Supplementary Materials

Distinct anharmonic characteristics of phonons driven lattice thermal conductivity and thermal expansion in bulk $MoSe_2$ and WSe_2

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The crystal structure of $MoSe_2$/WSe_2 is show in **Figure S1**. The structure consists of layers of $MoSe_6$/WSe_6 octahedral units in the *a*-*b* plane, with a stacking of layers along the *c*- axis shifted by (¼ ¼ 0). The probability distributions of atomic positions show a large anisotropy in both experiment and simulations. In **Figure S1 (b, c)**, we show the probability distribution for the transition metal in the *ab* and *bc*-planes obtained from the MLMD trajectory at 700 K. The structure parameters of $TMSe_2$ at ambient conditions are given in Table S1.

Table S1: The structure parameters and atomic positions of $MoSe_2$ and WSe_2 obtained from DFT calculation and X-ray diffraction measurements.

	Space group (194, $P6_3/mmc$)	
	$MoSe_2$	WSe_2
	DFT-relaxed (50 K expt.)	DFT-relaxed (50 K expt.)
a	3.276 (3.283)	3.275 (3.275)
c	12.722 (12.891)	12.777 (12.961)
Se(*x*,*y*,*z*) Wyckoff (4*f*)	(2/3, 1/3,0.118)	(2/3, 1/3,0.118)
Mo/W (*x*,*y*,*z*) Wyckoff (2*b*)	(1/3, 2/3, 1/4)	(1/3, 2/3, 1/4)

TABLE S2. Calculated elastic constants in GPa units of $MoSe_2$ and WSe_2, and experimental elastic constants of $MoSe_2$ [1]

	$MoSe_2$ Calc	**Expt.**	**WSe_2 Calc**	**Expt.**
C_{11}	187	177	203	-
C_{12}	42	-	38	-
C_{13}	13	-	13	-
C_{33}	66	70	68	-
C_{44}	23	-	24	-
Bulk-Modulus	47.9	-	49.4	-

TABLE-S3: The calculated in-plane(κ_{xy}) and out-of-plane (κ_z) lattice thermal conductivity, using ShengBTE-3ph, TDEP-3ph and ShengBTE 3ph+4ph methods, and the Green-Kubo method based on equilibrium molecular dynamics simulation that includes all order of anharmonicity. The reported measured lattice thermal conductivity obtained using the time-domain thermoreflectance technique[12].

(a) $MoSe_2$ (κ_{xy} / κ_z) (W/m-K)					
Temperature	Expt.	ShengBTE-3Phonon	ShengBTE-3+4Phonon	TDEP	Green-Kubo
100 K	90.0/2.7	260.7/49.6	260.5/43.2	169.8/11.1	102.0/14.2
200 K	51.0/3.1	119.7/22.9	112.7/14.9	77.4/5.2	
300 K	34.0/2.5	79.4/15.2	70.3/8.3	51.5/3.5	39.0/4.0
400 K	--	59.9/11.4	50.1/5.5	38.8/2.6	
500 K	--	48.2/9.2	38.3/3.9	31.3/2.1	18.5/3.0
600 K		40.5/7.7	30.5/3.0	28.6/1.9	
700 K		34.9/6.6	25.1/2.4	24.4/1.6	13.4/2.0
800 K		30.7/5.8	21.1/1.9	21.2/1.4	
900 K		27.3/5.2	18.0/1.6	18.8/1.3	
(b) WSe_2 (κ_{xy} / κ_z) (W/m-K)					
Temperature	Expt.	ShengBTE-3Phonon	ShengBTE-3+4Phonon	TDEP	Green-Kubo
100 K	120.0/2.9	319.6/47.5	267.2/26.9	213.0/11.6	119.5/39.0
200 K	58.0/3.0	136.7/20.3	97.2/7.9	89.9/5.1	
300 K	39.0/2.1	89.2/13.2	55.1/4.1	58.7/3.4	42.0/5.0
400 K		67.6/9.9	36.4/2.6	44.0/2.5	
500 K		54.4/7.9	26.1/1.8	35.3/2.0	28.2/9.0
600 K		45.6/6.6	19.7/1.3	29.5/1.6	
700 K		39.3/5.7	15.5/1.0	25.5/1.5	19.0/7.0
800 K		34.6/4.9	12.5/0.8	23.8/1.4	
900 K		30.8/4.4	10.3/0.6	21.0/1.2	

