An *Ab Initio* Perspective on the Key Defects of CsCu₅Se₃, a Possible Material for Optoelectronic Applications

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Abstract

We report herein a study of the native point defects of a newly synthesized chalcogenide material, CsCu_5Se_3 , using an *ab initio* approach (DFT + U, hybrid functional) to assess the electronic properties of the material through the supercell approach. The complex stability domain of this compound is investigated and defect formation enthalpies are calculated with respect to the synthesis conditions. It shows that the layered structure of this compound is very prone to cationic vacancies, leading to a very pronounced *p*-type behaviour. Depending on the conditions, V_{Cs} or V_{Cu} defects are the majority defects in the material and both play the role of acceptors. Chalcogen vacancies V_{Se} are always much less concentrated than cationic vacancies, despite being sometime quite low in enthalpy. The calculated interstitial defects are negligible. Defect concentrations with respect to crystal growth temperature were also simulated and rise up to $\simeq 10^{21} \text{ cm}^{-3}$ concentration for the majority defect above 500 K.

Introduction

Technical progress requires the constant discovery of new materials in a quest for ever improving properties. Among the current technological issues, more sustainable ways of producing energy are needed to address the challenges thrown by climate change and fossil fuel depletion. To that respect, photovoltaic electricity generation seems to be a promising solution. Indeed, industrial and academic researchers are looking for potential alternative materials overperforming the overwhelmingly deployed silicon-based solution. Different families of compounds are currently under investigation¹⁻³ and chalcogenides occupy a place of choice in this picture.⁴⁻⁸ Among the different approaches followed, original synthesis routes are developed in order to discover new absorber compounds. Recently, a solvothermal route allowed Xia *et al.*⁹ to obtain a new chalcogenide material, CsCu₅Se₃, exhibiting a strong 2D character and a suitable direct bandgap for optoelectronic applications ($\simeq 1.35$ eV). This newly discovered compound is isostructural to CsCu₅S₃, a layered material with caesium atoms sandwiched between copper-chalcogenide sheets. In order to assess the suitability of such new materials for the desired applications, it is important to understand the origin of their electronic properties (*n*-type/*p*-type). Hence, it is critical to evaluate the importance of the native point defects of a material as they are the key to rationalise the properties. To do so, the modelling community, following the pioneering work of Zunger, Lany, van de Walle among others,¹⁰⁻¹⁷ is now in possession of a mature methodology to tackle point defects, using the so-called supercell approach along with Density Functional Theory (DFT) computations.

No further investigation on CsCu₅Se₃ has been reported since its discovery. In order to identify the electronic properties of the material (*n*-type/*p*-type) and its origin, we report herein the very first study of the native point defects of this recently synthesized material using an *ab initio* approach (DFT + U, hybrid functional).

Computational details

The calculations were performed within the projector-augmented waves (PAW) scheme implemented in VASP^{18–21} using density functional PBE.²² Starting from pure GGA-PBE, one obtains a very tiny bandgap 0.09 eV. Thus, the semiconductor character of the material is not properly described with pure GGA and one needs to recover this semiconducting property in the model. Copper 3*d* localized electrons were thus treated by adding a Hubbard term of 6 eV within the formalism introduced by Dudarev *et al.*²³ in agreement with previous literature.²⁴ The cutoff for the plane-waves was set to 400 eV. Faulted supercells were built on a 2x2x2 ideal supercell containing 144 atoms. Reciprocal space was discretized following a Monkhorst-Pack scheme²⁵ on a $4 \times 8 \times 4$ grid leading to 64 irreducible *k*-points in the first Brillouin zone for structural relaxation and a Γ -centered grid of the same size (68 irreducible *k*-points) for DOS and energy calculations. Convergence criteria were set for the conventional cell optimisation to 10^{-6} eV and 10^{-3} eV/Å for the self-consistent cycle and forces, respectively, and to 10^{-5} eV and 10^{-2} eV/Å for the supercell relaxations. The GGA + U bandgap is obtained at 0.44 eV, to compare to an experimental value of 1.4 eV. Even if the material exhibits a marked 2D character, no van der Waals gap was expected since Cs atoms are sandwiched between $2/\infty$ [Cu₅Se₃] layers. Calculations *at posteriori* carried out fully confirmed this statement. To correctly assess the bandgap and correct the GGA+U calculations, the screened hybrid functional HSE06²⁶ including $\frac{1}{4}$ of Hartree-Fock exchange was employed using the standard value of range-separating coefficient $\omega = 0.2$. The electronic structures calculated using HSE06 on top of the GGA+U geometry, noted HSE06@PBE+U, and to confort it additionally performed consistently on top of the HSE06-optimised geometry, referred to as HSE06@HSE06, are given in Figures SI 1 and the position of the band extrema for the different methodologies in Figure SI 2.

