Comment on “Electron-phonon coupling in two-dimensional silicene and germanene”

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Abstract

In their work, Yan et al. [Phys. Rev. B 88, 121403 (2013)] employing density functional perturbation theory (DFPT) calculations, demonstrate that silicene and germanene show weaker Kohn anomalies in the Γ-\( E_g \) and \( K-A_1 \) phonon modes, compared to graphene. Furthermore, they compute the electron phonon (e-ph) coupling matrix elements using the frozen phonon approach and found that in silicene the average e-ph coupling matrix-element square over the Fermi surface, \( \langle g_{q\nu}^2 \rangle_F \), is about 50% of those in graphene, but in germanene is weaker and nearly negligible. However, Yan et al. argues that the smaller Fermi velocity in silicene compensates the reduced \( \langle g_{q\nu}^2 \rangle_F \), leading to phonon linewidths \( (\gamma_{q\nu}) \) slightly larger than those in graphene. In this Comment, we show that the DFPT and the frozen phonon results of Yan et al. for silicene are inconsistent. Additionally, we have evaluated the e-ph coupling using direct DFPT calculations, analytical relations, and frozen phonon calculations, and we found systematically that \( \langle g_{q\nu}^2 \rangle_F \) and \( \gamma_{q\nu} \) in silicene are one order of magnitude smaller than in graphene, in contrast to the conclusions of Yan et al.
In reference 1, Yan et al. report a first-principles study of the Kohn anomalies and electron-phonon (e-ph) coupling in low buckled monolayer silicene and germanene. The phonon frequencies and associated eigenvectors were computed using the density functional perturbation theory (DFPT), and the e-ph coupling matrix elements by a frozen-phonon approach (FPA), which was previously developed by the same authors for graphene, with results in very good agreement with other calculations. The phonon frequency shift and the linewidth were obtained from the phonon self-energy within the Migdal approximation.

By varying the electronic smearing occupation in the phonon calculations for silicene and germanene, Yan et al. demonstrate the presence of Kohn anomalies in the highest optical branch of the $q\nu$ phonon modes, i.e. $\Gamma-E_g$ and $K-A_1$. However, the range of frequency variation as a function of the smearing is significantly smaller than in graphene, implying a much weaker e-ph coupling in silicene and germanene. In order to perform a quantitative comparison, Yan et al. compute the average e-ph coupling matrix-element square over the Fermi surface ($\langle g_{q\nu}^2 \rangle_F$) for the $\Gamma-E_g$ and $K-A_1$ phonon modes. In silicene, they found that $\langle g_{q\nu}^2 \rangle_F$ is about 50% of those in graphene, while in germanene is weaker and nearly negligible. Finally, Yan et al. argue that the smaller Fermi velocity in silicene compensates the reduced $\langle g_{q\nu}^2 \rangle_F$, leading to phonon linewidths ($\gamma_{q\nu}$) slightly larger than those in graphene.

In this Comment, we show that for silicene, the FPA results of $\langle g_{q\nu}^2 \rangle_F$ reported by Yan et al. are inconsistent with their DFPT phonon dispersion, which gives rise to an artificially enhanced $\gamma_{q\nu}$. In addition, by computing $\langle g_{q\nu}^2 \rangle_F$ employing direct DFPT calculations, analytical relations, and frozen phonon calculations, we found systematically that the e-ph coupling in silicene is one order of magnitude smaller than in graphene, in contrast to the original conclusions of Yan et al.

We begin our analysis by briefly recovering the seminal work of Piscanec et al., which demonstrates that in graphene is possible to obtain the e-ph coupling entirely from the knowledge of the electronic band structure and phonon dispersion. In that work, it was shown that the slope $\alpha_{q\nu}$ of the phonon branches around the Kohn anomalies in the $\Gamma-E_{2g}$ and $K-A_{1}'$ phonon modes is proportional to the ratio between $\langle g_{q\nu}^2 \rangle_F$ and the slope $\beta$ of the electronic bands near the Fermi level:

$$\alpha_{q\nu} = \sqrt{\frac{3\pi^2}{\beta}} \langle g_{q\nu}^2 \rangle_F, \quad (1)$$

