Quantum effects in silicon isotopes at low temperatures under normal and high pressures

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Abstract

Precision studies of Raman scattering in isotopically pure $^{28}\text{Si}$, $^{29}\text{Si}$, and $^{30}\text{Si}$ single crystals have been performed in the temperature range from 8 to 300 K. It was found that the quantum effects manifest themselves noticeably at low temperatures ($T \leq 100$ K). This can be seen from the difference $\sim (0.4 \pm 0.1)$ cm$^{-1}$ between the normalized frequencies of two extreme $^{28}\text{Si}$ and $^{30}\text{Si}$ isotopes, while at room temperature, quantum effects are not visible and are comparable with the measurement error of frequencies (0.1 cm$^{-1}$). Raman scattering in silicon isotopes in the region of noticeable quantum effects has been studied under hydrostatic conditions at pressures to 12 GPa and at a temperature of $T = 80$ K. Quantum effects are not changed under compression within the accuracy of measurements.

1. Introduction

Silicon is one of the most abundant elements in nature and is used as the basic element of modern electronics. A continuous process of reducing the size of basic units of electronics makes it necessary to take into account the quantum properties of materials. Quantum effects are directly manifested when comparing the properties of different isotopes [1]. The zero-point energy in crystals is proportional to the square root of the mass of particles (isotopes) and its volume behavior is determined by the dependence of effective force constants on the interatom distance. An additional contribution from the zero-point energy to the classical part of the energy increases the equilibrium volume and this effect is more pronounced for lighter isotopes [1].

Measurements of Raman spectra constitute one of the most sensitive methods for studying isotopic effects. The frequency of the optical vibration mode in perfect single crystals can be determined with a very high accuracy (with a relative error of 0.01%). We have recently studied quantum isotope effects in diamond at high pressures [2]. Owing to a record high Debye temperature ($\sim 2200$ K), diamond is a quantum crystal even at room temperature. This property, together with a small mass of carbon atoms, made it possible not only to reliably establish the quantum contribution (difference of the frequency ratio from the classical limit) but also to study its nontrivial pressure dependence in Raman studies with the determination of the Raman frequency with an accuracy of 0.2 cm$^{-1}$.

Crystalline silicon is a typical diamond-like semiconductor. The most intense first-order line in Raman spectrum of silicon, as well as of diamond, is due to scattering by $F_{2g}$ optical phonons in the center of the Brillouin zone. At the same time, silicon is a much more challenging object for studying quantum effects because it has significantly lower Debye temperature ($\sim 640$ K), larger mass of atoms. The precision measurements of the lattice parameters of isotopically pure silicon single crystals [3, 4] showed that the difference between the specific volumes of two extreme $^{28}\text{Si}$ and $^{30}\text{Si}$ isotopes is no more than 0.017%–0.019% even at low temperatures (one third of that for $^{12}\text{C}$ and $^{13}\text{C}$ isotopes at room temperature). In addition, this quantity can be obtained within the simple Debye model. The relative volume expansion caused by quantum effects for each isotope can be represented in the form [5]
\[ \frac{\Delta V}{V_0} = 9/8 \cdot \gamma \cdot \left( \Theta_D / k_0 V_0 \right), \]

where \( \Theta_D \) is the Debye temperature, which is 641 and 616 K for the \(^{28}\)Si and \(^{30}\)Si isotopes, respectively [6]; \( \gamma \approx 1 \) is the Grüneisen parameter, and \( k_0 = -V_0 (\partial \rho / \partial V)_T = 97.8 \) GPa is the bulk modulus [7]. As a result,

\[ \frac{\Delta V^{28-30}}{V^{30}} = 1.9 \times 10^{-4}. \]

Although silicon crystals are reference objects for Raman measurements, systematic Raman studies of the quantum isotope effect in isotopically pure single crystals have not yet been performed. A number of Raman studies of crystals of different silicon isotopes were performed at fixed temperatures (e.g., at room temperature [8] and at a low temperature [9, 10]). In those studies, a very small contribution of quantum effects was revealed. The temperature and the pressure dependences of Raman frequencies were studied mainly for natural silicon whose isotopic composition is close to \(^{28}\)Si [11–13]. Raman studies of isotopically pure silicon single crystals under pressure have not yet been performed at all. Besides the quantum effects expected in silicon are small and it is very difficult to obtain isotopically pure high-quality single crystals.

