Electronic Structure of Germanium Phosphide Monolayer and Li-diffusion in Its Bilayer

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Description 1: Li-diffusion along *a* direction on the GeP monolayer

Here, we investigated the Li diffusion along the *a* (//X) direction. It will be quite reasonable to assume that the diffusion follows stepwise paths along the hollow sites in Figure 2, i.e., A → B → E → C → F → D → A, repeatedly. Figure 4 shows that the activation barriers are 0.09, 0.34, 0.08, 0.12, 0.04, and 0.01 eV for steps A → B, B → E, E → C, C → F, F → D, and D → A, respectively. We note that site E practically corresponds to the saddle point. Therefore, the rate-determining step is B → C, and the activation barrier (E_a) for the diffusion along the *a* axis is 0.43 eV. In turn, the barrier is inaccessible at room temperature, because the Boltzmann factor corresponding to the fraction of Li atoms with the barrier is only 5×10^{-8}. In short, the Li atoms cannot diffuse along the armchair path on the monolayer.

Description 2: Li-diffusion path P_b^1 in the interlayer region of GeP bilayer

Considering that site A is the most stable for the monolayer, we began our discussion on four nonequivalent steps to adjacent sites starting from site A_1F_2, i.e., $A_1F_2 \to B_1T_2$, $A_1F_2 \to D_1T_2$, $A_1F_2 \to T_1C_2$, and $A_1F_2 \to T_1D_2$. Our NEB calculation shows that the diffusion occurs along the first path exclusively, considering that their activation barriers are 0.24, 0.52, 0.53, and 0.57 eV, respectively. [Here, we recall that $A_1F_2 \to D_1T_2$ and $A_1F_2 \to T_1D_2$ steps are inequivalent, although D_1T_2 and T_1D_2 sites are equivalent.] Next, there are again four inequivalent steps from B_1T_2 to adjacent sites, i.e., $B_1T_2 \to A_1F_2$, $B_1T_2 \to E_1E_2$, $B_1T_2 \to T_1C_2$, and $B_1T_2 \to T_1D_2$, for which barriers are 0.07, 0.35, 0.37, and 0.71 eV, respectively. Therefore, the preferred path will be $A_1F_2 \to B_1T_2 \to A_1F_2$ repeatedly with barriers of 0.24, 0.07, and 0.24 eV, as shown in Figure 6(a).
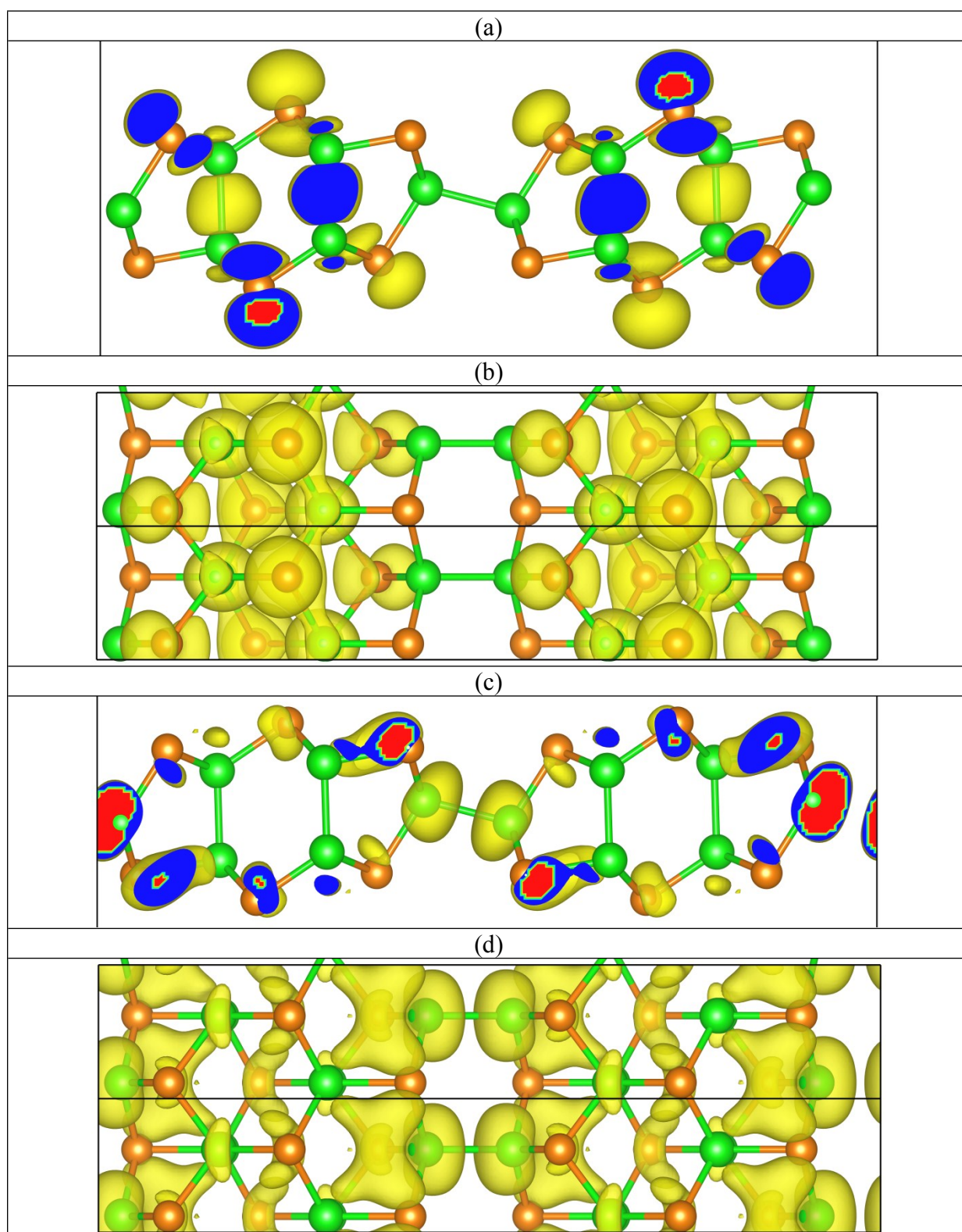
Description 3: Alternative Li-diffusion paths connecting P_b^1 to P_b^2 in the interlayer region of GeP bilayer

