DEPENDENCE OF THE CRYSTAL LATTICE CONSTANT ON ISOTOPIC COMPOSITION: THEORY AND AB INITIO CALCULATIONS FOR C, Si, AND Ge

Pasquale Pavone

Institut für Theoretische Physik, Universität Regensburg, D-93040, Germany

Stefano Baroni

Scuola Internazionale Superiore di Studi Avanzati (SISSA), Via Beirut 2/4, I-34014 Trieste, Italy

We consider the problem of the dependence of the lattice constant of a crystal upon its isotopic purity. After giving a brief account of the theoretical framework, we report on first-principles calculations for diamond, silicon, and germanium, performed by treating nuclear vibrations by density-functional perturbation theory. Our results are in good agreement with existing experimental data for diamond and germanium, and provide reliable predictions for silicon, which are relevant for metrological applications.

The high-accuracy determination of the equilibrium lattice constant of some crystals is important for metrological applications. In the specific case of silicon, for instance, this is an active field of research aiming at a better determination of the Avogadro constant [1]. Isotopic composition affects the equilibrium crystal volume through anharmonic effects and through the dependence of zero-point motions upon the nuclear masses. In this paper we present a theory of the dependence of the crystal lattice constant upon temperature and nuclear masses, and apply it to the determination of the isotopic effect on the equilibrium volumes of C, Si, and Ge crystals, using phonon frequencies calculated from first principles via density-functional perturbation theory [2].

The theory of the isotopic effect on the crystal equilibrium volumes is not new [3]. In the following, we derive some formulas which are relevant for the actual calculation of the effect. Let us consider a monoatomic crystal whose average atomic mass we indicate by μ. In the quasi-harmonic approximation, the crystal free energy is given by:

$$F(V,T,\mu) = E_0(V) + \int_0^\infty \left(\frac{1}{2}\hbar\omega + k_B T \log \left(1 - e^{-\frac{\hbar\omega}{k_B T}} \right) \right) n_{\mu V}(\omega) d\omega, \quad (1)$$

where $E_0(V)$ is the zero-temperature classical energy as a function of the crystal volume, k_B is the Boltzmann constant, and $n_{\mu V}(\omega)$ is the vibrational density of states of the crystal at volume V. If isotopic disorder is treated in the virtual-crystal approximation [4], the dependence of the vibrational density of states upon composition is given by a simple scale law:

$$n_{\mu V}(\omega) = x\, \bar{n}_V(x\omega), \quad (2)$$

where $x = \sqrt{\mu/\bar{\mu}}$, $\bar{\mu}$ being some reference isotopic mass (e.g. the average mass occurring in nature), and $\bar{n}_V$ the corresponding density of states. Inserting Eq. (2) into Eq. (1), one obtains:

$$F(V,T,\mu) = E_0(V) + \frac{1}{x} \bar{F}_{vib}(V, xT), \quad (3)$$

where $\bar{F}_{vib}$ is the vibrational contribution to the free energy (as given by the integral in Eq. (1)) of a crystal whose isotopic mass is $\bar{\mu}$. For a given average isotopic mass, μ, and temperature, T, the crystal equilibrium volume $V(T,\mu)$ is that which makes the volume derivative of the free energy, Eq. (3), equal to the negative of the pressure. For $\mu \approx \bar{\mu}$, the leading dependence of $\Delta V(T,\mu) = V(T,\mu) - V(T,\bar{\mu})$ upon $\Delta \mu$ can be obtained by expanding the volume derivative of Eq. (3) to linear order in ΔV and $x - 1 \approx \Delta\mu/(2\bar{\mu})$, and by equating the resulting expression to the negative of the pressure. The result reads:

$$\Delta V(T,\mu) \approx \bar{V}(T) \frac{\Delta\mu}{2\bar{\mu}\bar{B}} \left(\frac{\partial \bar{E}_{vib}}{\partial V} \right)_{V=\bar{V}(T)}, \quad (4)$$

where $\bar{V}(T) = V(T,\bar{\mu})$, $\bar{B}$ is the corresponding bulk modulus, and $\bar{E}_{vib}$ is the vibrational contribution to the internal energy of the crystal with average isotopic mass $\bar{\mu}$. In the quasi-harmonic approximation, $\bar{V}(T)$ is given by:

$$\bar{V}(T) = V_0 - \frac{V_0}{\bar{B}} \left(\frac{\partial \bar{F}_{vib}}{\partial V} \right)_{V_0, T}, \quad (5)$$

where V_0 is the volume which minimizes $E_0(V)$. In the practical implementation of Eqs. (4) and (5) we

TABLE I. Fractional lattice-parameter difference of ^{74}Ge with respect to natural isotopic Ge. Experimental values from Ref. [7].

T (K)	Theory	Experiment
78	-10.9×10^{-6}	-14.9×10^{-6}
300	-4.6×10^{-6}	-6.3×10^{-6}

approximate $\overline{B} \approx B_0 \equiv V_0 (\partial^2 E_0/\partial V^2)_{V=V_0}$. By expressing the derivative of the vibrational free and internal energies in terms of individual vibrational frequencies, $\overline{\omega}_\nu \equiv \omega_\nu(\overline{V},\overline{\mu})$, and mode Grüneisen parameters, $\overline{\gamma}_\nu = -(\overline{V}/\overline{\omega}_\nu) \times (\partial \overline{\omega}_\nu/\partial V)_{V=\overline{V}}$, one finally obtains:

$$\Delta V(T,\mu) \approx \frac{\Delta \mu}{4\overline{\mu}B_0} \times$$

$$\sum_\nu \hbar\overline{\omega}_\nu \, \overline{\gamma}_\nu \, \coth\left(\frac{\overline{\xi}_\nu}{2}\right)\left(\frac{\overline{\xi}_\nu}{\sinh(\overline{\xi}_\nu)} - 1\right), \quad (6a)$$

$$\overline{V}(T) = V_0 + \frac{1}{2B_0}\sum_\nu \hbar\overline{\omega}_\nu \, \overline{\gamma}_\nu \, \coth\left(\frac{\overline{\xi}_\nu}{2}\right), \quad (6b)$$

where $\overline{\xi}_\nu = \hbar\overline{\omega}_\nu/k_B T$, and $\nu \equiv (n, k)$ indicates the nth phonon branch at wavevector k.

