Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information of "Unusual phonon behavior and ultra-low thermal conductance of monolayer InSe"

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S1. Convergence test for the cut-off energy and k-points

The results of convergence test for the cut-off energy and k-points are shown in Table S1 and Table S2, respectively. We demonstrate that the cut-off energy of 70Ry and the k-points grid of 15×15×1 are accurate up to 6 digits. For the convergence of force, we adopt the value of 1×10^{-5} eV/Å.

Table S1. Convergence test for the cutoff energy

Cutoff energy (Ry)	Total energy (Ry)
46	-105.97566052
54	-105.97680654
62	-105.97740670
70	-105.97772339

Table S2. Convergence test for the k-points

K-grids	Total energy (Ry)
9×9×1	-105.97773522
10×10×1	-105.97772804
11×11×1	-105.97772664
12×12×1	-105.97772523
13×13×1	-105.97772386
14×14×1	-105.97772403
15×15×1	-105.97772339

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S2. Phonon properties of MoS_2

By using procedure (1) and procedure (3) listed in the main text, we calculate the phonon dispersion relation of MoS_2 and the results are shown in Figure S1, with panel (a) being exclusive while panel (b) being inclusive of long-ranged interaction. It is seen that the results of panel (b) match the dispersion relation of MoS_2 in the literature [s1]. Most importantly, for MoS_2, the effect of long-ranged interaction only causes a minor shift of phonon frequencies, and imaginary frequencies are completely absent even if the long-ranged interaction is not considered, which is in strong contrast to InSe, where the entire three acoustic modes become imaginary when the long-ranged interaction is not included.

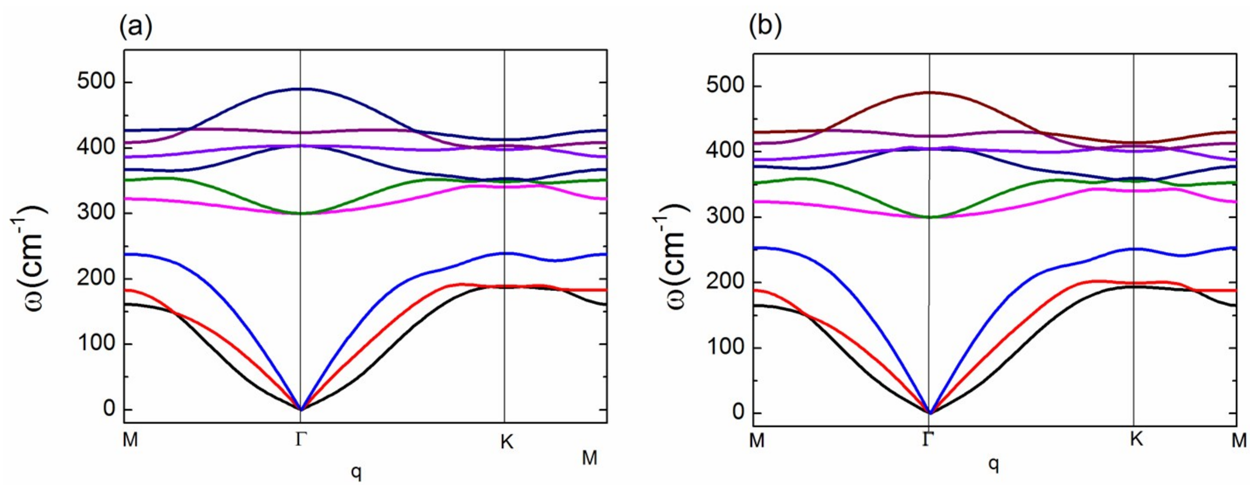

Figure S1. Phonon dispersion relation of MoS_2. (a)The result is obtained through procedure (1), where DDI is not taken into consideration. (b) The result is obtained through procedure (2), where the DDI is included.

