Supplementary materials for

Structural dimerization and charge-orbital ordering in ferromagnetic semiconductor LiV_2S_4 monolayer

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1. The effect of Hubbard U on the lattice constants of $LiVS_2$ bulk material.

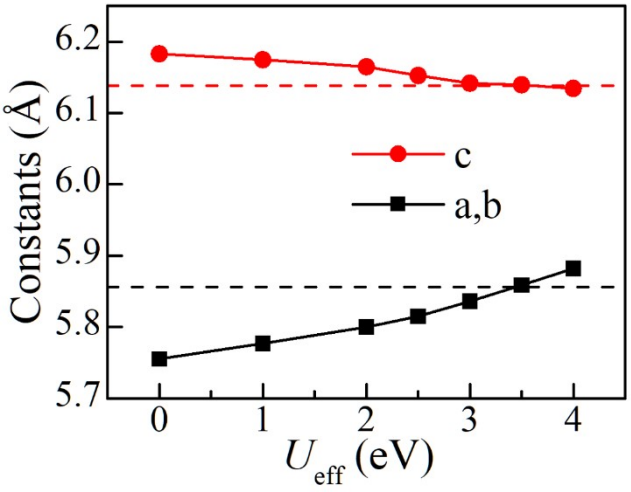

Fig. S1 (a) The diagram of the effective Hubbard U (U_{eff}) dependent lattice constants. The experimental values are shown by the dashed lines for reference.

2. Phonon modes analysis for the undistorted LiV_2S_4 monolayer using 2×2×1 supercell.

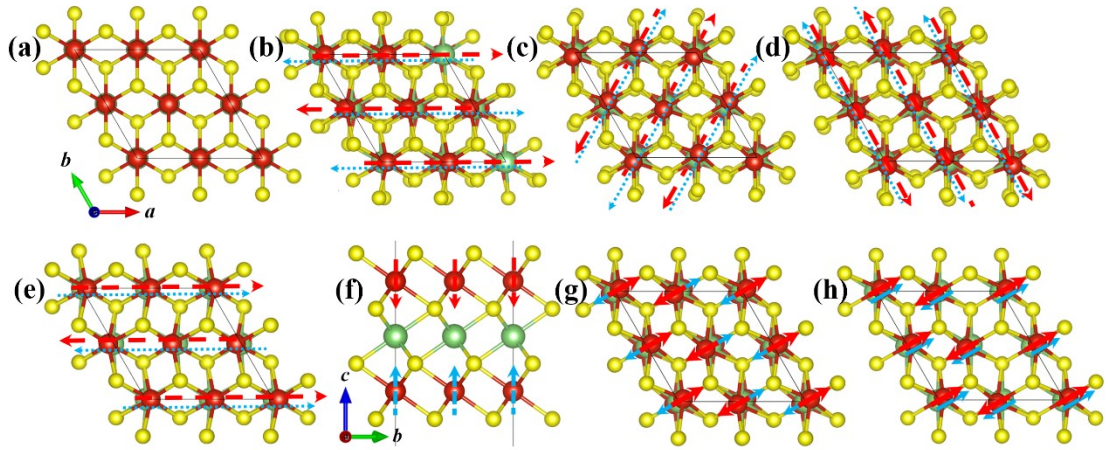

Fig. S2 (a) The undistorted LiV_2S_4 with perfect in-plane triangular lattice. Following the eigenvector of those phonon modes with imaginary frequency, several distorted structures have been found, which mainly originate from the relative displacement of V ions. (b-d) The in-plane stripe displacements of V with opposite directions between upper and lower VS_2 layers. All V ions shift along the stripe direction. In consideration of the rotation symmetry of triangular lattice, the energies for these three distorted structures are degenerate. In other words, these three distortion modes are equivalent. For simplicity, similar equivalent distortions will be ignored thereafter. (e) In-plane stripe displacement, but with same shift direction between upper and lower VS_2 layers. (f) The relative vertical displacements between upper and lower VS_2 layers with reverse direction, exhibiting longitudinal compressive behavior. This distortion mode is not observed in the ground state structure. (g, h) The in-plane stripe displacements with shift direction orthogonal to the stripes, and the displacement direction of V ions on adjacent stripes is opposite. The interlayer displacement is reversed in (g) but identical for (h). The relative displacement directions of V ions in the upper and lower VS_2 layers are represented by red and blue dashed arrows, respectively.