Next, we focused on various paths connecting $P_b{}^1$ to $P_b{}^2$ staring from B_1T_2. Its first step will be $B_1T_2 \rightarrow E_1E_2$, considering that its barrier is comparable to that for graphene bilayer. There are also four inequivalent steps from E_1E_2: $E_1E_2 \rightarrow T_1B_2$, $E_1E_2 \rightarrow B_1T_2$, $E_1E_2 \rightarrow C_1T_2$ and, $E_1E_2 \rightarrow T_1C_2$, for which barriers are 0.19, 0.20, 0.28, and 0.30, respectively, indicating that all of them are accessible. This is because their activation barriers are lower than or comparable to that (= 0.34 eV) for graphite. Now, we can define alternative paths connecting $P_b{}^1$ and $P_b{}^2$ paths. The one with the lowest barrier is denoted by $P_{a1}{}^1$: $B_1T_2 \rightarrow E_1E_2 \rightarrow T_1B_2$, for which stepwise barriers of 0.35 and 0.19 eV are certainly higher than those for a set of paths P_b by at least 0.11 eV. Consideration of the Boltzmann factor suggests that the diffusion from $P_b{}^1$ to $P_b{}^2$ along the a axis through $P_{a1}{}^1$ will be ~100 times slower than those along the b axis. It is clear that there are other less accessible paths connecting $P_b{}^1$ to $P_b{}^2$ in terms of the activation barriers comparable to that for graphite bilayer, such as $B_1T_2 \rightarrow E_1E_2 \rightarrow C_1T_2 \rightarrow F_1A_2$.
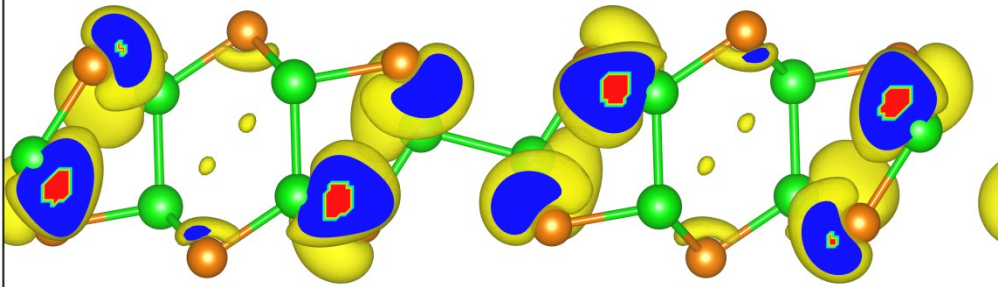
Description 4: an alternative Li-diffusion path connecting $P_b{}^2$ to $P_b{}^3$ in the interlayer region of GeP bilayer

