Phonon anharmonicity: a pertinent review of recent progress and perspective

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Anharmonic lattice vibrations play pivotal roles in the thermal dynamics in condensed matters and affect how the atoms interact and conduct heat. An in-depth understanding of the microscopic mechanism of phonon anharmonicity in condensed systems is critical for developing better functional and energy materials. In recent years, various novel behaviors in condensed matters driven by phonon anharmonic effects were discovered, such as soft mode phase transition, negative thermal expansion (NTE), multiferroicity, ultralow thermal conductivity (\(\kappa\)), high thermal resistance, and high-temperature superconductivity. These properties have endowed anharmonicity with many promising applications and provided remarkable opportunities for developing “Anharmonicity Engineering”—regulating heat transport towards excellent performance in materials. In this work, we review the recent development of studies on phonon anharmonic effect and summarize its origin, mechanism, research methods, and applications. Besides, the remaining challenges, future trends, and prospects of phonon anharmonicity are also discussed.

phonon, phonon anharmonicity, thermodynamics, inelastic neutron/X-ray scattering

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1 Introduction

1.1 Background

In a solid system, almost all atoms (ion cores) vibrate around their equilibrium positions. In such a context, many of the thermodynamics properties have been widely studied. However, a detailed description of these properties requires an understanding of the interactions between the normal phonon modes of these vibrations, especially for systems incorporating light atoms, with weak bonding, or at high temperatures \([1]\). Due to the limitations in the theory of harmonic or quasi-harmonic theory (i.e., the thermal effects depend only on the volume change) \([2-4]\), the lattice anharmonicity has begun to emerge as a considerable experimental and theoretical research topic over the last century.

In classical mechanics, anharmonicity is defined as the nonlinear relationship between oscillators with the generalized forces and the generalized displacement. However, such definition is not entirely accurate in the vibrational thermodynamics context due to the involvement of quasi-harmonic effects. Here, anharmonicity is more restrictively defined as the effect that occurs beyond the harmonic and quasi-
harmonic limits [5]. In this review, other than the harmonic and quasi-harmonic effects, only the “pure” (phonon-phonon interactions) anharmonicity is discussed. Interested readers can find elaborations extensively elsewhere [6,7].

In thermodynamics, anharmonicity was first introduced with the temperature-dependent lattice constant by Mie [8] and Grüneisen [9] in the early 1900s and was later studied by Born and co-workers [10-13]; however, the quasi-harmonic approximation was merely involved in their formulations. The influence of anharmonicity on the caloric equations of state, carried out beyond the quasi-harmonic approximation, was first investigated by Born and Brody et al. [14-16]. Later, Leibfried [17] modified the expressions for the free energy containing both thermal and caloric equations of state with anharmonic effects. In the 1930s, Born and Blackman [18,19] contributed the first papers on anharmonic effects in the absorption of infrared radiation by ionic crystals. Henceforth, many experimental and theoretical studies were performed in great detail to investigate the lattice anharmonicity [20-28] in some simple systems, which remarkably developed and promoted the research on anharmonicity in the mid-1990s. Among these, two review papers help us to understand the essence of anharmonicity historically: one is the review of lattice dynamics of metals by Joshi and Raja-gopal [20]; the other is the review of anharmonicity of ionic crystals by Cochran and Cowley [28]. In the 1960s, the developments of anharmonic effects in lattice dynamics were systematically reviewed by Leibfried and Ludwig [15]. Since then, with the maturity of the anharmonic theories and the development of modern measurement and computational technologies [5,29,30], light has been shed on investigating the area of anharmonicity [8-37].

In recent years, the study of anharmonicity has been tackled using a range of modern methods, including theoretical, experimental, and computational ones, which have given new insights into the microscopic mechanisms of anharmonicity [38-40]. Numerous novel phenomena, such as negative thermal expansion (NTE) [41], ultralow thermal conductivity [42], and multiferroicity [43], have been deeply understood in the context of anharmonicity over the past decades. Meanwhile, the concept of phonon “Anharmonicity Engineering” [39,44] has also been proposed to regulate the thermal properties in numerous materials, like thermoelectric materials and thermal barrier coatings [45-47]. For example, in the leading thermoelectric material SnSe, it was recently found that the coupled instability of electronic orbitals and phonon dynamics, and the anharmonicity is often known as phonon anharmonicity in thermodynamics. Here, the theories of phonon anharmonicity will be briefly revisited, and more details can be found in other works [7,60,61].

Due to the smallness of the atomic displacements \( \pi \) in crystals compared with interatomic distances \( d \), one can convert a problem of strongly interacting atoms to a problem of weakly interacting phonons. In the leading order of the parameter \( \eta = \pi / d \), the crystal lattice dynamics and thermodynamics can be described as ideal phonon gas (harmonic approximation). In fact, \( \eta \) increases with elevating temperature. From a semi-empirical Lindemann criterion [62], \( \eta \approx 0.1 \) at the melting point \( T = T_m \), higher-order (anharmonic) contributions to the thermodynamic properties are usually small up to the melting temperature [63,64]. However, for some peculiar phonon modes, anharmonicity could be crucially large and lead to many novel behaviors.

### 1.2 Phonon theory of anharmonicity

Crystal lattice dynamics is based on the concept of phonons, i.e., weakly interacting waves of atomic (or ionic) vibrations and corresponding quasi-particles. A phonon is a quantum mechanical description of a particular type of vibrational motion in which a lattice uniformly oscillates at the same frequency. In 1932, Tamm first introduced the concept of phonon. Phonon represents an excited state in the normal harmonic limits [5]. In this review, other than the harmonic and quasi-harmonic effects, only the “pure” (phonon-phonon interactions) anharmonicity is discussed. Interested readers can find elaborations extensively elsewhere [6,7].

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#### 1.2.1 Formulation of anharmonicity

One can expand the potential of lattice \( V(\{r_j\}) \) with \( j \) as the site index into the displacement vector \( \mathbf{\mu}_j = r_j - R_j \), \( r_j \) and \( R_j \), being the real and equilibrium position:

\[
V(\{r_j\}) = V_0 + \frac{1}{2} \sum_{j_1,j_2} \Phi^{\alpha_{j_1},\beta_{j_2}}_{\mu_{j_1},\mu_{j_2}} \alpha_{j_1} \beta_{j_2} + \frac{1}{6} \sum_{i,j,k} \Phi^{\alpha_{i},\beta_{j},\gamma_{k}}_{\mu_{i},\mu_{j},\mu_{k}} \alpha_{i} \beta_{j} \gamma_{k} + \ldots ,
\]

\( \Phi^{\alpha_{j_1},\ldots,\alpha_{j_n}}_{\mu_{j_1},\ldots,\mu_{j_n}} \) is the \( n \)-th order interatomic force constant (FC). The quadratic term corre-
sponds to the harmonic term, and the higher-order terms correspond to anharmonic ones. The potentials with displacements of harmonic (second-order) and the high-order anharmonic terms are shown in Figure 1 (middle and bottom panels), presenting the discrepancy induced by the large atomic displacements.

In the phonon representation, the total Hamiltonian of the lattice can be expressed as:

\[
H = V_0 + H_0 + \sum_{n=3}^{\infty} H^{(n)}, H_0 = \sum_i \hbar \omega_i \left( b_i^\dagger b_i + \frac{1}{2} \right),
\]

\[
H^{(n)} = \sum_{\lambda_1, \ldots, \lambda_n} \frac{\Phi^{(n)}_{\lambda_1, \ldots, \lambda_n}}{n!} A_{\lambda_1} \ldots A_{\lambda_n} A_{\lambda_n} = b_{\lambda_1}^\dagger + b_{\lambda_2}^\dagger + \ldots + b_{\lambda_n}^\dagger (i=1 \text{ to } n),
\]

where \(H_0\) is the Hamiltonian of the ideal phonon gas (harmonic approximation). \(\hbar\) is the Plank constant. \(\omega_{\lambda}\) is the phonon energy with the quantum index \(\lambda\) (\(\lambda \equiv q \xi, q\) is the wavevector running the Brillouin zone (BZ), and \(\xi\) is the phonon band index). \(b_{\lambda}\) and \(b_{\lambda}^\dagger\) are the phonon annihilation and creation operators. The multi-phonon scattering matrix elements \(\Phi^{(n)}_{\lambda_1, \ldots, \lambda_n}\) are the \(n\)th derivatives of the potential energy to atomic displacement (i.e., \(n\)th-order force constant). The matrix elements describe the processes of phonon-phonon interaction, such as a merging of two phonons into one (\(n = 3\)), or vice versa, decay of a phonon into two (\(n = 3\)), scattering of two phonons into two new states (\(n = 4\)), etc. (Figure 1 (top panel)).

### 1.2.2 Phonon self-energy

In classical mechanics, the oscillation frequency mainly depends on the oscillation amplitude for general nonlinear systems [65]. Therefore, the anharmonicity that leads to the temperature-dependent phonon spectra mostly results from the growth of average oscillation amplitudes with increasing temperature. In quantum mechanics, the same effect can be described in terms of the phonon self-energy [66,67] due to the phonon-phonon interactions. Phonon self-energy is a complex function, which is defined as \(\Sigma(\omega) = \Delta(\omega) + i\Gamma(\omega)\). The real part, \(\Delta(\omega)\), is associated with the phonon frequency shift due to scattering by other phonons and thus is responsible for the temperature dependence of the phonon frequency. The imaginary part, \(\Gamma(\omega)\), describing the probability of phonon decay, represents the inverse of the phonon lifetime. The real part of the self-energy, including three and four-phonon scattering processes, is shown in Figure 1 (bottom panel).
four phonon-phonon scattering processes, can be expressed as:

\[ \Delta \omega = \Delta_1^{(0)} + \Delta_1^{(3)} + \Delta_1^{(4)}, \]  

(3)

where \( \Delta_1^{(0)} = -\gamma \Delta V(T) / V \) is the quasi-harmonic contribution due to the temperature dependence of the volume \( V(T) \), \( \gamma \) is the Grüneisen parameter, \( \Delta_1^{(3)} \) and \( \Delta_1^{(4)} \) are the contributions of the three and four phonon-phonon scattering processes, correspondingly [24,68]:

\[ \Delta_1^{(3)} = \frac{1}{2\hbar^2} \sum_{k\mathbf{q}} \left| \Phi_1^{(3)}(k,\mathbf{q},\mathbf{q}^* - \mathbf{k} - \mathbf{q}) \right|^2 \]  

\[ \times \left( 1 + N_\mathbf{q} + N_{\mathbf{q}^* - \mathbf{k} - \mathbf{q}} + 1 + N_{\mathbf{q}^* - \mathbf{k}} \right), \]  

\[ \times \left( \delta(\omega_{\mathbf{q}^* - \mathbf{k} - \mathbf{q}} - \omega_{\mathbf{q}^* - \mathbf{k}}) + \left( N_{\mathbf{q}^* - \mathbf{k}} - N_{\mathbf{q}^* - \mathbf{k} - \mathbf{q}} \right) \right) \]  

\[ \times \delta(\omega_{\mathbf{q} - \mathbf{k} - \mathbf{q}} - \omega_{\mathbf{q} - \mathbf{k}}) + \left( N_{\mathbf{q} - \mathbf{k}} - N_{\mathbf{q} - \mathbf{k} - \mathbf{q}} \right) \right) \]  

\[ \times \left( \delta(\omega_{\mathbf{q}^* - \mathbf{k}} - \omega_{\mathbf{q}^* - \mathbf{k} - \mathbf{q}}) + \left( N_{\mathbf{q}^* - \mathbf{k}} - N_{\mathbf{q}^* - \mathbf{k} - \mathbf{q}} \right) \right) \right), \]  

