The isotopic mass and lattice parameter of diamond; a path-integral simulation

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Abstract
The dependence of the lattice parameter of diamond upon the isotopic mass has been studied by path-integral Monte Carlo simulations in the isothermal–isobaric ensemble. This computational method provides us with a quantitative and nonperturbative procedure for analysing such anharmonic effects. Atomic nuclei were treated as quantum particles interacting via a Tersoff-type potential. At 300 K, the difference Δa between the lattice parameter of isotopically pure crystals of ^{12}C and ^{13}C is found to be 6.1×10^{-4} Å, in good agreement with experimental results. This difference decreases under an applied external pressure, and for 4000 kbar we obtain $\Delta a = 2.4 \times 10^{-4}$ Å.

1. Introduction

In recent years, the effect of isotopic composition on the lattice dynamics and electronic properties of diamond-type materials has been investigated in great detail [1,2]. This has been feasible due to the availability of single crystals, either isotopically pure or with controlled isotope concentrations. For diamond in particular, some of the most interesting properties include changes in the energy gap [3], phonon spectrum [4–6], elastic constants [7], lattice parameter [8–10], and thermal conductivity [11–13] with the average isotopic mass. Other phonon-related properties, such as the thermal expansion, are also expected to depend on the isotope mass. Moreover, isotopic effects in diamond at high pressure are of particular interest due to the importance of the diamond anvil cell in high-pressure physics [14].

The dependence of the atomic vibrational amplitudes upon the atomic mass, along with the anharmonicity of the lattice vibrations, causes a change of lattice parameter with the average isotopic mass [8, 15]. This effect is most important at low temperatures, and disappears at $T > \Theta_D$ (Θ_D: the Debye temperature of the material). Recently, the isotopic effect on the lattice parameter of germanium has been measured with high precision by using an x-ray standing wave [16]. This is a promising technique for carrying out very precise determinations of the lattice parameter of other crystalline materials.

The isotopic dependence of the lattice parameter of diamond has been studied by x-ray diffraction techniques [8,9], as well as theoretical methods [10,17]. In particular, Pavone and Baroni [17] studied this isotope dependence using density-functional perturbation theory, in a

quasi-harmonic approximation. An alternative theoretical approach for studying many-body systems at finite temperatures is the Feynman path-integral (PI) method, which allows one to include directly quantum effects and anharmonicities in the numerical simulation of the crystal properties. Given an interatomic potential, structural properties can be obtained within the PI approach with arbitrary accuracy by Monte Carlo (MC) simulations [18, 19]. Thus, the PI MC method was employed earlier to study isotopic effects in solids, and in our context it was applied to analyse isotope effects upon the lattice parameter of solid neon [20], and more recently those of germanium [21] and silicon [22].

In this paper we present results for the cell parameter a of diamond, as derived from atomistic PI MC simulations in the isothermal–isobaric (NPT) ensemble. The cell parameter is studied as a function of temperature, pressure, and isotopic mass (M). The interatomic interaction is described by an effective Tersoff-type potential [23], which was employed earlier to obtain structural and thermodynamic properties of diamond by PI MC simulations [24].

2. Computational method

The implementation of the PI method for numerical simulations is based on an isomorphism between the quantum system and a classical one, obtained by replacing each quantum particle (here, the atomic nucleus) by a cyclic chain of L (Trotter number) classical particles. In the limit of classical mechanics, the cyclic chains collapse into single points and, therefore, classical simulations correspond to the limit $L = 1$. Details of this kind of quantum simulation can be found elsewhere [19, 25, 26].

