Theoretical study of the phosphorus vacancy in ZnGeP₂

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First-principles calculations are presented for the phosphorus vacancy Vₚ in ZnGeP₂, using full-potential linearized muffin-tin orbital supercell local density functional theory calculations. We find the Vₚ to have a high energy of formation compared to the Ge₂Zn antisite donor in Zn-poor material. Including a band gap correction to the Hamiltonian, the defect is predicted to be amphoteric with a donor +0 level at 0.6±0.1 eV and an acceptor 0− level at 1.25±0.1 eV above the valence band maximum.

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ZnGeP₂ is an important material for nonlinear optical frequency conversion with target wavelengths in the mid-infrared. Point defects play an important role in the efficiency of the material for these applications. However, the defects in ZnGeP₂ has not yet been thoroughly studied. Experimentally, a number of defect centers have been identified using electron paramagnetic resonance (EPR) and optically activated EPR. While the dominant defect in ZnGeP₂, present in as-grown samples is the V₂Zn acceptor, which is EPR active in the single negative charge state, two compensating donors have been found under optical activation: the Ge₂Zn antisite and the phosphor vacancy Vₚ. The material is usually strongly compensated but it is presently not clear which of these two donors is the most abundant. The EPR spectrum of the neutral phosphorus vacancy has been observed in as-grown ZnGeP₂ during illumination at low temperatures. Without illumination, the phosphorus vacancy is in a nonparamagnetic ionized state (Vₚ⁺). Subsequently, Gehlhoff et al. and Giles et al. used photoinduced EPR to investigate as-grown, postgrowth annealed, and electron irradiated ZnGeP₂ crystals to obtain information on the related defect energy levels. In particular, the Vₚ⁺ center becomes active above an optical excitation energy of 0.64 eV, suggesting a position of the energy Vₚ⁺/0 transition state at this energy above the valence band maximum. No other experimental or theoretical information is presently available to confirm this energy level.

On the computational side, there have been only a few studies. Zapol et al. presented an atomistic study using classical inter-atomic potentials. In a previous paper, we presented a first-principles study of the cation related defects V₉Zn, V₉Ge, Ge₂Zn, and Zn₉Ge. Here, we present results for the Vₚ and discuss its relation to the other previously studied defects.

We use a full-potential linearized muffin-tin orbital (FP-LMTO) method, which allows us to relax the structure around the defects by minimizing the total energy with a conjugate gradient method using analytically calculated forces. Density functional theory (DFT) in the local density approximation (LDA) is the underlying theoretical framework for our calculations. The FP-LMTO method used here has been shown in several cases to yield results comparable in accuracy to the well-known full-potential linearized augmented plane wave (FLAPW) or other all-electron methods. Although it uses a smaller basis set, the basis set is highly optimized by using smoothed Hankel function spherical waves in the interstitial region centered on muffin-tin spheres, augmented in the usual way inside the spheres in terms of solutions of the Schrödinger equation for the spherical part of the actual potential inside the sphere, and their energy derivative at some chosen energy. The smoothing of the Hankel functions adjusts the curvature of the basis functions in the region just outside the muffin-tin sphere. Fast Fourier transform techniques are used to solve the Poisson equation for the smooth part of the potential and to calculate the matrix elements of the Hamiltonian and overlap matrix while structure constant expansions are used for the sphere contributions. A double basis set with two sets of Hankel function decay constants and Gaussian smoothing radii per angular momentum channel is used in our calculations and found to be adequately converged. To model the defect, a 64 atom supercell is used. A 2 × 2 × 2 mesh of k points is used during the relaxation of the atomic positions, and a 4 × 4 × 4 mesh of k points is used to recalculate more accurately the energy differences for the final optimized geometry. Charged states of the defect are dealt with by adding a neutralizing homogeneous background charge distribution. To deal with the electrostatic artifacts of charged point defects in periodic boundary conditions, we use Blöchl’s approach to correct the total energies.

