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荷电对石墨烯的声子结构和电 - 声子耦合的影响研究

钟国华

（中国科学院深圳先进技术研究院 光伏太阳能研究中心　深圳　518055）

摘　要　石墨烯材料需要经过不同的改性处理才能够在电子器件领域大规模应用，其中荷电就是一种非常有效的手段。文章通过第一性原理计算方法研究了带有少量电荷(电子或空穴)的单层石墨烯的电子和声子态特征，以及电-声子相互作用变化，发现荷电可以使费米能级发生移动，导致石墨烯展现金属特征。在石墨烯中引入电荷没有改变 *z* 轴方向声学的振动模，不会引起石墨烯的弯曲。在石墨烯中注入电子，可以引起声子模式的软化，电-声耦合强度随着引入的电子浓度增加而增强。由于引入电荷可以调节纵向光学的声子频率的变化并且导致一个更强的电-声子相互作用，推断通过该途径可以提高石墨烯中载流子的迁移率。

关键词　石墨烯；声子；电-声子耦合；第一性原理

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The Study on Phonon Characteristic and Electron-Phonon Coupling of Charged Graphene

ZHONG Guohua

(*Center for Photovoltaic Solar Energy, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences,*
Shenzhen 518055, *China*)

Abstract　The modification such as introducing charge is an effective means to make the graphene applicable in the field of electronic devices. In this paper, the first-principle calculation was performed to investigate the electronic and phononic band structures as well as the electron-phonon interaction in a monolayer graphene doped by small number of electrons or holes. It was found that, the charged graphene exhibits metallic character due to the shift of Fermi level. The introducing charge did not affect the variation of bending in graphene since the *z*-axis acoustic mode was unchanged. The abnormal softened phonon mode was observed for electron-doped graphene. The electron-phonon coupling was constantly enhanced with the increasing of charge concentration. It was concluded that, the carrier mobility in graphene can be improved since the doping adjusts the longitudinal optical phonon frequency and results in a stronger electron-phonon interaction.

Keywords　graphene; phonon; electron-phonon coupling; first-principles

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作者简介：钟国华，博士，副研究员，研究方向为计算材料科学，E-mail：gh.zhong@siat.ac.cn。

1 Introduction

Carbon is one of the most intriguing elements in the periodic dable and plays a unique role in nature. It forms many allotropes, some known from ancient times (diamond and graphite) and some discovered 20 years ago (fullerenes and nanotubes). Interestingly, the two-dimensional (2D) form, graphene, recently attracting a great deal of attention[1-3]. The 2D plane of carbon atoms arranged in a honeycomb lattice is named as graphene which is the first example of a truly 2D crystal and also acted as ‘Mother’ of all graphitic materials[4]. With the fundamental research and possible applications, a graphene world has been opened[5,6].

The recent demonstration of a field-effect transistor (FET) based on monolayer and few-layers graphene sheets has boosted the interest in this system[1,7-20]. In particular, by tuning the FET gate voltage V_g, it is possible to dope graphene by adding an excess surface electron charge. The actual possibility of building a FET with just one graphene monolayer maximizes the excess charge corresponding to a single atom in the sheet. In a FET-based experiment, graphene can be doped up to 3×10^{13} cm^{-2} electron concentration[1,7,8], corresponding, in a monolayer, to a 0.2% valence-charge variation. The resulting chemical-bond modification could induce a variation of bond lengths and phonon frequencies of the same order, which would be measurable. This would realize the dream of tuning the chemistry, within an electronic device, by varying V_g.

The graphene is a good system to investigate the Kohn anomalies[21,22], since the variation of optical-phonon frequencies in graphene is much larger than 0.2% expected in conventional systems. At the same time, the phonon frequency change induced by FET doping could provide a much more precise determination of the Kohn anomalies, with respect to other experimental settings[23]. In addition, the interaction between electron and phonon plays an important role in understanding the high mobility of graphene at room temperatures. For the charged graphene, it remains an important open question[24], though extensive investigations have been done[7-20,23,25-29]. There is the obvious difference between experimental and theoretical electron-phonon interaction results. Especially for deep understanding the charged graphene from theoretical aspect, the variations in phonon frequency and electron-phonon interaction based on the first-principles calculations have been investigated.

