PCCP

Supporting information

The contribution of phonons to the thermal expansion of some simple cubic hexaboride structures: SmB_6, CaB_6, SrB_6 and BaB_6

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This document contains supporting data for the main paper. In particular it presents data for SrB_6 and BaB_6 corresponding to data for SmB_6 and CaB_6 shown in the main paper.

S1 Phonon dispersion curves

Phonon dispersion curves for SrB_6 and BaB_6 are presented in Figure **??**. These can be compared with the corresponding data for SmB_6 and CaB_6 shown in the main paper.

The mode eigenvectors for the modes with zero wave vector are shown in Figure **??**.

S2 Evaluation of elastic constants

The three elastic constants for a cubic crystal can be obtained from the acoustic modes of small wave vectors with propagation directions along the $[1,0,0]$ and $[1,0,0]$ directions according to the relationships

$$\mathbf{k}=[k_1,0,0]: \quad \rho\omega^2_{[001]} = C_{44}k_1^2 \tag{S1}$$

$$\rho\omega^2_{[100]} = C_{11}k_1^2 \tag{S2}$$

$$\mathbf{k}=[k_2,k_2,0]: \quad \rho\omega^2_{[001]} = 2C_{44}k_2^2 \tag{S3}$$

$$\rho\omega^2_{[1\bar{1}0]} = (C_{11}-C_{12})k_2^2 \tag{S4}$$

$$\rho\omega^2_{[110]} = (C_{11}+C_{12}+2C_{44})k_2^2 \tag{S5}$$

The bulk modulus is then calculated as $B=(C_{11}+2C_{12})/3$. We have computed the effective elastic constant values for a series of small wave vectors for the four systems, with plots given in Figures **??** and **??**. What is seen is that there are consistent trends except in the limit of very small wave vector, and to obtain best values we interpolated to zero wave vector values by fitting to a low-order polynomial. The resultant values of the elastic constants and bulk modulus are give in the main paper.

S3 Flexibility analysis and phonon dispersion curves

The results of the flexibility matching for SrB_6 and BaB_6 are shown in Figure **??**, where we plot the dispersion curves of Figure **??** and shade the curves towards black where there is a perfect match between the phonon and RUM eigenvectors – where $m_i(\mathbf{k})=1$ – and white where there is no match ($m_i(\mathbf{k})=0$), as described in the main text which shows corresponding results for SmB_6 and CaB_6.

S4 Thermodynamic properties from vibrational spectra

The phonon densities of states of SmB_6 and CaB_6 are shown in Figures **??** and **??** respectively, corresponding to data for SrB_6 and BaB_6 shown in the main paper. The densities of states show the gaps at frequencies of around 20 THz and just above 30 THz as seen in the phonon dispersion curves, Figure **??**. The same gaps are seen in SmB_6 and CaB_6.

Or relevance for the thermal expansion are the mode Grüneisen parameters γ_i as defined in the main paper. We have computed these for a random grid of wave vectors, and we plot a histogram of the distribution of values of γ as spread across the range of phonon frequencies. Figures **??** and **??** show these distributions for SrB_6 and BaB_6 respectively. Corresponding data for SmB_6 and CaB_6 are given in the main paper.

Figure **??** shows the distribution of significant values of γ across the dispersion curves of SrB_6 and BaB_6 shown in Figure **??**; corresponding diagrams for SmB_6 and CaB_6 are again given in the main paper.

