

Prediction of bulk modulus at high temperatures from longitudinal phonon frequencies: Application to diamond, *c*-BN, and 3C-SiC

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A general model relating mechanical and vibrational properties of binary cubic crystals is formulated by the combination of first Sziget and the Lyddane-Sachs-Teller relations. It is found that a direct correlation is expected to hold between bulk modulus and longitudinal optical phonon frequencies. We apply this model to calculate the bulk modulus of diamond up to 1800 K from available Raman measurements. Our results are in excellent agreement with experimental results derived from Brillouin scattering measurements up to 1600 K. We also apply this model to predict the bulk modulus of *c*-BN and 3C-SiC, for which no experimental data are available over a range of temperatures. Our predictions agree well with results derived Young modulus measurements and available calculations based on first principles. We discuss practical applications of our model in related scientific fields and possible extensions to study other materials.

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I. INTRODUCTION

The bulk modulus is a fundamental property in many areas of condensed matter physics. This quantity plays a central role in equation of state studies,¹ and it is usually invoked to give a measure of hardness in cubic crystals. It also plays an extremely important role in establishing stability criteria² and to calculate defect formation parameters in solids.³ Furthermore, the bulk modulus appears recurrently in studies including first-principles calculations because of its relation with the second derivative of the energy vs volume curves, so comparisons with experimental lattice parameters and bulk modulus results are used to check the quality of such calculations.⁴

High-pressure techniques⁵ and ultrasonic studies have provided extensive results of the bulk modulus at room temperature. Nevertheless, there is an important lack of experimental data at high temperatures. Theoretical equation of state models and first-principles calculations offer interesting alternatives to predict the qualitative thermodynamic behavior of crystalline solids; however, quantitative agreement with experimental data is not always achieved. Although temperature corrections can be introduced into equation of state models within the Debye-Grüneisen approximation,¹ information on key properties, such as the bulk modulus, based on experimental results at different temperatures is obviously preferred.

In a recent study,⁶ we introduced a successful phenomenological approach that relates the mechanical and spectroscopic properties of different binary cubic crystal families in a quantitative fashion. The most striking conclusion of this study is that the value of the bulk modulus is determined by an effective two-body spring constant associated to the longitudinal optical (LO) phonon frequency, regardless of the extent of polarization effects. Although this model can be applied to any binary cubic crystal, here we are interested in the study of the high-temperature behavior of tetrahedral solids. In particular, we shall focus on three hard materials

which exhibit high values of the bulk modulus. This class of materials has been studied for a long time both experimentally and theoretically⁴ due to their wide range of important technological applications. In principle, most hard materials are expected to exhibit outstanding mechanical properties and thermal stability; however, compressing these materials under static load is very difficult, and determination of the mechanical properties demands special measurement procedures.⁵ As a consequence, available experimental data on the mechanical properties of hard materials is quite limited, particularly at high temperatures, and only diamond, the archetype of the covalently bonded, tetrahedrally coordinated crystals, has been studied in detail.⁷

In our opinion, these circumstances turn the referred model particularly appealing in practical applications on diamond and other tetrahedral solids, because information on their mechanical properties over wide ranges of temperature is limited, but a large amount of spectroscopic data is currently available. In particular, Raman spectroscopy has been shown to be a powerful, well-established probe for diamond and other related materials,^{8,9} as it enables a distinction between various types of carbon. Furthermore, information about crystal size, stress and structure can be gained from spectroscopic results after separation of pressure, temperature, and phonon confinement effects. In the latter case, differences between finite-size and bulk crystalline systems are revealed through Raman spectroscopy experiments since sampling of confined systems is not limited to $\mathbf{k}=0$ in the Brillouin zone, and consequently a broadening and shifting of the signal is observed.¹⁰ A widely accepted procedure to determine the total residual stress in hard-coating films consists in referencing the shift of the (stressed) Raman band to the bulk value at a given temperature. Thus, a positive (negative) band shift reflects a compressive (tensile) stress on the sample that can be quantified if the pressure shift of the Raman bands is known at a given temperature. This procedure was used to estimate internal stress of diamond films up to 1200 K.¹¹ Characteristic pressure dependencies of optical phonons are also known for *c*-BN (Ref. 12) and 3C-SiC,¹³

