Supplemental Material

In Figure 7 we monitored the DOS transition in the 3d period, and in Figure 8 total DOS at E_F was given for both 3d and 4d periods, but information for 5d period was not supplied because there are only three mechanically stable 5d pernitrides, HfN_2, IrN_2 and PtN_2. We provide below in Figure A, the DOS of the adjacent IrN_2, PtN_2 and AuN_2 (unstable) in 5d period. We can see the reason why PtN_2 is a semiconductor but neither IrN_2 nor AuN_2. It is the left shift and width-narrowing behavior of DOS, placing a gap of states at the E_F of PtN_2.

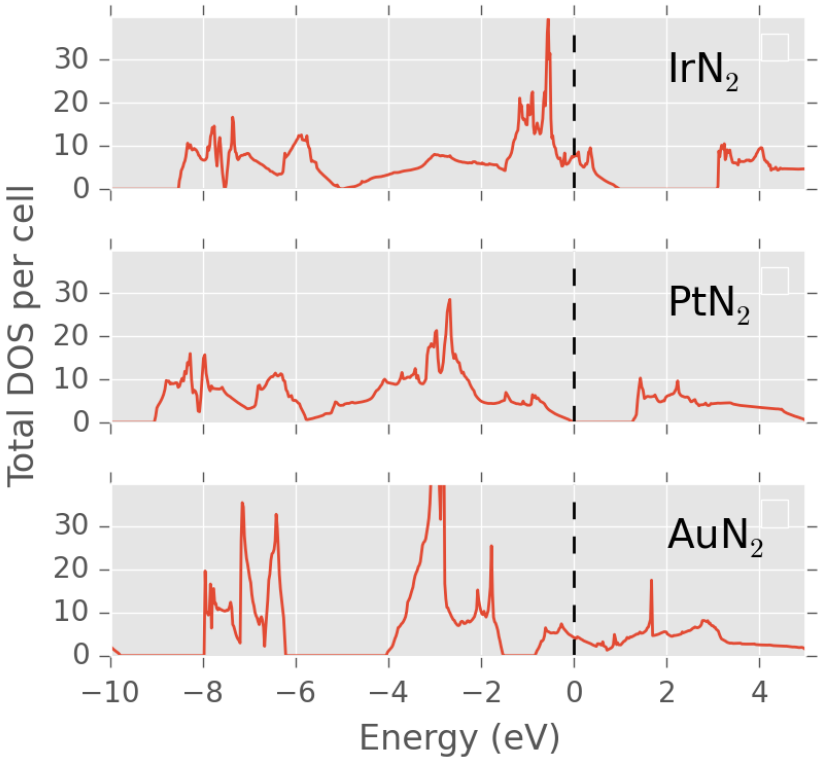

Figure A. Total density of states of pyrite-type IrN_2, PtN_2 and AuN_2.

Looking at the data by group number, in Figure 8, we see Group 10 metal pernitrides NiN_2 (3d), PdN_2 (4d) and PtN_2 (5d) having small values of total DOS at E_F. In Figure 7 there is a DOS plot for NiN_2 and there is a small notch between the two peaks at E_F; there is no gap, so it might not be appropriate to call it a semiconductor. But if we look at the cases of PdN_2 or PtN_2 in Figure B provided below, our calculations show that they are semiconductors with band gaps. The same situation goes for Group 4 pernitrides TiN_2, ZrN_2 and HfN_2 in Figure C, where E_F of TiN_2 lies in the valley between two peaks, but both ZrN_2 and HfN_2 are semiconductors.

