# Lattice Dynamics of SnSe Single Crystals Studied by Inelastic Neutron Scattering Spectrometers at the China Advanced Research Reactor (CARR)

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## Abstract

Inelastic neutron scattering (INS) is a powerful nondestructive nuclear detection technique, which plays a unique role in probing the lattice dynamical properties of advanced functional materials. The China Advanced Research Reactor (CARR) neutron science platform is equipped with a suite of high-performance inelastic neutron scattering spectrometers, providing crucial technical support for condensed matter physics and material science research. In this work, high-quality single-phase SnSe thermoelectric single crystals were prepared via the temperature gradient method, and their crystal structure, phase purity and orientation were characterized by combining XRD, SEM/EDS and neutron single-crystal diffraction techniques. Utilizing three complementary INS spectrometers (BOYA, Bamboo and CIAE-JCNS) at CARR, the lattice dynamical behaviors of longitudinal and transverse acoustic phonons at the (400) crystal plane of SnSe were systematically investigated at room temperature. We clearly clarified the physical origin of scattering intensity asymmetry along the (H00) longitudinal direction, the implication of off-principal-axis signals in two-dimensional phonon maps, the lattice dynamical responses in the high-Q region, and the competitive relationship between neutron scattering cross-section enhancement and Debye-Waller factor attenuation. The obvious phonon energy softening, slope transition of acoustic phonon branches and sharp reduction of phonon lifetime in the high-energy region directly reveal the strong lattice anharmonicity and intrinsic structural anisotropy of SnSe, which is the microscopic root cause for its ultra-low lattice thermal conductivity. This work not only deepens the understanding of the phonon transport mechanism in SnSe thermoelectric materials, but also further validates the excellent performance and application potential of CARR inelastic neutron scattering spectrometers in the field of

condensed matter characterization, enriching the application cases of nuclear scattering technology in advanced material research.

## Full Text

## Preamble

Lattice Dynamics of SnSe Single Crystals Studied by Inelastic Neutron Scattering Spectrometers at the China Advanced Research Reactor (CARR) Authors: Hongliang Wang[1],[2], Lijie Hao[1],[2],, *Siqin Meng[1],[2], Xiaoyan Ma[3], Shiliang Li[3], Jinchen Wang[4], Juanjuan Liu[4], Ao Shen[1],[2], Jianxiang Gao[1],[2], Kexuan Duan[1],[2], Tianfu Li[1],[2], Kai Sun[1],[2], Dongfeng Chen[1],[2],* Affiliations [1]Institute of Nuclear Physics, China Institute of Atomic Energy, Beijing 102413, China [2]Key Laboratory of Neutron Scattering Application Technology, CNNC, Beijing 102413, China [3]School of Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China [4]School of Physics, Renmin University of China, Beijing 100872, China *Dongfeng Chen. E-mail address: dongfeng@ciae.ac.cn* Lijie Hao. E-mail address: haolijie@ciae.ac.cn Abstract: Inelastic neutron scattering (INS) is a powerful nondestructive nuclear detection technique, which plays a unique role in probing the lattice dynamical properties of advanced functional materials. The China Advanced Research Reactor (CARR) neutron science platform is equipped with a suite of high-performance inelastic neutron scattering spectrometers, providing crucial technical support for condensed matter physics and material science research. In this work, high-quality single-phase SnSe thermoelectric single crystals were prepared via the temperature gradient method, and their crystal structure, phase purity and orientation were characterized by combining XRD, SEM/EDS and neutron single-crystal diffraction techniques.

Utilizing three complementary INS spectrometers (BOYA, Bamboo and CIAE-JCNS) at CARR, the lattice dynamical behaviors of longitudinal and transverse acoustic phonons at the (400) crystal plane of SnSe were systematically investigated at room temperature. We clearly clarified the physical origin of scattering intensity asymmetry along the (H00) longitudinal direction, the implication of off-principal-axis signals in two-dimensional phonon maps, the lattice dynamical responses in the high-Q region, and the competitive relationship between neutron scattering cross-section enhancement and Debye-Waller factor attenuation. The obvious phonon energy softening, slope transition of acoustic phonon branches and sharp reduction of phonon lifetime in the high-energy region directly reveal the strong lattice anharmonicity and intrinsic structural anisotropy of SnSe, which is the microscopic root cause for its ultra-low lattice thermal conductivity. This work not only deepens the understanding of the phonon transport mechanism in SnSe thermoelectric materials, but also further validates the excellent performance and application potential of CARR inelastic neutron scattering spectrometers in the field of condensed matter characterization, enriching the application cases of nuclear scattering technology in advanced material research.