from which the residual stresses have been also estimated.^{14–17} All these studies confirm that knowledge of the bulk modulus is required to introduce corrections in residual stress calculations at different temperatures. This again outlines the important role played by the bulk modulus in different areas of applied physics and materials science.

The purpose of this work is to demonstrate that the temperature dependence of the bulk modulus of binary cubic crystals can be accurately predicted from available spectroscopic results over a broad temperature range. We first introduce a model to justify the general behavior noted in Ref. 6 at room conditions. The model can be obtained through combination of the first Szigeti^{18,19} and the Lyddane-Sachs-Teller²⁰ (LST) relations. We provide estimates of the bulk modulus of diamond, *c*-BN, and 3C-SiC from available Raman spectroscopic results up to very high temperatures. Our predictions are in excellent agreement with both experimental and theoretical results of bulk moduli available in the literature. These results demonstrate that the method proposed here is well suited for quickly arriving at an estimate of missing bulk modulus data for materials of different bonding nature over wide temperature ranges.

II. THEORETICAL CONSIDERATIONS

We shall start this section with a brief introduction of the phenomenological model used to correlate some mechanical and spectroscopic properties of diatomic cubic crystals.⁶ According to our previous observations, the value of the isothermal bulk modulus, defined as

$$B_T = -V \left(\frac{dp}{dV} \right)_T, \quad (1)$$

with p the pressure and V the molar volume, is entirely determined by the magnitude of an effective two-body spring constant associated to the LO phonon frequency of the solid ω_{LO} . The relevant relationship is the following:

$$\omega_{LO}^2 = C_{LO} \left(\frac{B_0 d_0}{\mu} \right), \quad (2)$$

where C_{LO} is a parameter that depends on the crystal structure, d_0 is the equilibrium nearest-neighbor distance, μ the reduced mass of the two atoms considered, and B_0 refers to the value of the bulk modulus evaluated at zero pressure. The bulk modulus can be obtained from this at different temperatures, considering the temperature variation of ω_{LO} and d_0 , both experimentally available as explained hereafter.

Although Eq. (2) can be derived from early models,^{2,21} it has not been considered before, and it reflects the fact that both compressibility and longitudinal vibrations depend principally on short-range forces, while long-range interactions play an important role in transverse vibrations.^{18,19} This simple model provided an accurate correlation between tabulated results of B_0 and LO frequencies for different types of binary cubic crystals, including rock-salt (*B1*), cesium chloride (*B2*), zinc-blende (*B3*), and diamond (*A4*) structures. An empirical value of C_{LO} ranging between 9 and 10 was found for solids in the zinc-blende and diamond structures. This

result is in excellent agreement with the theoretical value $C_{LO} = 16/\sqrt{3}$ expected for the diamond structure,²² where the LO and transverse optical (TO) phonons are degenerate at the zone center.

The form of Eq. (2) can be justified by combination of the first Szigeti^{18,19} and the LST relation²⁰ relations. In the derivation of the classical theory of dielectric polarization, Szigeti¹⁹ obtained the following relation between B_0 and other measurable quantities:

$$B_0 = \frac{d_0^2}{3V} \left(\frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \right) \mu \omega_{TO}^2, \quad (3)$$

where ω_{TO} is the TO frequency, ϵ_0 and ϵ_∞ are the low (static) and high (electronic) frequency dielectric constants, respectively, and V is the unit cell volume. If this equation is written explicitly for the squared TO frequency, the quantity $(3VB_0/d_0^2)$ can be physically interpreted as a short-range interaction force constant.