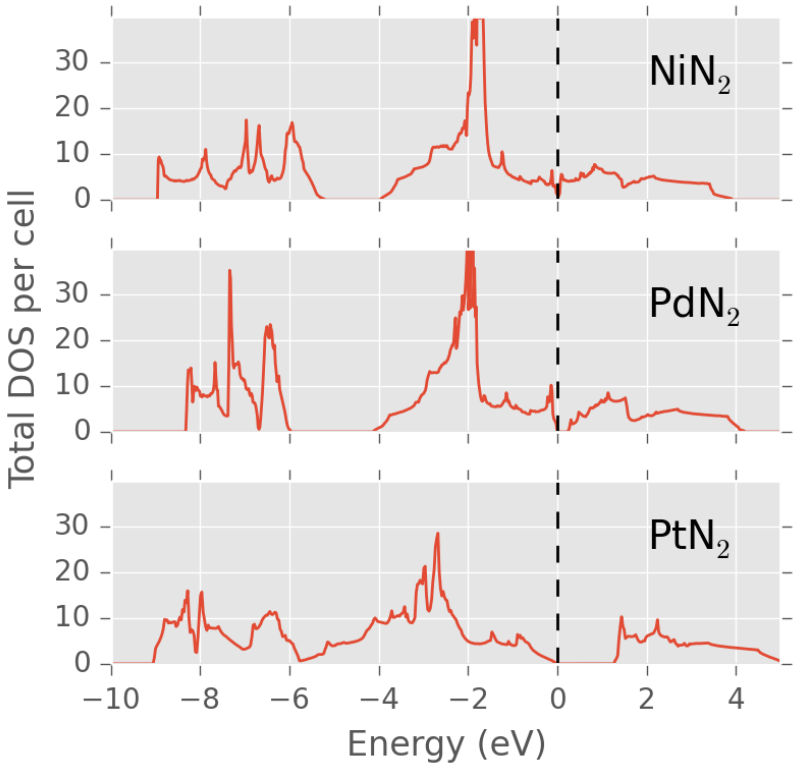

Figure B. Total density of states of pyrite-type NiN_2, PdN_2 and PtN_2.

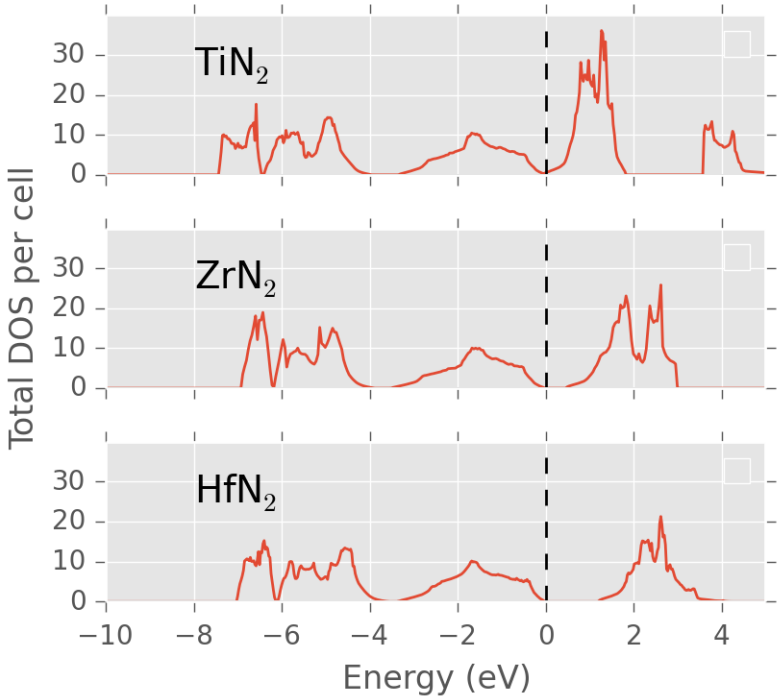

Figure C. Total density of states of pyrite-type TiN_2, ZrN_2 and HfN_2.

Summarizing the above, as the transition metal choice moves in the periodic table, the pernitride demonstrates metallic or non-metallic behavior, depending on the relative

position of E_F in DOS. This formation of the electronic band gap for a specific compound such as PtN_2 within the class of all structurally isomorphic transition metal pernitrides is determined by the correct appearance of E_F within the gaps between two energy bands available for filling electrons. These bands get filled as one adds one electron as the group number of the transition metal atom increases by one. The precise location of E_F on the energy x-axis of a figure like Figure 7 can only be obtained by detailed fully quantum mechanical computations as we have performed. Semiconductors can show up in various group numbers, and certainly can be analyzed along with metallic phases. The rules we are aiming to formulate apply to both.