(4)

\[ \Delta_1^{(4)} = \frac{1}{2\hbar^2} \sum_{k\mathbf{q}} \left| \Phi_1^{(4)}(k,\mathbf{q},\mathbf{q}^* - \mathbf{k} - \mathbf{q}) \right|^2 \]  

\[ \times \left( 1 + 2N_{\mathbf{q}^* - \mathbf{k} - \mathbf{q}} \right), \]  

(5)

where \( \varphi \) is the principal value symbol, \( N_\mathbf{q} = (\exp(h\omega_{\mathbf{q}^*}/kT) - 1)^{-1} \) the Bose occupation, \( h \) the Planck constant, \( \xi, \zeta, \eta \) and \( k, \mathbf{q} \) are the polarization indexes and wavevectors components in the quantum index \( \lambda \), respectively. At high temperature \( T \gtrsim \theta_D (\theta_D \) is the Debye temperature), \( N_{\mathbf{q}^*} \approx k_B T / \hbar \omega_{\mathbf{q}^*} \), and all three contributions in eq. (4) are linear in temperature. Figure 2(a) shows the real part of the self-energies of the transverse acoustic (TA), transverse optical (TO), and longitudinal acoustic (LA)-optical (LO) phonon modes at X-point \([\mathbf{q} = (0, 0, 0.8)]\) in germanium [69]. It can be seen that the calculated quasi-harmonic, third-order, and fourth-order contributions all show a linear relationship when the temperature is sufficiently high, especially above the Debye temperature (\( \theta_D = 371 \text{ K} [70] \)). The quasi-harmonic approximation gives a positive contribution to the energy shift (\( \Delta (0) \)) for TA, while it gives the negative contributions for TO and LA-LO modes. The third-order (\( \Delta (3) \)) and fourth-order (\( \Delta (4) \)) results give negative contributions to the energy shift for all three modes. All three contributions jointly drive a negative relationship between the total energy shift (\( \Delta (T) \)) and temperature for all the three modes, which indicates the significant role of anharmonicity on the lattice dynamics in germanium.

With the presence of anharmonicity, the phonons cannot be regarded as stable quasi-particles; e.g., they decay into other phonons through phonon-phonon interactions. As a result, the phonon damping (i.e., the inverse phonon lifetime) arises. In the lowest-order perturbation theory, the damping equals

\[ \Gamma_\mathbf{k} = \frac{\sigma}{2\hbar^2} \sum_{k\mathbf{q}} \left| \Phi_2^{(3)}(k,\mathbf{q},\mathbf{q}^* - \mathbf{k} - \mathbf{q}) \right|^2 \left( 1 + N_{\mathbf{q}^* - \mathbf{k} - \mathbf{q}} \right) \]  

\[ \times \delta(\omega_{\mathbf{q}^* - \mathbf{k} - \mathbf{q}} - \omega_{\mathbf{q}^* - \mathbf{k}}) + \left( N_{\mathbf{q}^* - \mathbf{k}} - N_{\mathbf{q}^* - \mathbf{k} - \mathbf{q}} \right) \]  

\[ \times \delta(\omega_{\mathbf{q} - \mathbf{k} - \mathbf{q}} - \omega_{\mathbf{q} - \mathbf{k}}) + \left( N_{\mathbf{q} - \mathbf{k}} - N_{\mathbf{q} - \mathbf{k} - \mathbf{q}} \right) \]  

\[ \times \delta(\omega_{\mathbf{q}^* - \mathbf{k}} - \omega_{\mathbf{q}^* - \mathbf{k} - \mathbf{q}}) + \left( N_{\mathbf{q}^* - \mathbf{k}} - N_{\mathbf{q}^* - \mathbf{k} - \mathbf{q}} \right) \]  

\[ \left( \delta(\omega_{\mathbf{q}^* - \mathbf{k}} - \omega_{\mathbf{q}^* - \mathbf{k} - \mathbf{q}}) + \left( N_{\mathbf{q}^* - \mathbf{k}} - N_{\mathbf{q}^* - \mathbf{k} - \mathbf{q}} \right) \right) \right), \]  

(6)

The delta functions correspond to the energy and momentum conservations of the decay processes. The damping shows a positive linear relationship with increasing temperature (Figure 2(b)), i.e., the higher the temperature, the stronger the phonon damping. It is worthwhile mentioning...
that in the previous theory derived by Maradudin and Fein [71], the fourth-order term contributes to the energy shift only (real part) but not to the phonon lifetime (imaginary part) [72,73]. Recently, Feng and Ruan [74] derive the anharmonic lattice formalism for four-phonon scattering by extending the derivation of Maradudin et al., and a comparable scattering rate to the third-order one is proposed for some material systems. More detailed descriptions can be found in refs. [36,75-77].

1.3 Scope of this review

In this review, the phonon anharmonicity will be described in detail, including its emergence, driving mechanism, characterization, and prospects. A general introduction to the background and the theory for phonon anharmonicity are discussed in sect. 1. The characterization tools to study the phonon anharmonicity in both experimental and theoretical methods are outlined in sects. 2 and 3. Then, we focus on the origin of the anharmonic behaviors: the intrinsic effects (sect. 4) and the evolutions under external stimuli (sect. 5) with some examples. Sect. 6 introduces a range of materials strongly influenced by the anharmonic effects and how the phonon mechanism is incorporated in them. Finally, in sect. 7, some remaining challenges, future works, and the prospects of phonon anharmonicity are discussed.

2 Experimental characterizations of phonon anharmonicity

After introducing the theory of phonon anharmonicity in the previous section, the characterizations are needed to validate it in real physical systems. As discussed in sect. 1, phonon anharmonicity comes from the large atomic displacements in the nonlinear system, which gives high-order contributions to thermodynamic properties. The anharmonic behaviors often manifest as temperature-dependence of mode softening/hardening and phonon damping in dynamics and phonon-phonon scattering processes in kinetics, which lead to the thermal expansion, finite thermal conductivity, and temperature-dependence of elastic moduli in thermodynamics. There are a variety of experimental methods to study phonon anharmonicity via characterizing these behaviors. It is beyond doubt that the lattice vibration spectrum is one of the most powerful and straightforward approaches to investigate the phonon dynamics and the inelastic neutron scattering (INS) made it possible for the first time to acquire detailed knowledge of the spectrum of lattice vibrations of a crystal [27]. The temperature dependence of mode softening/hardening and the phonon damping, which are the intrinsic reflections of phonon anharmonicity based on the self-energy, can thus be mapped out directly. In this section, the methods for the experimental characterization of anharmonicity will be outlined and discussed.

2.1 Inelastic neutron scattering

Phonons are quantized collective vibrations of atoms. Probing the lattice vibrational spectroscopy is an effective way to investigate phonon anharmonicity. Thermal neutrons (energy of about 5-100 meV and wavelength around 1-4 Å) have the same order of energy and momentum as lattice vibrations, which can exchange their energy and momentum with an excitation throughout the whole BZ when inelastically scattered off the samples. When a neutron is scattered by a crystalline solid, it can interact with nuclei through strong interaction and absorb/emit the energy of a phonon. This process annihilates/creates a phonon in which the neutron energy before and after the scattering differ by an amount (i.e., energy transfer). Being charge-neutral and carrying spin, neutron is a crucial tool that is widely used to study lattice order, transfer mechanics, and magnetism in the condensed matter [78,79].

By measuring the intensity of neutrons scattered off a sample as a function of wavevector transfer and frequency change relative to the incident monochromatic neutron source, one can measure the spatio-temporal correlations of the material. The phonon dispersion throughout the whole BZ can be obtained directly by measuring the coherent one-phonon INS cross-section in a single crystal. In this case, the double-differential coherent cross-section can be expressed as [78]:

$$\frac{\delta^2\sigma}{\delta E\delta E'}^{coh} = \frac{(2\pi)^3k_i}{2V_0\omega_{\lambda}}S(Q,\omega),$$  

(7)

where $\delta\sigma/\delta E_i$ is the number of neutrons scattered per second into the element of the solid angle $d\Omega$ with final energy between $E'$ and $E'+\delta E'$, and $V_0$ is the unit-cell volume. The dynamic structure factor, $S(Q,\omega)$, is defined by

$$S(Q,\omega) = \sum_\lambda \sum_{-\infty}^{+\infty} \frac{1}{\omega_\lambda} \sum_j \frac{b_j}{\sqrt{M_j}} \exp(-W_j) \exp(iQ \cdot r_j)(e_{\mu_j})^2 \times (N_j + 1) \delta(\omega - \omega_j) \delta(Q - q - \tau),$$  

(8)

where $Q = k_i - k_f = q + \tau$ and $\hbar\omega_{\lambda}(\pm) = E_i - E_f$ are the scattering vector and energy transfer to the sample. $E_i$ ($k_i$) and $E_f$ ($k_f$) are the incident and the scattered neutron energies (wavevectors). The $+(-)$ sign indicates that the phonon is created (annihilated) in the scattering process, $\tau$ the reciprocal lattice vector, $b_j^-$ the coherent neutron scattering length, $M_j$ the atomic mass in position $j$ of unit-cell, $e_{\mu_j}$ the polarization vector of normal phonon mode $\lambda$ for atom $j$. $W_j$ is the Debye-Waller factor defined as:
where $\mathbf{\mu}$ represents the displacement of atom $j$ in unit-cell $l$.

As described above, the phonon dispersion of a single crystal can be determined by the coherent one-phonon INS cross-section measurement, which provides detailed dynamics information, such as the mode energy (peak position), phonon scattering rate (full width at half-maximum of the peak), and sometimes multiple phonon-particle scatterings (peak asymmetry) \[80,81\]. Consequently, the phonon dynamics can be investigated by tracing the changes in phonon peaks. By performing the inelastic neutron scattering on polycrystalline samples, one can obtain frequency distribution of the phonons (phonon density of states, DOS), which is essential in its own right, especially for thermodynamic studies \[5\].

There are two typical techniques of INS measurements: the triple-axis neutron spectrometry (TAS) and the time-of-flight (TOF) spectrometry. TAS generally provides the constant-$Q$ or constant-$E$ scan, which has a significant advantage in seeking phonon energy at points or along high-symmetry lines in reciprocal space. TOF can map phonon dispersion, provide the four-dimensional (4D) data for single crystals across large volumes in reciprocal space \[82\], or give phonon DOS for polycrystalline. The interested readers can find more details of the principles of INS technologies in refs. \[5,78,79,83,84\].