where $\beta$ and $\alpha_{q\nu}$ are given in energy units, due to the momentum space was expressed in
units of $2\pi/a$, being $a$ the lattice constant. In a subsequent work, it was also demonstrated that the phonon linewidth of the $\Gamma$-$E_{2g}$ phonon mode is:

$$\gamma_\Gamma = \frac{2\sqrt{3}\pi^2}{\beta^2} \langle g_{q_v}^2 \rangle_F = \frac{2\alpha_\Gamma \omega_\Gamma}{\beta},$$

where $\omega_\Gamma$ is the phonon frequency. Thus, by extracting $\alpha_{q_v}$ and $\beta$ from their calculations and experimental results, Piscanec et al. demonstrate that the results obtained with Eqs. 1 and 2, are in good agreement with direct DFPT calculations of $\langle g_{q_v}^2 \rangle_F$.

It is important to note that in the derivation of Eqs. 1 and 2, it was considered a conic shape for the electronic bands near the Fermi level, a common feature in graphene, silicene, and germanene. Even more, the projection of the $\Gamma$-$E_g$ and $K$-$A_1$ phonon modes for the buckled structure in the hexagonal plane corresponds to the $\Gamma$-$E_{2g}$ and $K$-$A_1'$ phonon modes, respectively. Thus, it could be expected that Eqs. 1 and 2 hold for silicene and germanene.

In order to evaluate the agreement between the phonon dispersion and the e-ph coupling calculations of Yan et al., we use their reported values for the Fermi velocity $v_F$ ($\beta = hv_F/a$) and $\omega_\Gamma$, and then we perform two consistency tests. In the first one, by applying a linear fitting to the phonon frequencies of Fig. 2 in Ref. [1], we obtain the slope $\alpha$ of the phonon branches around the Kohn anomalies (see Fig. 1). Then, we evaluate the Eqs. 1 and 2 to get $\langle g_{q_v}^2 \rangle_{Fph}$ and $\gamma_{\Gamma ph}$, which represent estimated values from the phonon dispersion. In the second consistency test, using the reported values of Yan et al. for $\langle g_{q_v}^2 \rangle_F$, we obtain $\alpha_{epc}$ and $\gamma_{\Gamma epc}$, which correspond to estimated values from the e-ph coupling data.

In Table I, we summarize the phonon and e-ph coupling results of Yan et al., where for comparison we include the results of the two consistency tests described above. For silicene, the difference between the reported values for $\langle g_{q_v}^2 \rangle_F$ and $\gamma_\Gamma$, and the estimated ones $\langle g_{q_v}^2 \rangle_{Fph}$ and $\gamma_{\Gamma ph}$ is remarkable. Furthermore, as shown in Fig. 1, the slope $\alpha_{epc}$ is completely out of scale with respect to the phonon dispersion reported by Yan et al. In fact, it is important to note that the values for $\alpha_{epc}$ in silicene at $\Gamma$ (527 cm$^{-1}$) and $K$ (1130 cm$^{-1}$) are larger than in graphene ($\alpha_\Gamma = 396$ cm$^{-1}$ and $\alpha_K = 973$ cm$^{-1}$), indicating that the Kohn anomalies in silicene are stronger than in graphene. However, the values $\gamma_\Gamma$ and $\gamma_{\Gamma epc}$ show a very good agreement. On the other hand, for germanene there is a better consistency among all the analyzed parameters. For example, the phonon frequencies obtained using the slopes $\alpha$ and $\alpha_{epc}$ differs only 0.48 cm$^{-1}$ at $q = 0.03$ in the direction $\Gamma \rightarrow K$, close to the Kohn anomaly.
FIG. 1. Kohn anomalies for silicene around the Γ point (top) and the K point (bottom). The solid symbols are phonon frequencies obtained from Fig. 2 in Ref. [1], for a smearing parameter of 0.005 Ry. The blue line represents a linear fit to the phonon frequencies. The red line is the slope defined in Eq. 1 and obtained using the values of β and $\langle g^2_{q\nu}\rangle_F$ reported by Yan et al.\(^1\)

at Γ-$E_g$. Contrary to our analysis, in their article Yan et al. indicates that the computed $\langle g^2_{q\nu}\rangle_F$ in silicene is consistent with the direct phonon calculations, and that surprisingly in germanene the e-ph coupling is negligible.

