Determining sound velocities in the {111}-directions of 3C-SiC using FTIR spectroscopy

Emma Cherrie   Christian Johnsen   Fredrik Knapskog   Svein Åmdal

March 2019

Abstract: Vibrational modes of polyethylene and SiC were studied using FTIR spectroscopy. The effective force constant of polyethylene was found to be $442\,\mathrm{N\,m^{-1}}$. Finding similar values for the force constant of SiC, the sound velocity along the {111}-planes in SiC was found to be $10\,100\,\mathrm{m\,s^{-1}}$ for the longitudinal, and $9000\,\mathrm{m\,s^{-1}}$ for the transverse mode. These values yield a significant discrepancy with versus benchmark values.

1 Introduction

IR-spectroscopy is a widely used technique in solid state physics. We want to familiarize ourselves with this technique, by using a *Fourier Transform infrared* (FTIR) spectroscope. Using polyethylene as a sample, we will compare calculated and measured vibrational modes, and estimate the effective force constant in an approximated harmonic potential.

The SiC sample is assumed to be in cubic form (3C-SiC) and have a zinc blende structure with lattice parameter $4.359\,\mathrm{Å}$. A 2-atomic chain is then an approximation for the phonon dispersion of the {111}-planes. Using this approximation, we aim to find the sound velocity of SiC by recognizing different induced oscillation modes, and estimating similar effective force constants. We then investigate the validity of our assumptions by comparing with previously measured values.

2 Theory

The dispersion relation for photons is

$$\omega = ck, \tag{1}$$

where c is the speed of light in vacuum. By exposing the sample to EM-waves with a certain wavenumber k, one can induce phonons with a corresponding frequency ω. This process also requires the net induced dipole moment of the oscillation mode to be nonzero.

Using the fact that $\omega \approx \sqrt{2C/\mu}$ for a C-H bond[1](p.98), we find the effective force constant in an inter-atomic harmonic potential induced by some wave k to be

$$C = \mu(2\pi c\sigma)^2, \tag{2}$$

where $\mu = m_1 m_2/(m_1 + m_2)$ is the *reduced mass*, and σ is defined by $k = 2\pi\sigma$. We assume eq. (2) is valid for either of the two polyethylene stretching modes.

For a 2-atomic chain, one can model the atomic interactions in each unit cell as a set of coupled harmonic oscillators. For an effective force constant C, the exact solution is of the form

$$\omega_\pm = \sqrt{\frac{C}{\mu}}\sqrt{1 \pm \sqrt{1 - 4\gamma \sin^2\left(\frac{ka}{2}\right)}}, \tag{3}$$

where a is the lattice constant[1], and $\gamma = \mu^2/m_1 m_2$ is a dimensionless constant.

The *acoustic branch* is the solution where $\pm \to -$. Equation (1) shows that ω increases rapidly, so photons can only couple to phonons with small k-values.[2] In the limiting case where $k \to 0$, we Taylor-expand the acoustic ω^2 around 0 and obtain

$$\omega^2 = \frac{C}{\mu}(1 - [1 - \frac{1}{2}\gamma k^2 a^2 + \dots]). \tag{4}$$

The *group velocity* is the velocity at which acoustic phonons (sound) travel, which is given by

$$v_g = \frac{d\omega}{dk} = \pm a\sqrt{\frac{C\gamma}{2\mu}} = \pm a\sqrt{\frac{C}{2(m_1 + m_2)}}. \tag{5}$$

In the 2-atomic chain, both transverse acoustic (TA) and longitudinal acoustic (LA) vibrational modes are present. The difference in sound velocity between these modes is determined by the effective force constants C_{TA} and C_{LA}. We expect that the sound velocity is largest for the longitudinal modes.

3   Method

An FTIR spectrometer was used to measure the absorption spectrum of a (unknown) polyethylene sample and a silicon carbide sample. For each new sample, a background spectrum of the sample chamber was taken first, and then the sample was analyzed. The sample measurements from the spectrometer are in the form of a relative intensity $I(\sigma)/I_0(\sigma)$ where $I(\sigma)$ is the average of six[3] measured intensities for a given wavenumber σ and $I_0(\sigma)$ is the average of six measured background intensities for the same σ, giving transmission in %.

4   Results

From fig. 1, the three most distinct absorption lines are found to be $\sigma_1 = 2875\,\text{cm}^{-1}$,

---

[1]Here, a is the lattice constant of a one-dimensional chain. In the SiC sample, this corresponds to the distance between the {111}-planes, which is given by $a_{\text{SiC}}/\sqrt{3}$.

[2]Photons can only couple to phonons in the optical ($\pm \to +$) branch. By assuming the value of C is equal in the two branches, the result for the acoustic branch is still interesting.

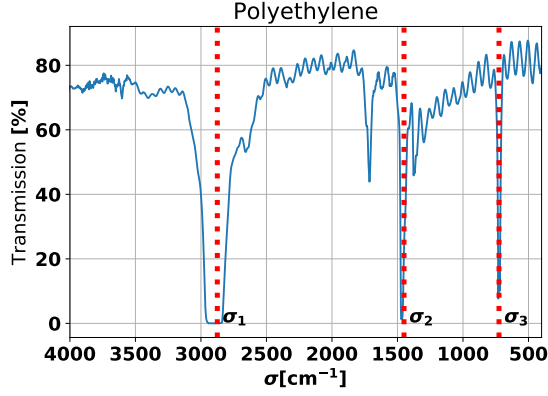[3]We use multiple measurements to reduce statistical anomalies.