Energy levels are obtained by a ΔSCF approach as energy differences between different charge state formation energies. The Gibbs free energy of a defect α is given by

\[ \Delta \Omega(\alpha,q) = E_w(\alpha,q) - E_w(0) - \sum_i \Delta n_i \mu_i + q \mu_e, \]

where \( E_w(\alpha,q) \), \( E_w(0) \) are the energies of the supercell containing the defect and that of the perfect crystal, respectively, and \( \Delta n_i \) is the change in number of atoms of a given species \( i \) in forming the defect and \( \mu_i \) their chemical potential. \( q \) is the charge state and \( \mu_e \) the chemical potential of the electron. \( \mu_e = E_{vbm} + E_F \) where \( E_{vbm} \) is the one-electron energy of the valence band maximum (VBM) of the perfect crystal relative to the average electrostatic potential far away from the defect in the defect containing supercell and \( E_F \) the Fermi level measured from the VBM and varies from zero to the band gap. As will be discussed later, however, the LDA underestimate of the band gap affects also the defect energy levels and an explicit correction for this effect will be included.
First, we establish the ranges of chemical potentials for the constituent elements assuming equilibrium with appropriate reservoirs. The chemical potential are restricted by the following equilibrium conditions: \( \mu_{Zn} + \mu_{Ge} + 2\mu_{P} = \Delta H_f(ZnGeP_2) \), representing equilibrium with ZnGeP_2, \( 3\mu_{Zn} + 2\mu_{P} = \Delta H_f(Zn_3P_2) \), \( \mu_{Ge} + \mu_{P} = \Delta H_f(GeP) \), required to prevent the formation of Zn_3P_2 and GeP, respectively, and \( \mu_{Zn} < 0 \), \( \mu_{Ge} < 0 \) and \( \mu_{P} < 0 \) to prevent precipitation of the elemental solids. Note that all chemical potentials here are actually “excess chemical potentials” with the zero reference level defined to correspond to the energy per atom in its elemental solid state. Using the first condition, we can choose two of the constituent elements as basic variables and eliminate the third. Whereas in the previous study of cation related defects, it was most convenient to pick \( \mu_{Ge} \) and \( \mu_{Zn} \) as basis variables because it allows us to discuss clearly the P-rich or P-poor limits. As a second variable we choose \( \mu_{Zn} \). Using experimental data \( \Delta H_f(ZnGeP_2) = -3.0 \text{ eV} \), \( \Delta H_f(Zn_3P_2) = -4.9 \text{ eV} \), \( \Delta H_f(GeP) = -0.22 \text{ eV} \), we can find the allowed ranges of Zn and P in ZnGeP_2, which are illustrated in Fig. 1.

Table I shows the energy of formation of the \( V_p \) in comparison with previously calculated point defects all in the neutral state under various chemical potential conditions. The labels A, B, C, D, E, and F refer back to Fig. 1. Clearly, the \( V_p \) is a high-energy defect. Even in the most P-poor Zn-rich condition, its energy of formation is 2.05 eV. As expected, as the system become richer in P and poorer in Zn the energy for formation increases. It is of particular importance to compare its energy of formation with that of the GeZn antisite because this is the only other donor among these defects. We can see that for conditions C and D, which are both P-poor and Zn-rich, the \( V_p \) energy of formation is slightly lower than the GeZn antisite. However, one usually expects ZnGeP_2 to be Zn-poor. Already for intermediate conditions like E and F, we see that the GeZn antisite has lower energy of formation than the \( V_p \) vacancy. Thus, one expects that under usual growth conditions, the dominant donor will be the GeZn antisite. Furthermore, the latter has a much shallower donor level.

In ZnGeP_2, the phosphorus atom is surrounded by two zinc atoms and two germanium atoms. In the perfect crystal, the distances among those atoms are almost the same, about 3.83 Å. After a phosphorus atom is removed, the relaxation shows the two zinc atoms move away from each other and from the vacancy. The distance between the two Zn now becomes 4.36 Å and they moved away from the vacancy by 0.33 Å. On the other hand, the two Ge atoms move inward toward the vacancy by 0.28 Å and the relaxed Ge-Ge distance is 3.37 Å. Still, we cannot interpret this as a Ge-Ge dimer formation since a typical Ge-Ge bond length for instance in bulk Ge is 2.45 Å.

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Next, we show the energies of formation of different charge states in Fig. 2. According to this figure, the \( V_p \) defect would be in the neutral charge state already when the Fermi level is at its lowest value, i.e., at the VBM. The crossing of the + and 0 energy of formation lines occurs in fact at 0.18 eV below the VBM. The above figure includes the Makov-Payne monopole correction. As is well known, however, the latter tends to somewhat overestimate the Coulomb interactions because it is based on a point charge model. As an opposite limit, we could ignore the Makov-Payne correction altogether. This would shift down the curve for the + charge state by 0.13 eV, in which case the +0 level would lie at –0.05 eV, i.e., closer to the VBM but still below the VBM. This would indicate the system is in the neutral charge state for as-grown p-type material. Experimentally, however, one finds that the EPR signal corresponding to the neutral \( V_p \) only occurs after illumination with photons of at least 0.64 eV.

