

## Lattice parameter and Raman spectra of isotopically mixed diamond

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The influence of isotope mass and anharmonicity on the lattice parameter of isotopically mixed diamond is studied in a simple theoretical model. The performed calculations confirm that in good approximation the lattice parameter changes linearly with the isotope concentration. We show that the stretching harmonic-force constants for pure  $^{12}\text{C}$  and  $^{13}\text{C}$  differ slightly and we explain why the Raman-frequency ratio is smaller than the square root of the ratio of the corresponding masses. Finally, the positive bowing of the Raman frequency in isotopically mixed diamond is discussed. [S0163-1829(97)02642-8]

### I. INTRODUCTION

Physical properties of crystals are affected by an isotopic mixture. For example, the lattice parameter and the Raman frequencies depend weakly on the isotopic composition, while the thermal conductivity is very sensitive to isotopic mixture. The isotopic substitution in a crystal is a perturbation with change of only one parameter—the isotopic mass. Contrary to substitutions by most other defects it does not change the largest interaction in a crystal—the Coulomb interaction. Therefore the properties of crystals upon isotopic substitution are changed due to isotopic mass change and due to the breakdown of the translational symmetry (site disorder) caused by substitution. The influence of isotopic substitution on properties of materials has been extensively studied and many aspects of these studies have been reviewed.<sup>1-3</sup> Recently the isotopic dependence of the lattice constant and the Raman frequency of diamond has attracted interest.<sup>4-8</sup> An isotopic mixture of a diamond structure crystal can be considered as an  $A_xB_{1-x}$  alloy in which  $A=^{13}\text{C}$  and  $B=^{12}\text{C}$ . The measurement of the lattice constant of the  $^{13}\text{C}_x^{12}\text{C}_{1-x}$  alloy in Ref. 4 shows that the lattice parameter is—with good accuracy—a linear function of the isotopic composition  $x$ . Contrary to Ref. 4, in Ref. 7 an x-ray-diffraction measurement was reported indicating very weak parabolic dependence of the lattice constant with composition. On the other hand, the Raman frequency  $\omega$  shows<sup>4</sup> a remarkable parabolic dependence on  $x$ . In Ref. 6 the pressure dependence of Raman frequencies for  $^{12}\text{C}$  and  $^{13}\text{C}$  was reported. The decrease of the ratio  $^{12}\omega/^{13}\omega$  with pressure was interpreted as a subtle but quite distinct quantum contribution to the physical properties of diamond.

The  $A_xB_{1-x}$  alloy system is attractive for comparing the experimental deviation from Vegard's rule with theoretical calculations. Because  $A$  and  $B$  are isotopes of the same atom there is only one crystal structure in the system and no effect of relative valency and electronegativity between the constituents. The main purpose of the present investigation is the theoretical study of the lattice parameter and Raman frequency as a function of the composition  $x$ . Our calculation will be based on the Harrison theory for the bond energy in tetrahedrally bonded crystals. Many properties of solids and molecules can be determined by calculating the bond energy.

Harrison,<sup>9,10</sup> using the tight-binding (TB) theory and some results following from the density-functional theory, simplified the calculation and the bond energy can be expressed in terms of one-electron atomic energies and some universal parameters. The universal parameters replace the complicated interaction integrals and are common for many covalent crystals.

From the bond energy we calculate the stretching force constant and thus the vibrational energy of the bond. Then we determine the bond length from the minimum of the Helmholtz free energy instead of the minimum of the adiabatic energy only.

