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The influence of the isotopic composition on the thermal expansion of crystalline Si

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Abstract. We report first-principles calculations of the dependence of the lattice parameter of Si on temperature and on the isotopic composition. Around 80 K (the minimum of the thermal expansion coefficient) the lattice parameter difference of different isotopic compositions is largest and then it decreases monotonically with increasing temperature. The results are explained in a simple physical picture.

The phonon spectra [1–4] of two crystals built from the same atomic species but with a different isotopic composition are quantitatively different due to the direct dependence of the vibrational frequencies on the atomic masses. This mass dependence also implies a change of the specific heat and the crystal lattice parameter. Some influence on the electronic bands [5–7] is to be expected as well. In this paper we analyse the influence of the isotopic composition on the lattice parameter using a first-principles approach which is essentially identical to that used in our study of the anomalous thermal expansion of Si [8].

The work reported in this paper was motivated by some recent highly accurate experimental measurements of the lattice parameter of isotopic enriched Si crystals. These crystals may potentially be used for a more accurate determination of the Avogadro constant [9, 10] which then can lead to a new definition of the mass unit. It is interesting to note that the mass unit is the only unit in the SI system which is still defined by a real piece of material and not expressed in terms of fundamental physical constants. A Si crystal is particularly well suited for precise measurements of the lattice parameter and Avogadro constant due to the relatively low concentration of intrinsic and extrinsic defects which normally cause some systematic errors. At this point a better and quantitative understanding of the isotopic composition and temperature effects is important.

For normal pressure, i.e. when the pressure term of the Gibbs free energy can be neglected, the equilibrium cell volume V_0 is determined by the minimum of the Helmholtz free energy F [8, 11]

$$F(V, T; M) = U^{\text{static}}(V) + \frac{1}{2} \sum_{n, \mathbf{k}} \hbar \omega_n(\mathbf{k}) + k_B T \sum_{n, \mathbf{k}} \ln \left[1 - \exp \left(\frac{-\hbar \omega_n(\mathbf{k})}{k_B T} \right) \right] \quad (1)$$

with respect to the volume V . The sums run over all vibrational modes of frequency $\omega_n(\mathbf{k})$, and k_B is the Boltzmann constant. The first term in (1) is the total energy as given by

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density-functional theory. The second term gives the zero-point vibrational energy and the third term contains the energy and entropy contributions due to thermal excitations. We also noted as an argument of the function F the average mass of the nuclei. Obviously, it only enters via the vibrational frequencies.

The phonon energies $\hbar\omega_n(\mathbf{k})$ entering (1) are calculated by diagonalizing the dynamical matrix $D_{ij} = d^2U^{\text{static}}/d\mathbf{R}_i d\mathbf{R}_j$. For the purpose of obtaining the second derivatives of the total energy we use an analytical expansion of the U^{static} up to second order in the atomic displacements in the form given by Keating [12]. It is well known that the Keating model gives a good but certainly not very accurate description of the phonon band structure. We would like to emphasize, however, that we are not interested in individual phonon frequencies $\omega_n(\mathbf{k})$ but 'only' in integral quantities of the band structure (see (1)).

In order to determine the Keating model force constants we calculate two types of the second derivatives of the total energy. One of these quantities is the bulk modulus $B = V(\partial^2 U^{\text{static}}/\partial V^2)$. The second quantity is the force constant k_b which is due to the change of the total energy under a breathing mode distortion of the four Si atoms around a particular lattice site. The theoretical value of $B = 0.947$ Mbar can be compared to the experimental one (0.992 Mbar) but k_b is only available from calculations. The bulk modulus B and the force constant k_b are related to the two Keating model parameters α and β [11]:

$$B = (1/a)(\alpha + \beta/3) \quad k_b = 16\alpha + 42\beta. \quad (2)$$

In this way the force constants α and β are determined as a function of volume (see figure 1) near the minimum of total energy U^{static} . As these force constants depend on the volume our theory accounts partly for anharmonic effects. This is quasi-harmonic approximation. The higher-order derivatives of $U^{\text{static}}(V)$ over atomic displacements cannot be reliably estimated from our density-functional theory calculation and their influence on the equilibrium distance is neglected. From the dynamical matrix we then evaluate the phonon frequencies as a function of volume, and the minimum of the Helmholtz free energy F (which defines the equilibrium lattice parameter a) is determined for any temperature of interest. Finally the linear thermal expansion coefficient

$$\alpha_1 = \frac{1}{a} \left(\frac{\partial a}{\partial T} \right)_p \quad (3)$$

follows from $a(T)$.

