

Supplementary information of the role of point defects in PbS, PbSe, and PbTe nanomaterials: a *first principles* study

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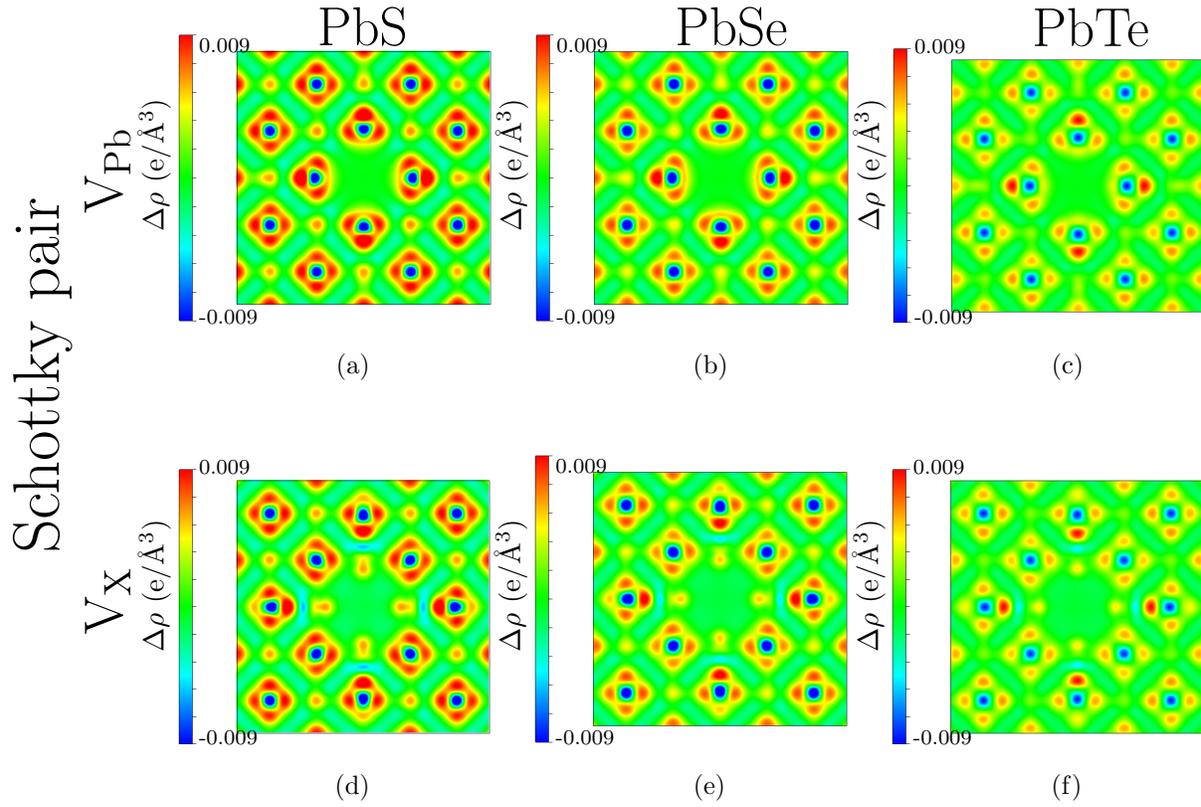


Figure 1. Charge density difference of PbX containing a Schottky dimer or a Schottky pair. Color red denotes charge accumulation, and color blue for charge depletion. The cross-section is the (100) plane for each system.

1. Introduction

In this Supporting Information (SI), we include the charge density difference of Schottky pair defects, and the detailed results of electronic structure calculations for V_{Pb} , V_{X} , the Schottky dimer and the Schottky pair.

2. Charge density difference of Schottky pair defects

The charge density difference of the Schottky pair is shown in Fig. 1. Due to the distant separation of the two vacancies, V_{Pb} and V_{X} in the Schottky pair configuration can be regarded as isolated vacancies and do not interact much with each other. Thus the pattern is very similar to those of the single V_{Pb} and V_{X} defects. But in the case of the Schottky pair, the charge polarization around V_{X} is stronger than around the V_{X} monovacancy, (Fig. 4 (i)–(l) in the main text).