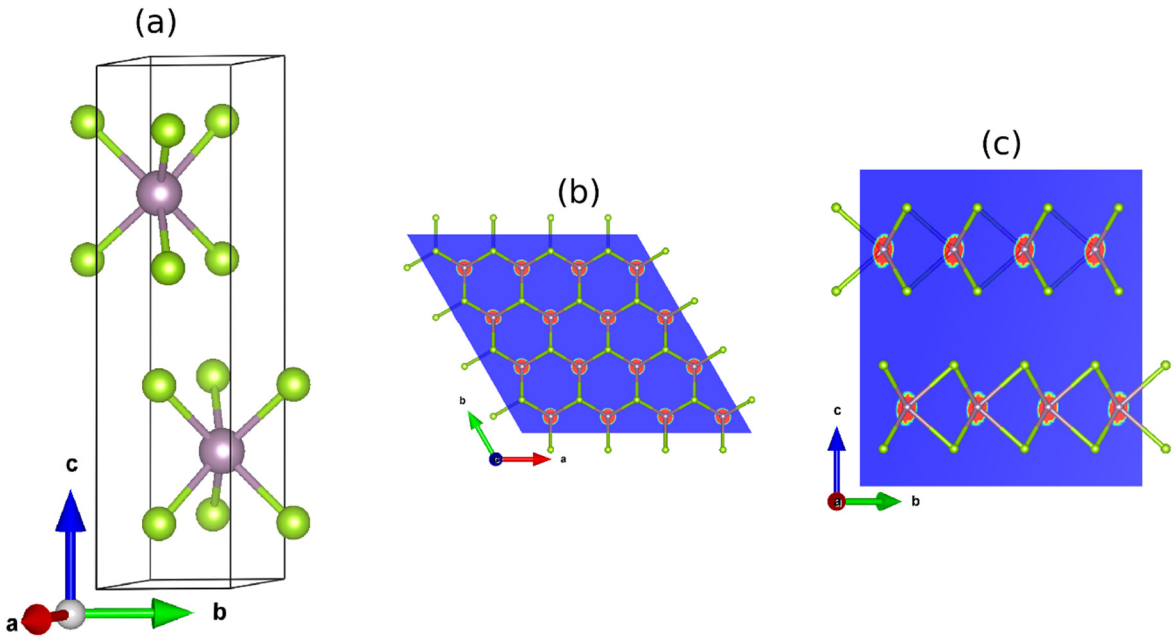

Figure S1. Crystal structure of MSe_2 (M=Mo, W) at ambient conditions (space group no. 194, $P6_3/mmc$). Light-purple and light-green colors, respectively, show M and Se elements. MLMD simulation of the atomic distribution of W at 700 K in (b) the a-b-plane and (c) in the b-c plane at 700 K for WSe2. The W atoms show a symmetric thermal amplitude in the a-b plane while its thermal distribution is more elongated along the c-axis, and asymmetric in the b-c plane. A similar distribution is also observed for the Se atoms.

