

Diffusion mechanism of Zn in InP and GaP from first principles

A. Höglund,¹ C. W. M. Castleton,² and S. Mirbt¹

¹Condensed Matter Theory Group, Department of Physics, Uppsala University, Box 530, SE-751 21 Uppsala, Sweden

²Department of Materials Chemistry, Box 538, SE-751 21, Uppsala, Sweden

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The diffusion mechanism of Zn in GaP and InP has been investigated using first-principles computational methods. It is found that the kickout mechanism is the favored diffusion process under all doping conditions for InP, and under all except *n*-type conditions for GaP. In *n*-type GaP the dissociative mechanism is probable. In both *p*-type GaP and InP, the diffusing species is found to be Zn_i^{+2} . The activation energy for the kickout process is 2.49 eV in GaP and 1.60 eV in InP, and therefore unintentional diffusion of Zn should be a larger concern in InP than in GaP. The dependence of the activation energy both on the doping conditions of the material and on the stoichiometry is explained, and found to be in qualitative agreement with the experimentally observed dependencies. The calculated activation energies agree reasonably with experimental data, assuming that the region from which Zn diffuses is *p* type. Explanations are also found as to why Zn tends to accumulate at *pn* junctions in InP and to why a relatively low fraction of Zn is found on substitutional sites in InP.

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The diffusion of dopants in semiconductors is of importance both to the implantation process for creating doped material and to the unwanted mobility of dopants in devices. Experiments are, however, most often carried out on diffusion either from an external source or from a highly doped material (from here on referred to as “unintentional” diffusion). The latter may reduce the number of active dopants and lead to a decrease in efficiency. Diffusion of *p* dopants into *n*-type regions can change the position of the *pn* junction with severe complications as a result. In this work we will study the diffusion of Zn, one of the most common *p* dopants in III-V materials, in GaP and InP and attempt to find the most energetically favorable diffusion mechanism.

It is fairly well accepted that Zn in GaP and InP diffuses by a substitutional-interstitial mechanism.¹ The interstitial zinc can either come from a substitutional dopant, leaving a vacancy behind (the dissociative mechanism), or from a native interstitial defect that replaces the substitutional dopant (the kickout mechanism). In InP it has long been believed that Zn becomes the mobile dissociative mechanism,¹ although recently Wittorf *et al.* found evidence for the kickout mechanism for diffusion into undoped and Fe-doped InP.² Unintentional Zn diffusion into undoped InP has been studied by Otsuka *et al.*, who also found that the diffusion profiles could be explained by the kickout mechanism.³ Far fewer studies have been carried out on Zn diffusion in GaP. Jäger *et al.* interpreted the formation of interface-type loops at the diffusion front in intrinsic GaP as a clear indication of the kickout mechanism.⁴ Stolwijk and Pöpping further found that their diffusion profiles could be fitted well by solely the kickout mechanism.⁵ In InP, activation energies of 1.35, 1.40, 1.36, and 1.52 eV have been reported for undoped InP, and 1.28, 2.34, and 2.40 eV in *n*-type InP.^{6–10} In GaP, only one activation energy, of 2.38 eV for *n*-type GaP, has been reported.⁹ Zn diffusion has also been studied in *n*-type $In_{1-x}Ga_xP$ where the activation energy was found to follow the relation $E_A(x)=1.28+2.38x$ eV (although these values compare better to those of undoped materials).⁹

Here, we show that Zn will diffuse by the kickout mechanism in InP and *p*-type GaP, but also that the diffusion mechanism depends on the doping and stoichiometry of the material. Our calculations are performed using plane wave *ab initio* density functional theory within the local density approximation (LDA).¹¹ 216 atom supercells are used together with ultrasoft pseudopotentials.¹² The stability of the defects is calculated through the use of the formation energy, which is the energy required to create a defect,

$$\mathcal{E}^{form}(q) = E_{def}^{tot}(q) - E_{ideal}^{tot} - \sum_i n_i \mu_i + q(\epsilon_F + \epsilon_V). \quad (1)$$

Here $E_{def}^{tot}(q)$ and E_{ideal}^{tot} are the total energies of the supercell with and without the defect in charge state q . n_i is the number of atoms of type i and chemical potential μ_i added in order to form the defect. ϵ_V is the energy of the valence-band maximum and ϵ_F is the Fermi level relative to it. Stoichiometric values are used for the chemical potentials: $\mu_{Ga} = -4.06$ eV and $\mu_P = -6.48$ eV in GaP, and $\mu_{In} = -3.48$ eV and $\mu_P = -6.24$ eV in InP. The most favorable Zn rich conditions are used for the chemical potential of Zn, $\mu_{Zn} = -1.89$ eV. A full technical description can be found in Ref. 13.