INS has been extensively used to characterize phonon anharmonicity by measuring the phonon dispersion relations and the lifetime of crystals in various sample environments (temperature, pressure, or magnetic). Three recent works are presented here as examples to introduce phonon anharmonicity using both TAS and TOF measurements. The first is to investigate the anharmonic lattice dynamics in SnTe and PbTe by TAS, TOF, and first-principles calculation with anharmonic lattice dynamics \[85\]. Figure 3 shows that the soft TO modes present strong broadening and softening with increasing temperature in both materials, indicating the large anharmonicity. In PbTe, the TO modes exhibit a splitting behavior (“new mode” pointed out by arrows) caused by the dispersion nesting between TO and TA. This nesting behavior enables more three-phonon scattering channels in PbTe than SnTe, and amplifies stronger anharmonicity. Such stronger anharmonicity in PbTe mainly results from the sharper resonance in the self-energy. The results reveal that the three-phonon scattering phase space and the combined lattice instability determine the TO ferroelectric soft mode.

The second example is the low thermal conductivity induced by the phonon anharmonicity in thermoelectric material Ba$_8$Ga$_{16}$Ge$_{30}$ \[86\]. The low-frequency optical phonon mode and the acoustic phonons were measured by using the TAS technique, showing an “avoided crossing” behavior between the TO and LA mode (Figure 4(a)). This behavior is reflected by the wide phonon linewidths (Figure 4(b)), indicating the strong phonon anharmonicity, and leads to the low thermal conductivity of Ba$_8$Ga$_{16}$Ge$_{30}$.

The third one is an example to study phonon anharmonicity by using the TOF technique. In Figure 5(a), It can be found that the measured phonon DOS mostly departs from the quasi-harmonic calculation, especially for the second optical phonon peak, indicating a strong anharmonic system of FeGe$_2$. Figure 5(b) shows the measured $S(Q, \omega)$ of FeGe$_2$ at 300, 500, and 635 K. From the cuts at [400] (Figure 5(c)), the three optical phonons localizing at 18, 21, and 31 meV show clear thermal softening and broadening (shaded region).
behaviors with the increasing temperature (Figure 5(d)) [87].

2.2 Inelastic X-ray scattering

X-ray diffraction is widely used in crystal structure characterization by focusing on accurate measurements of the positions and intensities of Bragg peaks. In reality, X-ray always acts on the vibrating lattice of crystals, leading to the energy exchange between X-ray and the lattice, i.e., energy loss for a phonon creation and energy gain for a phonon annihilation. It is a photon-in/photon-out spectroscopy where one may measure both the energy and momentum change from the scattered photon. The energy and momentum lost by the photon are transferred to phonons. Though the high energy of X-ray (keV) from synchrotron-radiation light source is about six orders of magnitude higher than that of phonons (meV), the technical developments have overcome the challenge in measuring small changes in high energy resolution ($\Delta E/E < 10^{-6}$), making it possible to determine the complete phonon dispersion. With similar principles of TAS, inelastic X-ray scattering (IXS) also operates the constant-$Q$ and constant-$E$ scans on single crystals. It is worthwhile mentioning that the IXS allows the measurement of phonon dispersion relations in micrograms of single crystal samples. This feature makes IXS technology have great advantages in investigating lattice dynamics for those systems, where a big single crystal is hard to grow.

Here, we introduce two recent works to show how IXS is used to investigate phonon anharmonicity. One example is represented on VO$_2$, in which the coherent neutron cross-section of V is very small, and thus IXS is a better choice for investigating the phonon anharmonicity. Figure 6 shows the phonon dispersions of VO$_2$ obtained by IXS [88], in which the phonon anharmonicity is revealed by the prominent broad phonon peaks (short lifetimes) with asymmetric shapes in Figure 6(b), and all low-energy TA and LA phonons are strongly damped (vertical error bars) in Figure 6(c). In addition, the unusual stiffening of the low-energy TA branches was observed on heating from 425 to 800 K, strongest along Γ-R and Γ-M directions, suggesting that the anharmonic mechanism is responsible for both phonon stiffening and damping [88].

The other example using IXS to investigate the phonon anharmonicity is in ScN films, which is impossible to carry out by INS due to the small sample size. Figure 7(a) shows the measured phonon dispersions of the epitaxial ScN film measured by IXS along Γ-K-X and Γ-X directions, which is verified by the first-principles calculation (Figure 7(b)) [89]. The LO modes exhibit large linewidths along Γ-X direction (Figure 7(c)). The calculated imaginary part of the self-energy has further confirmed this behavior and is in good agreement with the extracted phonon linewidths (due to the phonon-phonon interaction) (Figure 7(d)). The details of the phonon scattering were plotted in Figure 7(e), in which one pair of the phonons ($\omega_1$ and $\omega_2$, blue arrows) decays from the original (00q) phonon ($\omega_0$, green arrow) as a function of q. The linewidths of the LO mode also show broadening with the increasing temperature. This decay process is complicated and can be described by both the Ridley (LO → LA / TA + TO) [90] and Klemens-like (LO → 2LA / TA) [91] channels. Such strong anharmonicity induced by the three-body phonon-phonon interaction may be the origin of the low thermal conductivity in ScN film [89].

2.3 Raman spectroscopy

Light has a certain probability of being scattered by a material. Most of them are elastically scattered (Rayleigh scattering), while some are inelastically scattered (Raman and Brillouin scattering). Typically, Raman scattering in-
volves vibrational energy being gained/lost by a material as incident photons from a visible laser shift to lower/higher energy (Stokes/anti-Stokes Raman scattering). Due to the large difference between the magnitude of the wavevector of visible light \( k = 10^5 \text{ m}^{-1} \) and the first BZ \( \mathbf{q} = \pi/a \approx 0.1 \text{ Å}^{-1} \), only the phonons near the zone center can be probed (in the

**Figure 5** (Color online) Phonon DOS and the dispersions of FeGe\(_2\). (a) Measured phonon DOS by INS, overlaid by the quasi-harmonic calculation. (b) Measured phonon dispersions along [400] direction at 300, 500, and 635 K, respectively. The grey line indicates the region of the cut shown in (c). (c) Cuts at 4.0 r.l.u.. Error bars represent the width of the branches. (d) Fitted positions of the optical modes from (c). The red shaded regions represent the linewidth approximated by the full width at half maximum of peaks. The black line represents the high-energy mode predicted by the quasi-harmonic approximation [87]. Copyright (2018), American Physical Society.

**Figure 6** (Color online) Phonon dispersions measured with IXS in rutile VO\(_2\). (a) Reciprocal space of rutile VO\(_2\). (b) IXS scans at R point at 355, 425, and 810 K. Curves are the fitting results by the damped-harmonic-oscillator model. (c) Experimental results at 425 and 810 K. Vertical lines and shading regions indicate the large phonon linewidths [88]. Copyright (2014), Nature Publishing Group.
case of high-order processes are not involved). Raman spectroscopy is a fast and high-resolution tool for the characterization of electronic, optical, and phonon properties of materials. It is also utilized to investigate the phonon anharmonicity in various systems, such as two-dimensional (2D) materials [92-94], ferroelectric [95,96], thermoelectric [97,98], and multiferroics [99,100], associated with changes in temperature or pressure.

Here, we show one example to investigate the phonon anharmonicity in the popular thermoelectric SnSe using Raman and IR (infrared absorption spectroscopy). Figure 8(b) shows the normal reflectance spectra along a (lower) and b-axis (upper) of SnSe measured by far-transform IR (FTIR) [101], while Figure 8(c) shows the temperature-dependent Raman spectra along a- (left) and b-axis (right) of SnSe [102]. In comparison, the Raman-active modes (Figure 8(a)) arise at 70 cm$^{-1}$ (A$_g^1$), 108 cm$^{-1}$ (B$_{2g}$), 130 cm$^{-1}$ (A$_g^2$), and 150 cm$^{-1}$ (A$_g^3$) [103], while the IR-active modes arise at 80 cm$^{-1}$ (B$_{1u}^1$), 96 cm$^{-1}$ (B$_{2u}$), 123 cm$^{-1}$ (B$_{1u}^2$), and 150 cm$^{-1}$ (B$_{1u}^3$). It can be seen that the Raman and IR are complementarily used to probe the optical phonon modes due to the different microscopic mechanisms. Moreover, the phonon frequency softening and the linewidths broadening of the B$_{2g}$ and A$_g^2$ are shown in Figure 8(d). According to the Klemens decay model, the softening and broadening contributions are mainly dominated by the three-phonon scattering process [102].

2.4 Crystal structure methods

Beyond the lattice vibration spectra, some crystalline structural characterizations, such as X-ray and neutron diffraction [104], X-ray and neutron total scattering [105-107], and the extended X-ray absorption function spectroscopy (EXAFS) [108,109], are also applied to study phonon anharmonicity. Usually, large lattice vibration amplitude could induce strong phonon anharmonicity. Therefore, investigating the information of a crystal structure, especially the atomic position and atomic distance, could also provide clues to the anharmonicity. The main observations related to the phonon anharmonicity by these methods are the peak positions, peak widths, and peak asymmetry.

Here, we introduce one recent work of ScF$_3$, one of the NTE materials, to show the effectivity of the structural methods to study the phonon anharmonicity by the combination of neutron diffraction, X-ray total scattering, and EXAFS [110]. In Figure 9(a), the lattice constant contracts smoothly with increasing temperature over a large region, showing a prominent NTE behavior. This NTE behavior can be traced to the Sc-F and the Sc-Sc atomic pair distances in

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Figure 7  (Color online) Phonon properties of epitaxial ScN film [89]. (a) Phonon dispersions measured by IXS along Q~(3+q,−1,−1) (Γ-K-X, left) and Q=(1,1,3+q) (Γ-X, right) at room temperature. Color bars represent the intensities on a logarithmic scale. (b) Comparison between the IXS data (black circles) and the first-principles calculation (red lines). Black lines are guides to the eyes. (c) Constant-Q scans of the LO mode by IXS at RT. Lines are the fitting results. (d) Comparison between the extracted (solid black circles) and the calculated linewidths (red line) of LO mode, showing the good agreement. (e) Plots of the calculated decay phonons ($\omega_1$ and $\omega_2$, blue arrows) from the original (00q) phonon ($\omega_0$, green arrow) as a function of q ($q_1$ and $q_2$, black dots) in the reciprocal space of ScN. Copyright (2018), American Physical Society.
Figure 8  (Color online) Phonon anharmonicity investigated by both Raman and IR spectroscopy in SnSe. (a) Raman-active modes in orthorhombic SnSe [103]. Copyright (2018), American Chemical Society. (b) Normal reflectance spectra (blue) of $a$- and $b$-axis of SnSe by FTIR at room temperature, overlaid with the Drude-Lorentz fits (red) [101]. Copyright (2018), IEEE. (c) Temperature-dependence of the polarized Raman spectra for $B_{3g}$ (108 cm$^{-1}$) mode along $a$-axis (left), and for $A_{1g}$ (70 cm$^{-1}$), $A_{2g}$ (130 cm$^{-1}$), and $A_{3g}$ (151 cm$^{-1}$) modes along $b$-axis (right) [102]. (d) Anharmonic contribution to the phonon softening and linewidth broadening of the $B_{3g}$ mode (left) and $A_{2g}$ mode (right). The three-phonon, four-phonon, and volume expansion contributions are shown by blue, green, and magenta dashed lines, respectively [102]. Copyright (2016), American Chemical Society.