Keywords: Inelastic neutron scattering; China Advanced Research Reactor (CARR); Neutron scattering spectrometer; SnSe single crystal; Lattice dynamics; Phonon transport

## Introduction

Neutron scattering technology underpins cutting-edge interdisciplinary research and critical engineering detection, and has become a key enabling technique for fundamental research in physics, chemistry, materials science, life science, energy and environmental science[1]. It also plays an irreplaceable role in strategic fields pertaining to national security and national economic development, such as nuclear energy and the nuclear industry[2]. The China Advanced Research Reactor (CARR) is a state-of-the-art high-flux, multi-purpose research reactor with a maximum power of 60 MW and a peak thermal neutron flux of approximately 8.0$×10^{14}$ $\mathrm{n \cdot cm^{-2} \cdot s^{-1}}$, equipped with 25 vertical experimental channels and 9 horizontal neutron beam ports. Based on the high-flux neutron source provided by CARR, the China Institute of Atomic Energy (CIAE) has constructed a comprehensive neutron science platform housing 18 advanced neutron spectrometers through independent innovation and international collaborative efforts[3, 4]. Neutrons possess intrinsic magnetic moments, exhibit high sensitivity to light elements, and enable unambiguous discrimination of isotopes and adjacent elements, rendering neutron scattering a unique and indispensable analytical technique for probing the microstructural and dynamical properties of matter[1].

The CARR neutron science platform integrates three core technical capabilities: neutron scattering, neutron imaging and neutron activation analysis, with neutron scattering being the primary technique for investigating the microstructural and dynamical properties of materials.

Neutron scattering is categorized into elastic and inelastic scattering based on whether neutron energy is conserved during the scattering process. In elastic neutron scattering, neutrons only change their propagation direction upon colliding with atomic nuclei, with negligible energy variation; this technique is predominantly used to study the static structures of materials (e.g., crystal and magnetic structures). In inelastic neutron scattering, neutrons exchange energy with atomic nuclei or magnetic moments, leading to measurable changes in neutron energy; this method is dedicated to probing the dynamical properties of materials (e.g., lattice vibrations, magnetic excitations and molecular motions). Inelastic neutron scattering directly measures the dynamic behaviors and excitation spectra of microscopic particles inside materials by probing the energy-exchange process during neutron-matter collisions, and thus serves as a pivotal approach to exploring the internal structure of matter and understanding its intrinsic dynamic characteristics.

Fig.1. Inelastic neutron spectrometers at the China Advanced Research Reactor: (a) and (b) Thermal neutron triple-axis spectrometer CIAE-JCNS and BAM-

BOO; (c) Cold neutron triple-axis spectrometer XINGZHI; (d) Cold neutron wide-range spectrometer BOYA Characterizing the complex dynamical properties of condensed matter often cannot be accomplished with a single spectrometer, and inelastic spectrometers covering distinct energy- momentum ranges can complement each other' s advantages to provide a complete picture of material dynamics. Four state-of-the-art inelastic neutron spectrometers have been commissioned at the CARR neutron science platform, shown in Fig.1, namely the thermal neutron triple-axis spectrometer (TAS) CIAE-JCNS and BAMBOO, the cold neutron TAS XINGZHI and the cold neutron wide-range spectrometer BOYA: (1) The thermal neutron TAS CIAE-JCNS was jointly constructed by the Jülich Center for Neutron Science (JCNS) of Forschungszentrum Jülich, Germany and CIAE in 2010, marking the first inelastic scattering spectrometer at CARR[5, 6]. This spectrometer offers six selectable incident neutron energies (5 meV, 15 meV, 17 meV, 34 meV, 50 meV, 116 meV) via the combination of three fixed take-off angles (26.8°, 41.4°, 74.3°) and two switchable monochromators (PG(002), Cu(200)), covering a broad incident energy range to meet the diverse measurement requirements of the high-Q region and the high-energy optical phonon branch. Both the neutron monochromator and analyzer (PG[002]) adopt a double-focusing design, which increases the incident neutron intensity by an order of magnitude. The neutron flux at the sample position reaches 5.0$\times$10^{7}$ $\mathrm{n \cdot cm^{-2} \cdot s^{-1}}$ (at a reactor power of 10 MW, Ei=34 meV, PG(002) monochromator) or 6.3$\times$10^{6}$ $\mathrm{n \cdot cm^{-2} \cdot s^{-1}}$ (at a reactor power of 10 MW, Ei =116 meV, Cu(200) monochromator). Selectable filters (graphite PG, erbium) further eliminate the interference of higher-order neutrons on experiments at specific energies[7]. (2) The thermal neutron TAS BAMBOO was co-constructed by the Institute of Physics, Chinese Academy of Sciences and CIAE in 2013. Equipped with a sapphire/$B_4C$ filter and a velocity selector (with a transmittance of approximately 80%), this spectrometer effectively enhances the monochromaticity and flux of neutrons after reflection by the double-focusing monochromator (PG(002)), significantly suppresses the background from incoherent scattering neutrons, and achieves an extremely low experimental noise level[8]. The neutron flux at the sample position can reach 7$\times$10^{7}$ $\mathrm{n \cdot cm^{-2} \cdot s^{-1}}$ (at a reactor power of 60 MW, Ei =34 meV). Continuous variation of the take-off angle enables stepless adjustment of the energy resolution, with an energy resolution of 0.3 meV at an outgoing neutron energy Ef =7.5 meV.