Although numerical differences between the evaluation of Eqs. 1 and 2 with respect to direct calculations of the phonon dispersion or the e-ph coupling are expected, our analysis indicates two possibilities: the analytic relations developed for graphene does not hold for silicene, or there is a mistake in either the phonon or e-ph coupling calculations of Yan et al. Thus, we decide to perform DFT-based first principles calculations of the phonon dispersion and e-ph coupling in silicene and germanene, and then compare with the results of Yan et al.
TABLE I. Summary of the results from Yan et al.,\textsuperscript{1} and the two consistency tests. The superindex stands for parameters calculated with Eq. 1 and 2, (\textit{ph}) using a linear fit to the the phonon dispersion, and (\textit{epc}) using the reported values of \(\langle g_{q\nu}^2 \rangle_F\).

| \(\beta\) | \(\gamma_{q}\) | \(\omega\) | \(\alpha\) | \(\langle g^2 \rangle_F\) | \(\gamma\) | \(\langle g^2 \rangle^\text{ph}_F\) | \(\gamma^\text{ph}\) | \(\alpha^\text{epc}\) | \(\gamma^\text{epc}\) |
|-----|-----|-----|-----|------|-----|------|------|-----|-----|
| (eV) | (cm\(^{-1}\)) | (cm\(^{-1}\)) | (eV\(^2\)) | (cm\(^{-1}\)) | (eV\(^2\)) | (cm\(^{-1}\)) | (cm\(^{-1}\)) | (cm\(^{-1}\)) | (cm\(^{-1}\)) |
| Silicene | \(\Gamma\) | 562 | 64 | 0.0223 | 13.3 | 0.0027 | 1.5 | 527 | 12.6 |
| | \(K\) | 506 | 117 | 0.0478 | 21.5 | 0.0049 | - | 1130 | - |
| Germanene | \(\Gamma\) | 303 | 37 | 0.0021 | 0.6 | 0.0015 | 0.5 | 52 | 0.7 |
| | \(K\) | 267 | 73 | 0.0046 | 1.2 | 0.0030 | - | 114 | - |

In order to clarify the inconsistent results of Yan et al.,\textsuperscript{1} we try to keep our calculations as close as possible to that work. Thus, we employ the plane-waves and pseudopotential (PWPP) method, as implemented in the Quantum ESPRESSO code,\textsuperscript{8} and the local density approximation for the exchange-correlation functional.\textsuperscript{9} Core electrons were replaced by ultra-soft pseudopotentials taken from the PSLibrary,\textsuperscript{10} and the valence wave functions (charge density) were expanded in plane waves with a kinetic energy cut-off of 30 (360) Ry for silicene, and 60 (600) Ry for germanene. Dynamical matrices and e-ph coupling matrix elements were computed by means of DFPT. However, Yan et al. failed to report the \(k\)–grid employed in their phonon calculations, a critical numerical parameter. For that reason, after convergence tests, we employ a \(72 \times 72\) \(k\)–grid for a Methfessel-Paxton\textsuperscript{11} smearing of 0.005 Ry. The e-ph coupling matrix elements were computed in a series of \(k\)–grids from \(576 \times 576\) up to \(1008 \times 1008\), and the electronic smearing varying from 0.0002 to 0.005 Ry. Finally, phonon linewidths were calculated using Eq. 3 of Yan et al. using a temperature of 15 K in the Fermi-Dirac occupation. Employing DFPT calculations, we have previously\textsuperscript{5} obtained \(\langle g_{q\nu}^2 \rangle_F\) for graphene, and that result is in very good agreement with Piscanec et al.\textsuperscript{3} and the previous work of Yan et al. for graphene in Ref. [2].