S3. Phonon properties of β-phase InSe

In order to make a comparison, we also calculate the phonon properties of β-InSe. The results of Born effective charge, dielectric constant and self-interaction are summarized in Table S3. It is found that β-InSe possesses almost the same Born effective charge and dielectric constant as α-InSe. Therefore, the self-interaction of long-ranged forces in β-InSe is very close to that of α-InSe. However, due to the different geometry, β-InSe has a stronger short-ranged interaction. As a result, the percentage profile of long-range interaction in β-InSe (19-21%) is slightly smaller than that in α-InSe (25-27%), but it is still much larger than that in MoS_2 (3-6%). The dispersion relation of β-InSe is shown in Figure S2. Similar to α-InSe, β-InSe also presents imaginary frequencies in the acoustic modes if the dipole-dipole interaction (DDI) is not taken into consideration. However, in β-InSe, only two acoustic modes partially exhibit imaginary frequencies, which is different from α-InSe in which all the three acoustic modes are entirely in the imaginary regime. Once DDI is included, as shown in Figure S2(b), the imaginary frequencies disappear, and there is a frequency shift in the optical modes. The non-analytical behavior of the LO modes near the Γ point (at $187cm^{-1}$) is also present in β-InSe. Another observation is that in β-InSe, the out-of-plane mode ($109cm^{-1}$ and $240cm^{-1}$ at Γ point) no longer occupies a single frequency channel as that in α-InSe.

Using the non-equilibrium Green's function (NEGF) technique, we calculate the phonon transmission function and the thermal conductance of β-InSe, and the results are shown in Figure S3. It is found that there is only one frequency gap between $168\sim176cm^{-1}$. However, the optical modes have high transmission function. From Figure S3(b), we find that the high frequency modes ($>100cm^{-1}$) contributes about 60% of the thermal conductance, while it is only 40% for α-InSe. As a result, the thermal conductance of β-InSe, which is $0.49nWK^{-1}nm^{-2}$, is higher than that of α-InSe ($0.29nWK^{-1}nm^{-2}$).

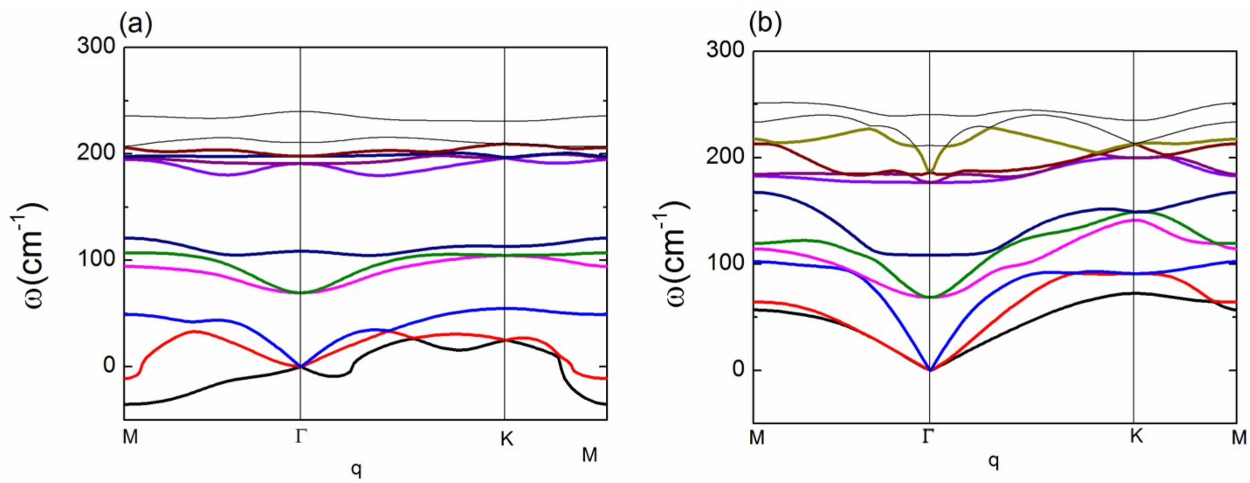

Figure S2. Phonon dispersion relation of β-InSe without DDI (a) and with DDI (b).