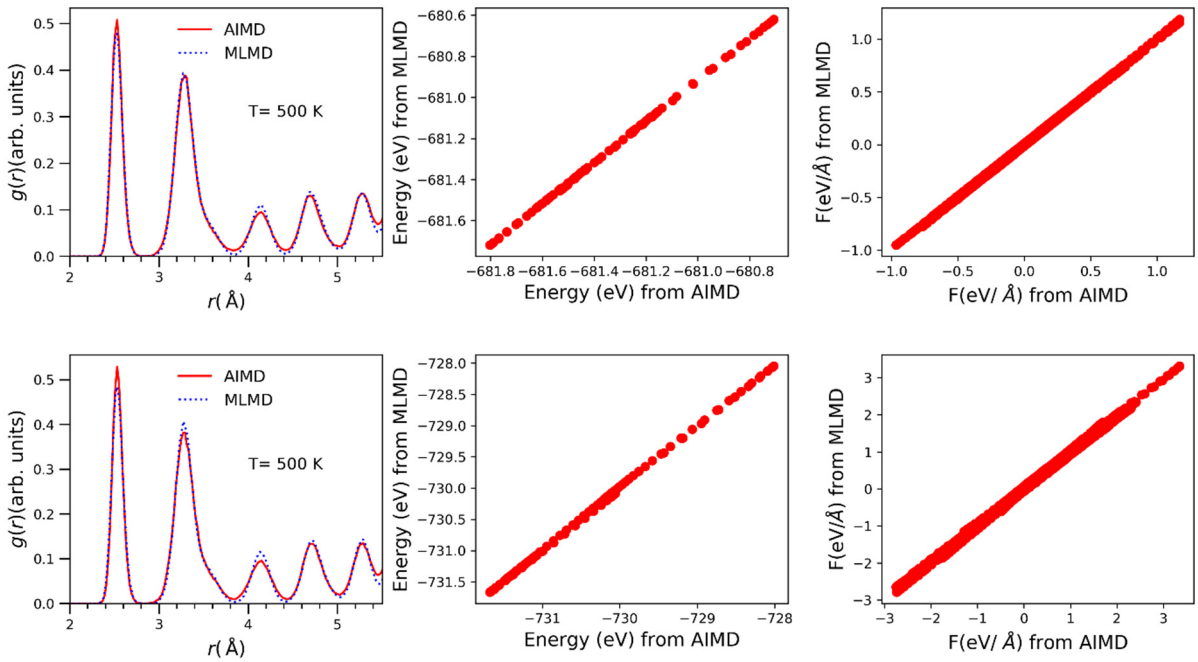

Figure S2: The AIMD and MLMD calculated pair-distribution function, total energies and forces for (top-panel) $MoSe_2$ and (bottom panel) WSe_2. The good agreement between the two simulations validates the machine-learned force field.