Our simulations have been carried out on a $2 \times 2 \times 2$ supercell of the diamond face-centred-cubic cell including 64 C atoms, with periodic boundary conditions. We have checked that using larger supercells does not change appreciably any of the results presented below. In particular, we have carried out PI MC simulations on a $4 \times 4 \times 4$ supercell at three different temperatures, and found that the results coincide (within error bars) with those obtained for the $2 \times 2 \times 2$ supercell. The C nuclei were treated as quantum particles interacting via a Tersoff-type potential [23, 27], according to which the interaction between atoms i and j is described as

$$V_{ij} = f_C(r_{ij}) \left[f_R(r_{ij}) + b_{ij} f_A(r_{ij}) \right] \tag{1}$$

where r_{ij} is the interatomic distance. The functions $f_R(r) = A \exp(-\lambda_1 r)$ and $f_A(r) = -B \exp(-\lambda_2 r)$ represent repulsive and attractive pair potentials, respectively, f_C is a smooth cut-off function, and b_{ij} is an effective measure of the bond order, as defined in reference [27]. We have taken the parameters given in reference [23], except $A = 1387.3$ eV and $B = 348.3$ eV. In fact, the original parameters were fitted to reproduce experimental values by using classical simulations. This is the case for the lattice parameter of diamond, for which classical simulations with the original Tersoff parameters give the measured room-temperature value (but not the actual temperature dependence, which includes quantum effects). However, these potential parameters are not totally adequate for the quantum simulations, as quantum zero-point effects change the low-temperature values of the calculated quantities (as they do in the real material). Thus, the parameters A and B were modified in order to reproduce the actual low-temperature value of the lattice parameter in the quantum simulations. In earlier work [24], we carried out PI MC simulations of diamond with this Tersoff-type potential, and found results for structural and thermodynamic properties (in particular, for the lattice parameter and thermal expansion coefficient) close to the experimental values.

Diamond crystals with average isotopic mass M have been modelled by setting a mass M for every atom in the simulation cell (virtual-crystal approximation). We have checked for

two different M-values that the results obtained by using this approximation coincide (within the precision of our results) with those yielded by actually distributing ^{12}C and ^{13}C atoms in the appropriate proportions over the simulation cell. In these simulations, both isotopes were randomly distributed over the lattice sites, and they were kept fixed at their respective positions (no diffusive positional change).

For each set of values considered for our variables (T, P, M), we generated 2×10^4 quantum paths per atom for system equilibration, and 2×10^6 paths per atom for the calculation of ensemble average properties. To keep a constant precision for the results at different temperatures, we have considered a Trotter number L that scales as the inverse temperature. In fact, we have taken L as the integer number closest to $\hbar\omega_c/(k_B T)$, with $\omega_c \sim 3\omega_D$ (ω_D: the Debye frequency of diamond), which is enough for convergence of the results. This means that $LT = 6000$ K, i.e., $L = 20$ at $T = 300$ K. The convergence of the lattice parameter with the Trotter number was studied in previous work [24]. Results for a obtained from simulations with $LT > 6000$ K lie within the error bars of the data shown below. The maximum change allowed for the lattice parameter a in a Monte Carlo step amounts to 0.02 Å at $T = 300$ K, and increases to 0.05 Å at $T = 2000$ K. More of the practical details on this computational method are given in reference [19].

3. Results and discussion

With the interatomic potential employed here, the minimum potential energy for the (classical) diamond crystal is found to be $E_0 = -481.302$ eV per simulation cell (64 atoms), which corresponds to a lattice parameter $a_{cl}(0) = 3.5493$ Å. This value for E_0 translates into a cohesive energy of 7.52 eV per atom. In figure 1 we plot the temperature dependence of the internal energy (kinetic plus potential) obtained in the PI MC simulations at atmospheric pressure for isotopically pure crystals of ^{12}C (squares) and ^{13}C (circles). In this figure we have taken as zero the minimum potential energy of the classical crystal (E_0). At 300 K, the internal energy found in the simulations amounts to -467.76 and -468.23 eV for ^{12}C and ^{13}C, respectively. This corresponds to a cohesive energy of about 7.31 eV per atom, close to the experimental value of 7.36 eV [28]. According to our calculations, the ^{13}C crystal is 7 meV per atom more stable than the natural crystal, as a consequence of the smaller vibrational energy
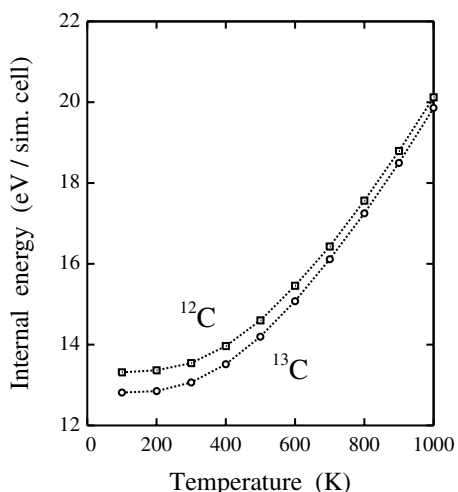

