Electronic Supplementary Material (ESI) for RSC Advances.

Electronic structure and magnetic properties of mixed-valence Fe-based metal-organic frameworks VNU-15: A theoretical study from linear response DFT+U calculations

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Section S1. Electronic structures

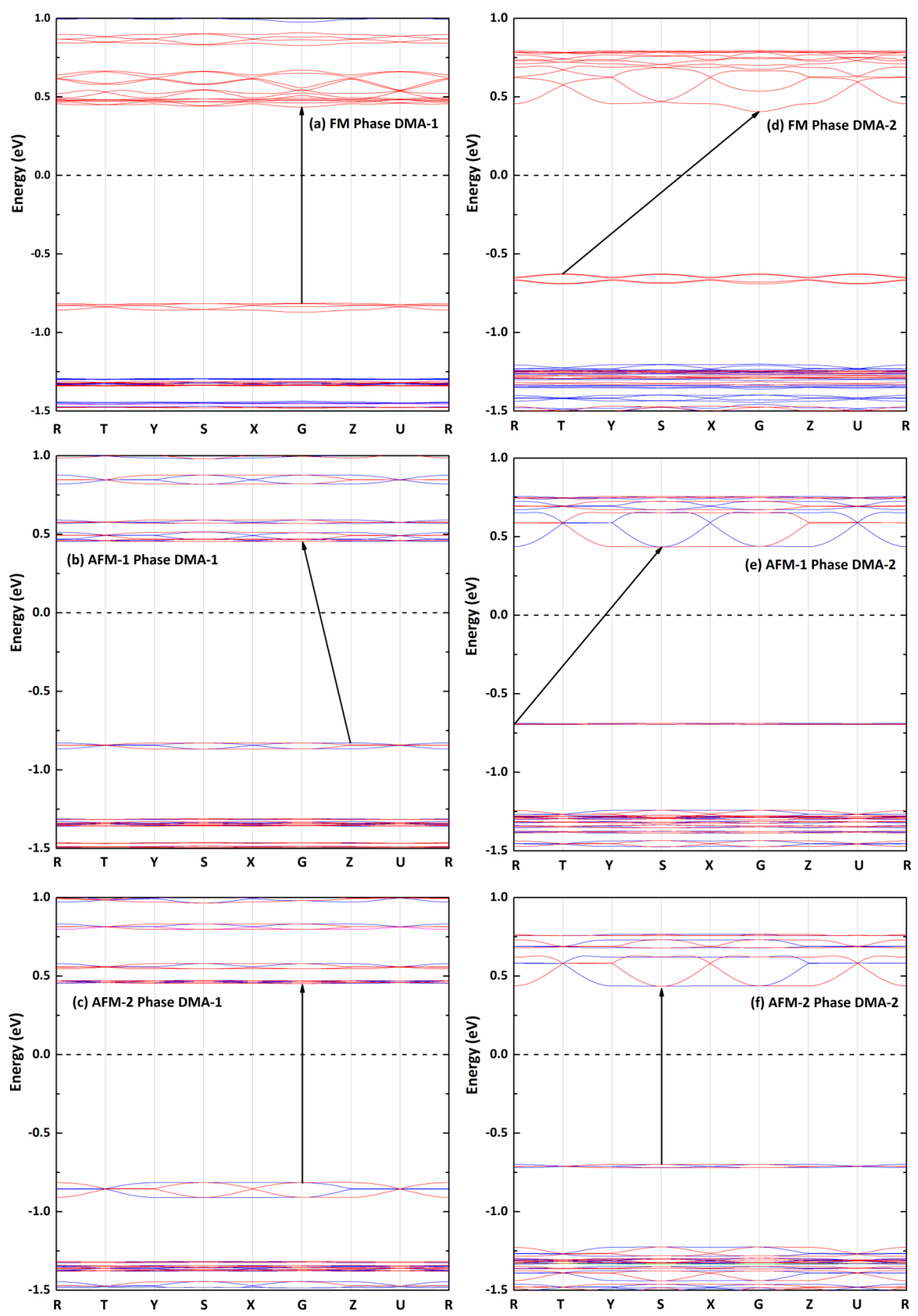

Figure S1. Band structure of (a) FM, (b) AFM-1, (c) AFM-2 of phase DMA-1 and (d) FM, (e) AFM-1, (f) AFM-2 of phase DMA-2 of VNU-15 by GGA+U calculation. The blue and red lines are for the up- and down-spins, respectively. The dotted line represents the Fermi level. High symmetry point S(-0.5, 0.5, 0), X(0, 0.5, 0), U(0, 0.5, 0.5), R(-0.5, 0.5, 0.5), G(0, 0, 0), Z(0, 0, 0.5), T(-0.5, 0, 0.5), Y(-0.5, 0, 0).

The electronic band structures for all magnetic configurations were calculated along the high-symmetry lines of the first Brillouin zone of VNU-15 structure, shown in Figure S1. The valence band and conduction band were formed from spin-down for FM states for both phases. The gap between the low-lying valence band and conduction band is about 1.76 eV and 1.62 eV for DMA-1 and DMA-2, respectively.