The incident neutron energy after filtration by the velocity selector can be continuously tuned in the range of 6–80 meV, with the outgoing neutron energy Ef $>$ 4 meV due to the limitation of the analyzer chamber, making this spectrometer particularly suitable for the accurate extraction of the lifetime of low-energy soft-mode phonons [9]. (3) The cold neutron TAS XINGZHI has been in operation since 2018[10], a collaborative effort between Renmin University of China and CIAE. This spectrometer employs a vertically focusing monochromator (PG(002)) and a double-focusing analyzer (PG(002)). The incident neutron beam is filtered for higher-order neutrons by a velocity selector, allowing the

incident neutron energy to be continuously adjusted in the range of 2.4–19.5 meV with an optimal energy resolution of 0.05 meV. Beyond the functionalities of a traditional neutron TAS, its most prominent feature is the integration of a complete neutron spin polarization analysis system, including an S-shaped bent tube polarizer and a mu-metal polarization analysis device[11]. (4) The cold neutron wide-range spectrometer BOYA was jointly built by Renmin University of China and CIAE in 2019. It adopts a vertically focusing monochromator (PG(002)) with an incident energy Ei range of 2.5–15 meV. The analyzer utilizes an innovative double curved crystal Rowland focusing (DCRF) technology, which simultaneously analyzes and detects signals across multiple energy channels (five fixed outgoing energies Ef : 3.0 meV, 3.5 meV, 4.0 meV, 4.5 meV, 5.0 meV) and a broad momentum range (covering a scattering angle of 119°). While optimizing the energy resolution (0.066 meV), its detection efficiency is two orders of magnitude higher than that of conventional TAS. This spectrometer can acquire wide momentum-energy space data in a single measurement, and is thus primarily dedicated to the study of low-energy lattice dynamics[10, 12].

Inelastic neutron spectrometers are important experimental apparatuses for probing the microscopic dynamical behaviors inside materials, with core functions including the measurement of magnetic excitations, phonon excitations, and crystal field excitations, as well as the determination of crystal and magnetic structures. By accurately measuring the energy and momentum transfer of scattered neutrons, these spectrometers directly acquire dynamic information of lattice and spin systems, with the dynamic structure factor $S(Q,\omega)$ as the core physical quantity, thereby revealing the underlying mechanisms of microscopic interactions in materials. Inelastic spectrometers possess meV-scale energy resolution and reciprocal space scanning capabilities, making them key tools for investigating low-energy elementary excitations in correlated quantum materials. Combined with various sample environments (e.g., electric field, magnetic field, high temperature, high pressure), can provide a complete physical picture from microscopic interactions to macroscopic physical properties for cutting-edge research directions including correlated electron systems and topological magnetic materials. Inelastic neutron spectrometers have important application value in the fields of thermoelectric materials, unconventional superconductors, quantum spin liquids, magnetically frustrated materials, and so on[13, 14].

Tin selenide (SnSe) single crystals have emerged as a research hotspot in the energy conversion field due to their ultra-low lattice thermal conductivity and excellent thermoelectric figure of merit (ZT) along specific crystal directions[15-19]. As a representative high-performance thermoelectric material, the outstanding thermoelectric performance of SnSe originates from strong lattice anharmonicity and intrinsic anisotropy, which jointly induce an extremely low lattice thermal conductivity. Taking advantage of the unique capabilities of inelastic neutron spectrometers in probing lattice dynamics, phonon spectrum measurements of SnSe single crystals can provide experimental support for identifying the key phonon modes dominating thermal transport, the strength of anharmonic inter-

actions, and the dynamical differences along different crystal directions. This work establishes the critical correlation between the microscopic lattice dynamics and macroscopic thermoelectric properties of SnSe, and provides a fundamental physical basis for understanding its exceptional thermoelectric performance[20-24]. By fully utilizing the complementary advantages of each inelastic spectrometer at CARR, we carry out a systematic experimental studies on the phonon dynamics of longitudinal and transverse acoustic phonons at the (400) crystal plane of SnSe thermoelectric single crystals at room temperature.

We elucidate the origin of scattering intensity asymmetry along the longitudinal (H00) direction, the physical implications of off-principal-axis signals in two-dimensional phonon maps, the dynamical behaviors in the high-Q region, and the competitive relationship between the enhanced scattering cross-section and Debye-Waller factor attenuation during measurements.

This study serves as a typical experimental paradigm for momentum-energy space selection in phonon excitation experiments using CARR inelastic spectrometers, and highlights the superior capabilities of inelastic neutron spectrometers for characterizing the lattice dynamics of thermoelectric materials over a broad momentum space.

## 2.1 Sample Preparation

High-quality SnSe single crystals were grown using the natural temperature gradient in a vertical tube furnace. Elemental Sn and Se with a stoichiometric ratio of 1:1 were sealed in a quartz tube with an outer diameter of 20 mm under high vacuum, which was then enclosed in a second quartz tube with an outer diameter of 25 mm to prevent sample oxidation caused by the rupture of the inner quartz tube during high-temperature sintering. The sealed sample assembly was placed obliquely in a vertical muffle furnace, heated to 1000 °C over a period of 1000 minutes, then slowly cooled from 1000 °C to 500 °C at a controlled rate of 1 °C per hour, and finally naturally cooled to room temperature. A single-phase SnSe single crystal with a mass of approximately 30 g was obtained via this method.

