Quantum lattice dynamics and their importance in superhydride clathrates

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Taking a detailed look at the dynamic stability of the recently predicted BaSiH₈ phase [Lucrezi et al., npj Comp. Mat. 8, 119 (2022)], we find that the inclusion of quantum ionic effects, anharmonicity, and phonon-phonon interaction within the framework of the stochastic self-consistent harmonic approximation (SSCHA) leads to an increase in the critical dynamical pressure to 20 GPa as compared to 5 GPa in a purely harmonic treatment of classical nuclei. We identify the change in the crystal structure due to quantum ionic effects to be the main driving force for this increase and demonstrate that this can already be understood at the harmonic level by considering zero-point energy corrections to the total electronic energy of the system. Importantly, the previously determined critical pressure of kinetic stability $p_{\text{kin}} = 30$ GPa still poses a stricter bound for the synthesizability of BaSiH₈ and similar hydride materials than the dynamical stability and therefore constitutes a more rigorous and accurate estimate for the experimental realizability of these structures. With respect to our methodology, we demonstrate the use of highly accurate machine-learned interatomic potentials to access considerably larger population sizes and supercell dimensions, enabling carefully converging and speeding up the SSCHA calculations.

INTRODUCTION

The discovery of high-temperature superconductivity in H₂S at extreme pressures [1] stimulated an intense hunt for novel hydride compounds with even higher $T_c$’s, spearheaded by computational material discovery [2–6]. One prominent example is LaH₁₀, which has been shown to superconduct up to temperatures of 205 K at pressures of ≈190 GPa [7,8]. While it is very tempting to continue searching for materials with record-breaking $T_c$’s [9–11], lowering the required stabilization pressures is even more important in view of technological applications [11,20].

In a recent paper [15], some of us proposed a strategy to bring the stabilization pressures of high-$T_c$ hydrides closer to ambient pressure, based on the concept of an optimized chemical precompression. In fact, we identified LaBH₈, a hydride superconductor with a $T_c > 100$ K, dynamically stable at an unprecedentedly low pressure. In a follow-up work, we showed that other hydride superconductors with the same $Fm\bar{3}m$ XYH₈ structural template can be identified with even lower critical pressures of stability, such as SrSiH₈ and BaSiH₈ [19]. The latter is particularly interesting, as it remains dynamically stable down to 3 GPa. We note in passing that these estimates of dynamical stability were based on anharmonic frozen-phonon calculations.

All of the mentioned $Fm\bar{3}m$ XYH₈ compounds are thermodynamically stable only at pressures above ≈100 GPa, and metastable below. A conceivable route to synthesize these materials would hence be to obtain them at high pressures where they are thermodynamically stable, and quench them to lower pressures.

The standard criterion employed in literature to estimate how far a metastable phase can be quenched down in pressure is dynamical (phonon) stability. However, dynamical stability indicates only that a structure is in a local minimum of the potential energy surface. To estimate its actual lifetime (kinetic stability) one needs also to estimate the height of the barriers that separate the current minimum from other minima. In Ref. [19], some of us introduced a rigorous method to assess the kinetic stability pressure $p_{\text{kin}}$ by explicitly calculating the energy barrier protecting the metastable $Fm\bar{3}m$ structure from decomposition as a function of pressure, using the variable-cell nudged elastic band method [21]. For BaSiH₈, for example, we found a $p_{\text{kin}}$ of ≈30 GPa, significantly higher than the dynamical value $p_{\text{dyn}} = 3$ GPa.

It was argued in a recent work [22] that quantum lattice effects treated within the stochastic self-consistent harmonic approximation (SSCHA) drastically increase the dynamical stabilization pressure $p_{\text{dyn}}$ for LaBH₈ and it was further suggested that a similar increase in $p_{\text{dyn}}$ should be expected for other $Fm\bar{3}m$ XYH₈ hydrides.

