Soft anharmonic phonons and ultralow thermal conductivity in Mg₃(Sb, Bi)₂ thermoelectrics

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The candidate thermoelectric compounds Mg₃Sb₂ and Mg₃Bi₂ show excellent performance near ambient temperature, enabled by an anomalously low lattice thermal conductivity (κₐ) comparable to those of much heavier PbTe or Bi₂Te₃. Contrary to common mass-trend expectations, replacing Mg with heavier Ca or Yb yields a threefold increase in κ₀ in CaMg₃Sb₂ and YbMg₃Bi₂. Here, we report a comprehensive analysis of phonons in the series AMg₃X₂ (A = Mg, Ca, and Yb; X = Bi and Sb) based on inelastic neutron/x-ray scattering and first-principles simulations showing that the anomalously low κ₀ of Mg₃X₂ has inherent phononic origins. We uncover a large phonon softening and flattening of low-energy transverse acoustic phonons in Mg₃X₂ compared to the ternary analogs and traced to a specific Mg-X bond, which markedly enlarges the scattering phase-space, enabling the threefold tuning in κ₀. These results provide key insights for manipulating phonon scattering without the traditional reliance on heavy elements.

INTRODUCTION
Thermoelectric (TE) materials directly interconvert electrical and thermal gradients, providing opportunities in waste heat recovery and cooling applications (1–4). Improving TE conversion efficiency requires minimizing the thermal conductivity κ tot = κL + κS (sum of electronic and lattice components) and simultaneously maximizing the electronic power factor (3, 4). While first-principles band structure calculations have enabled a predictive understanding of electronic transport properties and in silico material design, achieving a quantitative microscopic understanding of thermal transport in strongly anharmonic materials has remained challenging (3, 4). Impressive advances in TE performance have been achieved over the past decade at intermediate to high temperature (T > 450 K) (5–12), enabled in part because κS is strongly suppressed by anharmonic scattering for high phonon occupations (scaling with T). Around room temperature, a relative paucity of material candidates has hampered TE developments, with (Bi, Sb)₂(Te, Se)₃ alloys remaining the best for decades (13, 14). Recently, however, n-type Mg₃(Bi, Sb)₂ Zintl compounds were reported to achieve comparable performance near ambient conditions, potentially with much lower cost (15–18).

Despite their much lighter weight than conventional TE compounds PbTe or Bi₂(Te, Se)₃, these promising Zintl compounds exhibit strikingly low values of κ₀. For instance, κ₁ = 1.4 W m⁻¹ K⁻¹ was achieved in polycrystalline Mg₃Sb₂ at 323 K (19), despite its low mass and relatively simple crystal structure. This low κ₁ is comparable to those of 2.5× heavier compounds PbTe and Bi₂(Te, Se)₃ or barium clathrates with complex structures, contradicting the expected trend of κ₁ ∝ M⁻¹ [from the inverse relationship between the square of phonon frequency, ω, and mass, M, and the proportionality of group velocity vG and ω. κ₁ of polycrystalline PbTe, Bi₂Te₃, and Ba₈Ga₁₆Ge₃₀ are 2.0, 1.2, and 1.5 W m⁻¹K⁻¹ at room temperature (20–22). The mass densities of Mg₃Sb₂, PbTe, and Bi₂Te₃ are 4.02, 8.16, and 7.74 g/cm³, respectively.] Further, this surprisingly low κ₁ in Mg₃X₂ is strongly tunable upon targeted substitutions: Replacing A-site Mg with heavier Ca or Yb results in a striking anomalous increase in κ₁ by a factor of 2 to 3 (23, 24), again directly contradicting the expected suppression from more complex composition and heavier mass, and suggests heretofore unknown mechanisms capable of strongly suppressing phonon propagation in simple, lightweight crystalline compounds.

