and others. The recent discovery of superconductivity in boron-doped diamond [1] emphasizes further the importance of elastic constants. Specifically, elastic constants determine accurately the Debye temperature, which figures prominently in BCS-theory superconductivity and relates to an enormous variety of mechanical—physical—thermal properties.

This study has three principal purposes. First, extend our previous studies of second-order and third-order elastic properties of diamond [2]. Second, build on research of Vogelgesang and coworkers in which a quantum-mechanical analysis of zero-point

motion and lattice anharmonicity yielded the isotopic dependence of the bulk modulus [3], and extend their results by deriving expressions for $c_{11}(x)$ and $c_{12}(x)$. Third, clarify discrepancies between theory and measurement. Vogelgesang and coworkers predicted a very small isotope effect in the bulk modulus: only a 0.1% increase at $x = 1$ compared with the value at $x = 0$. That result is quite inconsistent with an ultrasonic measurement of $c_{12}(x)$ by Hurley and colleagues in which c_{12} at $x = 0.99$ was found to increase by 87% compared to the value at $x = 0$, inferring a 17% increase in the bulk modulus at $x = 1$ compared to $x = 0$ [4]. This discrepancy was mentioned by Plekhanov in an extensive review of isotope effects [5].

2. Computational method

Calculations used the *ab initio* implementation of density-functional theory embodied in GAPSS (Gaussian Approach to Polymers, Surfaces, and Solids). An overview of the GAPSS program, along with descriptions of the basis sets, computational parameters and methods for establishing convergence of computed physical properties, among other details, were reported in our previous study of diamond [2].

In this study, calculations use two distortions types labeled I and III, where the labels are consistent with the previous study [2]. The

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corresponding Eulerian tensor elements are $[\epsilon, \epsilon, \epsilon, 0, 0, 0]$ and $[\epsilon, \epsilon, -\epsilon, 0, 0, 0]$, using the six-component Voigt notation: $[\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4, \epsilon_5, \epsilon_6]$. Elastic coefficients and force constants are converted from an energy basis to a pressure basis by dividing by the volume of the rhombohedral unit cell (described below in the Theory section). All elastic properties are calculated in the Eulerian framework (infinitesimal strain). For comparison, the elastic properties associated with distortion I are also calculated in the Lagrangian framework (finite strain). The connection between the two is described in Appendix A.

Physical properties and statistical error were calculated as follows. Equilibrium total energy, lattice parameter, and second-order force constant were determined by fitting the computed total energies to Hooke's law over the harmonic region. The extent of the harmonic region was assigned at the strains beyond which the total energy deviated from Hooke's law. Force constants were then determined by fitting all energies to a third-order expression while holding equilibrium energy and lattice parameter fixed at their harmonic values, allowing only the second-order and third-order force constants to vary in a two-parameter fit. Statistical errors in the reported force constants were evaluated using five sets of computed data points. One set consisted of the force constant calculated using N points, where $N = 32$ (distortion I) and $N = 27$ (distortion III). The four remaining sets consist of $N-8$ data points. In each set, eight unique combinations of points are removed from the anharmonic region: four from the compression side (negative strain) and four from the expansion side (positive strain). Reported properties are arithmetic averages of the five sets; reported statistical error is the root-mean-square deviation from the mean for each distortion type.

Effects of internal relaxation were found to be negligible. In some cases, internal relaxation introduces additional degrees of freedom because symmetry departs from tetrahedral. For distortion III, the four bond lengths remain equal (particular to the value of strain), and the bond angles depart from the tetrahedral value (109.5°). Therefore, to quantify effects of internal relaxation, the total energy was minimized for distortion III, with respect to the three internal coordinates of the interior carbon atom C2, for zero strain and for strain near the harmonic limit (± 0.02). Fractional coordinates at the minimum were within 0.2% of the original values, and the total energy at the minimum decreased by less than 5×10^{-5} au, only slightly above the level of numerical precision (2×10^{-5} au). Consistent with these findings, changes in the nearest-neighbor bond length and changes in the bond angles, compared to the original values, were very small, within 0.09% and 0.8%, respectively. These results indicate that the level of internal relaxation is small, consistent with the high degree of point symmetry retained by C2 during distortion III. This finding agrees with the prediction that diamond's internal-strain parameter is especially small, much smaller than other group-IV elements: Si, Ge, and α -Sn [6].

3. Theory

To quantify the effect of isotopes on the elastic constants of a material, it is necessary to go beyond an ordinary classical treatment to a quantum-mechanical approach that accounts for zero-point motion of the nuclei. In this approach, the vibrational energy can be related to the isotopic mass and to the bond force constants that, in turn, can be related to the elastic coefficients.