### II. BOND ENERGY AND BOND LENGTH

In TB theory for the tetrahedrally coordinated crystals four orthogonal and normalized  $sp^3$  hybrids are chosen on each atom as the basic wave functions. The electronic bond energies are given as<sup>8,9</sup>

$$\varepsilon = \frac{1}{2}(\varepsilon_h^\alpha + \varepsilon_h^\beta) \pm q \sqrt{V_2^2 + V_3^2} + \frac{qV_2^2}{k|\bar{\varepsilon}_h|}, \quad (1)$$

where the energy with the minus corresponds to the bonding state, while the plus sign represents the energy of the antibonding state. In Eq. (1)  $V_3 = (\varepsilon_h^\alpha - \varepsilon_h^\beta)/2$ ,  $\varepsilon_h^{\alpha,\beta} = (\varepsilon_s^{\alpha,\beta} + 3\varepsilon_p^{\alpha,\beta})/4$ , where  $\varepsilon_s$  and  $\varepsilon_p$  are the free-atom energies for  $s$  and  $p$  states.<sup>9</sup>  $V_2 = f(\eta)\hbar^2/md^2$ , with  $m$  being an electron mass, determines the coupling between two atoms and the function  $f(\eta)$  is expressed in terms the four universal coefficients:  $\eta_{ss\sigma} = -1.40$ ,  $\eta_{sp\sigma} = 1.84$ ,  $\eta_{pp\sigma} = 3.24$ , and  $\eta_{pp\pi} = -0.81$ . For example, in the perfect Si crystal, for two  $sp^3-sp^3$  hybrids directed against each other on two neighboring atoms  $f_{sp^3-sp^3}(\eta) = \eta_{ss\sigma}/4 - 2\sqrt{3}\eta_{sp\sigma}/4 - 3\eta_{pp\sigma}/4 = -4.373$ . The  $q$  is the electron occupancy of the bond in units of electron charge and  $\bar{\varepsilon}_h$  is the average of  $\varepsilon_h^\alpha$  and  $\varepsilon_h^\beta$ . The parameter  $k$  is only one fitting coefficient entering this theory. It is determined from the requirement that calculated bond lengths for the C, Si, Ga crystals equal the experimental ones. The value of  $k$  is the same for all crystals built from the elements entering the same row of the periodic system. For example,<sup>9</sup> for the C row  $k=2.5$ , for the Si row  $k=1.455$ , and for the Ge row  $k=1.33$ .

The determination of the bond length from the minimum of the bond energy (or from the minimum of the total energy in *ab initio* theories) is only an approximation since the kinetic vibration energy is neglected. The vibrational energy depends on the interatomic distance and hence we should search for a minimum of both electrostatic and vibrational energies. The equilibrium interatomic distance can be determined from the minimum of the Helmholtz free energy  $F$  for the bond<sup>11</sup>

$$F(d, T; M) = \varepsilon(d) + \frac{1}{2} \hbar \omega + k_B T \ln \left[ 1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right) \right], \quad (2)$$

where  $k_B$  is the Boltzman constant and  $\varepsilon$  is the bond energy (1) for atoms interacting by the Coulomb forces.  $\omega$  is the harmonic vibrational frequency for atoms in a single bond and is given by

$$\omega = \sqrt{\frac{k_h}{\mu}}, \quad (3)$$

where  $k_h = \partial^2 \varepsilon / \partial d^2$  is the harmonic-force constant and  $\mu = M_A M_B / (M_A + M_B)$  is the reduced mass. This is the stretching-type vibration of atoms entering the bond. The second term in Eq. (2) is the energy of the zero-temperature vibration and it indirectly depends on the atomic mass  $M$ . At  $T=0$  K only the first and second terms in Eq. (2) influence the bond length. The mass dependence of the bond length originates from the quantum-mechanical effect of the zero-temperature vibration. We demonstrate that the anharmonicity of  $\varepsilon(d)$  directly influences this dependence. In order to determine the equilibrium distance at  $T=0$  we should set to zero the derivative of the Helmholtz energy. Thus using Eqs. (2) and (3) we arrive at the condition

$$\frac{\partial \varepsilon}{\partial d} + \frac{\hbar}{4\sqrt{\mu}} \frac{\partial^3 \varepsilon / \partial d^3}{\sqrt{\partial^2 \varepsilon / \partial d^2}} = 0. \quad (4)$$

