Identification of vibrational mode symmetry and phonon anharmonicity in SbCrSe₃ single crystal using Raman spectroscopy

Hong Wu^{1,2†}, Xiangnan Gong^{3†}, Yi Peng⁴, Long Zhang¹, Bin Zhang³, Kunling Peng¹, Jie Liu³, Guang Han⁵, Aifeng Wang¹, Yisheng Chai¹, Mingquan He¹, Haoshuang Gu⁴, Emmanuel Guilmeau⁶, Guoyu Wang^{2*}, Xu Lu^{1*} and Xiaoyuan Zhou^{1,3*}

ABSTRACT Developing an understanding of the physics underlying vibrational phonon modes, which are strongly related to thermal transport, has attracted significant research interest. Herein, we report the successful synthesis of bulk SbCrSe₃ single crystal and its thermal transport property over the temperature range from 2 to 300 K. Using angle-resolved polarized Raman spectroscopy (ARPRS) and group theory calculation, the vibrational symmetry of each observed Raman mode in the cleaved (001) crystal plane of SbCrSe₃ is identified for the first time, and then further verified through first-principles calculations. The ARPRS results of some Raman modes (e.g., $A_g^2 \sim 64 \text{ cm}^{-1}$ and $A_g^7 \sim 185 \text{ cm}^{-1}$) can be adopted to determine the crystalline orientation. More importantly, the temperature dependence of the lattice thermal conductivity (κ_L) is revealed to be more accurately depicted by the three-phonon scattering processes throughout the measured temperature range, substantiated by *in-situ* Raman spectroscopy analysis and the model-predicted κ_L . These results reveal the fundamental physics of thermal transport for SbCrSe₃ from a completely new perspective and should thus ignite research interest in the thermal properties of other low-dimensional materials using the same strategy.

Keywords: SbCrSe₃ single crystal, *in-situ* Raman, angle-resolved polarized Raman spectroscopy, lattice dynamics, thermal transport

INTRODUCTION

Low-dimensional bulk materials that have a quasi-one-dimensional (1D) or 2D structure have received growing research attention owing to their extraordinary electronic and thermal properties; they have emerged as highly attractive candidates used for next-generation electronic, optoelectronic, and thermoelectric devices [1–8]. In particular, low-dimensional intrinsic magnetic semiconductors—CrMX₃ ternary chromium trichalcogenides (M as a non-transition metal and X = S, Se or Te) have attracted considerable research interest in the magnetism and thermoelectricity fields owing to their appropriate band gaps and intrinsically low lattice thermal conductivity (κ_L) [9–15]. Intriguingly, the crystal structures of these compounds, by virtue of the different arrangements of CrX₆ octahedra, can transform from a quasi-2D layered structure into a 1D needlelike structure. For example, CrMX₃ has a laminar structure when M = Si, Ge, or Sn, with CrX₆ octahedra adopting a honeycomb lattice; in contrast, when Sb or Ga appears on M sites, it exhibits a pseudo-1D crystal structure, with CrX₆ octahedra forming infinite, edge-sharing, and double rutile chains, in which M atoms are linked to the neighboring chains. The relative angle between the double rutile chains is determined by the type of M atoms [16]. Although the crystal structures of these compounds have been fully

¹ College of Physics and Institute of Advanced Interdisciplinary Studies, Chongqing University, Chongqing 401331, China

² Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, China

³ Analytical and Testing Center of Chongqing University, Chongqing 401331, China

⁴ Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Hubei Key Laboratory of Ferro & Piezoelectric Materials and Devices, Faculty of Physics & Electronic Sciences, Hubei University, Wuhan 430062, China

⁵ College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China

⁶ Laboratoire CRISMAT, UMR-CNRS, Normandie University, Caen 14050, France

[†] These authors contributed equally to this work.

* Corresponding authors (emails: guoyuw@cigit.ac.cn (Wang G); luxu@cqu.edu.cn (Lu X); xiaoyuan2013@cqu.edu.cn (Zhou X))

comprehended, further investigation on their fundamental lattice vibration properties remains relatively slow.

Raman spectrum, as a fast and nondestructive tool, has been widely utilized to characterize phonon characteristics in the vicinity of the Brillouin zone center, the crystal structure, and electron–phonon interactions, particularly in many low-dimensional materials [17–20]. As a characteristic example of CrMX_3 compounds, SbCrSe_3 has an orthorhombic structure with 20 atoms in its primitive cell and is subject to the $Pnma$ space group and D_{2h} point group. Based on the group analysis, 60 vibrational modes at the Γ point in the Brillouin zone are generated, in which eight inequivalent irreducibles are included in the D_{2h} point group as follows: $\Gamma = 10A_g + 5B_{1g} + 10B_{2g} + 5B_{3g} + 5A_u + 10B_{1u} + 5B_{2u} + 10B_{3u}$. As can be observed, the symmetries of 30 Raman active modes, including $10A_g + 5B_{1g} + 10B_{2g} + 5B_{3g}$, are predicted using the group theory. Recently, angle-resolved polarized Raman spectroscopy (ARPRS) has emerged as a powerful tool for resolving and assigning Raman mode symmetries for some important crystals and for determining the crystalline orientation of films and nanotubes [21–24]. However, to the best of our knowledge, such a technique has never been used to identify the vibrational symmetries for experimentally observed Raman modes in low-dimensional CrMX_3 semiconductors.

