Supplementary Information for A Giant Thermal Switching in Ferromagnetic VSe$_2$ with Programmable Switching Temperature

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Supplementary Note 1

The first-principles calculation details

The phonon dispersion and phonon density of states (DOS) are calculated in Phonopy package.$^1$ The specific heat, phonon group velocity, weighted phonon-phonon scattering phase space, phonon-phonon scattering rates, thermal conductivity, and Grüneisen parameter are calculated in ShengBTE package.$^2$ The relaxed structure, second-order force constant, and third-order force constant needed by above two packages are calculated in Vienna Ab-initio Simulation Package (VASP).

The structure relaxation with (FM) and without (PM) spin polarization is performed in VASP with 19×19×1 K point mesh for monolayer VSe$_2$ (11×11×5 for bulk counterpart) and force tolerance of 0.005 eV/Å. The energy cut off of the plane wave basis set is 500 eV with the projector augmented wave (PAW) pseudopotentials.$^3$
The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) is applied for the electronic exchange-correlation functional. In order to describe the interlayer van der Waals interaction, DFT-D3 method is applied. A 5×5×1 supercell with 5×5×1 K point mesh and a 4×4×3 supercell with 1×1×1 K mesh are applied to calculate second-order force constant for monolayer and bulk VSe$_2$, respectively. A 6×4×1 supercell with 3×3×1 K point mesh and a 3×3×2 supercell with 2×2×2 K point mesh are applied to calculate third-order force constant for monolayer and bulk VSe$_2$, respectively. The cutoff is set as 0.65 nm for third-order force constant calculations.

Under the framework of linearized Boltzmann transport equation, the thermal conductivity $k$ can be calculated as following:

$$k_{\alpha\beta} = \frac{1}{k_B T^2 \Omega N} \sum_{\lambda} f_0 (f_0 + 1) (\hbar \omega)^2 v_\lambda^\alpha v_\lambda^\beta \tau_\lambda$$  \hspace{1cm} \text{(S1)}

$$\frac{1}{\tau_\lambda} = \frac{1}{N} \left( \sum_{\lambda} \Gamma_{\lambda\lambda\lambda}^+ + \frac{1}{2} \sum_{\lambda} \Gamma_{\lambda\lambda\lambda}^- + \sum_{\lambda} \Gamma_{\lambda\lambda\lambda}^x \right)$$ \hspace{1cm} \text{(S2)}

$$\Gamma_{\lambda\lambda\lambda}^+ = \frac{\hbar \pi}{4 \omega_\lambda \omega_\lambda \omega_\lambda} \left| V^{\lambda\lambda\lambda} \right|^2 \delta (\omega_\lambda + \omega_\lambda - \omega_\lambda)$$ \hspace{1cm} \text{(S3)}

$$\Gamma_{\lambda\lambda\lambda}^- = \frac{\hbar \pi}{4 \omega_\lambda \omega_\lambda \omega_\lambda} \left| V^{\lambda\lambda\lambda} \right|^2 \delta (\omega_\lambda - \omega_\lambda - \omega_\lambda)$$ \hspace{1cm} \text{(S4)}

Where $\alpha (\beta)$ denotes the direction $x$ or $y$ or $z$, $k_B$ is Boltzmann constant, $T$ is temperature, $\Omega$ is the volume of unit cell shown in Fig. 1, $N$ is the number of phonon modes $\lambda$ including phonon wavevector and branch, $f_0$ is equilibrium phonon distribution, $\hbar$ is the reduced Planck constant, $\omega$ is the phonon angular frequency, $v$ is the phonon group
velocity, \( r \) is phonon lifetime and \( V \) is the scattering matrix element.\(^4,^5\) The quantities \( \Gamma \) in equations (S3) and (S4) are phonon-phonon scattering rates and the superscripts “+” and “-” mean the adsorption and emission processes respectively. The Dirac delta functions inside the expressions of \( \Gamma \) mean the energy should be conserved during phonon-phonon scattering process. The conservation of quasi-momentum is not clearly shown here. Actually, the phonon mode \( \lambda'' \) in equations (S3) and (S4) is determined under the condition of quasi-momentum conservation \( \lambda'' = \lambda \pm \lambda' + G \), where \( G \) is the reciprocal lattice vector and the symbol “ \( \pm \) ” has same meaning as above.