The calculated HSE06@HSE06 electronic bandgap is 1.22 eV (-10% with respect to experiment). It is used to correct the band edge positions for all faulted supercell GGA+U calculations in the rest of the study. The trace of the dielectric tensor was found to be

$\epsilon = 22.16$ (static plus ionic contributions) and used for the image charge correction. All post-treatments were performed with the PyDEF 2.0 software.^{27,28}

Defect formation enthalpies and concentrations methodologies

The defect formation enthalpy, hereafter abbreviated DFE, can be assimilated to a formation energy because the variation in volume is negligible in the case of dilute defects. In that context, the formation enthalpy $\Delta H_{form}^{D,q}$ of a defect D in a state of charge q is given by a linear function of the Fermi level (chemical potential of the electron reservoir) μ_{EF} as expressed in the following equation:^{29–33}

$$\begin{aligned} \Delta H_{form}^{D,q}(\mu_{EF}) = & E_{total}^{D,q} - E_{total}^{host} + \sum_i n_i(\mu_i^0 + \Delta\mu_i) \\ & + q(E_{VBM}^{host} + \mu_{EF}) + corr(D, q) \end{aligned} \quad (1)$$

where $E_{total}^{D,q}$ is the energy of the faulted supercell, E_{total}^{host} is the total energy of the perfect (host) cell, $\mu_i = \mu_i^0 + \Delta\mu_i$ is the chemical potential of the i^{th} chemical element, expressed as the standard chemical potential of the i^{th} chemical element μ_i^0 , *i.e.* the energy per atom in the reference elemental phase of such element in standard conditions, and the chemical potential deviation $\Delta\mu_i$ from this value $n_i < 0$ for added atoms and $n_i > 0$ for removed atoms. The $corr(D, q)$ term corrects spurious effects introduced by the supercell model. Band-edge position, Makov-Payne-like, Moss-Burstein type and Perturbed Host States (PHS) corrections were included to account for finite-size effects. More details are given in SI, besides, we followed the same methodology as in our previous studies.^{34,35}

The value of the Fermi level at which the charge changes from q_0 to q_1 is the charge

transition level $\epsilon_{(q_0, q_1)}$, hereafter abbreviated CTL, given as stated in equation 2.

$$\epsilon_{(q_0, q_1)} = -\frac{\Delta H_{form}^{D, q_1}(0) - \Delta H_{form}^{D, q_0}(0)}{q_1 - q_0} \quad (2)$$

It is the Fermi level μ_{E_F} at which the formation enthalpies of q_0 and q_1 are equal as stated in equation 3.

$$\Delta H^{D, q_0}(\epsilon_{(q_0, q_1)}) = \Delta H^{D, q_1}(\epsilon_{(q_0, q_1)}) \quad (3)$$

CTL can be assimilated to a defect level.