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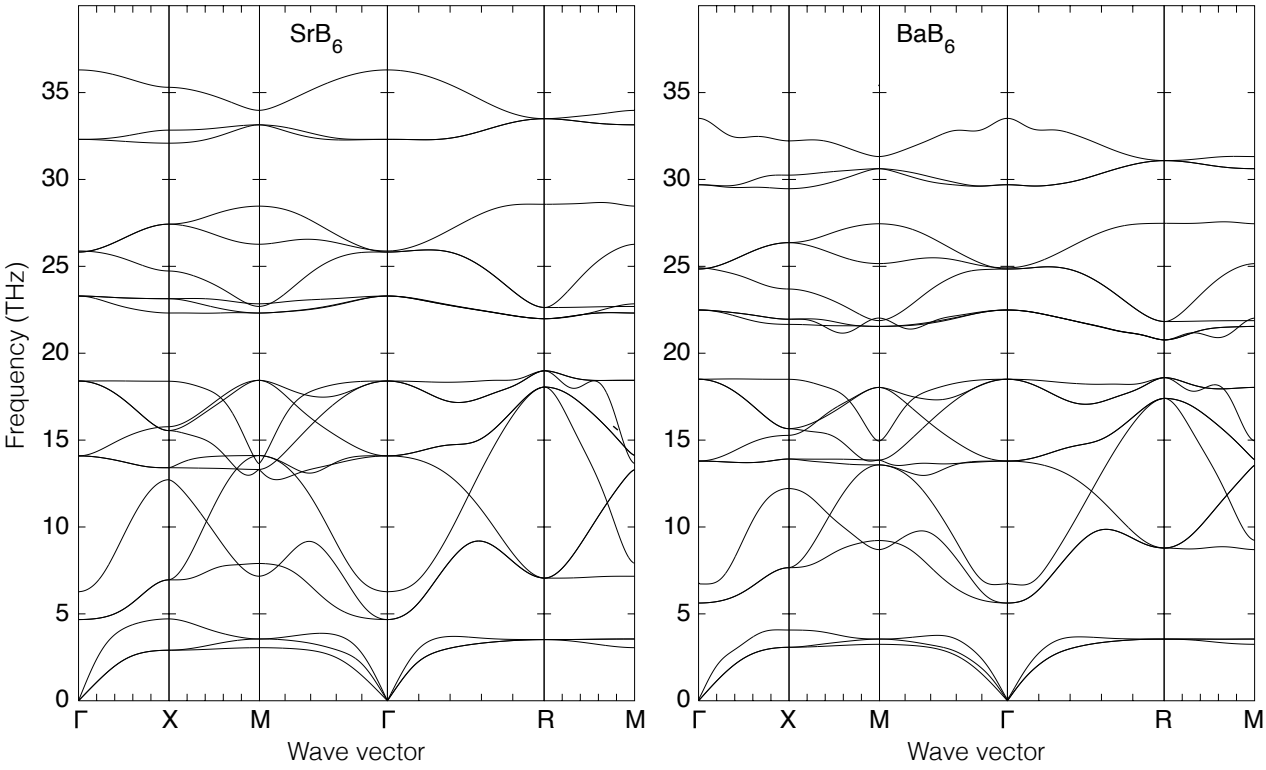
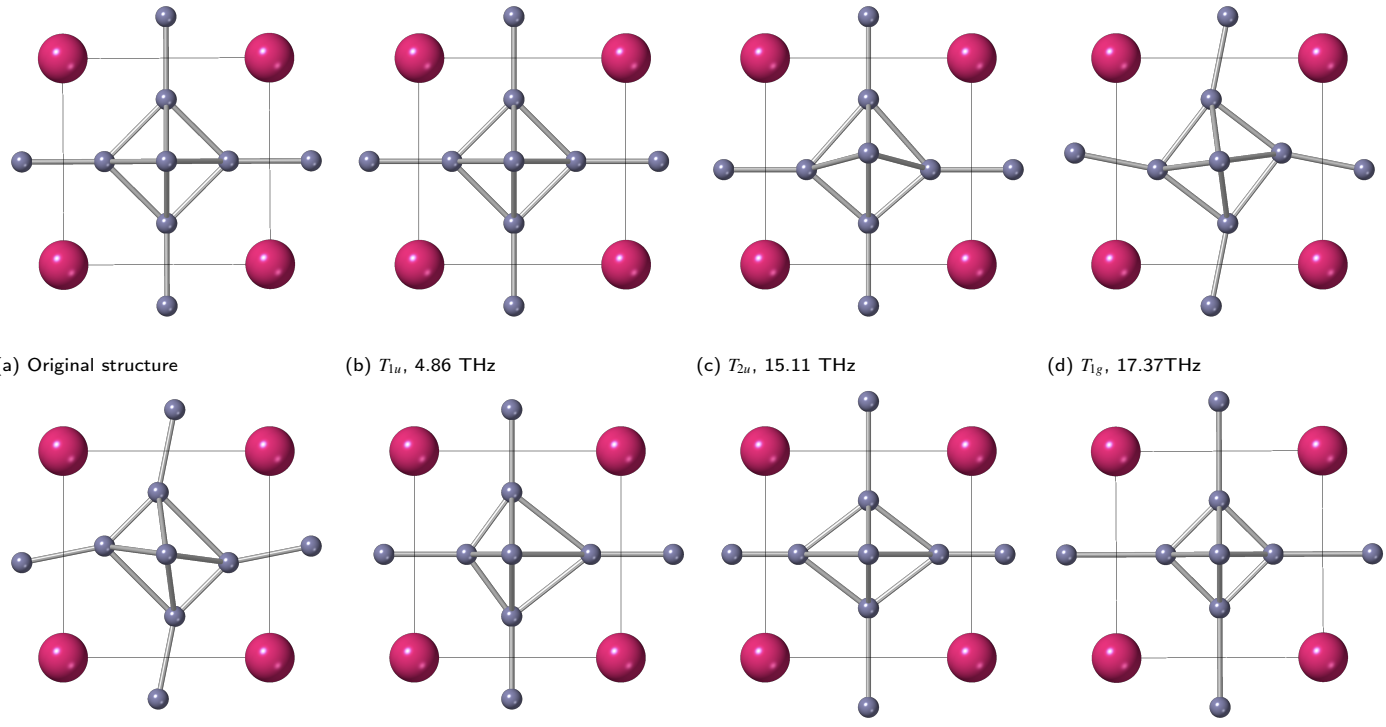


