Chemistry of Defect Induced Photoluminescence in Chalcopyrites: The case of CuAlS$_2$

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November 19, 2010

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Abstract

Hybrid exchange density functional theory is used to study the wide band gap chalcopyrite CuAlS$_2$. The formation energies of charged and neutral intrinsic defects are calculated for different environmental conditions, and it is shown that CuAlS$_2$ is a $p$-type material that cannot be type inverted through the formation of intrinsic defects. The calculated band gap states associated with the different intrinsic defects are used to comment on the origin of the observed CuAlS$_2$ photoluminescence emissions. The origin and stability of ordered defect compounds derived from CuAlS$_2$ are investigated, and it is concluded that CuAl$_5$S$_8$ is a stable ordered defect compound, albeit in a small region of phase space.

1 Introduction

The I-III-VI$_2$ chalcopyrite compounds (I=Cu, Ag; III=Al, Ga, In; and VI=S, Se, Te) have been attracting considerable attention as new materials for optical applications:
Variations in their composition result in significant changes in their lattice constants and energy gaps. In particular, Cu-III-VI$_2$ (III=Al, Ga and VI=S,Se) chalcopyrites have energy gaps ranging from 1.70 eV to 3.49 eV and are, therefore, promising candidates for light-emitting devices operating in the visible and ultraviolet spectral ranges. Among these Cu-III-VI$_2$ chalcopyrites CuAlS$_2$ has a 3.49 eV room temperature band gap, and its bulk single crystals usually exhibit values of room-temperature $p$-type mobility and hole concentration of the order of 0.9 Scm$^{-1}$ and $5.1 \times 10^{18}$ cm$^{-3}$ respectively.

Photoluminescence (PL), high resolution photoreflectance (HPR) and time resolved photoluminescence (TR-PL) experiments reveal the existence of luminescence emissions in CuAlS$_2$ at temperatures ranging from 10 K to 300 K. It has been suggested that these emissions might be due to: a) free excitons (FE), b) donor and acceptor-bound emissions and c) donor-acceptor pair recombination ($D^+A^-$) emissions. ($D^+A^-$) and donor-acceptor bound emissions are related to the intermediate optical band gap states that appear in defective CuAlS$_2$ and, therefore, PL emissions related with these excitons have wavelengths smaller than the optical band gap of CuAlS$_2$. In previous works, the orange PL emission observed in CuAlS$_2$ has been linked to a ($D^+A^-$) transition. As regards the so-called near-band-edge PL (NBEPL) emission, previous works have attributed it to either FE or defect-bound excitons, whose band gap states are near the valence band maximum (VBM) or the conduction band minimum (CBM).

The binding energy of the FE in CuAlS$_2$ is $R_s = 70$ meV, which is larger than the binding energies of other ultraviolet emitting materials such as ZnO (60 meV), ZnS (39 meV) and GaN (21 meV). This binding energy is calculated assuming that: (a) the effective masses of CuAlS$_2$ are given by the average value of the effective masses of CuGaS$_2$, ZnSe, ZnS, AgGaS$_2$ and GaN, and (b) the dielectric constant of CuAlS$_2$ is $\varepsilon = 7.0\varepsilon_0$. This large binding energy implies that FE in CuAlS$_2$ are stable at 298 K, a feature which means that CuAlS$_2$ has the potential to be a highly efficient ultraviolet emitter at room temperature.
The 3.49 eV optical band gap and the large FE binding energy suggest that CuAlS$_2$ could potentially be used for building blue and green light emitting devices. For producing such devices it is desirable to understand the nature of the PL emissions, which are strongly linked with the defect chemistry of CuAlS$_2$. So far, to the best of the authors knowledge, although there have been a number of experimental studies, there are no theoretical studies on the defect chemistry of CuAlS$_2$. NBEPL emissions have been observed in CuAlS$_2$ powder and epilayers within the 15 K–298 K temperature range. The intensity of NBEPL related emissions decreases in annealed samples, and the photoemission peaks are shifted towards lower energies. These peaks have been related to the formation of intrinsic defects. When defects are created, emissions related to (D$^+$A$^-$) pairs and donor-acceptor bound excitons prevail. It has been suggested, for instance, that the 1.9-2.0 eV orange emission is caused by (D$^+$A$^-$) recombination.

In the current work we calculate: a) the stability of pure CuAlS$_2$ with respect to other competing phases and, b) the stability of different intrinsic defects in CuAlS$_2$. Defects in various possible charge states, such as copper vacancies (V$_{Cu}^{0/1^-}$) and sulphur vacancies (V$_S^{0/1+/2+}$), aluminium substituting copper (A$_{Cu}^{0/1+/2+}$) and copper substituting aluminium (Cu$_{Al}^{0/1^-/2^-}$) are modelled. Moreover, the electronic structures associated with these defects and their influence in the PL emissions of CuAlS$_2$ are reported.

Among the CuAlS$_2$ competing phases are the ternary ordered defect compounds (ODCs). These ODCs are complex defect structures that have been observed in several chalcopyrites such as CuGaSe$_2$, CuGaTe$_2$, and CuInSe$_2$, and can be thought of as ordered structures of neutral (2V$_{Cu}^{1-}$ + (Ga/In)$_{Cu}^{2+}$)$^0$ compound defects. The existence of ODCs means that these materials have a structural tolerance to large anion-cation off-stoichiometry, and they do not undergo major structural changes as the composition is varied. The optoelectronic properties also show an unexpectedly weak variation with composition, as the ODCs have similar optoelectronic response to the stoichiometric phases. In CuInSe$_2$ this is because the (2V$_{Cu}^{1-}$ + In$_{Cu}^{2+}$)$^0$ compound defect is charge compensated, has no deep-gap levels, and thus does not impact in the opto-
Most of the theoretical works on the ODCs in the literature are limited to ODCs derived from CuInSe$_2$, CuGaTe$_2$ and CuGaSe$_2$ and the most commonly observed ODCs in these chalcopyrites are Cu(In/Ga/Al)$_5$(Se/Te)$_8$ and Cu(In/Ga/Al)$_3$(Se/Te)$_5$. The two ODCs simulated in this work are CuAl$_5$S$_8$ and CuAl$_3$S$_5$.