If the third derivative of  $\varepsilon$  is assumed to be zero (harmonic approximation) then we obtain the equilibrium distance from the minimum of the adiabatic energy, i.e.,  $\partial \varepsilon / \partial d = 0$ . The third derivative is usually negative and therefore the first derivative in Eq. (4) should be positive. This means that consideration of the vibrational energy makes the bond length longer than the bond length determined from the adiabatic energy only. Figure 1 shows the Helmholtz energy for single  $^{12}\text{C}-^{12}\text{C}$  and  $^{13}\text{C}-^{13}\text{C}$  pairs. Two crystals made of two different isotopes have different bond lengths (see Table I) because they differ in  $\mu$ . In both cases the adiabatic energy  $\varepsilon$  is the same but Eq. (4) is fulfilled at two different values of  $d$ . Therefore the harmonic-force constants for crystals composed from different isotopes of the same element differ slightly (see Table I) because they are calculated at different equilibrium positions  $d$ . The crystal composed of the heavier isotope has a smaller bond length than that made of the lighter one.

To test Eq. (1) we compare the bond length calculated using Eqs. (1)–(4) with the first-principles calculation<sup>11</sup> for Si crystals made of isotopes  $^{28}\text{Si}$ ,  $^{29}\text{Si}$ , and  $^{30}\text{Si}$ . We obtained the interatomic distance  $d(^{28}\text{Si}) = 2.35892 \text{ \AA}$  [taking  $k = 1.455$  in Eq. (1)],  $d(^{29}\text{Si}) = 2.35881 \text{ \AA}$ , and  $d(^{30}\text{Si})$

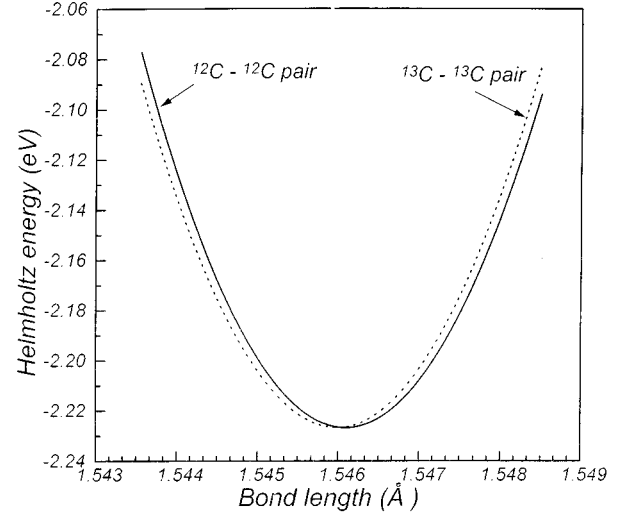


FIG. 1. The Helmholtz free energy (2) for single  $^{12}\text{C}-^{12}\text{C}$  (solid) and  $^{13}\text{C}-^{13}\text{C}$  (dotted) bonds at  $T=300$  K. The origin of the energy was shifted by 13.96 eV and the energy was then multiplied by 1000 to show the shape of the curves near minima. The relative shift of minima is seen distinctly.

$= 2.35870 \text{ \AA}$  at temperature  $T=0$  K. This gives  $\Delta d(^{28}\text{Si}-^{30}\text{Si}) = 0.00022 \text{ \AA}$  and  $\Delta d(^{29}\text{Si}-^{30}\text{Si}) = 0.00011 \text{ \AA}$ . The first-principles calculation of the lattice parameter cannot give precisely the absolute value of this parameter but the relative values for a crystal made of various isotopes are given quite accurately. From Fig. 4 of Ref. 11 one can read values of  $\Delta d(^{28}\text{Si}-^{30}\text{Si}) = 0.00017 \text{ \AA}$  and  $\Delta d(^{29}\text{Si}-^{30}\text{Si}) = 0.00009 \text{ \AA}$ , i.e., there is good agreement between calculations using essentially different techniques.

