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Numerical experiments on phonon properties of isotope and vacancy-type disordered graphene☆

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ABSTRACT

We have studied phonon properties of graphene theoretically with different concentrations of ^{13}C isotope and vacancy-type defects. The forced vibrational method, which is based on the mechanical resonance to extract the pure vibrational eigenmodes by numerical simulation, has been employed to compute the phonon density of states (PDOSs) and mode pattern of isotope-disordered graphene as well as a combined isotope and vacancy-type defective graphene structure. We observe a linear reduction of the E_{2g} mode frequencies with an increase in ^{13}C concentration due to the reduced mass variation of the isotope mixture. We find a downshift of the E_{2g} mode of 65 cm^{-1}, which is a very good agreement with the experimental results, and the phonon frequencies described by the simple harmonic oscillator model. The vacancy-type defects break down the phonon degeneracy at the Γ point of the LO and TO modes, distort and shift down the phonon density of states significantly. The PDOS peaks for the combined isotope and vacancy-type defects show the remarkable increase in the low-frequency region induced by their defect formations. Due to phonon scattering by ^{13}C isotope or vacancies, some graphene phonon wave functions become localized in the real space. Our numerical experiments reveal that the lattice vibrations in the defective graphene show the remarkably different properties such as spatial localization of lattice vibrations due to their random structures from those in the perfect graphene. The calculated typical mode patterns for in-plane K point optical phonon modes indicate that the features of strongly localized state depend on the defect density, and the phonon is localized strongly within a region of several nanometers in the random percolation network structures. In particular, for in-plane K point optical phonon modes, a typical localization length is on the order of $\approx$7 nm for isotope impurities, $\approx$5 nm for vacancy-type defects and $\approx$6 nm for mixed-type defects at high defect concentrations of 30%. Our findings can be useful for the interpretation of experiments on infrared, Raman, and neutron-diffraction spectra of defective graphene, as well as in the study of a wide variety of other physical properties such as thermal conductivity, specific heat capacity, and electron–phonon interaction.

1. Introduction

The unique properties of graphene [1–9] and its related materials arise from the relativistic behavior of electrons that give rise to great potential in numerous applications [10–19] and have stimulated an ever-growing interest in both basic and applied research. Thus, the characterization and investigation of their fundamental and application oriented properties are a crucial prerequisite for tomorrow's application. The study of fundamental properties such as vibrational modes in graphene-related materials has attracted considerable theoretical [20,21] and experimental [22–24] impetus in the past few years. Vibration modes and frequencies are the basis for understanding the thermal, transport, and optical properties of solids. Graphene has been considered as a prototypical bench-top relativistic quantum system that consists of a one-atom-thick planar sheet of the sp^2-bonded carbon atoms [2]. In sp^2 carbons, the phonons, like the electrons, depend on the atomic structure that are the main source of Raman spectra in the literature, and the Raman phonon spectra can be used to study the similarities and differences in the various materials within the sp^2 carbon family. The presence of disorder in sp^2 hybridized carbon systems leads to rich and intriguing phonon properties. For example, the effect of breaking the translational symmetry of crystal by introducing disorder into the lattice is the breakdown of momentum conservation, through the activation of phonons at interior K points of the Brillouin zone. Therefore, strong D band features are observed in the Raman spectra which are generally inactive for perfect graphene [25–27].

Naturally occurring carbon materials are made up of two stable isotopes, ^{12}C (abundance 98.9%) and ^{13}C (1.1%). The isotopic disorder in a crystal is a perturbation in which the average atomic mass is changed, and therefore, some physical properties, such as thermal conductivity and phonon scattering are sensitive to isotope mixing [28,29]. Among

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the physical properties of crystals, phonons are those which reflect most strongly differences in isotopic mass *M*, their frequencies being usually proportional to $M^{-1/2}$ [30]. Hence, the effects of *M* fluctuations should be best observed by spectroscopic techniques (Raman, infrared (IR) absorption, neutrons, possibly He-atom scattering, electron energy loss spectroscopy (EELS), and so on). Moreover, from a practical point-of-view, when graphene has been fabricated experimentally, they will have some structural defects. Vacancy and adatom–vacancy defects are among the most probable ones [31]. Even small concentrations of vacancy-type defects in graphene-based 1D and 2D structures may alter the vibrational properties significantly and thus change their optical absorption, low temperature specific heat and transport properties. Although isotopic defects do not interact directly with electrons, a strong influence of other defects such as vacancy-type defects on the electronic properties of graphene has been observed [32]. Costa et al. [33] studied the laser energy dependence of the D bands for pure ^{12}C and pure ^{13}C samples and showed that the slope of the D band, which is sensitive to the electronic structure, does not change with the isotope mass. This result serves as strong experimental evidence that isotope enrichment does not modify the electronic structure, and the presence of D band should originate from other types of defects. The transport of valence electrons in the garphene-related materials has been significantly affected by the lattice vibrations due to a strong electron–phonon coupling [34]. The investigation of the phonon properties of graphene including combined isotope-disorder and vacancy-type defects is thus of fundamental importance for the electron transport in electronic devices and of great general interest for the physical understanding of those structures.