Figure 1: The measured intensity relative to the background as a function of incident wavenumber σ for a polyethylene sample. The referenced graph features are marked vertically.
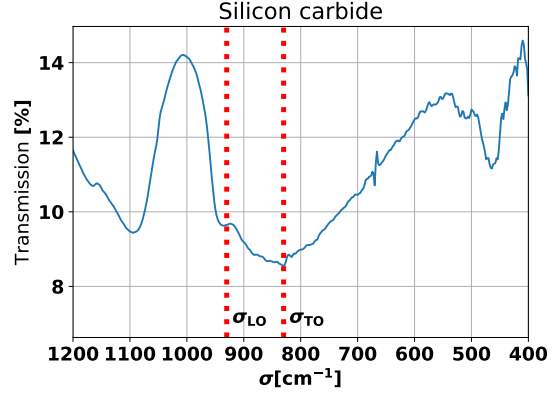

Figure 2: The measured intensity relative to the background as a function of incident wavenumber σ for a silicon carbide sample. The referenced graph features are marked vertically.

$\sigma_2 = 1450\,\mathrm{cm^{-1}}$ and $\sigma_3 = 725\,\mathrm{cm^{-1}}$. The force constant, C, is estimated by eq. (2) to be $442\,\mathrm{N\,m^{-1}}$.

From fig. 2, the absorption lines for the longitudinal optical (LO) and transverse optical (TO) modes are estimated to be respectively $\sigma_{\mathrm{LO}} = 930\,\mathrm{cm^{-1}}$ and $\sigma_{\mathrm{TO}} = 830\,\mathrm{cm^{-1}}$. Light dispersion is used to estimate the angular frequency. Equation (1) gives $\omega_{\mathrm{LO}} = 1.75 \cdot 10^{14}\,\mathrm{rad\,s^{-1}}$ for the LO mode and $\omega_{\mathrm{TO}} = 1.56 \cdot 10^{14}\,\mathrm{rad\,s^{-1}}$ for the TO mode. Using eq. (2), the following values are estimated $C_{\mathrm{LO}} = 214\,\mathrm{N\,m^{-1}}$ and $C_{\mathrm{TO}} = 170\,\mathrm{N\,m^{-1}}$. Assuming that these values for the force constant in the optical modes also can be used for the acoustic modes, eq. (5) can be used to calculate $v_{\mathrm{LA}} = 10\,100\,\mathrm{m\,s^{-1}}$ for the LA mode and $v_{\mathrm{TA}} = 9000\,\mathrm{m\,s^{-1}}$ for the TA mode.

5   Discussion

There is a slight discrepancy between all the tabulated calculated values of σ and the measured values for polyethylene. The discrepancy could be due to an erroneous adjustment of the spectrometer. More likely, however, it is due to inaccuracies in the calculation of the tabulated values.

Variable density in either of the samples may be co-responsible for the varying intensities. Also, the absorption is proportional to the change in atomic dipole moment.[4]

One can compare the results with a tabulated value of the force constant of a C-H bond in polyethylene, which is $448\,\mathrm{N\,m^{-1}}$.[2] As we don't know the exact type of polyethylene in the sample, we take this result as a verification that our results are somewhat accurate. Regrettably, we don't otherwise have a good approximation of the uncertainty produced by the apparatus.

Theoretically, all absorption lines should be infinitesimally thin as only discrete energies (i.e. wavenumbers) are allowed in transitions between vibrational modes. In practice, the width is influenced by the lifetime of the induced phonon, and the

---

[4]This explains why e.g. the symmetric stretch mode of CO_2 does not appear in the spectrum. Such a mode has no change in dipole moment, and as stated in section 2, it is impossible to induce it by EM-waves.

energy uncertainty of the measured and emitted light. Another contributing factor is differing cross-sections due to different orientations of molecules. When studied closely, it is noticeable that σ_1 in fig. 1 in fact has two absorption lines, one for symmetric stretch and one for asymmetric stretch.

Especially apparent in fig. 1 are the numerous absorption lines adjacent to the expected value. The discrepancies are likely due to induced molecular rotational modes, which have energy levels far below the vibrational modes.

Using the force constants given in [3] and the outlined method, along with the effectice force constants from [1] (p.83), the benchmark sound velocities are $v_{\mathrm{LA}} = 12\,950\,\mathrm{m\,s^{-1}}$, $v_{\mathrm{TA}} = 7160\,\mathrm{m\,s^{-1}}$. Our results are qualitatively comparable to these values, but the assumptions used clearly underestimate the distinctive nature of the two modes.

6 Conclusion

Comparing the measured and tabulated force constants in C-H bonds, one finds a small difference. Using a similar method of finding the force constant of SiC, we calculate the sound velocities of the longitudinal and transverse sound waves of Sic to be $10\,100\,\mathrm{m\,s^{-1}}$ and $9000\,\mathrm{m\,s^{-1}}$ respectively.

To obtain these values, we have assumed that the optical and aucoustic modes have the same value for the force constant, and that the {111}-direction in SiC can be approximated as a 2-atomic single chain. These approximations does not sufficiently distinguish between the vibrational modes, and the measured values are sandwiched between the benchmark values.

References

[1] C. Kittel, Introduction to Solid State Physics, 8th edition, John Wiley & Sons, Inc, (2005).

[2] W. M. Haynes, T. J. Bruno, and D. R. Lide, eds., CRC Handbook of Chemistry and Physics, Taylor and Francis, (2015).

[3] C. Z. Wang, R. Yu, H. Krakauer, Pressure dependence of Born effective charges, dielectric constant, and lattice dynamics in SiC, Physical Review B **53** (1996) 9.