Supporting Information: Exceptionally Enhanced Thermal Conductivity of Aluminum Driven by Extreme Pressures: A First-Principles Study

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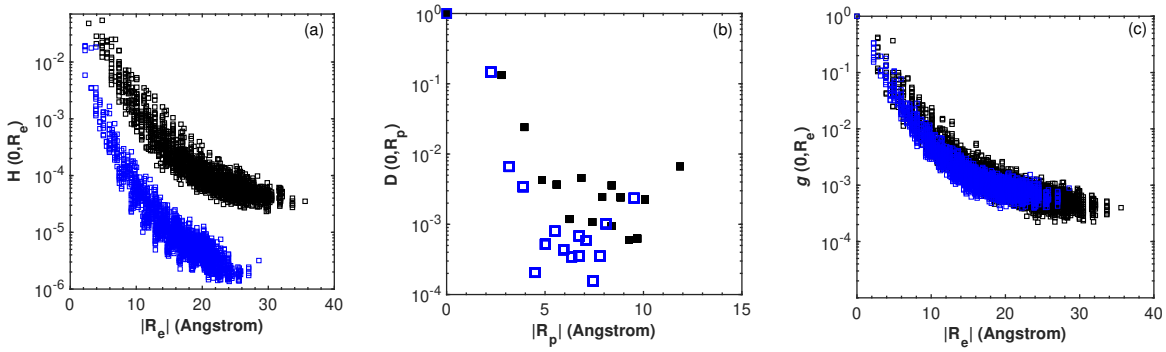

Figure S1: Spatial decays of (a) the Hamiltonian, (b) the dynamical matrix, and (c) the electron-phonon matrix elements for Al at 0 GPa (black black symbols) and 207 GPa (blue symbols).

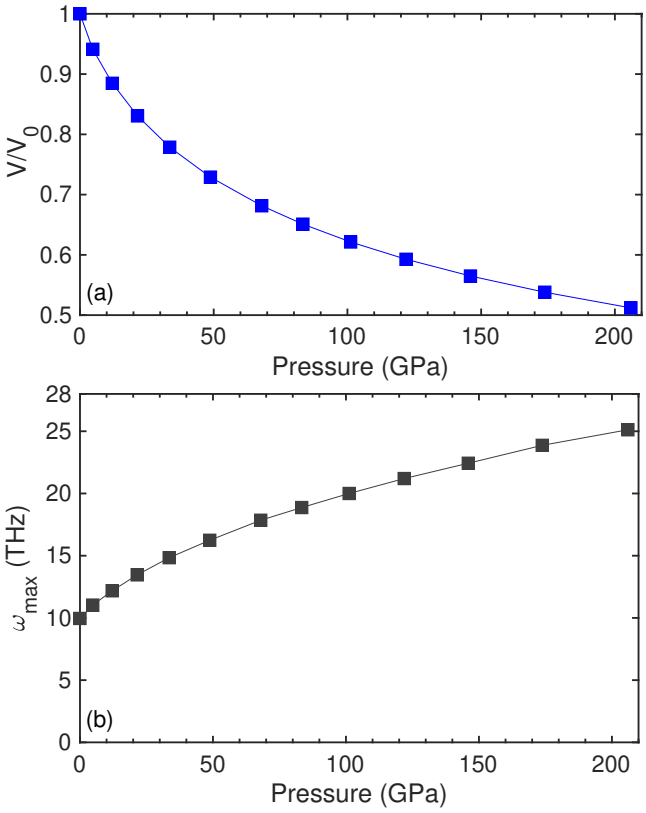

Figure S2: (a) The relative change of volume as a function of pressure for Al. The positive curvature suggests stiffening of the lattice. (b) Maximum phonon frequency vs pressure for Al.