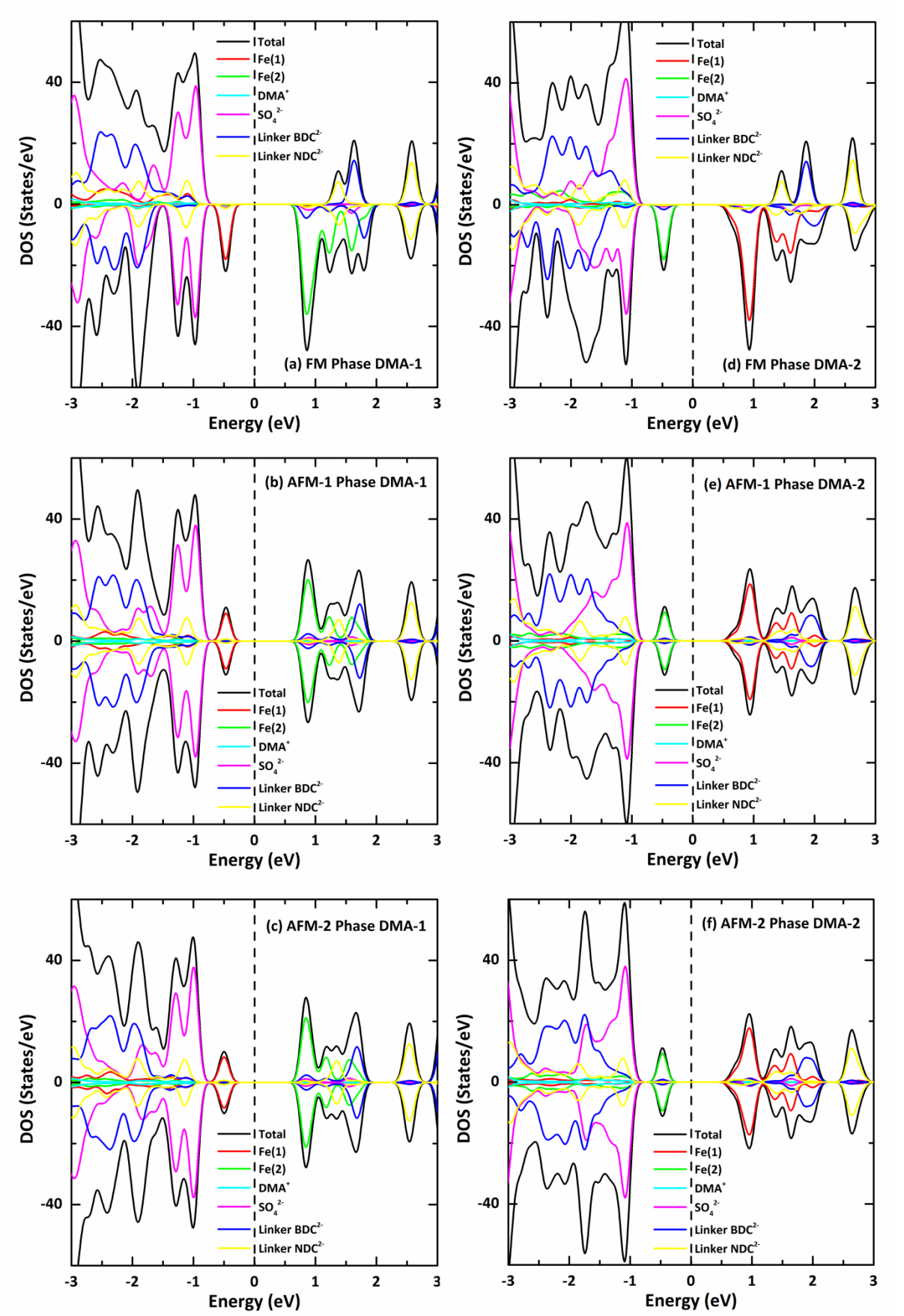

Figure S2. Partial Density of State (PDOS) of (a) FM, (b) AFM-1, (c) AFM-2 of phase DMA-1 and (d) FM, (e) AFM-1, (f) AFM-2 of phase DMA-2 of VNU-15 using GGA+U, where the top and bottom sides are for the up- and down-spins, respectively. The dotted line represents the Fermi level.

To further understand the nature of band structure, the total DOS of VNU-15 and the partial DOS of ions around the Fermi energy E_F in different magnetic configurations were examined, as displayed in Figure S2. In all magnetic configurations, the valence and conduction band for DMA-1 shows mainly Fe(1) and Fe(2) 3d orbitals contributions, respectively, whereas the situation is opposite for DMA-2. The low-lying band (below the valence band) is mainly centered on the orbitals of the $SO4^{2-}$ ions for both phases. The spin-polarized TDOS clearly displays a nearly symmetric feature in the spin-up and spin-down states for AFM configurations. On the other hand, in case of the ferromagnetic spin configuration, a remarkable difference between majority and minority spin is observed.

