

Isotope effects on the lattice parameter of cubic SiC

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Path-integral molecular-dynamics simulations in the isothermal-isobaric (NPT) ensemble have been carried out to study the dependence of the lattice parameter of 3C-SiC upon isotope mass. This computational method allows a quantitative and nonperturbative study of such anharmonic effect. Atomic nuclei were treated as quantum particles interacting via a tight-binding-type potential. At 300 K, the difference Δa between lattice parameters of 3C-SiC crystals with ^{12}C and ^{13}C amounts to 2.1×10^{-4} Å. The effect due to Si isotopes is smaller and amounts to 3.5×10^{-5} Å when replacing ^{28}Si by ^{29}Si . Results of the path-integral molecular-dynamics simulations are interpreted in terms of a quasiharmonic approximation for the lattice vibrations.

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It is well known that the lattice parameters of two chemically identical crystals with different isotopic compositions are not equal, lighter isotopes giving rise to larger lattice parameters. This is caused by a combination of two factors: the dependence of atomic vibrational amplitudes upon atomic mass and the anharmonicity of the vibrations. The isotope effect on the lattice parameter is most important at low temperatures, due to the change in zero-point vibrational amplitude with atomic mass, and disappears in the high-temperature (classical) limit at $T > \Theta_D$ (Θ_D —Debye temperature), where vibrational amplitudes are independent of the mass. In recent years, it has become feasible to measure the isotopic effect in lattice parameters of crystals with high precision.¹ Most of the work has been performed on elemental crystals, although binary and multinary materials offer the attractive possibility of isotopic substitution on different atoms.² Of these materials, SiC with three stable isotopes of Si and two of C, plus about 70 different polytypes, is a paragon. Here, however, we confine ourselves to the simplest polytype: zinc-blende-like 3C-SiC.

SiC has been suggested for a number of applications exploiting many of its superlative properties, close to those of diamond.^{3,4} Some of these applications take advantage of its hardness, large thermal conductivity, and low thermal expansion. Isotopically modified SiC may find applications exploiting the higher thermal conductivity⁵ and the dependence of its hardness on isotopic composition.⁶

Anharmonic effects in the vibrational properties of 3C-SiC have been studied earlier in detail, e.g., the pressure and temperature dependence of phonon frequencies^{7,8} and lifetimes.^{9,10} The thermal expansion of cubic SiC (another anharmonic effect) has been studied in detail both experimentally¹¹ and theoretically,^{12,13} the latter using a quasiharmonic approximation (QHA) for the lattice vibrations.

Isotopic effects on the lattice parameters of crystals have been usually calculated by employing the QHA and perturbative methods based on *ab initio* techniques.^{2,14,15} An alternative to perturbational approaches in solids is the combination of the path-integral formulation (to deal with the

quantum nature of the nuclei) with electronic structure methods. The path-integral approach to statistical mechanics allows one to study finite-temperature properties of quantum many-body problems in a nonperturbative scheme, even in the presence of large anharmonicities.¹⁶ An advantage of its combination with electronic structure methods is that both electrons and atomic nuclei are treated quantum mechanically in the framework of the Born-Oppenheimer approximation.^{17–19}

The path-integral molecular-dynamics (PIMD) method is based on an isomorphism between the quantum system under consideration and a classical one, obtained by replacing each quantum particle by a cyclic chain of classical particles, connected by harmonic springs.^{16,20,21} When calculating properties of crystals with isotopically mixed composition, it is usually assumed that each atomic nuclei in the solid has a mass equal to the average mass. This kind of *virtual-crystal approximation* has been used in density-functional calculations, as well as in atomistic simulations based on path integrals.^{2,21–24} In fact, in earlier path-integral simulations of diamond it was found that the results obtained by using this approximation are indistinguishable from those derived from simulations in which actual isotopic mixtures were considered.²⁴

Here we extend earlier path-integral calculations of the lattice parameter of group-IV solids^{21,23,24} (diamond, Si, and Ge) to a IV-IV compound such as 3C-SiC. The electronic structure has been treated with an efficient tight-binding Hamiltonian based on density-functional calculations.^{25,26} Simulations were performed on a $2 \times 2 \times 2$ supercell of the 3C-SiC face-centered-cubic cell with periodic boundary conditions, including 64 atoms. For a given temperature and isotopic composition, a typical run consisted of 2×10^4 PIMD steps for system equilibration, followed by 4×10^6 steps for the calculation of ensemble-average properties. Details on the actual implementation of the PIMD method to study structural and electronic properties of SiC were given elsewhere.²⁶