Fig. S1 Calculated phonon dispersion curves of SrB_6 (left) and BaB_6 (right). The wave vector labels have conventional meaning: Γ represents the wave vector $[0,0,0]$, X represents $(\frac{1}{2},0,0)$, M represents $(\frac{1}{2},\frac{1}{2},0)$ and R represents $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$.



(a) Original structure (b) T_{1u}, 4.86 THz (c) T_{2u}, 15.11 THz (d) T_{1g}, 17.37THz

(e) T_{2g}, 22.32 THz (f) T_{1u}, 25.94 THz (g) E_g, 34.44 THz (h) A_{1g}, 38.50 THz

Fig. S2 Representation of the mode eigenvectors of the seven normal modes of SmB_6 at zero wave vector. a) gives the original structure, and the other plots show the distortion of the crystal structure caused by each mode with corresponding irreducible representation and frequency.

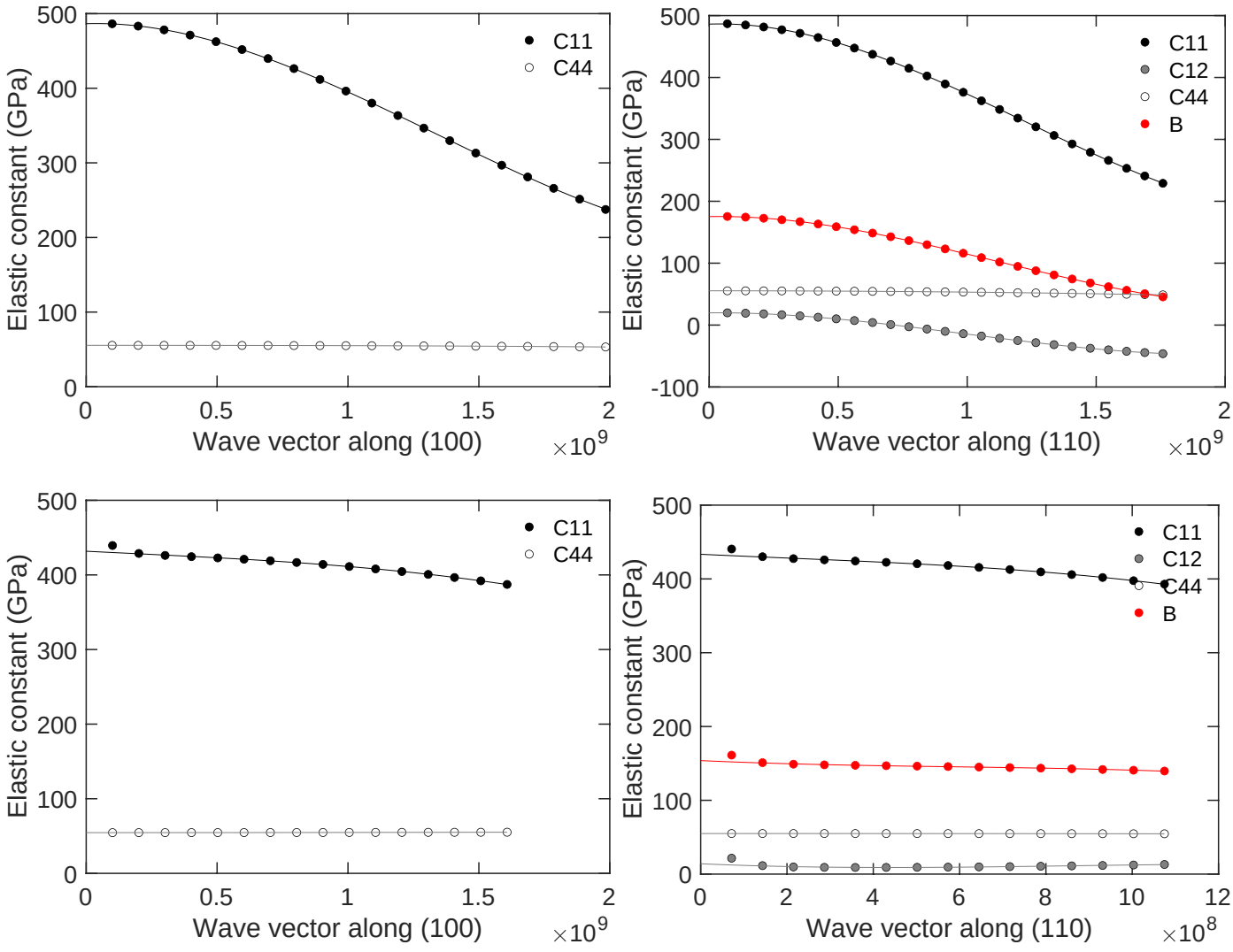


Fig. S3 Elastic constants of SmB_6 (top) and CaB_6 (bottom) evaluated for a range of wave vectors following equations **??** –**??**.

