

Supplementary Information

Enhanced Long-Range Quadrupole Effects in 2D MSi₂N₄: Impacts on Electric and Thermal Transport

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I. CRYSTAL STRUCTURE AND BANDSTRUCTURE

The optimized crystal structures for monolayer MoSi_2N_4 and WSi_2N_4 are shown in Figure S1(a-c), both of which possess an in-plane mirror symmetry and belong to the space group of P-6m2 (No.187) (point group D_{3h}), and the optimized lattice constants are $a = b = 2.89\text{\AA}$, $2.90\text{\AA}$, respectively, in good agreement with previous reports¹.

The phonon dispersions and partial phonon density of states (PDOS) at 0 K for monolayer MoSi_2N_4 and WSi_2N_4 are calculated by solving the eigenvalue equations with the dynamical matrix constructed from the harmonic inter-atom force constants (IFCs) obtained based on the density functional perturbation theory (DFPT), which are implemented in the PHONOPY package². Furthermore, by enforcing the rotational sum rules to the second IFCs implemented in the Hiphive package³, the calculated dispersion for ZA modes around the Γ point is guaranteed to manifest a quadratic shape, and those for TA and LA modes are linear. Subsequently, the results are shown in Figure S1(d,h) as orange solid lines, respectively, which show that both phonon dispersions possess no imaginary frequencies, indicating that these two monolayers are thermally stable at low temperatures. At 300 K, two optical-optical ($o-o$) phonon band gaps can be observed up to 0.99 THz and 1.48 THz for monolayer MoSi_2N_4 , and 1.55 THz and 1.61 THz for monolayer WSi_2N_4 . The phonon vibrations with low frequencies are contributed by heavy element Mo/W, while those with high frequencies are contributed by slight element N.

The calculated electronic band structures of monolayer MoSi_2N_4 and WSi_2N_4 using the PBE and PBE+SOC method projected by atomic orbitals are shown in Figure S1(f,j), and their partial density of states (PDOS) are shown in Figure S1(g,k). The electron bands near the Fermi level are mainly contributed by Mo/W-d orbitals and N-p orbitals. Both monolayers possess an indirect band gap with 1.79 eV and 2.11 eV, respectively, while considering SOC, the indirect band gaps are decreased to 1.78 eV and 2.09 eV, respectively. The conduction band minimum (CBM, C_1) is located at K point with six degeneracies in the full Brillouin zone (FBZ), and the valence band maximum (VBM, V_1) is located at Γ point with single degeneracy in the FBZ. As shown in Figure S1(f,j), the second local VBM (V_2) is located at K point with the energy difference of 0.25/0.26 eV compared to V_1 of monolayer $\text{MoSi}_2\text{N}_4/\text{WSi}_2\text{N}_4$, and the energy difference between C_1 and C_2 is 0.63/0.18 eV, respectively. The large energy difference between V_1 and V_2 , C_1 , and C_2 valleys indicates the absence of intervalley scatterings for VBM holes and CBM electrons.