First of all, we quantify the influence of quantum effects on the lattice parameter of cubic SiC. With this purpose we

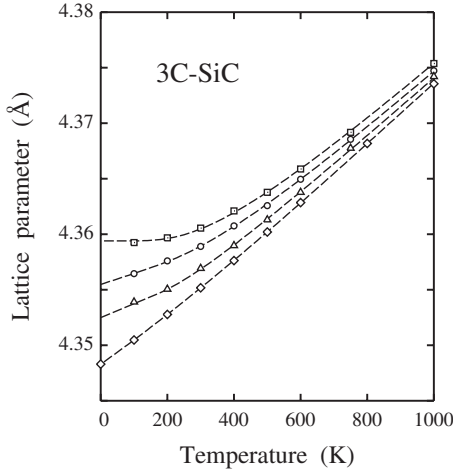


FIG. 1. Temperature dependence of the lattice parameter of 3C-SiC, as obtained from (a) PIMD simulations (squares), (b) simulations performed by setting the Si nuclei as classical particles (circles), (c) simulations carried out by considering classical C nuclei (triangles), and (d) all nuclei are assumed to be classical (diamonds). Lines represent empirical fits. The statistical error of the simulation results is less than the symbol size.

have performed simulations in which the atomic nuclei of either C or Si (or both) were considered as classical particles. We note that in the formalism used here, the classical limit for a given atomic nucleus is obtained by taking its mass as $M \rightarrow \infty$ (in fact, we took masses in the order of 10^5 amu).

In Fig. 1 we present the results of our molecular-dynamics simulations for the various cases considered. First, we compare the results of the full PIMD simulations (quantum atomic nuclei, open squares) with those of classical simulations (diamonds). The zero-point motion induces an increase in the lattice parameter of 0.011 \AA , which means a relative change of 2.5×10^{-3} . Second, we are interested in the lattice parameter obtained when nuclei of one of the elements (Si or C) are considered as classical and the other as quantum particles. Thus, triangles represent results for quantum Si and classical C, whereas circles indicate data for quantum C and classical Si. By comparing these results with those found in the full PIMD simulations, we find for $T \rightarrow 0$ that the lattice parameter a increases by 3.9×10^{-3} and $6.8 \times 10^{-3} \text{ \AA}$ due to having considered Si or C as quantum particles, respectively (assuming in each case that atomic nuclei of the other element are quantum particles). We note that these results are similar to those presented earlier in Ref. 26, but here the simulations extended over run ten times longer in order to improve the accuracy in the lattice parameter, and the present error bars are smaller by a factor of ~ 3 .

Results presented until now were obtained for SiC crystals with natural isotopic composition. We now turn to simulations of SiC crystals, in which one of the elements is taken to be isotopically pure. Thus, we carried out PIMD simulations of $^{nat}\text{Si};^{12}\text{C}$ and $^{nat}\text{Si};^{13}\text{C}$ (where the superscript “nat” refers to the mass of the natural isotopic composition) at several temperatures. Results for the difference Δa between lattice parameters of both kinds of crystals are shown in Fig. 2 (squares). At room temperature, we find $\Delta a = 2.1 \times 10^{-4} \text{ \AA}$, which translates into a relative change

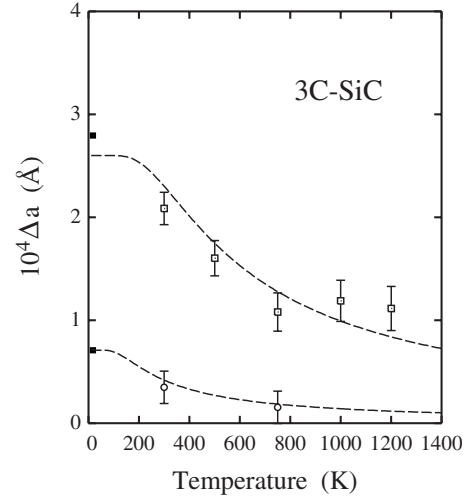


FIG. 2. Temperature dependence of the isotope effect on the lattice parameter of 3C-SiC. Squares represent the difference between lattice parameter of $^{nat}\text{Si};^{12}\text{C}$ and $^{nat}\text{Si};^{13}\text{C}$, whereas circles indicate the difference Δa between $^{28}\text{Si};^{nat}\text{C}$ and $^{29}\text{Si};^{nat}\text{C}$. Filled symbols indicate the low-temperature values derived from Eq. (5). Lines represent fits of the simulation results to Eq. (1).