The natural composition of Si crystals is a mixture of different isotopes. In [10] those are 92.232% of ^{28}Si , 4.677% of ^{29}Si , and 3.090% of ^{30}Si . The average nuclear mass is thus $M = 28.08538$. The isotopic composition affects the lattice vibrations, the greater inertia of the heavier isotope leading to lower frequencies. The method used for deriving the phonon spectrum differs from that used in our earlier calculations [8], when we diagonalized the dynamical matrix of a finite cluster of about 500 atoms. Here we diagonalize the wave-vector-dependent dynamical matrix of an infinite crystal, with summation over 47 independent wave-vectors in a 1/48 part of the Brillouin zone. We perform calculations for three isotopically pure Si crystals because to a very good approximation [3] any real crystal can be treated as a virtual composition of these three systems with a corresponding average mass. In figure 2 the thermal expansion coefficients for the three pure Si crystals are shown. The calculations reported in [8] were performed for a natural mixture $^{\text{nat}}\text{Si}$ of isotopes (i.e. for $M = 28.08538$) and they are close to the present result for the ^{28}Si isotope. Around 80 K the linear expansion coefficient exhibits a minimum with a negative

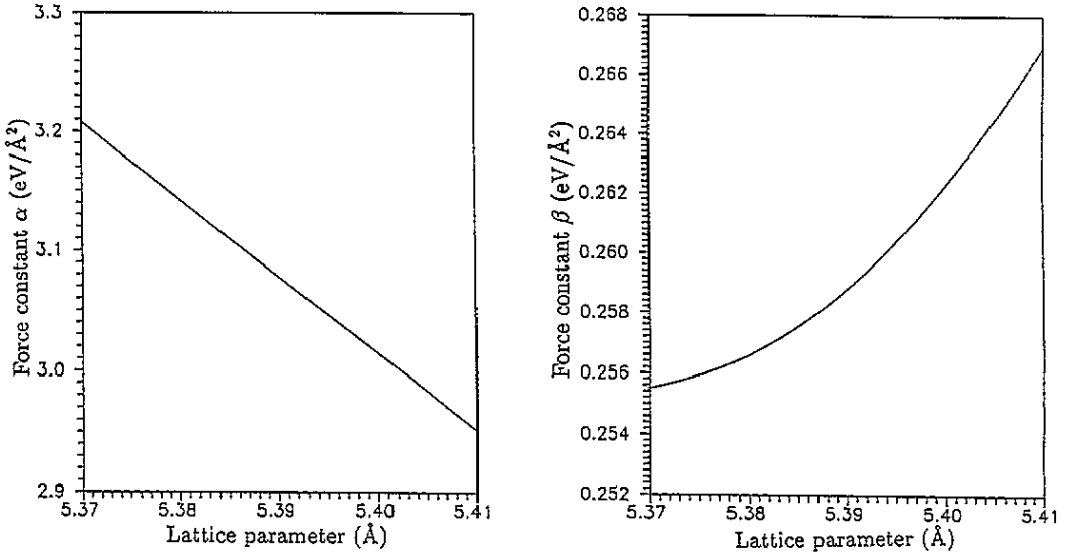


Figure 1. The two Keating model force constants α and β .

