Comment on "Quasi-One-Dimensional Metal-Insulator Transitions in Compound Semiconductor Surfaces"

Based on density-functional theory (DFT) calculations within the generalized gradient approximation (GGA), Zhao *et al.* [1] claimed that one-atom-wide metallic structures formed by selectively bonding of H or Li atoms to GaN($10\bar{1}0$) and ZnO($10\bar{1}0$) undergo the Peierls-type metal-insulator (MI) transitions, leading to a charge-density-wave (CDW) formation with periodic lattice distortion. However, we here demonstrate that such a CDW phase in GaN($10\bar{1}0$)-1H is due to the artifact of the GGA, while the antiferromagnetic (AFM) ground state is predicted by the hybrid DFT calculation and the exact-exchange plus correlation in the random-phase approximation (EX + cRPA).

For the 1D metallic structure composed of the surface metal atoms (Ga or Zn), Zhao *et al.* [1] found that the semiconducting $p(1\times2)$ phase with alternately up-and-down displacements is more stable than the metallic $p(1\times1)$ phase, and the $p(2\times2)$ phase is further stabilized. The relative total energies (ΔE) of these phases for GaN($10\bar{1}0$)-1H are listed in Table I.

For GaN($10\bar{1}0$)-1H, Zhao *et al.* [1] showed that the $p(1\times1)$ phase has a Fermi surface nesting that drives the CDW with the up-down buckling distortion. The resulting Peierls-type MI transition produced the $p(1\times2)$ phase with $\Delta E = -0.51$ eV and $E_g = 0.74$ eV (see Table I). The further lattice relaxation of $p(2\times2)$ gives $\Delta E = -0.57$ and $E_g = 0.99$ eV. Interestingly, a ferromagnetic (FM) phase appears in metallic $p(1\times1)$, but such spin ordering disappears in semiconducting $p(1\times2)$ and $p(2\times2)$ [1]. This disappearance of magnetic order may be due to the fact that the local density approximation or GGA tends to stabilize artificially delocalized electronic states due to their inherent self-interaction error (SIE) [2].

We optimize the structure of GaN($10\bar{1}0$)-1H using the all-electron Fritz-Haber-Institut *ab initio* molecular simulations [3] code with the GGA functional of Perdew-Burke-Ernzerhof (PBE) [4]. The present results of ΔE and E_g for the nonmagnetic (NM) $p(1\times2)$- and $p(2\times2)$-CDW phases agree well with those reported in the Letter (see Table I). In order to correct the SIE, we use the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional [5] to calculate ΔE and E_g of various phases including the AFM order. Here, we employed a mixing factor of $\alpha = 0.32$ controlling the amount of exact-exchange energy, which predicts well the observed bulk band gap of 3.51 eV [6]. We find that the HSE calculation stabilizes the magnetic phases with $\Delta E = -0.95$, -1.10, and -1.11 eV for $p(1\times1)$-FM, $p(1\times2)$-AFM, and $p(2\times2)$-AFM, respectively (see Table I). Meanwhile, ΔE of $p(1\times2)$ and $p(2\times2)$ CDW are -0.98 and -1.04 eV, respectively. Thus, the HSE calculation shows that the AFM phase is energetically more stable than the CDW formation. This result is confirmed by the EX + cRPA calculation [7,8].

TABLE I. Total energies [in eV per $p(2\times2)$ unit cell] of various phases relative to NM $p(1\times1)$ and band gaps (in eV).

	PBE (Ref. [1])		PBE		HSE	
	ΔE	E_g	ΔE	E_g	ΔE	E_g
$p(1\times2)$-CDW	−0.51	0.74	−0.51	0.71	−0.98	1.68
$p(2\times2)$-CDW	−0.57	0.99	−0.57	0.83	−1.04	1.82
$p(1\times1)$-FM	–	Metal	−0.12	Metal	−0.95	1.04
$p(1\times2)$-AFM					−1.10	1.85
$p(2\times2)$-AFM					−1.11	1.98

Our GGA and hybrid-DFT calculations showed the different predictions for the ground state of GaN($10\bar{1}0$)-1H. Contrasting with PBE predicting the $p(2\times2)$-CDW phase, HSE predicted the $p(2\times2)$-AFM phase. It is noted that the metallic $p(1\times1)$ phase of GaN($10\bar{1}0$)-1H has a narrow band width of 1.24 eV at the Fermi level, while that of ZnO($10\bar{1}0$)-1H has a wide band width of 4.08 eV [1]. Such more localized dangling-bond electrons in GaN($10\bar{1}0$)-1H are likely to favor the AFM order over the CDW formation, contrasting with the case of ZnO($10\bar{1}0$)-1H. Future experimental works are stimulated to confirm these theoretical predictions.

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[8] For the EX + cRPA calculation we used the periodic slab geometry and the electronic states obtained using the PBE functional. The EX+cRPA total-energy difference $\Delta E_{\mathrm{EX+cRPA}}$ between the CDW and AFM phases is 122 meV per 2×2 unit cell, which is somewhat larger than the corresponding one (68 meV) obtained using the HSE calculation with $\alpha = 0.32$. However, this value of $\Delta E_{\mathrm{EX+cRPA}}$ should be influenced by either the self-consistent EX + cRPA calculation or a more rigorous approach including the high-order diagrams beyond cRPA.