# Supplementary Information: $Cu_2SiSe_3$ as a promising solar absorber: harnessing cation dissimilarity to avoid killer antisites

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## S1. Lattice Parameters

Table S1: Calculated lattice parameters for $Cu_2SiSe_3$ using PBEsol and hybrid DFT (HSE06) with and without the inclusion of vdW dispersion interactions. Dispersion interactions are accounted for using the D3 correction with and without Becke-Johnson dampening. Percentage errors are with respect to experimental values.[S1]

|  | a | b | c |
|---|---|---|---|
| PBEsol | 6.64 Å (-0.4 %) | 11.65 Å (-1.3 %) | 6.66 Å (0.4 %) |
| HSE06 | 6.70 Å (0.4 %) | 11.84 Å (0.3 %) | 6.67 Å (0.6 %) |
| HSE06+D3 | 6.62 Å (-0.7 %) | 11.67 Å (-1.1 %) | 6.58 Å (-0.8 %) |
| HSE06+D3(BJ) | 6.60 Å (-1.0 %) | 11.67 Å (-1.1 %) | 6.57 Å (-0.9 %) |

# S2. Electronic Structure
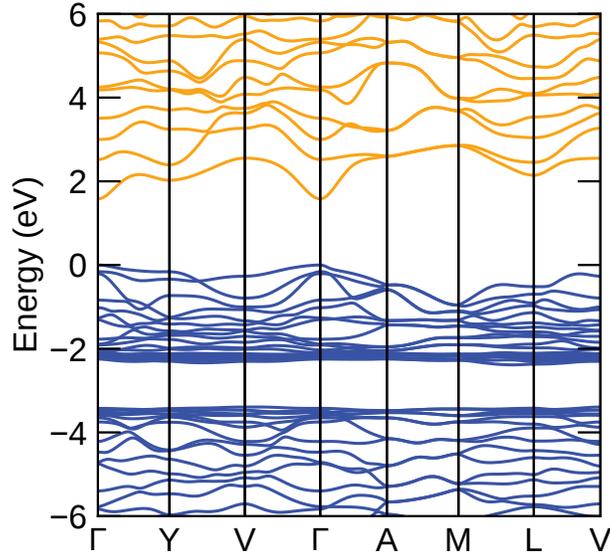


Figure S1: Electronic band structure of $Cu_2SiSe_3$ calculated with $QSG\hat{W}$. The valence band maxmimum is set to $0\,eV$, with valence bands in blue and conduction bands in orange.
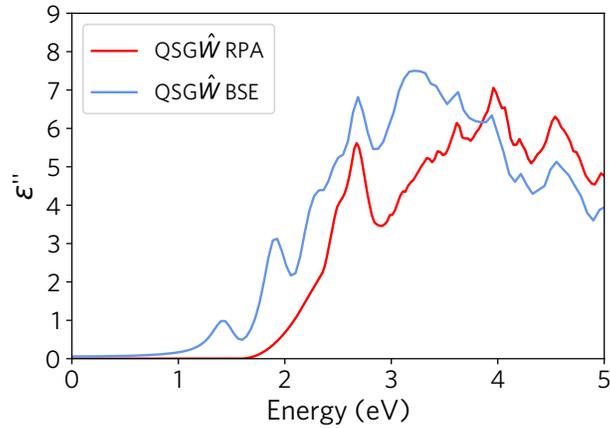