## 2.2 Sample Characterization

The structural quality and phase purity of the SnSe sample were verified by a Bruker D8 X-ray diffractometer (XRD, Cu K$\alpha$ radiation with $\lambda$=1.55406 Å, scanning rate of 2° per minute) and the CARR neutron four-circle diffractometer (incident neutron wavelength $\lambda$=0.9085 Å, reactor power 30 MW, counting time of 10 seconds per point), with the Fullprof software used for Rietveld refinement of the diffraction data. The surface morphology and elemental composition of the single crystal were characterized by a FEI Nova Nano field emission scanning electron microscope (SEM) coupled with an energy-dispersive X-ray spectroscopy (EDS) detector.

Phonon spectrum measurements focused on the transverse and longitudinal acoustic phonons near the (400) and (800) crystal planes. The cold neutron wide-range spectrometer BOYA and the thermal neutron TAS BAMBOO were used to measure the transverse (4K0) and longitudinal (H00) phonons at the (400) crystal plane in the constant-E scanning mode. For BOYA, incident energies of 5 meV, 7 meV, 9 meV and 11 meV were employed to obtain two-dimensional phonon maps of the (H, K) plane and high-resolution phonon spectra of the (H00) and (0K0) crystal planes. For BAMBOO, the incident neutron energy Ei was fixed at 14.88 meV, with a fine scan of the energy transfer range of 1–10 meV (step size of 0.5 meV) to resolve the detailed phonon features. The thermal neutron TAS CIAE-JCNS was used to measure the longitudinal (H00) phonons at the high-Q (800) crystal plane, with Ei fixed at 51.39 meV and a scan of the energy transfer range of 4–8 meV (step size of 1 meV) to investigate the dynamical response under large momentum transfer.

Specifically, BOYA was employed for two-dimensional imaging of the (H, K) plane near (400) to capture the hybridization behavior of acoustic and optical phonon branches in the off-principal- axis direction. Taking advantage of the ultra-low background characteristic of BAMBOO, a fine scan was performed to investigate the energy softening and linewidth broadening of the Ag soft mode. CIAE-JCNS, with its high incident neutron energy and broad Q coverage, was used for measurements at the high-Q (800) crystal plane to explore the lattice dynamical responses under large momentum transfer.

Fig.2. (a) XRD Rietveld refinement results of the SnSe single crystal, the inset shows the as- grown bulk SnSe single crystal; (b) Schematic diagrams of the ac and ab crystal planes of SnSe, illustrating the layered crystal structure; (c) and (d) Neutron single-crystal diffraction and Rietveld refinement results of SnSe, the inset shows the SnSe single crystal sample used for neutron diffraction measurements.

## 3.1 Physical Properties of SnSe Single Crystals

A portion of the as-grown SnSe single crystal was fully ground into a fine powder for XRD measurements, and the obtained diffraction patterns were refined using the Rietveld method, as shown in Fig.2(a). Strong preferred orientations are observed at $2\theta$ diffraction angles of 31.097° and 64.838°, corresponding to the (400) and (800) crystal planes, respectively. This pronounced texture originates from the unique layered crystal structure of SnSe, where the a-axis direction is the natural cleavage plane with low interlayer binding energy, as illustrated in Fig.2(b). Rietveld refinement yields a space group of Pnma with lattice parameters a = 11.49444 (45) Å, b = 4.15232 (28) Å and c = 4.44225 (31) Å, which is in excellent agreement with the reported values in the literature[25].

To verify the structural quality and phase purity of the single crystal, a portion of the sample was cut into a 3$×3×$3 mm cube (shown in the inset of Fig.2(d)) to ensure the uniformity of diffraction peak intensities in neutron diffractometer

measurements. The results of neutron single-crystal diffraction are presented in Fig.2(c), with partial diffraction peaks indexed according to the Pnma space group. No impurity phases were detected in the refined neutron single-crystal diffraction results, confirming the high phase purity of the as-grown SnSe single crystal. Fig.3 shows the surface morphology characterization results of the SnSe single crystal by SEM, where the well-defined layered structure of the sample surface is clearly observed, consistent with the XRD and neutron diffraction results. EDS mapping results further demonstrate the uniform distribution of Sn and Se elements on the surface of the SnSe single crystal, confirming the stoichiometric composition of the sample.

Fig.3. (a)-(c) SEM images of the SnSe single crystal surface at different magnifications, showing the well-defined layered crystal structure; (d)-(f) EDS elemental mapping results corresponding to the morphology in (c), demonstrating the uniform distribution of Sn and Se elements.