3. Electronic structure

We first discuss the electronic structure of perfect PbX systems before introducing the defect states. Since the electronic structures of PbS, PbSe and PbTe are similar (see for instance, the band structures of PbX calculated in Ref. [1]), we use PbS as an example to describe the characteristics of the electronic structures of perfect PbX crystals. The band structure, total density of states (TDOS), and projected density of states of the Pb atom and the S atom of primitive PbS are presented in Fig. 2. For a clearer description of the position of the bands, the Fermi level is set as zero energy. The band structure and DOSs can be categorized into three parts: semicore, valence, and conduction bands. In the semicore region, we have the S 3s state at -12 eV to -13.5 eV. In the valence window, we first have the Pb 6s state located at -9 eV to -6 eV. From -5 eV to VBM, the S 3p states overlap with mainly the Pb 6p states and the 6s state. It is noteworthy that the Pb 6s state is splitted into two peaks, one located at the bottom of the valence region, and one at the top, with an energy gap of around 3 eV. This is attributed to the interaction between the Pb 6s state and S 3p states, and corresponds respectively to the bonding and anti-bonding orbitals of these two states. The conduction bands are mainly composed of the Pb 6p states, with a slight overlap with the S 3p states. Therefore, it is expected that the defect states appearing in the band structures are related to the defect-induced perturbation of the Pb *s* and *p* states and the S *p* states.

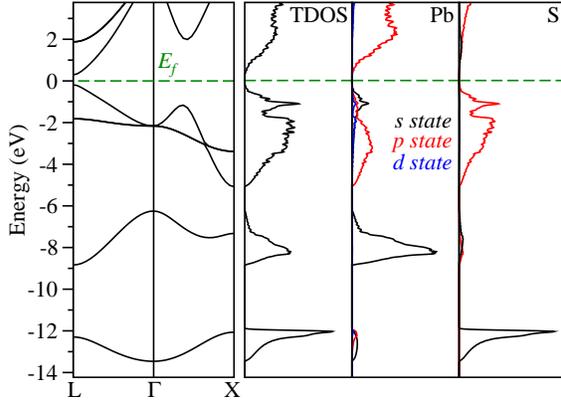


Figure 2. Bandstructure, total DOS (TDOS), and projected DOS of Pb atom and S atom of the PbS primitive cell. Fermi level is shifted to energy origin and is indicated as the dark green dashed line.

The electronic structures studied are the V_{Pb} , V_{O} , Schottky dimer and Schottky pair defects. The considered band structures of PbX are along the $L \rightarrow \Gamma \rightarrow X$ direction in the Brillouin zone. The DOS plots show the band gap region. Bandstructures are displayed in Fig. 3 to Fig. 6, and DOSs in Fig. 7 and Fig. 8. The DOS of defective systems are more smeared comparing to the ones of perfect systems. This is because the

presence of defects leads to additional dispersion. One remarkable observation is that only the V_X states cause a significant change in the electronic structure of PbX systems; V_{Pb} hardly modifies the original band structures. This finding echoes Slater's statement which said that in alkali halides the valence band and conduction band are dominated by the anion p states and s states, respectively[2, 3]. In other words, the chemical properties of alkali halide systems is determined by the anions. When comparing with Fig. 2, it is clear that at the top of valence band and at the bottom of conduction band, there are significant contributions from the Pb p and s states, and Slater's finding still applies to the partially-ionic PbX systems as the S p states also participate largely in the VBM region and partly in the conduction band.

In order to visualize more clearly the electron distribution of the defect states, the partial charge density corresponding to the defect states were also calculated and are plotted in Fig. 9 for V_{Pb} and V_X , and in Fig. 10 for the Schottky dimer and Schottky pair configurations.

Concerning the band structure of the PbX systems, we need to note two facts: 1) the symmetry of the system is broken because due to the presence of defects, thus the dispersion curves are changed. 2) In our calculations, the concentration of defects is around 0.5%, which is still considerably higher than the real concentration in experimental conditions. As a result, the defect states are rather dispersive. Because of these two concerns, we consider mainly the band structure at the L point.

