Supplementary Information (SI)

The Intrinsically Low Lattice Thermal Conductivity of Monolayer T-Au_6X_2 (X= S, Se and Te)

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1. Thermal Conductivity Based on 4th-phonon Scattering

1.1 Computational Methodology

From the solution of phonon BTE, the κ_l along the α axis is computed as[1]

$$\kappa_l^{\alpha\alpha} = \frac{\hbar^2}{k_B T^2 \Omega N_q} \sum_{qv} n_{qv}(n_{qv}+1)\omega_{qv}^2 v_{qv}^{\alpha} F_{qv}^{\alpha}$$

where $\hbar$, k_B, T, Ω, and N_q are the reduced Planck's constant, Boltzmann constant, absolute temperature, the volume of the unit cell, and the number of sampled $\boldsymbol{q}$ wave vectors, respectively. ω_{qv} and N_{qv} are the frequency and population of the phonon mode $|qv\rangle$ with mode index v. $v_{qv}^{\alpha\alpha}$ is the group velocity along the α axis, and F_{qv} is written as

$$F_{qv}^{\alpha} = \tau_{qv}(v_{qv}^{\alpha} + \Delta_{qv})$$

where τ_{qv} is the lifetime of mode $|qv\rangle$ under single-mode relaxation time approximation (SMRTA), Δ_{qv} works only for the iterative solution of BTE and is a quantity displaying the population deviation of phonons from the SMRTA scheme.

Normally, except τ_{qv} and Δ_{qv}, all phonon properties can be calculated within the harmonic approximation (HA) by diagonalization of a dynamic matrix transformed from harmonic interatomic force constants (IFCs). The computation of τ_{qv} and Δ_{qv} requires at least a 3*ph* scattering process, which is generally computed by dealing with cubic anharmonicity in a perturbation way to the HA, [2] as described by Eqs. (5)–(9) in Ref. 3. These approximations offer the most common model of the κ_l, hereinafter referred to as HA + 3*ph* and κ_{3ph}^{HA} for resulting κ_l. After the addition of quartic anharmonicity, there are three other models of the κ_l. First, if only 4*ph* scattering processes will modify τ_{qv} and Δ_{qv} are added (see Eqs. (2)–(7) in Ref. 4. for the expressions of τ_{qv} and Δ_{qv} with the inclusion of both 3*ph* and 4*ph* scatterings), the HA + 3*ph* model is changed into the HA + 3*ph* +4*ph* one, namely, κ_{3+4ph}^{HA}. Second, ω_{qv} and v_{qv} become temperature dependent when phonon frequency shifts arising from quartic anharmonic renormalization are taken into account.

To gain more precise harmonic, cubic and quartic IFCs, here we use the finite displacement approach with a displacement of 0.01 Å to generate the perturbed structures whose forces are computed subsequently by the static DFT. Due to the usage of 2 × 4 × 1 supercells for producing the IFCs, a fixed 15 × 15 × 1 q-mesh is utilized in the 3*ph*+4*ph* calculation process. It should be noted that the nearest-neighbor cutoff distance considered in the calculation of the four-phonon BTE is not large enough, resulting in a large error term, so the thermal conductivity is not accurate. However, if a large enough nearest-neighbor cutoff is considered, such a calculation would be unsustainable.

1.2 Results

The thermal conductivities of T-Au_6S_2, T-Au_6Se_2, and T-Au_6Te_2 calculated by 4th-phonon scattering are 0.062, 0.138, and 0.078, respectively, as shown in Fig. S1. It can be seen that

those values are significantly different from the results calculated by 3rd-phonon scattering in the main text. Meanwhile, there is no obvious pattern in this result (that is, like most S, Se, and Te compounds, the thermal conductivity of related compounds gradually decreases with the order of S, Se, and Te[5]). Therefore, in this context, we believe that the results of thermal conductivity obtained based on three phonon scattering calculations are more accurate than those obtained based on four phonon scattering calculations.

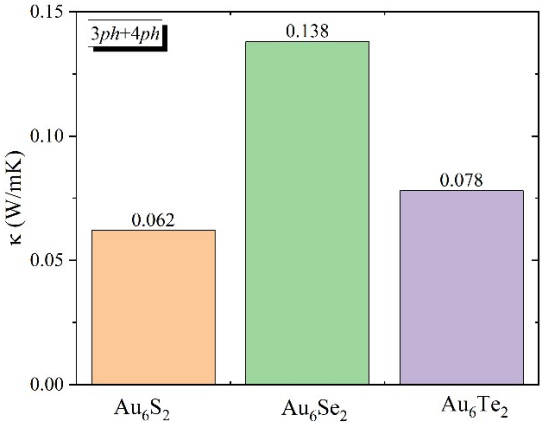

Fig. S1. The thermal conductivity of T-Au_6X_2 (X=S, Se, and Te) calculated by 4th-phonon scattering.

2. Electron Localization Function

As shown in Fig. S2 (electron localization function (ELF) map), the X atoms between layers do not share electron pairs, therefore the interlayer interaction of bulk T-Au_6X_2 is van der (Waals) vdW interaction. This also makes the preparation of two-dimensional T-Au_6X_2 relatively easy.

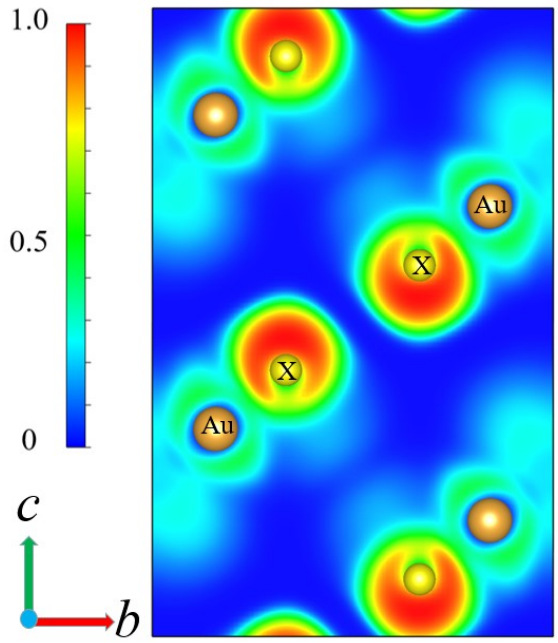

Fig. S1.The ELF maps for two-dimensional T-Au_6X_2. The blue (ELF=0.0) and red (ELF=1.0) represent no electron localization and full electron localization, respectively.

References

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