On the other hand, the LST equation relates the LO and TO frequencies with the dielectric constants in binary cubic crystals through the expression²⁰

$$\left(\frac{\omega_{LO}}{\omega_{TO}} \right)^2 = \frac{\epsilon_0}{\epsilon_\infty}. \quad (4)$$

Hence, by combination of Eqs. (3) and (4) one obtains the following identity for the C_{LO} parameter in Eq. (2):

$$C_{LO} = \left(\frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \right) \left(\frac{\epsilon_0}{\epsilon_\infty} \right) \left(\frac{g_B}{3} \right), \quad (5)$$

where g_B is a geometric constant defined as

$$\frac{g_B}{3} = \frac{3V}{d_0^3}. \quad (6)$$

An analogous relationship can be easily obtained for the TO phonons, since Eq. (3) can be also rewritten as

$$\omega_{TO}^2 = C_{TO} \left(\frac{B_0 d_0}{\mu} \right), \quad (7)$$

where

$$C_{TO} = \left(\frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \right) \left(\frac{g_B}{3} \right). \quad (8)$$

An inspection of Eqs. (5) and (8) indicates that a direct correlation between LO frequencies and B_0 must hold at any temperature, because the relative variations of the dielectric constants tends to cancel out in Eq. (5), so C_{LO} can be considered as independent of temperature. In other words, variations in the LO frequencies are expected to be less influenced by the sign and value of the temperature derivatives of the dielectric constants, in contrast to what is expected for the TO frequencies, as deduced from Eq. (8). This confirms that the effective strength associated with the LO displacements is directly related to the macroscopic value of B_0 , regardless of polarization effects.⁶ We emphasize that both early models and recent predictions²³ have always focused on the analysis of TO phonons. The above discussion suggests that analyses based on the temperature (or pressure) variation of TO

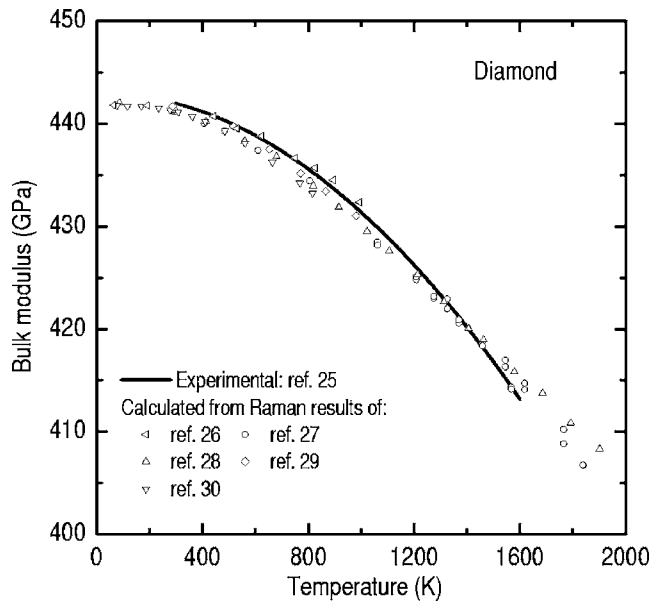


FIG. 1. Bulk modulus of diamond as a function of temperature predicted from Eq. (2) with $C_{LO}=16/\sqrt{3}$. References for the experimental sources of Raman measurements used in our calculations are indicated in the insert. Experimental results for the bulk modulus reported in Ref. 25 are represented by a continuous line.

phonons can be biased by changes of the dielectric constants with volume.