Figure S2: The z component of the imaginary dielectric spectrum of $Cu_2SiSe_3$ calculated with $QSG\hat{W}$ self-energy within the Random Phase approximation (RPA) and Bethe-Salpeter equation (BSE).
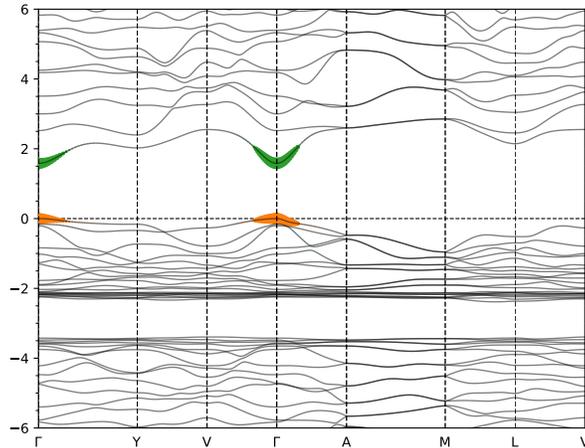
Figure S3: Electronic band structure of $Cu_2SiSe_3$ calculated with $QSG\hat{W}$, with exciton wavefunction weights projected onto the corresponding bands. The valence band maxmimum is set to $0\,eV$.
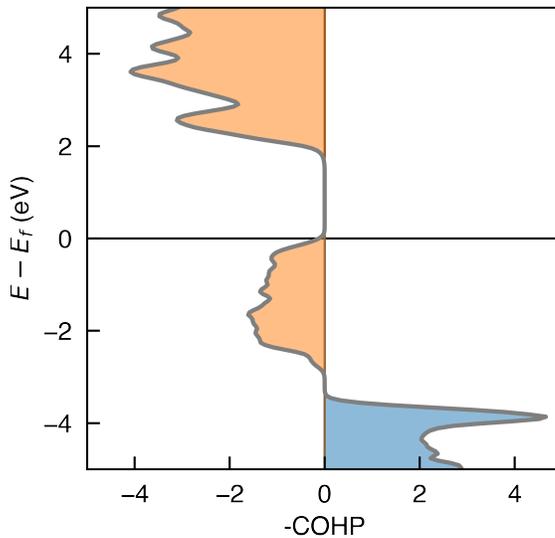


Figure S4: Cumulative Crystal Orbital Hamiltonian Population (COHP) analysis, which decomposes the density of states into bonding and anti-bonding orbital interactions.[S2–S4] Negative COHP values (blue) indicate bonding-type interactions and positive values (orange) indicate anti-bonding interactions.

## S3. Chemical potential space

To calculate the region of stability for $Cu_2SiSe_3$, the bordering competing phases were obtained from the Material Project.[S5] However, care must be taken due to the formation

energies predicted by the Material Projects (GGA/GGA+U) having a mean absolute error of 0.133 eV/atom.[S6] Furthermore, when looking at the predicted compositional phase diagram for Cu-Si-Se it can be seen that $Cu_2Se$ is found to lie 0.083 eV/atom above the hull, although it is found to be stable experimentally and is a commonly used precursor. Therefore, the formation energies of additional competing phases (found in the Inorganic Crystal Structure Database[S7]) were calculated using HSE06, rather than just the predicted bordering phases.

Calculating the formation energy of the competing phases using HSE06 predicts a much larger region of chemical stability, with the region no longer being bound only by $Cu_3Se_2$, $SiSe_2$ and Cu. Furthermore, using hybrid density functional theory (DFT), $Cu_2Se$ is found to be stable, lying on hull. The driving factor for this increase in stability is the lowering of the formation energy of $Cu_2SiSe_3$, when calculated using hybrid DFT, due to the lowering in energy of the Cu $d$ states. To check that the increase in stability was not due to errors introduced in modeling selenium containing phases, through the exclusion of Van der Waals interactions, the formation energies were also determined using the HSE06+D3 functional. The formations energies of $SiSe_2$ and $Cu_3Se_2$, calculated with HSE06+D3, were found to be within 14 meV/atom and 3 meV/atom of those predicted by the Material Project using R2SCAN, which has been shown to reduce the error in predicted formation energies by up to a factor of 2.5.[S8,S9] However, using HSE06/HSE06+D3 we find the formation energy of $Cu_2SiSe_3$ to lie 70/69 meV/atom lower in energy.

Table S2: The elemental chemical potentials at the intersections binding the chemical space for $Cu_2SiSe_3$. Intersection D and C correspond to Cu-rich conditions and G to Cu-poor.