Figure 1. The temperature dependence of the internal energy per simulation cell (64 C atoms), for isotopically pure crystals of ^{12}C (squares) and ^{13}C (circles), as derived from PI MC simulations. Dotted lines are guides to the eye.

of the former. The internal energy shown in figure 1 corresponds basically to the vibrational energy, E_{vib}, since changes in the elastic energy of the crystal, caused by lattice expansion, are much smaller and amount to 0.10 and 0.22 eV per cell at 300 and 1000 K, respectively (see reference [24]). For $T \to 0$ (zero-point motion) the vibrational energy amounts to 13.31 and 12.81 eV per simulation cell (208 and 200 meV per atom) for ^{12}C and ^{13}C, respectively. Thus, at 0 K we find a ratio $E_{vib}^{12}/E_{vib}^{13} = 1.039$, close to the value expected in a harmonic approach ($\sqrt{13/12} = 1.041$).

The anharmonicity of the lattice vibrations causes an increase in the average C–C distance (or in the lattice parameter) at $T = 0$. This interatomic distance is larger than that giving the minimum potential energy of the (classical) crystal, which corresponds to the infinite-mass limit ($d_{cl}(0) \equiv d_\infty(0) = 1.5369$ Å). Classical MC simulations give a linear temperature dependence for the interatomic distance, which converges at low T to $d_\infty(0)$ (see reference [24]). In the quantum simulations, we find a ^{12}C–^{12}C distance that extrapolates at zero temperature to $d_{12}(0) = 1.5443$ Å. This means that the increase in ^{12}C–^{12}C distance at $T = 0$ with respect to the classical minimum amounts to 7.4×10^{-3} Å. This quantum effect on the nearest-neighbour atom distance at low temperature translates into an increase in the lattice parameter of 1.70×10^{-2} Å, as compared with the 'classical' crystal. In fact, we find for the quantum crystal a zero-temperature lattice parameter $a_{12}(0) = 3.5663$ Å versus $a_{cl}(0) = 3.5493$ Å for the classical one. Note that this 'zero-point expansion' is of the order of the change in a due to thermal expansion between 0 K and the Debye temperature of diamond ($\Theta_D \sim 2000$ K) [24]. The difference $a - a_{cl}$ between the lattice parameter found in quantum and classical simulations goes down as temperature rises, and at $T \gtrsim \Theta_D$ it decreases as $1/T$ (see reference [22]). Our results for the lattice parameter of ^{12}C derived from PI MC simulations with the Tersoff-type potential follow closely the experimental results in the temperature range where data are available [24, 29]. In particular, at $T = 300$ K we find for ^{12}C a lattice parameter $a_{12} = 3.566\,60(2)$ Å versus $a = 3.567\,14(5)$ Å derived from room-temperature x-ray diffraction data for natural diamond ($M = 12.011$ amu) [8, 9].