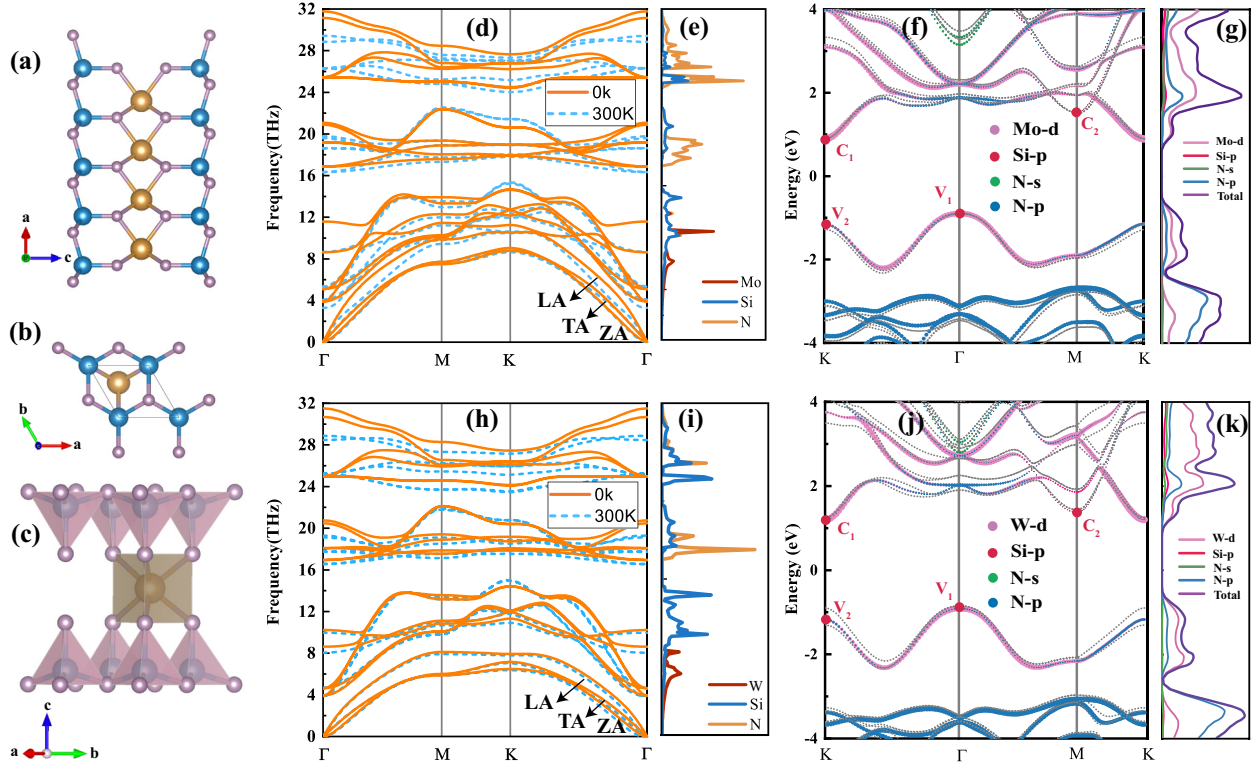


Figure S1. (a) Side and (b) top views of the crystal structure of MoSi_2N_4 and WSi_2N_4 . (c) Polyhedral cell. (d,h) The phonon dispersions and (e,i) phonon density of states of two monolayers. (f,j) The bandstructure and (g,k) PDOS of two monolayers.

II. ELECTRICAL AND THERMAL TRANSPORT

Table S1. Mode-resolved electron-phonon scattering rates (ps^{-1}) with/without the condideration of quadrupoles contributions of CBM electrons in monolayer MoSi_2N_4 and WSi_2N_4 at 300 K.

MoSi_2N_4					WSi_2N_4				
Mode	Noquad _{CBM}	Quad _{CBM}	Noquad _{VBM}	Quad _{VBM}	Mode	Noquad _{CBM}	Quad _{CBM}	Noquad _{VBM}	Quad _{VBM}
ZA	3.80×10^{-5}	1.01×10^{-3}	5.61×10^{-4}	2.96×10^{-4}	ZA	7.28×10^{-6}	1.23×10^{-5}	1.20×10^{-3}	9.82×10^{-4}
TA	0.06	0.11	0.42	0.12	TA	0.035	0.028	0.33	0.066
LA	0.26	0.06	1.79	2.50	LA	0.093	0.24	1.62	10.51
OPT	18.42	19.06	20.09	20.71	OPT	20.54	18.02	28.63	28.19
Total	18.57	19.22	22.30	23.33	Total	20.68	18.29	30.58	38.17

To reveal the underlying mechanisms for the phonon transport properties induced by the 3ph