Experimental and theoretical TE investigations of Mg₃X₂ have so far mainly focused on the electronic properties, for example, the origin of n-type behavior (25, 26), the multivalley character of the conduction band (27–30), and routes to increased carrier mobility (17, 18, 31–33). In contrast, the origin of the intrinsically low κ₀ of Mg₃X₂ and the counterintuitive increase of κ₁ in homologous ternary AMg₃X₂ have remained puzzling, although the low κ₁ plays an equally important role in achieving high zT. Previous computational studies suggested that the anharmonic interlayer shearing transverse acoustic (TA) modes (23, 24) and anharmonic mid-energy optical phonons (24) suppress κ₀. Simulations of alloys also predicted that doping 25% Ca or Yb on the A-site reduces κ₀ by reducing the averaged phonon velocity, while the averaged phonon lifetime remains unchanged (29). Measurements of elastic moduli revealed soft shear moduli in Mg₃Sb₂ and a higher rate of softening upon warming than in ternary AMg₃X₂, which was interpreted in terms of ion radii, unit cell volumes, and large negative Grüneisen parameters in TA modes (23). Yet, a clear microscopic picture of phonon scattering remains elusive because of the lack of detailed phonon measurements, precluding a clear understanding of the origin of the abnormally low κ₁ in Mg₃X₂.

Here, we reveal the phononic origins of the unusual thermal conductivity of Mg₃X₂ using both inelastic neutron scattering (INS) and inelastic x-ray scattering (IXS), supported by computational modeling based on density functional theory (DFT) and ab initio molecular dynamics (AIMD). We uncover a striking phonon softening (shift to...
lower energy) in Mg₃X₂ compared with ternary compounds (A = Ca or Yb) and an unusual flat low-frequency TA phonon branch in Mg₃X₂ that considerably stiffens upon substitution with Ca or Yb. Combining our extensive phonon measurements and simulations, we quantitatively determined the origin of the low ω₂ in Mg₃X₂. In particular, we identify the importance of a weak A-X nearest-neighbor bond in Mg₃X₂. This weak bond effectively destabilizes TA phonons, leading to a soft branch along Γ – M, overcoming expected mass trends between Mg and heavier A-site ions (A = Ca and Yb). Concomitant with a suppression in group velocities, we show how the phonon softening markedly increases (fivefold) the weighted scattering phase-space, overcoming an actual suppression (50%) in third-order force constants (FC). These results quantitatively account for the anomalous two- to threefold suppression in ω₂ in binary Mg₃X₂ compared to ternary AMg₃X₂ despite the lighter mass and simpler electronic structure are fairly isotropic (24). In the following, we refer to Mg on the octahedrally coordinated A-site by X atoms as Mg(1) and Mg on the tetrahedrally coordinated sites as Mg(2).

The phonon density of states (DOS) of six AMg₃X₂ (A = Mg, Ca, and Yb; X = Sb and Bi) powder samples were measured with INS as a function of temperature, using the wide angular-range chopper spectrometer (ARCS) at the Spallation Neutron Source (34). The contributions from different atoms are spectrally well separated, as seen from the calculated partial DOS (Fig. 2A and fig. S9). For instance, in Mg₃Bi₂, Mg(2) contributes mainly at energies greater than 20 meV, Bi contributes mostly below 10 meV, and Mg(1) dominates the intermediate region. The lower vibrational frequency of Mg(1) than Mg(2) thus suggests a weaker bonding environment of Mg(1). When replacing A-site Mg(1) with Ca or Yb, the Mg(2) modes at E > 20 meV remain almost unaffected in both experiments and simulations (figs. S5 and S9). This indicates relatively unchanged local environments and bondings for Mg(2) across compositions. Considering that the atomic mass directly shifts phonon frequencies (ω ≈ K/M, where K is the spring constant and M is the mass), all else being fixed, heavier atoms should exhibit lower phonon energies. Naturally, the heavier Yb atoms vibrate at a lower frequency than Mg or Ca (173, 24, and 40 atomic mass units, respectively). However, when comparing Mg(1) and Ca, the partial DOS of Mg(1) contributes more to the lower energy side and is substantially broader than for Ca (fig. S9). Substitution on the A-site also strongly affects the X partial DOS at low energy, reflecting a strong change in the A-X interaction, which we will explain later.

