Theoretical calculations on graphite and comparison of measured with calculated heat capacity

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In this paper the vibrational bands in phonon dispersion, heat capacity and the Debye curve are presented. An interesting thing is to compare for graphite, the simulated with the measured heat capacity within the temperature range from 100 to 350 K in a simple experiment. The Cambridge Serial Total Energy Package (CASTEP), a density functional theory based software is used for the theoretical calculations. The experimental heat capacity is determined in an experiment where a solid evaporates the mass of liquid nitrogen. It is illustrated for the graphite sample.

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1. Introduction

The calculations on the phonon spectrum and heat capacity have been performed by Tohei [1]. Here the thermodynamic properties of graphite such as vibrational modes in phonon dispersion, Debye temperature and the heat capacity are revisited. For simple teaching laboratories, introducing simulation as a tool for comparison of the theoretical calculations with the experimental results is indeed exciting. This simple exercise that correlates theoretical and measured heat capacity is worth mentioning and it can easily be replicated in any physics laboratory.

The discussion on heat capacity starts from Dulong and Petit who proposed a constant value 3R for metals with R as a molar gas constant [2]. Later, the unexpected behavior of heat capacity at low temperatures opened a new domain of calculations called as the quantum calculations that led Einstein [3,4] and Debye [5] to propose new models. Since then, phonons have been in discussions all the time. For studying properties of solids with temperature, phonons calculations are inevitable both in theory and experiments. In this paper, graphite, a soft allotrope of carbon is considered that shows interesting properties when compared to diamond, a hard material. Since, the properties related to temperature are discussed here, the optical phonons that contribute to the heat capacity will be talked about [1]. Tohei et al. have discussed phonon dispersion, stiffness of allotropes of carbon and Debye temperature. They have compared their theoretical calculations to experiments not readily available in the basic physics laboratory. Here is an attempt to compare heat capacity obtained through theoretical calculations with a basic laboratory experiment. Besides, the numerical solution of the heat capacity is compared to the simulation.

The simulation is performed in CASTEP [6] with built-in internal repository of structures. The graphite structure is simply imported into the working window from the structures folder. The calculation discussed here is a three step process. First, optimize the geometry of graphite and second, perform the energy calculation on graphite. Geometry optimization is the process to bring the molecule in its equilibrium configuration before moving ahead to the energy calculation. In the energy calculation run, phonon contribution is calculated. The last part is simply to analyze the obtained results. To relax the geometry, local density approximation [7] is used as it does not include the excited states. The geometry is optimized at 660 eV cutoff energy with the Monkhorst-Pack (MP) [8,9] grid of *k-points* 7×7×2.

2. Experiment

A Vernier Instruments force sensor (DFS-BTA) with an accuracy of 0.01 N is connected to the computer to continuously measure the weight of the vaporizing liquid nitrogen contained inside the styrofoam cup. The solid whose heat capacity is to be determined is first cooled down to a desired temperature in a vapor cryostat of liquid nitrogen and then, after achieving the desired temperature, it is transferred to the styrofoam cup containing the liquid nitrogen. The solid after heat exchange comes in equilibrium with the liquid nitrogen and the mass evaporated during this process is measured. The specific heat capacity is calculated using Eq. (10) as mentioned in Ref [10]. The temperature is monitored with a silicon diode attached to the sample. The schematic of the experimental setup is shown in the prior published article [10]. The data is measured down to 100 K.

3. Results and discussion

A. Vibrational states in phonon dispersion

The frequency of the vibrating atoms inside the solid changes and the main interest resides in looking at this change of frequency between two points inside the Brillouin zone. This information can be observed in the phonon dispersion curves. Therefore, to understand the phonon dispersion, consider the entire region of frequency as a three sub-frequency regions. The low frequency region for instance to say from 0 to 15 THz, the middle frequency region from above this region to 35 THz and the high frequency region further up to 50 THz. The vibrational bands are observed in the low-middle frequency region, however, the vibrational modes observed in current case are slightly less than those observed earlier [1]. This shows slightly less bending modes and layers shearing. The phonon dispersion obtained in this study is shown in Fig. 1.

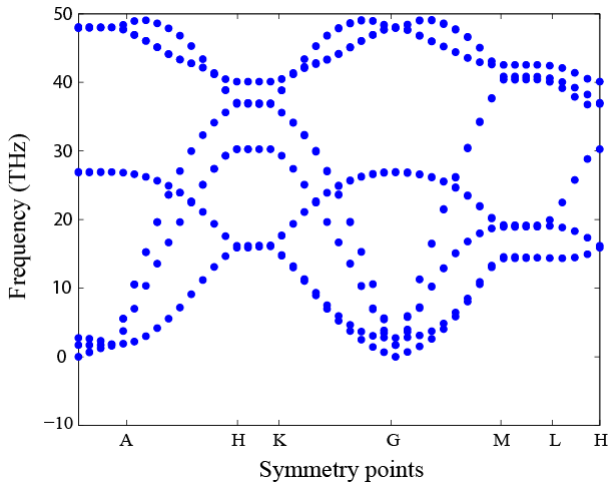

Fig. 1. The change in frequency of atoms inside the Brillouin zone for graphite.

