MilosevicKepcijaDobardzicDamnjanovicMohrMaultzschThomsen2011
Materials Science and Engineering B 176 (2011) 510–511

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Kohn anomaly in graphene

I. Milošević[a,*], N. Kepčija[a], E. Dobardžić[a], M. Damnjanović[a], M. Mohr[b], J. Maultzsch[b], C. Thomsen[b]

[a] NanoLab, Faculty of Physics, University of Belgrade, Studentski trg 12, P.O. Box 368, 11001 Belgrade, Serbia
[b] Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstrasse 36, 10623 Berlin, Germany

ARTICLE INFO

Article history:
Received 19 September 2009
Received in revised form 8 November 2010
Accepted 23 November 2010

Keywords:
Graphene
Kohn anomaly
Electron–phonon interaction
Symmetry

ABSTRACT

Symmetry based analysis of the Kohn anomaly is performed. Kohn phonon frequencies and displacements are calculated by force constant method. It is shown that Kohn phonon vibrations cause electronic band gap opening.

1. Introduction

Graphene has attracted tremendous attention for diversity of its unusual properties [1]. In particular, the research interest in its fundamental characteristics has increased rapidly after the discovery of an easy method to fabricate and identify these structures [2].

The electron–phonon coupling gives the main quantifying contribution to the phonons interaction with electrons. A key feature of graphene is its semimetallic character of the electronic structure. Generally, the atomic vibrations are partially screened by electrons. In a metal this screening can change rapidly for vibrations associated with certain points of the Brillouin zone, determined by the shape of the Fermi surface. The consequent anomalous behavior of the phonon dispersion is called Kohn anomaly [3]. It may occur only for phonons with wave vector connecting two electronic states at the Fermi surface. In graphene, the electronic gap is zero only at the two equivalent K points connected by the vector K. Thus, Kohn anomalies can occur for Γ and K point phonons which are manifested as two cusps in the optical phonon branches at these points.

In this work we perform numerical and symmetry based analysis of the Kohn anomaly and find that the Kohn normal displacements are followed by the corresponding electronic band gap oscillations. Finally, we introduce "kink phonons" in order to model kinks which emerge in the phonon dispersions as a consequence of the Kohn anomaly.

2. Symmetry

Graphene is a two-dimensional crystal with diperiodic symmetry [4] group $DG80 = TD_{6h}$. It is a single orbit system, generated by the subgroup $DG3 = TC_2$ and with the stabilizer group isomorphic to D_{3h} (still, it is a symmetry fixing set, i.e. graphene is not invariant under any Euclidean supergroup). This caused that its dynamical representation is significantly reduced, meaning that it does not contain many of the $DG80$ irreducible representations. An extraordinary consequence is that electron–phonon vibronic coupling (being an origin of Jahn–Teller effect [5]) is restricted, which is manifested in the electronic states uncoupled to phonons, and phonons which are not coupled to electrons, strongly indicating that symmetry is the key for full understanding of Kohn anomaly.

3. Electron–phonon coupling, Kohn anomaly and "kink phonons"

Although there is intensive research effort, the keynotes in understanding electron–phonon interaction in graphene, the phonons involved and the coupling strength of the interaction have not been resolved completely. Quite recently, angle-resolved photoemission spectroscopy has been successfully used to detect the signature of the electron–phonon interaction in the electronic spectra in the form of kink [6].

Diperiodic group based full symmetry analysis of the electron–phonon coupling in graphene starts with reduction of the dynamical representation into its irreducible components, which correspond to the normal mode displacements. Then the symmetrized squares of the irreducible representations

* Corresponding author.
E-mail address: ivag@rcub.bg.ac.rs (I. Milošević).

0921-5107/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2010.11.004

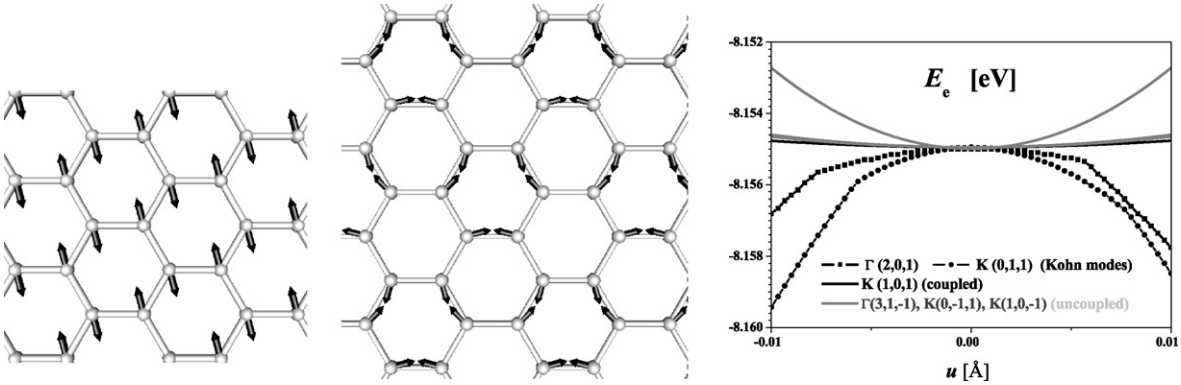

Fig. 1. Kohn phonons E_{2g} and A_{1g}, respectively, and electronic energy as function of the corresponding displacements.

describing electronic states are also reduced. The components pertaining to the both reductions couple electronic states to the particular phonons. Such a procedure shows that only three (out of six) optical modes at the Brillouin zone center Γ and at Dirac point K are symmetry allowed to couple to Fermi electrons.