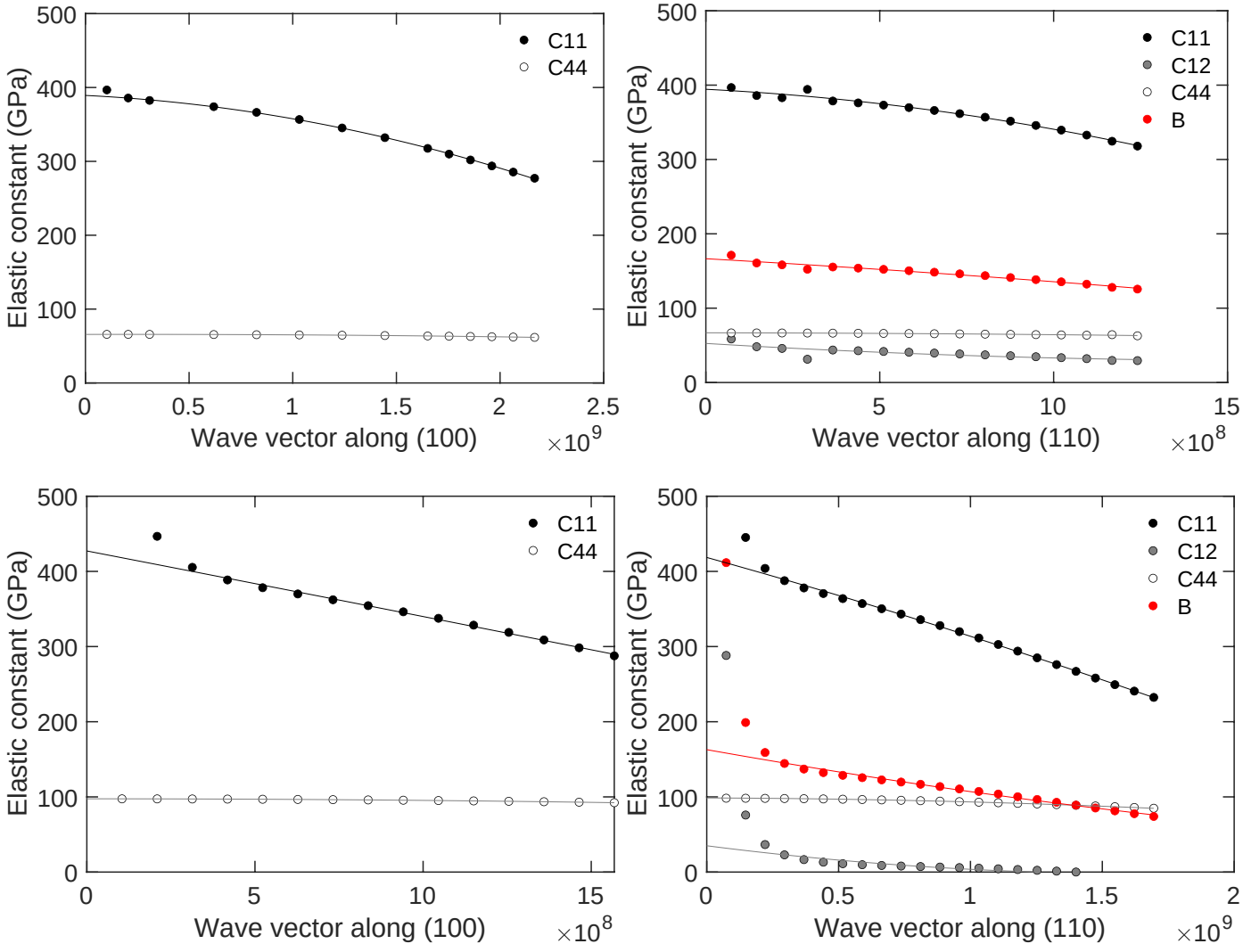


Fig. S4 Elastic constants of SrB_6 (top) and BaB_6 (bottom) evaluated for a range of wave vectors following equations **??–??**.