2 Methodology

2.1 Computational Details

Density functional theory (DFT) calculations were performed using CRYSTAL and the B3LYP hybrid exchange functional. This functional has been shown to provide a reliable description of the electronic structure, geometry and energetics in a wide range of materials. In particular, hybrid exchange functionals, such as B3LYP, provide a much better prediction of the band gap of semiconductors than local density approximation (LDA) or generalised gradient approximation (GGA) DFT functionals.

Polarised triple valence Gaussian basis sets, which have been used in previous studies, were used throughout and detailed information is included in the supplementary material. In CRYSTAL, real space summations of the Coulomb and exchange contributions to the Hamiltonian matrix are controlled by five overlap criteria. In these calculations, four of these overlap criteria have values of 10$^{-6}$ and the last one has a value of 10$^{-12}$. The control of these approximations is described in detail elsewhere. A Monkhorst-Pack shrinking factor of eight was used to sample the first Brillouin zone, and a Gilat net of eight points was used in the evaluation of the Fermi energy and density matrix. Defects were calculated within 64 atom supercells, obtained by doubling the $a$ and $b$ axes of the conventional cell.
2.2 Energy Correction for Charged Defects

The use of periodic boundary conditions within electronic structure calculations leads to the conditional convergence of the Coulomb potential. For neutral systems the Ewald summation may be used to ensure that the Coulomb potential and total energies converge to well defined values. In charged systems, however, the total energy can only be calculated to within a constant offset value. This offset is corrected through the electrostatic potential alignment correction ($\Delta E_v$). The $\Delta E_v$ correction can be explicitly computed by calculating the change in the energy of the neutral system when an electron is removed from it. When the size of the system tends to infinity, the change in the energy converges to the value of the energy offset. To calculate the value of $\Delta E_v$ in CuAlS$_2$, the change in energy between a neutral system, and a system with a single electron removed, was calculated for increasing system size until convergence (to within 0.04 eV) of the energy offset was obtained. The results of these calculations are given in table 1. In this work a 64 atom supercell, obtained by doubling the $a$, $b$ and $c$ axes of the primitive lattice, has been adopted. In the calculations of charged defect energies, a value of 6.518 eV is used for $\Delta E_v$ for the CuAlS$_2$ system.

<table>
<thead>
<tr>
<th>No. of Atoms</th>
<th>$\Delta E_v$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>6.220</td>
</tr>
<tr>
<td>32</td>
<td>6.520</td>
</tr>
<tr>
<td>64</td>
<td>6.518</td>
</tr>
<tr>
<td>128</td>
<td>6.523</td>
</tr>
</tbody>
</table>

Table 1: Convergence on the value of $\Delta E_v$ for increasing system size.

The \textit{ab initio} calculation of the formation energy of charged defects involves the addition of a uniform background charge to neutralise the cell: The total energy would diverge for a periodically repeating charged system. The total energy of a charged defect in a periodic system includes terms due to defect-defect, defect-background, and background-background Coulomb interactions. The values of these terms are required for the accurate calculation of the energy of an isolated defect and, assuming the defect...
charge $q$ is localised, they can be approximated by the multipole correction:

$$\Delta E = \frac{q^2 \alpha_M}{2\varepsilon_r V^{\frac{1}{3}}} + \frac{2\pi q Q}{3\varepsilon_r V} + O(V^{-\frac{5}{3}})$$

(1)

where $\alpha_M$ is the lattice dependent Madelung constant and $V$ is the volume of the supercell. $Q$ is the quadrupole moment of the defect. Finally, $\varepsilon_r$ is the static relative dielectric constant, measured in units of the vacuum dielectric constant, $\varepsilon_0$. In this work, an experimental value of $7.0\varepsilon_0$ is used for the $\varepsilon_r$ in CuAlS$_2$.

Previous theoretical calculations on CuGaS$_2$ used 64 atom unit cells, which were sufficiently large to render the second order term in equation (1) as negligible relative to the defect formation energies. In this work a 64 atom supercell is used as well and the value of $\Delta E$ is also calculated using only the first term in equation (1). For a 64 atom supercell, the calculated value of $\Delta E$ in CuAlS$_2$ is 0.27 eV and 1.08 eV for the single and double charged defects.

### 2.3 Phase Stability

At equilibrium, the Gibbs free energy of CuAlS$_2$ with respect to its elemental solids is given by:

$$G_{\text{CuAlS}_2} = \mu_{\text{Cu}} + \mu_{\text{Al}} + 2\mu_{\text{S}}$$

(2)

$\mu_i$ ($i = \text{Cu, Al, S}$) is the absolute value of the chemical potential of element $i$. Equation (2) can be re-written as:

$$\Delta G_{\text{CuAlS}_2} = \Delta \mu_{\text{Cu}} + \Delta \mu_{\text{Al}} + 2\Delta \mu_{\text{S}}$$

(3)

where $\Delta G_{\text{CuAlS}_2}$ is the Gibbs free energy of formation of CuAlS$_2$, and $\Delta \mu_i$ ($\Delta \mu_i = \mu_i - \mu_i^0$) is the difference between $\mu_i$ and the value of $\mu_i$ when the element $i$ is in its standard state. This state is defined at a temperature of 298.15 K and a pressure of
I atm. The allowed values of \( \mu_i \) are determined from a set of thermodynamic limits. The upper bound of \( \mu_i \) is the chemical potential of the corresponding element in its standard state, as to avoid precipitation of the later. That is,

\[
\Delta \mu_i \leq 0 \tag{4}
\]

We are primarily interested in the region of phase space in which CuAlS\(_2\) is stable. In this stability region the chemical potentials of the constituent atoms must equal the Gibbs free energy of formation of the compound, as stated in equation 3, and they are further restricted by other competing phases. To identify the stability region of CuAlS\(_2\) it is necessary to calculate the relative stability of these competing phases, such as Cu\(_2\)S. For instance:

\[
2\Delta \mu_{\text{Cu}} + \Delta \mu_{\text{S}} \leq \Delta G_{\text{Cu}_2\text{S}} \tag{5}
\]

The following competing phases have been considered: Cu\(_2\)S low chalcocite, Al\(_2\)S\(_3\), CuAl\(_3\)S\(_5\) and CuAl\(_5\)S\(_8\). The allowed values of \( \Delta \mu \) are bound by values that preserve the stability of CuAlS\(_2\), avoiding the formation of competing phases.