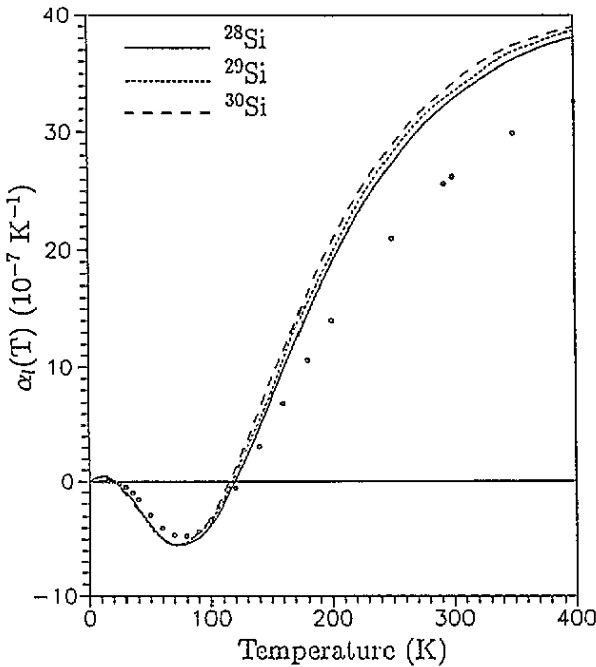


Figure 2. The thermal expansion coefficient α_l for Si crystals composed of three different isotopes. The open dots are experimental data [14, 15] for natural Si crystal.

value, which reflects a contraction of the crystal compared to the zero-Kelvin geometry. This contraction is maximal at 120 K (see figure 3). The calculations reproduce well the expansion coefficient for lower temperatures. The discrepancies between calculation and experiment for higher temperatures indicate the influence of higher- (than second-) order derivatives of $U^{static}(V)$. These results show that at a given temperature the heavier isotope gives rise to a smaller lattice parameter. In figure 4 we show the differences $\Delta\alpha$ between

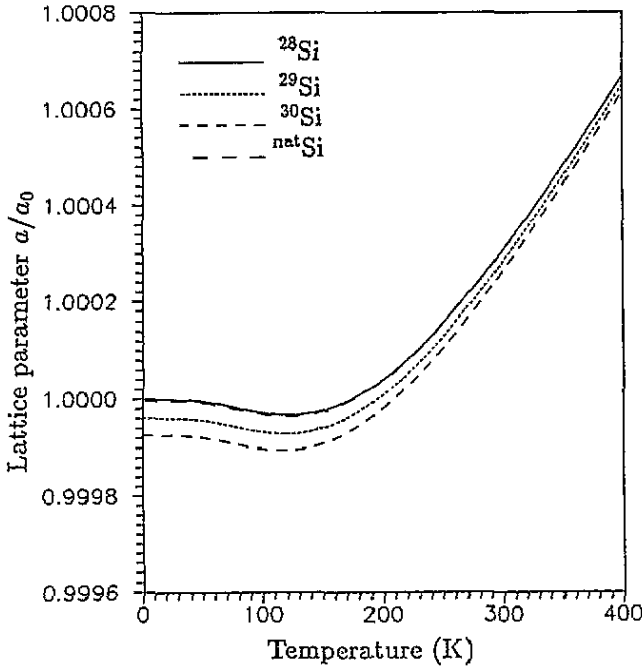


Figure 3. The relative lattice parameter of Si as a function of temperature. a_0 is the lattice parameter of ^{28}Si at zero temperature.

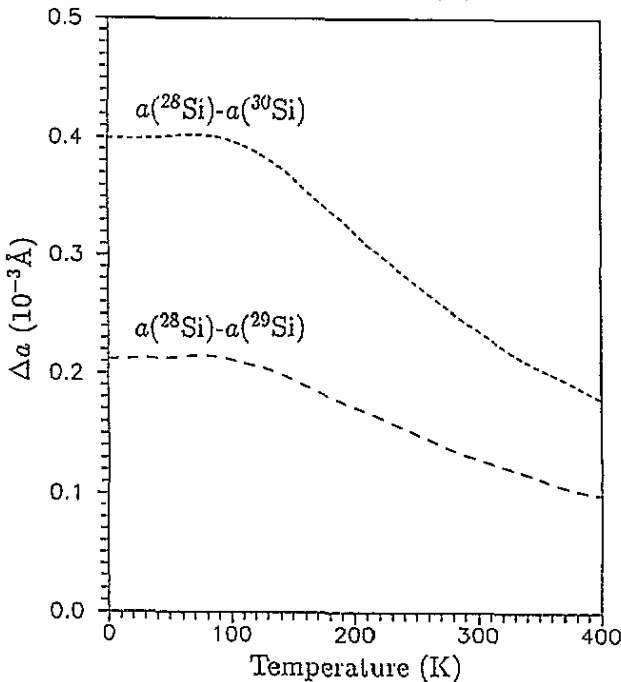


Figure 4. The difference Δa between lattice parameters of two different Si crystals. Note that differences $a(^{28}\text{Si}) - a(^{30}\text{Si})$ (upper curve) and $a(^{28}\text{Si}) - a(^{29}\text{Si})$ are largest for small temperatures and decrease with increasing temperature.