$\Delta a/a = 4.8 \times 10^{-5}$. Something similar has been done for $^{28}\text{Si};^{nat}\text{C}$ and $^{29}\text{Si};^{nat}\text{C}$ crystals, and the difference Δa yielded by our simulations is much lower: at 300 K we found $\Delta a = 3.5 \times 10^{-5} \text{ \AA}$ or $\Delta a/a = 8 \times 10^{-6}$. The temperature dependence of Δa can be fitted to a function with the shape of the mass derivative of a Bose-Einstein function, namely,

$$\Delta a = C \left[1 + \frac{2}{e^x - 1} \left(1 - \frac{xe^x}{e^x - 1} \right) \right], \quad (1)$$

where $x = T_a/T$ and C and T_a are fit parameters. Dashed lines in Fig. 2 represent this function with $T_a = 1200$ (upper curve) and 600 K (lower curve). Equation (1) is basically equivalent to Eq. (3) of Ref. 26 except that the adjustable parameter b has been replaced by well-defined physical variables more convenient for the subsequent treatment. The minor deviations of the PIMD points from the fitted curves are not surprising since we have used a single Einstein-oscillator fit. They could be decreased by using two oscillators.²⁷

The results of our PIMD simulations can be further analyzed in terms of a QHA for the lattice vibrations. In such an approximation, the lattice parameter $a(T)$ for a given isotopic composition at temperature T can be derived by minimizing the Helmholtz free energy with respect to the crystal volume.^{2,22} One finds

$$a(T) = a_\infty + \frac{1}{3Ba_\infty^2} \sum_{n,\mathbf{q}} \gamma_n(\mathbf{q}) E_n(\mathbf{q}, T), \quad (2)$$

where

$$E_n(\mathbf{q}, T) = \frac{1}{2} \hbar \omega_n(\mathbf{q}) \coth \left(\frac{\hbar \omega_n(\mathbf{q})}{2k_B T} \right). \quad (3)$$

Here, $\omega_n(\mathbf{q})$ are the frequencies of the n th mode in the crystal, B is the bulk modulus, a_∞ is the zero-temperature lattice parameter in the limit of infinite atomic mass (classical

limit), and $\gamma_n(\mathbf{q}) = -\partial \ln \omega_n(\mathbf{q}) / \partial \ln V$ is the Grüneisen parameter of mode n and \mathbf{q} . Then, at $T=0$ the difference $a(0) - a_\infty$ is given by

$$a(0) - a_\infty = \frac{1}{6Ba_\infty^2} \sum \hbar \omega_n(\mathbf{q}) \gamma_n(\mathbf{q}). \quad (4)$$

Let us consider now for simplicity two isotopically pure monatomic crystals with a mass difference ΔM . The difference between the corresponding lattice parameters, Δa , can be related to the zero-point renormalization, $a_{\text{nat}}(0) - a_\infty$, for the natural crystal. This can be achieved through a first-order expansion for the lattice parameter as a function of the mass M and taking into account that the frequencies $\omega_n(\mathbf{q})$ scale as $1/\sqrt{M}$. One finds for the change in lattice parameter at $T=0$,

$$\Delta a = -\frac{1}{2} [a_{\text{nat}}(0) - a_\infty] \frac{\Delta M}{M_{\text{nat}}}. \quad (5)$$

This means that the low-temperature changes in a due to isotopic mass can be obtained from the zero-point renormalization of the lattice parameter in the natural crystal.

For binary compounds such as SiC, one can use a formula similar to Eq. (5) to obtain the separate contributions of each kind of atoms (i.e., Si or C). To first order, the contributions of both types of atoms will be additive. Then, from the difference $a_{\text{nat}}(0) - a_\infty$ discussed above and presented in Fig. 1, we obtain in the low-temperature limit, using Eq. (5), $\Delta a = 2.8 \times 10^{-4}$ Å when replacing ^{12}C by ^{13}C and $\Delta a = 7.0 \times 10^{-5}$ Å for substitution of ^{28}Si by ^{29}Si . These are the values shown in Fig. 2 as filled squares at $T=0$.