A strong phonon stiffening (energy increase) is observed at E < 12 meV when substituting Mg(1) with Ca or Yb. This is clearly seen

RESULTS AND DISCUSSION

Soft phonons in Mg₃X₂

The Zintl compounds AMg₃X₂ (A = Mg, Ca, and Yb; X = Sb and Bi) belong to the CaAl₂Si₂-type family that crystallize in a trigonal conventional cell with space group P3m1 (no. 164). Their structures consist of alternating [Mg₃X₂] and A atom layers, as shown in Fig. 1A. Despite the structural anisotropy, the bonding and electronic structure are fairly isotropic (24). In the following, we refer to

Fig. 1. Soft phonons from inelastic neutron scattering. (A) Crystal structure of AMg₃X₂ and illustration of octahedral A-site and tetrahedral Mg(2) atoms. Red, orange, and blue represent A, Mg(2), and X, respectively. d₁ and d₂ are the nearest- and second-nearest-neighbor Mg(2)-X bonds. The nearest-neighbor A-X bond is d₃. Comparison of experimental neutron DOS E = 20 meV at 300 K of (B) Mg₃Bi₂ (blue) and YbMg₃Bi₂ (purple) and (C) Mg₃Sb₂ (red) and CaMg₃Sb₂ (orange). Significant stiffening is observed in ternary compounds despite a heavier mass of Ca or Yb than Mg. Extra shoulders at low energy are observed only in binary compounds. Neutron dynamical structure factor S(|Q|, ω) of (D) Mg₃Bi₂, (E) YbMg₃Bi₂, (F) Mg₃Sb₂, and (G) CaMg₃Sb₂, the same datasets as in (B) and (C). Total intensities are normalized to the value of Mg₃Bi₂. Much stronger intensities at the low-energy region can be observed in binary compared to ternary compounds.
in the $E = 20$ meV INS data at 300 K, as shown in Fig. 1 (B and C) and fig. S4. Compared with Mg$_3$X$_2$, all the peaks in CaMg$_3$X$_2$ below 12 meV are stiffened, with relative shifts ($\Delta E/E$) as large as +6.4, +15.1, and +4.6% in Bi compounds, and +12.3, +12.7, and +6.2% in Sb compounds (see table S1). On the basis of mass alone, one would predict a softening of $-3\%$ in CaMg$_3$X$_2$ from DFT. Even for the heavy YbMg$_3$Bi$_2$, where Yb contributes significantly below 12 meV, stiffer phonon energies are observed compared to Mg$_3$Bi$_2$ for $8 < E < 12$ meV (see fig. S4B). The frequency stiffening of the X partial DOS in ternary compounds relative to the binaries again suggests that the interactions between Ca-X and Yb-X are stronger than Mg(1)-X. While a 10% stiffening on average is observed in the DOS, specific modes stiffen significantly more. Our DFT calculations show that the lowest TA mode at the zone boundary M-point stiffens by more than 60% ($E = 3.33, 5.40, \text{ and } 5.53$ meV for Mg$_3$Bi$_2$, CaMg$_3$Bi$_2$, and YbMg$_3$Bi$_2$; see fig. S8). Notably, an extra shoulder is seen at low energy around 3.5 meV in Mg$_3$Bi$_2$ (5 meV in Mg$_3$Sb$_2$) that does not exist in the ternaries.

The powder-averaged dynamical structure factor from INS, $S(|Q|, \omega)$, shown in Fig. 1 (D to G), reveals more details. In all four compounds, vertical intensity streaks disperse out from the elastic line (at 0 meV), corresponding to acoustic phonons. The top of the acoustic phonon and the low-energy optical phonons contribute to the strong intensity between 6 and 10 meV. At 2 to 4 meV, only the binary Mg$_3$X$_2$ show strong intensity, especially visible at higher $Q$, which originate from the softest acoustic phonons, and give rise to the extra shoulder in the DOS.

The soft phonon and low-energy shoulder seen in Mg$_3$X$_2$ with INS are well captured by our DFT simulations, as shown in fig. S6. We resolve the low-$E$ shoulder as a softened TA branch in binaries, as shown by the red curves in fig. S7 (a peak/shoulder in the DOS arises from a less dispersive branch over an extended volume of the Brillouin zone). The lowest-energy TA branch along $\Gamma - M$ is drastically less dispersive in Mg$_3$X$_2$ than in CaMg$_3$X$_2$ or YbMg$_3$X$_2$ (highlighted in red in fig. S8). We note that previous studies (24) reported an unphysical unstable phonon branch for Mg$_3$Bi$_2$ in particular around the L-point. Our simulations resolved this issue by using the Perdew-Burke-Ernzerhof revised for solids (PBEsol) functional and including spin-orbit coupling (SOC). The softer dispersion and flat TA branch in Mg$_3$X$_2$ result in suppressed phonon group velocities ($v_g = |\nabla \omega|$, where $E = \hbar \omega$). Simultaneously, the three-phonon scattering phase-space is strongly expanded, as detailed below and in section S4.