|   | Cu (eV) | Si (eV) | Se (eV) |
|---|---------|---------|---------|
| A | -0.08   | -0.08   | -0.76   |
| B | -0.10   | -1.10   | -0.41   |
| C | 0.00    | -0.72   | -0.60   |
| D | 0.00    | -0.39   | -0.71   |
| E | -0.29   | -1.60   | -0.11   |
| F | -0.41   | -1.71   | 0.00    |
| G | -0.46   | -1.59   | 0.00    |
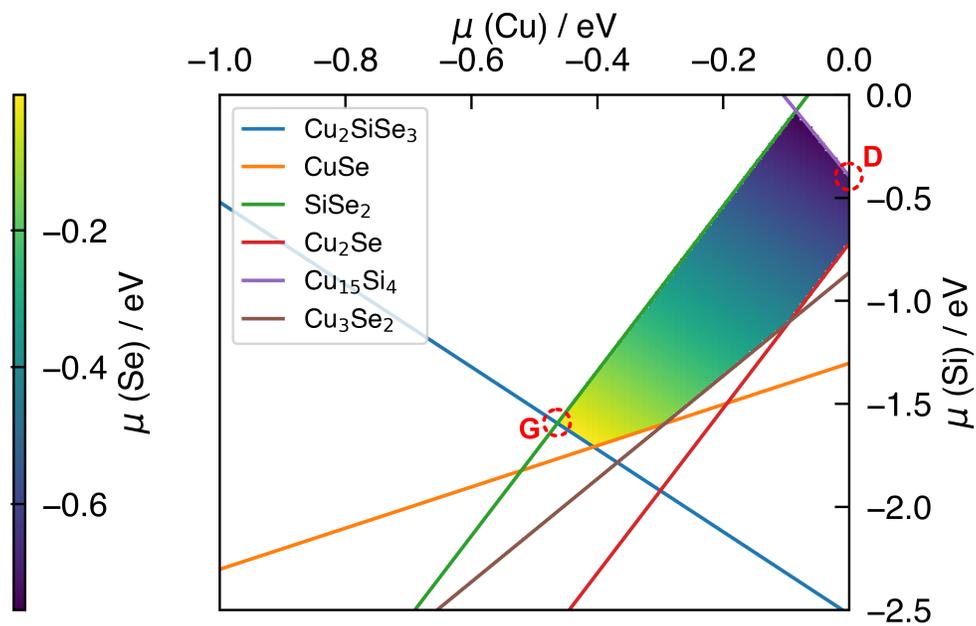
Figure S5: The chemical potential space of $Cu_2SiSe_3$. Intersection D corresponds to Cu-rich conditions and G to Cu-poor.