We note that the virtual-crystal approximation has been employed in our simulations, i.e., for crystals with the natural isotopic composition of Si or C we have assumed that the atoms have the average mass. In this respect it is worthwhile considering the validity of assuming an effective mass M_{eff} for all the atoms in a given crystal to describe changes in the lattice parameter. In view of Eq. (4), one has²²

$$\frac{a(0) - a_\infty}{a_\infty} \sim \frac{\hbar}{BV_c} \langle \omega_n(\mathbf{q}) \rangle \langle \gamma_n(\mathbf{q}) \rangle, \quad (6)$$

where V_c is the volume of the primitive cell and $\langle \dots \rangle$ indicates an average over all branches of the Brillouin zone. Now we may assume a dependence of the average frequency on effective mass as

$$\langle \omega_n(\mathbf{q}) \rangle \sim M_{\text{eff}}^{-1/2}, \quad (7)$$

which, in fact, is expected when one considers M_{eff} as

$$\frac{1}{M_{\text{eff}}} = \frac{1}{2} \left(\frac{1}{M_C} + \frac{1}{M_{\text{Si}}} \right). \quad (8)$$

To check this point we have carried out PIMD simulations for SiC crystals with various effective masses for both Si and C. The results are displayed in Fig. 3 as open symbols. For comparison with the result derived for M_{eff} given by Eq. (8)

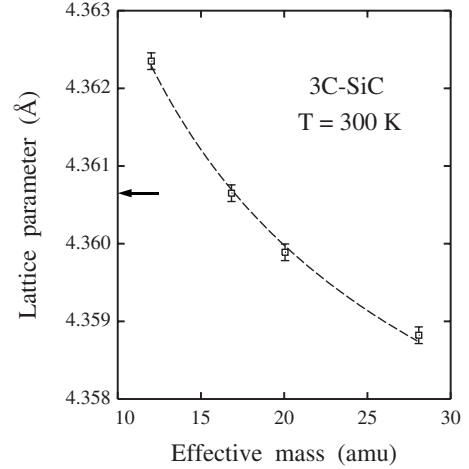


FIG. 3. Lattice parameter of 3C-SiC as a function of M_{eff} in a virtual-crystal approximation, in which all atoms in the simulation cell (Si and C) are assumed to have the same effective mass. Open squares indicate results of PIMD simulations in this approximation. The dashed line is a fit to Eq. (9). An arrow indicates the lattice parameter derived from PIMD simulations with C and Si atoms having the mean isotopic masses of natural material.

(~ 16.8 amu), we also show those obtained by assuming an effective mass given either by the average $(M_C + M_{\text{Si}})/2$ or by the mass of Si or C. All these results can be fitted well to the expression

$$a = b + \frac{c}{\sqrt{M_{\text{eff}}}}, \quad (9)$$

where b and c are fit parameters. Such an expression can be expected from Eq. (4) when one considers an effective mass for both types of atoms at temperatures $T \ll \Theta_D$ (for SiC, $\Theta_D \sim 1100$ K). The actual lattice parameter of SiC yielded by the simulations above is indicated in Fig. 3 by an arrow. It coincides within error bars with that derived assuming $M_{\text{eff}} = 16.8$ amu, as given in Eq. (8). Note that taking the effective mass as the average of the masses (at about 20 amu) yields a lattice parameter clearly lower than the actual one obtained using the separate masses of C and Si.

The agreement between the result for $M_{\text{eff}} = 16.8$ amu and the real crystal can be interpreted in terms of perturbation theory as follows. Looking at Eq. (4), changes in the lattice parameter are mainly due to TO phonons, as can be derived from Fig. 9 in Ref. 13 for the appropriate values of γ_n and Fig. 2 for the density of phonon states. The TO band in SiC is rather symmetric,¹³ and according to second-order perturbation theory,^{22,28} mass fluctuations cause an increase in the high frequencies and a reduction in the low ones by a similar amount. All together the effect in the lattice parameter is expected to be negligible, as observed in the results of the simulations. If some effect appears due to mass fluctuations, it has to be of third or higher order and should be less than the statistical uncertainty of our results. This gives further support to the virtual-crystal approximation for calculating lattice parameters of this kind of semiconductors.

In summary, we have calculated the isotope effect on the lattice parameter of cubic SiC by PIMD simulations. This procedure gives a quantitative estimation of such effect, which amounts to $\Delta a/a=4.8 \times 10^{-5}$ for replacement of ^{12}C by ^{13}C and to $\Delta a/a=8 \times 10^{-6}$ for substitution of ^{29}Si for ^{28}Si . These results have been interpreted in terms of a quasi-harmonic approach for the lattice vibrations. The virtual-

crystal approximation is found to be valid in all cases considered here. Second order perturbation theory, as implied by Eq. (5), has also been shown to be valid.

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