Results and discussion

Cristallographic structure

CsCu₅Se₃ cristallizes in a Pmma (n 51) structure with two formula unit per conventional cell, as drawn in Figure 1.⁹ It is a layered structure with nona-coordinated caesium atoms sandwiched between copper selenide sheets roughly 5 Å-thick. Copper is split between three distinct cristallographic sites. Cu₁ atoms sit slightly above a triangle whose corners are occupied by two Se₁ and one Se₂ with a relatively short copper-copper distance ($d_{\text{Cu}_1-\text{Cu}_1} \simeq 2.52$ Å). To some regards, the [Cu₍₁₎Se₃]₂ fragment could be viewed as an “ethane-like” group with a slight Cu₁–Cu₁ interaction. Cu₂ is also tricoordinated by selenium and form Cu₍₂₎Se₃ fragments capped with two equidistant Cu₃ atoms while Cu₃ exhibits a linear configuration bonded to two Se atoms. Detailed interatomic distances are available in Table 1.

Stability domain

The stability domain of the material was investigated by comparing the formation enthalpies of all known crystallised compounds in the Cs-Cu-Se system using the aforementioned

Figure 1: CsCu_5Se_3 structure (SG Pmma). The conventional cell is delimited by black lines. Purple spheres correspond to Cs atoms (2e site). Beige ones represent Cu_1 atoms (4j site). Cu_2 atoms (4i site) are represented in orange and Cu_3 atoms (2f site) in brown. Light green spheres represent Se_1 atoms (2e site) and darkgreen ones Se_2 (4j position). The interatomic distance values shown are those of the XRD data from Xia *et al.*⁹

Table 1: Interatomic distances ($\text{\AA}$) for copper environments in the CsCu_5Se_3 structure.

($\text{\AA}$)	ICSD ⁹	PBE + U	Δ_{rel} (%)
$\text{Cu}_1\text{-Cu}_1$	2.517	2.532	0.6
$\text{Cu}_1\text{-Se}_1 \times 2$	2.495	2.511	0.6
$\text{Cu}_1\text{-Se}_2$	2.364	2.404	1.7
$\text{Cu}_2\text{-Cu}_3$	2.725	2.714	-0.4
$\text{Cu}_2\text{-Se}_1$	2.440	2.476	1.5
$\text{Cu}_2\text{-Se}_2 \times 2$	2.449	2.475	1.0
$\text{Cu}_3\text{-Se}_2 \times 2$	2.355	2.380	1.1
$\text{Cu}_3\text{-Cu}_2 \times 2$	2.725	2.714	-0.4

GGA+U parameters. Starting point for the geometry optimisations were taken from the Inorganic Crystallographic Structure Database (ICSD).³⁶ The 16 different phases considered are listed in SI. As the system exhibits lots of phases, are presented in Figure 2a only the compounds limiting the stability domain of CsCu_5Se_3 , the material of interest. Another representation in the $(\mu_{\text{Cs}}, \mu_{\text{Cu}})$ plane is displayed on Figure 2b. The chemical potential values are summarised in table 3. To simplify, the complex shape of the stability domain was approximated by the triangle $AF\frac{C+D}{2}$. The latter point, half of the CD segment, will hereafter be labelled CD. The A synthesis conditions correspond to the limit of formation of Cu_3Se_2 and Cu, they are the most copper-rich conditions of the stability domain. CD corresponds to the limit of formation of CsCuSe_4 and F of Cu and $\text{Cs}_3\text{Cu}_8\text{Se}_6$. Table 2 sums it up; A corresponds to Cu-rich growth conditions, CD to Cu-poor and Se-rich conditions and F to Cs-rich and Se-poor ones.

Table 2: Limit growth conditions considered.

	Cs	Cu	Se
A	poor	rich	intermediate
CD	intermediate	poor	rich
F	rich	rich	poor

(a)

(b)

Figure 2: Stability domain of CsCu_5Se_3 in $(\mu_{\text{Se}}, \mu_{\text{Cu}})$ (a) and $(\mu_{\text{Cs}}, \mu_{\text{Cu}})$ (b) chemical potential planes, simplified to the grey triangle. A, CD and F correspond to $(\mu_{\text{Cs}}, \mu_{\text{Cu}}, \mu_{\text{Se}})$ equal to $(-3.24 \text{ eV}, -1.76 \text{ eV}, -4.09 \text{ eV})$, $(-2.97 \text{ eV}, -2.125 \text{ eV}, -3.57 \text{ eV})$ and $(-2.06 \text{ eV}, -1.76 \text{ eV}, -4.49 \text{ eV})$, respectively. The three chemical potentials are linked by the equation of the formation enthalpy of CsCu_5Se_3 $H_f(\text{CsCu}_5\text{Se}_3) = \mu_{\text{Cs}} + 5\mu_{\text{Cu}} + 3\mu_{\text{Se}}$. All coordinates are available in Table 3.