Figure 9  (Color online) Temperature-dependent structural properties of ScF$_3$ [110]. (a) Relative lattice constant measured by X-ray diffraction (blue square), X-ray PDF (red circle), and neutron powder diffraction (black diamond). Inset shows the coupled rocking motion of ScF$_6$. Red arrows represent the motion of F. (b) The Sc–F and Sc–Sc (inset) lengths were extracted from the EXAFS (open) and the X-ray PDF (filled). The red triangles represent the Sc–F distance extracted from neutron powder diffraction. (c) Parallel (left), Perpendicular (middle), and the anisotropy atomic MRSDs of the vibrations of Sc–F and Sc–Sc atomic pairs extracted from EXAFS. Curves are fits by the Einstein model. (d) Schematic ellipsoids of the Sc–F (larger) and Sc–Sc (smaller) thermal vibrations. Copyright (2016), American Chemical Society.
the cubic ScF₃ from the EXAFS data. The Sc–F bond shows a steep expansion with increasing temperature, while the nearest-neighbor Sc–Sc distance shows a slow shrinking behavior (Figure 9(b)). The atomic mean square relative displacement (MSRD) can quantitatively investigate the correlated motion between the selected atomic pairs. It can be seen that the MSRD parallel to the bond directions of the Sc–F shows the moderate temperature-dependency (left panel in Figure 9(c)), while the perpendicular one shows the significant-high temperature-dependency (middle panel in Figure 9(c)). The ratio of the anisotropy (MSRD connection/MSRD perpendicular) reaches around 20, which is an extremely large value among the present popular NTE materials [110]. This high anisotropic behavior indicates that the anharmonic transverse thermal vibration of F is the dominant mechanism of the NTE behavior in ScF₃. The thermal vibration of F will distort the corner-shared ScF₆ octahedrons around the center of the structural frame (dynamic motion in the inset of Figure 9(a)), which shrinks the volume of the system and thus the NTE behavior of ScF₃. Therefore, phonon anharmonicity of ScF₃ was successfully investigated by the crystal methods, and the relationship between phonon anharmonicity and NTE could be studied with the INS technique (details can be found in sect. 6).

In this section, three vibrational spectroscopy techniques and crystal structure methods for studying phonon anharmonicity were discussed. Additionally, there are other vibrational spectra techniques used for phonon-related properties. Unlike Raman scattering, IR photon could be absorbed by the optical mode, showing a sharp peak in the absorption spectrum (Figure 8(b)). Like Raman scattering, Brillouin scattering is another phonon-related inelastic light-scattering that probes acoustic phonons due to its scattering feature. Inelastic electron tunneling spectroscopy (IETS) is sensitive to the vibrations of adsorbed molecules but only from the first few atomic layers on conductive substrates [111]. The latest work reported that the single-defect phonon could be successfully imaged by the newly developed angle-resolved electron energy-loss spectroscopy (EELS); however, resolving phonon dispersions is still challenging due to the momentum resolutions [112]. Table 1 lists the comparison of different phonon anharmonic-related experimental methods, including principles, applications, advantages, and limitations [112-115], which could help the readers understand and choose the appropriate one when dealing with the problems on hand.

### 3 Computational characterizations of phonon anharmonicity

As described in sect. 2, phonon anharmonicity can be ex-
perimentally characterized in various materials through a combination of vibrational spectroscopy and crystal structure methods. With the development of computational methods and techniques, phonon anharmonicity, especially its microscopic origin, is extensively explored from the first-principles method and molecular dynamics (MD) calculations, such as the density functional perturbation theory (DFPT) method [116], the DFT-based methods with non-perturbation including the self-consistent phonon (SCP) [35,117,118] and the self-consistent-field (SCF) theory [1,119], and the ab initio MD (AIMD)-based temperature-dependent effective potential (TDEP) method [120-123]. Here, we will briefly review typical features to characterize the phonon anharmonicity from simulations, such as non-parabolic frozen phonon potential, large third-order force constants, and phonon energy shifting and damping. The basic theory of these methods will not be introduced in detail, and the interested readers can refer to the above literature [1,35,116-120,122,123].

3.1 Phonon calculations with harmonic approximation

Calculation of harmonic phonon dispersion is usually based on the DFPT method and supercell method [35]. A linear response theory DFPT is one of the standard first-principles methods for calculating harmonic interatomic FC. With the assumption of infinitesimally small atomic displacements, the harmonic dynamical matrix for an arbitrary $q$-point can be obtained from the perturbation theory [116,124]. The supercell method is another approach to calculate harmonic FC. In this approach, harmonic FCs are estimated from the first-order numerical derivative of the atomic forces [125]. It is the basis to investigate the lattice dynamics and thermodynamics of weak anharmonic materials. Although, the harmonic approximation hardly works for the strongly anharmonic systems, it can signify the strong anharmonicity of the materials to some extent, e.g., imaginary phonon frequencies [120,126] and frequency mismatching [120,127]. For example, by using both the PBE and PBE+U functional harmonic calculations (Figures 10(a) and (b)), rutile structure VO$_2$ shows the unstable phonon modes. This indicates the presence of strong anharmonicity, which was verified from the large phonon linewidth from IXS measurement as shading regions shown in Figure 10(c). When considering the anharmonicity by using the TDEP method [120], the unstable phonons are stabilized, and phonon dispersion is in good agreement with the experiment result (Figure 10(c)) [88].

![Figure 10](Color online) Comparison between the phonon dispersions calculated from harmonic approximation and TDEP methods with the anharmonic effect considered. Results produced by harmonic methods at 0 K. (a) PBE and (b) PBE+U functionals. (c) Phonon dispersions calculated by TDEP methods at 425 K (blue lines) and 800 K (red lines). Diamonds and shading regions represent the phonon energies and linewidths at 425 K [88]. Copyright (2014), Nature Publishing Group.
3.2 Non-parabolic frozen phonon potential

Harmonic phonons correspond to parabolic frozen phonon potentials, while the strong anharmonic phonons correspond to non-parabolic phonon potentials. Therefore, it is a straightforward approach that one can explore the anharmonicity by calculating the frozen phonon potential for a specific phonon mode. In this method, all atoms are displaced according to the corresponding phonon eigenvectors and the frozen phonon potential can be obtained as a function of atomic displacements. The larger the frozen phonon potential deviate from the parabolic potential, the stronger the anharmonicity is expected in the systems. As shown in Figure 11(a) and (b), when the V atoms vibrate with large displacements, the potential of the phonon mode at R-point departs far from the parabolic curve, showing strong anharmonicity of VO$_2$ in the rutile phase. However, at the low-temperature monoclinic phase, the potential of the same vibration mode follows a nearly parabolic profile, indicating the weak anharmonicity at the low-temperature phase in VO$_2$ [88]. Similar non-parabolic frozen phonon potentials occur in many advanced materials, such as SnSe [39], ScF$_3$ [128], and Cu$_3$SbSe$_3$ [129] systems (discuss later).

The frozen phonon potential method is not only convenient to evaluate the strength of anharmonicity for a particular mode, but also help to investigate the atomic interactions between specific atoms and explore the origin of the anharmonicity. For example, the Sn atoms in Figure 11(c) vibrate with large displacements, which cause the large deviation from the harmonic potential in TOe mode (vibrating along c-axis) (Figure 11(d)), leading to strong anharmonicity in SnSe. Recently, Parlinski [130] has developed a large displacement method to compute anharmonicity without calculating the third-order FCs, in which a larger atomic amplitude corresponding to the given temperature is used to calculate the anharmonic phonon peaks and the dispersion curves. This method is applicable in cubic W, perovskite MgSiO$_3$, and superconductor MgB$_2$ crystals.

3.3 Third-order interatomic force constant

Based on the interatomic potential expressed in eq. (1), anharmonicity depends on the high-order terms, which can be the most direct quantification of the anharmonicity. Therefore, an effective way to characterize the anharmonicity quantitively is to calculate the third-order force constants. It can be seen in Figure 12(a), the Pd atom has square-planar coordination formed by [Se$_2$]$^{2-}$ and Se$^{2-}$. The larger third-order FCs of [Se$_2$]$^{2-}$ dimers (Figure 12(b)) reveals that the formation of [Se$_2$]$^{2-}$ dimers are the origin of the strong anharmonicity in Pd$_2$Se$_3$ directly [131]. Therefore, it is critical to calculate third-order FC accurately in characterizing

![Figure 11](image-url) (Color online) Frozen phonon potentials to investigate the anharmonicity. (a) and (b) are the frozen phonon potentials of VO$_2$ (a-b) in rutile and monoclinic phases [88]. (c) is the illustration of a strongly anharmonic triplet in SnSe, and (d) is the frozen phonon potential of the TOe mode [39]. Insets are the related vibration modes in these systems. Copyright (2015), Nature Publishing Group.
phonon anharmonicity. There are several methods to deal with the anharmonic FCs, basically in two ways. One is to make a small correction on the harmonic terms by the many-body perturbation theory [71]. This perturbation method is helpful to explore the temperature effects with relatively small anharmonicity [132]. However, due to the challenge of converging higher-order derivatives of the electronic orbitals in DFPT calculations, the application is limited to investigating the systems with large supercells or strong anharmonicity [130].

In order to overcome the limitations of perturbation methods, some non-perturbation methods based on DFT have been developed recently. These approximations supplement the conventional treatments, including the self-consistent ab initio lattice dynamics (SCAILD) [117] and the stochastic self-consistent harmonic approximation (SSCHA) [118]. In these methods, atoms are displaced in a supercell with the corresponding temperature and the thermal average of the “exact” potential (or force) is evaluated. In these cases, for example, by the SCP method, the temperature-dependent phonon dispersions can be successfully predicted and show an excellent agreement with the experiment [35] (SrTiO$_3$ in Figure 12(c)).

Additionally, the molecular dynamics approach is powerful in investigating phonon anharmonicity because it naturally includes all effects of anharmonicity in the trajectories while the system is evolving dynamically [120,133,134]. One successful approximation is the TDEP method [120-122], which used the atomic configurations from a molecular dynamic run and fitted the calculated forces to an effective harmonic model. They used the crystal symmetry to reduce the number of FCs and performed a least-square fit to extract the inequivalent FCs. The effective FCs are temperature dependent in this method because the MD snapshots were taken from a constant temperature run. Thus, the temperature-dependent phonon dispersion can be successfully calculated, as shown previously discussed in VO$_2$ (Figure 10(c)) and SrTiO$_3$ (Figure 12(d)) [135]. It can be seen in Figure 12(c) that the TDEP results have good agreement with the experiments and the results by SCP method.