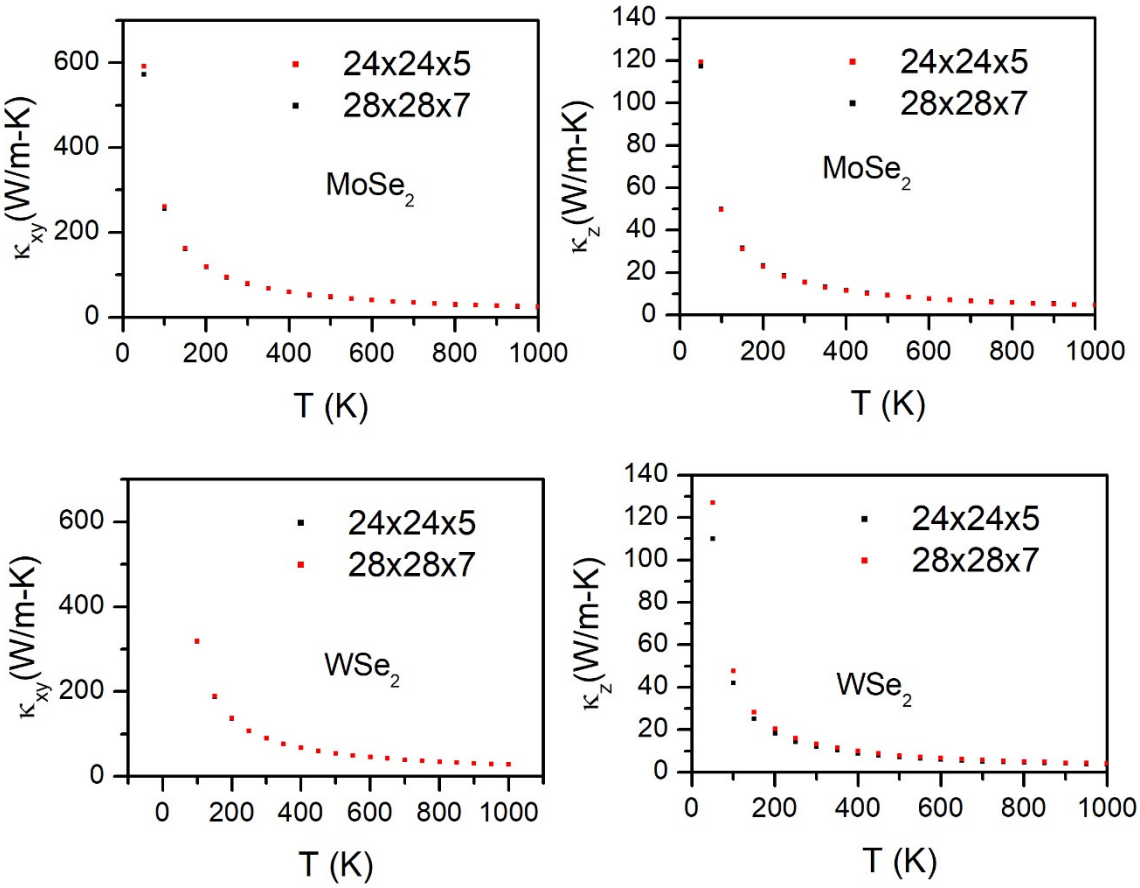

Figure S3: The calculated lattice thermal conductivity from three-phonon scattering using ShengBTE using a q-point grid of 24×24×5 and 28×28×7. The computed values do not show any significant difference, and hence a 24x24x5 q-point grid in BZ was used for all other calculations.

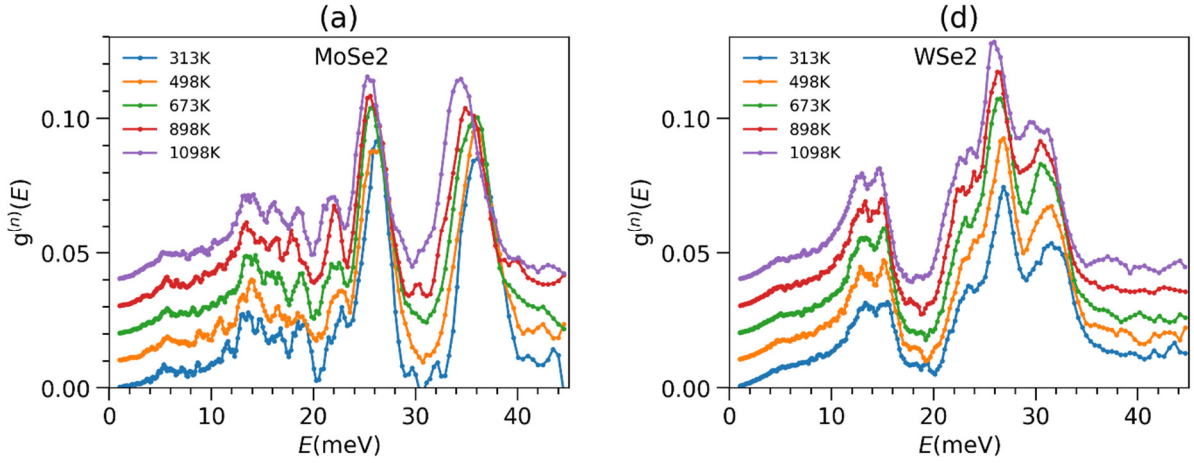

Figure S4: The measured temperature dependence of neutron-weighted phonon density of states of $MoSe_2$ and WSe_2.