We further compare the INS DOS with first-principles simulation including anharmonic effects. We performed temperature-dependent effective potential (TDEP) simulations, which include anharmonic frequency renormalization but no anharmonic broadening, and calculations of the velocity autocorrelation function (VACF) from AIMD, capturing anharmonic mode broadening as well as shifts. As seen in Fig. 2A, peak positions from TDEP (gray) agree well with the INS DOS for Mg(2) and Bi-dominated modes at 300 K (blue). However, a stronger broadening is seen in INS for 10 < $E < 20$ meV, corresponding to Mg(1) modes, reflecting an anharmonic bonding environment for Mg(1). This broadening is well captured by the VACF at 300 K (black). Additional INS results for all compounds as a function of temperature are shown in figs. S2 and S3. The entire spectrum broadens upon warming as a result of anharmonic lifetime suppression when vibrational amplitudes increase, but the Mg(1) modes broaden the most in panels (A) and (D).

**Origin of soft TA modes in Mg$_3$X$_2$**

To fully elucidate the origins of the anomalous low-$E$ acoustic modes, we performed $Q$-resolved dispersion measurements with IXS on small single crystals of Mg$_3$Bi$_2$ ($T =$ 80, 300, and 600 K) and YbMg$_3$Bi$_2$ ($T =$ 300 K), using the high-energy-resolution inelastic x-ray spectrometer (HERIX) beamline (sector 30) at the Advanced Photon Source (35, 36). The IXS spectra show well-defined peaks (see fig. S16), enabling accurate estimates of the phonon energies. The phonon energies from IXS are compared with our DFT simulations in Fig. 2 (B and C). Very good agreement is observed for YbMg$_3$Bi$_2$, which exhibits strongly dispersive TA along $\Gamma - M$, $\Gamma - A$, and the long-wavelength portion of $\Gamma - L$ (we track the lowest-energy TA by phonon polarization; see fig. S13). Good agreement is also found in Mg$_3$Bi$_2$. Upon warming Mg$_3$Bi$_2$ from 80 to 600 K, most phonons soften and broaden, but the TA branch at the $L$-point anomalously stiffens, consistent with the negative Grüneisen parameter from our quasi-harmonic simulations (fig. S10) and those in (23).

The lowest TA branch along $\Gamma - M$ is significantly softer in Mg$_3$Bi$_2$ than in YbMg$_3$Bi$_2$, which explains the extra shoulder observed in the DOS. To rationalize this soft TA branch, we analyze the modulus of the second-order FC ($|\Phi^{(2)}|$, ) from DFT for Mg$_3$Sb$_2$ (red), CaMg$_3$Sb$_2$ (orange), Mg$_3$Bi$_2$ (blue), and YbMg$_3$Bi$_2$ (purple), respectively, as shown in Fig. 3A and as a function of bond length in fig. S14A. The two strongest bonds are the nearest-neighbor ($d_1$) and

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**Fig. 2. Anharmonic Mg(1) phonon modes and momentum-resolved measurements from inelastic x-ray scattering.** (A) Phonon DOS of Mg$_3$Bi$_2$ from INS at 300 K (blue) and 600 K (red), compared with VACF calculation at 300 K (black) and renormalized DOS from TDEP (gray). The computed total DOS is NW and convolved with the experimental resolution. (B and C) Momentum-resolved IXS measurements on single crystals (markers), compared with DFT phonon dispersions (solid lines) for Mg$_3$Bi$_2$ and YbMg$_3$Bi$_2$. Blue, green, and red markers correspond to the fitted phonon energy at 80, 300, and 600 K. (D) Brillouin zone (irreducible wedge in red) and high-symmetry points.
1.17 and 0.75 eV/ed partial COHP for bonds d1 through d5 are defined in (C) and (D). The largest change is found for the d1 bond, which is much weaker in binaries than in ternaries. The negative integrated pCOHP (−IpCOHP) for multiples of the corresponding |(2)|. While a slightly larger charge transfer in the case of CaMg2Sb2, the charge density formation charge density (Fig. 3, C and D) shows that despite the deflection charge density near the Fermi energy (E Fermi) in CaMg2Sb2 and Mg3Sb2, respectively. This large increase in |(d5)| by 105% (Sb) and 56% (Bi) in the ternary compounds reveals a strong change in A-X bonding. The much smaller |(d1)| for d1 than d2 also leads to the lower phonon frequency of Mg(1) than Mg(2) in the DOS. The weak d3 bond directly controls the TA branch along the Γ−M direction. As we show in Fig. S14F, artificially replacing (d1) in Mg3Bi2 with that from YbMg3Bi2 leads to a more dispersive TA branch along Γ−M, while changing (d2) for d1 or d2 has relatively little effect.

