The Complex Defect Chemistry of Antimony Selenide: Supporting Information

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Lattice parameters

Table 1: Calculated lattice parameters of Sb_2Se_3, with percentage differences from the original structure of Voutsas *et al.*[1]

Lattice Parameter	a(Å)	b(Å)	c(Å)	volume(Å^3)
HSE06	11.9455	3.9762	11.5287	547.583
Experiment	11.7938	3.9858	11.6478	547.537
% difference	+1.29	−0.24	−1.02	+0.01

Defect Methodology

For a defect X in charge state q, the formation energy of that defect, $\Delta_f E(q)$, is given by:

$$\Delta_f E(q) = [E_X(q) - E_H] + q(\epsilon_H^{VBM} + \Delta E_F) + \sum_i n_i(E_i^0 + \Delta\mu_i) + E_{corr}, \quad (1)$$

where E_H is the energy of the host (pure) supercell and $E_X(q)$ is the energy of the defective supercell in charge state q; E_i^0 is the elemental reference energy of the n atoms of species i being removed or added and $\Delta\mu_i$ are the elemental chemical potentials defined with respect to those elemental references. For charged defects, $q \neq 0$ and the formation energy of the defect is also a function of the Fermi level position ΔE_F above the host valence band energy ϵ_H^{VBM}. E_{corr} defines the three additional terms associated with the potential alignment, 'band-filling' and 'image-charge' corrections, mentioned in the Computational Methods section of the manuscript.

The thermodynamic transition levels, as depicted in Figure 2 of the manuscript, are defined as the Fermi level position for which a given defect changes from charge state q to q':

$$E(q/q') = \frac{\Delta_f E_X(q) - \Delta_f E_X(q')}{(q' - q)}. \quad (2)$$

Defect Transition Levels

Table 2: Vacancy and selenium interstitial defect transition levels in Sb_2Se_3, with positions in energy given with respect to the valence band maximum.

Transition Level	$V_{Sb,\,1}$	$V_{Sb,\,2}$	$V_{Se,\,1}$	$V_{Se,\,2}$	$V_{Se,\,3}$	Se_i
+4/+2						0.2859
+2/+1			0.2120		0.4042	
+2/0				0.8543		0.4312
+1/0			0.6259		0.5372	
0/−1		0.0412				
0/−2						1.2548
0/−3	0.0987					
−1/−2		0.0956				
−2/−3		0.1413				

Table 3: Antisite and antimony interstitial defect transition levels in Sb_2Se_3, with positions in energy given with respect to the valence band maximum.

Transition Level	$Sb_{Se,\,1}$	$Sb_{Se,\,2}$	$Sb_{Se,\,3}$	$Se_{Sb,\,1}$	$Se_{Sb,\,2}$	Sb_i
+5/+3						−0.1401
+3/+2				−0.1281	−0.0951	
+3/+1	0.3870	0.1144				0.7762
+3/−1			0.4152			
+2/+1				−0.1161	−0.0819	
+1/0		0.4512				
+1/−1	0.4938			0.6464	0.6971	1.1797
0/−1		0.8885				
−1/−3						1.3010

References

(1) Voutsas, G.; Papazoglou, A.; Rentzeperis, P.; Siapkas, D. The crystal structure of antimony selenide, Sb_2Se_3. *Zeitschrift für Kristallographie – Crystalline Materials* **1985**, *171*, 261–268.