Table I. Energies of formation of native point defects in ZnGeP_2 (in electron-volts) in the neutral state and for different values of the chemical potentials as indicated.

<table>
<thead>
<tr>
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<th>A</th>
<th>B</th>
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<th>D</th>
<th>E</th>
<th>F</th>
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<tbody>
<tr>
<td>( \Delta \Omega (V_p) )</td>
<td>4.83</td>
<td>4.93</td>
<td>2.38</td>
<td>2.05</td>
<td>3.44</td>
<td>3.83</td>
</tr>
<tr>
<td>( \Delta \Omega (V_{Zn}) )</td>
<td>0.47</td>
<td>1.71</td>
<td>3.25</td>
<td>3.25</td>
<td>1.86</td>
<td>2.28</td>
</tr>
<tr>
<td>( \Delta \Omega (V_{Ge}) )</td>
<td>4.01</td>
<td>2.95</td>
<td>3.68</td>
<td>4.01</td>
<td>4.01</td>
<td>3.02</td>
</tr>
<tr>
<td>( \Delta \Omega (Ge_{Zn}) )</td>
<td>3.35</td>
<td>1.14</td>
<td>0.24</td>
<td>0.57</td>
<td>1.96</td>
<td>0.73</td>
</tr>
<tr>
<td>( \Delta \Omega (Ge_{Zn}) )</td>
<td>-0.20</td>
<td>2.19</td>
<td>2.91</td>
<td>2.58</td>
<td>1.18</td>
<td>2.42</td>
</tr>
</tbody>
</table>
rounded by cations. In addition, we may expect that empty sphere band gaps by adding shifts to the cation-elements. Experience has shown us that we can adjust the wave function to localize on Zn atoms. The reason for this discrepancy is related to the LDA band gap problem. A study of the highest occupied defect orbital shows it to be localized primarily on the nearest neighbor Ge atoms, and two of the P atoms attached to these Ge, as shown in Fig. 3. In fact, the Ge atoms move inward to the vacancy from a normal Ge-P distance of 2.35 to 2.07 Å and the Zn move away from the vacancy from a Zn-P distance of 2.36 Å to 2.70 Å. This inward motion of the Ge also stretches the distance to one of its other P neighbors to 2.42 Å. The defect level thus has a mixed Ge and P atomic orbital character. One would expect a shallow donor level to shift along with the conduction band minimum (CBM). However, in this case, the donor level is very deep with a mixed valence band (P) and conduction band (Ge) derived character. We note that the defect wave function character differs from the conjecture of Giles et al., who state that they expect the wave function to localize on Zn atoms.

In order to determine how much the defect level shifts, we need to explicitly change the band gap by adding self-energy shifts to the Hamiltonian. We can do this most easily in the atomic sphere approximation (ASA) to the LMTO method. In the ASA LMTO, the “atomic orbital energies” are known as the center of the band potential parameter C_Ri. By shifting both the corresponding C_Ri and the linearization energy E_c, we basically add shifts to the diagonal Hamiltonian matrix elements. Experience has shown us that we can adjust the band gaps by adding shifts to the cation-s levels and the empty sphere s states of the empty spheres directly surrounded by cations. In addition, we may expect that the Zn d levels should be shifted down by quasiparticle self-energy effects and this will also contribute to the opening of the gap because the VBM is pushed up by its interaction with lower Zn d states. We thus first adjusted the band gap of pure ZnGeP₂ by adding a Zn d shift estimated from the Zn d band position in photoemission experiments for various Zn-VI compounds. Then, we added shifts to the cation and empty sphere s states so as to adjust the band gap to its experimental value of 2.2 eV. The same shifts were then used in the supercell calculations of the perfect and V_P containing crystal. We found that the highest occupied level at Γ [in other words, the highest occupied molecular orbital (HOMO)] of the defect system shifts by 0.7 eV relative to the next level below, while the lowest unoccupied molecular orbital (LUMO) shifts by 1.1 eV. Although we cannot really assign the lower level (HOMO-1) to the VBM, we can expect it to be unshifted like the VBM. In fact, from the total energy charge state calculations, we expect the VBM to be just above or at the HOMO level. We should note that the ASA calculation used an unrelaxed idealized geometry and in this case, the V_P does appear to induce a one-electron level in the gap, whereas in the FP-LMTO calculation, consistent with the ΔSCF calculation, no state appears clearly separated in the gap. This circumstance made it easier to recognize the defect one-electron level in the ASA calculation. The purpose of this ASA calculation is only to determine how much it is expected to shift by the gap correction. The shift of the LUMO is consistent with the band gap shift of about 1.1 eV determined separately for the perfect crystal. Thus, we conclude that the defect level should shift by about 0.7±0.05 eV. This furthermore is consistent with its atomic orbital character being slightly more than half Ge like and slightly less than half P like. Given that the unshifted position of the level in FP-LMTO and as determined from the ΔSCF calculation is slightly below the VBM, we obtain the final +0/0 level estimate of 0.6±0.1 eV, which is in good agreement with the optically induced EPR results.