Gibbs free energies are computationally very expensive to calculate from first principles and, therefore, they are usually approximated. In this case, the approximations are applied when defining the variational limits of \( \Delta \mu_i \) \((i = \text{Cu, Al, S})\), which is done through the formation energies of CuAlS\(_2\) and its competing phases. In the following, the methodology is exemplified using the Gibbs formation energy of CuAlS\(_2\),
which is defined in equation (3). This equation can be written as follows:

$$
\Delta G_{\text{CuAlS}_2} = G_{\text{CuAlS}_2} - G_{\text{Al}} - G_{\text{Cu}} - 2G_{\text{S}} \\
= \varepsilon^{\text{DFT}}_{\text{CuAlS}_2} - \varepsilon^{\text{DFT}}_{\text{Cu}} - \varepsilon^{\text{DFT}}_{\text{Al}} - 2\varepsilon^{\text{DFT}}_{\text{S}} \\
+ F_{\text{vib}}^{\text{CuAlS}_2} - F_{\text{vib}}^{\text{Cu}} - F_{\text{vib}}^{\text{Al}} - 2F_{\text{vib}}^{\text{S}} \\
+ p(V_{\text{CuAlS}_2} - V_{\text{Cu}} - V_{\text{Al}} - 2V_{\text{S}})
$$

(6)

In this equation, the Gibbs free energy, $G = E - TS + pV$, is written as

$$
G = \varepsilon^{\text{DFT}} + F_{\text{vib}} + pV.
$$

(7)

$\varepsilon^{\text{DFT}}$ is the \textit{ab initio} total energy of the material, $F_{\text{vib}} = E_{\text{vib}} - TS_{\text{vib}}$ is the \textit{Helmholtz} vibrational energy, which depends on the phonons and is a function of temperature, and $pV$ is the pressure-volume term.

The $pV$ and $F_{\text{vib}}$ terms are small for crystalline incompressible materials such as CuAlS$_2$, and equation (6) uses differences between these quantities to define the $\Delta \mu_i$ variational limits. Consequently, the $pV$ and $F_{\text{vib}}$ contributions can be considered as negligible, and $\Delta G_{\text{CuAlS}_2}$ can be written as:

$$
\Delta G_{\text{CuAlS}_2} = \varepsilon^{\text{DFT}}_{\text{CuAlS}_2} - \varepsilon^{\text{DFT}}_{\text{Cu}} - \varepsilon^{\text{DFT}}_{\text{Al}} - 2\varepsilon^{\text{DFT}}_{\text{S}}
$$

(8)

where $\varepsilon^{\text{DFT}}_{\text{CuAlS}_2}$, $\varepsilon^{\text{DFT}}_{\text{Cu}}$, $\varepsilon^{\text{DFT}}_{\text{Al}}$ and $\varepsilon^{\text{DFT}}_{\text{S}}$ are the \textit{ab initio} total energies of these materials in their solid standard states. $\varepsilon^{\text{DFT}}_{\text{CuAlS}_2}$ is the total energy of bulk CuAlS$_2$ in its tetragonal phase and $\varepsilon^{\text{DFT}}_{\text{S}}$ is calculated in its pure orthorombic $\alpha$ phase. As regards Cu and Al, the B3LYP approximation does not provide accurate energies for metals and, therefore, $\varepsilon^{\text{DFT}}_{\text{Cu}}$ and $\varepsilon^{\text{DFT}}_{\text{Al}}$ are calculated using the experimental standard formation enthalpies,
\( \Delta H^0 \), of \( \text{Al}_2\text{S}_3 \) and \( \text{Cu}_2\text{S} \) as,

\[
E_{\text{Al}}^{\text{DFT}} = \frac{1}{2} \left[ E_{\text{Al}_2\text{S}_3}^{\text{DFT}} - 3E_{\text{S}}^{\text{DFT}} - \Delta H_0^{\text{Al}_2\text{S}_3} \right] \quad (9)
\]

\[
E_{\text{Cu}}^{\text{DFT}} = \frac{1}{2} \left[ E_{\text{Cu}_2\text{S}}^{\text{DFT}} - E_{\text{S}}^{\text{DFT}} - \Delta H_0^{\text{Cu}_2\text{S}} \right] \quad (10)
\]

### 2.4 Defect Energetics

The formation of a defect can be considered in terms of an exchange between the host material and notional atomic and electronic reservoirs. The formation energy of a defect in the charge state \( q \) can be written as

\[
\Delta G_{D,q}(E_F, \mu) = G_{D,q} - G_{\text{CuAlS}_2} + \Sigma_i n_i \mu_i + q(\Delta E_v + E_F) \quad (11)
\]

where \( G_{D,q} \) and \( G_{\text{CuAlS}_2} \) are the Gibbs free energies of \( \text{CuAlS}_2 \) with and without defect \( D \), and they are calculated as described in section 2.2. The value of \( G_{D,q} \), for charged defects, includes the first order multipole correction described in section 2.2. The third term represents the free energy term due to the loss of \( n_i \) atoms of type \( i \) that occurs when the defect is formed (a negative value of \( n_i \) denotes addition of atoms). The fourth term represents the free energy change due to exchange of electrons and holes with the carrier reservoirs. \( \Delta E_v \) is the electrostatic potential alignment correction, which represents the offset between the VBM in the neutral and charged systems. Finally, \( E_F \) is the Fermi energy relative to the VBM, which is bound between the VBM and the CBM.