### 3.2.1 Phonon Excitation Spectra Measured by the BOYA

Two-dimensional phonon maps of the (H, K) plane obtained by the Boya inelastic spectrometer are shown in Fig.4, which clearly exhibit the dispersive behaviors of transverse and longitudinal acoustic phonons around the reciprocal lattice point (400). Fig.4(a) shows the results of elastic scattering, with an extremely strong scattering intensity at (400), consistent with the XRD and neutron diffraction results. At low energy transfers dE (0.5–1.5 meV), the high-intensity region is still concentrated near (400) but becomes slightly diffuse; the significant broadening of diffraction peaks at (400) and (040) crystal planes masks the weak signals of phonon excitation spectra in this low-energy range, as shown in Figures 4(b)-(d). With the increase of dE to 2–3.5 meV, the original strong elastic scattering spot evolves into a distinct annular feature with a significantly increased radius, which directly demonstrates the linear proportional relationship between phonon energy and wave vector q along the principal axis directions, a characteristic feature of acoustic phonons in the long-wavelength limit.

Fig.4. (a)-(p) Two-dimensional phonon maps of the (H, K) plane at different energy transfers dE, showing the evolution of acoustic phonon dispersion rings around the reciprocal lattice point (400).

As dE further increases to the intermediate energy range of 4–6 meV (Figures 4(e)-(m)), the phonon dispersion ring continues to expand and its contour becomes rougher and more diffuse.

The intrinsic anisotropy of SnSe lattice dynamics, which leads to different sound velocities along the [H, 0, 0] and [0, K, 0] directions, causes the deformation of the dispersion ring; the intensity distribution is no longer a single closed ring, and fractures or overlaps with excitations near other Bragg points begin to appear. When dE reaches the high-energy region of 6.5–7.5 meV (Figures 4(n)-(p)), the acoustic phonon branch gradually approaches the Brillouin zone bound-

ary, the signals of transverse and longitudinal phonons become more diffuse, and the transverse phonon signals and low-q phonon signals disappear preferentially. In this high-energy region, acoustic phonon branch signals start to be strongly affected by the optical phonon branch, indicating the onset of acoustic-optical phonon hybridization.

The two-dimensional phonon maps reveal rich phonon information deviating from the high- symmetry axes, manifested as well-resolved phonon dispersion rings. These off-principal-axis signals are not experimental noise but contain extremely valuable lattice dynamic information, with their physical implications mainly as follows: (1) Anisotropy of lattice interactions. For isotropic materials (e.g., amorphous or polycrystalline materials), the dispersion relation of acoustic phonons is approximately a conical surface, i.e., $\omega$ v q (where v is the sound velocity), and a perfect circular cross- section is obtained in the dE slice. However, in single crystals with intrinsic anisotropy, the interatomic forces vary with crystal directions, leading to a non-perfect circular dispersion ring (e.g., elliptical, rhombic, or rounded square), which directly reflects the difference in sound velocity along different lattice directions. When the wave vector q deviates from the principal axis, off-principal-axis signals are crucial for fitting the interatomic force constant matrix; the full tensor parameters cannot be uniquely determined by the principal-axis data alone. (2) Hybridization of polarization vectors. Along the high-symmetry directions (principal axes), phonons are typically pure longitudinal (LA/LO) or transverse (TA/TO) modes, with atomic vibration directions strictly parallel or perpendicular to the wave vector q. Once deviating from the principal axes (entering the asymmetric region of the (H, K) plane), phonon modes often exhibit a significant hybridization effect of longitudinal and transverse polarization, leading to the complex intensity distribution observed in the two-dimensional phonon maps. (3) Scattering cross-section and selection rules. The brightness of the dispersion ring is inhomogeneous, which is determined by the structure factor of inelastic neutron scattering: ( , ) where Q is the scattering vector and is the phonon polarization vector (i.e., the atomic vibration direction). According to the neutron scattering selection rule, neutrons can only detect a phonon when the vibration direction has a non-zero projection along the scattering vector Q. At off-principal-axis positions, the dot product relationship leads to intense intensity fluctuations due to the variation of the direction of Q and the change of the phonon polarization vector with q. By analyzing the intensity variation of off-principal- axis signals, the directional evolution of phonon polarization vectors in reciprocal space can be deduced, and the correctness of atomic vibration modes in theoretical models can be experimentally verified. This is particularly important for materials with strong anharmonicity such as SnSe, as anharmonicity often causes the polarization vector to deviate significantly from the direction predicted under the harmonic approximation.

Fig.5 shows the experimental phonon dispersion data and corresponding theoretical calculation results along the [H, 0, 0] and [4, K, 0] directions. In the low-energy region (dE $<$ 4 meV) near the (400) reciprocal lattice point, the

slope of the "V" shape formed by the experimental data points is in almost perfect agreement with the theoretical calculation, as shown in Figures 5(a)-(b). This excellent agreement proves that the elastic constants or low-order interatomic force constants used in the theoretical model are highly accurate and can well predict the sound velocity of SnSe in the long-wavelength limit. The maximum energy of the acoustic phonon branch in the theoretical calculation is approximately 8.5 meV, and the scattered phonon signals measured in the experiment gradually disappear or become blurred near 8 meV, which not only verifies the upper energy limit of the acoustic phonon branch in SnSe but also confirms the correctness of the theoretical model in describing the strength of short-range interatomic interactions. Figures 5(c)-(d) show the dynamical behaviors of transverse acoustic phonons along the [4, K, 0] direction; although the experimental data in Fig.5(c) are sparser than those in Fig.5(a), the dispersive profile of the transverse acoustic phonon branch is still clearly outlined near K = 0. Both experimental and theoretical calculation results show that the transverse acoustic phonon branch reaches a maximum value of approximately 7 meV at K 0.5, which is in good agreement with the theoretical prediction, further confirming the reliability of the experimental measurements and the validity of the theoretical model.