Taking into account interaction with twenty-four nearest neighbors, we calculated electronic band structure by the tight-binding density functional method [7], and phonon dispersions within symmetry based force constants approach [8]. The both dispersions are assigned by the complete set of quantum numbers, enabling straightforward detection of the coupled electronic states and phonons (using the above described algorithm). It turns out that only optical phonons at K and Γ point can be coupled to the Fermi level electrons. In particular, optical phonons E_{2g} (at K point), A_{1g} (at Γ point) and E_1^+ (at K) could cause Kohn anomaly, while the remaining phonons, B_{3g} (at Γ), E_0^B and E_1^- (at K), are totally vibronically uncoupled.

Optical phonon branches exhibit two cusps, at Γ point and at K point which are symmetry allowed to couple to the Fermi electrons. These normal displacements are illustrated in Fig. 1. Their calculated frequencies are 1577 cm^{-1} and 1293 cm^{-1}, in accordance with the experimentally obtained values [6].

We calculate dependence of the electronic energy on the all six Γ and K optical phonons displacements as a function of displacement. As shown in Fig. 1 only the Kohn modes, substantially coupled to Fermi level electrons, show unusual behavior of the electronic energy. While for other modes band gap ΔE does not appear, for these two modes it is linear in displacement u: $\Delta E = cu$, with $c = 33$ eV/Å. Stronger influence on the electronic band structure of the symmetric Dirac point Kohn displacements is evident which is in agreement with recent angle-resolved photoemission spectroscopy measurements [6].

Also, our numerical calculations show that the total energy (electronic plus ionic) as a function of the Kohn phonons displacements has a form of a kink which can be well approximated by intersection of two parabolas $V_{\pm}(x) = 1/2\omega^2(x \pm a)^2$. We analytically determined the spectrum $E(n)$ of the corresponding "kink phonon" Hamiltonian in a form which is similar to that of the classical phonons. Only instead of natural number n there is a function $f(n) = n + a\sqrt{m\omega/\hbar}\sqrt{0.13 + 0.81n} + 0.4a\sqrt{m\omega/\hbar}$, falling off rapidly with n. Hence, the deviations can be observed for the lowest states only.

4. Conclusions

Numerical and symmetry based analysis of the Kohn anomaly in graphene have been performed within Born–Oppenheimer approximation [9]. The model independent, symmetry based analysis predicts the Kohn anomalies, their Brillouin zone positions and complete set of good quantum numbers. Force constant calculations give frequencies and vectors of the Kohn displacements. Dispersion of "kink phonons" is calculated and found to be similar to the classical phonons spectrum. It is shown that Kohn phonon vibrations cause the Fermi level oscillations. If tunable, such a band gap opening opens a room for electronic applications.

Note that the use of Born–Oppenheimer approximation may be subjected to certain criticism; in particular, experimental verification can be difficult, as the samples are doped, while numerical results are reasonable for undoped graphene only. Still, the part of analysis based on symmetry only is quite reliable as model independent.

Acknowledgements

This work is supported by Serbian Ministry of Science (Project No. ON141017) and European Union (FP6 INCO-WBC 026303 project).

References

[1] A.K. Geim, Science 324 (2009) 1530.
[2] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Gregorieva, A.A. Firsov, Science 306 (2004) 666.
[3] W. Kohn, Phys. Rev. 2 (1959) 393.
[4] E.A. Wood, 80 Diperiodic Groups in Three Dimensions (Bell System Monograph No. 4680).
[5] I. Milošević, M. Damnjanović, B. Nikolić, M. Krčmar, J. Phys. A: Math. Gen. 31 (1998) 3625.
[6] S.Y. Zhou, D.A. Siegel, A.V. Fedorov, A. Lanzara, Phys. Rev. B 78 (2008) 193404.
[7] I. Milošević, B. Nikolić, E. Dobardžić, M. Damnjanović, I. Popov, G. Seifert, Phys. Rev. B 76 (2007) 233414.
[8] M. Mohr, J. Maultzsch, E. Dobardžić, S. Reich, I. Milošević, M. Damnjanović, A. Bosak, M. Krisch, C. Thomsen, Phys. Rev. B 76 (2007) 035439.
[9] S. Pisana, M. Lazzeri, C. Casiraghi, K.S. Novoselov, A.K. Geim, A.C. Ferrari, F. Mauri, Nat. Mater. 6 (2007) 198.