3.0.1. V_{Pb} By combining Fig. 3 and 7, one can see the electronic structure change of PbX upon the presence of V_{Pb} . The presence of the defect causes a downward shift to the Fermi levels such that the Fermi levels pass through the VBM. The location of the V_{Pb} defect state at the L point is beyond the Fermi level. Based on the projected wave function analysis, we found that the V_{Pb} defect states at the L point have zero occupancy, thus they are p -type defect states consisting of two holes. The wave function analysis also shows that this defect state is composed of three degenerate states, and each of these states have some Pb s character, and p character from the X atoms. Furthermore, the three X p states interacting with the Pb s state have the same magnitude, reflecting the spherical symmetry of the Pb $5s$ state which interacts with the p_x, p_y and p_z orbitals of X atoms to the same extent. The partial charge density of V_{Pb} is shown in Fig. 9, and the s - p interaction is also confirmed as the NN X p charge density and the NNN Pb s charge density are both polarized towards each other. However, the results of Ref. [4] and [5] for V_{Pb} in PbTe only attribute the V_{Pb} state to the $5p$ orbitals of the NN Te atoms.

3.0.2. V_X In Figures 4 and 8, one can see the electronic structure change of PbX due to the presence of V_X . Contrary to the V_{Pb} states, V_X will cause Fermi levels to undergo an upward shift. For PbS and PbSe, the Fermi level penetrates the VBM, while for PbTe, the Fermi level is shifted to above the VBM. The wavefunction analysis shows that the occupancy of the V_X defect state is a singlet doubly occupied state, with two

electrons coming from NN Pb p orbitals, as shown in Fig. 9. This makes the V_X n -type. Our results are in good agreement with the results of Ref. [4] and [5].

3.0.3. Schottky dimer and Schottky pair Schottky dimer and Schottky pair systems give rise to both V_{Pb} and V_X defect states. In these two cases, the Fermi level is almost fixed at the original position because of the presence of V_{Pb} and V_X . This is Fermi level pinning, where the two electrons at the V_X state and the two holes at V_{Pb} are present in combination. As a result, the Fermi level is pinned at the original place because of the unchanged net carrier concentration. The wavefunction analysis confirms the argument that in the Schottky defects, the two electrons originally occupying the V_X state are now transferred to the V_{Pb} state.

It is noteworthy that with decreasing inter-vacancy distance, the position of the V_X state shifts closer towards the CBM. That is, if we define $\Delta E = E(CBM) - E(V_X)$, then $\Delta E(V_X) > \Delta E(\text{Schottkypair}) > \Delta E(\text{Schottkydimer})$.

We present the partial charge density for the V_{Pb} and V_X states in Schottky configurations in Fig. 10. The partial charge densities for V_{Pb} and V_X in the Schottky pair are identical to their counterparts in perfect PbX systems. This implies that there is not a significant interaction between the two vacancy sites. However, the picture of the Schottky dimer is more complex because of the interaction between the next-neighbor V_{Pb} and V_X vacancies. For V_{Pb} in the Schottky dimer, the charge density located on the NN X atoms is polarized towards the V_X site (which also confirms that now the V_X site is electron deficient). At the V_X site, the charge density from the V_{Pb} site is lacking. And the charge density at the NN Pb atoms of V_X is slightly polarized toward the V_{Pb} site.

For all the four abovementioned defect configurations, the degree of charge redistribution is inversely proportional to the size of X anions; the larger the X anion, the less its electronegativity, thus less the charge redistributes. This finding echoes the discussion we gave in the main text.

4. Derivation of the free energy

The number of configurations at thermal equilibrium Ω is defined as

$$\Omega = \frac{n!}{n_d!(n - n_d)!}, \quad (1)$$

where n is the the total number of atoms and, n_d is the number of defects. The entropy of the system is given by

$$S = k_B \ln \Omega, \quad (2)$$

After substituting Eq. 1 into Eq. 2, and defining $x_d = \frac{n_d}{n}$ as the equilibrium defect concentration, we obtain the expression of entropy S in terms of x_d

