# Supplementary Information

# Abnormal behavior of preferred formation of cationic vacancy from the interior in γ-GeSe monolayer with the stereo-chemical antibonding lone-pair state

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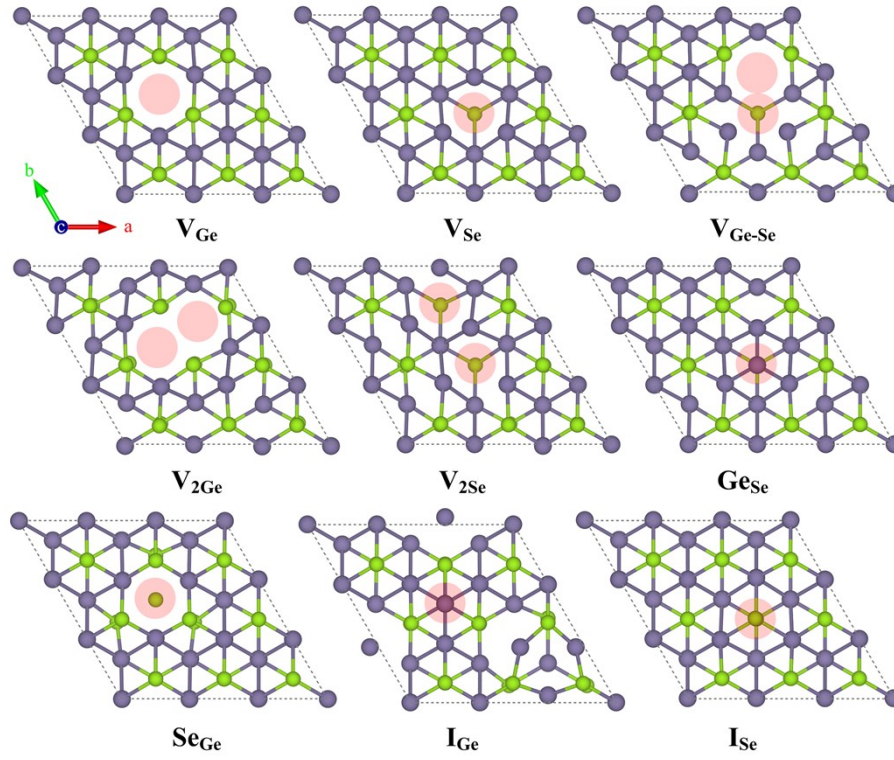E-mail: yongqingcai@um.edu.mo; keqingq@mail.sysu.edu.cn

**Fig. S1**  Top views of γ-GeSe monolayer with vacancies, anti-sites, and interstitials, where defect sites have been highlighted by translucent red-circles.
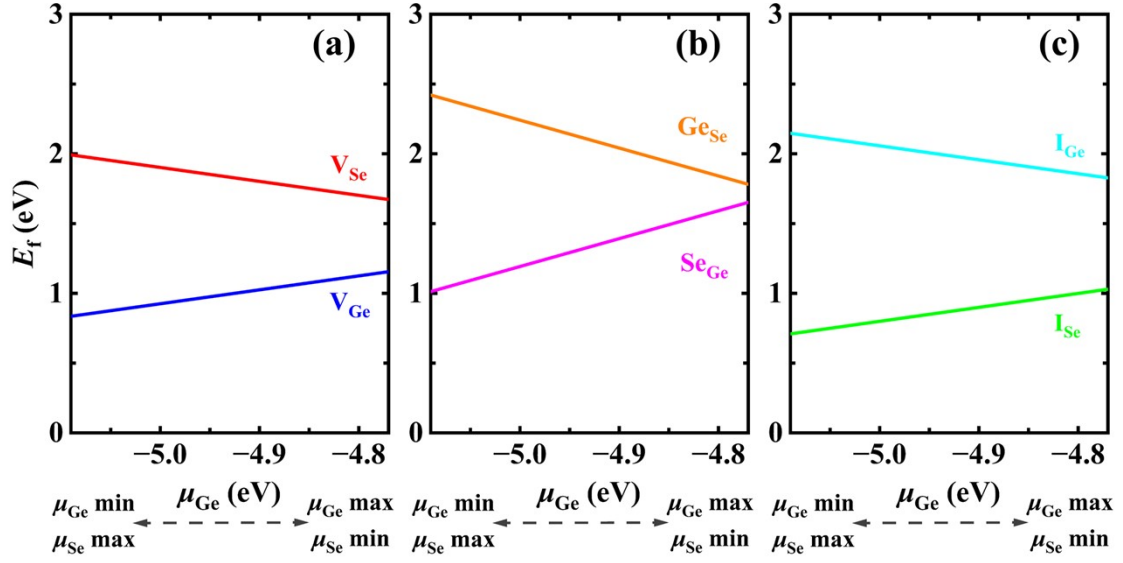