Fig.5. (a) and (b) Experimental and theoretical phonon spectra of the (H00) crystal plane[26]; (c) and (d) Experimental and theoretical phonon spectra of the (0K0) crystal plane

### 3.2.2 Phonon Excitation Spectra Measured by the BAMBOO

Inelastic signal scanning in the Constant-E mode was performed using BAMBOO spectrometer, which resolved the detailed phonon signals of SnSe in the range of $3 < H < 5$ along the [H00] direction at room temperature. A significant scattering intensity asymmetry was observed in the measurement of longitudinal [H00] phonons of SnSe: the phonon intensity on the right side of [H00] ($H > 4$) is much higher than that on the left side ($H < 4$). This pronounced intensity asymmetry originates not only from the $Q^2$ dependence of the neutron scattering cross-section but also involves the critical matching mechanism of the spectrometer resolution function. The differential cross-section for single-phonon coherent inelastic neutron scattering is given by[27]: ) , where ki and kf )) are the incident and final neutron wave vectors, $n(\omega)$ is the Bose-Einstein distribution function, and the squared dynamic structure factor term includes the dot product of the polarization vector [27]: , ) , and the scattering vector , − ( ) , ) where bd、Md、rd are the neutron scattering length, mass, and crystallographic position of the d- th atom in the unit cell, respectively. − ( ) is the Debye-Waller factor, which describes the attenuation of coherent neutron scattering intensity caused by thermal atomic vibrations. The term leads to a significant variation in the intensity of acoustic and optical phonon branches in different Brillouin zones.

For longitudinal phonons in the low-q region, the polarization vector is almost parallel to the wave vector q. When observing near the (400) reciprocal lattice point and scanning along the H direction (i.e., ), the dot product term can be simplified to This $Q^2$ dependence leads to a significant enhancement of the scattering intensity with increasing Q. In addition to the intensity enhancement by a factor of , the effects of diffraction extinction and weak incoherent scattering must be considered. This combined effect explains why the phonon signal in the region $H > 4$ near [400] is stronger than that in the region $H < 4$ and also stronger than the phonon signal in the region $H > 5$ near [500], as shown in Fig.6(a).The resolution function of the TAS is an inclined ellipsoid in the , ) space. The experimentally observed intensity asymmetry is often stronger than the theoretical , ) predicted value from pure dependence, which is due to the different matching degrees between the resolution focusing and the slope of phonon dispersion. When the group velocity of the phonon dispersion curve ( ) is consistent with the slope of the major axis of the resolution ellipsoid, the effective integral intensity of the scanning path passing through the ellipsoid is maximized, which is called "focusing" ; the opposite case is called "defocusing" . In SnSe, on the right side of the (400) reciprocal lattice point ($H > 4$), the dispersion slope of longitudinal phonons is positive, which has a higher matching degree with the inclination angle of the BAMBOO resolution ellipsoid. In contrast, on the left side ($H < 4$), the dispersion slope is negative, resulting in a defocusing state. This resolution focusing/defocusing mechanism further explains the sharper peak shape and significantly higher intensity on the right side of [400] observed in Fig.6(a).

Fig.6(b) shows the magnified partial results of Fig.6(a); the acoustic phonon branch signal gradually weakens with the increase of excitation energy and completely disappears at an energy transfer of 8.5 meV, which is consistent with the results measured by BOYA and the reported results in the literature[26], confirming the upper energy limit of the acoustic phonon branch in SnSe. The weak abnormal phonon signals observed at $H > 5$ with energy transfers of 8 meV and 8.5 meV are attributed to the contribution of the acoustic phonon branch near the Brillouin zone boundary. Fig.6(c) shows the longitudinal phonon spectrum along the [H 0 0] direction fitted from the experimental data, which can be divided into two approximately linear parts in both the $H > 4$ and $H < 4$ regions, a feature highly similar to the theoretical calculation results.

Fig.6. (a) and (b) Longitudinal phonon spectra along the [H00] direction at different excitation energies measured by BAMBOO; (c) Fitted longitudinal phonon dispersion spectrum along the [H 0 0] direction; (d) Full width at half maximum (FWHM) of the phonon excitation peak as a function of energy for $H > 4$ along [H 0 0].

