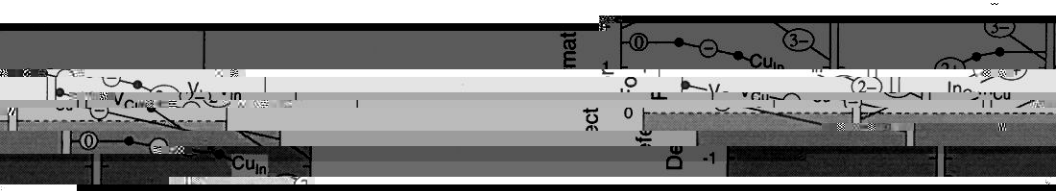
agreement with the available experimental data.

2. Method of Calculation



electron Fermi energy, ϵ_F, at chemical potentials A, B and C (defined in the inset). Charge state q determines the slopes of each line segment. The shaded area highlights negative formation energies. Solid dots denote transition energies.

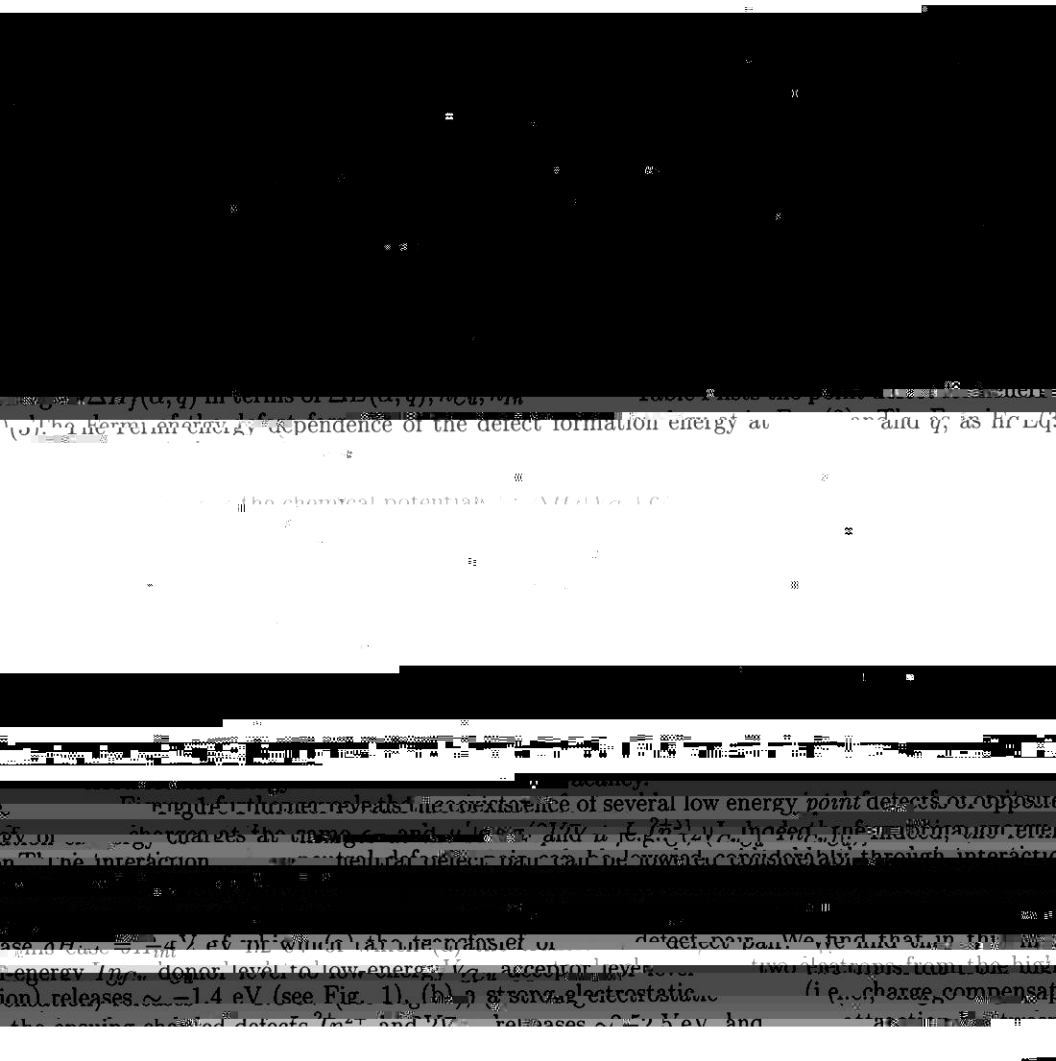
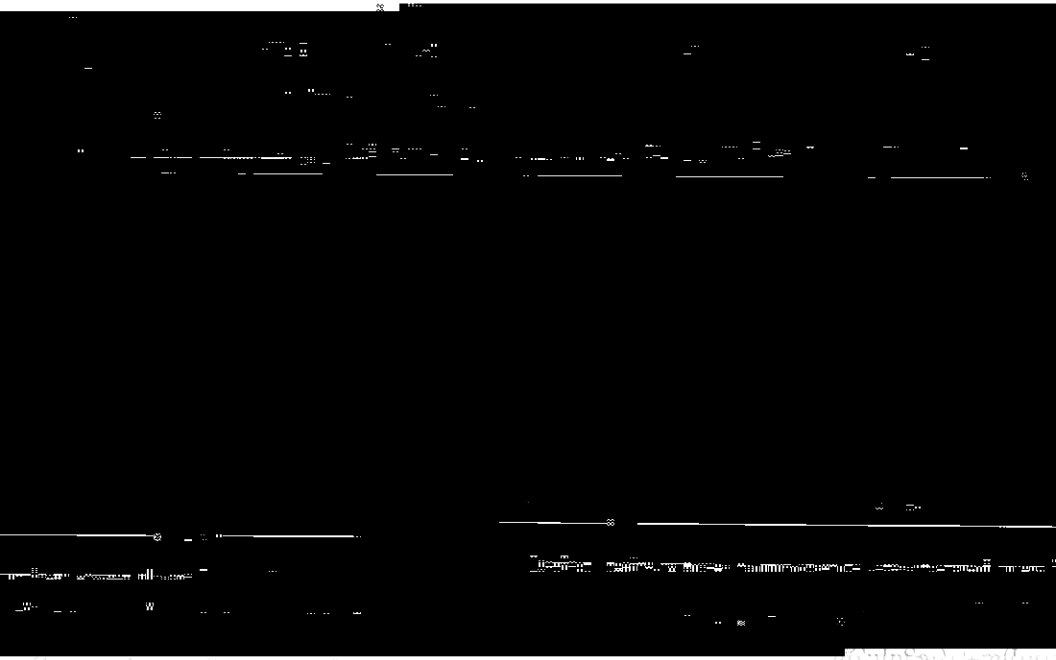