**Fig. S2** Formation energies of α-GeSe monolayer with vacancy (a), anti-site (b), and interstitial (c) defects as functions of $\mu_{Ge}$ in the range from −5.09 eV to −4.77 eV, where γ-GeSe can remain stable with respect to the formation of bulk Ge ($\mu_{Ge}$ = −4.77 eV) or $Se_6$ moleculer crystal ($\mu_{Ge}$ = −5.09 eV).
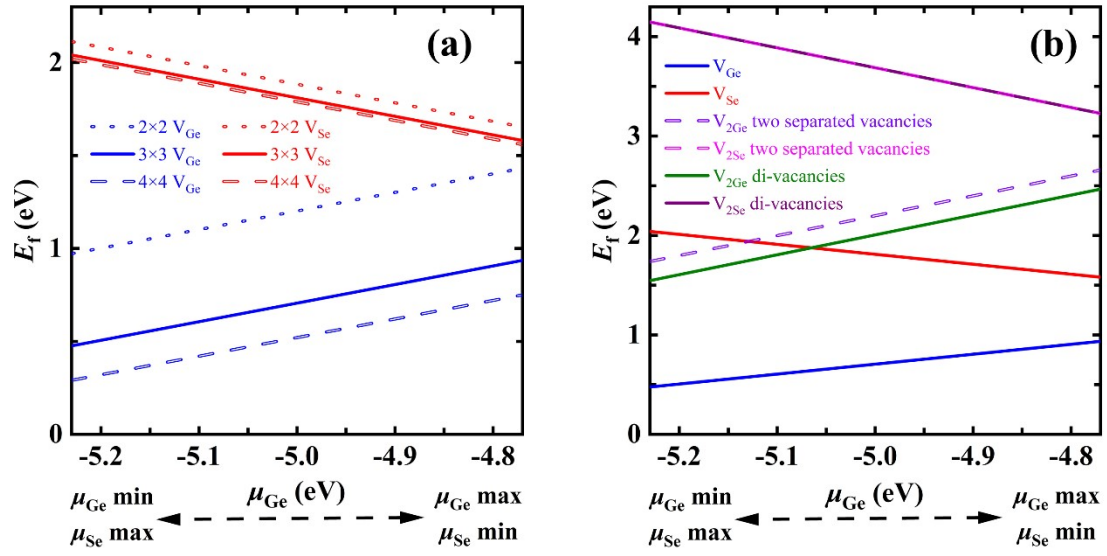
**Fig. S3**　(a) The $E_f$ of the single vacancy in a 2×2, 3×3, 4×4 supercell, and (b) the $E_f$ of the single vacancy and double vacancies in a 3×3 supercell.