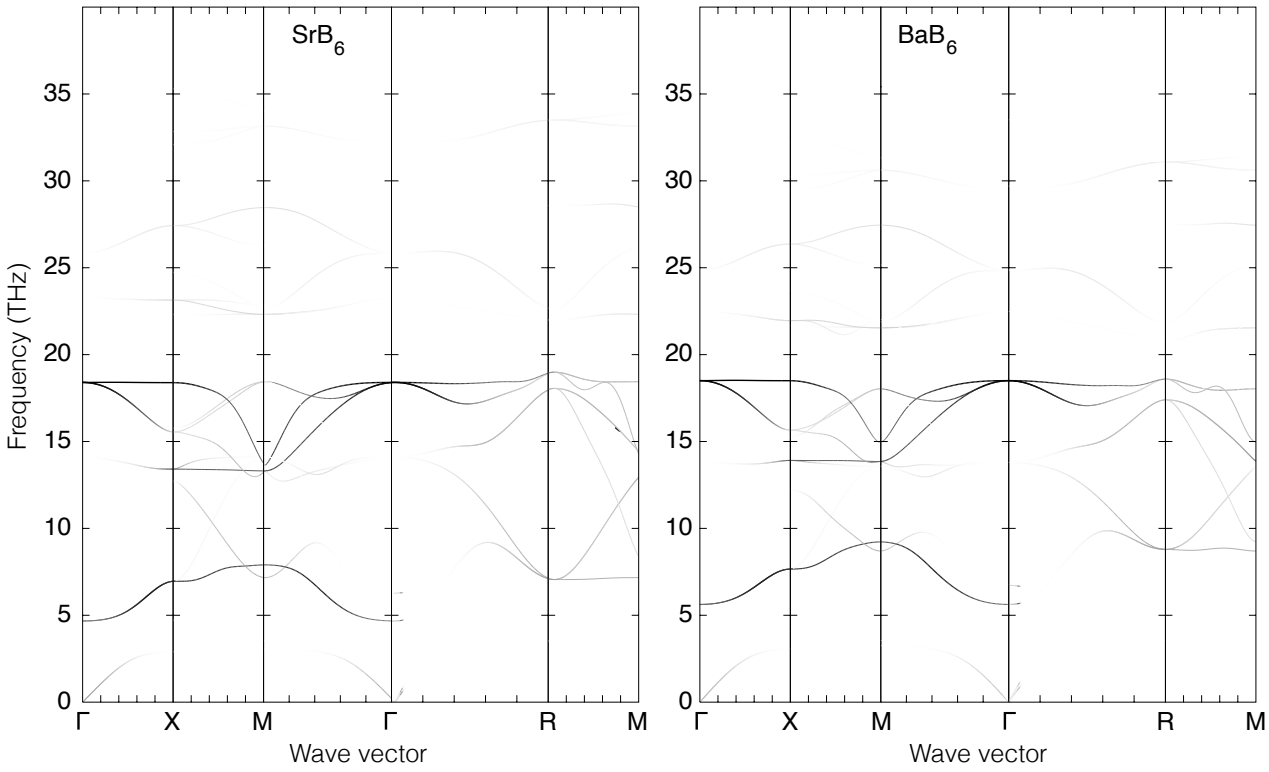
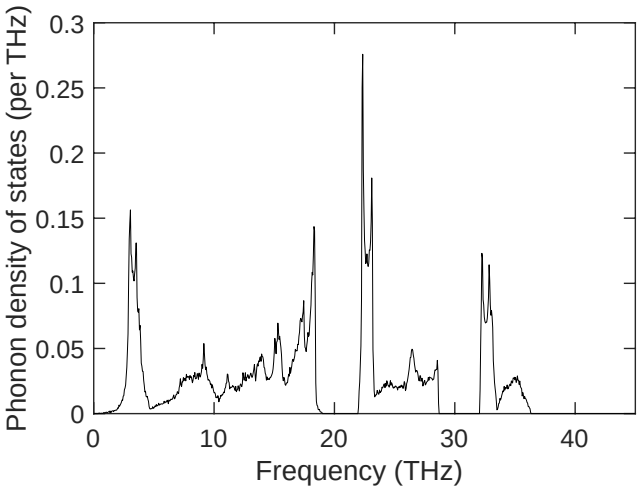
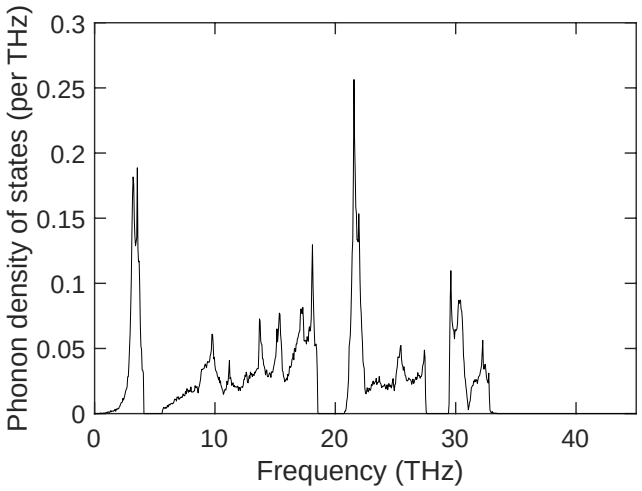