The formation energies of Zn in GaP and InP are presented in Fig. 1. The formation energies have been scaled to the infinite supercell limit according to Ref. 14, in order to overcome the supercell approximation errors. This correction is necessary to get the $(0|-)$ transition level of the Zn acceptor inside the band gap as it should be. With the correction the $(0|-)$ level is located 0.02 and 0.12 eV above the valence band for InP and GaP, respectively, which compares well with the experimental values of 0.035 and 0.070 eV.¹⁵ Since Zn is an acceptor in III-V semiconductors it should be most stable on cation sites, which is indeed found in our calculations.²⁴ From Fig. 1 it is seen that in both GaP and InP, Zn is most common in the substitutional form, $Zn_{III}^{0/-}$, and at the P surrounded tetragonal interstitial site, Zn_{iP}^{+2} . It is

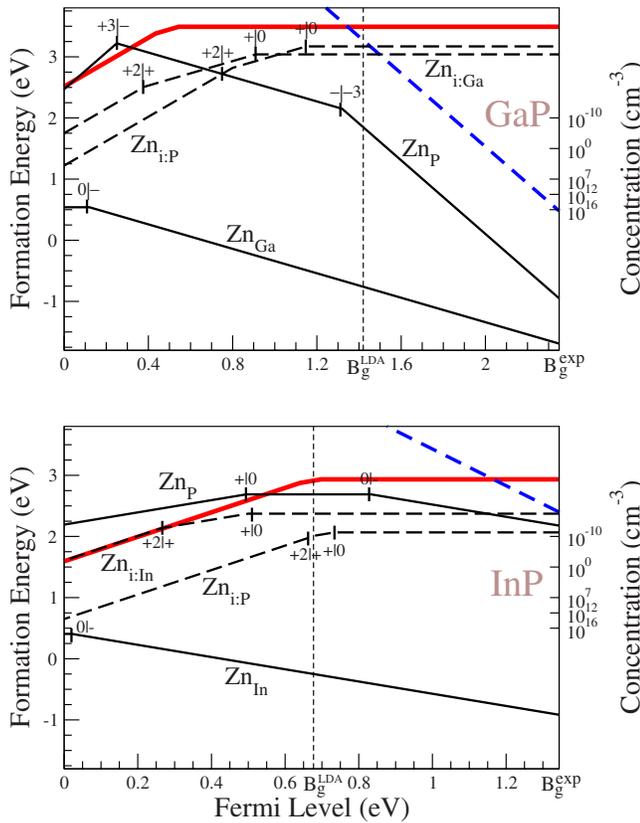


FIG. 1. (Color online) Formation energies of Zn in GaP (top) and InP (bottom). $i:X$ stands for the tetragonal interstitial position, surrounded by X atoms. The red line gives the activation energy of the kickout mechanism, under the assumption of a constant kickout barrier for the different charge states. The blue line is a lower bound of the activation energy for the dissociative mechanism. (In InP, $Zn_{i:In}$ is actually unstable and is only included here to show the migration barrier dependence on the Fermi level.) The concentration estimation on the right y axis is calculated at 300 K and with a vibrational entropy contribution of $5k_B$. (Ref. 13)

therefore these that will most likely be involved in the diffusion process in p -type material. The charge state of interstitial Zn is the same as found by Chu *et al.* in an experimental study of unintentional Zn diffusion into undoped InP.¹⁶ The biggest difference between GaP and InP is that Zn_i is much more stable in InP, so a larger interstitial concentration is expected at equilibrium. (The formation energy difference between them, ~ 0.6 eV, corresponds to a concentration difference of several orders of magnitude.) This explains why a relatively small fraction of Zn is observed occupying substitutional sites for high Zn concentration in InP, unlike in most other III-V semiconductors.¹ Substitutional zinc, $Zn_{III}^{0/-}$, is also lower in energy in InP than in GaP (~ 0.15 eV). Therefore Zn is, in general, more stable in InP than in GaP and in heterojunctions Zn would tend to accumulate in regions of InP.