$$S = -k_B n (x_d \ln x_d + (1 - x_d) \ln 1 - x_d), \quad (3)$$

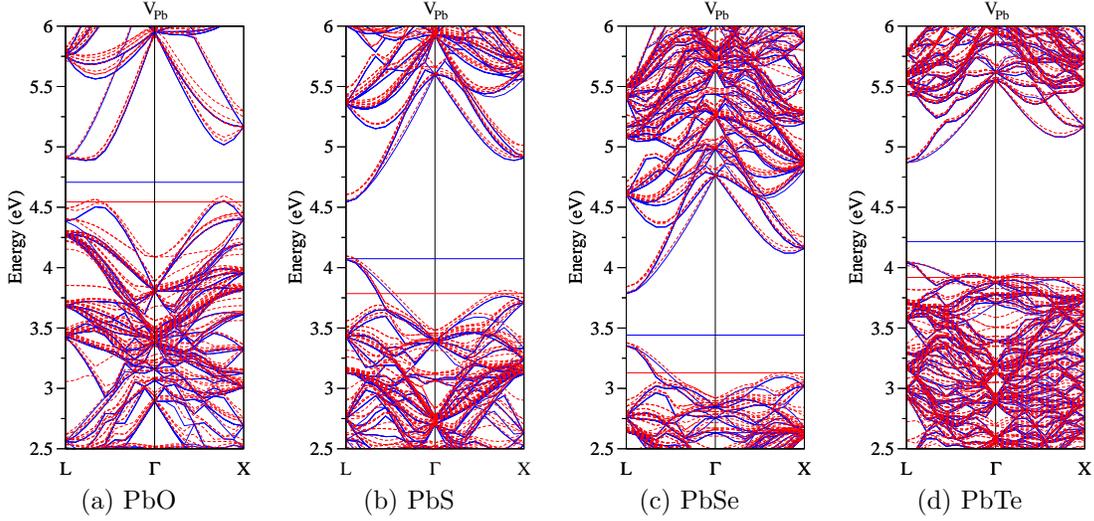


Figure 3. Band structure of PbX supercells containing a V_{Pb} , as shown in red dotted lines. Band structure of perfect PbTe is shown in dotted blue lines. The solid red and solid blue lines are Fermi levels of the defective and perfect supercells, respectively.

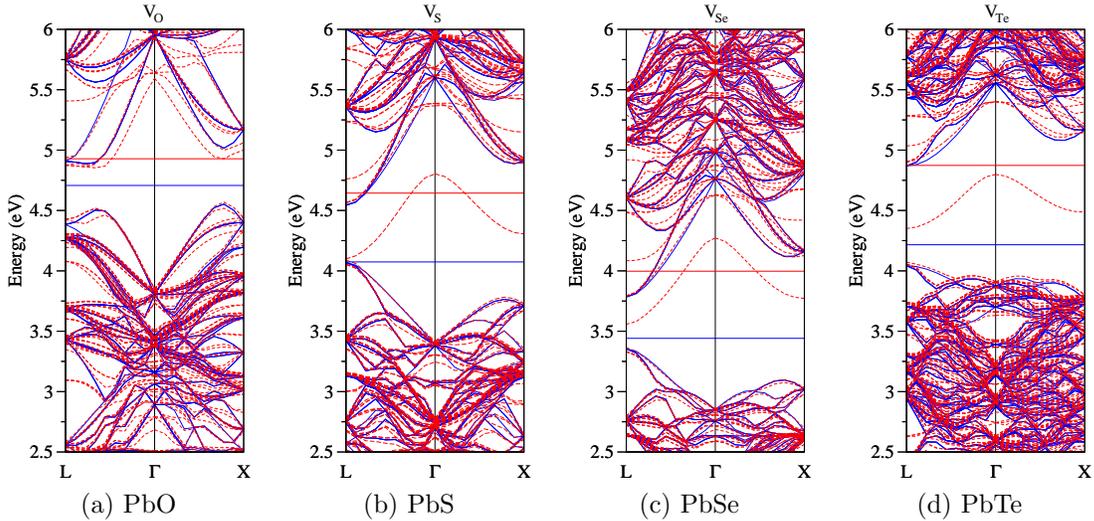


Figure 4. Band structure of PbX supercells containing a V_O , as shown in red dotted lines. Band structure of perfect PbTe is shown in dotted blue lines. The solid red and solid blue lines are Fermi levels of the defective and perfect supercells, respectively.