Finally, let us analyze the effect of temperature on the equilibrium distance d_0 , and its consequences on the temperature shift of the phonon frequencies. According to Eq. (2), the variation of the nearest neighbor distance as a function of temperature must be approximately known to separate the neat effect of the bulk modulus. Since a downshift is experimentally observed in phonon frequencies at temperatures above the Debye temperature θ_D a pronounced decrease in B_0 is expected at high temperatures, even for small frequency shifts, because the thermal expansion causes a steady increase of d_0 above θ_D . In this regard, tabulated results of the thermal expansion coefficient are available for diamond and other tetrahedral solids.²⁴ We have used these tabulated results in all our calculations. Alternatively, in the absence of experimental results of thermal expansion coefficient, estimations based on the Debye-Grüneisen approximation¹ usually gives reasonable results for the thermal expansion of the lattice up to the melting temperature. It must be emphasized that the well-known anomalies in the thermal expansion coefficient found in tetrahedral solids at low temperatures have negligible effect on the correlation.

III. RESULTS AND DISCUSSION

The predictions of our model are compared with available data of diamond, *c*-BN, and 3C-SiC in Figures 1–3, respectively. In the case of diamond, there is a good knowledge of its spectroscopic and mechanical properties at high temperature. The most reliable results of bulk moduli for diamond are those based on the recent Brillouin scattering experiments reported by Zouboulis *et al.*²⁵ up to 1600 K, which are

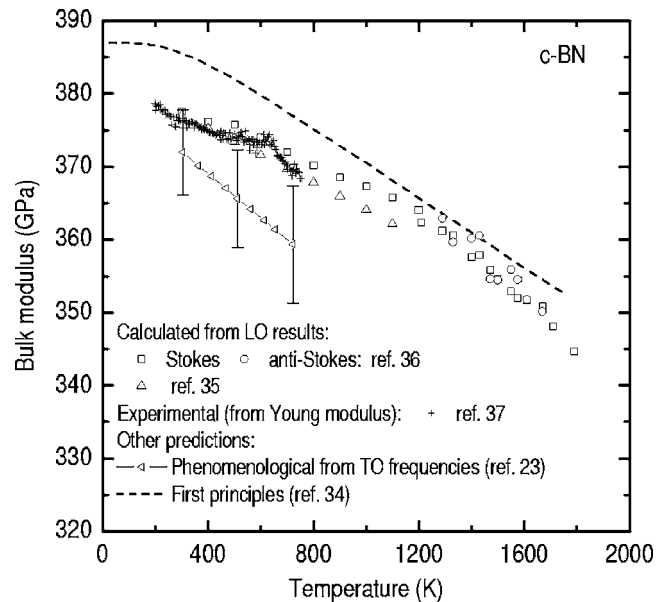


FIG. 2. Bulk modulus of *c*-BN predicted from Eq. (2) with $C_{LO}=10.4$ (Ref. 31), and the following experimental LO phonon frequencies at different temperatures: Alvarenga *et al.* (Ref. 35) (triangles) and Herchen and Cappelli (Ref. 36) (squares: Stokes bands, circles: anti-Stokes bands). Estimations given by Datchi and Canny (Ref. 23) from TO phonon frequencies (left triangles) are plotted for comparison. Experimental results derived from scaled experimental results of Young modulus in polycrystalline samples (Ref. 37) (crosses) are also included. In addition, the theoretical calculations of Albe (Ref. 34) are depicted by means of a dashed line.

represented in Fig. 1 by a continuous line. On the other hand, the shift with temperature of the triply degenerate Raman band of diamond has been experimentally studied by a number of authors. We have used the following sources to perform our calculations: Borer *et al.*,²⁶ Herchen and Capelli,²⁷ Zouboulis and Grimsditch,²⁸ Cui *et al.*,²⁹ and Liu *et al.*³⁰ Despite the differences found among the frequencies reported by the different authors, the overall agreement with experimental results of B_0 is extremely satisfactory. This suggests that a good prediction of the bulk modulus, which is usually accurate within 5–10 %, can be derived from typical spectroscopic measurements with accuracies of 4 cm^{-1} or better.