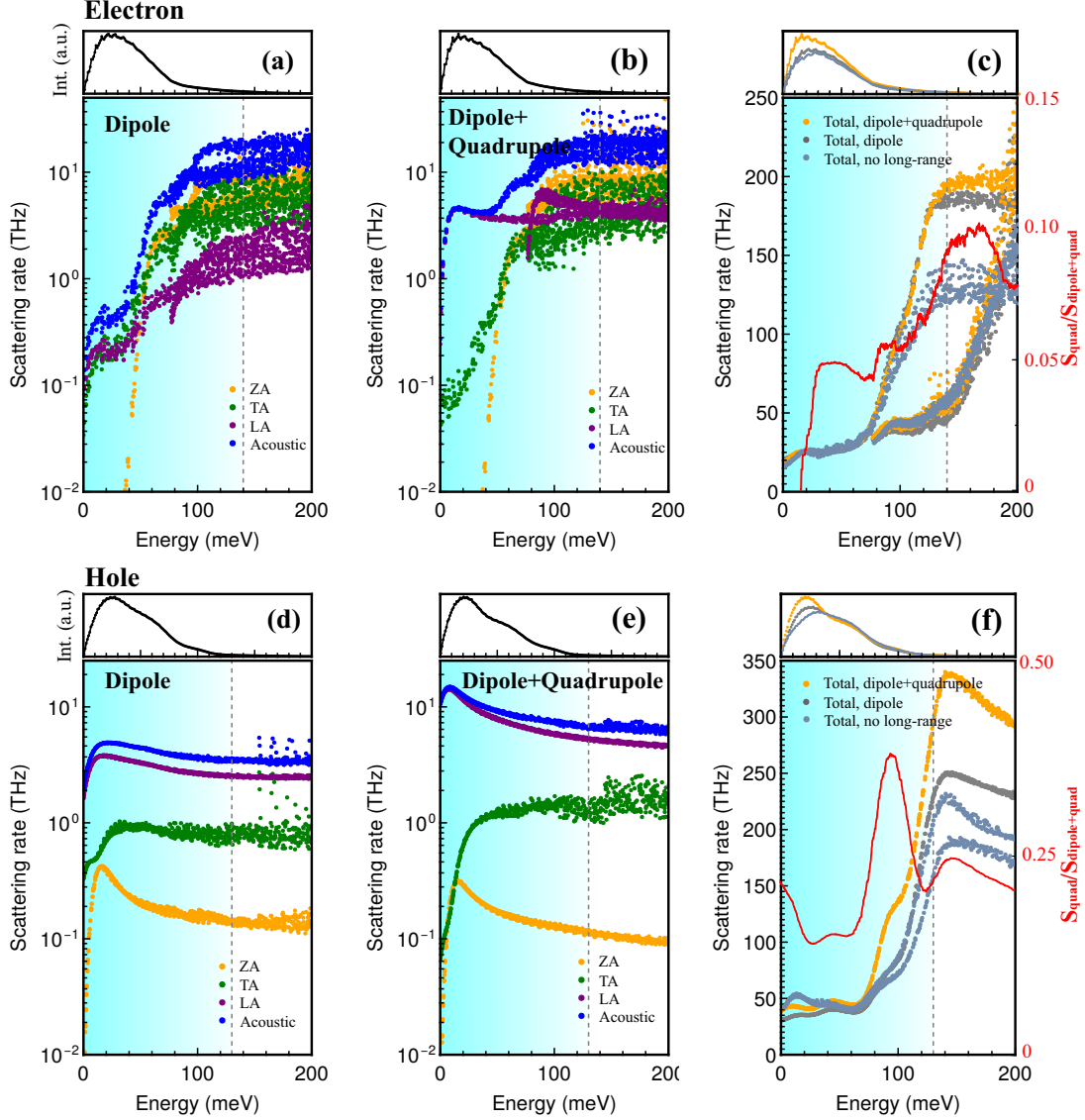


Figure S2. The calculated mode-resolved e -ph (a-c) electrons and (d-f) holes scattering rates with dipole, dipole+quadrupole and no long-range within 200 meV from the band edges for monolayer WSi_2N_4 at 300 K.

interactions for monolayer MoSi_2N_4 and WSi_2N_4 , the scattering channel-resolved phonon phase space for 3ph interactions $P_{\lambda\lambda'\lambda''}$, also called as the 3ph selection rules, can be defined according to the energy and momentum conservation, i.e. $\mathbf{q} \pm \mathbf{q}' = \mathbf{q}'' + \mathbf{G}$ and $\omega_{\lambda\mathbf{q}} + \omega_{\lambda'\mathbf{q}'} = \omega_{\lambda''\mathbf{q}''}$, where $\mathbf{G}$ is a reciprocal lattice vector with zero for Normal processes and nonzero for Umklapp processes,

$$P_{\lambda\lambda'\lambda''} = \frac{2}{3\Omega_0} \left(P_3^+ + \frac{1}{2} P_3^- \right) \quad (1)$$