### 2.5 Electronic Transition Energies

The transition energy \( \epsilon(D, q/q') \) is defined as the Fermi energy at which the charge state of defect \( D \) spontaneously transforms \( q \leftrightarrow q' \). Therefore, at \( E_F = \epsilon(D, q/q') \) the formation energies of both defects are the same: \( \Delta G_{D,q}(E_F, \mu) = \Delta G_{D,q'}(E_F, \mu) \). Using equation (11) the transition energy can be expressed as:

\[
\epsilon(D, q/q') = \frac{G_{D,q} - G_{D,q'}}{(q' - q)} - \Delta E_v \quad (12)
\]
2.6 Defect Concentration

At equilibrium the defect concentration obeys Boltzmann statistics and so it is given by

\[ c_{D,q}(E_F, \mu_i, T) = N \exp \left[ -\frac{\Delta G_{D,q}(E_F, \mu_i)}{k_B T} \right] \]  

(13)

where \( N \) is the total number of atomic sites where the defect can occur, \( k_B \) is the Boltzmann constant and \( T \) is temperature. The condition that the overall system must remain charge neutral enables \( E_F \) to be determined self consistently. The neutrality condition is given by

\[ \sum_D q_D c_D = 0 \]  

(14)

where \( q_D \) is the charge of defect \( D \) and \( c_D \) is the concentration of the defect.

2.7 Ordered Defect Compounds (ODCs)

The procedure Zhang and coworkers applied to CuInSe\(_2\) was used to construct the unit cells for CuAl\(_5\)S\(_8\) and CuAl\(_3\)S\(_5\). The method involves creating compound defects in CuAlS\(_2\) supercells. For instance, CuAl\(_5\)S\(_8\) is obtained by creating a \((2V_{\text{Cu}}^- + \text{Al}^{2+})_0\) compound defect in a 16 atom CuAlS\(_2\) supercell. Figure 1 shows a schematic picture of CuAlS\(_2\).

3 Results

3.1 CuAlS\(_2\) Bulk

The computed and experimental lattice parameters are given in table 2. The lattice parameters are overestimated by around 2% for CuAlS\(_2\), which is typical for B3LYP calculations on wide bandgap insulators. The calculated density of states for CuAlS\(_2\) is shown in figure 2. The calculated band gap is 3.5 eV, which is in agreement with the
Table 2: Calculated lattice constants for CuAlS\(_2\). The experimental values\(^\text{[11]}\) are given in parenthesis.

<table>
<thead>
<tr>
<th>Material</th>
<th>(a) (Å)</th>
<th>(c) (Å)</th>
<th>(a/c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAlS(_2)</td>
<td>5.47 (5.32)</td>
<td>10.55 (10.43)</td>
<td>1.93 (1.96)</td>
</tr>
</tbody>
</table>

experimental values measured for the optical band gap of CuAlS\(_2\): 3.55 eV\(^\text{[6]}\) and 3.5 eV\(^\text{[37]}\)

### 3.2 Phase Stability

Figure (3) is the computed phase diagram as a function of the aluminium and copper chemical potentials. It was calculated as explained in section 2.3 and highlights the stability region for CuAlS\(_2\). This figure is a phase diagram projected in the \((\Delta\mu_{\text{Cu}}, \Delta\mu_{\text{Al}})\) plane. \(\Delta\mu_{\text{S}}\) is constrained by equation (3), and the diagonal line which links the \(\Delta\mu_{\text{Cu}}\) and \(\Delta\mu_{\text{Al}}\) axes represents \(\Delta\mu_{\text{S}} = 0\) eV. Points 1-2-3-4 indicate the corners of the stability region. The strip region stretching parallel to the line defined by points 1 and 4 indicates the stability region for the CuAl\(_5\)S\(_8\) ODC.

### 3.3 Defect Energies

The formation energies of the calculated defects along the boundary of the CuAlS\(_2\) stability region are shown in figure (4). The formation energies of all the defects studied are depicted: The copper and sulphur vacancies \(V_{\text{Cu}}^{0/1+/2+}\) and \(V_{\text{S}}^{1-/0}\); the copper substituting aluminium \(\text{Cu}_{\text{Al}}^{2-/1-/0}\); the aluminium substituting copper \(\text{Al}_{\text{Cu}}^{0/1+/2+}\) and the compound \((2V_{\text{Cu}}^{1-} + \text{Al}_{\text{Cu}}^{2+})^0\) defect. The equilibrium defect concentration is calculated using equation (13), and the temperature adopted is 900K, which is a typical temperature for the growth of CuAlS\(_2\).\(^\text{[45]}\) The defect concentrations depend explicitly on the equilibrium Fermi energy, \(E_F\), through the defect formation energies and, in turn, \(E_F\) depends on the concentration of the charged defects through the neutrality condition expressed in equation (14). Therefore, the values of the defects concentrations and \(E_F\) are determined self consistently.
Along lines 1-2 and 4-1, and part of line 2-3, the point defects with the lowest formation energies are $V^{1-}_{\text{Cu}}$ and $Al^{2+}_{\text{Cu}}$. Along the remainder of line 2-3 the $Cu^{0}_{\text{Al}}$ defect dominates, having its minimum formation energy at point 3. Finally, along line 3-4 the most stable point defects are $Cu^{0}_{\text{Al}}$, $V^{0}_{\text{Cu}}$, $V^{1-}_{\text{Cu}}$ and $Al^{2+}_{\text{Cu}}$. The formation energy of the compound defect $(2V^{1-}_{\text{Cu}} + Al^{2+}_{\text{Cu}})^0$ is also plotted in figure (4): This defect is comprised of point defects $V^{1-}_{\text{Cu}}$ and $Al^{2+}_{\text{Cu}}$. The interaction energy of the compound defect, $\Delta E_{\text{int}}$, is defined as:

$$\Delta E_{\text{int}} = E((2V^{1-}_{\text{Cu}} + Al^{2+}_{\text{Cu}})^0) - 2E(V^{1-}_{\text{Cu}}) - E(Al^{2+}_{\text{Cu}}).$$

(15)

At all points along the path bordering the stability region of CuAlS$_2$ $\Delta E_{\text{int}}$ has a value of -1.45 eV, which is independent of $\Delta \mu_i$ and $E_F$. Point defects $V^{1-}_{\text{Cu}}$ and $Al^{2+}_{\text{Cu}}$ are, hence, stabilised by the formation of the $(2V^{1-}_{\text{Cu}} + Al^{2+}_{\text{Cu}})^0$ compound defect. This implies that at high concentrations of $V^{1-}_{\text{Cu}}$ and $Al^{2+}_{\text{Cu}}$, their energies are further lowered by interactions with nearby defects. The $(2V^{1-}_{\text{Cu}} + Al^{2+}_{\text{Cu}})^0$ compound defects are most stable along the line 1-4. This is expected as this line represents the region in which CuAlS$_2$ is at equilibrium with the CuAl$_5$S$_8$ ODC, which consists of ordered arrangements of the $(2V^{1-}_{\text{Cu}} + Al^{2+}_{\text{Cu}})^0$ compound defect.

