Comment on “Stability of the Bulk Phase of Layered ZnO”

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Bog G. Kim

Department of Physics, Pusan National University, Busan 609-735, Korea

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In a recent letter, B. Rakshit and P. Mahadevan [1] reported an *ab initio* calculation on the structural stability of the bulk phase of layered ZnO using LDA (local density approximation) and LDA+U calculations. The authors claimed to have found a new stable form of the α-BN structure of ZnO. By analyzing the phonon spectrum given by the LDA calculation, they found that the original α-BN structure of ZnO is unstable and finally they showed the optimized α-BN structure of ZnO (Figure 5 of ref. 1) using the LDA+U calculation. Our detailed calculations show that the α-BN structure of ZnO is only stable using the LDA+U calculation, but it seems unstable (or metastable) against spontaneous transformation into the wurtzite structure of ZnO when examined using the GGA+U (generalized gradient approximation) and hybrid functional calculations.

We performed *ab initio* calculations using LDA [2] and GGA [3] on the density functional with a project-augumented-wave method as implemented in VASP (Vienna ab initio simulation package) [4]. In order to correct the *e-e* interaction error in LDA and GGA, a Hubbard U-like term is introduced within the Dudarev scheme [5]and the effective U (U_{eff}) is set to 12 eV as in ref. 1. We have also done a similar calculation by using the HSE06 hybrid functional calculation [6]. Phonon calculations have been done by using the finite differences method as implemented in VASP [7].

Table 1(a) shows the optimized geometry of layered ZnO with space group (SG) 194 ($P6_3/mmc$) with GGA+U, HSE06 hybrid, and LDA+U functionals. In this space group using GGA+U and HSE06, the lowest phonon mode has symmetry of A_u (depicted in Figure 1). In the LDA+U calculation, A_u has a finite frequency (180.0 cm^{-1}) at the zone center. However, GGA+U and HSE06 calculation shows that the lowest A_u mode has an imaginary frequency, which means the system is unstable against spontaneous displacement along the A_u

eigenvector [7].

After relaxation along the A_u eigenvector and further optimization, the system is now stabilized and spatial group analysis shows that this stable structure is wurtzite ZnO (SG 186, $P6_3mc$), as shown in table 1(b) [7]. It is quite clear that A_u itself is a soft mode from the $P6_3/mmc$ to $P6_3mc$ structural phase transition. We would like to make two comments on the final optimized structure. To begin with, since we have the optimized structure from $P6_3/mmc$, the *z* positions of Oxygen and Zinc are shifted with some offset. The relevant structural parameter is *u* value (difference between z positions of Oxygen and Zinc), which takes on the value of 0.3371 in GGA + U and 0.3854 in HSE06. In addition to this, the effective U parameter is 12 eV, which is a large value for wurtzite ZnO. The volume of the optimized GGA + U structure is quite small compared with the experimental value of wurtzite ZnO. We do not have this kind of problem using the hybrid functional HSE06. In conclusion, by using the LDA+U, GGA+U, and HSE06 phonon calculations with symmetry analysis, we have shown that the proposed optimized structure of α-BN structure of ZnO [1] is only stable in the LDA+U approximation, but unstable against spontaneous structural transformation into the wurtzite structure of ZnO in the GGA+U and HSE06 calculations.

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[7] see supplementary information for detail.

Caption

Table 1: Optimized geometry, *z* position of atoms, and unstable modes of layered ZnO within GGA + U (U_{eff} = 12 eV), HSE06 hybrid, and LDA + U. b) Optimized structure with displacement along A_u mode.

Figure 1: (color online) Phonon eigenmode of soft A_u and acoustic E_{1u} in layered ZnO ($P6_3/mmc$). Blue and red symbols represent Zinc and Oxygen respectively.

		a(Å)	c(Å)	Zn(z)	O(z)	Unstable Mode (cm^{-1})
a)	GGA+U (194)	3.26409	4.25717	0.25	0.75	A_u 118.61i
	HSE06 (194)	3.42522	4.51244	0.25	0.75	A_u 138.56i
	LDA+U (194)	3.16881	3.98214	0.25	0.75	None
b)	GGA+U (186)	3.08828	4.97064	0.3399	0.7170	None
	HSE06 (186)	3.27219	5.16108	0.3373	0.7227	None
	LDA+U (186)	2.97516	4.70701	0.3081	0.6919	None

TABLE 1 Bog G. Kim

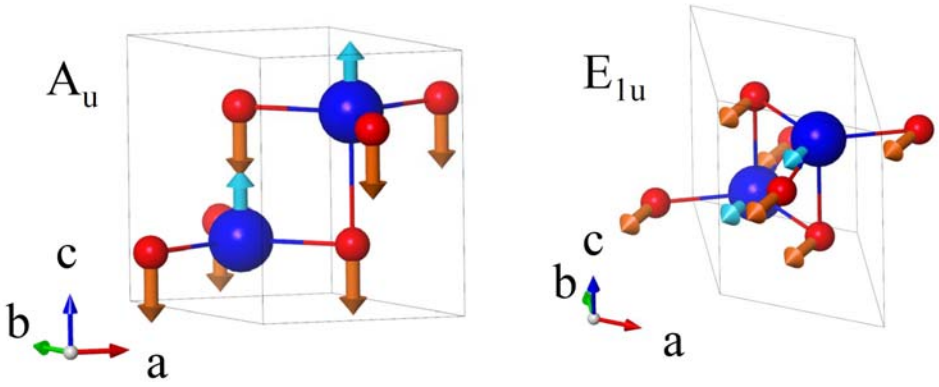

Figure 1 Bog G. Kim