In Table II, we report our DFPT results of the phonon dispersion and e-ph coupling for silicene and germanene, as well the two consistency tests previously applied to the data of Yan et al. For easy comparison and analysis, we use the same format as in Table I. We found that our phonon results (\(\omega\) and \(\alpha\)) are in very good agreement with the work of Yan et al., but our direct DFPT calculations of \(\langle g^2 \rangle_F\) and \(\gamma\) are one order of magnitude lower than their
TABLE II. Summary of our DFPT results for the phonon dispersion and e-ph coupling in silicene and germanene, and the two consistency tests. The superindex stands for parameters calculated with Eq. 1 and 2, ($ph$) using the slope $\alpha$, and ($epc$) using the obtained value of $\langle g^2 q^\nu \rangle_F$.

|       | $\beta$ | $q$ | $\omega$ | $\alpha$ | $\langle g^2 \rangle_F$ | $\gamma$ | $\langle g^2 \rangle_{ph}^F$ | $\gamma_{ph}^F$ | $\alpha_{epc}$ | $\gamma_{epc}$ |
|-------|---------|-----|----------|----------|-----------------------|---------|--------------------------|----------------|-------------|-------------|
|       | (eV)    | (cm$^{-1}$) | (cm$^{-1}$) | (eV) | (eV$^2$) | (cm$^{-1}$) | (eV$^2$) | (cm$^{-1}$) | (cm$^{-1}$) | (cm$^{-1}$) |
| Silicene | 5.84 | $\Gamma$ | 561 | 64 | 0.0031 | 1.8 | 0.0027 | 1.8 | 78 | 1.0 |
|         |       | $K$ | 504 | 117 | 0.0063 | 3.3 | 0.0049 | - | 148 | - |
| Germanene | 5.61 | $\Gamma$ | 309 | 35 | 0.0017 | 0.6 | 0.0015 | 0.5 | 41 | 0.6 |
|       |       | $K$ | 278 | 78 | 0.0037 | 1.1 | 0.0030 | - | 91 | - |

reported values. However, it is important to note that the evaluation of Eqs. 1 and 2 within our DFPT calculations give consistent results for both silicene and germanene, indicating that something is missed in the results of Yan et al. for silicene. Evenmore, the results for $\langle g^2 q^\nu \rangle_{ph}^F$ and $\gamma_{ph}^F$ obtained from the estimated value of $\alpha$ from the phonon dispersion of Yan et al. are in very good agreement with our corresponding results, clearly indicating that the frozen phonon calculation of Yan et al. for the e-ph coupling matrix elements in silicene is wrong.

To rule out that the difference between our results and those of Yan et al. comes from numerical sources such as the use of different pseudopotentials or $k-$ grids, we perform frozen phonon calculations employing the full-potential linearized augmented plane-wave with local orbitals (FP-LAPW+lo) method, as implemented in the ELK code. We use a muffin-tin radii ($R_{MT}$) of 2.11 and 2.21 a.u. for silicene and germanene, respectively, and a $R_{MT} \times |G+k|_{MAX} = 8.0$. The angular momentum cut-off for the muffin-tin charge density and potential were expanded in crystal harmonics up to $l = 8$.

For the FPA calculations, the atomic positions were displaced according to the $\Gamma-E_g$ and $K-A_1$ phonon modes by a small distance $d$ of up to 0.010 Å. The phonon frequencies were computed by a quadratic fitting of the electronic total energy as a function of the atomic displacement, as in our previous works. Then, from the electronic band structure we obtain the band gap $\Delta E$ for each displacement, and for the evaluation of $\langle g^2 q^\nu \rangle_F$ we use the
TABLE III. Phonon frequencies, $\Delta E/d$, and $\langle g^2 \rangle_F$ for silicene, calculated using the frozen phonon approximation, by means of two different DFT methods: plane-waves and pseudopotential (PWPP), and the full-potential linearized augmented-plane wave with local orbitals (FP-LAPW+lo).