2 Computational method

The calculations were performed, using QUANTUM-ESPRESSO package[30]. The exchange-correlation energy was treated as local density approximation (LDA), since the calculated phonon frequency from LDA is better according to the experimental value[31,32] than from generalized gradient approximation (GGA). We adopted the Andrea Dal Corso-type ultrasoft pseudopotential with a cutoff energy of 35 and 350 Ry for the wave function and the charge density, respectively. $36\times36\times1$ Monkhorst-Pack k-point grids with Gaussian smearing of 0.02 Ry were used for the phonon calculations at $6\times6\times1$ q-point mesh, and double k-point grids were used for calculation of the electron-phonon interaction matrix element. The 2D graphene crystal is simulated using a supercell geometry with the interlayer spacing of 8 Å, 12 Å, 16 Å and 20 Å, respectively. The Fermi-energy (E_F) shift is simulated by considering an excess electronic charge which is compensated by a uniformly charged background. The electron number variation was set to $-0.06\,e$, $-0.04\,e$, $-0.02\,e$ and $-0.02\,e$, $-0.04\,e$, $-0.06\,e$ corresponding to the decrease and increase of electron number respectively, where e represents the quantity of electrons. The maximum change extent of doping electrons is about $\pm 9\times 10^{13}$ cm^{-2}.

3 Results and discussion

For the zero-doped graphene, the optimized lattice constant (~2.44 Å) in plane is slightly less than GGA result (~2.46 Å)[31], with the distinction of 0.8%. The difference of lattice constants obtained from LDA and GGA is also observed in other materials. The doping results in the change of Carbon-Carbon (C-C) bond lengths, accompanying the variation of lattice constants in plane. The C-C bond becomes long due to adding electrons into the graphene, on the contrary, the C-C bond shrinks because of taking electrons out from the graphene. For instances, the C-C bond length for zero doping is 1.409 Å, it is 1.406 Å for the doping of $-0.06\,e$, and it is 1.414 Å for the doping of $\times 0.06\,e$, as the vacuum is set at 16 Å. With the electron concentration change of 3×10^{13} cm^{-2}, the lattice constant variation in plane is about ±0.1%.

It is well-known that a direct zero band gap is between bands crossing at each corner K (K') point of the 2D hexagonal Brillouin zone. The charge doping induces the shift of energy bands. The Dirac point is below the E_F after adding electrons, on the contrary, the Dirac point is just above the E_F after subtracting electrons. Comparing with the zero-doped semimetallic graphene, these charged graphenes exhibit metallic character. The density of states at E_F appear large variation. The typical electron concentration obtained in experiments[1,7,8] corresponds to an important Fermi energy shift ~0.6 eV. For this shift, the linearized bands are still a good approximation[23].

Fig. 1 presents the variations of phonon frequency of longitudinal optical /transverse optical (LO/TO) mode at Γ k-point with the doping. The calculated zero-doped phonon frequency is 1 591 cm^{-1}, which is unchanged with the interlayer distances. This frequency obtained from LDA is slightly different from previous theoretical and experimental values[33-35]. It is closer to 1 590 cm^{-1} of graphite[23], but larger than 1 554 cm^{-1} of graphene from GGA[23,31]. The lattice parameter variation is important, since it nearly doubles the frequency shift. As mentioned above, thus big phonon frequency of 1 591 cm^{-1} is just due to the smaller lattice constant induced by LDA than GGA[35]. From Fig. 1, the phonon frequency increases with the increase of hole number relative to neutral graphene, while the phonon frequency decreases with the