One can also estimate in advance whether it is possible to observe in principle the change in quantum effects in silicon upon compression. The atomic volume of silicon at normal pressure is 12.1 cm\(^3\) mol\(^{-1}\), at a pressure of 10 GPa it is 11.05 cm\(^3\) mol\(^{-1}\). The bulk modulus increase from 97.8 GPa up to 139 GPa, respectively. The biggest uncertainty is related to the Debye frequency (temperature). At normal pressure Debye temperatures are 641 K for \(^{28}\)Si and 616 K for \(^{30}\)Si. If we assume that their ratio will be constant, then Debye temperatures at 10 GPa should be 701.9 K and 674 K, respectively. The difference in densities for \(^{30}\)Si and \(^{28}\)Si is 1.9 \times 10^{-4} at normal pressure and 1.8 \times 10^{-4} at a pressure of 10 GPa. The classical frequency ratio is 1.0351. The actual value of the frequency ratio at low temperature is 1.034 35; at pressure of 10 GPa, it is 1.034 28. The accuracy of frequency measurement for determination of the pressure dependence then should be no worse than 0.02 cm\(^{-1}\), but we have in a real experiment only 0.1–0.15 cm\(^{-1}\). It is clear that in this case we cannot trace the change of the quantum contribution to the physical properties of silicon under compression. On the other hand, the behavior of the Debye frequencies (temperatures) with increasing pressure is unknown \textit{a priori}, and we nevertheless decided to study the pressure dependences of the Raman frequencies at low temperatures with pressures up to 12 GPa.

The aim of this work is to study Raman spectra for isotopically pure \(^{28}\)Si, \(^{29}\)Si, and \(^{30}\)Si single crystals in a wide temperature range from 8 to 300 K at high hydrostatic pressures up to 12 GPa. The maximum pressure of 12 GPa used in the measurements is dictated by the phase diagram of silicon. A further increase in the pressure is accompanied by a structural transition in silicon [14], after which the intensity of Raman lines decreases by two or three orders of magnitude, which affects the accuracy of measurements and the interpretation of results.

2. Experimental details

High-purity \(^{28}\)Si, \(^{29}\)Si, and \(^{30}\)Si single crystals were grown by float zone melting in the high-purity argon atmosphere. The structural perfection of single crystals was estimated by the x-ray diffraction and selective etching methods. The purity of each isotope in all three types of crystals was above 99.9%. The concentration of carbon and oxygen impurities in the samples measured by the infrared spectroscopy method was no more than 5 \times 10^{15} \text{ cm}^{-3}.

The temperature dependence of the spectra of silicon isotopes was measured in the range of 80–300 K in a Linkam THMS600 cryogenic chamber. The low-temperature table was mounted on an Olympus BX51 microscope. The microscope with a 50\times objective ensured the focusing of exciting laser radiation on the sample and collection of Raman radiation. The error of measurement of the Raman frequency in this temperature range for all isotopes was estimated as about 0.1 cm\(^{-1}\). At lower temperatures, Raman spectra were obtained with the use of an optical helium cryostat (Oxford Optistat SMX), which allows measurements in the temperature range of 4.2–300 K with a temperature accuracy of \approx 0.1 K.

An Ar\(^+\) laser with a wavelength of 488 nm and a power of 30 mW was used for excitation. To estimate the possible effect of heating of the sample by laser radiation, we measured spectra in the range of powers on the sample from 1 to 3 mW. In subsequent measurements, we used radiation with a power less than 1.5 mW, which did not heat the samples within the accuracy of the measurements. Scattered light was analyzed in the backscattering geometry using a Princeton Instruments TriVista 555 triple spectrometer with a liquid-nitrogen-cooled CCD detector. The spectral width of the slit was 0.6 cm\(^{-1}\). The spectral positions of Raman peaks were calibrated with respect to the lines of a neon lamp.

Studies under pressure were performed with a homemade high-pressure diamond anvil cell [15]. The diameter of the working area of diamond anvils was 450 \mu m, and a hole in a metal (steel) gasket had a diameter of 150 \mu m. Samples of three isotopes and ruby pieces were placed in the hole in the gasket; after that, the working
volume of the chamber was filled with compressed helium by means of a system described in [15]. The pressure was measured from the shift of the luminescence line of ruby.

All $^{28}\text{Si}$, $^{29}\text{Si}$, and $^{30}\text{Si}$ samples were studied simultaneously. This circumstance made it possible to exclude the effect of errors in the measurements of pressure and temperature on the comparison and analysis of the results. After each measurement under pressure at low temperatures, the high-pressure cell with samples was removed from the cryostat and was heated to room temperature. Then, the pressure was increased and measurements were continued.

3. Results and discussion

The Raman frequencies for the $^{28}\text{Si}$, $^{29}\text{Si}$, and $^{30}\text{Si}$ isotopes at room temperature are 521.3, 512.6, and 503.9 cm$^{-1}$, respectively. Figure 1 shows the Raman spectra of the $^{28}\text{Si}$, $^{29}\text{Si}$, and $^{30}\text{Si}$, single crystals measured at room temperature and a temperature of 8 K. Raman peaks have a Lorentzian shape with a half-width of 3.3 cm$^{-1}$ at room temperature and 1.5–1.6 cm$^{-1}$ at temperature of 8 K, which is in good agreement with the data reported in [8, 13].

Figure 2 shows the line positions for all silicon single crystals as a function of the atomic mass of isotopes at room and low temperatures. The solid and dashed lines are the dependences of the phonon frequency on the atomic mass of the isotope obtained in the virtual crystal approximation for room and low temperatures, respectively. These lines represent the expression $\omega = \omega_0 \cdot (28/m)^{1/2}$ valid in the classical limit.