crystals of different isotopes. This figure shows that the relative difference is largest for temperature around 80 K and then decreases monotonically with the temperature increases. This behaviour is in agreement with measurements by Buschert *et al* [3] for the Ge crystals with a natural and ^{74}Ge -enriched composition. The measured ratio $\Delta a/a$ was approximately twice as large at liquid-nitrogen temperature than at room temperature. Our calculations for ^{28}Si and ^{29}Si given $\Delta a/a = -3.62 \times 10^{-5}$ at liquid-nitrogen temperature and -2.12×10^{-5}

at room temperature. Buschert *et al* also performed a theoretical estimation for $\Delta a/a$ based on the London theory [13] of the variation in the crystal volume with isotopic composition. The starting point in this theory is the same as in the present calculation, i.e. the expression (1) for the Helmholtz free energy.

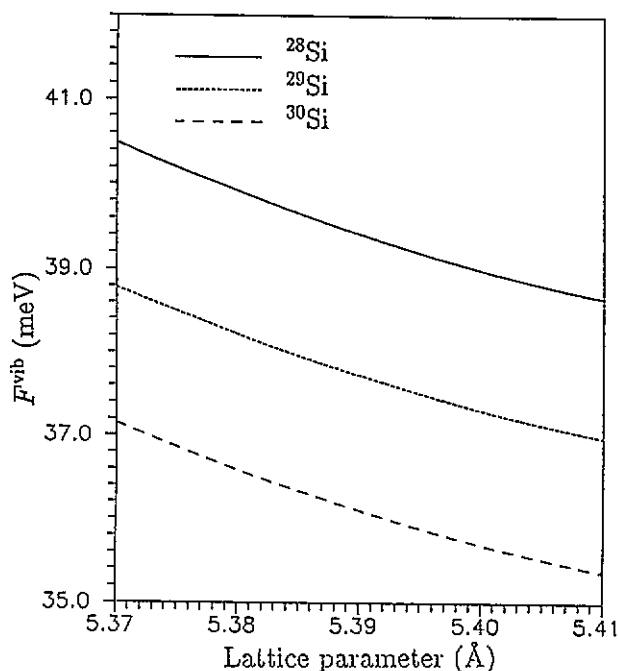


Figure 5. The vibrational part F^{vib} of the Helmholtz free energy (at room temperature) as a function of the lattice parameters.

When we analyse the sum of the second and third terms of (1), i.e. F^{vib} as a function of the lattice parameter (see figure 5) we find that this quantity has a negative slope. This implies that the equilibrium geometry is at a bigger lattice parameter than the minimum of $U^{\text{static}}(V)$. The reason is that $\sum_{nk} \hbar \omega_n(k)$ is the leading term and it decreases with increasing crystal volume (we note that this holds only for the sum over all phonons). Obviously, the absolute value of the slope of $\sum_{nk} \hbar \omega_n(k)$ is smaller for heavier atoms because $\omega \propto 1/\sqrt{M}$. Thus, as long as the term of the zero-point vibrations dominates the vibrational part of the free energy, it follows that heavier isotopes should give rise to a smaller lattice constant than lighter isotopes.

The vibrational contribution to the Helmholtz free energy is due to the vibrational energy U^{vib} and the vibrational entropy $-S^{\text{vib}}T$ (see also [8]). At zero temperature only U^{vib} survives; thus, here the isotope dependence of the lattice parameter is a pure quantum mechanical effect. With increasing temperature the entropy term becomes dominant and acts in the opposite direction to the vibrational energy. Therefore the decrease of Δa (see figure 4) with increasing temperature is an entropy driven effect.

In summary, we calculated the dependence of the lattice parameter for Si crystals composed of various Si isotopes. The relative difference in the lattice parameter for two neighbouring isotopes depends on the temperature and it is about 0.002–0.004%. This can be neglected in most measurements but it might be important in high-accuracy measurements like those relevant for the determination of the Avogadro constant. In those measurements the required accuracy of the lattice parameter is 10^{-8} or better. We have discussed the origin of the effects and compared the calculated values of $\Delta a/a$ for Si at liquid-nitrogen and room temperatures with results measured for Ge crystals.

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