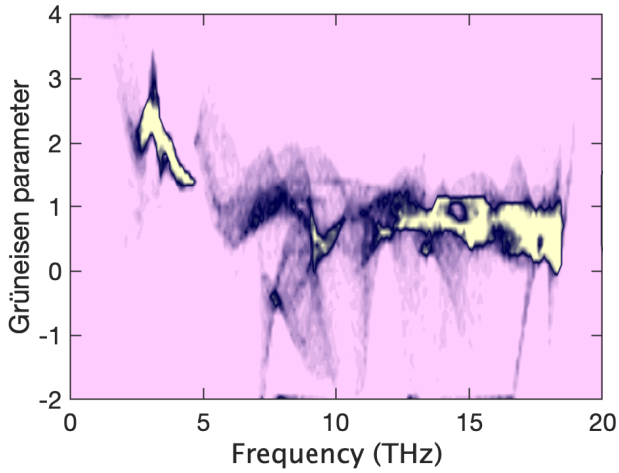
Fig. S5 Calculated phonon dispersion curves of SrB_6 (left) and BaB_6 (right) coloured between white and black to indicate the degree to which the mode eigenvectors can be described as a combination of the RUMs identified in a simple flexibility model, where black indicates close alignment of the phonon eigenvectors with the RUMs. The wave vector labels have conventional meaning: Γ represents the wave vector $[0,0,0]$, X represents $(\frac{1}{2},0,0)$, M represents $(\frac{1}{2},\frac{1}{2},0)$ and R represents $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$.



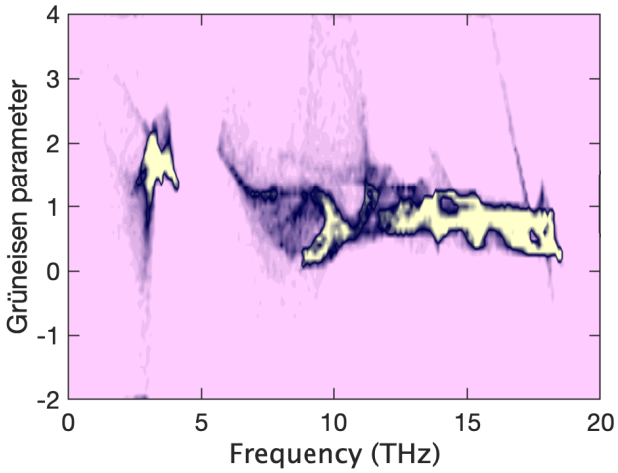
(a) SrB_6 density of states



(b) BaB_6 density of states



(c) SrB_6 mode Grüneisen parameters



(d) BaB_6 mode Grüneisen parameters

Fig. S6 Calculation of phonon densities of states for SmB_6 (a) and CaB_6 (b), and distribution of values of mode Grüeisen parameters across the range of frequencies for SmB_6 (c) and CaB_6 (d). In the latter two, pink represents a zero of phonon modes with a particular pair of values of frequency and Grüeisen parameters, yellow corresponds to the maximum in the distribution function, and the colour scheme passes from pink to yellow through dark blue. In order to highlight the existence of the distribution function for which there are fewer modes we saturate the scale of the histogram.