The activation energy of a diffusion process is the sum of the formation energy for the diffusing species and the migration barrier, $E_A = E^{form} + E_m$.¹⁷ (This is simply the highest energy along the diffusion curve in a plot of the formation energy versus position.) The dominant diffusion mechanism

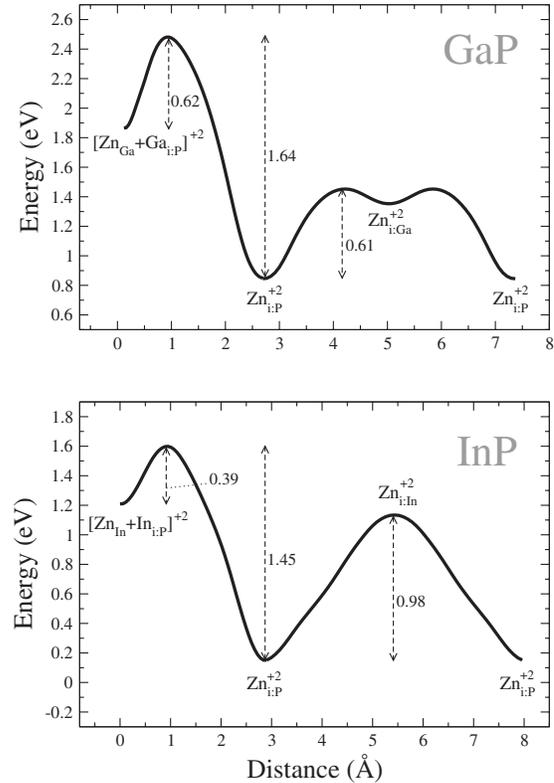


FIG. 2. Diffusion path of interstitial Zn in p -type GaP (top) and InP (bottom).

is therefore largely determined by the concentration of the native defect with which the Zn diffusion is associated. A high formation energy for any species involved in the diffusion mechanism will thus make the process unlikely. The dissociative mechanisms will be controlled by the concentration of vacancies, and the kickout mechanism will be controlled by the concentration of cation interstitials. As we have found in earlier studies,^{13,18} the formation energies of cation vacancies are high in p -type material, which results in the activation energy for the dissociative mechanism being at least 4.8 eV in GaP and 4.7 eV in InP. As will be shown, these high values cause the dissociative mechanism to be much less favorable than the kickout mechanism. The kickout mechanism starts from a Zn substitutional atom and a cation interstitial, which are found to have a binding energy of 0.48 eV in GaP and 0.27 eV in InP. The $[Zn_{III}+III_i]$ complex is found to be most stable in a +2 charge state, which is also the charge state of interstitial Zn. The diffusion path of this complex is shown in Fig. 2, where the first energy barrier is the barrier for the kickout of the Zn atom and the second is the barrier for the movement of Zn_i from one interstitial site to the next. The migration barrier for diffusion of Zn_i^{+2} is 0.61 eV in GaP and 0.98 eV in InP, with corresponding activation energies of 1.44 and 1.23 eV, respectively. Zn_i should therefore be more mobile in GaP. In InP Zn_i is not even metastable at the In surrounded interstitial site. Considering the whole path, GaP and InP have similar barriers for the kickout process, 0.62 and 0.39 eV, respectively, but due to the larger formation energy of Ga_i (1.82 eV) in comparison to that of In_i (1.08 eV), the activa-

tion energies differ by almost 1 eV, being 2.49 eV in GaP and 1.60 eV in InP. From the whole kickout process, Zn is therefore concluded to diffuse faster in InP than in GaP, in agreement with the available literature. In both *p*-doped GaP and InP, it is also seen that once in the interstitial form, Zn is not expected to return easily to the substitutional form since the formation energy of III_i is much larger than that of Zn_i and V_{III} is essentially absent under these doping conditions.