At a given temperature, the lattice parameter is expected to decrease linearly for increasing isotopic mass [17, 21, 30]. In figure 2 we show PI MC results for the lattice parameter of
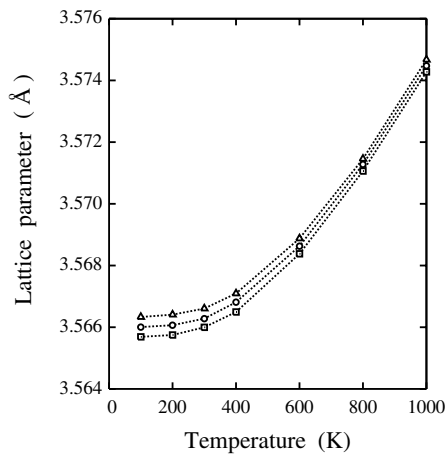

Figure 2. Lattice parameter of diamond as a function of temperature for isotopically pure crystals of ^{12}C (triangles), ^{13}C (squares), and for a crystal with average isotopic mass $M = 12.5$ amu (circles). Symbols represent results of PI MC simulations at $P = 1$ atm and dotted lines are guides to the eye. Error bars of the simulation results are smaller than the symbol size.

diamond for three different average masses M and temperatures lower than 1000 K, where the isotopic effect is clearly observable. In this figure, different symbols correspond to different masses: triangles for $M = 12$, circles for $M = 12.5$, and squares for $M = 13$ amu. The change in lattice parameter, $\Delta a = a_M - a_{12}$, for $M = 13$ and 12.5 amu is displayed in figure 3. Open circles and squares correspond to results derived from our PI MC simulations, and dotted lines are guides to the eye. At low temperatures ($T \leqslant 200$ K), we obtain $\Delta a = -6.5\ (\pm 0.2)$ and $-3.3\ (\pm 0.2) \times 10^{-4}$ Å for $M = 13$ and 12.5 amu, respectively. For increasing temperature, the difference Δa decreases, as quantum effects become less important for describing the atomic motion. This isotopic effect is still seen in the results of our MC simulations at temperatures of about 2000 K (of the order of Θ_D). At higher T, it becomes more difficult to observe due to the noise present in the values of Δa derived from the simulations, which increases as temperature is raised.
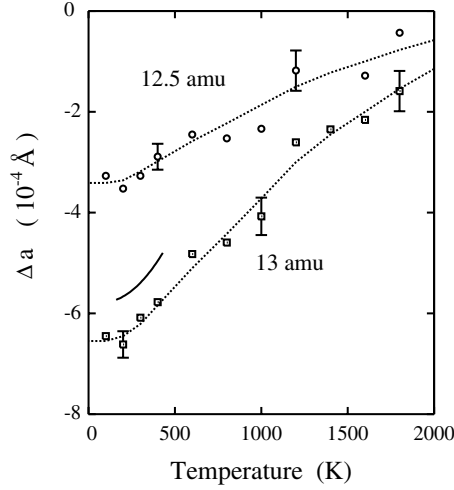

Figure 3. Difference between lattice parameters, $\Delta a = a_M - a_{12}$, versus temperature for $M = 13$ (squares) and 12.5 amu (circles), as derived from PI MC simulations at atmospheric pressure. Dotted lines are guides to the eye. The solid line is a parabolic fit to the results of a quasi-harmonic approximation for ^{12}C, given in reference [17].

The low-temperature changes in a due to isotopic mass can be explained quantitatively from the zero-point lattice expansion, $a_{\text{ref}}(0) - a_\infty(0)$, for a crystal with a reference isotopic mass M_{ref}. In fact, in a quasi-harmonic approach the difference $\Delta a(0) \equiv a_M(0) - a_{\text{ref}}(0)$ at $T = 0$ can be expressed as [22, 30]

$$\Delta a(0) = [a_{\text{ref}}(0) - a_\infty(0)]\left(\sqrt{M_{\text{ref}}/M} - 1\right). \qquad (2)$$

Taking ^{12}C as our reference, we have $a_{12}(0) - a_\infty(0) = 1.70 \times 10^{-2}$ Å (see above), and equation (2) gives $\Delta a(0) = -3.4$ and -6.7×10^{-4} Å for $M = 12.5$ and 13 amu, respectively. These values are close to the low-temperature results found from direct calculation of the lattice parameters corresponding to different atomic masses (squares and circles in figure 3). We note that an expression for $\Delta a(0)$, linear in $\Delta M = M - M_{\text{ref}}$, can be obtained by Taylor expanding the square root on the r.h.s. of equation (2), and neglecting terms of second and higher order in ΔM (see [22]).