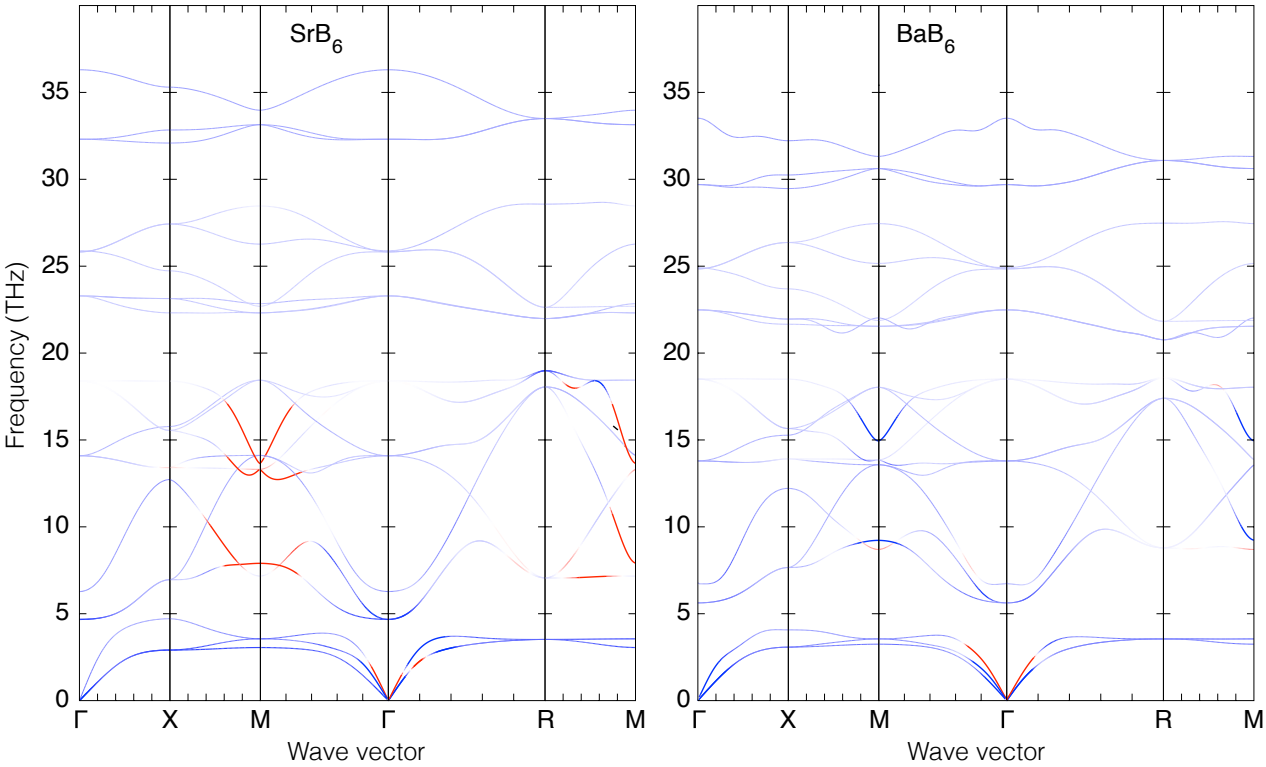


Fig. S7 Calculated phonon dispersion curves of SrB_6 (left) and BaB_6 (right) coloured between red and blue to indicate the values of the mode Grüneisen parameters γ_i, where the strongest red indicates values of $\gamma_i < -1$ and the strongest blue indicates values of $\gamma_i > +3$. The wave vector labels have conventional meaning: Γ represents the wave vector $[0,0,0]$, X represents $(\frac{1}{2},0,0)$, M represents $(\frac{1}{2},\frac{1}{2},0)$ and R represents $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$.