Table 1. Defect formation energies $\Delta E(q, \mu_{Cu}, \mu_{In}, \mu_{Se})$ and defect transition levels



$$(Cu_{(n-m)}In_{(n+m)}Se_{2n} + 3m(Cu) - \Delta H_f(n, m),$$

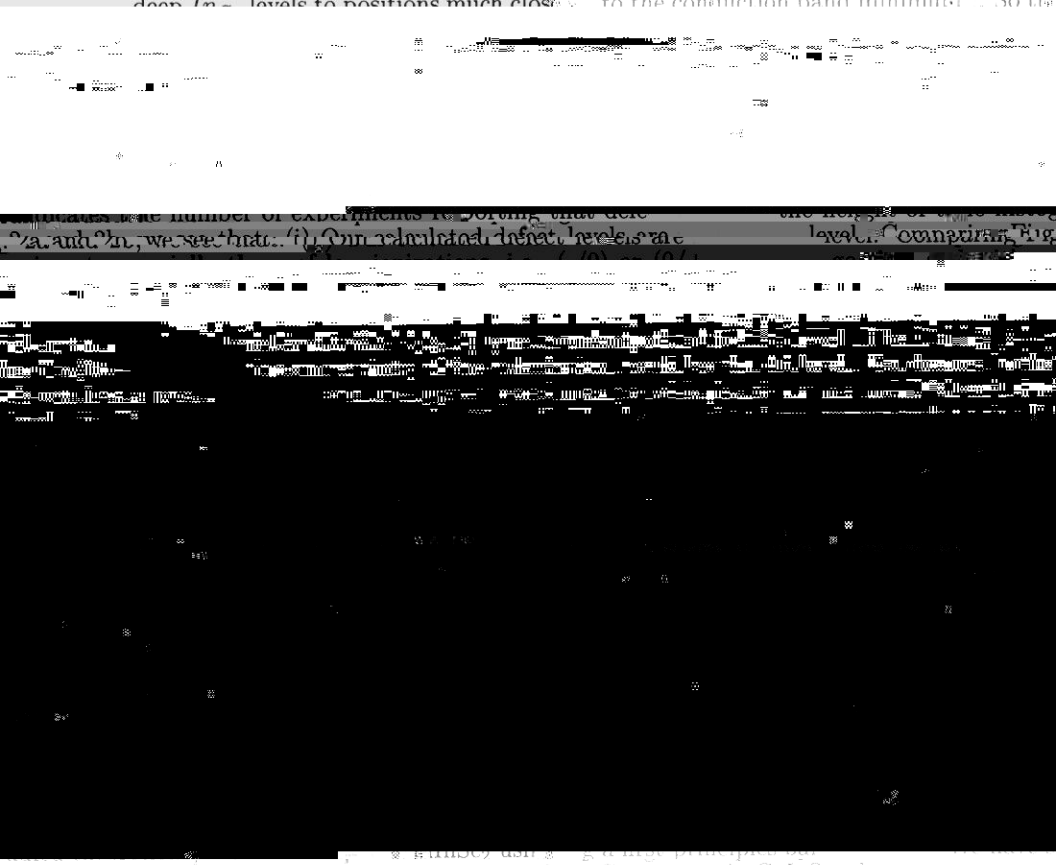
where m = 1, 2, 3, ... and n = 3, 4, 5, ... and