### III. EFFECT OF ISOTOPIC SUBSTITUTION

The Bragg x-ray-diffraction averages the influence of foreign atoms in a crystal on the lattice constant over many diffraction surfaces. This results in a dependence of the average lattice parameter on the concentration. Many properties of crystals are studied using the virtual crystal approximation (VCA). The simplest example of this approximation is Vegard's rule.<sup>12</sup> It gives the lattice constant of an alloy as the concentration-weighted sum of the lattice constant of the components. In terms of the bond length, Vegard's rule can be written as

$$d_{\text{av}} = x d_{AA} + (1-x) d_{BB}. \quad (5)$$

Zen<sup>12</sup> suggested to calculate the average lattice constant from the concentration-weighted sum of the specific volumes of the end-point materials. This results in the following equation for the average bond length:

$$d_{\text{av}} = d_{BB} \left[ 1 - x \left( 1 - \frac{d_{AA}^3}{d_{BB}^3} \right) \right]^{1/3}. \quad (6)$$

Equations (5) and (6) totally neglect the way in which atoms are distributed in an alloy. The average lattice parameter determined from x-ray measurements does not always coincide with the average parameter calculated in the VCA. The atoms  $A$  and  $B$  can be randomly distributed among the  $2N$

TABLE I. The results of the bond length and vibrational frequency calculation for the  $^{13}\text{C}$ - $^{13}\text{C}$  ( $AA$ ),  $^{12}\text{C}$ - $^{12}\text{C}$  ( $BB$ ), and  $^{12}\text{C}$ - $^{13}\text{C}$  ( $AB$ ) pairs.  $d_{\text{av}}$ ,  $k_{\text{av}}$ ,  $\omega_{\text{av}}$  are linear interpolations of bond length, force constant, and frequency at  $x=0.5$ . We give more digits than follows from the accuracy of the absolute values of calculated quantities to show the relative change with the isotopic mass. To obtain  $k_h$  in Eq. (3) it is necessary to multiply the force constant from this table by a factor of 4.

Quantity	Calc. $T=0$ K	Calc. $T=300$ K	Expt. $T=300$ K
$d_{AA}$ (Å)	1.545427	1.545988	1.54436(3) [8]
$d_{AB}$ (Å)	1.545538	1.546038	
$d_{BB}$ (Å)	1.545647	1.546093	1.54460(2) [8]
$d_{\text{av}}(x=0.5)$ (Å)	1.545537	1.546040	
$\Delta d/d = \Delta a/a$	$1.42 \times 10^{-4}$	$0.68 \times 10^{-4}$	$1.5 \times 10^{-4}$ [5,8]
$k_{AA}$ (eV/Å <sup>2</sup> )	11.48179	11.44412	
$k_{AB}$ (eV/Å <sup>2</sup> )	11.47433	11.44077	
$k_{BB}$ (eV/Å <sup>2</sup> )	11.46700	11.43708	
$k_{\text{av}}(x=0.5)$ (eV/Å <sup>2</sup> )	11.47440	11.44060	
$\omega_{AA}$ (cm <sup>-1</sup> )	1381.09	1378.82	1281.2 [6]
$\omega_{AB}$ (cm <sup>-1</sup> )	1409.11	1407.05	
$\omega_{BB}$ (cm <sup>-1</sup> )	1436.56	1434.68	1332.1 [6]
$\omega_{\text{av}}(x=0.5)$ (cm <sup>-1</sup> )	1408.82	1406.75	