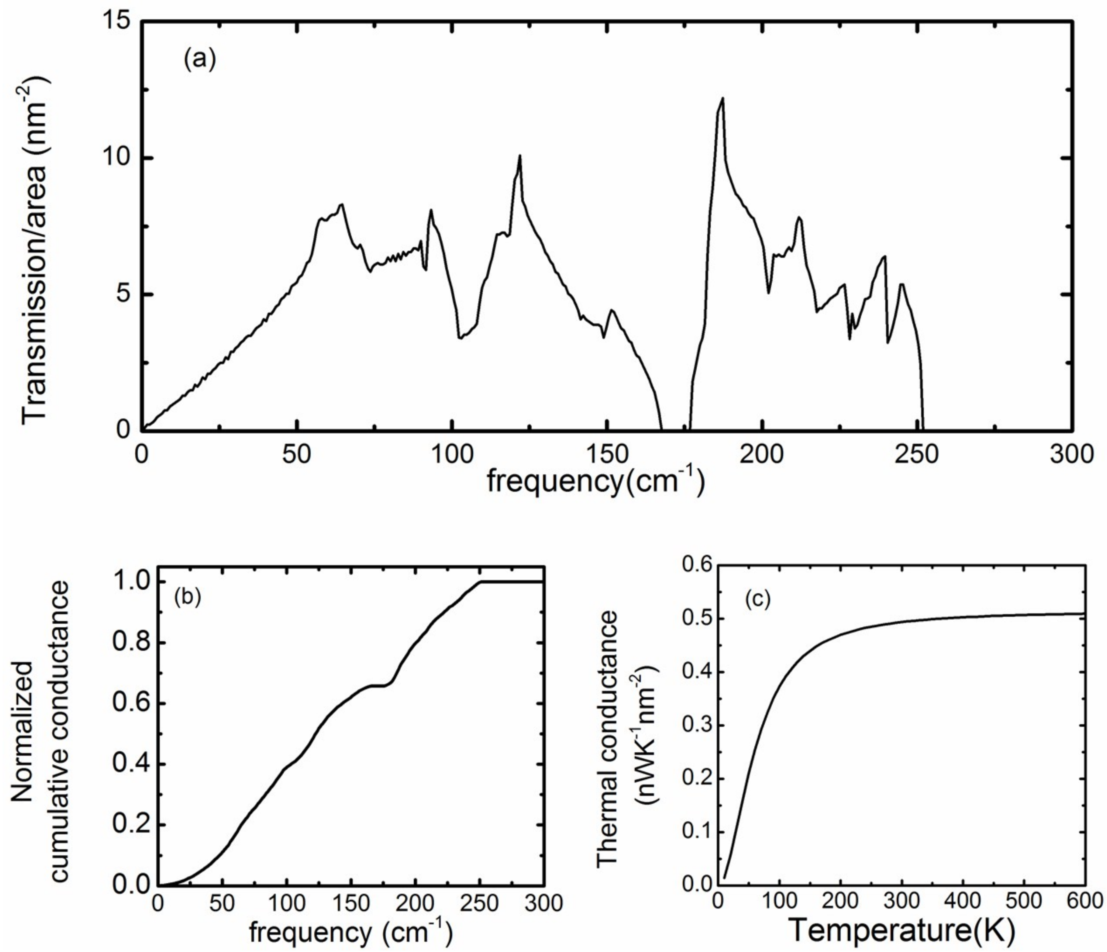

Figure S3. Transport properties of β-InSe. (a) The transmission function per cross-sectional area of β-InSe. (b) The cumulative thermal conductance of InSe at room temperature (300K). (c) Thermal conductance of β-InSe against temperature.

Table S3. Comparison of Born effective charge, dielectric constant and self-interaction in α-InSe and β-InSe. The self-interaction of InSe is in units of Ry/Bohr[2].

	Atom	$Z^*_{xx}=Z^*_{yy}$	Z^*_{zz}	ϵ_{xx}	ϵ_{zz}	$C_{xx}(\approx C_{yy})$ Short range	$C_{xx}(\approx C_{yy})$ Long range	C_{zz} Short range	C_{zz} Long range
α-InSe	Se	2.33	0.27	3.88	1.55	0.12435	0.04191 (25%)	0.13694	-0.00274 (2%)
	In	-2.33	-0.27			0.11421	0.04113 (27%)	0.22758	-0.00269 (1%)
β-InSe	Se	2.37	0.26	3.85	1.55	0.16306	0.04345 (21%)	0.13363	-0.00263 (2%)
	In	-2.37	-0.26			0.17859	0.04259 (19%)	0.22743	-0.00258 (1%)

References

S1. Y. Cai, J. Lan, G. Zhang and Y.-W. Zhang, Physical Review B **89** (3), 035438 (2014).