The change in |(d2) can be related to the electronic bonding via the crystal orbital Hamiltonian population (COHP), here calculated with the LOBSTER software (37–40). Figure S15 shows the projected partial COHP for bonds d1, d2, and d3, comparing Mg3Sb2 (solid lines) and CaMg2Sb2 (dashed lines). Bonding states are negative and antibonding states are positive. All states are bonding below −2 eV. In the valence band near the Fermi energy (E Fermi = 0 eV), Mg3Sb2 and CaMg2Sb2 have similar pCOHP for d1 and d2. However, for d3, Mg(1)-Sb remains nonbonded down to −1 eV, while Ca-Sb has antibonding interaction in the valence band down to −2 eV. The pCOHP for Mg(1)-Mg(2) (d2) in Mg3Sb2 was shown to involve nonbonding states at the valence band maximum but bonding states at the conduction band minimum in (33). The integrated pCOHP (IpCOHP) probes covalency and relative bond strength, where a more negative value corresponds to a stronger covalent bonding (41). We note that all AMg2X2 compounds are isostructural with only A-site substitution, so comparing their pCOHP is justified. As seen in Fig. 3B, the −IpCOHP values at E Fermi for d1 are slightly larger than d2 in both Mg3Sb2 and CaMg2Sb2, and much larger than d3, which matches the trend of the corresponding |(d2)|. While a slightly smaller −IpCOHP for d1 and d2 is found in CaMg2Sb2 than in Mg3Sb2, the −IpCOHP for d3 is larger, which supports the observation of weaker Mg(1)-Sb than Ca-Sb bonds. Meanwhile, the deformation charge density (Fig. 3, C and D) shows that despite the larger charge transfer in the case of CaMg2Sb2, the charge density around Mg(2) is similar in both cases. A more ionic character was found in Ca-Mg(2) compared to Mg(1)-Mg(2) (d3) in agreement with a prior study (29).

Differences in Mg(1)-X versus Ca-X bonding character cannot explain the surprising disparity in d3 FC. The softer Mg(1)-X bonds likely arise in part from negative chemical pressure experienced by Mg(1). Although Mg is much smaller than Ca (atomic radii: 1.45 versus 1.94; ionic radii: 0.72 versus 1.00 Å), the difference between the Ca-Sb versus Mg(1)-Sb bond lengths (d2) is only 0.14 Å. In the binary compounds, the Mg(1) coordination environment can thus be described as an oversized pnictide cage. The MgX6 octahedra in the binaries are highly distorted compared with the near-ideal octahedral geometry of the ternary compounds. Both binaries exhibit a high-temperature β-phase in which Mg is tetrahedrally coordinated by X (42). The formation of the Mg3X2 compounds in the CaAl2Si2 structure type at lower temperatures is a testament to the extreme chemical adaptability of Mg (43). The binaries can be seen as a textbook example of driving a system to the edge of structural stability to achieve soft TA modes by negative chemical pressure.

**Thermal conductivity analysis**

We now rationalize the anomalously low k1 in Mg3Sb2 and Mg3Bi2. Replacing Mg(1) with Ca or Yb leads to two- to threefold higher k1 in polycrystalline samples, as shown in Fig. 4 (A and B) (filled markers) (24, 44, 45). The k1 of Mg3X2 is twice higher in single crystals (46) versus polycrystals owing to the absence of boundary scattering. Our calculated k1 using TDEP (details in the Supplementary Materials) matches very well with the single-crystal measurements in Mg3X2 at 300 K (red and blue hollow markers versus solid lines). Further, we find an almost isotropic k1 at all temperatures (e.g., 2.38 in-plane, 2.29 out-of-plane for Mg3Sb2 and 6.30 in-plane, 6.05 out-of-plane for CaMg2Sb2 at 300 K), in agreement with previous Mg3Sb2 simulations (29). The calculated k1 of CaMg2Sb2 is about 5× higher than for Mg3Sb2 (2× in Bi compounds), matching the experimental trend (only polycrystalline data available).