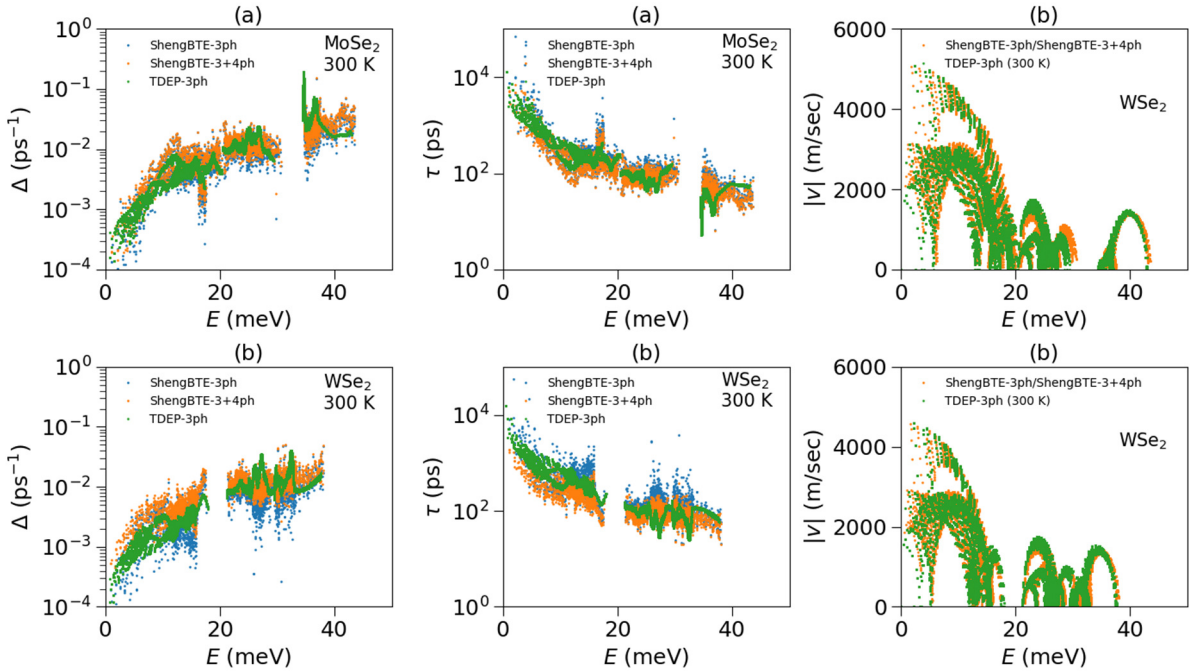

Figure S5. The calculated mode-resolved phonon scattering rate, life time and group velocities on a (24×24×7) q-point grid in BZ in $MoSe_2$ and WSe_2, calculated from 2nd and 3rd-order force-constants at 0 K (ShengBTE-3ph), calculated from 2nd, 3rd- and 4th order force-constants at 0 K (ShengBTE-3ph+4ph) and renormalized 2nd and 3rd-order force-constants at 300 K (TDEP-3ph). Both the ShengBTE-3ph and ShengBTE-3ph+4ph calculation use the same 0 K harmonic phonon group velocity, while the TDEP uses the temperature renormalized phonon group velocities.