# S4. Defect Formation Energy Diagrams
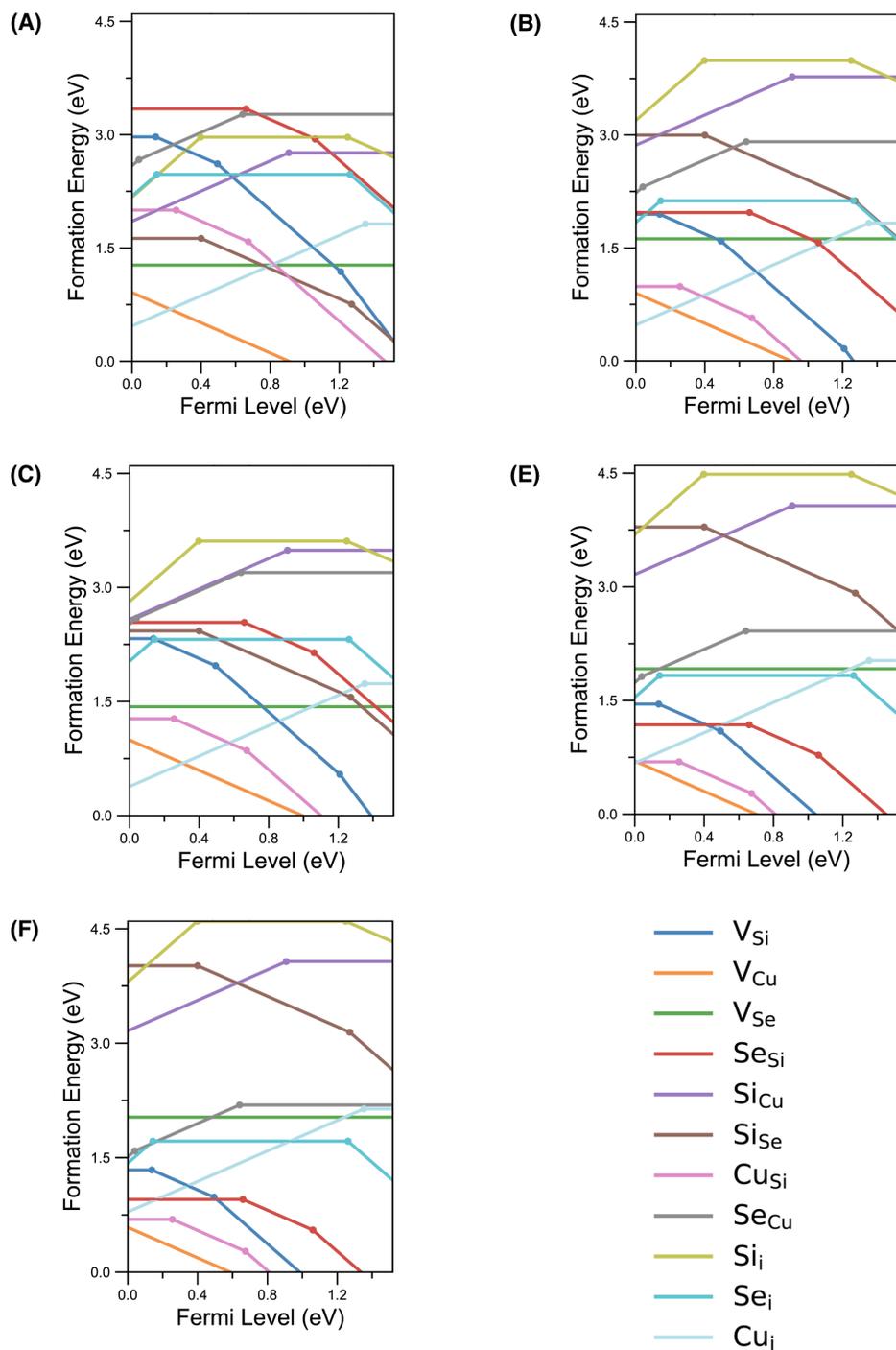


Figure S6: Formation energies as a function of Fermi level for the intrinsic defects in Cu$_2$SiSe$_3$. Labelling refers to the position on the chemical phase diagram, Table S3. For each defect species, only the lowest energy defect site has been plotted.
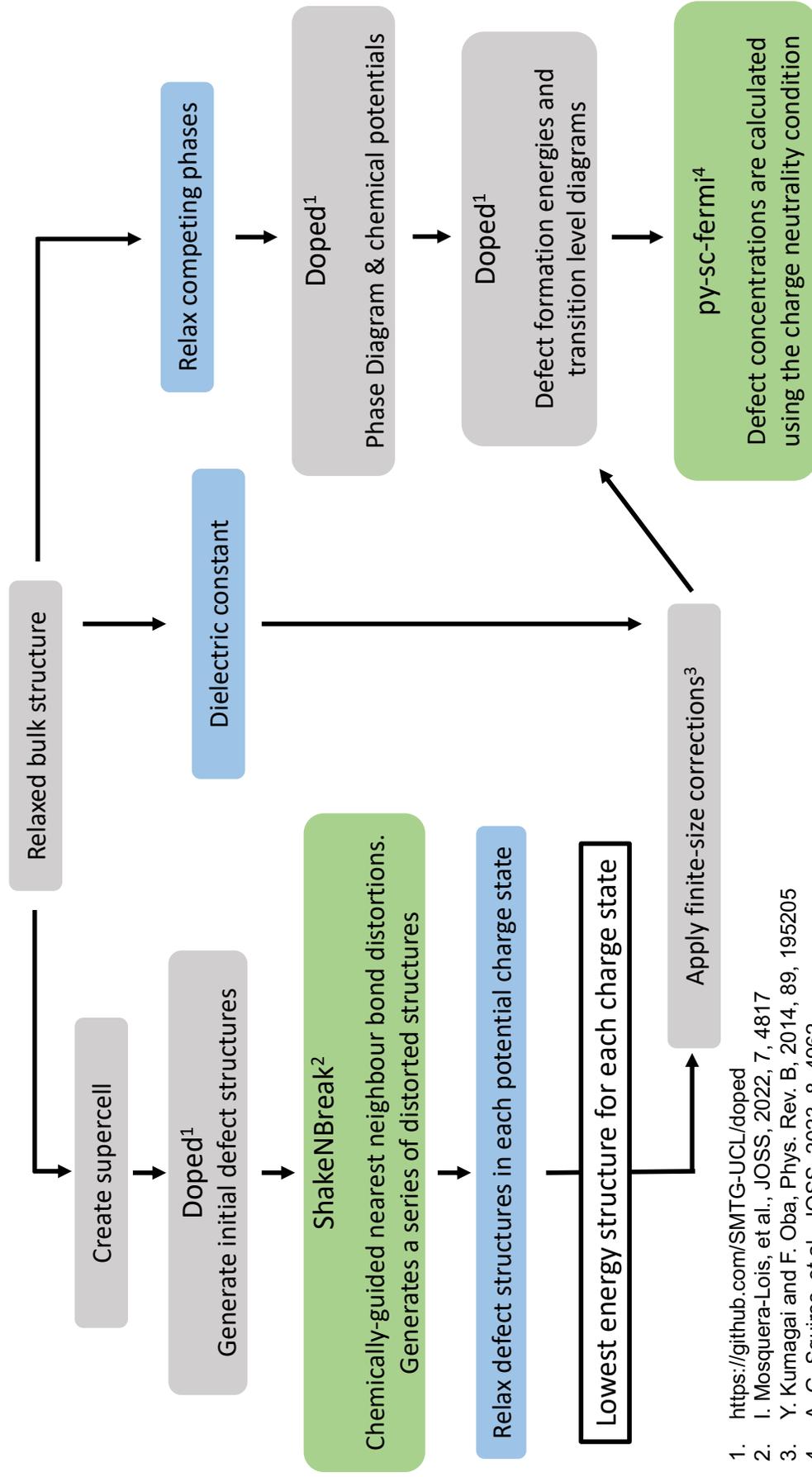
Figure S7: Defect calculation workflow.