lattice sites (on two face-centered sublattices) by various ways. The real crystal possesses only one particular distribution. Two real crystals with the same concentration of atoms  $A$  and  $B$  will possess different random distributions. The total number of distributions can be calculated for a given number of atoms  $A$  and  $B$ . Then it is necessary to calculate the number of the  $AA$ ,  $AB$ , and  $BB$  pairs for each distribution. The difficulty consists of separating the distributions with a given number of corresponding pairs of atoms. Each such distribution corresponds to a crystal with a particular lattice parameter. In general, this task is not tractable.<sup>13</sup> Therefore, the number of pairs is usually calculated statistically. Namely, the probability that two nearest lattice sites are occupied by  $^{13}\text{C}$  atoms is  $x^2$ . Similarly,  $2x(1-x)$  is the probability that on two neighboring sites either the pair of  $^{12}\text{C}$ - $^{13}\text{C}$  or  $^{13}\text{C}$ - $^{12}\text{C}$  is found. The average number of  $AA$  pairs is  $N_{AA} = x^2 pN/2$  and the average number of  $AB$  pairs is  $N_{AB} = 2x(1-x)pN/2$ . Here  $p=4$  is the coordination number of atoms around a given lattice site. The  $N_{AB}$  calculated in this way is smaller than the number of similar pairs calculated from various distributions (this can be directly checked by calculating distributions for a ‘‘crystal’’ with a small number of atoms, say,  $N=4,5,6$  and with various contents of  $A$  and  $B$  atoms inside). The number of various pairs of atoms calculated in this way has a purely statistical nature. Additionally, there is a physical factor which influences the distribution of pairs. In the approximation, where the alloying is considered as a chemical reaction of the type  $AA + BB \rightleftharpoons 2AB$ , the equilibrium is reached when<sup>13</sup>

$$\frac{\langle N_{AB} \rangle^2}{\langle N_{AA} \rangle \langle N_{BB} \rangle} = 4 \exp\left(\frac{-2\varepsilon_{AB} + \varepsilon_{AA} + \varepsilon_{BB}}{k_B T}\right). \quad (7)$$

If the nominator in the exponent containing the bond energy of various pairs is positive, the real number of  $N_{AB}$  pairs in the crystal will exceed the number of these pairs calculated on a statistical basis.

Using the statistical weight of various pairs of atoms, the average interatomic distance  $d_{\text{av}}$  between two atoms in an alloy can be determined as

$$d_{\text{av}} = x^2 d_{AA} + 2x(1-x)d_{AB} + (1-x)^2 d_{BB}. \quad (8)$$

The above formula, contrary to formulas given by Eqs. (5) and (6), requires for an estimation of  $d_{\text{av}}$  the knowledge of  $d_{AB}$ . Equation (8) gives the linear dependence on  $x$  provided  $d_{AB} = (d_{AA} + d_{BB})/2$ . This is, in good approximation, the case of the  $^{13}\text{C}_x^{12}\text{C}_{1-x}$  alloy. The Zen formula (6) applied to diamond at  $x=0.5$  does not show a deviation from Vegard’s rule.

In the approximation, where the vibrational energy is neglected, the bond length is determined from the setting to zero of the derivative of the bond energy  $\varepsilon$  with respect to the interatomic distance  $d$ . The minimum of the total energy (the adiabatic potential) depends upon the electronic structure and not upon the masses of the atoms. Two different isotopic species of the same atom will have different vibrational frequencies only because of the difference in isotopic masses. The ratio  $r$  of the vibrational frequencies for the  $^{12}\text{C}$  and  $^{13}\text{C}$  in the  $^{12}\text{C}$ - $^{12}\text{C}$  and  $^{13}\text{C}$ - $^{13}\text{C}$  bond pairs is given [see Eq. (3)] in this approximation as

$$r \equiv \frac{\omega(^{12}\text{C})}{\omega(^{13}\text{C})} = \sqrt{\frac{M_B}{M_A}} = \sqrt{\frac{13}{12}} = 1.040\ 833, \quad (9)$$

where  $M_A$  and  $M_B$  are the masses of  $^{13}\text{C}$  and  $^{12}\text{C}$ , respectively. For diamond-structure crystals, the optical frequency  $\omega(\Gamma)$  at the  $\Gamma$  point is related to the vibrational frequency (3) as follows:  $\omega(\Gamma) = \sqrt{4/3}\omega$ . Therefore, the ratio  $r$  of the Raman frequencies for crystals composed from  $^{12}\text{C}$  and  $^{13}\text{C}$  isotopes should be given by Eq. (9). The ratio  $r$  for the observed Raman frequencies in  $^{12}\text{C}$  and  $^{13}\text{C}$  crystals at  $T=300$  K (see Table I) is  $r = 1332.1/1281.2 = 1.0397$ . The ratio of calculated bond pair frequencies is  $r = 1436.56/1381.09 = 1.040\ 16$  at  $T=0$  K and  $r = 1434.68/1378.82 = 1.040\ 51$  at  $T=300$  K. We find that

the ratio  $r$  is smaller than the value given by Eq. (9). This implies that in crystals made of different isotopes the harmonic-force constants are not the same and this is a direct consequence of anharmonic term in the interatomic potential.