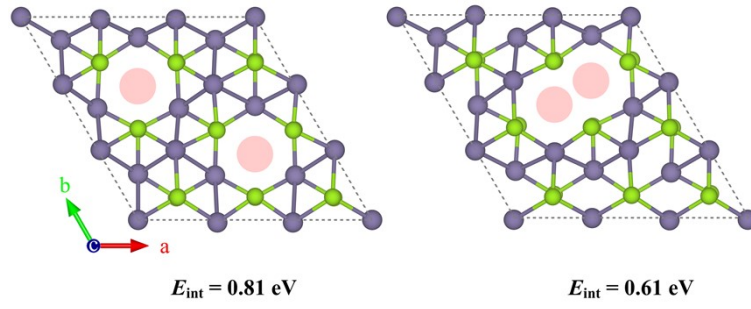$E_{int} = 0.81$ eV             $E_{int} = 0.61$ eV

**Fig. S4** The structures and interaction energies of mono-vacancies in two representative configurations. The configurations stability between two Ge-vacancies can be investigated by their interaction energies ($E_{int} = E_{2V} + E_p - 2E_{1V}$), where $E_{2V}$ and $E_{1V}$ mean that there are 2 mono-vacancies and 1 mono-vacancy within a 3×3 supercell, respectively.
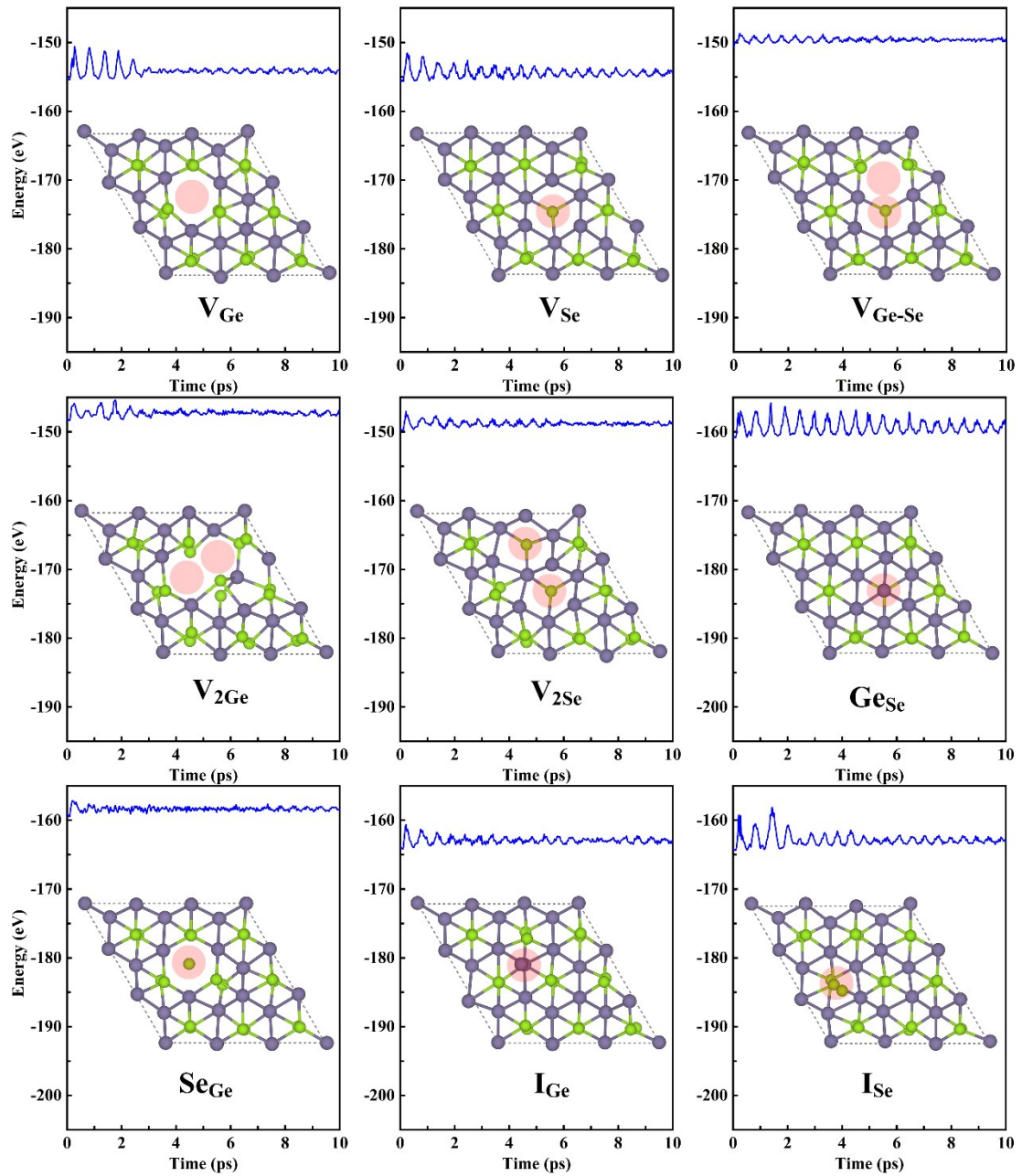
**Fig. S5** Evolution of the total energy from ab initio molecular dynamics calculations (AIMD) of γ-GeSe monolayers containing different defects at 300 K and a snapshot at 10 ps.