In most materials, the anharmonicity is mainly dominated by the three-phonon scattering process, i.e., third-order FC successfully estimates the anharmonicity in the systems. However, in some systems within (1) strongly anharmonic vibrations, (2) large acoustic-optical phonon band gaps, and (3) 2D materials with reflection symmetry, the fourth-order

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**Figure 12** (Color online) Different methods to estimate the third-order FCs. (a) Top view of the crystal structure of Pd$_2$Se$_3$. (b) Third-order FCs with different triplets in Pd$_2$Se$_3$ by the DFPT [131]. Copyright (2018), American Chemical Society. (c) Phonon dispersions of cubic SrTiO$_3$ by experiments (red circles), harmonic calculations (black dash lines), and the temperature-dependent SCP calculations (solid grey lines, the green lines are highlighted curves at 300 K) [35]. Copyright (2018), Institute of Pure and Applied Physics. (d) Phonon dispersions of cubic SrTiO$_3$ by experiments (magenta circles), DFPT (grey dash lines), and TDEP (blue and orange solid lines are results at and 200 and 300 K, respectively) [135]. Copyright (2018), American Physical Society.
FC can be large and need to be taken into consideration [36]. Since 2017, the calculation of fourth-order FC has been available from DFT [75], and the anharmonicity was investigated successfully in BAs [76], graphene [77], and PbTe [136]. In recent years, the role of fourth-order FC has attracted increasing attention in various materials such as Tin Selenide [137], Lead-Free Halide Double Perovskites [123], MgO [138], Tl$_3$VSe$_4$ [139], and thus the thermodynamic properties (e.g., the thermal conductivity and the thermal expansion) can be predicted more accurately and reliably.

3.4 Phonon energy shifting and damping

The anharmonic phonon shifting and damping are both determined by the third-order FC according to eqs. (4) and (6). After obtaining accurate second and third-order FCs, the phonon softening/hardening and the phonon broadening are accessible for further analysis. For example, in silicon, the temperature-dependence of the calculated phonon softening and broadening (linewidth, 1/τ) from stochastically initialized TDEP (s-TDEP, including anharmonic and thermal expansion) show good agreement with the experiments (markers). In contrast, the results from quasi-harmonic approximation show a significant discrepancy with the experiments (Figure 13(a) and (b)) [140]. Additionally, the difference of calculated shifts (broadening) between s-TDEP and the quasi-harmonic model are of 65% (15%) at 1500 K (Figure 13(c)). The temperature dependence of shifts and broadenings exist throughout the BZ in silicon, indicating strong anharmonicity in this system (Figure 13(d)).

As discussed above, depending on the developments of computational methods, various advanced computing methods are accessible for the study of phonon anharmonicity, which provides a microscopic picture of phonon-phonon interactions. By combining phonon anharmonicity measurements and calculations, it is possible to obtain a comprehensive investigation of anharmonic lattice dynamics and kinetics, as well as the microscopic origin of the phonon anharmonic interactions. Table 2 lists the comparison of different computational characterization methods, including...

Figure 13  (Color online) Phonon anharmonicity of silicon [140]. Temperature-dependence of shifts (a) and broadening (b) of the phonon modes at $\mathbf{q}=(0.75, 0.25, 0.25)$. Markers, solid, and dash lines represent the experimental, s-TDEP, and quasi-harmonic results, respectively. Inset represents the phonon modes marked by the purple circle, red square, blue pentagon, green hexagon, and black triangle as the increased energy. (c) Comparison between the s-TDEP and quasi-harmonic calculations at 300 and 1500 K. (d) Temperature-dependence of shifts and broadenings throughout the BZ. Copyright (2018) by the author.
the principle, application, and feature [34-36,73,141], which provides the reference for readers to choose the appropriate simulation method when dealing with the problems on hand.

4 Origin of the anharmonic interactions

In previous sections, it shows what phonon anharmonicity is and how it is characterized. However, how the anharmonicity emerges in a real system can be complicated. In recent years, the origin of anharmonicity has been successfully understood in many systems [39,82,142-144] by combining phonon measurements and calculations (as mentioned in sects. 2 and 3). In this section, we will introduce three typical microscopic mechanisms that cause anharmonicity (Figure 14), including lone pair electrons, resonant bonding, and rattle models [145,146].

4.1 Lone pair electrons

In chemistry, lone pair electrons (LPEs) refer to a pair of outermost valence electrons not shared with other atoms. The mechanism behind the relationship between LPEs and phonon anharmonicity is that the LPEs are non-bonding and expected to form a shell of a relatively large radius, causing the bonding asymmetry. As atoms approach one another during thermal vibration, the overlapping wave functions of the non-interact LPEs and nearby valence electrons will induce a nonlinear repulsive electrostatic force, leading to the anharmonic atomic displacements and structural instability, thus the phonon anharmonicity [142,147-149]. The formation of LPEs usually requires a strong interaction between the cation $s$ and anion $p$ orbitals and the crystal structure distortion [145]. For example, for an $n s^2 n p^m$ valence configured atom, if the valence electron of $n p$ orbitals alone participate in bonding with the anion, the bond will not share the $n s^2$ electrons and lead the $n s^2$ electron pair to an isolated (“lone pair”) state, hence form the LPEs.

The LPEs induce strong anharmonicity in various materials, such as binary oxides [150-152], binary chalcogenides [39,153-155], ternary oxides [156,157], ternary chalcogenides [142,148,158,159]. SnSe is a typical example to show this issue due to the active $5 s^2$ lone pair electrons of Sn atoms, visualized by the “caps” in the space between bilayers in Figure 15(a) and (b), which originate from the hybridization with Se $p_x$-state [39]. Combined with the resonant bonding (discuss later) of $p$-orbitals of Se atoms, the lone pairs induce the off-centering of Sn atoms and the strong Sn–Se bond anharmonicity, especially for the $d_2$ and the $d_3$ bonds in Figure 11(c). These anharmonic bond vibrations cause giant anharmonicity of the TO phonon modes (Figure 11(d)), which are reflected by the temperature-dependent broadening and softening of the TO modes (Figure 15(b) and (c)) extracted from the INS measurements (Figure 15(d)-(f)). Consequently, such orbitally driven giant anharmonicity acts as the primary origin of the ultralow thermal conductivity in SnSe.

LPEs will usually induce the distortion of the bonding...
structure, which is related to the strength of the repulsive electrostatic force between LPEs and neighboring atoms. Structural distortion mainly depends on the delocalization of LPEs (the distance between LPEs and the nucleus), which can be observed by the bond angle of a single atom. The Cu-Sb-Se ternary system presents a direct example to study this issue. As shown in Figure 16(a), the Se-Sb-Se bond angles of Cu₃SbSe₄ without LPEs are 109.5°, and the bond angles of CuSbSe₂ and Cu₃SbSe₃ with LPEs are 95.24° and 99.42°, respectively. In this case, the LPEs are far away from Sb in Cu₃SbSe₃ and yet do not form bonding, which leads to the strong bond anharmonicity, hence the lowest thermal conductivity among the three compounds (Figure 16(b)) [142].

Figure 14 (Color online) Three typical mechanisms leading to the intrinsic phonon anharmonicity. The left and the right picture are adapted from refs. [145,146], respectively.

4.2 Resonant bonding

Unlike the LPEs, the resonant bonding [160] can also result in lattice anharmonicity even in structures with high symmetry, such as the rocksalt and rocksalt-like structures [161-163]. In these cases, a single, half-filled p-band forms two bonds to the left and right (more than that is allowed by the 8-N rule, N for the valence), and can be easily understood by the schematic illustrations in Figure 17. For the (001) plane of a hypothetical simple cubic crystal of Sb [162], two valence p-electrons of each Sb atom alternately occupy four covalent bonds between the adjacent atoms, as shown on the left and right panels in Figure 17. If the valence bonds frequently change between these two cases and thus reduce the total energy, a superposition of these electronic configurations emerges (middle panel in Figure 17), resulting in resonance bonding. The remarkable electron delocalization characterized by resonant bonding leads to a significant increase in electronic polarizability.

The resonant bonding can commonly induce strong anharmonicity of long-range interatomic FCs in rocksalt structures [164,165]. Figure 18 shows the trace of the FCs of materials in typical IV-VI, V₂-VI₃, and V groups [153]. Compared with the NaCl (ionic bonding) and InSb (sp-hybridized covalent bonding) shown in Figure 18(b), the long-ranged interactions of the resonant bonding ones (IV-VI, V₂-VI₃, and V groups) are much larger and non-negligible even for the fourteenth-nearest neighbors.

Figure 19(a) shows the resonant bonding behavior in the rocksalt structure in ferroelectric PbTe. In PbTe, only the p-electrons are considered for valence states, and each atom has three valence electrons on average (Pb: 2 and Te: 4). This bonding configuration will form a long-range resonance bond of PbTe, leading to the softening of the TO modes [161,164,166]. It is reported that there is a large coupling between TO and LA mode due to the softening of TO mode [164,167]. Such behavior was later experimentally confirmed by the INS measurement, as shown in Figure 19(b) [166]. It reveals an avoided crossing between LA and TO branches around \( q = (0, 0, 1/3) \) due to anharmonic repulsion between these modes, in contrast with the harmonic dispersions (shown as white solid lines) calculated by DFT. Such an anharmonic TO mode leads to an intrinsic scattering of LA modes and thereby largely suppresses the thermal conductivity of PbTe, which is significant for thermoelectric applications, shown in Figure 19(c) [168].
4.3 Rattling vibrations

The rattling vibration can be described as follows: the guest atoms (or molecules) are weakly bound and somewhat independent of the other atoms in an oversized atomic cage, which vibrate anharmonically with large displacements. Such a rattling behavior was first described by Sievers and Takeno [169] and was first introduced into thermoelectric materials with cage structures by Slack [170]. Figure 20(a) shows the anharmonic potential induced by the rattling vibration of off-center guest Ba atoms (6k site) in type-I clathrate β-Ba8Ga16Sn30. The potential of the rattling Ba atoms can be described as $V=Ax^2+Bx^4$, containing a harmonic (quadratic) term and an anharmonic (quartic) term [171,172].

In general, one of the main features of the guest atoms inducing rattling vibrational behaviors is that when the available space in the host cages becomes larger than their ionic radii, the restoring forces on them will become weaker. The phonon frequencies will decrease accordingly and behave anharmonically in a more localized region. Therefore, these guest phonon dispersions become low-lying and flat [173-175]. The rattling guest atoms usually have two types of positions in the cage: on-center and off-center, which depend on the relative size of the cage to the guest atom [176]. As a result, the on-center and the off-center atoms will lead to the difference between their respective phonon dispersions (Figure 20(b) and Figure 4 for the on-center one) [177]. Compared with the on-center one, the phonon linewidth of the off-center one becomes much broader and
gapless in the region of the avoided crossing (Figure 20(c)),
which is attributed to the random orientation of guest atoms.

Recently, rattling vibration has been widely observed in
materials with cage structures (e.g., skutterudite [178]
and clathrate [86,171,176]), non-cage structures (e.g., CsPbI3
[179], and Cu12Sb4S13 [180]), and even 2D-layered structures
(e.g., Mg3Sb2 [181]). This behavior can be effectively stu-
died by simulations and experimental techniques, such as X-
ray and neutron diffraction [182,183], EXAFS [184], in-
elastic X-ray and neutron scattering [86,185-187], Raman
spectroscopy [175,188], and optical conductivity [189].

Though the rattling phenomenon has been extensively stu-
died, the origin of the low-lying soft modes is still not fully
understood, except for the case of lone pair electrons
[180,190].

Unlike the rattling motion that is vibrating locally in cage
structures, similar states could exist in which the weakly
bonded atoms vibrate with much larger thermal atomic dis-
placement parameters (ADPs) in the system, called rattling-
like motion [142]. In materials such as filled skutterudites
and Cu3SbSe3 (Figure 21(a)), this vibration will lead to the
atomic-level heterogeneity and the mixed part-crystalline-
part-liquid structure, and thus the rattling-like thermal
damping due to the collective soft-mode vibrations, which is
similar to the Boson peak in amorphous materials [191].