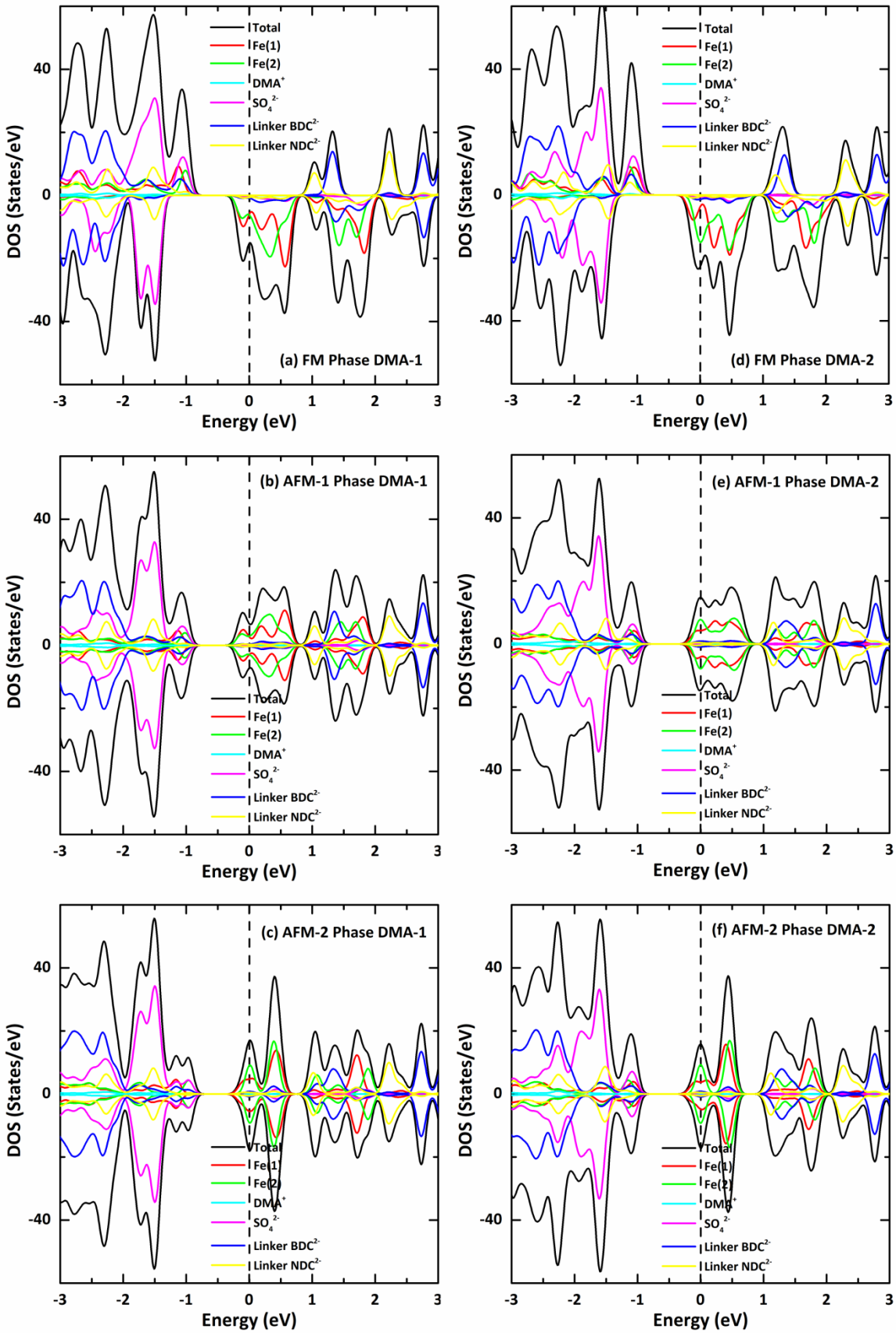

Figure S3. Partial Density of State (PDOS) of (a) FM, (b) AFM-1, (c) AFM-2 of phase DMA-1 and (d) FM, (e) AFM-1, (f) AFM-2 of VNU-15 using GGA (collinear) calculations, where the top and bottom sides are for the up- and down-spins, respectively. The dotted line represents the Fermi level.