Table 3: Limits of CsCu₅Se₃ stability domain. Chemical potential deviation from the standard state of reference $\Delta\mu$ are indicated between brackets. All energies are given in electronvolts.

	$\mu_{Cs} (\Delta\mu_{Cs})$	$\mu_{Cu} (\Delta\mu_{Cu})$	$\mu_{Se} (\Delta\mu_{Se})$
A	-3.24 (-2.40)	-1.76 (0.00)	-4.09 (-0.59)
B	-3.21 (-2.37)	-2.04 (-0.28)	-3.64 (-0.14)
C	-3.06 (-2.22)	-2.12 (-0.36)	-3.55 (-0.05)
D	-2.88 (-2.04)	-2.13 (-0.37)	-3.60 (-0.10)
E	-2.51 (-1.67)	-1.98 (-0.22)	-3.97 (-0.47)
F	-2.06 (-1.22)	-1.76 (0.00)	-4.49 (-0.99)
$\frac{CD}{2}$	-2.97 (-2.13)	-2.13 (-0.37)	-3.58 (-0.08)

Defect formation enthalpies

The DFE *vs.* Fermi level are presented in Figures 3a, 3b and 3c. Distinguishing between the different cristallographic sites, three copper vacancies (V_{Cu}), two selenium vacancies (V_{Se}) and the caesium vacancy (V_{Cs}) were considered. Additionally, the calculations were performed on two interstitials, a copper one and a selenium one (Cu_i and Se_i). Both interstitials were arbitrarily initialized in a position in the void between caesium and the Cu-Se layers before relaxation. The detailed positions before and after relaxation are given in Table SI 5.

All cation vacancies will exhibit a 0/-1 CTL making them acceptor defects (favouring *p*-type conductivity). The selenium interstitial Se_i ($q = 0/-1/-2$) is an acceptor too. The closest to the Valence Band Maximum (VBM) this CTL sits in the gap, the more holes will be created at the top of the VB if the Fermi level is pinned near the CTL. Conversely, selenium vacancies ($q = +2/+1/0$) and copper interstitial ($q = 0/+1$) are donor defects (favouring *n*-type conductivity).

Se_i is a very deep acceptor defect with a negative U-behaviour ($\epsilon_{0/-2} = 0.79$ eV) as the intermediate state of charge $q = +1$ is not thermodynamically stable. It is moreover very high in formation enthalpy (for the neutral state of charge, 3.11 eV at A, 2.59 eV at CD and 3.02 eV at F), thus it is of no interest regarding the targeted electronic properties of the material for a possible application in photovoltaics. All the other acceptors (V_{Cu} and V_{Cs}) have CTL exceptionally close to the VBM ($\epsilon(0/-1) \leq 0.09$ eV). Numerical values are

detailed in SI. Their DFE is less than 1 eV and most importantly they are lower in enthalpy than the donor defects, whatever the synthesis conditions. Thus, the hole concentration will be expected to be more important than the concentration of donors. Donor defects for their part are all deep defects, their CTL being far from the CBM.

Now let us look at the different synthesis conditions in more details. At the A limit of the stability domain (Cu-rich atmosphere), V_{Cs} is the major defect, 0.32 eV lower in enthalpy than V_{Cu1} with the second lowest DFE. Its DFE is positive but very low in absolute value ($\simeq 0.10$ eV). It means that the vacancy is very easy to form in such conditions. Additionally, V_{Cu1} has a DFE inferior to $\simeq 0.50$ eV (0.38 eV) and is much more concentrated than V_{Se1} , the most concentrated donor defect in this atmosphere with a DFE of 0.60 eV. V_{Se} DFE is the lowest at A compared to CD and F. Selenium vacancies DFE do not change by more than 0.60 eV between the different conditions.