Relaxed bulk structure

Relax competing phases

Doped[1]

Phase Diagram & chemical potentials

Doped[1]

Defect formation energies and transition level diagrams

py-sc-fermi[4]

Defect concentrations are calculated using the charge neutrality condition

Dielectric constant

Create supercell

Doped[1]

Generate initial defect structures

ShakeNBreak[2]

Chemically-guided nearest neighbour bond distortions. Generates a series of distorted structures

Relax defect structures in each potential charge state

Lowest energy structure for each charge state

Apply finite-size corrections[3]

1. https://github.com/SMTG-UCL/doped
2. I. Mosquera-Lois, et al., JOSS, 2022, 7, 4817
3. Y. Kumagai and F. Oba, Phys. Rev. B, 2014, 89, 195205
4. A. G. Squires, et al., JOSS, 2023, 8, 4962

Table S3: Number of defect types and charge states studied in this work

|  | Defect species | Sites | Charge states |
|---|---|---|---|
| Vacancy | $V_{Cu}$ | 2 | -1,0 |
|  | $V_{Si}$ | 1 | -4,-3,-2,-1,0 |
|  | $V_{Se}$ | 3 | 0,1,2 |
| Antisite | $Cu_{Si}$ | 1 | -4,-3,-2,-1,0 |
|  | $Si_{Cu}$ | 2 | 0,1,2,3 |
|  | $Si_{Se}$ | 3 | -2,-,1,0 |
|  | $Se_{Cu}$ | 2 | 0,1,2,3,4,5 |
|  | $Se_{Si}$ | 1 | -4,-3,-2,-1,0,1,2,3,4 |
| Interstitial | $Cu_i$ | 17 | 0,1 |
|  | $Si_i$ | 17 | -4,-3,-2,-1,0,1,2,3,4 |
|  | $Se_i$ | 17 | -2,-1,0,1,2,3,4,5,6 |

# S5. Copper Vacancy and Copper Antisites

A quantitative way to determined if a defect state is a perturbed host state (PSHS) is to use the screening method developed by Kumagai et al.,[S10] which defines a PHS as being a VBM-like state within 0.5 eV of the VBM (Figure S10b) and having an orbital dissimilarity less than 0.4. They define orbital dissimilarity as,

$$\Delta_m = \sum_{e,i} |\phi_{vacancy}^{m,e,i} - \phi_{bulk}^{e,i},\tag{S1}$$

where $\phi_{vacancy}^{e,i}$ is the sum of the projections on element $e$ and orbital $i$ ($i = s, p, d,$ or $f$) at the $m$th band in the supercell with the vacancy and $\phi_{perfect}^{e,i}$ is that at the VBM in the perfect supercell. Using their metric, the neutral vacancy is found to be VBM-like with an orbital dissimilarity of 0.01. This indicated that in the case of $V_{Cu}$, the neutral defect state is actually a $V_{Cu}^-$ plus a delocalized hole. This can be seen by visualizing the charge density of the neutral defect where the defect state is delocalized across the supercell and comping to the bulk, Figure S8a and S9. To accurately calculate the energy of such a shallow acceptor level, a supercell of several thousand of atoms is required.[S11] Increasing the size of the supercell from 96 atoms to 160 atoms reduced the transition level from 0.16 eV above the VBM to 0.10 eV. For a PHS it is expected for the formation energy of the neutral vacancy to