To investigate this, we apply the SSCHA formalism to BaSiH₈, which, so far, has the lowest $p_{\text{dyn}}$ among all $Fm\bar{3}m$ XYH₈ hydrides. In SSCHA, a major bottleneck is represented by the need to use large supercells and large numbers of individuals if one wants to fully converge the calculation. We overcome this problem by employing machine-learned moment tensor potentials (MTP) [23,24] that allow us to obtain total energies, forces, and stresses with DFT accuracy but at a fraction of the computational cost [25,27]. To our knowledge, this work represents the first combination of MTPs with the SSCHA method. In addition, we introduce a method to discern the contribution of quantum ionic (QI) effects...
from those of anharmonic and phonon-phonon (ph-ph) effects.

We find that $p_{\text{dyn}}$ increases from 3 GPa to about 20 GPa within the SSCHA and that this rise can almost entirely be attributed to QI effects, with actual anharmonic and ph-ph effects playing only a subordinate role. In fact, the same crystal structure that minimizes the free energy within SSCHA can already be obtained in density-functional theory (DFT) by including zero-point energies (ZPE).

Importantly, we demonstrate that even after including QI, anharmonic, and ph-ph effects within the framework of SSCHA, the actual limit of stability is still set by $p_{\text{kin}}$ ($\sim$ 30 GPa), as stated in our previous work [19].

RESULTS

Ab-initio machine-learned interatomic potentials

In the self-consistent harmonic approximation, the full anharmonic and interacting lattice is mapped onto an auxiliary harmonic system and the free energy $F$ of the full system is approximated by the minimum of the free energy of the auxiliary harmonic system [28–31]. In the SSCHA, this minimization is performed stochastically via Monte-Carlo summation and importance sampling over several consecutive ensembles (populations) of a large number of individuals. Each individual here corresponds to a supercell structure with displaced atomic positions, where the supercell size determines the density of phonon wave vectors in the Brillouin zone [32]. More details are provided in the Method section, the Supplementary Material (SM) [33], and in Refs. [34–40].

In practice, to calculate accurate phonon frequencies within SSCHA, in particular for slow-converging soft modes, one needs to consider population sizes of several ten or hundred thousands individuals. In addition, one also needs to converge the supercell size.

Doing this fully at a DFT level is computationally prohibitive, which is why we made use of MTPs in this work. For every pressure, MTPs were trained on DFT results of 50 structures randomly chosen out of the SSCHA random-displacement individuals in $2 \times 2 \times 2$ supercells. We then validated the trained MTPs for all other individuals by comparing the total energies, forces and stress components. This validation is shown in Fig. 1 demonstrating the exceptional accuracy of the used MTPs (see Supplementary Fig. 2 in the SM for other pressures, as well as forces and stresses). As can be appreciated in this figure, the root-mean-squared error (RMSE) is below 1 meV/atom, i.e., at the same level as the error in DFT. The inset also shows that the potential energy surface of the slow-converging, $T_{2g}$ mode at $\Gamma$ is reproduced very nicely with the MTPs.

As a final validation, we compare the SSCHA phonon dispersions obtained using only DFT with those employing only MTPs (see Supplementary Fig. 3 in the SM) and find very good agreement, with only minor differences in the $T_{2g}$ mode at $\Gamma$ and the $E_g$ at $X$. To fully converge these modes within 1 meV, we increased the populations sizes within MTP-SSCHA up to 100 000 individuals compared to 10 000 for the DFT-SSCHA calculations.

The use of MTPs does not only substantially speed up the calculations [41], but also gives access to larger supercells. In this work, we performed additional SSCHA calculations using MTPs on $n \times n \times n$ supercells with $n = 1, 2, 3, 4$ at all studied pressures. The convergence of the free energy, the structural parameters, and the phonon dispersions with respect to the supercell size is provided in Supplementary Figs. 4-6 in the SM. An overview of all performed SSCHA runs is given in Supplementary Tab. 1 in the SM. Unless stated otherwise, all SSCHA results presented in the following have been obtained with MTPs for 100 000 individuals in $4 \times 4 \times 4$ supercells.

