Comment on "Observation of anomalous peaks in the photoelectron spectra of highly oriented pyrolytic graphite: Folding of the band due to the surface charge density wave transition"

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In a recent paper by Tanaka, Matsunami, and Kimura [Phys. Rev. B **84**, 121411(R) (2011)], the surface charge density wave transition at low temperature is proposed to explain the superperiodicity observed in the angle-resolved photoelectron spectroscopy measurement of highly oriented pyrolytic graphite. We have performed density-functional theory and density-functional perturbation theory calculations to investigate the electronic structure and lattice dynamics of the graphite (0001) surface. Neither instability nor anomaly is found in the calculated electronic and phonon band structures. Thus, the surface charge density wave in a *pristine* graphite surface is less likely, and another clue is necessary to explain the observed superperiodicity.

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Tanaka *et al.*[1] have investigated the electronic structure of highly oriented pyrolytic graphite (HOPG) by using the angle-resolved photoelectron spectroscopy. They found an anomalous peak just below the Fermi level in the surface normal photoelectron spectra below ∼30 K. The peaks are assigned to the π band at the $K(H)$ point, which is backfolded into the $\Gamma(A)$ point as a result of the formation of the superperiodicity of $(\sqrt{3}\times\sqrt{3})R30^\circ$. The authors proposed the surface charge density wave (CDW) transition at low temperatures to explain this surface reconstruction.

To investigate CDW in the graphite surface, we performed electronic structure calculations based on density-functional theory within the local density approximation (LDA). We also performed lattice dynamics calculations with density-functional perturbation theory.[2] Electron-ion interactions were described by ultrasoft pseudopotentials,[3] and the wave functions and the augmentation charge density were expanded in terms of a plane wave basis set with cutoff energies of 40 and 480 Ry, respectively. The graphite (0001) surface is modeled by a 13-layer-thick slab with a (1×1) periodicity, which is separated by a vacuum equivalent to a nine-layer thickness (∼31–32 Å). We used a symmetric slab to avoid spurious electrostatic interactions[4] between image slabs. The slab was constructed using the LDA-optimized lattice constants ($a = 2.449$ Å and $c = 6.456$ Å). Brillouin zone integration was performed with a 16×16 **k**-point set in the surface Brillouin zone, and the Fermi surface was treated by cold smearing[5] with a width of 0.27 eV. Dynamical matrices were calculated on a 4×4 **q**-point mesh, and the full phonon dispersion curves were obtained by the Fourier interpolation technique. All the calculations were performed with the QUANTUM ESPRESSO package.[6]

The calculated LDA band structure along the Γ-M, M-K, and K-Γ directions is shown in Fig. 1(a). It is very similar to that for the bulk graphite, and no peculiar electronic states to the graphite surface were observed. It was also found that our phonon dispersion curve [Fig. 1(b)] is almost identical to that of the bulk,[7] i.e., the surface phonon of graphite is almost identical to that of the bulk, and shows no dynamical instability (imaginary frequency), which leads to the formation of a superperiodicity. We note that the Kohn anomalies in the Γ-E_{2g} and K-A_1' directions (Ref. 8) were not present in our LDA phonon dispersion curve, because of insufficient **k**-point sampling to describe the Kohn anomalies. Furthermore, the electron-phonon interaction in graphene and graphite is significantly underestimated with LDA, resulting in a small Kohn anomaly, and hence a much smaller slope of the

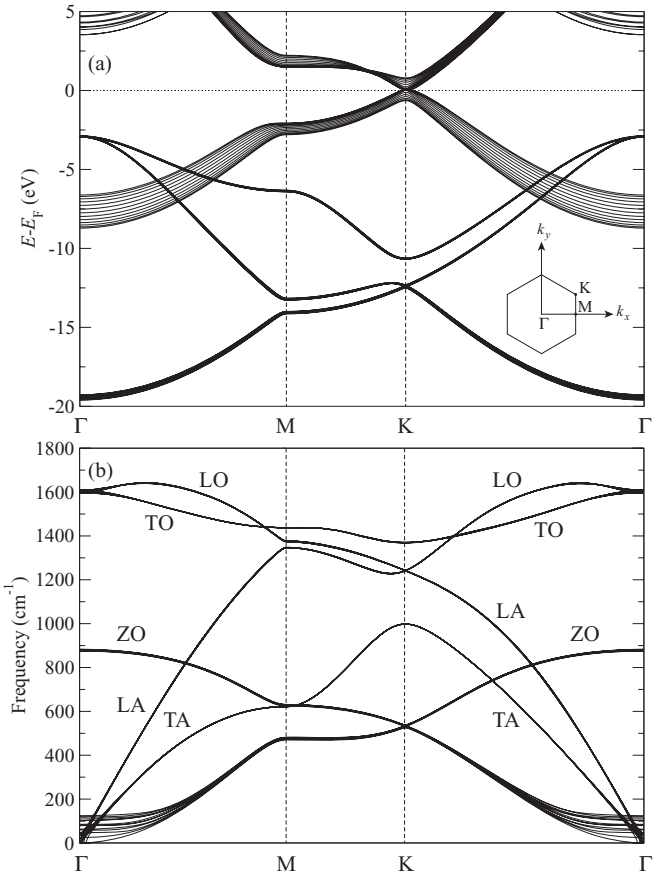

FIG. 1. (a) Band and (b) phonon dispersion curves of graphite (0001) slab. The zero of the electronic energy is set to the Fermi level (E_F). The Brillouin zone and symmetry points of the graphite surface are indicated in the inset.

highest optical phonon near the K point than the experimental one.[9] To calculate accurate phonon dispersion, especially that around the K point, the electron-electron correlation effect should be taken into account (for, e.g., via the GW approximation).[9,10] Nevertheless, LDA is able to describe the Kohn anomaly qualitatively. The electronic as well as lattice dynamical properties of the graphite surface (slab) are almost identical to those of bulk, and it is unlikely that, at the surface, electron-phonon coupling is significantly large, which leads to the surface CDW of graphite at a low temperature. Thus, a surface effect alone is inadequate to explain the anomalous electronic states observed in the experiment. Our LDA electronic and phonon band structures indicate that the graphite (0001) (1×1) surface (slab) is statically as well as dynamically stable, and thus we concluded that the CDW transition does not take place in a pristine graphite surface.

The $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure at the surfaces of HOPG has been observed in scanning tunneling microscopy (STM) experiments, in the vicinity of step edges[11,12] and of vacancies.[13,14] Theoretical calculations have been performed and have shown that it is possible to reproduce the STM images (local density of states) for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure in the presence of vacancy,[15,16] step edges,[11] and chemisorbed hydrogen.[17] Thus, it is more plausible that the superperiodicity is due to the step edges and/or defects in the graphite surface. Indeed, Niimi *et al.*[12] show from theoretical calculations the coexistence of honeycomb and $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructures in graphene with armchair (zigzag) edges mingled with a small amount of zigzag (armchair) edges, which extend spatially over 40 Å. Kondo *et al.*[14] also report the propagation of the nonbonding π state with the periodicity of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ up to 30–40 Å, which is originated from the zigzag edges formed at a single carbon vacancy.

Although the detailed mechanism is yet to be explored, the present results, as well as the experimental and theoretical studies mentioned above, indicate that the defects at the surfaces are a more likely origin of the formation of the superstructure, instead of the surface CDW in the *pristine* graphite surface.

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