Figure (5) shows the defect formation energies of the point defects at the four corners of the stability region of CuAlS$_2$. At each of these four points, the chemical potentials have fixed values and, therefore, the formation energy given by equation (11) is only a function of $E_F$, and can be written as:

$$\Delta G_{D,q}(E_F) = K_D + qE_F$$

(16)

where $K_D$ is a constant characteristic of each defect.

Figure (5) may be used to analyse the possibility of type-inversion in CuAlS$_2$. In principle, any semiconductor can be either n or p-doped. In practice, however, semiconductor dopability is limited. For instance, ZnO and ZnS are n-type semiconductors.
that cannot be made $p$-type, and CuAlSe$_2$ is a $p$-type semiconductor that cannot be made $n$-type. Doping limits exist because doping with donors (acceptors) moves the equilibrium Fermi energy towards the CBM (VBM). In this way, the formation energy of acceptors (donors) is lowered, and is easier for the acceptors (donors) to form spontaneously. This mechanism compensates the intentional donor (acceptor) dopants, and leads to the pinning of the Fermi energy at an energy we label as $E_{F}^{p,\text{pin}}$ ($E_{F}^{n,\text{pin}}$). This mechanism can be understood from an examination of equation (16).

Ideally, for a system to become $n$-type, $E_{F}^{n,\text{pin}}$ should be as high in the band gap as possible, even inside the conduction band. Figure (5) shows that, at points 1, 2, 3 and 4 the maximum value for $E_{F}^{n,\text{pin}}$ is less than half of the band gap energy. Conversely, $E_{F}^{p,\text{pin}}$ is $\approx 1$ eV above the VBM at point 1 and below the VBM at all the other points.

The position of $E_{F}$ in the band gap ($E_{G}$) determines the type of doping: if $E_{F} \geq \text{VBM} + \frac{E_{G}}{2}$, the system is $n$-type; if $E_{F} \leq \text{VBM} + \frac{E_{G}}{2}$, the system is $p$-type. In figure (4) the value of $E_{F}$ is always smaller than half the band gap, which indicates that CuAlS$_2$ is a $p$-type material under these environmental conditions, a prediction that agrees with experimental evidence.

### 3.4 Electronic Transition Energies

Table (3) and figure (6) show the transition energies calculated using equation (12). $V_{Cu}$ and Cu$_{Al}$ defects both contribute acceptor levels while Al$_{Cu}$ defects contribute donor levels. As regards $V_{S}$ defects, they are expected to form donor levels, as one or two electrons are donated to the system when $V_{S}^{1+}$ and $V_{S}^{0}$ are formed. In the case of CuAlS$_2$, it has been suggested that these electrons $n$-dope the system. Experimental measurements on CuGaSe$_2$ and CuInSe$_2$ have shown, however, that $V_{Se}$ defects could cause persistent hole photoconductivity ($p$-type PPC). This is because the two electrons left behind by the neutral Se vacancy form a defect localised state that lies at energies below the VBM. Therefore, optical excitement of the $V_{Se}^{2+}$ defect initiates...
Table 3:
Calculated transition energies of vacancies and substitutional defects as defined by equation (12). The corresponding charge states for these transitions are given in parentheses. The transition energies are relative to the VBM for acceptors and to the CBM for donors. The transition energy (0/1+) in $V_S$ is below the VBM.

<table>
<thead>
<tr>
<th>Defect</th>
<th>$(q/q')$</th>
<th>$\varepsilon (D, q/q')$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{Cu}$</td>
<td>(1/-0)</td>
<td>0.11</td>
</tr>
<tr>
<td>$AICu$</td>
<td>(0/1+)</td>
<td>1.10</td>
</tr>
<tr>
<td>$AICu$</td>
<td>(1+/2+)</td>
<td>1.20</td>
</tr>
<tr>
<td>$CuAl$</td>
<td>(2/-1-)</td>
<td>1.68</td>
</tr>
<tr>
<td>$CuAl$</td>
<td>(1/-0)</td>
<td>0.48</td>
</tr>
<tr>
<td>$V_S$</td>
<td>(0/1+)</td>
<td>-0.24</td>
</tr>
<tr>
<td>$V_S$</td>
<td>(1+/2+)</td>
<td>0.99</td>
</tr>
</tbody>
</table>

The reaction $V_{Se}^{2+} \rightarrow V_{Se}^0 + 2h$, which traps two electrons, releasing two holes to the valence band. Similarly, $V_{Se}^{1+}$ releases one hole to the acceptor level. To the best of the authors knowledge, there are no experimental data suggesting that PPC occurs in CuAlS$_2$. However, figure (6) shows the transition energies associated with $V_S$, and it can be clearly seen that the (0/1+) transition state lies below the VBM, and that the (1+/2+) transition state lies below the middle of the band gap. These results suggest that $V_S$ is behaving as an acceptor and could potentially $p$-dope the system.