Structural parameters and electronic dispersion

The $Fm\bar{3}m$ phase of BaSiH$_8$ has a face-centered cubic unit cell with 10 atoms in the primitive cell, where
Table I. **Structural parameters**: Lattice constant $a$, Wyckoff parameter $x$, H-Si distance $d_{\text{H-Si}}$, and pressure $p$ after the relaxation with respect to the DFT total energy and after the constant-volume relaxation within SSCHA ($\tilde{x}$, $\tilde{d}$, and $\tilde{p}$).

| $a$ [Å] | $x$ | $d_{\text{H-Si}}$ [Å] | $p$ / GPa | $\tilde{x}$ | $\tilde{d}_{\text{H-Si}}$ [Å] | $\tilde{p}$ / GPa |
|---------|-----|------------------|--------|--------|------------------|--------|
| 6.541   | 0.1434 | 1.625             | 10    | 0.1459 | 1.653             | 12.2   |
| 6.323   | 0.1471 | 1.611             | 20    | 0.1498 | 1.640             | 22.6   |
| 6.242   | 0.1483 | 1.603             | 25    | 0.1510 | 1.633             | 27.9   |
| 6.171   | 0.1494 | 1.597             | 30    | 0.1521 | 1.626             | 33.1   |

Ba and Si occupy Wyckoff 4$f$ sites and the H occupy 32$f$ sites. The eight H atoms form rhombicuboctahedral cages around the Ba atoms and cubic cages around the Si atoms. The structure has only two free parameters, namely the lattice constant $a$ and the Wyckoff coordinate of the 32$f$ sites $x$, defining the H-H distance $d_{\text{H-H}} = 2a \cdot x$ (side length of the cubic cage) and the H-Si distance $d_{\text{H-Si}} = a \sqrt{3} \cdot x$ (half the space diagonal of the cubic cage).

Relaxing the structure within DFT to target pressures of 10, 20, 25, and 30 GPa, we obtained lattice constants between 6.5 Å and 6.2 Å, and H-Si distances of about 1.6 Å, as shown in Table I. An extensive list of the structural parameters from ambient pressure up to 100 GPa, as well as the fit to the Birch-Murnaghan equation of state can be found in Supplementary Note 1 in the SM.

Starting from the atomic positions obtained in DFT and the harmonic dynamical matrices obtained in density-functional perturbation theory (DFPT) calculations at each pressure, we performed constant-volume SSCHA relaxation calculations [12]. The corresponding parameters, indicated by $\tilde{x}$, $\tilde{d}$, and $\tilde{p}$, are reported in Table I.

We observe an elongation of $d_{\text{H-H/Si}}$ of about 30 mÅ (2%) for all pressures and an increase in pressure of about 2 to 3 GPa, i.e. $\sim 20\%$ at 10 GPa and $\sim 10\%$ at 30 GPa. The change in atomic positions introduces only small changes in the electronic structure, as demonstrated in Fig. 2 where we compare the electronic bands and densities of states (DOS) for $x$ and $\tilde{x}$. The largest differences are found above and below the Fermi energy, whereas electronic bands and DOS at the Fermi energy, and hence the Fermi surface, remain essentially unchanged.

**Phonon dispersions and lattice instability**

Moving on, we evaluate and compare the DFPT and SSCHA phonon dispersions at all studied pressures, as shown in Fig. 3. Similar to the results for LaBH$_8$ in Ref. [22], we find that the high-energy optical modes are strongly renormalized to lower frequencies. In particular, a significant softening occurs for the threefold degenerate $T_{2g}$ mode at $\Gamma$ (harmonic values around 50 meV in Fig. 3), which becomes imaginary and indicates a (dynamic) lattice instability for lattice constants $a > 6.323$ Å, corresponding to $p = 20$ GPa and $\tilde{p} = 22.6$ GPa. Thus, the inclusion of quantum lattice effects within the SSCHA shifts the dynamical stability pressure from the anharmonic frozen-phonon value $p_{\text{dyn}} = 3$ GPa to $\tilde{p}_{\text{dyn}} = 20$ GPa (see Supplementary Fig. 7 in the SM). This $\sim 17$ GPa difference is substantial, but considerably smaller than the $\sim 40$ GPa shift reported for LaBH$_8$ [22].

We want to note in passing that we also calculated the fourth order corrections to the phonon frequencies in SSCHA and find, in contrast to Ref. [22], but in accordance with other works employing SSCHA [35, 36, 38–40], only minor differences to the results obtained only up to third order. The maximum phonon energy differences are on the order of about 1 meV for all pressures. The phonon dispersions in the $2 \times 2 \times 2$ supercells [41] with second (auxiliary), third, and fourth order terms for all studied pressures are shown in Supplementary Fig. 8 in the SM.