The solid line in figure 3 corresponds to calculations by Pavone and Baroni [17]. These authors studied the dependence of the unit-cell volume upon isotopic mass by using density-functional perturbation theory in a quasi-harmonic approximation. They presented a parabolic

fit to their results for $\Delta V/V$ as a function of temperature, in a region centred around 300 K. Their fitted parabola for ^{13}C, translated to values of Δa, is presented in figure 3. This quasi-harmonic approximation gives an isotopic effect on the lattice parameter somewhat smaller than that found from our PI MC simulations. In particular, for ^{13}C at $T = 300$ K, this method yields $\Delta a = -5.4 \times 10^{-4}$ Å, to be compared with a value of -6.1 (± 0.2) $\times 10^{-4}$ Å, derived from the PI MC simulations presented here.

In figure 4 we show the difference Δa as a function of the average isotopic mass M. Results of our PI MC simulations at 300 K (black squares) are compared with room-temperature experimental data from Holloway *et al* [8] (open circles) and Yamanaka *et al* [9] (diamonds). Taking into account the error bars associated with the experimental results and MC simulations, these three sets of data points are compatible with each other. Our simulation results for Δa follow a linear dependence on M (dashed line), with a slope slightly larger than that found by Pavone and Baroni [17] (dotted line). The experimental results in the range from $M = 12$ to 13 amu are also compatible with this linear dependence. Nevertheless, Yamanaka *et al* [9] proposed a parabolic dependence for Δa, in view of their x-ray diffraction results (diamonds). Such a dependence is, however, very difficult to reconcile with the present and other theoretical analyses [10, 17], as well as with the current understanding of isotopic effects in the lattice parameters of crystals [30–32]. Moreover, that parabolic dependence would produce spurious features, such as a minimum in the lattice parameter for $M = 13.2$ amu, and an increase in a for larger M (which corresponds to a hypothetical crystal with large concentration of ^{14}C). Although it is clear that corrections to the linear dependence will appear due to higher-order effects, not included in approximations such as the quasi-harmonic one, they are too small to be detected, considering the precision of the experimental data in figure 4. The PI MC simulations can, in principle, detect such deviations from linearity, but also in this case the present error bars preclude the observation of such a small effect.
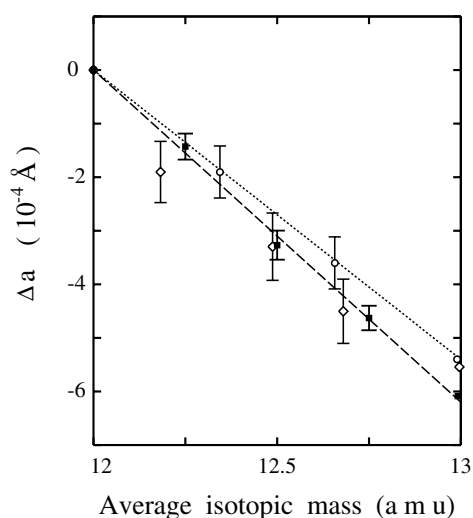

Figure 4. Change in the lattice parameter, $\Delta a = a_M - a_{12}$, as a function of the average isotopic mass M, at atmospheric pressure. Black squares: PI MC results at $T = 300$ K; open circles and diamonds: room-temperature experimental data obtained by Holloway *et al* [8] and Yamanaka *et al* [9], respectively. Error bars for the data points at $M = 13$ amu are similar to those for smaller M, and are not shown for the sake of clarity. The dashed line is a linear fit to the PI MC data, and the dotted line corresponds to the quasi-harmonic approximation in reference [17].