B. Heat capacity

Fig. 2 displays both the calculated and measured heat capacity of graphite with temperature. The simulated data is within the temperature range from 0 to 1000 K. However, the possible experimental readings are from 100 to 350 K. The calculated values are shown with blue squares and red triangles represent the experimental values. It is visible from the plot that the experimental findings are in fair agreement with the simulated data. Keeping in view the statistical minimization of errors and the prior mentioned Eq. (14) [10], the error bars are plotted on the experimental data points. From Fig. 2, it seems obvious that both simulation and experiment are fairly close.

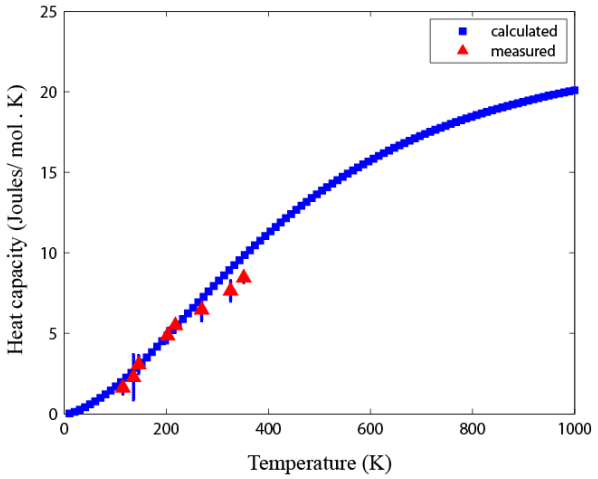

Fig. 2. Calculated heat capacity (blue squares) and measured heat capacity of graphite (red triangles).

C. Debye curve

The Debye curve with temperature obtained from simulation is shown in Fig. 3. In comparison to the Debye curve shown by Tohei [1], current values are slightly underestimated. From the simulated curve, at 300 K on the temperature axis, a horizontal line is drawn to meet the y-axis. The value at the y-axis is approximately 1570 K, close to the data point shown by Tohei [1].

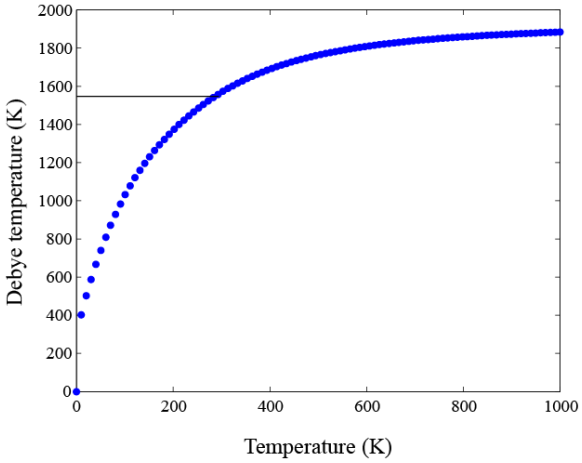

Fig. 3. Calculated Debye curve of graphite.

D. Numerical and simulation curves

The heat capacity at constant volume (C_V) is calculated by following the Debye model [5] and is given by,

$$C_V = \frac{4\pi k_B^4}{h^3}\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right)\frac{\partial}{\partial T}\left(T^4 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx\right)$$

where h is the Plank's constant, k_B is the Boltzmann's constant, c_l is the longitudinal speed of the wave, c_t is the transverse speed of the wave, T is the temperature and the integrand is a factor essential for the evaluation of C_V for the Debye model. θ_D is the Debye temperature and its relation with the Debye frequency (ν_D) is $\theta_D = (h\ \nu_D) / k_B$. After evaluating this integral, a numerical plot of the heat capacity from 0 to 1000 K is obtained and it is shown in Fig. 4 with black triangles.

The simulated plot of the heat capacity is also shown in Fig. 4 with blue squares. In the high temperature limit, both the curves are fairly close. However, in the region of low temperature, it is observed that the two plots are slightly far. The reason attributes to the local density functional that is implemented in the simulation.

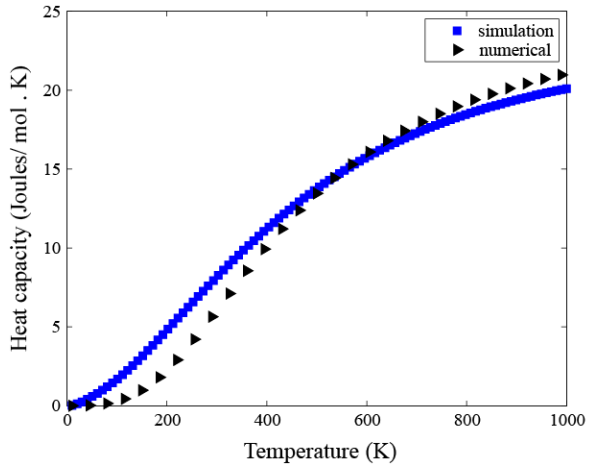

Fig. 4. Numerical (black triangles) and simulated (blue squares) heat capacity.

4. Conclusion

This work reviews the phonon dispersion, vibrational modes and the Debye curve of graphite in a simple way. Besides, a comparison of the simulation on heat capacity with the measured heat capacity from an experiment easily accessible in the basic physics laboratory is provided. The simulated and measured experimental data are fairly close in the temperature range from 100-350 K. In the last part of current work, a comparison between simulation and the numerical curves is shown. At higher temperature, both of the curves are fairly close. However, at low temperature, slight difference arises due to the functional used in the simulation. This simple activity also helps us understanding some limitations of the software's.

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