Figure 21(b) shows that in Cu3SbSe3, the large ADPs of a set
of Cu atoms (Cu1z atoms vibrate along the z-direction, and
Cu2xz atoms vibrate along the x-z plane), which dominate
the rattling-like vibration, present the strong anharmonic
potentials. Accordingly, such a rattling-like mode induces
the fluid-like flow of atoms and presents a more thermal
damped peak in the phonon density of states compared with
the single rattling mode, as shown in Figure 21(c) and (d). As
a result, the dynamic fluctuations of a set of atoms, which are
weakly bonded to the rest of the lattice, can cause the part-
crystalline-part-liquid states, leading to strong phonon
damping.

5 Effect of external stimuli

In sect. 4, we discussed the intrinsic origin of phonon an-
harmonicity and introduced how the electrons, atoms,
bonding, and phase structures account for the anharmonic
behaviors. However, phonons are very sensitive to the ex-
ternal environment, such as temperature [40,87,140], pres-
sure [87,192], electric fields [193,194], and magnetic fields
[195,196], which may dramatically influence the lattice dy-
namics and cause various novel phenomena in solids.
Herein, the temperature and pressure-induced phonon an-
harmonicity will be shortly introduced. Details can be found

![Figure 16](Color online) Low thermal conductivity induced by the lone
pair electrons in the Cu-Sb-Se compounds [142]. (a) Schematic plots of the
local environment of Sb atoms in Cu3SbSe4, Cu3SbSe2, and CuSbSe2.
Shaded sticks represent the Sb–Se bonds, and dashed lines represent lone
pair 5s electron orbital of Sb atoms. (b) Measured thermal conductivities of
these three compounds. Copyright (2011), American Physical Society.

![Figure 17](Color online) Schematic plots of origin of resonance bonding for Sb [162]. The same limited bonding states in an undistorted Sb phase are
shown in the left and right panels. The resonance bonding phase, formed from the minimizing energy by a hybrid wave function in solids, is shown in the
middle panel. Copyright (2017), American Chemical Society.
Figure 18  (Color online) Normalized traces of the interatomic FCs tensors versus the atomic distances [153]. (a) Lead chalcogenides and SnTe, (b) NaCl and InSb, (c) Bi₂Te₃, and (d) Bi and Sb. Circled elements indicate the interactions between the corresponding atom and other atoms. Copyright (2014), Springer Nature.

Figure 19  (Color online) Strong anharmonicity induced by the resonant bonding that leads to the low thermal conductivity of PbTe. (a) Electron charge density of cubic PbTe in the (001) plane, revealing the large delocalized electron density [164]. Copyright (2011), American Physical Society. (b) Phonon dispersions obtained from INS for PbTe at 300 K, showing the avoided crossing of LA and TO phonon branches. The harmonic dispersions calculated with the DFT are shown as white solid lines [166]. Copyright (2011), Springer Nature. (c) Cumulative thermal conductivity \( \kappa_c \) as a function of the mean free path \( \lambda \). \( \kappa_{ave} \) represents the averaged values of the two TA branches. The much smaller value of LA originates from the strong scattering by the anharmonic TO phonons [168]. Copyright (2012), American Physical Society.

Figure 20  (Color online) Phonon anharmonicity in cage structure. (a) Schematic of the cage structure and guest potential well for the Ba(2) in \( \beta \)-Ba₈Ga₁₆Sn₃₀. The fourfold potential minima (24k site) are offset by 0.43 Å away from the cage center (6d site) of the cage \[171\]. Copyright (2008), AIP Publishing. (b) Phonon dispersions for the on-center Ba₈Ga₁₆Sn₃₀. (c) Phonon dispersions for the off-center \( \beta \)-Ba₈Ga₁₆Sn₃₀. Solid and dash lines represent the longitudinal and transverse modes, respectively. The shaded regions bounded by the solid and dash lines indicate the broadening induced the off-center vibrations. Dotted lines represent the long-wave limited acoustic branches \[177\]. Copyright (2011) by the author.
from the cited work mentioned above.

5.1 Temperature effect

Theoretically, the temperature-dependent effect is the primary stimulus that leads to the anharmonicity introduced in phonon systems [6]. At elevated temperatures, the higher-order (anharmonic) terms in eq. (1) cannot be negligible, and the anharmonic effects will become more and more prominent with increasing temperatures. The temperature effects, such as the phonon frequency shifting and damping, were discussed in various materials above. Here, we will discuss another interesting anharmonic phenomenon related to the temperature, which is known as the liquid-like thermal vibration in the superionic compounds, such as Cu$_{2-\delta}$X (X=Se/S) [197,198], MCrX$_2$ (M=Cu/Ag, X=Se/S) [199-202] and AgCuX (X=S/Se/Te) [203,204]. In these materials, the lattice exhibits crystalline order, while the atoms follow the long-range diffusion [205]. Thus, the thermal conductivity is strongly reduced in a solid-state by a remarkable strong anharmonic effect—the breakdown of acoustic phonon transport in a host lattice with a liquid-like component, based on the notion that liquids do not propagate shear waves [206].

In this case, the acoustic phonons (both the longitudinal and the transverse phonons) are significantly damped as temperature rises in the ordered phase. Interestingly, above the order-disorder transition temperature, the transverse acoustic phonons are dramatically suppressed (melting) through the ultrafast dynamical disorder. Such behavior may be explained beyond the rigorous definition of phonon, which is a collective excitation in a well-defined lattice. Meanwhile, the LA mode is strongly scattered but survives and is thus responsible for the intrinsically ultralow lattice thermal conductivity [207,208]. Despite such context, it has still been argued that the strong anharmonic low-lying rattling phonons could be the source of thermal transport suppression [185,209,210]. For example, in a recent work of CuCrSe$_2$, there exists an order-disorder transition around 363 K [211] (Figure 22). At low temperature (Figure 22(a)), the Cu ions occupy only the $\alpha$ sites ($R3m$ symmetry); warming across $T_{\text{ord}} \sim 363$ K (Figure 22(e)), the Cu ions across $\alpha$ and $\beta$ sites with equal occupancies; above $T_{\text{ord}}$, the Cu ions undergo “superionic” quasi-2D diffusion in their occupied sublattice ($R3m$ symmetry) [212]. By tracking the evolution of the CuCrSe$_2$ lattice dynamics from 10 to 650 K (Figure 22(b)-(d)), it can be seen that the low-energy phonon band ($\sim 8$ meV) softens and broadens on heating and eventually spread over the low-energy transfer range above $T_{\text{ord}}$. 

Figure 21 (Color online) Ratting-like motion in Cu$_3$SbSe$_3$ [129]. (a) Crystal structure of Cu$_3$SbSe$_3$. (b) Calculated ADPs and the corresponding atomic projections for the different atoms. Inset is the calculated potentials for the five nonequivalent atoms. (c) Schematic plots of the rattling-like thermal damping (upper left) in materials with chemical bond hierarchy and single-rattle phonon in filled CoSb$_3$ (upper right). The lower panel represents the part-crystalline part-liquid structure. (d) Partial phonon DOS of Cu$_3$SbSe$_3$. $x$, $y$, and $z$ indicate the vibration directions. Copyright (2014), PNAS.
With increasing temperature, this behavior shows a strong anharmonic effect and the intensities of Bragg peaks and acoustic phonons (both LA and TA) remaining visible.

Such behavior can be further understood from Figure 23, in which the low-energy peak of phonon DOS noticeably softens and broadens with increasing temperature (Figure 23(a)). In Figure 23(b) and (c), the projected partial phonon DOS reveals that the 8 meV peak arises from in-plane phonons dominated by the vibrations of Cu atoms, which indicates the Cu atoms undergo large-displacement quasi-two-dimensional (quasi-2D) vibrations in this energy region in the ordered phase. Subsequently, the vibration of Cu atoms becomes delocalizing and diffusive upon heating into the superionic phase, leading to an overdamped peak (corresponding to large anharmonic oscillations). The strong anharmonic vibration of Cu atoms is revealed by the AIMD trajectories (Figure 23(d) and (e)). It is found that the Cu atoms localize around the $\alpha$ site at 300 K (ordered), while delocalize across $\alpha$ and $\beta$ ($z=1$) sites at 500 K (disordered). This evidence indicates that the temperature-dependent anharmonic TA modes remain well defined through the superionic transition, whereas the specific phonon quasi-particles break down due to lattice anharmonicity and disorder.

### 5.2 Pressure effect

It is worthwhile mentioning that the temperature effect includes two components: change of lattice volume and increase of vibrational amplitude of atoms. The former is known as the implicit anharmonicity, i.e., the quasi-harmonic behavior in lattice dynamics, while the latter is known as the explicit anharmonicity [192,213]. Pressures distort the electron cloud and affect the equilibrium spacings between

![Figure 22](image1.png)

**Figure 22**  (Color online) Anomalous atomic dynamics in CuCrSe$_2$ [211]. Crystal structures of room- (a) and high-temperature (e) phase of CuCrSe$_2$. The half-white-half red spheres represent the occupancy of Cu atoms on both $\alpha$ and $\beta$ sites in the high-temperature phase. (b)-(d) $S(Q, E)$ measured by INS at 200 (b), 350 (c), and 650 K (d). (b)-(d) show that the dispersive acoustic phonons remain visible in the superionic phase. Copyright (2018), Springer Nature.

![Figure 23](image2.png)

**Figure 23**  (Color online) Temperature-dependent anharmonic evolutions of Cu-dominated phonon modes [211]. (a) Neutron-weighted DOS with increasing temperatures. The trace labeled by shading is the DFT results renormalized by neutron weighting and convolution with the instrument energy resolution. (b) and (c) are the out-of-plane and in-plane DOS, respectively. The AIMD trajectories for the Cu atoms show the localization of Cu atoms around $\alpha$ site ($z=0$) at 300 K (d), compared with the delocalization of Cu atoms across $\alpha$ and $\beta$ ($z=1$) sites at 500 K (e). Copyright (2018), Springer Nature.
nuclei, thus the volume of the lattice is changed. Although the phonon frequencies also shift versus pressure at a fixed temperature, this mechanism ignores the vibrational amplitude of atoms, which can only be regarded as quasi-harmonic behavior. However, it is beneficial to decouple the pure anharmonic and quasi-harmonic effects by comparing the temperature and the pressure measurements (sect. 5.3). Therefore, it is necessary to have a brief introduction to the pressure-induced phonon frequency shifts.

In Figure 24(a), the solid curves are fits with the quadratic functions: \( \omega_{\text{Si}} = 523.88 + 5.1P - 0.062P^2 \) and \( \omega_{\text{Ge}} = 304.64 + 4.02P - 0.059P^2 \) for Si and Ge, respectively [214]. It can be seen that the quadratic terms are sufficiently small and can be ignored, then, the frequency shifts linearly with pressure. This is analogous to the temperature-induced quasi-harmonic effect in eq. (3). As discussed above, the pressure stimuli changes the unit-cell volume only, and the phonon-phonon interactions can be ignored at zero temperature. At the fixed temperature of 6 K, the pressure-dependent phonon line-widths, which were fitted by the least square functions, are follow the linear functions \( \Gamma_{\text{Si}} = 1.08 + 0.137P \) and \( \Gamma_{\text{Ge}} = 0.51 + 0.037P \) (Figure 24(b)). Although these linewidths are small to be considered (without considering the involved finite temperature and the sample mosaic), it is still associated with the phonon decay channels changed by the pressure-induced phonon frequency shifts [214].