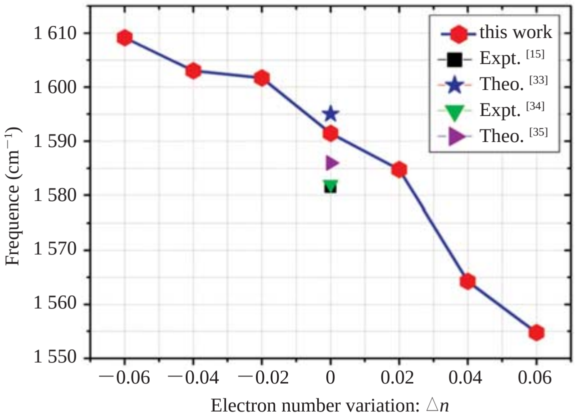
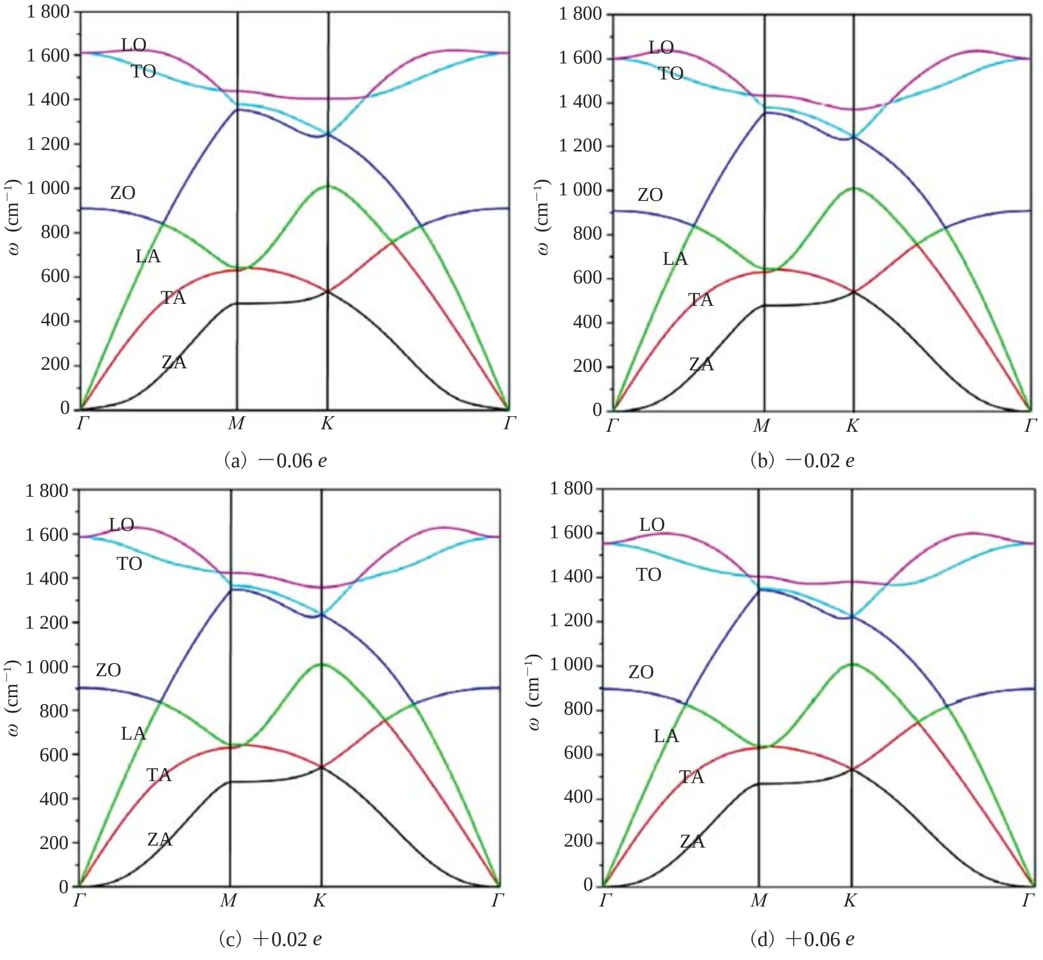