PL measurements carried out by Chichibu et. al. on low-grade CuAlS$_2$ defective samples showed three shallow acceptor levels at 0.08 eV, 0.175 eV and 0.250 eV. They did not specify the growing conditions and did not assign any of these levels to any particular defect. Moreover, inductively coupled plasma spectroscopy found that CuAlS$_2$ single crystals, grown by the chemical vapour transport technique, are copper deficient. Electron spin resonance (ESR) and thermal quenching measurements on these samples identified an isotropic signal. This ESR signal was linked to a copper vacancy, whose associated defect level had an ionisation energy of $E_A = 0.190 \pm 0.01$ eV. This conclusion is in agreement with the data presented here (figure 4) which suggest that $V_{Cu}$ is the most stable defect at most points along the phase stability region.
3.5 Photoluminescence in defective CuAlS$_2$

A wide variety of processes have been suggested as interpretation of the observed PL emissions that are listed in table (4), these include:

- FE recombination
- Radiative recombination of a free hole and a donor (hD$^0$)
- Radiative recombination of a free electron and an acceptor (free-to-bound emission) (eA$^0$)
- Excitonic emission bound to a neutral acceptor (A$^0$X)
- Excitonic emission bound to a singly-charged acceptor (A$^-$.X)
- Excitonic emission bound to a neutral donor (D$^0$X)
- Excitonic emission bound to a singly-charged donor (D$^+$X)
- Donor acceptor pair recombination (D$^+$.A$^-$).

It is suggested, from our calculations, that D is Al$_{Cu}$, and A is either V$_{Cu}$, V$_S$ or Cu$_{Al}$. Since the data is insufficient to unambiguously associate the observed PL emissions with specific defects, the experiments need to be complemented with theoretical data, such as the calculated energy of the PL emissions associated with each of the studied defects. The energy of a PL emission is given by:

$$h\nu = E_G - E_{BE}$$ (17)

where $E_G = 3.5$ eV is the calculated band gap and $E_{BE}$ is the binding energy associated with the given emission. The $E_{BE}$ for a FE recombination is $R_x$. In PL emissions associated with the radiative recombination of a free hole and a donor (hD$^0$), or a free electron and an acceptor(eA$^0$), $E_{BE}$ can be estimated as the electronic transition energies $\epsilon(D,q/q')$ or $\epsilon(A,q/q')$ respectively. If excitons are bound to neutral and ionized donors or acceptors the value of $E_{BE}$, although still dependent on $\epsilon(D,q/q')$
or \( \varepsilon(\mathcal{A}, q/q') \), is modified. For instance, PL experiments on II-IV compounds yielded PL emissions that were interpreted as resulting from an exciton-neutral-defect complex. These results showed that the \( E_{BE} \) of the exciton-neutral-defect complex is about 0.20 times the \( E_{BE} \) of the corresponding radiative recombination process of the associated defect (\( E_{BE} = 0.20 \varepsilon(\mathcal{D}, q/q') \)). Sharma and Rodriguez\(^{46} \) and Atzmuller et al.\(^{47} \) estimated \( E_{BE} \) for bound excitons as a function of the ratio between the effective masses of the electrons and holes: 

\[
s = \frac{m_e^*}{m_h^*} = (\frac{\partial^2 E_{CB}(k)}{\partial k^2})_\Gamma / (\frac{\partial^2 E_{VB}(k)}{\partial k^2})_\Gamma,
\]

where the second order derivatives have been calculated along the \((-100) \rightarrow (000) \rightarrow (100), (0-10) \rightarrow (000) \rightarrow (010) \) and \((00-1) \rightarrow (000) \rightarrow (001) \) directions in the reciprocal space. The value adopted for \( s \) in \( \text{CuAlS}_2 \) is the average between these three values: \( s = 0.165 \). Using the calculated values for the effective masses we have also estimated the reduced mass of the electron-hole pair and, with it, the value of binding energy for the free exciton: \( R_x = 62 \) meV. Within the model proposed by Sharma and Rodriguez, the expressions for calculating the energy of the PL emissions associated with defect-bound excitons in \( \text{CuAlS}_2 \) are:

\[
\begin{align*}
E_{BE} &= R_x + 1.00 \varepsilon(\mathcal{D}, 0/1+) \text{ for } (\mathcal{D}^+ X) \quad (18) \\
E_{BE} &= R_x + 1.18 \varepsilon(\mathcal{A}, 1-) \text{ for } (\mathcal{A}^- X) \quad (19) \\
E_{BE} &= R_x + 0.29 \varepsilon(\mathcal{D}, 0/1+) \text{ for } (\mathcal{D}^0 X) \quad (20) \\
E_{BE} &= R_x + 0.11 \varepsilon(\mathcal{A}, 0/1+) \text{ for } (\mathcal{A}^0 X) \quad (21)
\end{align*}
\]

where \( \varepsilon(\mathcal{D} \text{ or } \mathcal{A}, q/q') \) is the activation energy of the donor or acceptor involved in the process. Finally, \( E_{BE} \) for PL emissions associated with \( (\mathcal{D}^+ \mathcal{A}^-) \) transitions is given by:\(^{48} \)

\[
E_{BE} = (\varepsilon(\mathcal{D}, q/q') + \varepsilon(\mathcal{A}, q/q')) + \frac{e^2}{\varepsilon r} + C(r). \quad (22)
\]

The \( E_{BE} \) of a \( (\mathcal{D}^+ \mathcal{A}^-) \) transition depends on the distance \( r \) between the two defects. \( \frac{e^2}{\varepsilon r} \) is a Coulomb contribution and \( C(r) \) is a correction used for small values of \( r \). \( C(r) \) tends to zero when \( r \) tends to infinity. In table 5 the calculated PL emissions are sum-
marised. The PL emissions associated with $(\mathbb{D}^+\mathbb{A}^-)$ have been estimated at $C(r) = 0$, an assumption that will be discussed later.

To simplify the comparison between experimental and theoretical results, the PL emissions observed by Kuroki et al., Shirakata et al. and Chichibu et al. are classified into three sets: a) Free exciton PL emissions of 3.52 eV and 3.55 eV; b) near band edge PL (NBEPL) emissions of 3.34 eV, 3.43 eV, 3.0 eV, and emissions at 3.45 eV; and c) mid-band gap emissions of 1.90 eV, 2.76 eV and 2.10 eV.