For comparison, we have also considered another path staring from T_1B_2 instead. Along the same direction, there is only one inequivalent step: $T_1B_2 \rightarrow D_1T_2$, for which the barrier of 0.64 eV is even lager.
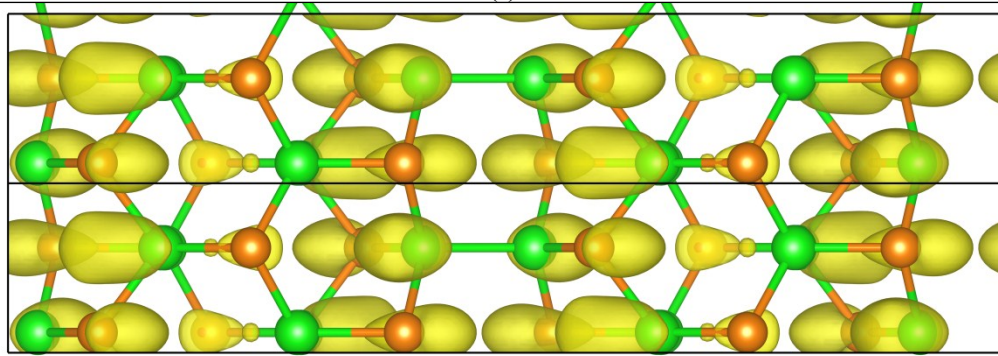
Figure S1. Two different views of the charge density plot for the VBM at S' point (a,b), the CBM at Y'' (c,d), the second CBM at the Γ points (e,f) , and the VB-1 at Γ (g,h). The brown and green colors represent phosphorus (P) and germanium (Ge) atoms, respectively.
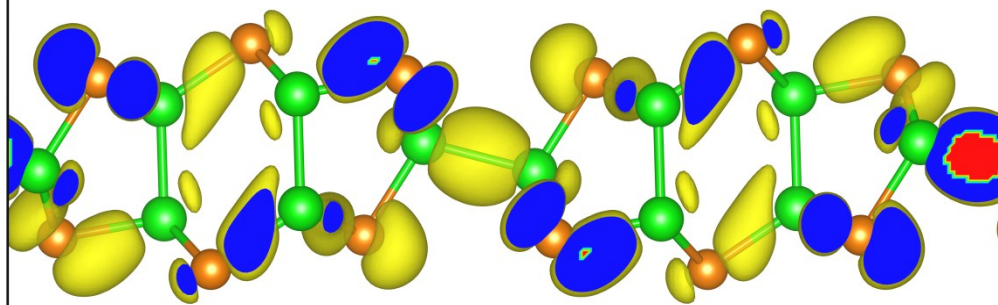
(e)

(f)

(g)

(h)