Figure 4E and Fig. S18 show the spectrally decomposed thermal conductivity, k(E), revealing that phonons below 15 meV dominate the overall k1 in both Mg3Sb2 and CaMg2Sb2 (12 meV in AMg3Bi2). The peak contribution to k(E) corresponds to the top of the acoustic...
As shown in table S5, served in INS indicates a strong change in phonon linewidths below 4 meV in Mg$_3$Bi compounds (Fig. 4, C and D, and fig. S18). The much larger $\kappa_l$ from TDEP for (A) AMg$_3$Sb$_2$ and (D) AMg$_3$Bi$_2$. Binary compounds exhibit a factor of 2 to 3 larger linewidths, similar to the ratio in $\kappa_l$, (B) Spectrally decomposed $\kappa_l$ in Mg$_3$Sb$_2$ and CaMg$_2$Sb$_2$. Inset shows the corresponding weighted phase-space ($W$). A three times larger $W$ is observed in Mg$_3$Sb$_2$ below 10 meV. (F) $\kappa_l$ comparison of Mg$_3$Sb$_2$ and CaMg$_2$Sb$_2$. Red and orange markers are the same $\kappa_l$ in (A). Blue, green, and black hollow markers represent the $\kappa_l$ when replacing $\nu_g$, $\tau$, and $C_v$ with the values from CaMg$_2$Sb$_2$ (details in the main text).

branches, around 5 meV in Mg$_3$Sb$_2$ and 7 meV in the CaMg$_2$Sb$_2$. A marked suppression of $\kappa_l$ is observed in Mg$_3$Sb$_2$ over the range 1 < $E$ < 15 meV. The $\kappa_l$ ratios (2 to 3) between binaries and ternaries are directly reflected in their phonon linewidths (= $\kappa_l^{-1}$) in both Sb and Bi compounds (Fig. 4, C and D, and fig. S18). The much larger phonon linewidths below 4 meV in Mg$_3$X$_2$ correspond to the flat TA mode (e.g., along $\Gamma$ – $M$). These are strongly scattered, as they satisfy the energy conservation rules for phonon-phonon scattering easily. They also have low phonon group velocities and thus contribute little to the total $\kappa_l$. In ternary compounds, these phonon branches are more dispersive, are less scattered, and carry more heat. Zhang et al. (24) emphasized these TA phonons and mid-energy optical phonon (13 to 20 meV) as the main suppression mechanism. However, this is insufficient, as the suppression happens over the entire energy range. The anharmonic scattering rates (= linewidth) calculated in (24), using harmonic $\Phi^{(2)}$, are almost 10 times larger in Mg$_3$Sb$_2$ than in CaMg$_2$Sb$_2$, leading to an underestimated $\kappa_l$ even lower than polycrystalline data. We note that using harmonic phonon dispersions significantly overestimates the scattering phase-space.