The Fermi level during crystal growth cannot enter regions of the bandgap where at least one defect has a negative DFE, otherwise the creation of the defect would be favoured over the formation of the structure and it would lead to the formation of another phase instead of the one expected. The defect with the lowest DFE sets the dopability limit: the maximum value allowed for the Fermi level during synthesis. This value is given by the solution to the $(\Delta H_f(\mu_{E_F}) = 0)$ equation of variable μ_{E_F} for the most concentrated defect. Indeed, as the concentration dependence in ΔH_f is the inverse of an exponential, a Fermi level value higher than the dopability limit would compromise the charge neutrality of the material. There would be so much defects of the lowest DFE that it would be impossible to compensate the created charges. In A conditions, the dopability limit is set by V_{Cs} at $\simeq 0.10$ eV. It means that the Fermi level, the chemical potential of the electrons, has to stay within the vicinity of the VBM for $CsCu_5Se_3$ to be synthesised. This leads us to believe the material will exhibit a very good hole conductivity, *i.e.* it is an exceptional *p*-type semiconductor, even more as the Fermi level is pinned by cationic vacancies.

Then, let one examine the CD case (Cu-poor, Se-rich). As expected, the lowest DFE

in such conditions is that of a copper vacancy, V_{Cu1} . It is undoubtedly easier to form copper vacancies in growing conditions which are slightly under stoichiometric in terms of copper. The second lowest DFE, $\simeq 0.30$ eV higher, is that of V_{Cu3} . Copper vacancies in such conditions are the major defect of the material, although the caesium vacancy has still a small DFE of $\simeq 0.35$ eV. The dopability domain is limited to a 0.07 eV-wide region above the VBM due to the tiny DFE of V_{Cu1} . This stability domain is tiny due to the extremely low DFE of V_{Cu1} . The material obtained at such theoretical limit, if experimentally possible, is expected to be heavily faulted and may be difficult to stabilise in practical terms. Anyway, it still highlights the very good p -conductivity of $CsCu_5Se_3$ due to a dopability domain very close to the VBM and very concentrated donor defects (DFE as low as 0.09 eV).

In contrast to the situation at A, V_{Cu1} is the major defect at F (Cs-rich, Se-poor), thanks to a very low DFE of 0.18 eV. At F, all three copper vacancies are more concentrated than V_{Cs} and than the donor defects. In F conditions, V_{Se} still exhibit a DFE inferior to 1 eV, quite close to A values, however as pointed out previously, they are still higher in enthalpy than the acceptor defects.

From the analysis of the DFE, one can conclude that $CsCu_5Se_3$ has a high propensity to exhibit acceptor defects, both as caesium and copper vacancies, the major defect depending on the conditions. Of all the copper vacancies, V_{Cu1} is the easiest to form. This is independent from the point on the stability domain (A, F, $\frac{CD}{2}$) as the DFE are all shifted by the same μ_{Cu} value. This may be explained by the fact that Cu_1 has a shorter Cu-Cu distance than Cu_2 , so that the repulsion between the two cations is stronger for Cu_1 than for Cu_2 . Besides, the removal of one Cu_1 atom leads to a bicoordinated Cu_1 in a linear environment that is chemically stable.