The free energy is defined as

$$F = U - TS, \quad (4)$$

where U is the enthalpy, and T is temperature in K . At pressure of zero Pa, U is equal to the sum of the formation energy of every defect, $n_d E_d$. Thus, Eq. 4 can be rewritten as

$$F = n_d E_d + nk_B T [X_d \ln X_d + (1 - X_d) \ln (1 - X_d)]. \quad (5)$$

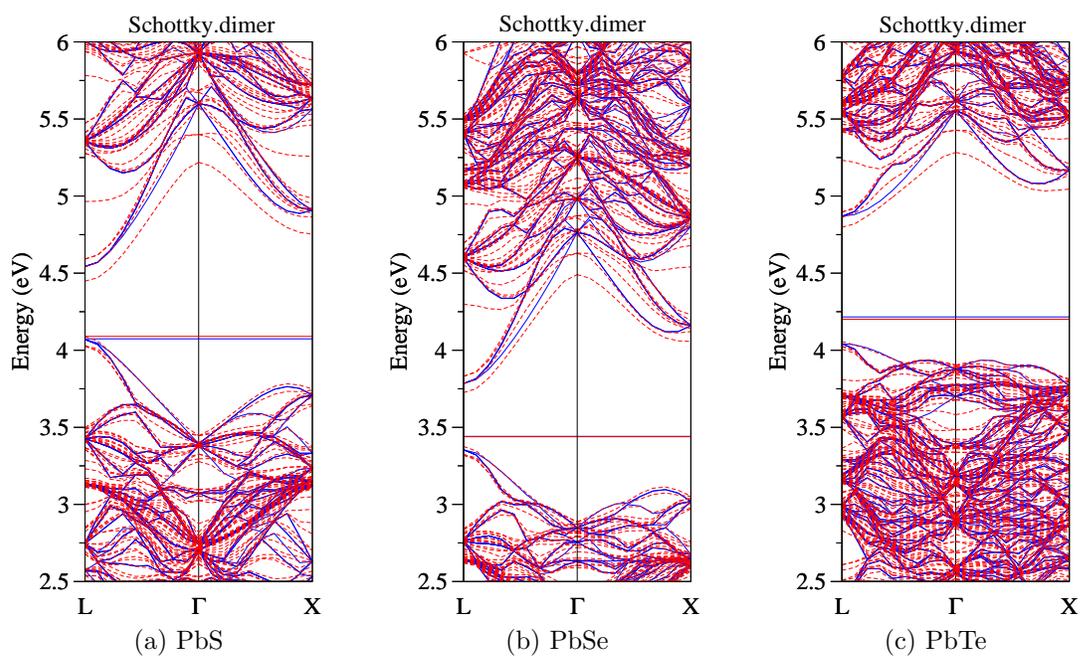


Figure 5. Band structure of PbX supercells containing a Schottky dimer, as shown in red dotted lines. Band structure of perfect PbTe is shown in dotted blue lines. The solid red and solid blue lines are Fermi levels of the defective and perfect supercells, respectively.