Fig. 1　The shift of phonon frequency of LO/TO branches at Γ k-point with the variation of net charge

increase of electron concentration in graphene. A monotonous decrease relation of phonon frequency on the doping concentration is observed, which is different from the experimental result[10], especially for the electron-doped case. When doping electron in graphene, a softening G phonon is obtained in our result, while G phonon becomes hardening as doping electron into graphene at experiment[10]. In particular, the G phonon stiffness changes from softening to hardening in the bilayer graphene as carrier density increases[15-18]. The same variation trends were observed in monolayer graphene and billayer graphene, which means that the difference between experiment and theory does not come from the interlayer coupling interactions. By comparing the sample size, we find that the possible reason is from the difference of system sizes between experimental and theoretical observations. In our calculation, the graphene is a real plane due to the size below nanometer. In experimental study, on the contrary, the size of sample is far bigger than that of simulated system. The bending or folding will occur when the size of graphene is big enough, which introduces some new phonon modes such as bending mode. This bending or folding mode increases with the increase of carrier concentration. As a result,



(a) −0.06 *e*　(b) −0.02 *e*

(c) +0.02 *e*　(d) +0.06 *e*

ZA: *z*-axis acoustic　ZO: *z*-axis optical　LA: longitudinal acoustic　LO: longitudinal optical　TA: transverse acoustic　TO: transverse optical

Fig. 2　The phononic band structure for different charge concentrations

the phonon hardening, a different phenomenon from theoretical simulation, was observed from experiments.

Furthermore, the phononic band structure along special k points for doping $-0.06\ e$, $-0.02\ e$, $+0.02\ e$, and $+0.06\ e$ are shown in Fig. 2. It is found that the phonon frequency variation induced by doping mainly occurred at LO and TO two optical branches. The longitudinal acoustic (LA), transverse acoustic (TA), and z-axis acoustic (ZA) three acoustic modes as well as z-axis optical (ZO) mode have not visible change with doping. Among these six phonon modes of LO, TO, ZO, LA, TA, and ZA, the ZA mode is described as the transversal polarization out-of-plane. In general, the phonon frequency for such mode increases when the in-plane lattice parameter is increased, contrary to the usual behavior, since upon stretching atoms in the layer will be less free to move in z direction (just like a string that is stretched will have vibrations of smaller amplitude and higher frequency). And the thermal contraction was found to be greatly reduced with respect to graphene, comparing with graphite[31]. Thus ZA mode results in a big oscillation out-of-plane. The ZA mode is also called as bending mode. In fact, graphene is a flexible membrane embedded in three-dimensional space[36]. The doping from holes to electrons makes the in-plane lattice constant somewhat become big. However, the phonon frequencies for three acoustic modes are almost unchanged. Clearly, the doping does not induce the variation of bending in graphene. Interestingly, the variation of in-plane lattice constant is not responsive to the unchanging of phonon frequency of long-wave acoustic modes (especially for LA mode), which indicates that a unusual phenomenon of phonon softening is observed in this charged graphene.

The visible increase of phonon frequencies for LO and TO optical modes is observed when doping holes into graphene, while the frequency decrease is formed in electron-doped systems, as shown in Fig. 2. Our results differ from previous report in which the phonon frequency is increased when adding electrons into graphene[23]. The lower optical phonon frequency corresponds to the bigger in-plane lattice constant. After doping, the coupling between electric-magnetic fields and optical modes induces the dispersion variation of optical phonon branches and influences the optics properties of graphene.

We have also investigated the electron-phonon interaction in the doped graphene. The electron-phonon coupling constant variation with the doping is shown in Fig. 3. A monotonously increased electron-phonon coupling constant is obtained during the doping electrons, which is in good agreement with that in previous reports[25,29]. The electron-phonon interaction of graphene doped by holes also enhances with the increase of holes