In order to describe FM orderings effects on phonon-phonon scattering, the weighted phonon-phonon scattering phase space \( WP3 \) is calculated and written as:\(^6,^7\)

\[
W_{\lambda}^{\pm} = \frac{1}{2N} \sum_{\lambda, \lambda'} \left\{ \frac{2(f_{\lambda} \pm f_{\lambda'})}{f_{\lambda} + f_{\lambda'} + 1} \right\} \frac{\delta(\omega_{\lambda} \pm \omega_{\lambda'} - \omega_{\lambda''})}{\omega_{\lambda} \omega_{\lambda'} \omega_{\lambda''}}
\]

(S5)

Where the symbols have the same physical meanings as above. The upper part in the bracket means the absorption process while the lower part means the emission process. By comparing equations (S3) or (S4) and (S5), the weighted scattering phase space describes the allowed number of phonon-phonon scattering channels.

A \( 60 \times 60 \times 1 \) \( q \)-mesh with a scalebroad of 1.0 for monolayer 2H-VSe\(_2\) (a \( 21 \times 21 \times 7 \) \( q \)-mesh with a scalebroad of 1.0 for bulk counterpart) is chosen to calculate the thermal conductivity. To guarantee the convergence of calculations, different \( q \)-mesh (the number of \( q \) points) and scalebroad (Gaussian width) are tested in FM monolayer 2H-VSe\(_2\) and shown in Fig. S4. From the figure, \( 60 \times 60 \times 1 \) \( q \)-mesh is large enough to
guarantee the convergence and scalebroad of 1.0 is also well enough. In addition, the isotope scattering is considered and BTE is iteratively solved.

Supplementary Note 2

The magnetic transition temperature calculation of bulk 2H-VSe$_2$

To evaluate the strength of spin interactions between V atoms in monolayer VX$_2$, the parameters $J$ in spin Hamiltonian is derived. Based on the Heisenberg model,$^8$ the spin Hamiltonian is described as

$$H = -J \sum_{i} \sigma_i \sigma_{i+1},$$

where $\sigma_i$ is the net spin induced by the $i$th V atom site. Based on the model, the energy difference $\Delta E$ between the AFM and FM phases is

$$E^{\text{AFM}} - E^{\text{FM}} = 2J|\sigma_i|^2,$$

from which the energy of exchange interactions $J$ can be obtained. The Curie temperature can be simply estimated by $J/k_B$,\textsuperscript{10} where $k_B$ is the Boltzmann constant. The $J$ of bulk VSe$_2$ is 7.17 meV and the Curie temperature is estimated about 80 K.

The mode dependent phonon group velocity
Fig. S1 The mode (frequency) dependent phonon group velocity of monolayer (a) and bulk (b) 2H-VSe$_2$ at the magnetic transition temperature from FM (hollow symbols) to PM (solid symbols) phase.

Fig. S2 Phonon dispersion of monolayer FM 2H-VSe$_2$ with (red dotted lines) or without (blue lines) introducing spin-orbit coupling.
Fig. S3 Phonon dispersion (a) and thermal conductivity (b) of bulk PM 1T-VSe$_2$. Since the experimental thermal conductivity of 2H-VSe$_2$ is still lacking, our calculated value of 4.5 W/m-K for bulk 1T-VSe$_2$ at room temperature is consistent with previous experimental measurement, indicating the accuracy of our calculations.

Fig. S4 Scalebroad and number of q points dependent thermal conductivity in FM monolayer 2H-VSe$_2$ at 430 K.
**Fig. S5** (a) Phonon frequency dependent three-phonon scattering phase space (P3) and four-phonon scattering phase space (P4) of monolayer FM 2H-VSe$_2$ at 430 K. (b) Number of q points dependent thermal conductivity for three-phonon and both three- and four-phonon process at 430 K. The calculated thermal conductivity with both three- and four-phonon process is about 10% smaller than that with only three-phonon process at 430 K for monolayer FM 2H-VSe$_2$. Thus, the four-phonon process is not that important in 2H-VSe$_2$.

**Fig. S6** Phonon dispersion of monolayer FM phase (red lines), PM phase with (black lines) or without spin polarization (blue dotted lines). The phonon dispersion of PM structure with spin polarization is similar to that of FM structure but much different to that of PM structure without spin polarization, indicating that the large thermal conductivity variation in 2H-VSe$_2$ is caused by magnetic order while structural change has weak effects.
The lattice parameters of VSe$_2$

Table S1. The lattice parameters of monolayer and bulk VSe$_2$ in PM and FM phases, respectively.

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<tr>
<th>Thickness</th>
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References