The region near the Bragg point (400) corresponds to the long-wavelength limit region of the longitudinal acoustic (LA) phonon branch, where the slope of the dispersion curve represents the sound velocity along this direction and reflects the elastic response of the lattice to long-range perturbations. The slope in

the region 4.1 < H < 4.5 is 9.872 meV per reciprocal lattice unit (r.l.u.), corresponding to a group velocity of approximately 2744 $m \cdot s^{-1}$. The region far from the (400) Bragg point (near the Brillouin zone boundary) corresponds to the nonlinear dispersion region; according to the sine dispersion model for acoustic phonons the group velocity is given by . As H moves from the Bragg point (400) to the next Brillouin zone 핌푠 boundary, the cosine term decreases rapidly, the dispersion curve bends significantly with the increase of wave vector q, and the group velocity gradually decreases. The slope in the region 4.6 < H < 5 decreases to 4.573 $meV \cdot r.l.u.^{-1}$, corresponding to a group velocity of approximately 1271 $m \cdot s^{-1}$, which clearly indicates that phonons exhibit a strong dispersion effect in this high-q region.

SnSe exhibits a strong anharmonic interaction between the acoustic phonon branch and the low- frequency optical phonon branch. When the acoustic phonon branch extends upward in energy and approaches the low-frequency optical phonon branch, the slope of the acoustic phonon branch is "distorted" or flattened near the intersection point, which is manifested as an obvious slope transition in the experimental fitting. Since the lattice thermal conductivity can be expressed as (where C is the specific heat capacity and $\tau$ is the phonon lifetime), the significant reduction in group velocity directly leads to a substantial decrease in the contribution of high-frequency phonons to the lattice thermal conductivity. This strong dispersion bending effect reflects the complex lattice dynamics inside SnSe and its intrinsic inhibitory effect on phonon transport, which is the physical origin of the ultra-low lattice thermal conductivity.

In an ideal perfect crystal, the phonon dispersion curves on both sides of the Bragg point should be strictly symmetric. However, in this work, the slope in the region 3.7 < H < 3.9 is -10.607 $meV \cdot r.l.u.^{-1}$, corresponding to a group velocity of approximately 2948 $m \cdot s^{-1}$ at the long- wavelength limit, which is about 7.4% higher than that in the region 4.1 < H < 4.5. This difference usually originates from the convolution effect of the spectrometer resolution function and the weak experimental background. The slope in the region 3.3 < H < 3.6 is -7.178 $meV \cdot r.l.u.^{-1}$, corresponding to a group velocity of approximately 1995 $m \cdot s^{-1}$ in the nonlinear dispersion region. In the H > 4 region, the phonon branch is highly focused with the spectrometer resolution ellipsoid, and the measured dispersion curve is closer to the real "softened" state of the phonons. In the H < 4 region, the signal is in a defocusing state, and the signal envelope may include contributions from partial optical phonon branches or other experimental backgrounds, leading to a "gentler" observed slope attenuation. Despite the small experimentally induced asymmetry, the significant slope transitions on both sides of the (400) Bragg point clearly indicate the strong lattice dynamical anharmonicity of SnSe. When the phonon wavelength decreases (q increases) to a certain extent, the unique layered crystal structure and its strong anharmonicity cause phonons to no longer propagate effectively in the form of harmonic waves transform into hybrid modes with complex polarization, leading to a greatly reduced propagation efficiency. he rapid decrease in phonon group velocity directly results in the extremely low lattice thermal conductivity

of SnSe, a key feature for its excellent thermoelectric performance.

Fig.6(d) shows the variation of the corrected FWHM with excitation energy on the focusing side (H > 4); the FWHM is narrow and remains relatively constant at excitation energies dE < 6.5 meV, corresponding to a long phonon lifetime, where phonons are mainly scattered by grain boundaries or minor point defects. When the excitation energy dE > 6.5 meV, the FWHM increases sharply, indicating a significant reduction in phonon lifetime. The combined effect of reduced phonon velocity and shortened phonon lifetime greatly limits the contribution of mid-to- high frequency phonons to the lattice thermal conductivity, which is a critical factor for the excellent thermoelectric performance of SnSe.

The significant change in the slope of the phonon dispersion curve is often accompanied by an increase in phonon scattering probability and a corresponding reduction in phonon lifetime. The phonon lifetime and the intrinsic energy level broadening (intrinsic full width at half maximum, FWHM) satisfy the Heisenberg uncertainty principle, with the relationship in the energy space: . Since the experimentally measured raw FWHM includes the contribution of spectrometer resolution, a rigorous correction is required extract the intrinsic phonon linewidth. A Gaussian convolution model is usually used for approximate processing: , where R is the spectrometer resolution at the corresponding (Q,E). For the focusing side = (H > 4) of SnSe, the resolution R is small, the measured is thus closer to the true intrinsic value, and the calculated phonon lifetime is more reliable. Fig.6(d) shows the variation of the corrected FWHM with excitation energy on the focusing side (H > 4); the FWHM is narrow and remains relatively at excitation energies dE < 6.5 meV, corresponding to a long phonon lifetime, where phonons are mainly scattered by grain boundaries or impurities.

When the excitation energy dE > 6.5 meV, the FWHM increases sharply, indicating a significant reduction in phonon lifetime. The combined effect of reduced phonon velocity and shortened phonon lifetime greatly limits the contribution of mid-to-high frequency phonons to the lattice thermal conductivity, which is a critical factor for the excellent thermoelectric performance of SnSe.