Fig. 1 shows the unit cell used in our calculations. That unit cell is the asymmetric rhombohedral subunit of the standard diamond f.c.c. unit cell (space group Fd3m, No. 227) whose vertices are at Cartesian fractional coordinates $(0, 0, 0)$, $(1/2, 0, 1/2)$, $(0, 1/2, 1/2)$,

and $(1/2, 1/2, 0)$ [7]. The lattice parameters a , b , and c measured at equilibrium (zero strain) are related according to $a_0 = b_0 = c_0$ and $\alpha = \beta = \gamma = 60^\circ$. The cell contains two carbon atoms C1 and C2 located at $(0, 0, 0)$ and $(1/4, 1/4, 1/4)$ [7]. The observed bonding symmetry between C2 and its four nearest neighbors (the four vertices of the asymmetric subunit) is tetrahedral with bond length $\sqrt{3}a_0/4$. The equilibrium volume of the rhombohedral cell is $V_0 = 16d_0^3/3\sqrt{3}$, which is one fourth the volume of the f.c.c. super cell. The labeling convention used to define strain in the rhombohedral cell is depicted by the two smaller diagrams in Fig. 1 and described in Appendix B.

The change in a material's electronic energy relative to the equilibrium (unstrained) configuration is denoted by $\Delta\bar{U}$, defined by the equation

$$\Delta\bar{U} = \frac{1}{2} \sum_{ij} c_{ij} \epsilon_i \epsilon_j + \frac{1}{6} \sum_{ijk} c_{ijk} \epsilon_i \epsilon_j \epsilon_k + \dots, \quad (1)$$

in which terms are shown through third order. Here, $\Delta\bar{U}$ is the change in total electronic energy (kinetic, Coulomb, and exchange-correlation) per unit volume at zero-temperature. Parameters ϵ_i , ϵ_j , and ϵ_k denote strain in fractional units, c_{ij} and c_{ijk} denote the second- and third-order elastic coefficients, and indices $\{i, j, k\}$ take the values one through six.

In diamond, symmetry dictates three independent c_{ij} (c_{11}, c_{12}, c_{44}) and six independent c_{ijk} ($c_{111}, c_{112}, c_{123}, c_{144}, c_{166}, c_{456}$). For distortions that retain the orthogonality of the f.c.c. unit cell, that is $\epsilon_4 = \epsilon_5 = \epsilon_6 = 0$, Eq. (1) takes the following form:

$$\Delta\bar{U} = \frac{1}{2} \left[c_{11} (\epsilon_1^2 + \epsilon_2^2 + \epsilon_3^2) + 2c_{12} (\epsilon_1 \epsilon_2 + \epsilon_1 \epsilon_3 + \epsilon_2 \epsilon_3) \right] + \frac{1}{6} \left[c_{111} (\epsilon_1^3 + \epsilon_2^3 + \epsilon_3^3) + 3c_{112} (\epsilon_1^2 \epsilon_2 + \epsilon_1^2 \epsilon_3 + \epsilon_1 \epsilon_2^2 + \epsilon_3 \epsilon_2^2 + \epsilon_2^2 \epsilon_1 + \epsilon_3^2 \epsilon_2) + 6c_{123} \epsilon_1 \epsilon_2 \epsilon_3 \right], \quad (2)$$

where fourth- and higher-order terms are omitted.

For distortion I (uniform dilation), Eq. (2) simplifies as follows:

$$\Delta\bar{U}^{(I)} = \frac{1}{2} (3c_{11} + 6c_{12}) \epsilon_1^2 + \frac{1}{6} (3c_{111} + 18c_{112} + 6c_{123}) \epsilon_1^3, \quad (3a)$$

$$k_I = 3c_{11} + 6c_{12}, \quad (3b)$$

$$g_I = 3c_{111} + 18c_{112} + 6c_{123}, \quad (3c)$$

thus yielding definitions of the corresponding second-order and third-order force constants k_I and g_I , respectively.

For distortion III, the analysis in Appendix C shows that $\Delta\bar{U}$ can be expressed solely in terms of ϵ_1 , akin to Eq. (3a). Specifically, the four nearest-neighbor bond lengths are equal at each value of strain, and the contribution of changes in bond angles is negligible compared to the contribution of changes in bond length. As a result, the angular dependence in $\Delta\bar{U}$ can be omitted, thus yielding the following expressions for change in total electronic energy and associated force constants of distortion III.

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