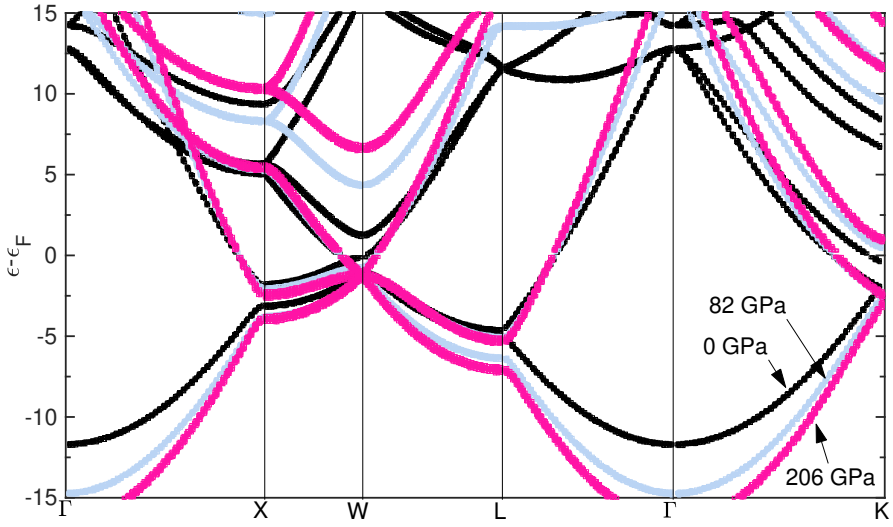

Figure S3: Bandstructure calculations for Al at three different pressures.

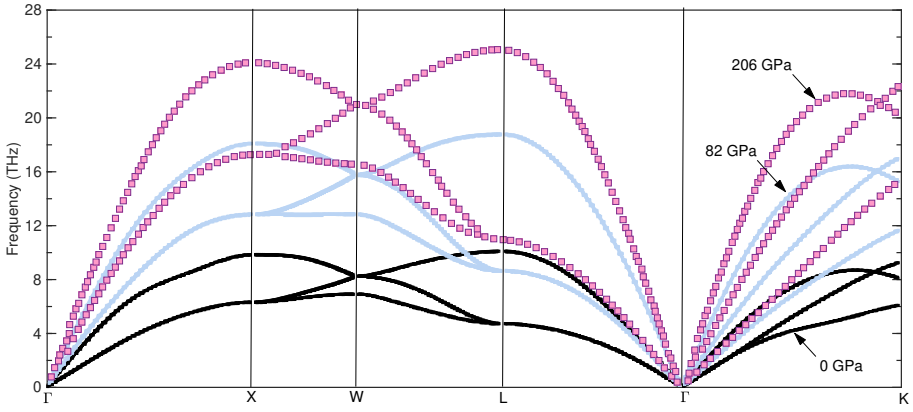

Figure S4: Phonon dispersions for Al at three different pressures.

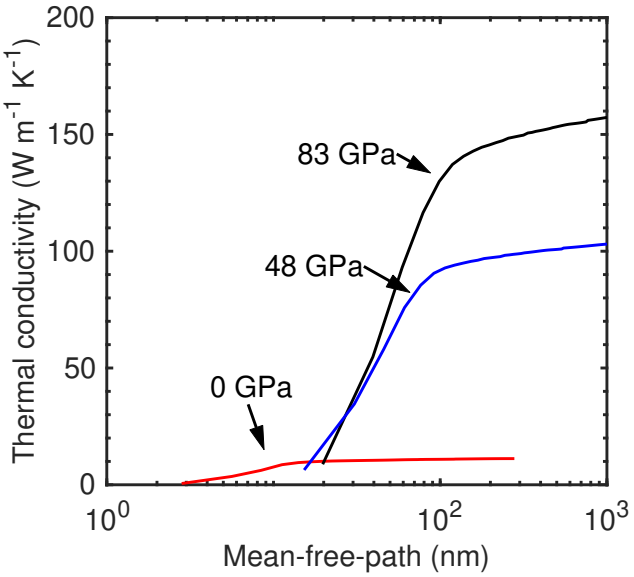

Figure S5: Lattice thermal conductivity accumulation as a function of phonon mean free paths for Al at three different pressures.