**Different effects contributing to frequency shifts**

The observed changes in the phonon dispersions when employing SSCHA and the resulting different dynamical stabilization pressures result from a combination of several effects that are not included at the level of standard DFT and DFPT. These are most importantly the vibrational contributions of the ions to the free energy, phonon anharmonicity, and ph-ph interactions. In the following, we will present an attempt to disentangle and determine the importance of each of these effects for BaSiH$_8$. 

Figure 2. **Difference in electronic properties**: a electronic bands, and b density of states for the structure with H positions defined by $x$ (DFT minimum, blue line) and $\tilde{x}$ (SSCHA minimum, red line) for $a = 6.242$ Å.
**QI effects:** First, we want to look at the contributions to the total energy originating from the so-called zero-point vibrations, i.e., vibrations of the ions around their equilibrium positions due to the quantum mechanical treatment of the nuclei, absent in the classical, clamped-nuclei picture [45]. In the Born-Oppenheimer approximation, the total energy $E_{\text{tot}}[\mathbf{R}]$ (at $T = 0\,\text{K}$) for ionic positions $\mathbf{R}$ is given by the sum of the internal electronic energy $E_{\text{el}}[\mathbf{R}]$ and the ZPE contributions of the nuclei $E_{\text{ZP}}[\mathbf{R}]$. In most solids, $E_{\text{ZP}}$ is much smaller than $E_{\text{el}}$ and can be safely neglected. However, due to the small mass of H and the resulting high phonon frequencies in hydrides, the ZPE can become substantial and thus cause a modification of the equilibrium crystal structure.

At the harmonic level, the true ZPE can be approximated via $E_{\text{ZP}}[\mathbf{R}] \approx \int_{0}^{\infty} d\omega \rho_{\mathbf{R}}(\omega)\hbar\omega/2$, where $\rho_{\mathbf{R}}(\omega)$ is the DFPT phonon density of states and $\hbar\omega/2$ the ZPE of a quantum harmonic oscillator. At constant volume, the only free parameter in the $Fm\bar{3}m$ structure is the Wyckoff parameter $x$, for which we have plotted $E_{\text{tot}}$, $E_{\text{el}}$, and $E_{\text{ZP}}$ in Fig. 4 for a lattice constant of $a = 6.242\,\text{Å}$. The results for other lattice constants, i.e., pressures, are provided in Supplementary Fig. 9 in the SM.

As can be appreciated in this figure, the inclusion of the ZPE, even at the harmonic level, shifts the position of the minimum of the total energy considerably and puts it almost exactly at the minimum position $\tilde{x}$ predicted by the SSCHA. The differences in $d_{\text{LaSi}}$ between the SSCHA calculations and the ZPE analysis are, in fact, of the order of 1 mÅ, i.e., well within the observed stochastic noise in SSCHA. We want to note that the same is true for LaBH$_8$ (see Supplementary Fig. 10 of the SM). Furthermore, inclusion of ZPE reduces the total energy at its minimum by $\sim 30\,\text{meV/uc}$, agreeing very nicely with the result from SSCHA ($\sim 27\,\text{meV/uc}$).

This is a quite remarkable result as it demonstrates the importance of QI effects of the light H ions on the dynamic stability of the hydride materials, and shows that the minimum structure from SSCHA can already be obtained at the level of harmonic ZPE corrections, at least for this class of materials.

Having established that the ZPE has a crucial effect on the structure, we investigate the effect of the changed structure on the phonon dispersions. In Fig. 5a, we present the harmonic dispersions for atomic positions defined by $x$ and $\tilde{x}$. We observe large differences for the high-energy optical modes above 150 meV, but also for the low $T_{2g}$ mode at $\Gamma$. The energy shifts for these modes are between 15 and 25 meV.