During the past few years, several studies have been performed on the phonon properties of graphene using various theoretical approaches, including force constant fittings [24,35], density functional theory [20,21,36], and the first-principles calculations [37–39], the most of which focus on the pristine graphene only. Some studies have considered the influence of the isotopic composition on the phonon-related properties of single wall carbon nanotube (SWCNT) [29,33,40], graphene [41,42], and BN nanotubes [43]. However, to our best knowledge, no study has attempted to calculate the phonon properties of graphene due to the combined effects, especially the mixture of isotope and vacancy-type defects. When vacancy or other types of defects present in a system, they may induce the symmetry breakdown of elemental topological arrangements, which generate more complex lattice structures. Therefore, the dynamical matrix method requires huge computational resources. These long computational times and convergence problems in the dynamical matrix calculations limit the systems of interest to benchmark molecules. However, a significantly larger-scale model is essential for an in-depth understanding of vibrational properties of defective atomic structures. It is thus crucial to build a reliable model to measure the physical properties of the defective graphene or to observe the vibrational mode directly.

We are here interested in the systematic investigation of isotope and vacancy-type defect effects on the phonon properties of graphene. When some disorder is present in a system, there may appear vibrational modes [44,45] lying outside of the allowed frequency range of the perfect crystal. These are called localized vibrational modes or local modes because the mode energy is spatially concentrated at the defect site, which is similar to Anderson's localization for electronic wave functions in the disordered lattice. If the vibration modes or the phonons are localized, the mean free path of the phonon becomes finite and proportional to the square of the localization length. Generally, when the electron–phonon interaction of graphene is discussed [46,47], the phonon wave function is treated as delocalized in the crystal. However, in a real graphene sample, we know that 1.1% of the atoms are ^{13}C and also present some vacancy-type defects. Thus, phonons have a finite lifetime and a finite localization length due to the scattering by ^{13}C or vacancy-type defects, which is one of the main contributions to the natural linewidth of the Raman spectra. Therefore, we need an insightful understanding on how the isotope disorder combined with vacancy-type defects influences the phonon properties of graphene.

Recently, Chen et al. [48] has studied the thermal conductivity of isotopically modified graphene experimentally and matched their results with molecular dynamic (MD) simulations, corrected for the long-wavelength phonon contributions by means of the Klemens model. They showed by the MD simulations that thermal conductivity of the natural graphene (1.1% ^{13}C) reduced by ~40% relative to that of the isotopically pure ^{12}C graphene. They elucidated that the evolution of thermal conductivity with isotope content is mostly produced by a change in the phonon-point defect scattering rate through the mass difference. The phonon group velocity and mass density do not undergo substantial modification through the isotope composition. However, the long-wavelength region acoustic modes are significant heat carriers due to their high group velocities than the optical modes. On the other hand, the density of states of the high-frequency optical mode is high. It has been speculated that impurities (i.e. isotope or vacancy-type defects) interrupt the crystallinity and impede the flow of thermal energy through the localization of phonon. Since localization virtually immobilizes phonons and makes them non-conducting, these phonons lose their nature as heat carriers. These strongly notice that there is a possibility of interruption of the thermal conductivity of isotopically modified graphene by the localization of short-wavelength phonons. Moreover, some discrepancies may be related to the wave interference effects are observed [49,50] in SWCNTs and boron nitride nanotubes with large isotope impurity concentrations (>10%). Savic et al. [49], and Yamamoto et al. [50], both they observed three transport regimes (ballistic, diffusive, and localized) due to the wave interference effects of isotope-enriched samples, and calculated the localization length via atomistic Green's function formalisms, while localization effects of the phonon wave function are not discussed. As pointed out by Savic et al. [49], localization effects are difficult to observe in thermal transport measurements because the thermal conductance is mostly dominated by the ballistic and diffusive contributions. The localization regime appears in the high-energy optical modes, and thus special experimental techniques capable of probing these high-energy modes are required to observe any localization effects. Hence, it is particularly very important to uncover information about the different localized modes in graphene due to these types of defects.

In this work, we have performed a computer experiment on the phonon properties of graphene considering the combined effects of isotope and vacancy-type defects for a large number of lattices. We apply the forced vibrational method suitable to treat physical systems, which is based on the mechanical resonance to extract the vibrational eigenmodes for very complex and large systems by numerical calculations to describe the change in the phonon density of states due to the ^{13}C isotope and vacancy-type defects. The ^{13}C isotope and vacancy concentration are the most important parameters in this study that have been varied over a broad range. To study the nature of phonon states, we have calculated the mode pattern in the presence of ^{13}C isotope and vacancy-type defects. We focus particularly on the *K* point in-plane TO modes because of their importance in the Raman D band, the dominant feature in the Raman spectra. Moreover, we calculate the localization length as a function of impurity density to study the localization effects caused by different types of impurities.

2. Theoretical background

Here, we briefly elucidate the forced vibrational method relevant to treat physical structures with much large size, in which we obtain the expressions that will be useful for the calculation of phonon density of states and mode patterns. A short description of the model which is used for the estimation of phonon localization length is also given in this section.