We will briefly describe the calculations of basic physical quantities that are used to ultimately calculate the lattice and electron thermal conductivity. Our calculations of the electron-phonon coupling coefficients requires the calculations of the imaginary part of the electron and phonon self-energies given as,[S1,S2]

$$\Sigma_{n\mathbf{k}}(\omega,T) = \sum_{m\nu}\int_{\mathrm{BZ}}\frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}}|g_{mn,\nu}(\mathbf{k},\mathbf{q})|^2 \times\left[\frac{N_{\mathbf{q},\nu}(T)+f_{m\mathbf{k}+\mathbf{q}}}{\omega-(\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{\mathrm{F}})+\omega_{\mathbf{q},\nu}+i\delta}+\frac{N_{\mathbf{q},\nu}(T)+1-f_{m\mathbf{k}+\mathbf{q}}(T)}{\omega-(\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{\mathrm{F}})-\omega_{\mathbf{q},\nu}+i\delta}\right], \quad (1)$$

$$\Pi_{\mathbf{q}\nu}(\omega,T) = 2\sum_{mn}\int_{\mathrm{BZ}}\frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}}|g_{mn,\nu}(\mathbf{k},\mathbf{q})|^2 \times\frac{f_{n\mathbf{k}}(T)-f_{m\mathbf{k}+\mathbf{q}}(T)}{\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}-\omega-i\delta}, \quad (2)$$

where ε_{F} is the Fermi energy, $N_{\mathbf{q},\nu}$ is the Bose-Einstein distribution, $f_{n\mathbf{k}}(T)$ is the Fermi-Dirac distribution at band n, $g_{mn,\nu}(\mathbf{k},\mathbf{q})$ is the electron-phonon matrix element computed using density functional perturbation theory over all phonon and electron wave-vectors, $\mathbf{q}$, and

$\mathbf{k}$, respectively, and quantifies the scattering process between the Khon-Sham states $m\mathbf{k}'$ and $n\mathbf{k}$, δ is a small positive real parameter to avoid numerical instabilities guaranteeing the correct analytical structure of the self-energies, and the integrals are extended over the Brillouin Zone (BZ) of volume Ω_{BZ}, and the factor of 2 in the electron self-energy accounts for spin degeneracy.[S1,S2] Note, the commonly used approximation known as the "double-delta function" approximation that neglects the phonon frequencies $\omega_{\mathbf{q}\nu}$ and takes the limit of small broadening δ is not required in the electron-phonon Wannier (EPW) package used for the calculations of the self-energies.[S1,S3]

We calculate the Eliashberg transport spectral function, $\alpha^2_{\mathrm{tr}}F(\omega)$, which measures the probability of specific phonon modes with energy $\hbar\omega$ to decay into an electron-hole pair from an electron eigenstate in the Fermi surface to another. The average of the electron-phonon coupling over all phonon wave-vectors, $\mathbf{q}$ with branch index ν, throughout the entire Brillouin Zone is given as,[S4]

$$\alpha^2_{\mathrm{tr}}F(\omega) = \frac{1}{N(\varepsilon_{\mathrm{F}})}\sum_{\mathbf{q}\nu}\sum_{\mathbf{k}nm}|g^{\mathbf{q}\nu}_{\mathbf{k}+\mathbf{q}m,\mathbf{k}n}|^2\delta(\hbar\omega-\hbar\omega_{\mathbf{q}\nu})\delta(\varepsilon_{\mathbf{k}n}-\varepsilon_{\mathrm{F}})\delta(\varepsilon_{\mathbf{k}+\mathbf{q}m}-\varepsilon_{\mathrm{F}})\eta_{\mathbf{k}+\mathbf{q}m,\mathbf{k}n}, \quad (3)$$

