Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Novel Metastable Compounds in the Zr-B System: An *ab initio* Evolutionary Study

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I. Structural Information of ZrB_{12}

Table S1 Optimized Crystallographic Data of ZrB_{12}

Space group	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	*Z*
$Fm\bar{3}m$ (No. 225)	7.39	7.39	7.39	403.6	4
atom	position	*x*	*y*	*z*	
Zr	4*a*	0.0000	0.0000	0.0000	
B	48*i*	0.500	0.6695	0.6695	

II. Convergence of Different xc-functionals of DFT

To check the convergence of the"metallicity" property of the studied novel phases Zr_2B_3 and Zr_3B_2. Different xc-functionals of DFT were tested (See figure 1 to figure 4). It was found that, the studied two novel phases are both metallic, independent on the xc-functionals of DFT used.

1. non-GGA functional: LDA (See figure S1)

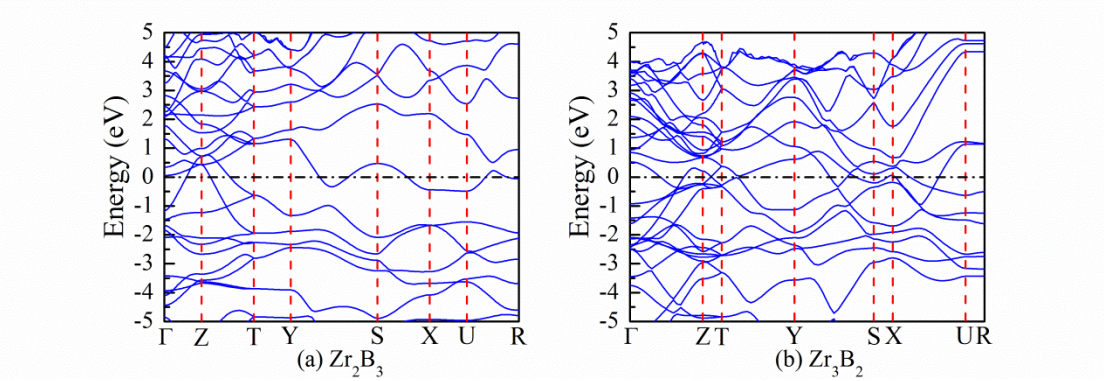

Figure S1：Calculated band structure for Zr_2B_3 and Zr_3B_2 by LDA

2. GGA functional: PBEsol (See figure S2)

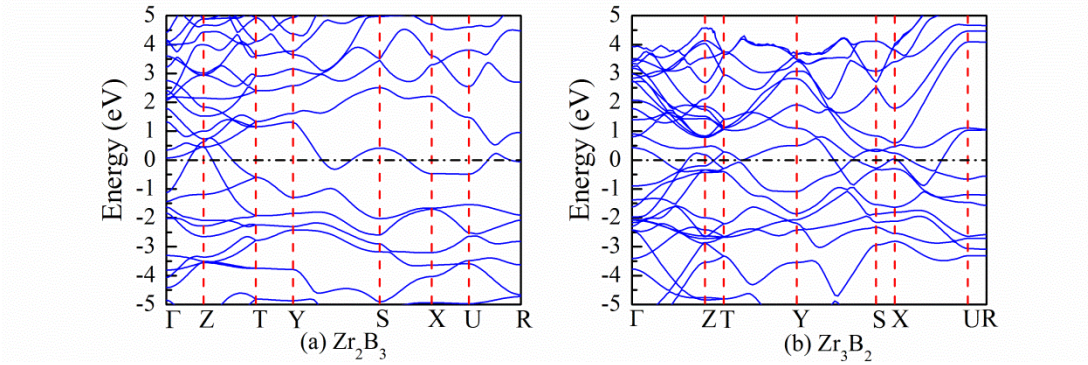

Figure S2：Calculated band structure for Zr_2B_3 and Zr_3B_2 by PBEsol

3. Full-potential linearized augmented plane waves (FLAPW) method as implemented in the WIEN2k code, GGA functional: PBE (See figure S3). (other important parameters are: the muffin-tin radii were selected to be 2.36 and 1.63 (2.47 and 1.68) for the Zr and B atoms in the Zr_2B_3 (Zr_3B_2) system; the convergence of the basis set is controlled by a cutoff parameter $R_{mt} \times K_{max}=7$, in which K_{max} is the magnitude of the largest k vector and the k points are 2000 in the Brillouin zone) .