| Method        | $q$ | $\omega$ (cm$^{-1}$) | $\Delta E/d$ (eV/A) | $\langle g^2 \rangle_F$ (eV$^2$) |
|---------------|-----|----------------------|---------------------|-------------------------------|
| PWPP          | $\Gamma$ | 561                | 6.83                | 0.0031                        |
|               | $K$   | 504                | 6.54                | 0.0064                        |
| FPLAPW+lo     | $\Gamma$ | 566                | 6.89                | 0.0031                        |
|               | $K$   | 510                | 6.62                | 0.0064                        |

the following relations previously reported by Lazzeri et al.$^{15}$ for graphene:

$$\langle g^2 \rangle_F = \lim_{d \to 0} \frac{\hbar}{32M\omega_{\Gamma}} \left( \frac{\Delta E}{d} \right)^2,$$

$$\langle g^2 \rangle_{K} = \lim_{d \to 0} \frac{\hbar}{16M\omega_{K}} \left( \frac{\Delta E}{d} \right)^2,$$

where $M$ is the atomic mass. In the case of the $K$-$A_1$ phonon mode we use a $\sqrt{3} \times \sqrt{3}$ supercell, where the $K$ point and the band gap is refolded in the $\Gamma$ point.

The results of our frozen phonon calculations are presented in Table III, where for comparison we have included the FPA results obtained using the PWPP method. It is clear that the effects of using different DFT methods for the calculation of the studied parameters are practically negligibles. It is important to note that our frozen phonon results for $\langle g^2 \rangle_F$ are in good agreement with the values in Table II obtained from DFPT calculations and the analytical relation of Eq. 1, indicating consistency and giving support to our results.

Finally, we want to comment that it is well established that FPA and DFPT calculations should agree when those are performed carefully under the harmonic approximation, as we found between our DFPT and FPA results. Thus, in this work we are not criticizing the use of the FPA to compute the e-ph coupling in silicene. However, given the above explained consistence between the three methodologies to compute the e-ph coupling, even when using two DFT codes with different approaches, it is clear that the FPA implementation of Yan et al. has some mistake in the case of silicene.

In conclusion, in this comment we show that the result of Yan et al.$^1$ for e-ph coupling
in silicene is wrong. From direct DFPT calculations, evaluation of analytical relations, and frozen phonon calculations, we found systematically that the e-ph coupling in silicene is one order of magnitude smaller than in graphene.

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1 J. A. Yan, R. Stein, D. M. Schaefer, X. Q. Wang, and M. Y. Chou, Phys. Rev. B 88, 121403 (2013).
2 J. A. Yan, W. Y. Ruan, and M. Y. Chou, Phys. Rev. B 79, 115443 (2009).
3 S. Piscanec, M. Lazzeri, F. Mauri, A. C. Ferrari, and J. Robertson, Phys. Rev. Lett. 93, 185503 (2004).
4 M. Lazzeri, S. Piscanec, F. Mauri, A. C. Ferrari, and J. Robertson, Phys. Rev. B 73, 155426 (2006).
5 M. E. Cifuentes-Quintal, O. de la Peña-Seaman, R. Heid, R. de Coss, and K.-P. Bohnen, Phys. Rev. B 94, 085401 (2016).
6 J. Maultzsch, S. Reich, C. Thomsen, H. Requardt, and P. Ordejón, Phys. Rev. Lett. 92, 075501 (2004).
7 At least in absence of spin-orbit coupling, as was considered in the article of Yan et al.1.
8 P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Scandolo, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys.:
Condens. Matter 21, 395502 (2009).

9 J.-P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).

10 A. D. Corso, Comput. Mater. Sci 95, 337 (2014).

11 M. Methfessel and A. T. Paxton, Phys. Rev. B 40, 3616 (1989).

12 http://elk.sourceforge.net.

13 O. De la Peña-Seaman, R. de Coss, R. Heid, and K. P. Bohnen, Phys. Rev. B 76, 174205 (2007).

14 E. Martínez-Guerra, F. Ortíz-Chi, S. Curtarolo, and R. de Coss, J. Phys.: Condens. Matter 26, 115701 (2014).

15 M. Lazzeri, C. Attaccalite, L. Wirtz, and F. Mauri, Phys. Rev. B 78, 081406 (2008).