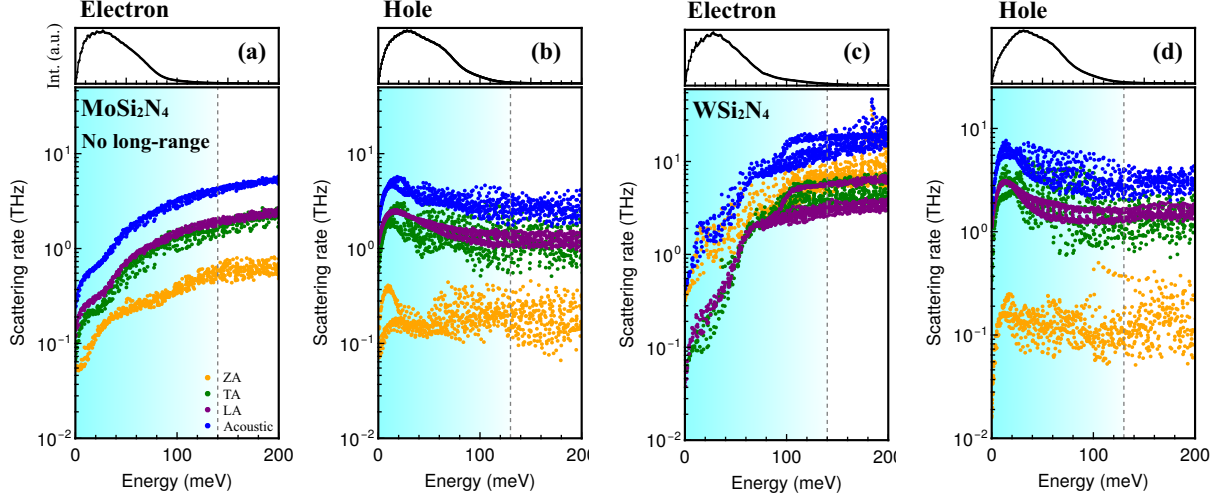


Figure S3. The calculated mode-resolved no long-range e - ph electron and hole scattering rate of monolayer MoSi_2N_4 and WSi_2N_4 .

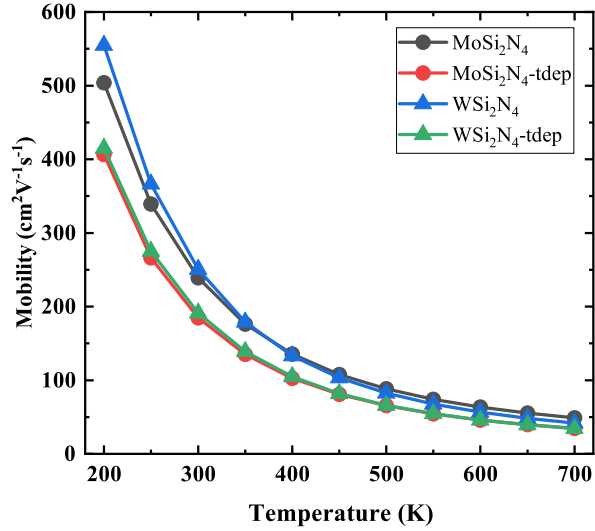


Figure S4. The calculated dipole-like electron mobility of monolayer MoSi_2N_4 and WSi_2N_4 with and without the consideration of temperature-induced effects by TDEP calculations.

$$P_{\lambda\lambda'\lambda''}^{\pm} = \int d\mathbf{q}d\mathbf{q}'\delta(\omega_{\lambda}(\mathbf{q}) \pm \omega'_{\lambda'}(\mathbf{q}') - \omega''_{\lambda''}(\mathbf{q} - \mathbf{q}' - \mathbf{G})) \quad (2)$$

where Ω_0 is a normalization factor, $\pm$ describes absorption processes and emission processes.