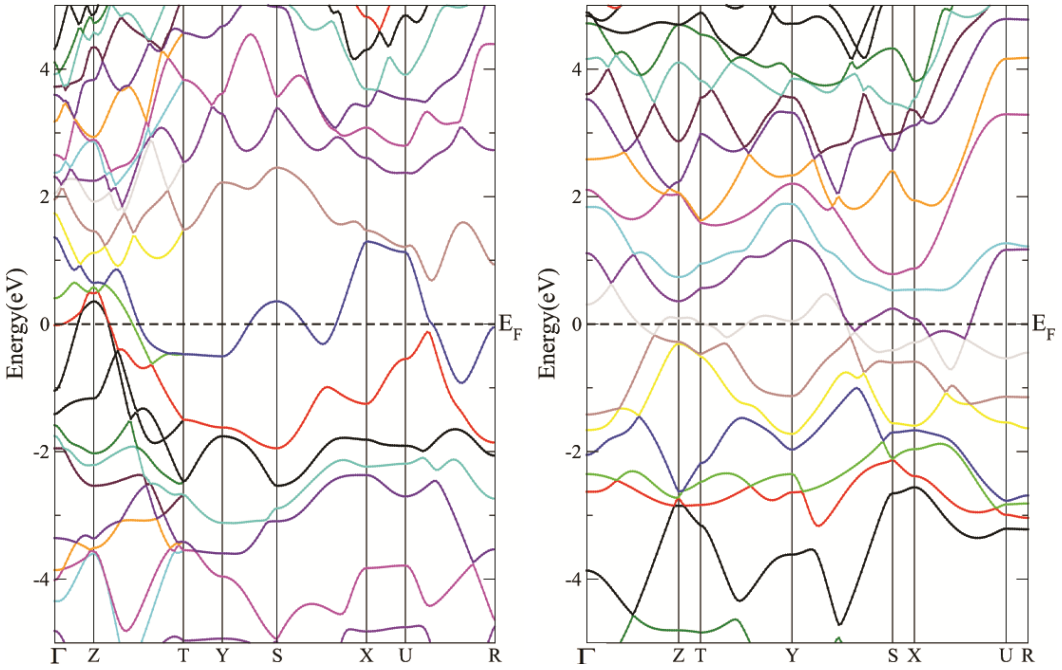

Figure S3：Calculated band structure for Zr_2B_3 and Zr_3B_2 by FLAPW and PBE
(Left: Zr_2B_3; Right: Zr_3B_2)

4. FLAPW method as implemented in the WIEN2k code, GGA functional: PBEsol (See figure S4). (other parameters are the same as part 3)

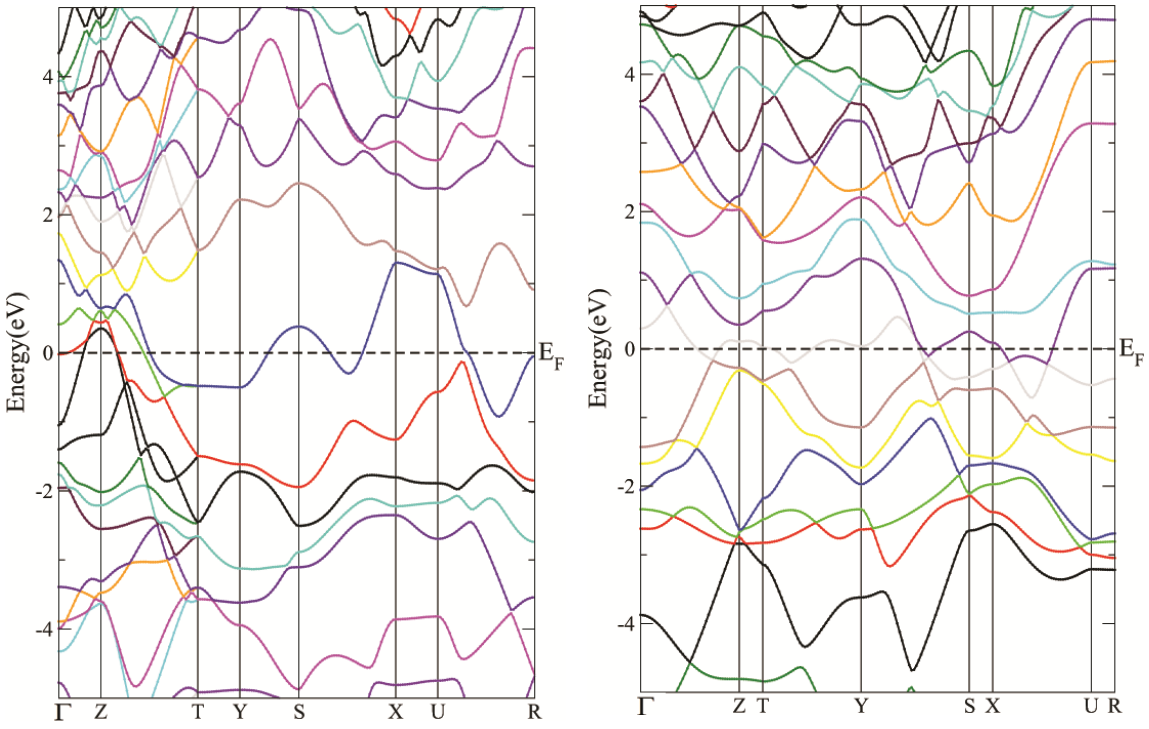

Figure S4：Calculated band structure for Zr_2B_3 and Zr_3B_2 by FLAPW and PBEsol
(Left: Zr_2B_3; Right: Zr_3B_2)