The ingredients entering Eqs. (6), ω_ν and γ_ν, have been calculated from density-functional perturbation theory [2], using the same technical ingredients as in Refs. [2] and [5] for silicon and germanium and for diamond respectively. In Fig. 1 we compare the dependence of the diamond lattice constant upon the average nuclear mass, as predicted from Eqs. (6), with the experimental data of Ref. [6]. In the case of germanium, the experimental data [7] are scarcer, and probably not as accurate. However, also in this case the agreement between our predictions and experiments is quite satisfactory, as shown in Table I.

In Fig. 2 we display the temperature dependence of the equilibrium lattice constants of the materials studied here, corresponding to different pure isotopic
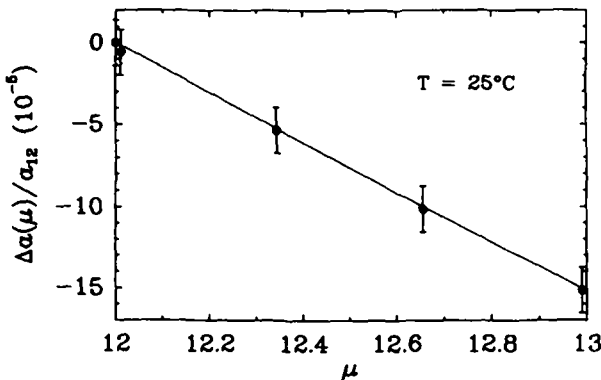

Fig. 1. Dependence of the equilibrium lattice constants of diamond upon average isotopic mass. Full circles indicate experimental data from Ref. [6].
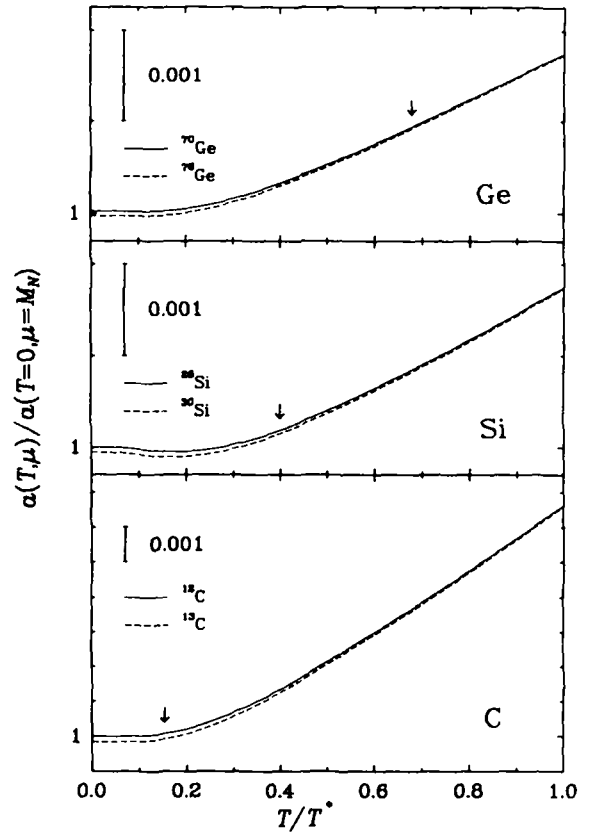

Fig. 2. Dependence of the equilibrium lattice constants of C, Si, and Ge upon temperature for different isotopic masses. The temperature is given in units of T^* (see text), ($T^*(C) = 1941$ K, $T^*(Si) = 744$ K, and $T^*(Ge) = 440$ K). The arrows indicate the room temperature (25°C). The lattice constants are in units of the zero-temperature lattice constants at the natural isotopic compositions ($a_C = 6.71$, $a_{Si} = 10.23$, and $a_{Ge} = 10.61$ a.u.). Note the different units in the three panels, which are indicated by the vertical bars.

compositions. The temperatures have been scaled to the temperature corresponding to the maximum frequencies of the spectra of the different materials, $T^* = \hbar\omega_{max}/k_B$; also note the different vertical scales. According to Eqs. (6), the relative variation of the equilibrium volume is linearly related to the relative variation of the average isotopic mass, the ratio between the two variations being a function of temperature. We have found that this temperature dependence can be accurately interpolated by the formula:

$$\frac{\Delta V(T,\mu)}{\overline{V}(T,\mu)} \approx \frac{\Delta \mu}{\mu} \times \left(A + B(T - T_0) + C(T - T_0)^2\right), \quad (7)$$

where $T_0 = 25°C$ indicates the room temperature. The values of the A, B, and C coefficients as fitted to our theoretical data for the three materials studied here are reported in Table II. The quality of the fit is such that, Eq. (7) provides 3 significant figures for C and Si and 2 for Ge in a range of $200°C$ centered around T_0.

TABLE II. Coefficients of the polynomial fit to the temperature dependence of the fractional volume variation with isotopic mass (Eq. (7)).

	A	B	C
C	-5.48×10^{-3}	3.55×10^{-6}	8.21×10^{-9}
Si	-1.60×10^{-3}	3.94×10^{-6}	-6.90×10^{-9}
Ge	-0.72×10^{-3}	2.27×10^{-6}	-6.40×10^{-9}

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