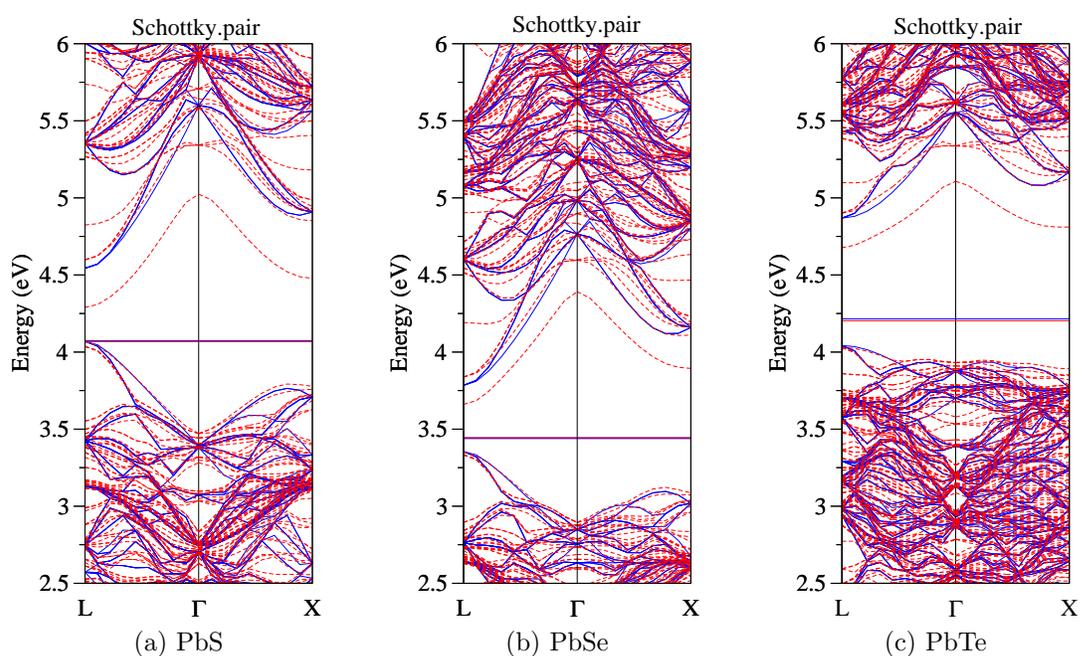


Figure 6. Band structure of PbX supercells containing a Schottky pair, as shown in red dotted lines. Band structure of perfect PbTe is shown in dotted blue lines. The solid red and solid blue lines are Fermi levels of the defective and perfect supercells, respectively.

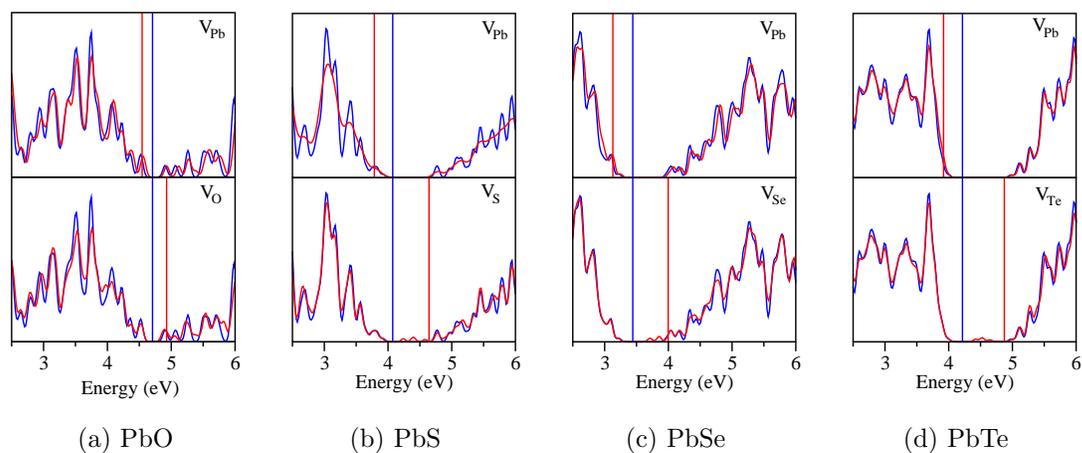


Figure 7. Density of states (DOS) of PbX supercells containing a Pb vacancy or a X vacancy. The red dotted curve and blue dotted curve are DOS of defective supercell and perfect supercells, respectively.