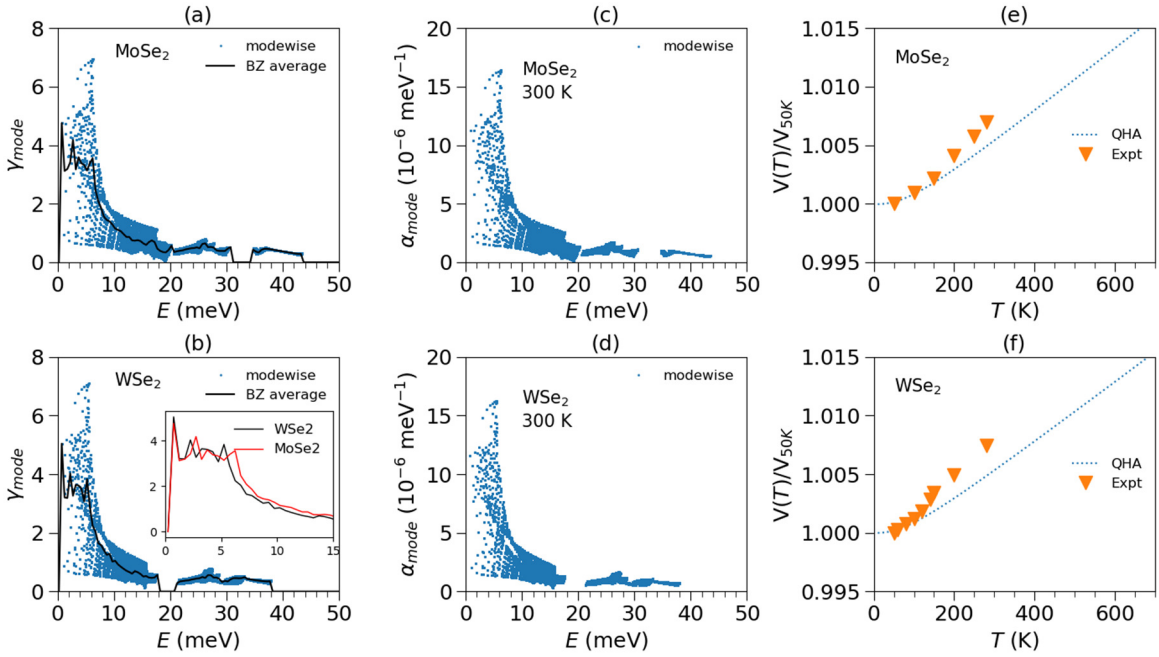

Figure S6. (a-b) The calculated mode Grüneisen parameters in $MoSe_2$ and WSe_2 using pressure dependence of phonon frequencies and (c-d) mode-resolved contribution to thermal expansion coefficient at 300 K in $MoSe_2$ and WSe_2, (e, f) The fraction change in volume with temperature calculated within QHA and compared with our X-ray measurements.

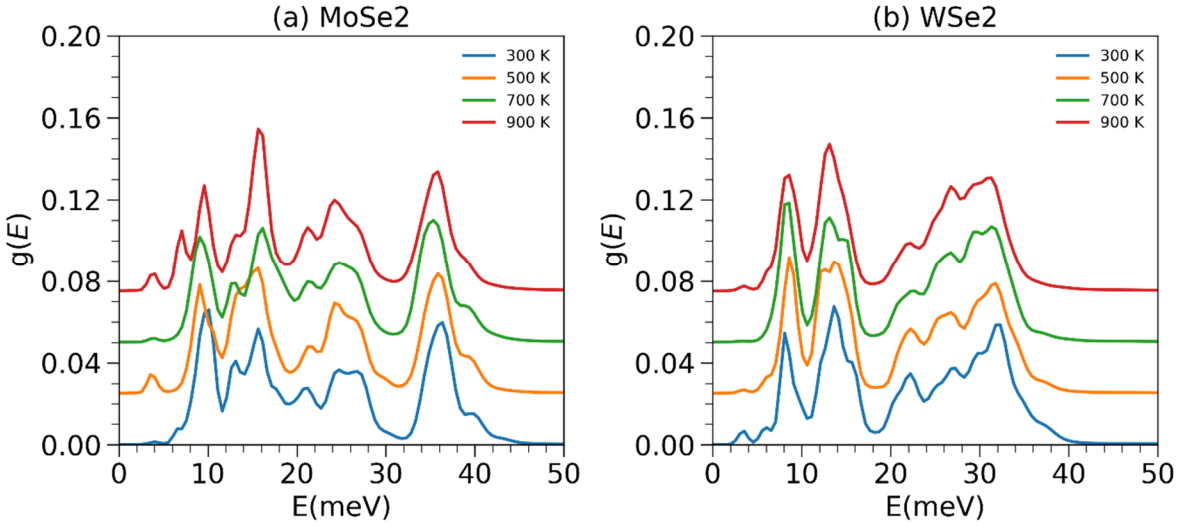

Figure S7. The calculated temperature dependence of PDOS, g(E), of $MoSe_2$ and WSe_2 using AIMD simulation by calculating the Fourier transform of the velocity autocorrelation function. For better visibility, the subsequent PDOS curves are vertically shifted by 0.025.

[1] V. Babacic, D. Saleta Reig, S. Varghese, T. Vasileiadis, E. Coy, K.-J. Tielrooij, and B. Graczykowski, Advanced Materials **33**, 2008614 (2021).