Section S2. Effective masses

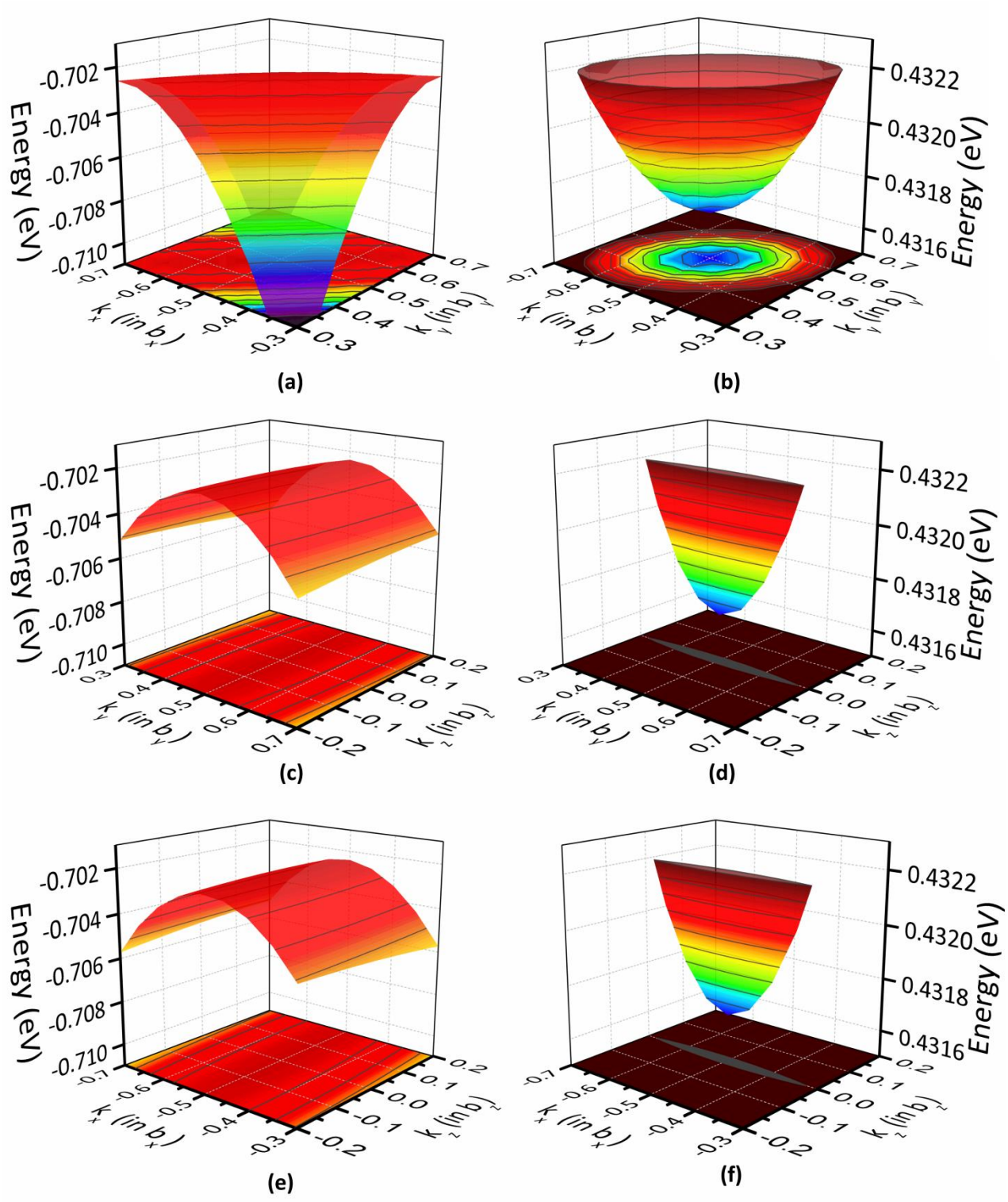

Figure S4. Three dimensional band structure for AFM-2 of phase DMA-2 of VNU-15 in majority spin. (a), (b), (c) the valence band in the $\boldsymbol{k_x - k_y}$, $\boldsymbol{k_y - k_z}$, $\boldsymbol{k_x - k_z}$ plane, respectively. (d), (e), (f) the conduction band in the $\boldsymbol{k_x - k_y}$, $\boldsymbol{k_y - k_z}$, $\boldsymbol{k_x - k_z}$ plane, respectively. The chosen k-points are all centered at S point.