The calculated FE emission is 3.44 eV (table 5). This result suggests that the observed emissions of 3.55 eV and 3.52 eV (with a FWHM of 0.05 eV) are due to FE emissions. The NBEPL emissions of 3.43 eV and 3.34 eV were observed in samples known to be $p$-type and their intensities were linearly proportional to the power of the exciting laser radiation. These emissions where therefore assumed to be due to free-to-bound type transitions related to an acceptor. The free-to-bound transition (table 5) has a PL emission of 3.39 eV and involves the $V_{Cu}$ acceptor, which is the most stable intrinsic defect in CuAlS$_2$ under a wide range of environmental conditions (figure 4). It is therefore concluded that either of the observed 3.43 eV and 3.34 eV PL emissions is due to emission 8. Since the FWHM of the observed emissions is 0.1 eV, it is not possible to determine specifically which of the two emissions is related with $V_{Cu}$. The other two NBEPL emissions of 3.45 eV and 3.00 eV were observed on samples grown under stoichiometric and Cu-rich conditions, respectively. The origin of these PL emissions was not concluded from these experiments. On the basis of the calculated PL emissions and thermodynamic stability, emission 6 (3.44 eV) in table 5 might be the origin of the 3.45 eV NBEPL emission. Emission 6 is also related with $V_{Cu}$. The calculated PL emissions and thermodynamic stability suggest the 3.0 eV NBEPL emission can be assigned to emission 12 (3.02 eV) on table 5. This emission is linked with Cu$_{Al}$ which is stabilised under Cu-rich conditions.

---

*It has already been stated that the underlying recombination process of NBEPL can be identified from the behaviour of the PL intensity as the excitation power is varied.*
The 2.76 eV, 2.10 eV and 1.90 eV mid-band gap emissions are broad-peak emissions. The 2.76 eV emission has been observed in \( p \)-type systems but, for the other two emissions, there is no information available on whether the samples are \( p \) or \( n \)-type doped or on the nature of the defect causing the PL emission. Low temperature broad emissions are generally linked with \((D^+A^-)\) type transitions. As the defect concentration increases, the Coulomb-type term in equation \(22\) increases as the distance between distant defect pairs is reduced, resulting in a broad emission band. It is shown in figure \(4\) that the \((D^+A^-)\) pair formed by \(V_{Cu}^{1-}\) and \(Al_{Cu}^{2+}\) is stable. Moreover when the concentration of these defects is large enough, the interaction between them leads to the formation of the \(CuAl_3S_8\) ODC, and it is assumed this renders the \(C(r)\) term in equation \(22\) as negligible. The 1.90 eV and 2.10 eV emissions were observed in samples annealed at 1073 K and 1123 K respectively, and in Al-rich Cu\(_{0.97}Al_{1.03}S_2\) samples. The stable pair formed by \(V_{Cu}^{1-}\) and \(Al_{Cu}^{2+}\) defects is likely to have been formed under these conditions, and transition 19 in table \(5\) indicates it has an associated PL emission of 2.19 eV, which will be broadened by the interaction of distant defect pairs. Therefore, the combined experimental and theoretical evidence suggests that the \((D^+A^-)\) pair as being responsible for the 2.10 eV and 1.90 eV broad emissions. The 2.76 eV emission has been experimentally linked with a bound-to-free (BF) transition involving a deep acceptor whose thermal quenching process was dominated by non-radiative recombination centers. Although the theoretical results suggest PL emissions, that are associated with deep acceptor levels, occur at values that are comparable with experiments (For instance, emission 10 in table \(5\): 2.87 eV), none of these can account for the broadness of the experimentally observed PL emission. Therefore, the experimentally proposed BF transition has to coexist with a \((D^+A^-)\) transition. The theoretical results suggest the \((D^+A^-)\) transition has to be between the pair formed by the \(V_{Cu}^{1-}\) and \(Al_{Cu}^{2+}\) defects.
4 Conclusions

*Ab initio* thermodynamics has been used to study the thermodynamic stability of CuAlS$_2$ and its intrinsic defects. It has been shown that the CuAlS$_2$ is a $p$-type material, and that depending on the environmental conditions, the compound defect ($2V_{Cu}^{1-} + Al_{Cu}^{2+}$)$_0$ has the lowest formation energy of all the defects considered. This is consistent with the stability of the predicted CuAl$_3$S$_8$ ODC, which originates from a high concentration of this type of compound defect.

In addition, our results suggest that CuAlS$_2$ broad visible PL emission, centred at around 2 eV, is due to radiative recombinations that occur between the band gap states related to the $Al_{Cu}^{2+}$ and $V_{Cu}^{1-}$ defects. As regards the room-temperature ultraviolet emission, our results match and complement current experimental evidence, suggesting that UV emissions are related with: a) FE emissions in non-defective CuAlS$_2$; and b) NBEPL emissions connected with $V_{Cu}$ and Cu$_{Al}$ defects.

5 Acknowledgements

The calculations performed for this work were carried out in part on the facilities of Imperial College High Performance Computing Service (URL: http://www.imperial.ac.uk/ict/services/teachingandresearchservices/highperformancecomputing), and in part on the national high-performance computing service of the UK, HECToR, where computer time has been provided via our membership of the HPC Materials Chemistry Consortium of the UK and funded by the EPSRC (portfolio Grant No EP/F067496).

This work was funded by the EPSRC under the "Nanostructured Functional Materials for Energy Efficient Refrigeration, Energy Harvesting and Production of Hydrogen from Water" grant (EP/G060940/1).
References


[25] See Basis Sets file included as supplémentary information.


Figure 1: (Color online) The (16 atom) conventional unit cell of CuAlS$_2$ is shown. Figure (a) indicates the CuAlS$_2$ crystalline structure. Figure (b) shows the $2V_{Cu}^1$ + Al$_{Cu}^{2+}$ defect in CuAlS$_2$ and figure (c) indicates the crystalline structure of CuAl$_3$S$_8$.


Figure 2: (Color online) Projected density of states (PDOS) for bulk CuAlS$_2$. The Fermi energy is the zero of energy.

Figure 3: (Color online) Calculated phase diagram for the Cu-Al-S system indicating the stable phases in the vicinity of CuAlS$_2$. $\Delta \mu_{\text{Cu}} = 0$ and $\Delta \mu_{\text{Al}} = 0$ indicates Cu-rich, Al-rich regions. Since $\Delta \mu_S$ is defined through equation (2), the $\Delta \mu_{\text{Cu}} = \Delta \mu_{\text{Al}} = 0$ also indicates a S-poor region. The diagonal line which links the $\Delta \mu_{\text{Cu}}$ and $\Delta \mu_{\text{Al}}$ axes represents a sulphur rich region with $\Delta \mu_S = 0$. 