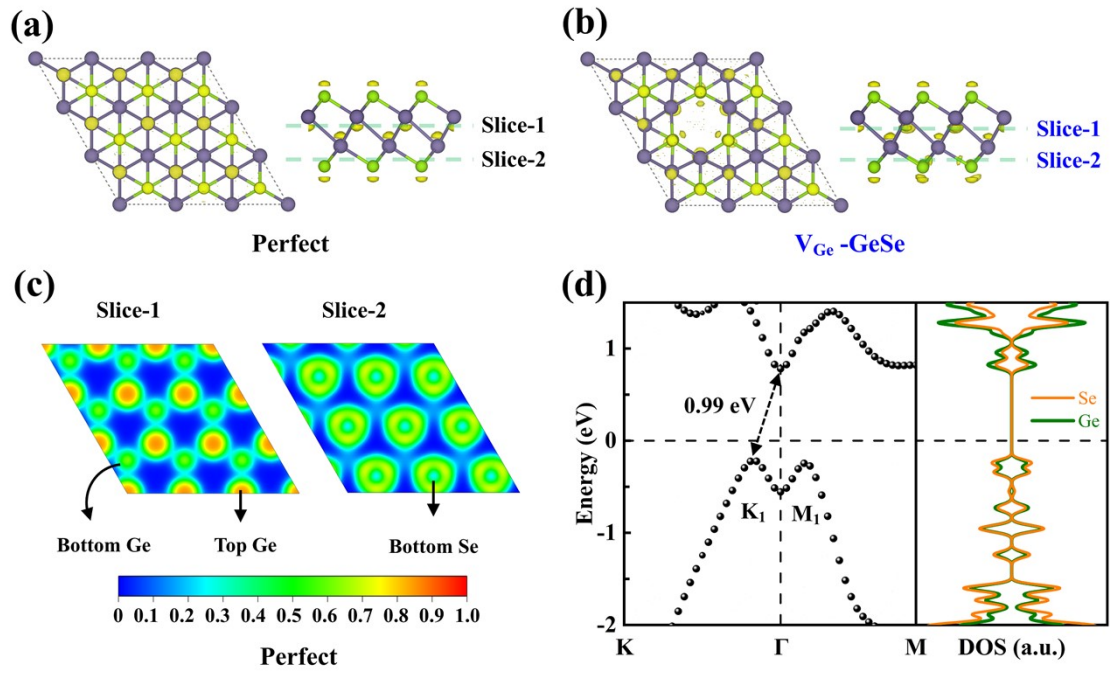
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**Fig. S6** ELF (isosurface level: 0.813) of perfect γ-GeSe (a) and γ-GeSe with $V_{Ge}$ (b) , (c) 2D ELF contour mapping of the (001) plane marked by the dashed lines in (a), and (d) unfolded band structures and local density of states of the perfect γ-GeSe monolayer supercell.