The pressure dependence of the unit-cell volume for ^{12}C was studied earlier with PI MC simulations [24]. At $T = 300$ K and $P = 4000$ kbar, we found $a = 3.093\,70(2)$ Å, and the crystal volume is reduced to a value of 0.653 times the zero-pressure volume. Moreover, the isotopic effect on the crystal volume (or lattice parameter) is expected to decrease as pressure rises, due to the change in bulk modulus with isotopic mass [7]. In figure 5 we present the pressure dependence of Δa at $T = 300$ K for $M = 12.5$ and 13 amu, as derived from our PI MC simulations. For increasing pressure, Δa is lowered, and we find for ^{13}C a change from $\Delta a = -6.1\ (\pm 0.2) \times 10^{-4}$ Å at atmospheric pressure to $-2.4\ (\pm 0.2) \times 10^{-4}$ Å at 4000 kbar. Hence, the fractional volume change $\Delta V / V$ between ^{13}C and ^{12}C decreases from -5.1×10^{-4} at zero pressure to -2.3×10^{-4} at 4000 kbar. As a result, Δa for $M = 12.5$ amu is half the value found for ^{13}C over the whole range from 0 to 5000 kbar. The important change in Δa as a function of pressure is basically due to an increase in the bulk modulus, B, of the material as the pressure is raised. In fact, at a given temperature, one can write $a_M - a_{12}$ as a function of the Grüneisen parameters of the material, and see that, to first order in these parameters, Δa is proportional to $1/B$ [22, 30]. In other words, the decrease in isotopic effect as pressure rises is associated with a reduction of the zero-point lattice expansion (see equation (2)), that in turn is caused by an increase in the bulk modulus of the material.
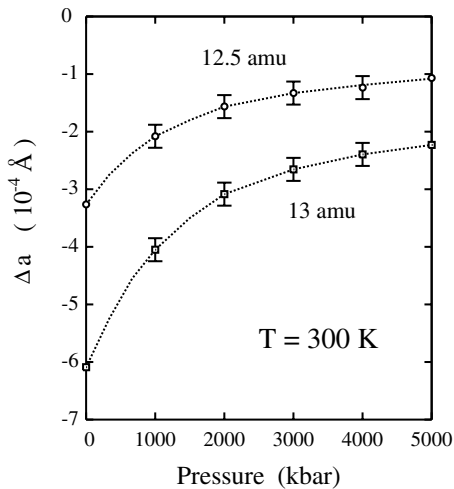

Figure 5. Difference $\Delta a = a_M - a_{12}$ as a function of pressure at 300 K. Symbols are data points derived from PI MC simulations for $M = 13$ (squares) and 12.5 amu (circles). Dotted lines are guides to the eye.

We finally note that, in spite of the limitations associated with using an empirical potential originally optimized for classical simulations, good agreement has been found between PI MC and experimental results for the isotope effect in the lattice parameter of diamond. An alternative to the use of this kind of empirical potential in condensed-matter simulations consists of calculating the system energy by standard electronic structure methods, as in the Car–Parrinello approach [33]. Although the original formulation of this method considered the atomic nuclei as classical particles, new approaches that take into account the quantum nature of both electrons and nuclei have been developed in recent years. In this way, *ab initio* path-integral molecular dynamics simulations have become feasible for small molecules [34], and they can now be applied to condensed-matter problems [35]. This is a promising tool for studying anharmonic effects in solids.

In summary, we have studied the dependence of the lattice parameter of diamond on isotopic mass, at different temperatures and pressures, by path-integral Monte Carlo simulations. These quantum simulations allow us to study phonon-related properties of solids, without the usually employed harmonic or quasi-harmonic approximations. Thus,

anharmonicities in the lattice vibrations are taken into account in a natural way, which permits us to check results obtained from different theoretical approaches. Our results at atmospheric pressure agree well with those derived from x-ray diffraction experiments, and we hope that our prediction for the isotopic effect at high pressures will stimulate experimental studies under these conditions.