**Anharmonicity and ph-ph interaction effects:** Having established the QI effects on the structure and the phonon dispersions, we now want to assess the contributions of phonon anharmonicity (anh) and ph-ph interactions. To do that, we perform a SSCHA calculation while keeping the ions fixed at the DFT equilibrium positions, thus qualitatively removing structural effects on the phonon frequencies. The phonon dispersions obtained from this calculation are presented in Fig. 5b, where we find that all H-dominated optical modes in the whole BZ experience a sizable frequency renormalization. It is worth noting that fixed-ions SSCHA calculations indicate the onset of dynamical instability just between 5 and 10 GPa (8.4 and 12.2 GPa, respectively, for the SSCHA pressure $\tilde{p}$, see Supplementary Fig. 11 in...
Figure 4. Electronic total energy, ZPE and resulting total energy as a function of H-Si distance, where the DFT minimum \( x \) and the SSCHA minimum \( \tilde{x} \) are marked explicitly, the latter coinciding with the minimum position of \( E_{\text{tot}} \). The three energy curves are plotted relative to their respective values at \( x \). The solid lines represent a cubic spline for \( E_{\text{el}} \) and second order polynomial fits for the other energies.

Superconductivity

As BaSiH\(_8\) is potentially a very promising high-\( T_c \) superconductor, we also want to assess the implications of the above mentioned effects on its superconducting (SC) properties. To do that, we solved the anisotropic Migdal-Eliashberg (ME) equations as implemented in EPW \(^{17}\) for the four cases in Tab. II. Details about the calculation within EPW are provided in the Method section and in the SM, at this point we only want to highlight that for each case we used the corresponding force constants to compute the dynamical matrices, and computed the electron-phonon (\( ep \)) coupling matrix elements as the self-consistent first-order variation of the potential using the equilibrium positions as defined in Tab. II \(^{18}\). In Table III, we summarize the obtained values for quantities characterizing the SC state, i.e., the \( ep \) coupling strength \( \lambda \), the logarithmic average of the phonon frequencies \( \omega_{\log} \), and the SC critical temperature \( T_c \) \(^{49}\). The corresponding Eliashberg spectral functions \( \alpha^2 F(\omega) \) and the cumulative coupling strengths \( \lambda(\omega) \) are shown in Supplementary Fig. 12 in the SM. We want to stress that the provided values for \( T_c \) are obtained by the solution of the full ME equations. The distribution of the SC gap function \( \Delta_k \) indicates no change in the distinct two-gap shape calculated in Ref. \(^{19}\), and is therefore not shown here.

Table II. Overview of ionic treatment: The separate cases are classified according to the structural and phonon treatment. The phonons are obtained either via DFPT or SSCHA. The ground-state (GS) structure is determined by minimizing either the electronic energy within DFT or the total energy including the ZPE (using DFPT or SSCHA.)

| \( \Delta E \) / meV | \( \lambda \) | \( T_c \) / K |
|-------------------|-------|--------|
| x = min\( (E_{\text{el}}) \) | DFT | SSCHA |
| x = min\( (E_{\text{el}}) \) | DFT | SSCHA |
| x = min\( (E_{\text{el}}) \) | DFT | SSCHA |
| x = min\( (E_{\text{el}}) \) | DFT | SSCHA |
| x = min\( (E_{\text{el}}) \) | DFT | SSCHA |

The differences in \( \omega_{\log} \), \( \lambda \), and \( T_c \) are in the order of 10-15% except for the full SSCHA calculation, where we see a considerable increase in \( \lambda \) to almost double the harmonic value, but also a decrease in \( \omega_{\log} \), compensating the enhancement of \( \lambda \). The resulting \( T_c \) is increased from 84 to 96 K, showing that the full inclusion of all discussed effects results only in \( \sim 15\% \) change in \( T_c \) for BaSiH\(_8\).
DISCUSSION

In this work, we study the effects of quantum lattice dynamics within the SSCHA framework on the structure and the dynamical stability of the \(Fm\bar{3}m\) phase of BaSiH\(_8\). The SSCHA structure relaxation suggests a 2% elongation of the H-H and H-Si bonds for the studied pressure range of 10 to 30 GPa (\(\sim 30\) m\(\text{˚A}\)).

In the phonon dispersions, we find an overall softening of the high optical modes, as well as a dynamic lattice instability characterized by imaginary SSCHA phonon frequencies in the \(T_{2g}\) mode at \(\Gamma\) below 20 GPa, setting the estimate for the critical dynamical pressure to \(\tilde{p}_{\text{dyn}} \approx 20\) GPa. We have further demonstrated the importance of QI effects over anharmonicity and ph-ph interactions, and found that the change in structure, and consequently in pressure, can already be understood by considering harmonic ZPE corrections to the total electronic energy of the system alone (which can be obtained much faster and easier than performing a full SSCHA calculation).