be almost the same as the charge defect state when the Fermi level is at the VBM. Therefore, we have set the transition level for a $V_{\text{Cu}}$ in $Cu_2SiSe_3$ to 0 eV above the VBM.

**(a)**



**(b)**
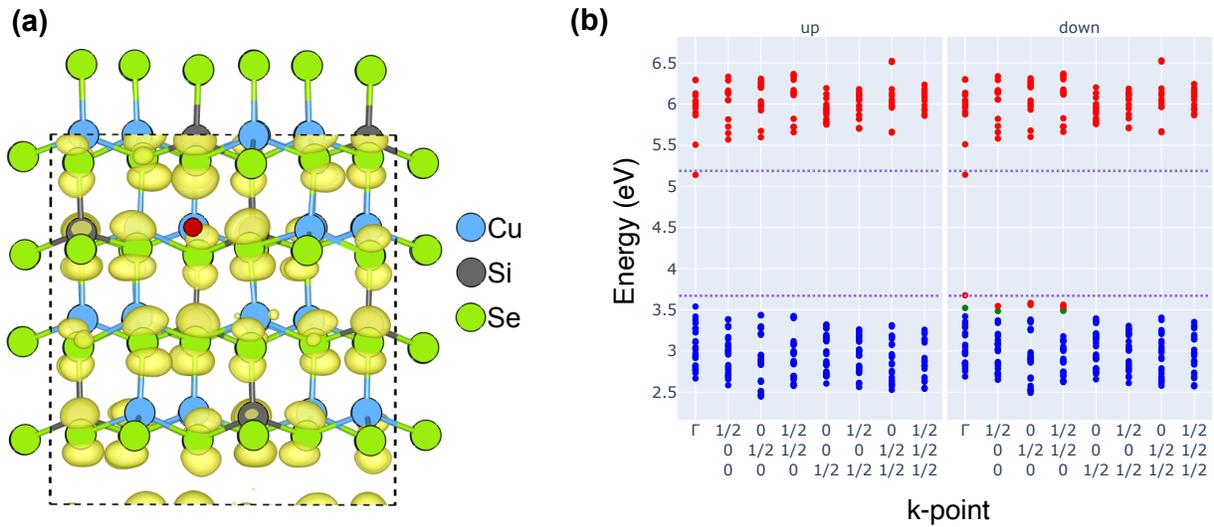


Figure S8: (a) Structure and spin down charge density of a neutral copper vacancy defect state at the VBM. Copper vacancy represented by the red circle. Isovalue set to $1 \times 10^{-3}$ $e/\text{Å}^3$. (b) Plot of the eigenvalues of a neutral copper vacancy defect state. Occupied levels are blue, unoccupied red, and partially occupied are colored green. The VBM and CBM of the pristine supercell are shown by the dashed line.
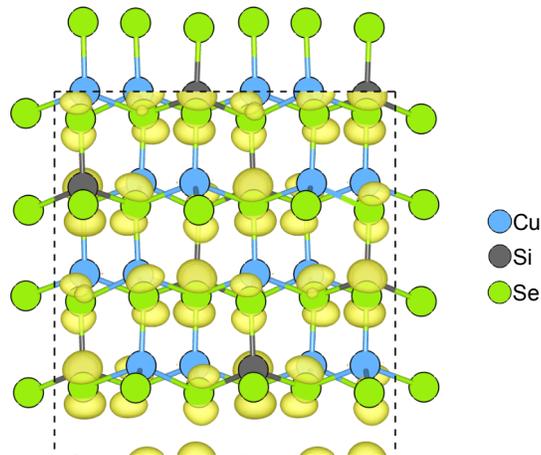