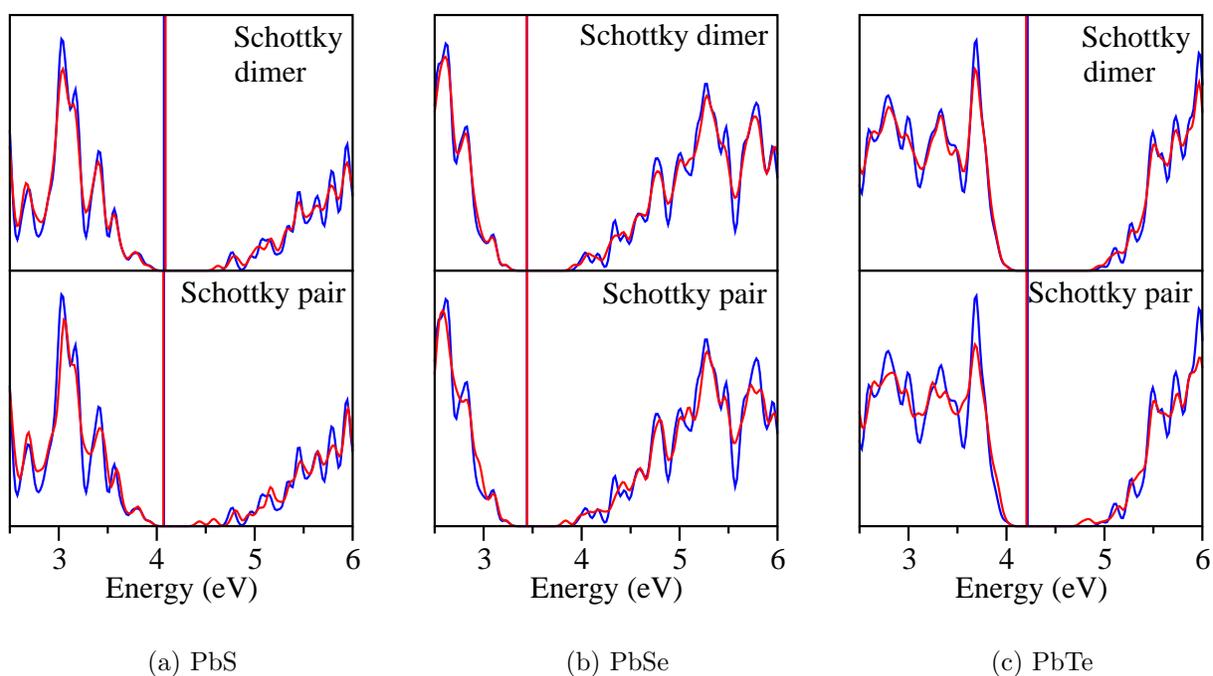


Figure 8. Density of states (DOS) of PbX supercells containing a Schottky dimer or a Schottky pair. The red dotted curve and blue dotted curve are DOS of defective supercell and perfect supercells, respectively.

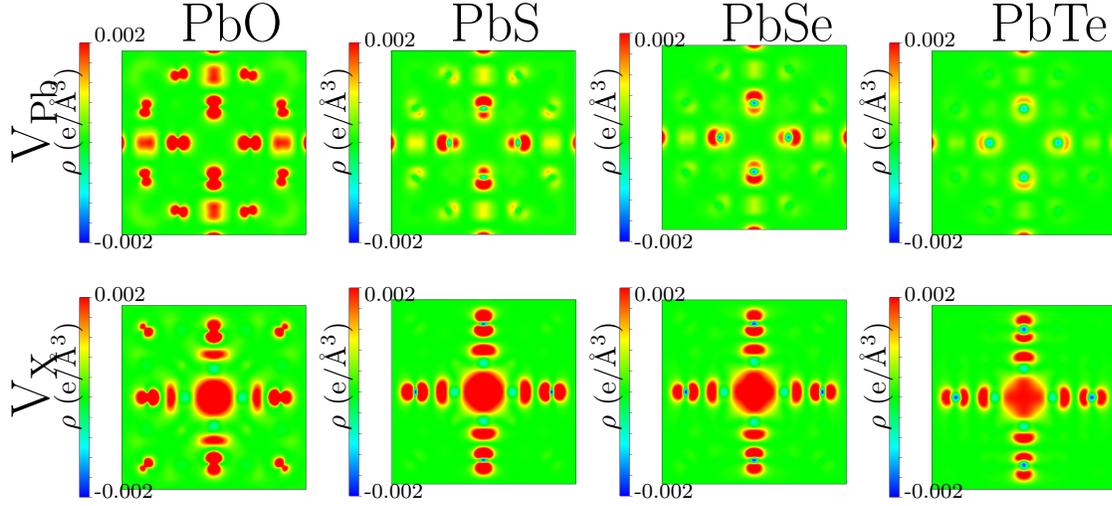


Figure 9. Partial charge density of the defect states at L point of V_{Pb} and V_X of PbX . Color red denotes charge accumulation, and color blue for charge depletion. The cross-section is the (100) plane for V_{Pb} , and (001) for V_X . The band of the defect state was specifically selected

Finally, the free energy per atom f is

$$f = \frac{F}{n} = x_d E_d + k_B T (x_d \ln x_d + (1 - x_d) \ln(1 - x_d)). \quad (6)$$

Hence, by determining the x_d for which f is at the minimum, the equilibrium defect concentrations at different temperatures can be found.