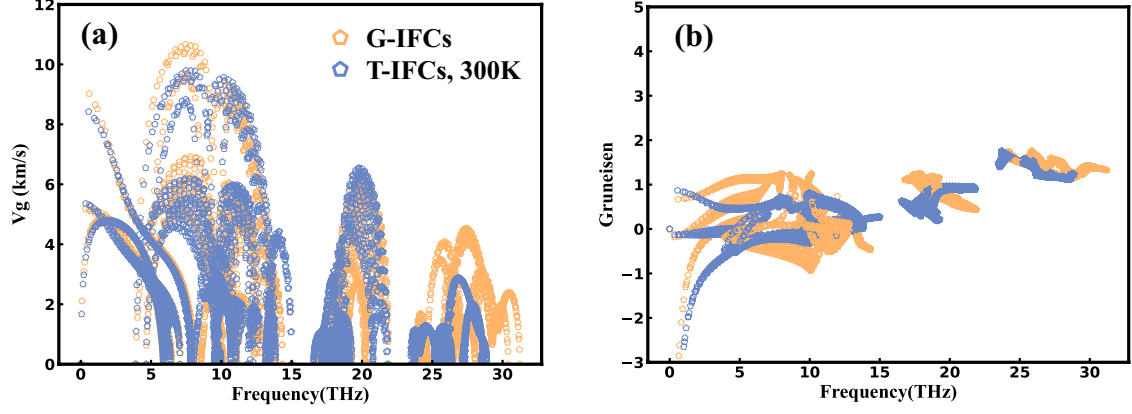


Figure S5. (a) Phonon group velocity and (b) Gruneisen constant based on G-IFCs and T-IFCs for monolayer WSi_2N_4 .

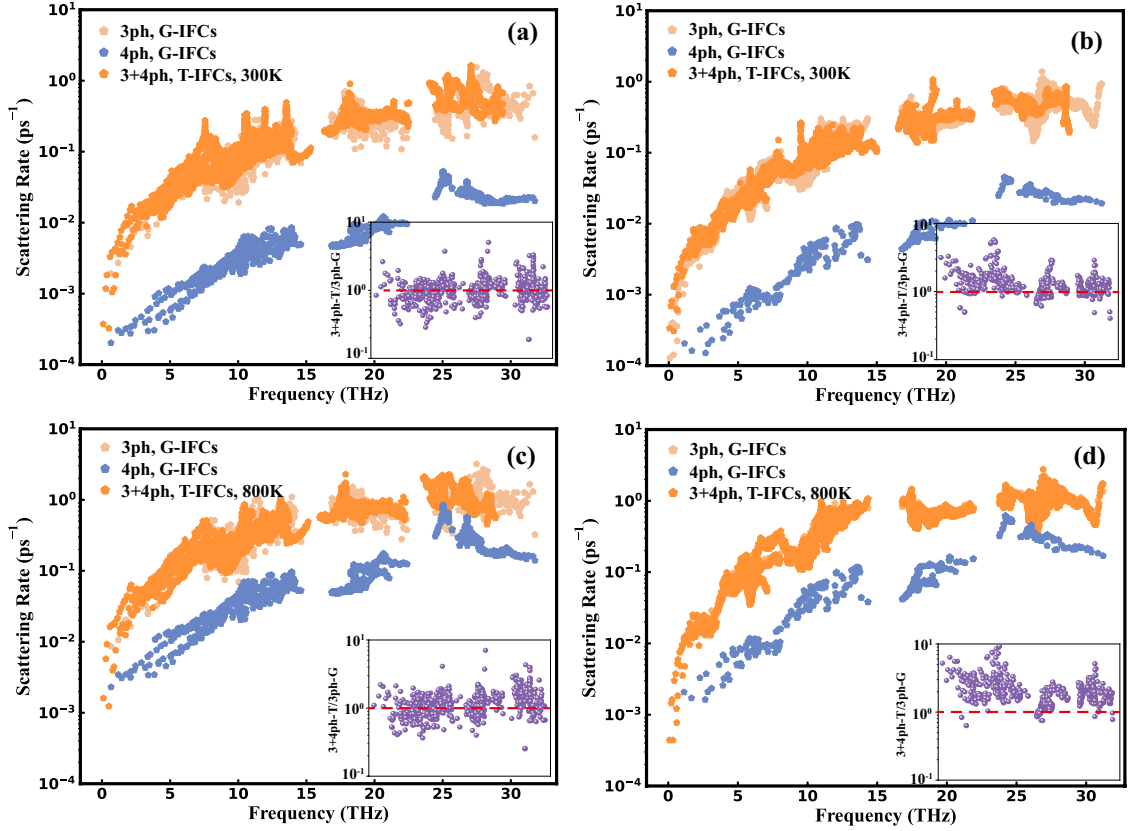


Figure S6. The 3ph, 4ph and with T-IFCs scattering rates at 300K and 800K of monolayer (a,c) MoSi_2N_4 and (b,d) WSi_2N_4 .

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- ³ Fredrik Eriksson, Erik Fransson, and Paul Erhart. The hiphive package for the extraction of high-order force constants by machine learning. *Adv. Theory Simul.*, 2(5):1800184, 2019.