We further examine the thermal transport mechanism by isolating the relative contribution of $C_v$, $\nu_g$, and $\tau$ in $\kappa_l$, and revealing the critical contribution of the $d_3$ bond in modulating the scattering phase-space. We use the TDEP $\kappa_l$ of Mg$_3$Sb$_2$ and CaMg$_2$Sb$_2$ as references and replace each component in Mg$_3$Sb$_2$ with its counterpart from CaMg$_2$Sb$_2$, as shown in Fig. 4F. For instance, the blue curve labeled as $\nu_g$ Ca” represents $\kappa_l$ = $\frac{3}{2}C_v$ Mg$_3$Sb$_2$ $\nu_g$ Mg$_3$Sb$_2$ $\tau$ Mg$_3$Sb$_2$. As one would expect, the heat capacity effect is minimal, which almost overlaps with the $\kappa_l$ of Mg$_3$Sb$_2$ (black hollow circles). The energy shift observed in INS indicates a strong change in $\nu_g$. As shown in table S5, at some Q vectors, $\nu_g$ is enhanced by more than 50% in CaMg$_2$Sb$_2$, showing a corresponding increase in mode $\kappa_l$ compared to Mg$_3$Sb$_2$. However, the overall increase in $\kappa_l$ is only 22% (blue), which is a small part of the actual difference (~3×) in total $\kappa_l$. On the other hand, replacing $\tau$ leads to a 2.4× higher $\kappa_l$ (green). The scattering rate ($\propto \tau^{-1}$) results from a product of the scattering phase-space, weighted by the phonon occupation factor, and the scattering probability $|V_{g}^{X_{2s}}|^{2}$ involving phonon modes $\lambda$, $\lambda'$, and $\lambda''$. The latter can be viewed as the mass-, frequency-, and eigenvector-weighted Fourier transform of the third-order FC $(\Phi^{(3)})$. $\Phi^{(2)}$ controls the phonon group velocity, frequency, and eigenvector and determines the scattering phase-space. $\Phi^{(3)}$ only determines the scattering probability. By separately replacing $\Phi^{(2)}$ and $\Phi^{(3)}$ of Mg$_3$Sb$_2$ with those of CaMg$_2$Sb$_2$, we further break down the contributions to $\kappa_l$. As can be seen in fig. S14B, $\Phi^{(3)}$ only differs by 10% on average between the two Sb compounds, while weak Mg(1)-X bonds are again found. These weaker $d_3$ bonds result in a 50% smaller scattering probability, and substituting the Ca $\Phi^{(3)}$ (blue) leads to 50% decrease in $\kappa_l$ (fig. S19). However, substituting the Ca $\Phi^{(2)}$ (green) results in a 5× increase in $\kappa_l$, arising from frequency and scattering phase-space renormalization by the $d_3$ bond. The weighted scattering phrase-space ($W$), defined by equation S7, is shown in the inset of Fig. 4E. A large increase in $W$ is observed for Mg$_3$Sb$_2$ compared with CaMg$_2$Sb$_2$, in the same energy range where $\kappa_l$ is suppressed. This renormalization is controlled by $\Phi^{(2)}$ as shown in fig. S18E.

Through a systematic investigation of phonons and thermal transport in AMg$_3$X$_2$ compounds with INS, IXS, and first-principles modeling including AIMD, we revealed how the superior thermal properties of Mg$_3$X$_2$ for TE applications originate from specific bonding characteristics, especially a weak $d_3$ bond associated with Mg(1)-X. This weak bond plays a critical role in destabilizing TA phonons, leading to a soft flat branch along $\Gamma$ – $M$, overcoming expected mass trends between Mg and heavier A-site ions (Ca and
Our thermal conductivity analysis fully accounts for the unexpected threefold suppression in the $\kappa_{\text{f}}$ of Mg$_3$X$_2$ compared to heavier ternaries, revealing the impact of this soft $d_{\text{f}}$ bond. While group velocity suppression reduces $\kappa_{\text{f}}$ by a modest 20%, the soft anharmonic dispersion enables a threefold increase in phonon scattering primarily by enhancing the scattering phase-space. These findings rationalize the microscopic origins of the outstanding thermal properties of AMg$_3$X$_2$ compounds and provide fundamental insights into means to control thermal transport properties, which will enable the further design of highly efficient TE materials.

MATERIALS AND METHODS
For a detailed description of methods, see the Supplementary Materials. Neutron experiments were performed on AMg$_3$X$_2$ powders using the ARCS time-of-flight neutron spectrometer at the Spallation Neutron Source, Oak Ridge National Laboratory. The samples were measured in a 1.27-centimeter-diameter thin-walled aluminum can and placed in a high-$T$ closed-cycle refrigerator in an inert atmosphere. IXS measurements were performed on single crystals mounted on standard copper post bars with a beryllium dome and heated with high-$T$ closed-cycle refrigerators in vacuum, using the HERIX beamline at Sector 30 at the Advanced Photon Source, Argonne National Laboratory. Powder samples were grown by solid-state reaction and single crystals were synthesized by the self-flux growth method.

Theoretical calculations were performed with the Vienna ab initio simulation package (VASP 5.4) (47–49), using PBEsol (50–52). SOC was included for Bi compounds. Phonon and thermal conductivity calculations were performed with Phonopy (53), ShengBTE (54), and TDEP (55, 56).

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/7/21/eabg1449/DC1

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