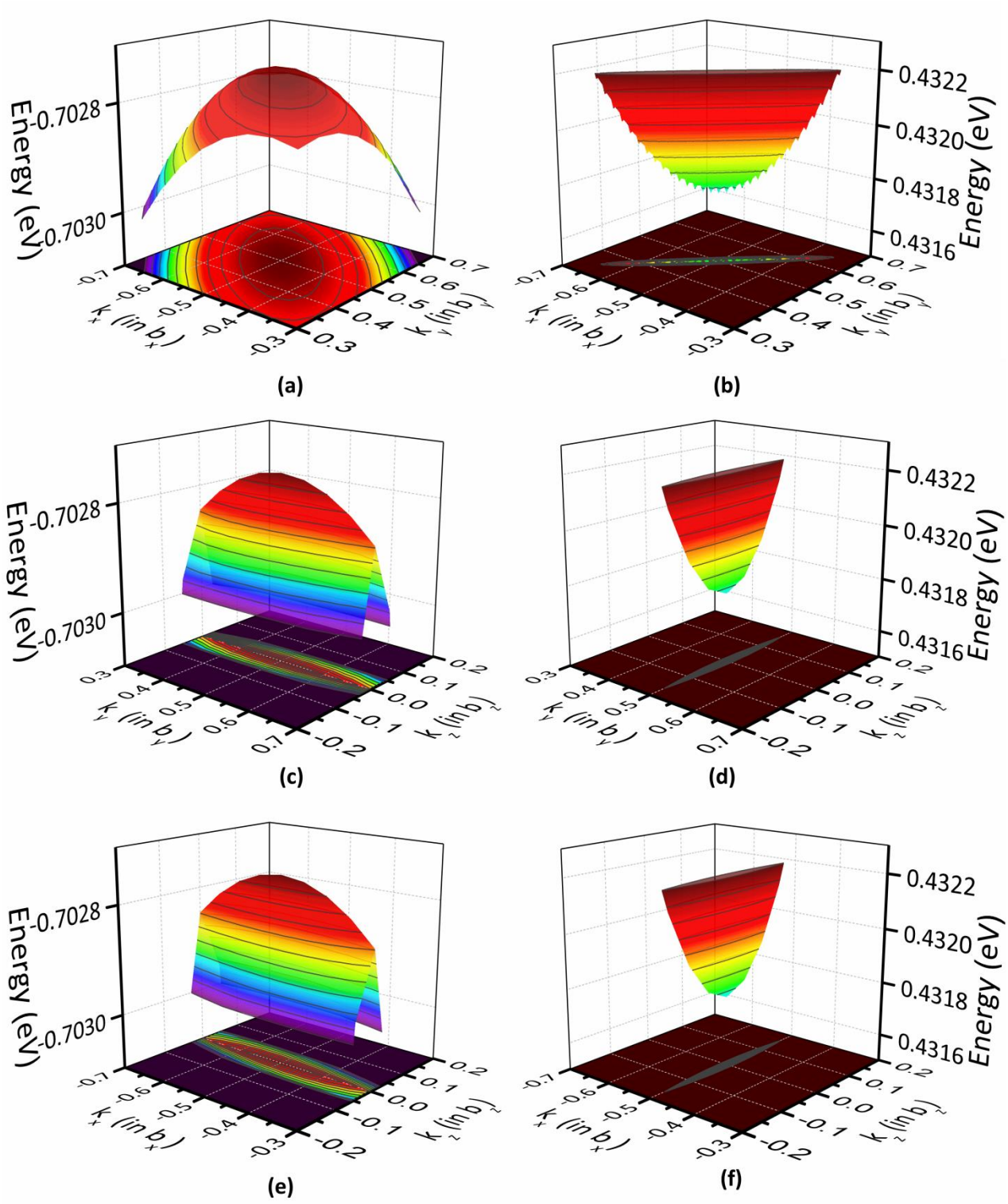

Figure S5. Three dimensional band structure for AFM-2 of phase DMA-2 of VNU-15 in minority spin. (a), (b), (c) the valence band in the $\boldsymbol{k_x - k_y}$, $\boldsymbol{k_y - k_z}$, $\boldsymbol{k_x - k_z}$ plane, respectively. (d), (e), (f) the conduction band in the $\boldsymbol{k_x - k_y}$, $\boldsymbol{k_y - k_z}$, $\boldsymbol{k_x - k_z}$ plane, respectively. The chosen k-points are all centered at S point.

Section S3. Structural Data

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