Since the formation energy of $[\text{Zn}_{\text{III}}+\text{III}_i]^{+q}$ depends on the Fermi level (ϵ_F), the activation energy of the kickout mechanism will depend on the overall doping of the material. This dependence is shown in Fig. 1, taking the variation of the most stable charge state of the complex into account (and assuming that the variation in the kickout barrier is small). This therefore gives the activation energy of the kickout mechanism under all types of doping conditions. It has been found that the diffusivity of Zn in InP is concentration dependent at low Zn concentration, but that this dependence is saturated for higher concentrations.¹⁹ This could be explained by the dependence on ϵ_F ; since Zn is an acceptor, increasing the Zn concentration will lower ϵ_F from a midgap position, but at sufficiently high concentrations it will be pinned at the $\text{Zn}_{\text{In}}^{0|}$ acceptor level close to the valence-band maximum.

In GaAs, which has been studied extensively, it has been found that dopants that occupy group III sites diffuse via $\text{V}_{\text{Ga}}^{-3}$ in *n*-type and semi-insulating material (dissociative mechanism), and via Ga_i^{+2} in *p*-type material (kickout mechanism).²⁰ A lower bound of the dissociative mechanism is the sum of the formation energies for Zn_i and V_{III} , which is plotted in Fig. 1. The conclusion from this will depend on how the LDA band gap error is treated, but unless the migration barrier is less than 0.5 eV, the dissociative mechanism is plausible only in *n*-type GaP.

Considering that the number of interstitial cations is the bottleneck for the kickout mechanism, the activation will depend on the stoichiometry of the material through the forma-

tion energy of III_i (although strictly speaking, the complex itself has no dependence on the chemical potentials). The variation of the chemical potentials leads to a variation in activation energy with stoichiometry of 2.49 ± 0.45 eV in GaP and 1.60 ± 0.22 eV in InP, where the lower values correspond to cation-rich conditions.¹³ Jakiela *et al.* found a higher activation energy of 1.61 eV in *p*-rich InP than in stoichiometric InP (both *n* type), where it was found to be 1.36 eV.¹⁰ According to our prediction it would be 0.22 eV higher in *p*-rich InP which gives 1.58 eV, in close agreement to the 1.61 eV. Since the concentration of V_{In} increases under *p*-rich conditions but that of In_i decreases, this trend indicates that the dominating process is the kickout mechanism even in *n*-type InP, and not the dissociative mechanism as expected in GaAs and probably GaP.

The experimental activation energies given in the introduction compare well with our calculated values, using ϵ_F of the region from which the Zn diffuses. This is a reasonable assumption since it is in this region that the rate limiting kickout step takes place. It would be enlightening to compare our results to those from an experimental study of unintentional doping, but unfortunately no such study has been performed (to our knowledge).

Since III_i and V_{III} are high in energy in *p*-type material, Zn_i will remain in interstitial form after being kicked out. Vacancies are only common in *n*-type material, so Zn_i will remain interstitial until it reaches a V_{III} in an *n*-type region, where it will lower its energy by becoming substitutional. This tendency for Zn to migrate from *p*- to *n*-type material could explain the often observed pileup of Zn at *pn* junctions in InP.²¹⁻²³

In conclusion, we have shown that the kickout mechanism will be the dominant diffusion mechanism for Zn in *p*-type and semi-insulating GaP and InP. We provide the activation energies under all doping conditions, although since the rate limiting step always occurs in *p*-type Zn doped regions, only the values there should be relevant.

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- ²⁴ Zn_p introduces a triply degenerate Kohn-Sham level in the band gap which is occupied by three electrons. In GaP this level lies

in the middle of the band gap making it possible for Zn_p to act both as a triple donor and a triple acceptor (charge states ranging from -3 to $+3$). Strong Jahn-Teller effects also lead to a negative-U effect for the transition states as seen in Fig. 1. In InP, however, the defect level lies close to the conduction band and merges with it for more extreme charge states, so that the possible charge states range only from -1 to $+2$.