The VCA can be used to derive the equation for the forbidden electronic-energy gap or for the Raman frequency. In VCA the vibrational frequencies at the point  $\Gamma$  are determined from the dynamical matrix

$$\begin{pmatrix} 4M_{AA} - \omega^2, & 4M_{AB} \\ 4M_{BA}, & 4M_{BB} - \omega^2 \end{pmatrix},$$

where the matrix element  $M_{AA} = xxk_{AA} + 2x(1-x)k_{AB} + (1-x)(1-x)k_{BB}/(xM_A + (1-x)M_B)$  and  $M_{BB} = -M_{AB} = M_{AA}$ . Using the values of the force constants from Table I one obtains at  $x=0.5$  the small negative bowing  $\Delta\omega = -0.8 \text{ cm}^{-1}$ . This is due to the fact that the ‘‘reduced’’ mass  $[xM_A + (1-x)M_B]/2$  of the  $AB$  pair in the VCA is larger than the reduced mass  $\mu = M_A M_B / (M_A + M_B)$ .

#### IV. RESULTS AND DISCUSSION

The difference in the bond lengths of  $^{12}\text{C}$  and  $^{13}\text{C}$  crystals comes out from the difference in the masses of nuclei and from the anharmonicity of the interatomic potential. As seen from Eq. (4), both crystals would have the same bond length in harmonic approximation. Because the third derivative of the potential is negative, the real bond length is always larger than that calculated in the harmonic approximation. The difference in the isotope masses induces by means of the anharmonic-force constant the zeros of Eq. (4) at different  $d$  for each isotope. In this sense, the harmonic-force constant calculated at different  $d$  (see  $k_{AA}$  and  $k_{BB}$  in Table I) depends indirectly on the isotopic mass.

We did not attempt to obtain very accurately the bond lengths for the end-point materials by a suitable choice of parameter  $k$  in Eq. (1) (we have used the commonly accepted value). However, since the parameter  $k$  was chosen we can calculate the difference of the lattice constant between the end point materials. At  $T=0 \text{ K}$  this difference is  $\Delta a = 4\Delta d/\sqrt{3} = 0.000 51 \text{ \AA}$  and at  $T=300 \text{ K}$  it is  $0.000 11 \text{ \AA}$ . The experimental value at  $T=300 \text{ K}$  is  $0.000 53 \text{ \AA}$ , i.e., it is in agreement with the calculated value at  $T=0 \text{ K}$ . The reason why our calculated difference at  $T=300 \text{ K}$  is too small, can be explained by the crudeness of the Einstein approximation where the real phonon-dispersion curves are replaced by a single frequency of the bond-pair atoms.

We have assumed that the change of the lattice parameter is due to two effects. First, this is the formation of the bond length between the solute and solvent atoms. Second, the disorder influences the average bond length (if alloy system contains more vacancies than end-point crystal then they will also influence the average value, additionally to disorder effect). The first effect we can estimate accurately. The bond-length effect reaches its maximum when the alloy is an ordered system, i.e., when  $^{13}\text{C}_x^{12}\text{C}_{1-x}$  has zinc-blende structure. For diamond  $d_{AB} \cong d_{av} = (d_{AA} + d_{BB})/2$  and Eq. (8) transforms to Eq. (5). We confirm in this approximation the result of Ref. 4, i.e., the validity of Vegard’s rule. We have performed our calculation of the  $^{13}\text{C}_x^{12}\text{C}_{1-x}$  system keeping one digit more than experimental precision which is of the