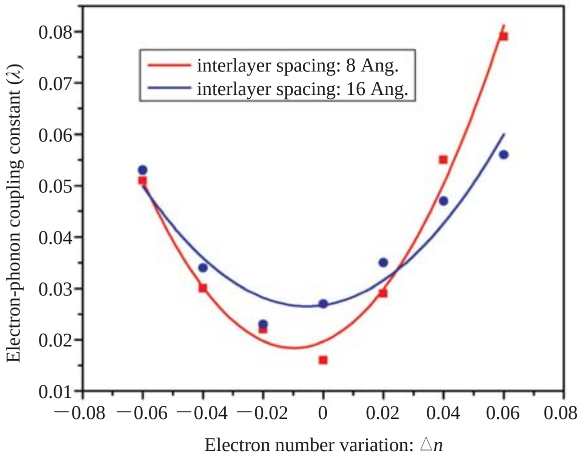


Fig. 3 The variation of electron-phonon coupling constant λ

(The solid lines are obtained by fitting to $\lambda=0.354\,\Delta n+0.077$)

concentration, which has no references to compare. However, the electron-phonon interaction is also still opened question due to the Dirac point at *K*. The interaction mainly results from electrons and three optical modes (LO, TO, and ZO) in doped graphene, especially the role of LO and TO modes. The vibration of optical phonon modes forms a polarized electric field. This field can makes frequency of LO phonon higher than that of TO phonon. And this field also interacts with conductive electrons which is stronger than the interaction between LA phonon and conductive electrons. Hence, the carrier mobility is mainly affected by the interaction between LO phonon and conductive electrons. The carrier mobility will been improved by doping charge since the doping can tune the frequency of LO phonon.

4 Conclusions

In the presented paper, the in-plane lattice parameter, electronic band structure, phonon frequency, and electron-phonon interaction in charged graphene have been investigated theoretically. During the whole doping, the in-plane lattice constant increases with the increase of electron concentrations, with a high Fermi energy more and more. The doped graphenes exhibit metallic character. The doping does not affect the variation of bending in graphene since the ZA mode is unchanged. The softened phonon mode is observed when adding small number electrons into graphene. The electron-phonon coupling constant monotonously increases with the doping concentration. The doping can possibly improve the carrier mobility in graphene due to the interaction between electron and LO phonon.

References

[1] Novoselov KS, Geim AK, Morozov SV, et al. Electric field effect in atomically thin carbon films [J]. Science, 2004, 306(5696): 666-669.

[2] Katsnelson MI. Graphene: carbon in two dimensions [J]. Materials Today, 2007, 10(1-2): 20-27.

[3] Geim AK. Graphene: status and prospects [J]. Science, 2009, 324(5934): 1530-1534.

[4] Geim AK, Novoselov KS. The rise of graphene [J]. Nature Material, 2007, 6(3): 183-191.

[5] Noorden RV. Moving towards a graphene world [J]. Nature, 2006, 442(7100): 228-229.

[6] Brumfiel G. Graphene gets ready for the big time [J]. Nature, 2009, 458(7237): 390-391.

[7] Novoselov KS, Geim AK, Morozov SV, et al. Two-dimensional gas of massless Dirac fermions in grapheme [J]. Nature, 2005, 438(7065): 197-200.

[8] Zhang Y, Tan YW, Stormer HL, et al. Experimental observation of quantum Hall effect and Berry's phase in grapheme [J]. Nature, 2005, 438: 1-7.

[9] Ferrari AC, Meyer JC, Scardaci V, et al. The Raman fingerprint of graphene [J]. Physical Review Letters, 2006, 97: 187401.

[10] Yan J, Zhang Y, Kim P, et al. Electric field effect tuning of electron-phonon coupling in graphene [J]. Physical Review Letters, 2007, 98(16): 166802.

[11] McChesney JL, Bostwick A, Ohta T, et al. Massive enhancement of electron-phonon coupling in doped graphene by an electronic singularity [J]. 2007, http://arxiv.org/abs/0705.3264v1.

[12] Casiraghi C, Pisana S, Novoselov KS, et al. Raman fingerprint of charged impurities in graphene [J]. Applied Physics Letters, 2007, 91(23): 233108-233108-3.

[13] Pisana S, Lazzeri M, Casiraghi C, et al. Breakdown of the adiabatic Born-Oppenheimer approximation in graphene [J]. Nature Material, 2007, 6(3):198-201.

[14] Maland LM, Elias DC, Alves ES, et al. Observation of distinct electron-phonon couplings in gated bilayer graphene [J]. Physical Review Letters, 2009, 101(25): 1-30.