where $g^{\mathbf{q}\nu}_{\mathbf{k}+\mathbf{q}m,\mathbf{k}n}$ is the electron-phonon matrix elements that quantifies the scattering of an electron eigenstate $|\mathbf{k}n\rangle$ at Fermi surface to the state $|\mathbf{k}+\mathbf{q}m\rangle$, and $N(\varepsilon_{\mathrm{F}})$ is the density of states of electrons per spin at the Fermi level. The efficiency factor

$$\eta_{\mathbf{k}+\mathbf{q}m,\mathbf{k}n} = 1 - \frac{\mathbf{v}_{\mathbf{k}n}\cdot\mathbf{v}_{\mathbf{k}+\mathbf{q}m}}{|\mathbf{v}_{\mathbf{k}n}|^2}, \quad (4)$$

which depends on the electron velocity $\mathbf{v}_{\mathbf{k}n}$ and accounts for the anisotropy by considering different scattering directions, is the difference between the transport spectral function and the spectral function, $\alpha^2F(\omega)$.[S2,S5] We calculate the electron-phonon mass enhancement parameter (λ) and the transport constant (λ_{tr}) given as,

$$\lambda_{(\mathrm{tr})} = 2\int_0^\infty \frac{\alpha^2_{(\mathrm{tr})}F(\omega)d\omega}{\omega}. \tag{5}$$

We calculate the electron-phonon coupling matrix within the framework of the EPW package.[S2] From an initial coarse grid of 18×18×18 and 6×6×6 electron ($\mathbf{k}$) and phonon wave vector grids ($\mathbf{q}$), respectively, we use the recently formulated maximally localized Wannier functions basis,[S6] to interpolate to uniform (and denser) grids of 50×50×50 and 30×30×30, for $\mathbf{k}$ and $\mathbf{q}$, respectively, to conduct integration via the tetrahedron method. Note, for all of our calculations, we use a plane wave energy cutoff of 816.3 eV (60 Ry) and a gaussian smearing of 0.34 eV (0.025 Ry).

We ensure that the interpolated wavevector grids are dense enough to produce numerically converged values of λ as detailed in our earlier works in Refs. S5,S7. We also check the accuracy of the Wannier representation by confirming their localized nature by considering the spatial decay of the Hamiltonian, dynamical matrix, and the e-p coupling matrix elements, which have to decrease to zero to confirm the localization of the Wannier functions and validate their use for high-quality interpolation.[S8] We plot the spatial decays of the Hamiltonian, the dynamical matrix and the electron-phonon coupling matrix elements in the Wannier functions representation for Al at 0 GPa and 206 GPa in Fig. S1. The electron Hamiltonian is obtained as,

$$H^{\mathrm{el}}_{\mathbf{R}_e,\mathbf{R}'_e} = \sum_{\mathbf{k}} w_{\mathbf{k}} \mathrm{e}^{-i\mathbf{k}\cdot(\mathbf{R}'_e-\mathbf{R}_e)} U^\dagger_{\mathbf{k}} H^{\mathrm{el}}_{\mathbf{k}} U_{\mathbf{k}}, \tag{6}$$

where $w_{\mathbf{k}}$ is the weight of the $\mathbf{k}$ points, $\mathbf{R}_e$ is the electron unit-cell and the guage matrix $U_{\mathbf{k}}$ yields the transformation between Bloch eigenstates and maximally localized Wannier functions (MLWFs).[S8,S9]