The analysis above shows that the sum of interaction and ordering energies ... for the defect pair array $(2V_{Cu}^- + In_{Cu}^{2+})$ is about ... $\Delta H_f(In_{Cu}^0) = 4.5$ eV at point A in Fig. 1. The total formation energy of the defect array could be as low as -6.1 eV at point B. Thus, spontaneous formation of stable defect compounds ($CuIn_5Se_8$, $CuIn_3Se_5$, etc.) is predicted in this system.

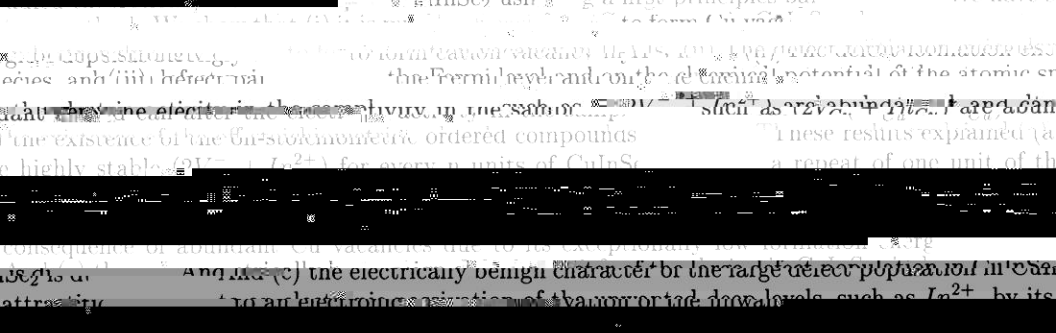
... defect levels are relatively deep including the two ... 0.67 eV above E_V, respectively. The Cu_{In} antisite ... at 0.29 and 0.58 eV above E_V. The deep donors in ... with two levels ... below ... and the ... with one level at 0.20 eV below ... respectively.

... vacancy acceptor levels at 0.41 and ... also has two deep acceptor levels ... $CuInSe_2$ are the In_{Cu} antisite ... interstitial with ...

For isolated interacting $(2V_{Cu}^{-} + In_{Cu}^{2+})$ pair, we find that the pairing pushes up t
deep In_{Cu} levels to positions much clos
the conduction band minimum. So, the In



the number of experiments to doping that defe
level. Comparing Fig
and 2h, we see that: (i) Our calculated defect levels are



the Fermi level and on the chemical potential of the atomic sp
such as Zn_{Cu}. Therefore,
the existence of the on-stoichiometric ordered compounds
These results explained
highly stable $(2V_{Cu}^{-} + In_{Cu}^{2+})$ for every n units of $CuInSe_2$
a repeat of one unit of th

consequence of abundant Cu vacancies due to its exceptionally low formation ener
and (c) the electrically benign character of the large defect population in Cu
attractive
to an electronic excitation of the unoccupied deep levels, such as In^{2+}, by its

References

[17] Laks, D. B., et al., 1992. Phys. Rev. B 45, 10965; Van De Walle, C. communication.