Defect concentrations

Derived from the DFE by applying a Boltzmann statistics as expressed in equation 4, one can obtain the defect concentrations with respect to the growth temperature, T_{gr} as shown in

Figure 4 and in SI. N_D^{sites} stands for the number of sites available for the defect, typically the multiplicity of the cristallographic site for a vacancy. The Fermi level during crystal growth E_F^{gr} used in equation 4 is determined by solving the global charge neutrality equation 5. The graphs are presented with a wide temperature range to highlight the trends of the model. Xia *et al.*⁹ used a soft-chemistry solvothermal route at 200°C to synthesize the product, however we will focus our attention on a wider range of temperatures (100-900 K) which comprises the experimental one. The defect concentrations increase with temperature, which captures well the physical intuition of temperature favoring disorders due to the increasing weight of entropy. This concentration model exhibits an inflexion point at low temperature and reaches a plateau at high temperature. The order of magnitude for the major defect concentration is 10^{21} cm^{-3} at the plateau, *i.e.* V_{Cs} in A conditions above 500 K ($\simeq 800^\circ\text{C}$). One can notice that the second most concentrated defect is roughly a thousand times less concentrated than the previous one. The other synthesis conditions have similar behaviours. Experimentally, the material was synthesised using a solvothermal route whereas the calculations are conducted at thermodynamic equilibrium. This soft-chemistry route may induce metastable states which may if present result in behaviour different from the ones predicted in the thermodynamic limit.

$$n_D = N_D^{sites} \cdot \left(e^{\frac{-\Delta H_{form}^{D,q(E_F^{gr})}(E_F^{gr})}{k_B T_{gr}}} \right) \quad (4)$$

$$-n_{e^-}(E_F^{gr}) + n_{h^+}(E_F^{gr}) + \sum_D q_D n_{D,q,T_{gr}}(E_F^{gr}) = 0 \quad (5)$$

Conclusion

Our supercell calculations using GGA-PBE functional within a PAW scheme along with a “+U” Hubbard correction term for copper 3d electrons show that CsCu_5Se_3 layered struc-

ture is very prone to cationic vacancies, leading to a very pronounced *p*-type behaviour. Depending on the conditions, V_{Cs} or V_{Cu} is the major defect in the material. Both are very good acceptor defects. We have identified the preferential V_{Cu} site as Cu_{4j} . The relatively short Cu-Cu distance in Cu_1 environment is probably responsible for this. V_{Se} , although sometimes quite low in enthalpy, are always way less concentrated than cationic vacancies. Thus, they play no detrimental role regarding hole conduction. Our calculation prove that in this case interstitial defects are negligible. Defect concentrations with respect to crystal growth temperature were also simulated and point to a 10^{21} cm^{-3} concentration for the major defect. The very strong *p*-type character due to the identified defects is encouraging for its use as an absorber in photovoltaic solar cells.

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI xxxxxxxx

- electronic band structure and DOS
- positions of the band extrema
- computed cell parameters *vs.* methodology

- details on the corrections to the defect formation enthalpies
- comparison before/after BS+PHS correction
- detailed correction values
- positions of the interstitial defects
- Charge Transition Levels
- intrinsic defect concentrations

Figure 3: a) Defect formation enthalpies of intrinsic defects in CsCu_5Se_3 in A synthesis conditions (Cu/ Cu_3Se_2 , Cu-rich/Cs-poor), $(\mu_{\text{Cs}}, \mu_{\text{Cu}}, \mu_{\text{Se}}) = (-3.24 \text{ eV}, -1.76 \text{ eV}, -4.09 \text{ eV})$; b) in CD synthesis conditions (CsCuSe_4 , Cu-poor), $(\mu_{\text{Cs}}, \mu_{\text{Cu}}, \mu_{\text{Se}}) = (-2.97 \text{ eV}, -2.13 \text{ eV}, -3.58 \text{ eV})$; c) and in F synthesis conditions (Cu/ $\text{Cs}_3\text{Cu}_8\text{Se}_6$, Cu-rich/Cs-rich), $(\mu_{\text{Cs}}, \mu_{\text{Cu}}, \mu_{\text{Se}}) = (-2.06 \text{ eV}, -1.76 \text{ eV}, -4.49 \text{ eV})$.

Figure 4: Intrinsic defect concentrations *vs.* growth temperature in CsCu₅Se₃ in A synthesis conditions (Cu/Cu₃Se₂).

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Graphical TOC Entry