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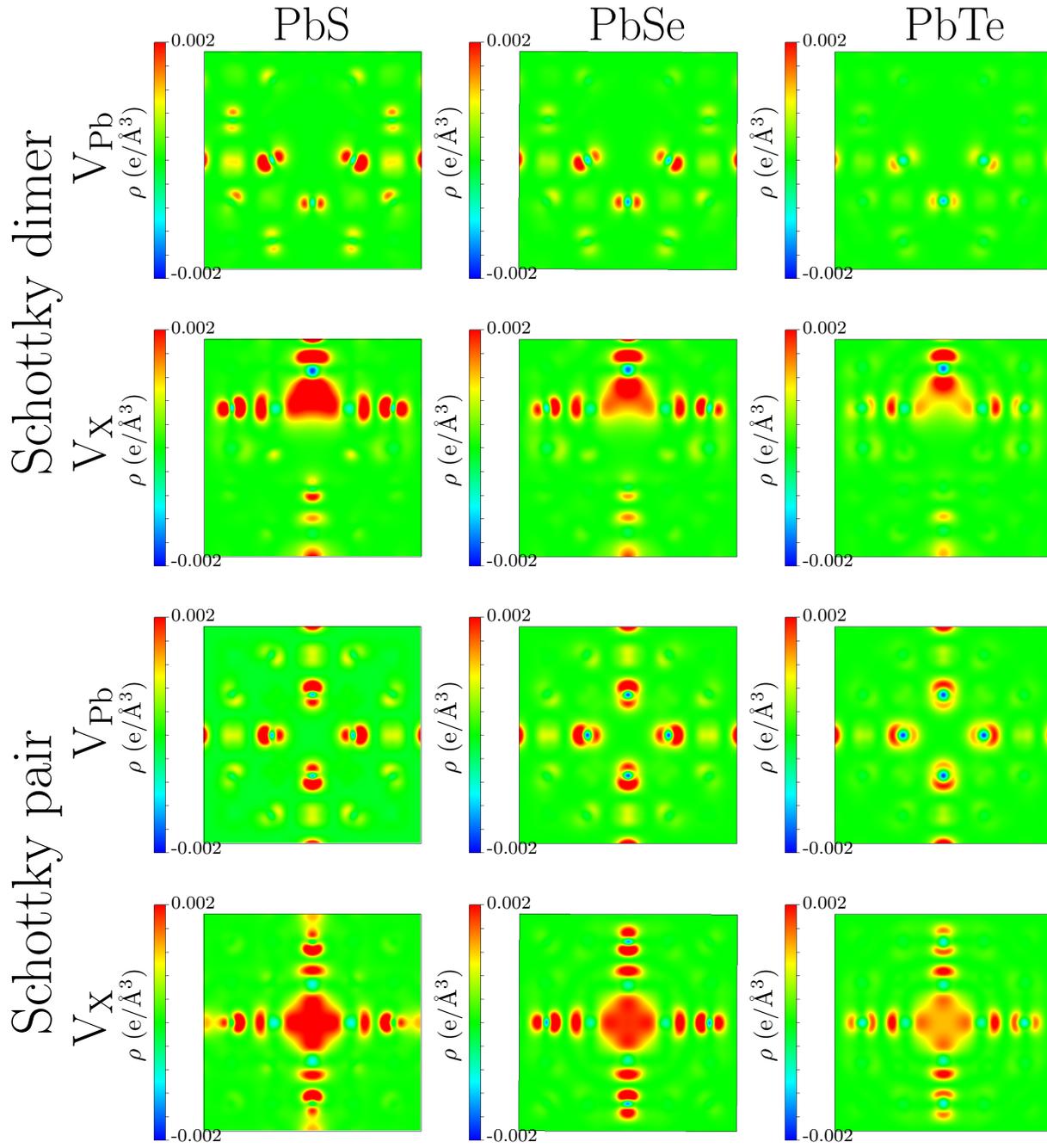


Figure 10. Partial charge density of the V_{Pb} and V_X defect states at L point for Schottky dimer and Schottky pair defects in the PbX systems. Color red denotes charge accumulation, and color blue for charge depletion. The cross-section is (100) for all the systems.