We now consider the higher transition levels 0/− and −/2−. How do we interpret these levels in a simple molecular orbital model? Basically, we can think in terms of Ge and Zn dangling bonds surrounding the V_P. Using atomic energy levels from Harrison’s periodic table, a P, Ge, and Zn dangling bond related levels. The Ge dangling bonds are clearly much lower than the Zn related dangling bonds. They may be assumed to form a bonding and antibonding state with the bonding state occurring well below the VBM and taking two of the electrons. Thus, a Ge antibonding combination of dangling bonds is expected to form a lower level in the gap, consistent with Fig. 3, and this level will be empty in the − charge state and be occupied with one electron in the neutral state. Thus, the 0/− level is derived from the same one-electron level and also must be shifted up by 0.7 eV, placing it at 1.25±0.1 eV. This means that adding a second electron in this state moves it up by a Coulomb energy of about 0.6 eV. The next −/2− transition corresponds to a Zn-like mostly conduction band level and thus should be shifted as the gap by about 1.1 eV, placing it above the conduction band minimum. In the single negative charge state, the electrons in the defect level would be paired and the state

FIG. 3. (Color online) Probability density isosurface (yellow) for the highest occupied defect state of the P vacancy. The P-vacancy position is indicated by the small grey sphere in the center. Zn, Ge, and P are represented by blue, magenta, and green spheres, respectively. The figure was made with XCrySDen (see Ref. 20).
would no longer be EPR active. This predicts that the $V_P$ is actually an amphoteric defect which could act either as a deep donor by giving up its electron or as an acceptor by accepting a second electron. Usually, ZnGeP$_2$ is compensated $p$ type because of $V_{Zn}$ which has a 0/− level at 0.03 eV above the VBM. Under those circumstances, the $V_P$ will lose its electron to the $V_{Zn}$ defects and will be in a positive, and thus EPR inactive, state. It becomes active either if the Fermi level is above 0.6±0.1 eV or by illumination with photons of at least this energy. Our calculation furthermore predicts that in $n$-type doped ZnGeP$_2$ with the Fermi level high enough in the gap (above 1.25±0.1 eV), the $V_P$ related EPR center could be quenched, with the $V_P$ now playing the role of an acceptorlike trapping center. To the best of our knowledge, $n$-type ZnGeP$_2$ has so far not been achieved or even pursued. It would presumably require to grow Zn-rich material to suppress formation of $V_{Zn}$ and to add dopants like S or Se substituting the P site. The presence of a 0/− level at 1.25±0.1 eV however does not predict that the EPR signal would be quenched when illuminating with energy above this level, unless the illumination is so strong that it changes the Fermi level. One might expect though that there is a slight decrease in efficiency of activating the EPR signal when this energy of illumination is reached. In fact, in the data of Gehlhoff et al. on may notice a slight decrease in the $V_P$ EPR signal above 1.2 eV.

In conclusion, we have found that the $V_P$ is a very deep donor with an energy level likely to be about 0.6±0.1 eV above the VBM, in agreement with photoinduced EPR studies. It is a high energy of formation defect in Zn-poor ZnGeP$_2$ and thus unlikely to be the dominant compensating donor for the $V_{Zn}$ related acceptor. The $V_P$ related EPR spectrum is expected to be quenched in $n$-type ZnGeP$_2$ when the Fermi level exceeds the 0/− acceptor level of 1.25±0.1 eV of this amphoteric defect. Our calculations indicate a defect state primarily located on nearest neighbor Ge atoms and P atoms attached to those Ge, which implies that it would be useful to look for corresponding hyperfine structure.

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