### 3.2.3 Phonon Excitation Spectra Measured by CIAE-JCNS

To investigate the lattice dynamical behaviors under high momentum transfer, phonon scanning in the room-temperature Constant-E mode was performed at the high-Q (800) Bragg point using the CIAE-JCNS spectrometer, as shown in Fig.7(a). Similar to the (400) crystal plane, the factor determines the baseline of the scattering intensity (stronger in the high-Q region), and the spectrometer resolution focusing effect further amplifies this intensity asymmetry. The factor at the (800) diffraction peak is four times that at the (400) peak; theoretically, the neutron scattering cross-section should be significantly enhanced. However, the scattering intensity simultaneously exhibits an attenuating trend following the Debye-Waller exponential factor.

As a typical thermoelectric material with excellent performance, SnSe has an

extremely soft lattice and strong intrinsic anharmonicity, which means that the mean-square thermal vibration displacement of atoms increases sharply with increasing temperature. Since the scattering vector Q appears in the exponential term of the Debye-Waller factor, the attenuation rate of this factor for high-index crystal planes (e.g., (800)) is much faster than the linear gain of the $Q^2$ factor, leading to a significant "collapse" of the phonon signal intensity in the high- temperature or high-Q region. This competitive interplay between the $Q^2$-enhanced scattering cross-section and the Debye-Waller factor-induced intensity attenuation is clearly observed in our experiment; therefore, no detectable phonon signals are observed at an energy transfer of 8 meV at the (800) crystal plane.

Fig.7(b) shows the direct comparison of longitudinal phonon spectra along the [H 0 0] direction at an energy transfer of 4 meV measured by the BAMBOO (low-Q, (400) plane) and CIAE-JCNS (high-Q, (800) plane) spectrometers. The BAMBOO spectrometer exhibits an extremely high signal-to-noise ratio and sharp peak shape in the low-Q region, a direct result of its ultra-low experimental background. Despite the strong Debye-Waller (D-W) attenuation of the signal at the high-Q (800) crystal plane, clear and well-resolved phonon signals are still observed near (800) thanks to the high thermal neutron flux and high incident energy of CIAE-JCNS. A higher incident neutron energy not only enables high-Q measurements but also provides the capability to study the low-energy optical phonon branches in SnSe, which is crucial for a complete understanding of the lattice dynamics of SnSe. By taking advantage of the respective strengths of the three inelastic spectrometers at CARR, we have systematically characterized the phonon dispersion relations of SnSe single crystals near the (400) crystal plane, and the obtained experimental results were compared with published experimental data and density functional theory (DFT) calculations. The results show that the experimental data obtained from the CARR neutron spectrometers are in high agreement with the literature reports, which verifies the high reliability and accuracy of the data obtained by the CARR inelastic neutron spectrometers, and demonstrates the superior capabilities of the CARR neutron science platform for characterizing the lattice dynamics of condensed matter materials.

Fig.7. (a) Longitudinal phonon spectra along the [H00] direction at different excitation energies measured by the CIAE-JCNS spectrometer at the high-Q (800) crystal plane; (b) Comparison of longitudinal phonon spectra along the [H 0 0] direction at an energy transfer of 4 meV measured by BAMBOO and CIAE-JCNS

## Conclusion

In this work, high-quality SnSe thermoelectric single crystals with ideal layered structure and favorable preferred orientation were successfully synthesized via the temperature gradient method, and their basic structural properties were accurately characterized by multi-technique characterization methods including

neutron diffraction. Based on the high-performance inelastic neutron scattering spectrometers at the CARR neutron science platform, the lattice dynamical properties of SnSe single crystals at the (400) crystal plane were systematically studied at room temperature, and a series of key phonon dynamical behaviors were revealed. The experimental results demonstrate that the acoustic phonon branches of SnSe exhibit significant energy softening and obvious slope transition with the increase of energy transfer, and the phonon lifetime drops sharply in the high-energy region, which directly reflects the strong lattice anharmonicity and intrinsic structural anisotropy, and explains the ultra-low lattice thermal conductivity of SnSe at the microscopic level. Meanwhile, the scattering intensity asymmetry, off-principal-axis phonon signals and high-Q dynamical responses were thoroughly analyzed, which further supplements the lattice dynamical database of layered thermoelectric materials.

This work fully verifies the outstanding performance of CARR inelastic neutron scattering spectrometers in characterizing the fine lattice dynamical behaviors of materials, highlighting the unique advantages of nuclear scattering technology in condensed matter characterization. It not only provides key experimental evidence for revealing the phonon transport mechanism of high- performance thermoelectric materials, but also enriches the application cases of reactor-based neutron scattering technology in advanced material research, providing a valuable experimental paradigm for the combination of nuclear technology and material science research. The relevant research results can also provide technical reference for the optimization and application of inelastic neutron scattering spectrometers at CARR.

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Figure 1

Figure 1: Figure 1

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## Figures