The transformation of the dynamical matrix to real-space representation is carried out using,

$$D^{\mathrm{ph}}_{\mathbf{R}_p,\mathbf{R}'_p} = \sum_{\mathbf{q}} w_{\mathbf{q}} \mathrm{e}^{-i\mathbf{q}\cdot(\mathbf{R}'_p-\mathbf{R}_p)} \mathbf{e}_{\mathbf{q}} D^{\mathrm{ph}}_{\mathbf{q}} \mathbf{e}^\dagger_{\mathbf{q}} \tag{7}$$

where $w_{\mathbf{q}}$ is the weight of the $\mathbf{q}$ points, $\mathbf{e}_{\mathbf{q}}$ are the orthonormal eigenvectors of the dynamical matrix. Consequently, the e-p matrix elements are given as,

$$g(\mathbf{R}_e, \mathbf{R}_p) = \frac{1}{N_p} \sum_{\mathbf{q},\mathbf{k}} w_{\mathbf{q}} \mathrm{e}^{-i(\mathbf{k}\cdot\mathbf{R}_e + \mathbf{q}\cdot\mathbf{R}_p)} U^{\dagger}_{\mathbf{k+q}} g(\mathbf{k},\mathbf{q}) U_{\mathbf{k}} \mathbf{u}^{-1}_{\mathbf{q}}, \tag{8}$$

Here, $U_{\mathbf{k}}$ and $U_{\mathbf{k+q}}$ are the electronic matrices, $\mathbf{u}_{\mathbf{q}}$ are the phonon eigenvectors scaled by the atomic masses, and N_p is the number of unit cells in the period supercell.[S8,S9] As is clear from Fig. S1, all quantities decay to zero for the two extreme pressure conditions very quickly with distance in the electron or phonon unit cells. This suggests that high quality interpolation has been achieved via the wanniarization technique. Note, the phonon frequencies and band energies at ambient condition obtained via the interpolation also agree with those calculated directly by the density functional theory calculations and previous works,[S10,S11] which provides confidence in our approach for calculating electron-phonon interactions at high pressures. We calculate the electron thermal conductivity by utilizing the electron-phonon scattering rates calculated from the above mentioned methodology in conjunction with the BTE.

The application of pressure has a positive curvature on the relative volume change, which suggests that the lattice is hardening with pressure. We also find that the spectrum of vibrations also broadens to higher frequencies with pressure (Fig. S2). The application of pressure is also shown to broaden the both the electronic band structure and phonon dispersion as shown in Fig. S3 and Fig. S4, respectively, along high symmetry directions in the Brillouin zone.

The BTE is solved to calculate the phonon thermal conductivity tensor that is given by[S12]

$$\kappa_{p,\alpha\beta} = \sum_{qv} c_{qv} v_{qv,\alpha} v_{qv,\beta} \tau_{qv} \tag{9}$$

here, c_{qv} denote the volumetric specific heat capacity, $v_{qv,\alpha}$ gives the α component of the

group velocity vector v_{qv} of the phonons and τ_{qv} represents the lifetime of the phonon.The computation carried out in Eq. 9. is in the first Brillioun zone for all the phonon modes. The volumetric specific heat capacity for phonons is given by Bose-Einstein statistics as $c_{qv} = \frac{\hbar\omega_{qv}}{V}\frac{\delta n^0_{qv}}{\delta V}$, where n^0_{qv} is the Bose-Einstein distribution. The group velocity and the mode frequency are related as v_{qv}=$\frac{\delta\omega_{qv}}{\delta q}$. The commonly used method for calculating the phonon lifetime is by employing the inverse of the phonon scattering rate, under the relaxation time approximation of the BTE and is given by, $\frac{n_{qv}}{\delta t}$.[S13]

The phonon frequencies are obtained by employing the Harmonic lattice dynamics calculations.[S14] The elements of the dynamical matrix elements are

$$D^{\alpha\alpha^{'}}_{\tau\tau^{'}}(q) = \sum_{R^{'}} \frac{1}{\sqrt{m_\tau m_{\tau^{'}}}} \Phi^{\alpha\alpha^{'}}_{0\tau,R^{'}\tau^{'}} exp(iq.R^{'}). \tag{10}$$