We are now left with the question: what is the stability boundary of \(Fm\bar{3}m\)-BaSiH\(_8\)? In our previous work on BaSiH\(_8\) [19], we challenged the common practice of assuming the range of metastability of high-pressure hydrate phases to coincide with the range of (an)harmonic dynamical stability, which systematically underestimates the stabilization pressures needed to synthesize these materials in reality [50,53]. Dynamical stability is only a prerequisite for thermodynamic metastability, which is characterized by the existence of a distinctive enthalpy barrier that protects a metastable phase from decomposition into other phases (kinetic stability). We calculated the enthalpy transition path to the thermodynamic groundstate at different pressures (corresponding to a decomposition of the \(Fm\bar{3}m\) BaSiH\(_8\) phase into BaSiH\(_6\) + H\(_2\) in molecular form), and could estimate the barrier height from the intermediate structures. In combination with the calculated convex hulls for the B-S-H system, we can argue with confidence that the \(Fm\bar{3}m\) BaSiH\(_8\) phase could be synthesized above 100 GPa, and retained down to \(\sim 30\) GPa, where a distinctive enthalpy barrier still exists. At lower pressures, metastable \(Fm\bar{3}m\) BaSiH\(_8\) will decompose, even though (anharmonic) lattice dynamics calculations predict it to be stable. Hence, kinetic stability poses a stricter bound for synthesizability than dynamical stability.

In conclusion, employing \textit{ab-initio} machine-learned MTPs, we were able to perform SSCHA calculations for BaSiH\(_8\) at various pressures for supercells up to \(4 \times 4 \times 4\) and more than 100 000 individuals. The inclusion of QI effects, anharmonicity, and ph-ph interactions within the SSCHA-framework increases the pressure of dynamical stability from \(p_{\text{dyn}} \approx 3\) GPa to \(\tilde{p}_{\text{dyn}} \approx 20\) GPa. We identified the change in structure due to QI effects to be the main driving force here, something that can already be captured to good approximation at the level of harmonic zero-point energy corrections.

Most importantly, the determined \(\tilde{p}_{\text{dyn}} \approx 20\) GPa is still below \(p_{\text{kin}} \approx 30\) GPa posed by the concept of kinetic stability, thus the latter represents a much stricter bound for the stability and realizability in these materials.
METHODS

DF(P)T calculations

All DFT and DFPT calculations of electronic and vibrational properties were carried out using the plane-wave pseudopotential code Quantum ESPRESSO \cite{PPE1, PPE2}, scalar-relativistic optimized norm-conserving Vanderbilt pseudopotentials \cite{PPE3}, and the PBE-GGA exchange and correlation functional \cite{PPE4}. The unit cell calculations are done in the fcc primitive unit cell with 10 atoms, a 12×12×12 k-grid, and a plane-wave cutoff energy of 80 Ry. The 2×2×2 supercell calculations were done on a 6×6×6 k-grid. Further details are provided in Supplementary Method 1 in the SM.

SSCHA calculations

The calculations in the SSCHA are done in the constant-volume relaxation mode, i.e. minimizing the free energy with respect to the average atomic positions \(R\) and the force constants \(\Phi\), as implemented in the SSCHA python package \cite{PPE5}. We use the DFT equilibrium atomic positions and the DFPT dynamical matrices on a 2×2×2 \(q\)-grid as initial guesses for \(R\) and \(\Phi\), respectively. The starting point for the larger supercells is obtained by interpolating the previously converged auxiliary dynamical matrices.

The total energies, forces, and stress tensors for the individuals are obtained from DFT calculations or from machine-learned interatomic potentials in the framework of MTPs, see below. At the end of a minimization run, a new population with higher number of individuals is obtained from DFT calculations or from the previously converged auxiliary dynamical matrices.