3. The statistical analysis of the Molecular Dynamics (MD) simulation under room temperature (RT, 300 K).

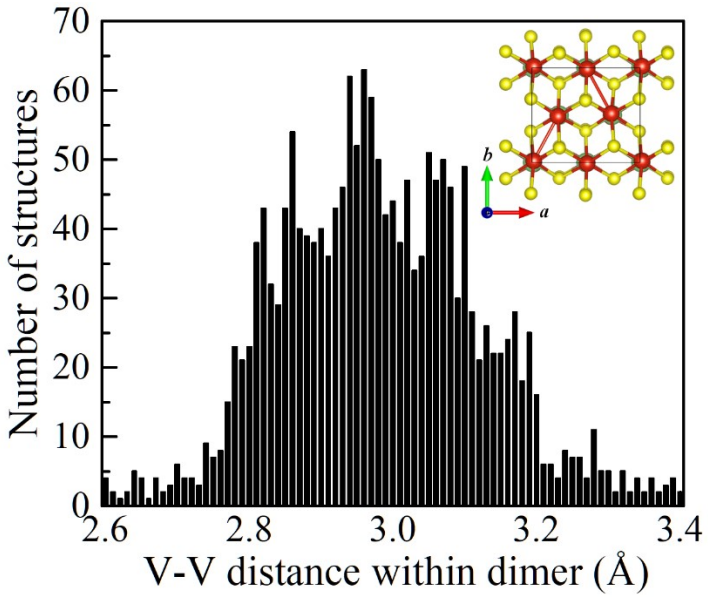

Fig. S3 The statistical results of the V-V distance versus the corresponding number of simulated structures. The V-V distance within the dimer is denoted by red line in the inset.

4. The non-magnetic DOS of LiV_2S_4 monolayer in the high symmetric and low-temperature phases.

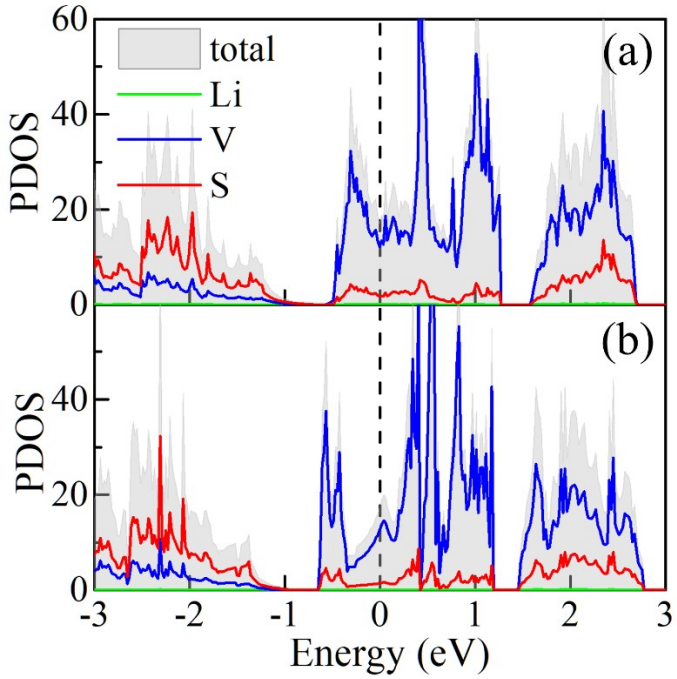

Fig. S4 (a) The atomic projected DOS (PDOS) of high symmetric LiV_2S_4 with perfect in-plane triangular lattice (*P*-3m1 phase). (b) The PDOS of V dimerized LiV_2S_4 monolayer (*P*2/c phase). The Fermi level is represented by dashed lines.

5. Table S1. The optimization results of 2D LiV_2S_4 with FM and four possible AFM magnetic orders. The in-plane lattice constants (*a* and *b*) and the nearest V-V distances (*s*: short; *m*: medium; *l*; long) are in units of Å, and the relative energies are in units of meV/V. The distorted FM ground state is taken as the reference.

Space group	Order	Energy	*a*	*b*	*s*	*m*	*l*
P-3m1	FM	90.1	7.097	5.955	/	/	/
	A-AFM	90.5	7.108	5.954			
	Stripe	138.7	6.849	6.008			
	Zigzag	899.6	6.626	5.757			
*P*2/c	FM	0.0	6.955	6.080	3.27	3.44	3.57
	A-AFM	0.3	6.955	6.080	3.26	3.43	3.57
	Stripe	43.6	6.960	6.028	3.27	3.43	3.53
	Zigzag	4.8	6.967	6.033	3.33	3.54	3.58
*P*1	Y-AFM	22.8	6.069	5.960	3.41	3.46	3.53