Acknowledgments

References

[1] Cardona M, Etchegoin P, Fuchs H D and Molinás-Mata P 1993 *J. Phys.: Condens. Matter* **5** A61
[2] Cardona M 2000 *Phys. Status Solidi* b **220** 5
[3] Collins A T, Lawson S C, Davies G and Kanda H 1990 *Phys. Rev. Lett.* **65** 891
[4] Hass K C, Tamor M A, Anthony T R and Banholzer W F 1992 *Phys. Rev.* B **45** 7171
[5] Muinov M, Kanda H and Stishov S M 1994 *Phys. Rev.* B **50** 13 860
[6] Vogelgesang R, Alvarenga D, Kim H, Ramdas A K, Rodriguez S, Grimsditch M and Anthony T R 1998 *Phys. Rev.* B **58** 5408
[7] Ramdas A K, Rodriguez S, Grimsditch M, Anthony T R and Banholzer W F 1993 *Phys. Rev. Lett.* **71** 189
[8] Holloway H, Hass K C, Tamor M A, Anthony T R and Banholzer W F 1991 *Phys. Rev.* B **44** 7123
     Holloway H, Hass K C, Tamor M A, Anthony T R and Banholzer W F 1992 *Phys. Rev.* B **45** 6353 (erratum)
[9] Yamanaka T, Morimoto S and Kanda H 1994 *Phys. Rev.* B **49** 9341
[10] Biernacki S W 1997 *Phys. Rev.* B **56** 11 472
[11] Anthony T R, Banholzer W F, Fleischer J F, Wei L, Kuo P K, Thomas R L and Pryor R W 1990 *Phys. Rev.* B **42** 1104
[12] Wei L, Kuo P K, Thomas R L, Anthony T R and Banholzer W F 1993 *Phys. Rev. Lett.* **70** 3764
[13] Olson J R, Pohl R O, Vandersande J W, Zoltan A, Anthony T R and Banholzer W F 1993 *Phys. Rev.* B **47** 14 850
[14] Vohra Y K and Vagarali S S 1992 *Appl. Phys. Lett.* **61** 2860
[15] Buschert R C, Merlini A E, Pace S, Rodriguez S and Grimsditch M H 1988 *Phys. Rev.* B **38** 5219
[16] Kazimorov A, Zegenhagen J and Cardona M 1998 *Science* **282** 930
[17] Pavone P and Baroni S 1994 *Solid State Commun.* **90** 295
[18] Ramírez R and Herrero C P 1993 *Phys. Rev.* B **48** 14 659
[19] Noya J C, Herrero C P and Ramírez R 1996 *Phys. Rev.* B **53** 9869
[20] Müser M H, Nielaba P and Binder K 1995 *Phys. Rev.* B **51** 2723
[21] Noya J C, Herrero C P and Ramírez R 1997 *Phys. Rev.* B **56** 237
[22] Herrero C P 2000 *Phys. Status Solidi* b **220** 857
[23] Tersoff J 1988 *Phys. Rev. Lett.* **61** 2879
[24] Herrero C P and Ramírez R 2001 *Phys. Rev.* B **63** 024103
[25] Gillan M J 1988 *Phil. Mag.* A **58** 257
[26] Ceperley D M 1995 *Rev. Mod. Phys.* **67** 279
     Ceperley D M 1999 *Rev. Mod. Phys.* **71** S438
[27] Tersoff J 1988 *Phys. Rev.* B **37** 6991
[28] Kittel C 1975 *Introduction to Solid State Physics* (New York: Wiley)
[29] *Landolt–Börnstein New Series* 1982 Group III, vol 17a, ed O Madelung (Berlin: Springer)
[30] Debernardi A and Cardona M 1996 *Phys. Rev.* B **54** 11 305
[31] Garro N, Cantarero A, Cardona M, Göbel A, Ruf T and Eberl K 1996 *Phys. Rev.* B **54** 4732
[32] Biernacki S and Scheffler M 1994 *J. Phys.: Condens. Matter* **6** 4879
[33] Car R and Parrinello M 1985 *Phys. Rev. Lett.* **55** 2471
[34] Marx D and Parrinello M 1995 *Nature* **375** 216
     Marx D and Parrinello M 1996 *Science* **271** 179
[35] Benoit M, Marx D and Parrinello M 1998 *Nature* **392** 258
     Marx D, Tuckerman M E, Hutter J and Parrinello M 1999 *Nature* **397** 601