Figure S9: Charge density at the valence band in bulk $Cu_2SiSe_3$. Isovalue set to $1 \times 10^{-3}$ $e/\text{Å}^3$.
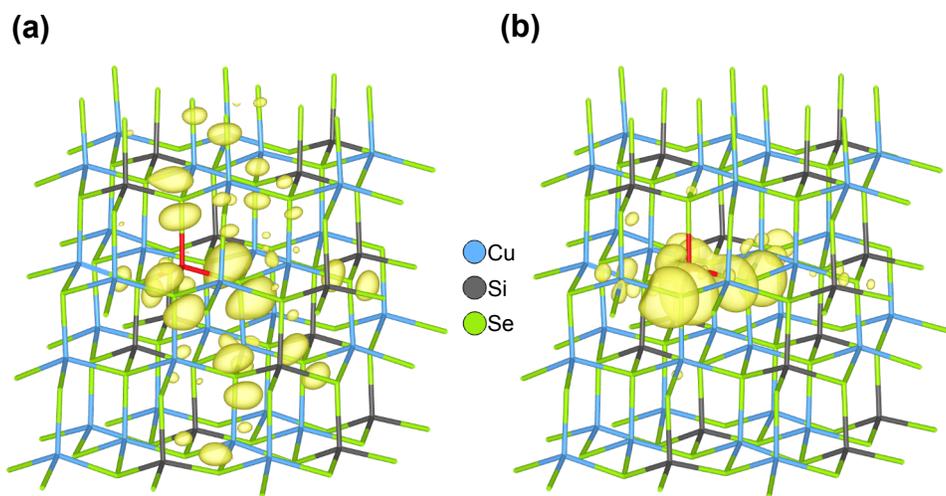
Figure S10: Structure and charge density ((a) spin up and (b) spin down) of a neutral copper on silicon antisite. The $Cu_{Si}$ site is colored red. Isovalue set to $6 \times 10^{-3}$ $e/\text{Å}^3$.

# S6. Ground State Structure Searching

**(a)**



**(b)**



Figure S11: (a) $V_{Se}$ bond distortion method (BDM) plot; nn refers to the number of nearest-neighbours distorted around the defect site. (b) Unperturbed defect structure (top) and energy lowering reconfiguration (bottom). Vacancy indicated by red circle. The lowest energy defect structure was also identified as the ground state structure for all charge states.
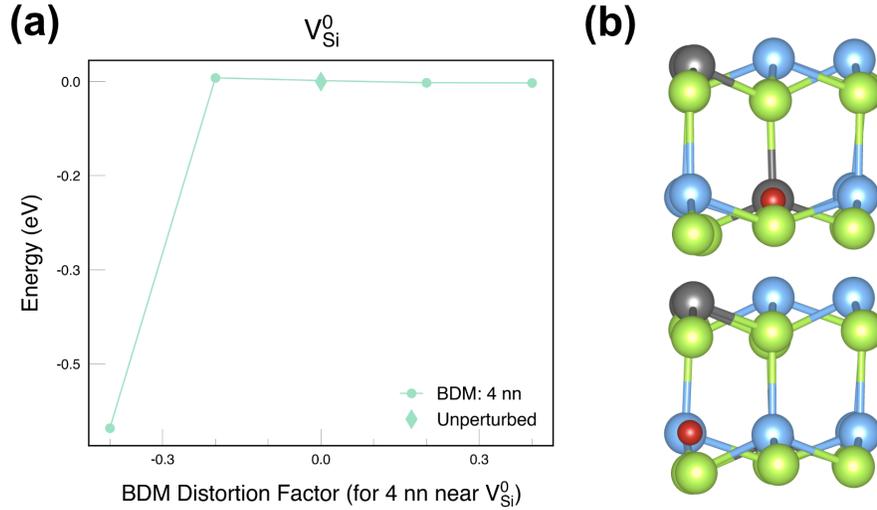
Figure S12: (a) $V_{Si}$ bond distortion method (BDM) plot; nn refers to the number of nearest-neighbours distorted around the defect site. (b) Unperturbed defect structure (top) and energy lowering reconfiguration (bottom). Vacancy indicated by red circle. The lowest energy defect structure was also identified as the ground state structure for all charge states.



Figure S13: (a) $Se_{Si}$ bond distortion method (BDM) plot; nn refers to the number of nearest-neighbours distorted around the defect site. (b) Unperturbed defect structure (top) and energy lowering reconfiguration (bottom). Antisite colored red. The lowest energy defect structure was also identified as the ground state structure in the -1 charge state.

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