As indicated earlier, bulk modulus results are not experimentally available for most tetrahedral solids over wide ranges of temperature. For instance, the bulk modulus of *c*-BN is only accurately known at low temperatures. For the sake of comparison, the bulk modulus of *c*-BN at room temperature derived from our model is 377 GPa.³¹ This result is in excellent agreement with those derived from the pressure dependence of the lattice constants (369–385 GPa),^{32,33} and density functional theory calculations (385 GPa).³⁴ In the absence of experimental B_0 results for *c*-BN at high temperatures, we compare in Fig. 2 our predictions using Raman LO frequencies up to 1800 K (Refs. 35 and 36) with values of the bulk modulus derived from experimental measurements of the temperature dependence of Young modulus E

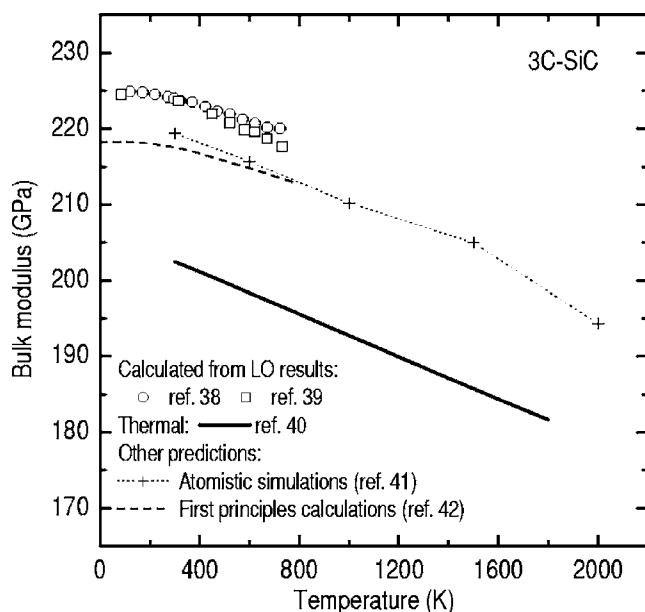


FIG. 3. Bulk modulus of SiC predicted with our model using LO phonon frequencies at different temperatures. Our results are referred to accepted values of $B_0=224\text{--}225$ GPa at room temperature (Refs. 44 and 45). Experimental LO phonon frequencies used in our calculations are those reported by Werninghaus (Ref. 38) (circles) and Olego and Cardona (Ref. 39) (squares). Solid line: calculated from results reported in Ref. 40; crosses: bulk modulus obtained from atomistic simulations by Tang and Yip Ref. 41; dashed line: first principles calculations by Karch *et al.* (Ref. 42).

on *c*-BN thin films.³⁷ Both properties are related through the expression

$$B_T = \frac{E}{3(1 - 2\nu_p)}, \quad (9)$$

where ν_p is the Poisson ratio. The experimental results of the Young modulus have been scaled to recover the bulk modulus of *c*-BN at room temperature using the value $\nu_p=0.2$,³⁷ which has been considered constant with temperature. In general, our predictions show a nice agreement with the scaled results deduced directly from the experiment. The squares and circles represent the Stokes and anti-Stokes predictions of the present model using experimental results given in Ref. 36, and the triangles represent the predictions using the Raman experiments of Alvarenga *et al.*³⁵ We complete the comparison in Fig. 2 with first-principles calculations by Albe,³⁴ that include temperature corrections based on the Debye-Grüneisen theory, and the recent predictions of Datchi and Canny²³ using their Raman TO results. It must be noted that in order to extract B_0 values using the phenomenological method proposed by Datchi and Canny, the mode Grüneisen parameter γ_{TO} and the pressure derivative of the bulk modulus $B'_0=(dB_0/dP)_T$, must be known at a reference temperature. In contrast to the method proposed here, knowledge of γ_{TO} and B'_0 requires accurate high pressure measurements, and even so, both quantities are usually accompanied of large uncertainties. In addition, these authors assumed that γ_{TO} was independent of temperature and that the variation