The summation shown in Eq. 10 is carried out over all the unit cells located at position vector $R^{'}$, m_τ denotes the mass of the atom τ in the unit cell, $\Phi^{\alpha\alpha^{'}}_{0\tau,R^{'}\tau^{'}}$ is for the second-order (harmonic) force constant which links the motion of atom (0,τ) (atom τ in the unit cell at 0) in the α direction and atom $(R^{'},\tau^{'})$ in the $\alpha^{\prime}$ direction. The eigenvalue problems are solved to obtain the eigenvectors, e_{qv}, and the phonon frequencies. The eigenvalue problem is given by,

$$(\omega_{qv})^2 e_{qv} = D(q) e_{qv} \tag{11}$$

For these calculations, we consider phonon-phonon and phonon-electron interactions interactions[S15]

$$\begin{aligned}\frac{1}{\tau^{pp}_{qv}} =& \frac{\pi\hbar}{16N}\sum_{q^{'}v^{'}}\sum_{q^{''}v^{''}}\left|V^{qq^{'}q^{''}}_{vv^{'}v^{''}}\right|^2 \Big[(n^0_{q^{'}v^{'}} + n^0_{q^{''}v^{''}} + 1)\delta(\omega_{qv} - \omega_{q^{'}v^{'}} - \omega_{q^{''}v^{''}}) + (n^0_{q^{'}v^{'}} - n^0_{q^{''}v^{''}}) \\ & \times \left[\delta(\omega_{qv} + \omega_{q^{'}v^{'}} - \omega_{q^{''}v^{''}}) - \delta(\omega_{qv} - \omega_{q^{'}v^{'}} + \omega_{q^{''}v^{''}})\right]\end{aligned} \tag{12}$$

here, N denotes the total number of phonon modes, $V^{qq'q''}_{vv'v''}$ represents the matrix elements for three phonon scattering. The three phonon scattering depend on the third order force constants $\Phi^{\alpha\alpha^{'}alpha^{''}}_{0\tau,R'\tau',R''\tau''}$ and can be defined as,

$$V^{qq'q''}_{vv'v''} = \sum_{R''\tau''\alpha''} \sum_{R'\tau'\alpha'} \sum_{\tau\alpha} \delta_{q+q'+q''} \Phi^{\alpha\alpha^{'}\alpha^{''}}_{0\tau,R'\tau',R''\tau''} \times \frac{e^{i(q^{'}\cdot R^{'}+q^{''}\cdot R'')} e^{\tau\alpha}_{qv} e^{\tau^{'}\alpha^{'}}_{q'v'} e^{\tau^{''}\alpha^{''}}_{q''v''}}{\sqrt{m_\tau m_{\tau'} m_{\tau''} \omega_{qv} \omega_{q'v'} \omega_{q''v''}}}$$

(13)

here $e^{\tau\alpha}_{qv}$ denote the α-component of the eigenvector e_{qv} for atom τ. For phonon mode qv, the scattering is,[?]

$$\frac{1}{\tau^{ep}_{qv}} = \frac{2\pi}{\hbar} \sum_{\kappa mn} \omega_{kappa} \left| g^{v}_{mn}(\kappa\kappa^{'}, q \right|^2 (f_{\kappa m} - f_{\kappa^{'}n}) \times \delta(\epsilon_{\kappa m} + \hbar\omega_{qv} - \epsilon_{\kappa^{'}n}) \tag{14}$$

here, ω_κ represents the weight of the κ point which is normalized to two for non-magnetic calculations and $\kappa^{'} = \kappa + q$. The effective lifetime of the phonon mode qv is obtained by combining the phonon-phonon and phonon-electron relaxation time using the Matthiessen's rule in which the lifetime is given as,

$$\frac{1}{\tau_{qv}} = \frac{1}{\tau^{pp}_{qv}} + \frac{1}{\tau^{ep}_{qv}}. \tag{15}$$

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