5.3 Practical evaluation of anharmonic interactions

As discussed above, the frequency shifts can be induced either by pressure or temperature. However, it is valuable to clarify that whether the frequency varies the same when it is induced by temperature, measured at constant pressure and when, for the same volume variation induced by pressure, measured at a constant temperature. In other words, whether \((\text{dln} v / \text{dT})_p\) equals \((\text{dln} v / \text{dP})_T\)? Such problem can be investigated by the isothermal \((\gamma_T)\) and isobaric \((\gamma_P)\) mode Grüneisen parameters, which both quantify the change in frequency of a given mode to the change in volume of the unit cell \(V\), expressed respectively as:

\[
\begin{align*}
\gamma_T &= \left( \frac{\partial \ln v}{\partial \ln V} \right)_T, \\
\gamma_P &= \left( \frac{\partial \ln v}{\partial \ln V} \right)_p.
\end{align*}
\]

The relationship between the implicit and explicit terms can be described as:

\[
\frac{\partial v}{\partial T} = \frac{\partial \ln v}{\partial T} \times \left( \frac{\partial \ln V}{\partial v} \right)_p + \left( \frac{\partial \ln V}{\partial T} \right)_v.
\]

The term \((\partial v/\partial T)_p\) can be determined by measuring the phonon spectrum as a function of temperature at constant pressure, while the volume-dependent implicit term \([\partial v(P, T)/\partial P]_T\) can be obtained by measuring the phonon spectrum under pressure at a constant temperature. The explicit contribution of anharmonicity is

\[
\left( \frac{\partial \ln V(P, T)}{\partial T} \right)_v = \alpha(\gamma_T - \gamma_P) = A,
\]

where \(\alpha\) is the volume coefficient of thermal expansion, and \(A\) is the anharmonic parameter.

In the quasi-harmonic approximation, \(\gamma_T\) and \(\gamma_P\) are equal, and the anharmonic parameter \(A\) is zero. The ratio \(\gamma_T/\gamma_P\) is

Figure 24  Pressure-induced phonon frequency shifting (a) and broadening (b) for Si and Ge by Raman spectra [214]. The solid lines represent the fitted functions. The dashed lines are calculated results. Copyright (1997), American Physical Society.
called the implicit fraction [215,216]. Thus, the explicit anharmonicity, determined by the thermal population of vibrational levels, can be successfully extracted by experiments under external temperature and pressure stimuli. The temperature dependence of the different implicit and explicit contributions is defined as [217,218]:

\[ v(T) = v_0 + \Delta \varphi(T) + \Delta \varphi(T). \]  \hspace{1cm} (13)

The implicit frequency shift can be written as [71]:

\[ \Delta \varphi(T) = -v_0kT/16[\Phi^{(2)}/ \Phi^{(0)}]. \]  \hspace{1cm} (14)

and the explicit frequency shift can be written as [219]:

\[ \Delta \varphi(T) = \Omega(T) = \frac{C[1 + N(x_1) + N(x_2)]}{1 + 3N(x_1) + 3N(x_2)^2}. \]  \hspace{1cm} (15)

where \( C \) and \( D \) correspond to a three-phonon and a four-phonon process, respectively, \( N(x) \) is the Bose-Einstein population factors of the different interacting phonons, and \( x \) is the index of the phonon mode \( (\omega_i) \).

The temperature and pressure-induced thermodynamic properties make it possible to decouple the quasi-harmonic and anharmonic effects experimentally. Based on the description above, such decoupling can be obtained not only by the difference between the isothermal \( \gamma_T \) and the isobaric \( \gamma_P \) mode Grüneisen parameters but also by the corresponding heat capacity, thermal expansion coefficient, and phonon entropy, etc. [4,5,87,216].

6 Examples of phonon anharmonicity in advanced materials

As discussed above, anharmonic phonons involve the vibrations of atoms with large amplitudes. Such anomalous lattice vibration often determines the thermodynamics (e.g., thermal expansion and thermal conductivity), elastic, dielectric properties, and crystal structure of materials. In recent decades, a number of novel phenomena induced by the phonon anharmonic effects have been observed, such as ferroelectric phase transition [220,221], negative thermal expansion [41,222], ultralow thermal conductivity [39,42], making the concept of “anharmonic engineering” ever-increasingly valued by scientists. In this section, some applications of phonon anharmonicity that account for the novel physical phenomena in the related advanced materials will be introduced.

6.1 Negative thermal expansion materials

Thermal expansion is quantified by the relative change in volume, \( \Delta V/V \), for a given change of the temperature \( \Delta T \). The thermal expansion coefficient [223]:

\[ \alpha_v = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \]  \hspace{1cm} (16)
equals zero in the harmonic approximation (\( P \) is the pressure and \( T \) is the temperature). This can be easily derived from the Gibb distribution for the potential energy [224], which is quadratic in the atomic displacements \( \mu_j \). The thermal expansion coefficient is a positive quantity in the usual case when a positive change in temperature results in an increase in volume. However, in the negative thermal expansion (NTE), the volume change is negatively related to the elevated temperature.

Even though the thermal expansion is an inherent process that comes from the anharmonic effect, one can employ the Grüneisen theory, phonon frequencies change depending on the volume (quasi-harmonic approximation), to explain the NTE behavior. In a crystal, we have a great number of normal phonon modes, so one defines a set of mode Grüneisen parameters:

\[ \gamma_i = -V \frac{\partial \omega_i}{\partial \ln V} = -\frac{\partial \ln \omega_i}{\partial \ln V}. \]  \hspace{1cm} (17)

These are combined to give the mean Grüneisen parameter:

\[ \gamma(T) = \frac{1}{C_v(T)} \sum c_i \gamma_i, \]  \hspace{1cm} (18)

where \( C_v(T) \) is the heat capacity and \( c_i \) the contribution of each phonon to the overall heat capacity, and thus, the volume thermal expansion for a crystal can be expressed as:

\[ \alpha_v = \frac{\gamma(T)C_v(T)}{VB_T}, \]  \hspace{1cm} (19)

where \( B_T = -V(\partial P/\partial V)_T \) is the isothermal bulk modulus. Since \( C_v, B \) and \( V \) are necessarily positive for materials in thermodynamic equilibrium, the mode Grüneisen parameters are the critical quantities for whether thermal expansion is positive or negative. It is worth noting that if we anticipate that the Grüneisen theory applies to NTE, it is required that the overall Grüneisen parameter is a negative value, not just one specific mode Grüneisen parameter.

Here, we introduce another recent work of ScF3 as an example to explain how phonon anharmonicity acts on NTE behavior. In Figure 25 [128], the low-energy rigid unit modes (RUM), [ScF6] octahedra pivot about corner-shared F atoms (see the crystal structure in Figure 25(d)), have ultralow phonon energies (Figure 25(a)) and large negative Grüneisen parameters (Figure 25(b)), such as at \( M \) and \( R \) points. The lowest energy mode at \( R \) point exhibits a quartic potential (Figure 25(c)), which suggests the quasi-harmonic is not reliable here, showing strong anharmonic effect. The simple mechanical model in Figure 25(d) and (e) [128], describing the transverse motion of F atoms, helps to explain the inherent relationship between phonon anharmonicity and NTE. For a static state (\( T = 0 \)), the two Sc atoms and the F atom
(x=0) are positioned in equilibrium. In this case, there is no net force on the atoms. When the F atom starts moving (assuming the Sc atoms are fixed at their lattice positions), the transverse restoring force on the F atom mostly depends on the elongations of the springs. It goes as \(1 - \cos \theta\) times the resolved transverse force, giving a transverse restoring force going as \(x^3\). In this case, the total potential of the F atom is \(U = kx^4/4d^7\), which is consistent with the quartic potential of the \(R^{4+}\) mode.

NTE exists in an extensive range of materials [128,222,225], such as zirconium tungstate [226], zirconium vanadate [227], scandium tungstate [228], most of which can be described in terms of networks, or frameworks, of coordination polyhedra (e.g., perovskite or perovskite-like). Due to their novel structures, the origin of the NTE is closely related to phonon anharmonicity. With the NTE behaviors, a number of potential applications are available for these materials [229], for example, producing composites with near-zero thermal expansion for applications where rapid temperature changes limit the performance.

### 6.2 Ferroelectrics and soft mode

Ferroelectric materials have garnered much attention owing to their remarkable properties and potential applications [230], such as storages [231], transducers [232], and detectors [233]. In displacive ferroelectrics, the phase transition is directly influenced by the soft anharmonic phonon mode [234-236]. The soft mode has a low frequency resulting from the interplay between the local restoring force and the long-range dipole interaction [237]. Due to the unique temperature-dependent damping and softening behavior, the soft mode usually behaves anharmonically in the system. In this section, the soft mode and displacive phase transitions will be briefly reviewed.

The soft mode theory of phase transitions was firstly proposed by Cochran [238] and Anderson [239]. Typically, a soft mode is a low-frequency transverse optic phonon mode in the high-temperature symmetric phase at the zone center, whose frequency decreases on cooling until it falls to zero [234]. At Curie temperature, the crystal is unstable and undergoes a phase transition to a lower-symmetry phase by freezing the atomic vibration of the soft mode. In a microscopic view, the ferroelectric phase transition originates from the relative displacement of anion and cation atoms, which gives rise to a net dipole moment of the unit cell, and hence the breakdown of inversion-symmetry (Figure 26(a) and (b)). Figure 26(c) shows the temperature dependence of the central phonon mode of typical ferroelectric BaTiO\(_3\) [234]. It can be seen that the central mode softens with decreasing
temperature. The transition on cooling also occurs at any point where a phonon frequency approaches to zero. There is a soft mode on the low-temperature side of the transition as well, which increases in frequency on cooling, associated with the instability that occurs on heating.

The other way to describe the soft mode is based on the harmonic phonon dispersion calculations, in which the calculated phonon frequency in a high-temperature symmetric phase is imaginary. However, it reaches a real value in the corresponding lower-temperature and lowers symmetric phase. The lower symmetry structure can be regarded as a small distortion from the higher-symmetry structure, in which the soft mode is frozen. With the soft modes from the harmonic approximation calculations, one can reach the possible ferroelectric structures by freezing the sole soft mode or a combination of soft modes. This is a standard approach in the ferroelectric community [240-242].

Another type of phase transition is related to the soft mode with wave vectors at zone boundaries, which usually emerges in anti-ferroelectric systems. In this case, the soft phonons can be either acoustic or optic modes since the distinction between the two types of mode is unclear at zone boundary (Figure 26(d) and (e)). The zone boundary soft mode leads to the unit cell of the low-temperature phase doubling in one or more directions. When the soft mode at zone boundary is frozen below Curie temperature, it induces the relative displacement of anion and cation atoms in opposite directions in the neighboring unit cell, canceling the dipole moments and forming the anti-ferroelectricity. Figure 26(f) shows the temperature dependence of the zone center and boundary optical mode frequencies of PbZrO$_3$ [236]. With decreasing temperature, all the modes soften completely at $T_c$ (507 K), driving the anti-ferroelectric phase transition of PbZrO$_3$.