with temperature of B'_0 was negligible. Again, it must be noted that no further approximations are required to evaluate B_0 from Eq. (2). The comparison depicted in Fig. 2 lends considerable support to the assumptions included in our model, as it provides insight into the trend expected for bulk modulus at high temperatures with a quality comparable to more elaborated treatments. Since first-principles calculations are usually available only at 0 K, it is interesting to discuss the prediction of our model at low temperatures. Although the lowest temperature for which experimental data are available for *c*-BN is 298 K, extrapolation to 0 K of our results is feasible by using a Debye-like function to fit the bulk modulus over the whole range of temperatures considered here. In this case, as the Debye temperature of *c*-BN is rather high, the value predicted at 0 K is only slightly higher than that calculated at 298 K (around 378 GPa). This comparison yields a reasonable good agreement between our model and first principles calculations.

Finally, our B_0 results for 3C-SiC considering LO phonon frequencies obtained from Raman experiments^{38,39} are plotted in Fig. 3. In this case, instead of calculating the absolute values of B_0 from Eq. (2), our predictions are referred to accepted values of B_0 at room temperature. The squares and circles represent the predictions of the present model using experimental results of LO phonons given in Refs. 38 and 39. In the absence of experimental data on bulk 3C-SiC over a range of temperatures, we compare our predictions with available results obtained from thermal measurements.⁴⁰ The adiabatic bulk moduli reported in Ref. 40 have been corrected to isothermal values using standard thermodynamic relations. Overall, the temperature dependence of B_0 is rather well reproduced. Available theoretical results from atomistic simulations⁴¹ and first-principles calculations⁴² are also included for comparison. In general, in spite of the lower values for the bulk modulus derived from thermal measurements, all data sets show excellent agreement in the temperature derivative of B_0 above room temperature. This suggests that our method can also serve as a useful aid for extrapolating B_0 results into the high-temperature regime.

IV. SUMMARY AND CONCLUSIONS

We have demonstrated in this work that it is possible to obtain an accurate estimation of the bulk modulus over the wide range of temperatures from spectroscopic results of LO phonons for crystals in the diamond and zinc-blende structures. Our results for diamond are in excellent agreement with B_0 results derived from Brillouin scattering measurements up to 1600 K. Our predictions for *c*-BN and 3C-SiC, for which no direct experimental data are available over a range of temperatures, agree with results derived from diverse measurements, first-principles calculations, and other phenomenological models based on the variation of TO frequencies with temperature.

The quality of the present results allow us to conclude that (1) combination of the first Szigeti and the LST relations provides an adequate framework to correlate mechanical and vibrational properties of crystalline solids over the whole temperature range, (2) the observed correlation holds prima-

rily for LO frequencies and B_0 values, since the temperature variations of the dielectric constants tend to cancel out only for LO phonons, in contrast to what is expected for TO phonons, and (3) the present method may serve as a useful aid to estimate the mechanical properties at high temperature for other families of solids, such as $B1$ and $B2$ binary crystals. In such a case, only the value of the geometrical constant g_B must be changed accordingly. In addition, on the basis of the results obtained in ref. 6 at room conditions, results for wurzite-type solids using Eq. (2) should be of similar quality to those presented here, provided that average values of the LO and TO along the two nondegenerated directions are used.⁶

In summary, it is hoped that the method proposed here will be of considerable interest in obtaining reliable estimates of bulk modulus in a variety of solids for which experimental information is lacking. This model, together with high-pressure–high-temperature Raman spectroscopic

techniques⁴³ can be used to extract valuable information on the equation of state of other covalent solids in a straightforward way. Finally, we believe that other researchers might find interesting applications of our model in other fields, because bulk modulus data over a range of temperatures are needed in to calculate residual stresses in coating and semiconductor materials, or vacancy formation parameters (Gibbs energy and volume) in many different types of crystals.³

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