[15] Yan J, Henriksen EA, Kim P, et al. Observation of anomalous phonon softening in bilayer graphene [J]. Physical Review Letters, 2008, 101(13): 6216-6220.

[16] Das A, Chakraborty B, Piscanec S, et al. Phonon renormalization in doped bilayer graphene [J]. Physical Review B Condensed Matter, 2009, 79(15): 897-899.

[17] Kuzmenko AB, Benfatto L, Cappelluti E, et al. Gate tunable infrared phonon anomalies in bilayer graphene [J]. Physical Review Letters, 2009, 103(11): 116804.

[18] Ando T. Anomaly of optical phonons in bilayer graphene [J]. Journal of the Physical Society of Japan, 2007, 76(10): 104711.

[19] Faugeras C, Amado M, Kossacki P, et al. Tuning the electron-phonon coupling in multilayer graphene with magnetic fields [J]. Physical Review Letters, 2009, 103(18): 186803.

[20] Sääskilahti K, Harju A, Passnen P. Gate-controlled current switch in graphene [J]. Applied Physics Letters, 2009, 95(9): 092104-092104-3.

[21] Kohn W. Image of the Fermi surface in the vibration spectrum of a metal [J]. Physical Review Letters, 1959, 2(9): 393-394.

[22] Piscanec S, Lazzeri M, Mauri F, et al. Kohn anomalies and electron-phonon interactions in graphite [J]. Physical Review Letters, 2004, 93(18): 10445-10458.

[23] Lazzeri M, Mauri F. Nonadiabatic Kohn anomaly in a doped graphene monolayer [J]. Physical Review Letters, 2006, 97(26): 2305-2311.

[24] Peres NMR, Ribeiro RM. Focus on graphene [J]. New Journal of Physics, 2009, 11(9): 095002.

[25] Tse WK, Sarma SD. Phonon-induced many-body renormalization of the electronic properties of graphen [J]. Physical Review Letters, 2007, 99(23): 236802.

[26] Verdaguer A, Cardellach M, Segura JJ, et al. Charging and discharging of graphene in ambient conditions studied with scanning probe microscopy [J]. Applied Physics Letters, 2009, 94(23): 233105-233105-3.

[27] Wang F, Zhang Y, Tian C, et al. Gate-variable optical transitions in graphene [J]. Science, 2008, 320(5873): 206-209.

[28] Zhang Y, Brar VW, Girit C, et al. Origin of spatial charge inhomogeneity in graphene [J]. Nature Physics, 2009, 6: 722-726.

[29] Calandra M, Mauri F. Electron-phonon coupling and electron self-energy in electron-doped graphene: calculation of angular-resolved photoemission spectra [J]. Physical Review B, 2007, 76(20): 205411.

[30] Giannozzi P, Baroni S, Bonini N, et al. Quantum ESPRESSO: a modular and open-source software project for quantum simulations of materials [J]. Journal of Physics Condensed Matter, 2009, 21(39): 395502-395520.

[31] Mounet N, Marzari N. First-principles determination of the structural, vibrational and thermodynamic properties of diamond, graphite, and derivatives [J]. Physical Review B, 2005, 71(20): 205214.

[32] Oshima C, Aizawa T, Souda R, et al. Surface phonon dispersion curves of graphite (0001) over the entire energy region [J]. Solid State Communications, 1988, 65(12): 1601-1604.

[33] Dubay O, Kresse G. Accurate density functional calculations for the phonon dispersion relations of graphite layer and carbon nanotubes [J]. Physical Review B Condensed Matter, 2004, 67(8): 089906.

[34] Maultzsch J, Reich S, Thomsen C, et al. Phonon dispersion in graphite [J]. Physical Review Letters, 2004, 92(7): 2835-2842.

[35] Yan JA, Ruan WY, Chou MY. Phonon dispersions and vibrational properties of monolayer, bilayer, and trilayer graphene: density-functional perturbation theory [J]. Physical Review B Condensed Matter, 2009, 77(12): 125401.

[36] Meyer JC, Geim AK, Katsnelson MI, et al. The structure of suspended graphene sheets [J]. Nature, 2007, 446(7131): 60-63.