There are also many other non-ferroelectric phase transitions related to soft modes, such as quartz with the soft mode at zone center [243], ferroelastic phase transition with transverse acoustic soft mode [244], and incommensurate phase transition with the soft mode at q wave vector between zone center and zone boundary [245]. In all these cases, they are all symmetry-breaking phase transitions driven by atomic displacements and associated with soft modes.

### 6.3 Thermoelectrics and low thermal conductivity

Thermoelectric materials are widely known for the direct and reversible conversion of heat to electricity. It is a most urgent and primary goal to enhance the heat-to-electricity conver-
sion efficiency in the past few decades \cite{246-248}. The thermoelectric figure of merit, $ZT=S^2\sigma T/(\kappa_e+\kappa_l)$, which determines the maximum efficiency of the conversion, depends on the Seebeck coefficient ($S$), the electric conductivity ($\sigma$), and the electric ($\kappa_e$) and lattice ($\kappa_l$) thermal conductivities \cite{247,249}. Due to the complexity of interactions between the electrical parameters, tuning the lattice thermal conductivity was proposed as a powerful stage to enhance $ZT$ \cite{250}. With this concept, reducing the lattice thermal conductivity by a so-called “phonon engineering” has been studied in many thermoelectric materials \cite{44,251}. In this section, the phonon anharmonicity and the driving mechanism of thermal conductivity reduction will be discussed.

When only harmonic phonons are considered, i.e., neglecting the phonon-phonon interactions and phonon scattering by any defects or quasi-particles, the phonon mean free path $l$ approaches to infinity. This means the lattice thermal conductivity will be infinitely large for perfect, isotopically homogeneous, insulating crystals. It is the anharmonic effect that induces the finite thermal conductivity in materials. The lattice thermal conductivity is determined by the phonon group velocity $v_\lambda$ and phonon scattering rate $\tau_\lambda$:

$$\kappa_1 = \frac{1}{3\nu} \sum_{\lambda} C_{A\lambda} v_\lambda^2 \tau_\lambda.$$  \hfill (20)

The scattering rate in the mean free path $l=v_\lambda\tau_\lambda$ is inversely related to the phonon damping $\Gamma$ in eq. (6), $\tau_\lambda^{-1} = 2\Gamma_\lambda$. However, from a continuum medium theory, any process of phonon-phonon interaction cannot lead to a finite thermal conductivity since the momentum is conserved for any specific phonon-phonon process, and any redistribution of the momentum among the phonons will not change the energy current of the phonon gas as a whole. In crystals, Umklapp processes are possible when the momentum is conserved with the accuracy of some nonzero reciprocal lattice vector $q$, and only these processes will lead to the relaxation of the energy current and the finite $\kappa_l$ \cite{252}.

Here, we introduce a recent work of $\alpha$-MgAgSb, a new type of promising thermoelectric material \cite{253-255}, to show the relationship between phonon anharmonicity and $ZT$ (Figure 27) \cite{254,256}. In the primitive cell of $\alpha$-MgAgSb, there are a large number of atoms (24 atoms), giving a very complicated phonon dispersion. Mg and Sb atoms jointly form the distorted rocksalt sublattice, while Ag atoms are filled in the distorted cubes (Figure 27(a)), leading to the intrinsic weak Ag-Sb bonding. On the one hand, the TA phonons are almost fully scattered by the intrinsic distorted rocksalt sublattice (Figure 27(b)), making LA phonons the primary heat carrier. However, on the other hand, the slope of the LA is abruptly suppressed by the strong anharmonic LO

Figure 27 (Color online) Relationship between phonon anharmonicity and $ZT$ in $\alpha$-MgAgSb. (a) Crystal structure of $\alpha$-MgAgSb with the distorted Mg–Sb rocksalt sublattice, where half of the Mg–Sb distorted cubes are filled with Ag atoms. (b) Dynamic (upper) and static (lower) structure factors measured by neutron scattering (left panel). The magenta and green lines are calculated transverse and longitudinal phonons, respectively. The energy-cut data at 2.0, 2.5, and 3.0 meV are shown in the right panel. Copyright (2020) by the author. (c) Schematic illustration of the microscopic origin of low lattice thermal conductivity for $\alpha$-MgAgSb. (d) and (e) show the lattice thermal conductivity and $ZT$ values of Yb doped $\alpha$-MgAgSb, respectively. (a) and (b) are figures from ref. [256], while (c), (d), and (e) are figures from ref. [254]. Copyright (2017), Elsevier.
phonon, known as the “avoided crossing” interaction, which further blocks the heat transport [254]. Such unique properties make α-MgAgSb a highly anharmonic system (Figure 27(c)), which leads to its intrinsic ultralow thermal conductivity (Figure 27(d)) via suppressing the group velocities and increasing the phonon scattering rates, and thus the high ZT (Figure 27(e)).

In addition to the examples mentioned in this section, other thermoelectric materials related to phonon anharmonicity are discussed above as well, such as the SnSe, PbTe Cu3SbSe3, and Ba8Ga16Sn30. For thermoelectric materials, phonon anharmonicity is an important topic because it helps to reduce the thermal conductivity and thus enhances the ZT value. There are many strategies to reduce the thermal conductivity, such as “Phonon-glass Electron-crystal” [257], “Phonon-liquid Electron-crystal” [258], and lowering the dimensions [259]. Several classes of thermoelectric materials are currently under investigation, including complex chalcogenides [260,261], skutterudites [262], half-Heusler alloys [263], and metal oxides [264], etc. Besides thermoelectric materials that required low thermal conductivity, there are also various applications in materials related to low thermal conductivities, such as thermal barrier coating, thermal insulators, and heat sinks.

6.4 Two-dimensional materials

2D materials have attracted great interest due to their remarkable physical properties, making them to be ideal candidates for next-generation nanoscale devices and ideal platforms for fundamental physical researches. Recently, the study on phonon anharmonicity has been reported in various 2D materials, such as graphene [92] and transition metal dichalcogenides, MX2 (M=Mo, W; X=S, Se, Te) [92,265].

Here, we introduce one recent work to show how phonon anharmonicity emerges in graphene-based materials [92]. As shown in Figure 28(a) and (b), compared with the Si mode in silicon, the typical featured G and 2D modes of graphite both soften with nonlinear dependence of increasing temperature. For G mode, the four-phonon scattering process dominates the softening, while for the 2D mode, it also softens nonlinearly with temperature but was not suitable to use the three- and four-phonon scattering processes to account for the contributions from anharmonicity. The slope dPos(2D)/dPos(G) is 1.52. Figure 28(c) shows the phonon linewidths of G, 2D, and Si modes. It is found that the 2D and Si modes both show linear-like dependence on temperature. For G mode, the linewidth shows nonlinear temperature dependence. The contribution of electron-phonon coupling to the phonon linewidth dominates below 700 K, leading to the decreasing profile, while the contribution of anharmonicity increases with temperature, leading to the increasing profile after 700 K.

6.5 Other materials

The present review mainly focuses on phonon anharmonicity and the dominated phenomena in advanced materials. However, there are also materials closely related to phonon-particle interactions, such as ferromagnetics [266], multiferroics [267], superconductors [268], charge density wave materials [269], and some Weyl semi-metals [270]. In these cases, phonons can be scattered by electrons or spins, and the driving mechanism is known as electron-phonon or spin-phonon coupling. For example, the electron-phonon coupling drives the formation of the electron pairs responsible for superconductivity [268,271]; the spin-phonon coupling drives multiphase transitions in perovskite oxides [272]. For such strong multi-body interactions involving phonons, one can treat them as non-harmonic behaviors [4] beyond the scope of the anharmonic effects. The interested readers can find more details in the cited works.

7 Summary and outlook

Anharmonicity is, for a long time, considered as a perturbation from the ideal harmonic ground state. With the development of anharmonic phonon theories, modern experimental techniques, and computational methodologies, phonon anharmonicity and many novel thermodynamic properties of materials are well investigated. In this review, we summarized the recent progress of phonon anharmonicity, including the fundamental theory, the characterization techniques with both experiments and computational simulations, the origin that induced intrinsically and extrinsically, and some novel phenomena induced by phonon anharmonicity in various advanced materials. Although great progress has been made in the study of phonon anharmonicity in recent years, it is still a complicated, challenging, but exciting research field. The challenge arises because one should consider how phonons interact with other phonons or with other particles (or quasi-particles), while it is exciting because this interaction induces many novel properties. Phonon anharmonicity attracts more and more attention, and the following aspects are still rarely concerned and potentially promising.

(1) Anharmonic phonon interactions with other particles. In some systems, one should consider not only how phonons interact with other phonons but also with other particles, such as electron-phonon coupling [271,273], spin-phonon coupling [274,275], and phonon-spin-orbit coupling [276,277]. These complicated correlations will jointly induce many novel properties. However, since the particles are sensitive to the crystal field and thus have a significant impact on the atomic vibrations of lattice, it is a challenge to distinguish or extract how much phonon anharmonicity...
contributes to the novel property, and the origin of phonon anharmonicity in these systems. Investigations on such issues are essential for not only acquiring an in-depth understanding of the microscopic mechanism but also developing the anharmonic theories in the application of these novel properties.

(2) Quantifying the phonon anharmonicity. To our knowledge, most of the mentioned works above are focused on whether the phonon anharmonicity exists or estimating the strength of phonon anharmonicity in the system. However, due to the experimental and simulative difficulty, there is not yet a standard criterion for quantifying the anharmonicity of a real system, and this can be of importance for anharmonic engineering. Therefore, it is necessary to develop experimental techniques and simulation approaches to quantify the phonon anharmonicity.

(3) Investigating phonon anharmonicity in extreme conditions. Although extensive investigations of phonon anharmonicity have been studied, less attention has been paid in extreme conditions. Properties of materials in extreme

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Figure 28  (Color online) Phonon anharmonicity in graphene-based material [92]. (a) Contour plot of Raman intensity of G (left) and 2D, (middle) modes in graphite and Si (right) mode in silicon. (b) Phonon softening of G (left) and 2D, (middle) modes and their correlation (right). (c) Phonon linewidths of G (left), 2D, (middle), Si (right) modes. Measured thermal conductivities of these three compounds. Squares are the experimental data extracted from the Raman spectrum. Solid lines are the overall fitting data. Dashed lines are individual contributions. Copyright (2019), Elsevier.
conditions become more complicated, especially for phonon anharmonicity, which originates from anharmonic potentials that can be changed by external stimuli. Potential areas perhaps to be concerned in the future include the extreme temperature and pressure conditions, phase transition, interface, and nanoparticles where the bonding state and the phonon scattering processes are more complicated.

(4) Developing the anharmonic engineering techniques. Up to now, the research on phonon anharmonicity mainly focuses on its characterization, mechanism, and its driving novel properties. However, little attention has been paid to anharmonic engineering, e.g., utilizing anharmonicity to optimize the performance of materials. Therefore, the approaches and techniques of anharmonic engineering are in urgent need for manufacturing novel devices with better performance.

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