order of  $10^{-5} \text{ \AA}$ . Therefore even if the ordered-alloy approximation accounts for only, say 20–40% of the effect, it still confirms the experimental accuracy of Vegard’s rule for diamond. The effect of disorder can be treated by considering a crystal as a large cluster of randomly distributed atoms which interact not only in the nearest-neighbor approximation. In such a crystal the nearest-neighbor atoms have many different bond lengths scattered between the values for the end-point materials. In view of the above results we think that the lattice parameter measurements in Refs. 4, 5 and 7, 8 do not contradict each other. In both measurements different crystals were used. Even for the same concentration they differ in the distribution of isotopes (homogeneity) and this might slightly influence the measurements at a precision of the order of  $10^{-5} \text{ \AA}$ . The measured fractional difference  $\Delta a/a$  at  $T=300 \text{ K}$  is in reasonable agreement with the theoretical estimation at  $T=0 \text{ K}$ . The decrease of  $\Delta a/a$  with a temperature increase is in agreement with the experimental observation for Ge crystals made of different isotopes<sup>14</sup> as well as with first-principles calculations for Si crystals.<sup>11</sup>

The positive or negative bowing of the bond length can be observed when  $d_{AB}$  is larger or smaller than  $(d_{AA} + d_{BB})/2$ , respectively. The average zero-temperature vibrational amplitude  $u$  of an atom in a crystal is given approximately by  $u = \sqrt{\hbar(n+1/2)/(\mu\omega)}$ , where  $n$  is the phonon occupation number. We obtained  $u=0.063$  and  $0.061 \text{ \AA}$  for  $^{12}\text{C}$  and  $^{13}\text{C}$  at  $T=0 \text{ K}$ , respectively. At  $T=300 \text{ K}$  the average amplitudes are  $u(^{12}\text{C})=0.086 \text{ \AA}$  and  $u(^{13}\text{C})=0.085 \text{ \AA}$ , i.e., they are  $\approx 5.5\%$  of the interatomic distance.

The ordered-alloy approximation predicts for the difference  $\omega_{AB} - \omega_{av}$  a small positive bowing of  $\approx 0.3 \text{ cm}^{-1}$  at  $x=0.5$ . The measured bowing of Raman frequency is  $\approx 5 \text{ cm}^{-1}$  and thus we should ascribe about 95% of the bowing to the effect of structural disorder (the influence of vacancies is neglected). This can be seen even for two atomic chains  $ABAB$  and  $AABB$  containing four atoms. They possess the same concentration  $x=0.5$ . Using the force constant as given in Table I we find that the largest (Raman) frequencies for both chains differ by  $2 \text{ cm}^{-1}$ . The conclusion that a large positive bowing of the Raman frequency is a consequence of isotopic disorder was drawn earlier in Ref. 5. There, including a small *ad hoc* correction for the change of force constants on interatomic distance (in this way was partly accounted the anharmonic effect), this bowing was reproduced by the coherent-potential approximation method. The calculation performed there in the VCA gave a small bowing of negative sign.

The calculated vibrational frequency for the  $^{12}\text{C}$ - $^{12}\text{C}$  pair at  $T=0 \text{ K}$  is  $1436.56 \text{ cm}^{-1}$ , while for natural diamond it is  $1332.1 \text{ cm}^{-1}$ . This means that our bond energy is a slightly steeper function of  $d$  than the real thermal potential. At this point we stress that the adiabatic energy is given analytically by Eq. (1) and since its minimum was adjusted (by adjusting the parameter  $k$ ), further properties are calculated using its fixed shape. The difference  $\Delta\omega$  between the end-point materials is  $55.47 \text{ cm}^{-1}$  at  $T=0 \text{ K}$  and  $55.86 \text{ cm}^{-1}$  at  $T=300 \text{ K}$  (see Table I). It is in reasonable agreement with the experimentally determined value  $50.9 \text{ cm}^{-1}$  at  $T=300 \text{ K}$ . The Raman frequency in an alloy with a given concentration  $x$  is not sensitive to a particular distribution of isotopes. The reason

for this is that the vibrational wave comprises the whole crystal and the weight of a particular crystal site in the wave is very small. Hence, the frequency is determined by the average of the force constant and mass over all atoms.

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