The phonon density of states \(\rho_{\text{phon}}(\omega)\) is obtained using DFPT on a 2×2×2 \(q\)-grid, interpolated on a 16×16×16 \(q\)-grid. Smooth ZPE and total energy curves are obtained by second-order polynomial fits in \(x\). Due to the shift out of the DFT equilibrium structure, forces on the individual H atoms arise at the DFT level. Around the total energy minimum, the force components are in the order of 150 meV \(\text{Å}\) for the force components, and 0.3-0.4 GPa for the diagonal stress tensor components. We further validated the MTPs on 30 randomly chosen individuals in a 3×3×3 supercell and achieve similar RMSEs. The validations and RMSEs for each pressure are shown in Supplementary Fig. 2 and Supplementary Note 2 in the SM.

ZPE and total energy

The internal electronic energy \(E_{\text{el}}[R(x)]\) is obtained from DFT calculations at fixed volume by varying the Wyckoff parameter \(x\) of the H positions. The explicit positions \(R(x)\) are given in the SM. The phonon density of states \(\rho_{\text{phon}}(\omega)\) is obtained using DFPT on a 2×2×2 \(q\)-grid, interpolated on a 16×16×16 \(q\)-grid. Smooth ZPE and total energy curves are obtained by second-order polynomial fits in \(x\). Due to the shift out of the DFT equilibrium structure, forces on the individual H atoms arise at the DFT level. Around the total energy minimum, the force components are in the order of 150 meV \(\text{Å}^{-1}\), i.e., small enough to warrant the use of linear-response theory to gain qualitative and systematic insights. DFT diagonal stress tensor components (pressures) are decreased by about 2 GPa.

Migdal-Eliashberg theory

The Wannier interpolation of the \(ep\) matrix elements onto dense \(k\)- and \(q\)-grids, and the subsequent self-consistent solution of the fully anisotropic Migdal-Eliashberg equations were done in EpW \cite{PPE6, PPE7}, for all the cases in Tab. \(\text{III}\) We used coarse 6×6×6 and fine 30×30×30 \(k\)- and \(q\) grids, a Matsubara frequency cutoff of 1 eV, and a Morel-Anderson pseudopotential \(\mu^* = 0.10\). Further details are provided in Supplementary Method 3 in the SM.
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AUTHOR CONTRIBUTIONS

R.L., E.K., and S.D.C. performed the calculations, M.A. introduced the idea of MTP, and C.H. and L.B. conceived and supervised the project. All authors contributed to the discussion of the results and participated in preparing the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

DATA AVAILABILITY

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials. Further information is available upon request.

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[42] Within SSCHA, the stress tensor is obtained as $P_{\alpha\beta} = -V_{sc}^{-1} \left( \partial \mathcal{F} / \partial \varepsilon_{\alpha\beta} \right) |_{\varepsilon=0}$, where $V_{sc}$ is the supercell volume, $\mathcal{F}$ the free energy functional, and $\varepsilon_{\alpha\beta}$ the strain tensor. The pressure is then obtained as $P = \sum_{\alpha} P_{\alpha\alpha}/3$.

[43] The small imaginary dip near $\Gamma$ in $\mathbf{b}$ is due to interpolation, all phonon frequencies at wave vectors commensurate with the supercell are positive.

[44] Calculating fourth-order corrections on larger supercells is computationally unfeasible with our currently available resources. This calculation in an $n \times n \times n$ supercell requires 4D arrays with $(3 \cdot n^3 \cdot < \text{number of atoms in uc} >)^4$ elements. For 10 atoms in the unit cell and $n = 3$, this yields 810⁴ double-precision entries, for which 3.13 TB of RAM are needed on a single shared-memory node.

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A more rigorous treatment would require the replacement of the polarization vectors $e^{\nu}$, as well as either the inclusion of the force term arising in the DF(P)T description of the structure defined by $\bar{x}$, or an $F$-based description of the $ep$ matrix elements within the SSCHA.

The $ep$ coupling strength $\lambda(\omega) = 2 \int_0^\omega d\omega' \frac{\alpha^2 F(\omega')}{\omega'}$ and the logarithmic average phonon frequency $\omega_{\text{log}} = \exp \left( \frac{2}{\hbar} \int_0^\infty d\omega \frac{\alpha^2 F(\omega) \ln \omega}{\omega} \right)$ are obtained from the Eliashberg spectral function $\alpha^2 F(\omega)$.

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