It is seen that the points corresponding to the frequencies of the $^{29}\text{Si}$ and $^{30}\text{Si}$ isotopes at room temperature are close to the harmonic approximation (difference is only slightly larger than the accuracy of the measurements). At the same time, the points corresponding to the Raman frequencies of the $^{29}\text{Si}$ and $^{30}\text{Si}$ isotopes at a temperature of $T = 80$ K are no longer on a straight line but noticeably deviate from the linear dependence of the classical limit.

The temperature dependences for all three isotopically pure silicon single crystals are shown in figure 3, where four series of experimental data are presented; three of them were measured to 80 K and the fourth one, to 8 K. We used the dependences $\omega(T)$ determined by the contribution to the phonon–phonon scattering, which describes the decay of an optical phonon corresponding to the $\Gamma$ point of the Brillouin zone into two acoustic phonons that have opposite momenta and belong to the same branch (Klemens model) [16]. The temperature dependence of the shift of the Raman frequency is described in this case by the expression

$$\omega(T) = \omega_0 - A[2/(\exp(\hbar\omega_0/2k_BT) - 1)],$$

where $\omega_0$ is the energy of a phonon at the $\Gamma$ point of the Brillouin zone at $T = 0$ and $A$ is the third-order anharmonic coefficient. The values of Klemens approximation parameters $\omega_0$ and $A$ for different isotopes are 524.19 ± 0.03 cm$^{-1}$ and 3.6 ± 0.1 cm$^{-1}$ for $^{28}\text{Si}$, 515.3 ± 0.04 cm$^{-1}$ and 3.6 ± 0.1 cm$^{-1}$ for $^{29}\text{Si}$ and 506.76 ± 0.02 cm$^{-1}$ and 3.4 ± 0.1 cm$^{-1}$ for $^{30}\text{Si}$ respectively.

The temperature dependences of the reduced frequencies of the extreme $^{28}\text{Si}$ and $^{30}\text{Si}$ isotopes are shown in figure 4, where the frequency for the $^{30}\text{Si}$ isotope is multiplied by the square root of the inverse mass ratio. The points are the experimental data for two silicon samples, whereas the lines are approximations of the

![Figure 1. Raman spectra of different silicon isotopes measured at room temperature and a temperature of 8 K.](image-url)
experimental frequencies by expressions corresponding to the anharmonic decay of optical phonons for normal crystals without phase transitions.

According to the plotted data, the difference between two lines, which corresponds to the quantum contribution, increases with a decrease in the temperature. The difference of the ratio of frequencies from the classical value at room temperature is close to the accuracy of the measurements. At the same time, the quantum contribution to the vibration frequencies at low temperatures is determined quite reliably: the difference between the frequency of the $^{28}\text{Si}$ isotope and the normalized frequency of the $^{30}\text{Si}$ isotope is $(0.4 \pm 0.1) \text{ cm}^{-1}$, whereas the accuracy of the measurements with large statistics is $0.1\ldots0.15 \text{ cm}^{-1}$. A reduction of the temperature below 80–100 K only weakly affects a further increase in quantum effects in silicon. The same behavior was previously observed for the quantum contribution to the difference between specific volumes of the silicon isotopes \[3\]. Consequently, to estimate the behavior of quantum effects in silicon, studies can be performed at a temperature 80 K.

The pressure dependences of the ratio of the Raman frequencies for silicon isotopes at a temperature of 80 K and at room temperature are shown in figure 5. It is seen that the ratio of frequencies at a low temperature noticeably differs from the classical value, whereas quantum effects at room temperature are almost invisible. At the same time, the difference of the ratio of frequencies of different isotopes from the classical value even at low temperatures is an order of magnitude smaller than that for carbon isotopes (see \[2\]). It is seen that the ratio of frequencies almost does not vary with the pressure. This is more clearly seen from the approximation of the data.
by a linear function $y(P) = a + b \cdot P$, where the coefficient $a$ corresponds to the ratios of the frequencies at zero absolute temperature and the coefficient $b$ is the slope of the line. Then, for the ratio of the frequencies of the $^{28}$Si and $^{30}$Si isotopes at a temperature of 80 K, these parameters are

$$a = 1.034 \pm 6.9 \times 10^{-5}, \quad b = (-7.16 \times 10^{-6} \pm 1.2 \times 10^{-5}) \text{ GPa}^{-1}.$$

The slope of the linear dependence is much smaller than the error of the measurements. To reveal a probable effect of the pressure on the quantum contribution in silicon isotopes, it is necessary to measure the Raman frequency with an accuracy of no worse than $0.02 \text{ cm}^{-1}$, which is currently impossible.

To conclude, we note that quantum effects in silicon isotopes measured by Raman spectroscopy at a temperature of $T = 80$ K and below are several times larger than the error of the measurements. Conclusions on the effect of high pressures on these quantum effects cannot be made at the current accuracy of the measurements. Anyway, the experimental results obtained can serve as a test for *ab initio* calculations of the relative contribution of zero point energy in silicon to the total energy under compression. Also it is an undoubted interest to observe quantum effects in germanium isotopes, where they are smaller than in silicon and should be manifested at much lower temperatures.
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