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<table>
<thead>
<tr>
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<tr>
<td>Chichibu et. al.</td>
<td>LP-MOVPE, high grade</td>
<td>10</td>
<td>3.52 (0.1), 2.76 (0.4)</td>
<td>A, (Δ^0X) or (Δ^-X)</td>
<td>A, (Δ^+Δ^-)</td>
</tr>
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<td>Chichibu et. al.</td>
<td>LP-MOVPE, low grade</td>
<td>10</td>
<td>3.43 (0.1), 3.34 (0.1), 2.76 (0.4)</td>
<td>(ΔΔ^0), (ΔΔ^0), (Δ^0X) or (Δ^-X)</td>
<td>(ΔΔ^0), (ΔΔ^0), (Δ^+Δ^-)</td>
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<td>Kuroki et. al.</td>
<td>Pellets ann. at 1073, defective K</td>
<td>298</td>
<td>1.90 (0.3)</td>
<td>(Δ^+Δ^-)</td>
<td>(Δ^+Δ^-)</td>
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<td>Pellets ann. at 1123 K, defective</td>
<td>298</td>
<td>1.90 (0.3)</td>
<td>(Δ^+Δ^-)</td>
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<td>Kuroki et. al.</td>
<td>Pellets ann. at 937 K, defective + CuS</td>
<td>15, 30, 50, 70</td>
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<td>A, N/A</td>
<td>A, (ΔΔ^0)</td>
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<td>CVT, Al rich, defective</td>
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<td>3.55 (0.05), 2.11 (0.3)</td>
<td>A, N/A</td>
<td>A, (Δ^+Δ^-)</td>
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</table>

Table 4: Observed PL emissions on CuAlS₂ samples. The synthesis methods are indicated in the second column. The temperature at which the PL emission was observed and its corresponding intensity and FWHM are indicated in the third and fourth columns. Columns five and six show the proposed experimental and theoretical origins of the observed PL emissions: (A) FE recombination; (ΔΔ^0X) excitonic emission bound to a neutral donor; (Δ^+X) excitonic emission bound to a singly-charged donor; (ΔΔ^0) radiative recombination of a free hole and a donor; (Δ^0X) excitonic emission bound to a neutral acceptor; (Δ^-X) excitonic emission bound to a singly-charged acceptor; (ΔΔΔ^0) radiative recombination of a free electron and an acceptor (free-to-bound emission); and (Δ^+Δ^-) is a donor acceptor pair recombination. The subscript s indicates a strong PL intensity.
Table 5: Calculated values of the PL emission energies, $h\nu_{\text{CAL}}$, associated with different defect states in CuAlS$_2$. $E_G = 3.5 \ eV$ is the calculated band gap and $R_x = 0.07 \ eV$ is the FE binding energy. The second column shows the form equation (17) adopted depending on the type of PL emission and the defects involved. The values of the electronic transition energies $\epsilon(Dor\ A, q/q')$ used on the expressions on the second column were taken from table [3].

<table>
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<tr>
<th>Identifier</th>
<th>Type</th>
<th>Expression for PL emission</th>
<th>$h\nu_{\text{CAL}} [\text{eV}]$</th>
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</thead>
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<tr>
<td>1</td>
<td>FE</td>
<td>$E_G - R_x$</td>
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<td>2</td>
<td>$I_{D'X}$</td>
<td>$E_G - 0.29\epsilon(Al_{Cu},0/1+) - R_x$</td>
<td>3.12</td>
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<td>$I_{D'X}$</td>
<td>$E_G - 1.00\epsilon(Al_{Cu},0/1+) - R_x$</td>
<td>2.34</td>
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<td>$I_{D'^0}$</td>
<td>$E_G - \epsilon(Al_{Cu},0/1+)$</td>
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<tr>
<td>5</td>
<td>$I_{D'^0}$</td>
<td>$E_G - \epsilon(Al_{Cu},1+/2+)$</td>
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<tr>
<td>6</td>
<td>$I_{A'X}$</td>
<td>$E_G - 0.11\epsilon(V_{Cu},1-/0) - R_x$</td>
<td>3.44</td>
</tr>
<tr>
<td>7</td>
<td>$I_{A'X}$</td>
<td>$E_G - 1.18\epsilon(V_{Cu},1-/0) - R_x$</td>
<td>3.31</td>
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<tr>
<td>8</td>
<td>$I_{A'^0}$</td>
<td>$E_G - \epsilon(V_{Cu},1-/0)$</td>
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<td>9</td>
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<td>10</td>
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<td>2.87</td>
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<td>22</td>
<td>$I_{D'^A}$</td>
<td>$E_G - [\epsilon(Al_{Cu},1+/2+) + \epsilon(V_{S},1+/2+)]$</td>
<td>1.31</td>
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Figure 4: (Color online) Defect formation energies at the border of the CuAlS$_2$ stability region. This region is defined by the lines connecting the points 1-2-3-4 in figure 3.
Figure 5: (Color online) Defect formation energies at the four corners of the stability region of CuAlS$_2$ (figure 3). At these four points, labeled 1, 2, 3 and 4, the chemical potentials $\mu_i$ have fixed values, and the defect formation energy is a function of the Fermi energy, whose values range have been assumed to be vary from the VBM up to the CBM. The breaking points of each line indicates the transition energies between different charged states of the defect. In each plot, vertical dash-dotted lines mark the $n$ and $p$-type doping limits, and a red dash-dotted line indicates the equilibrium Fermi energy $E_F$, which has been calculated self-consistently using the neutrality condition (equation (3)) at a temperature of 900K.

![Figure 5](image.png)

Figure 6: (Color online) Calculated defect transition energies as defined by equation (12). Their precise values are given in table 3. The transitional charge states are indicated in parenthesis. The thick black lines at the top and bottom represent the CBM and VBM respectively.

![Figure 6](image.png)