Moreover, SbCrSe_3 exhibits intrinsically low κ_L [15], indicating that it could be a promising thermoelectric material following electrical property optimization [25–30]. Regardless, the underlying physics for the low thermal conductivity of SbCrSe_3 , which relies on the analysis of phonon modes, remains unclear. Through *in-situ* Raman spectroscopy analysis, the temperature-dependent lattice vibration characteristics can be precisely attained, thereby further illustrating the anharmonic interactions between phonons by analyzing the temperature-dependent evolution of Raman peaks and corresponding full width at half maximum (FWHM) [31–33]. Hence, an essential task is to unveil the phonon scattering mechanisms in bulk low-dimensional materials such as SbCrSe_3 by using the combination of *in-situ* Raman experiment and lattice dynamics.

Herein, we report the determination of mode symmetry for each observed Raman peak in SbCrSe_3 single crystal. Three-phonon scattering processes dominate the thermal transport for SbCrSe_3 throughout the measured temperature range, as suggested by the temperature dependence of Raman mode frequency and linewidth, which is further corroborated by the good consistency between experimental and calculated thermal conductivity. Our

findings highlight the utilization of the Raman spectrum as a fast, precise, and nondestructive method to identify the vibrational mode symmetry, crystalline orientation, and phonon anharmonicity of low-dimensional materials.

EXPERIMENTAL AND THEORETICAL METHODS

Synthesis

SbCrSe_3 single crystals were grown through the self-flux method [34]. Starting elements (chunks, 99.99%, Sigma-Aldrich) were weighted according to a molar ratio of Cr:Sb:Se = 2:38:60 and loaded into an alumina crucible. The alumina crucible was placed into a quartz tube, and another alumina crucible with silica wool was placed inverted onto the prior one. Then, the quartz tube was evacuated to a pressure of 5×10^{-4} Pa and sealed. The quartz tubes were heated to 1000 K over 12 h, slowly cooled to 900 K, and maintained at this temperature for 144 h. Then, the molten liquid was separated from the crystals in a centrifuge, with silica wool serving as a filter. Finally, the obtained needle crystals were evacuated, encapsulated in a fused quartz tube, and annealed at 780 K for 24 h. Consequently, millimeter-long malleable SbCrSe_3 single crystals were obtained.

Characterizations

The diffraction intensity data of single crystal SbCrSe_3 were collected on an Agilent Technologies SuperNova single-crystal X-ray diffraction (SCXRD, SuperNova, Agilent Technology, Poland) instrument equipped with graphite-monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 295 K. The structures were solved using the SHELXT structure solution program and refined with the SHELXL refinement package. The XRD pattern was recorded via a PANalytical X-ray diffractometer (X'Pert Powder, PANalytical, Netherlands) that was operated at 40 kV and 40 mA using Cu $K\alpha$ ($\lambda = 1.5418$ Å) radiation. Raman spectrum measurements were performed using HORIBA JobinYvon HR Evolution, and 600 and 1800 groove mm^{-1} holographic gratings combined with thermoelectric cooled Synapse charge-coupled device were used for the ARPRS and temperature-dependent Raman experiments, respectively. Solid-state Nd:YAG (HR Evolution, HORIBA Scientific, France) laser with a wavelength of 532 nm was used as the excitation source. The thermal conductivity was measured on a Physical Property Measurement System DynaCool 9 (PPMS, DynaCool 9, USA). High-resolution transmission electron microscopy (HRTEM, Talos F200S, ThermoFisher Sci-

entific, Netherlands) and scanning transmission electron microscopy high-angle annular dark field (STEM-HAADF) were used to characterize the microstructure. The corresponding energy-dispersive X-ray spectroscopy (EDX) mapping was performed using a transmission electron microscope (Talos F200S G2) operating at 200 kV. An electron probe microanalyzer (EPMA, JXA-8530F Plus, JEOL, Japan) was used to determine the distribution of Sb, Cr, and Se in the single crystal with a spatial resolution of 1 μm .

Density functional theory calculations

Under the precondition of density functional theory (DFT) [35], the Vienna *ab-initio* Simulation Package code using the projector augmented plane wave methods was implemented for all calculations [36]. A generalized gradient approximation of Perdew–Burke–Ernzerhof is defined as the relevant exchange–correlation functional [37]. For the relaxation of the crystal structure, the total energies of electronic self-consistent interactions were numerically converged to 1×10^{-8} eV with a basis set energy cutoff of 600 eV, and the forces on the atoms were 1×10^{-4} eV $\text{\AA}^{-1}$ for optimizing the atomic positions. For the Brillouin zone integrations, the k -mesh grid ($5 \times 11 \times 3$) centered at Γ was used for the primitive cell. To calculate phonon dispersion, finite displacement methods using $2 \times 3 \times 1$ supercell were performed in the Phonopy package to investigate the lattice dynamics of SbCrSe_3 [38]. The κ_L was calculated using the ShengBTE package using a cutoff of 10 $\text{\AA}$ for the interaction range and $1 \times 3 \times 1$ supercell to obtain third-order anharmonic interatomic force constants (IFCs) [39].

RESULTS AND DISCUSSION

Phase characterization

The structure of our SbCrSe_3 single crystal, with the lattice parameters $a = 9.1475(6)$ $\text{\AA}$, $b = 3.7872(3)$ $\text{\AA}$, and $c = 13.4264(11)$ $\text{\AA}$ obtained by the refinement of SCXRD, is orthorhombic with $Pnma$ space group (No. 62) and D_{2h} point group. Corresponding structural data are listed in Table S1. Fig. 1a shows the refined crystal structure of SbCrSe_3 , which is regarded as a quasi-1D structure with double chains of CrSe_6 octahedra aligned parallel to the b -axis shown in Fig. 1b. Within the double chain, the Cr cations follow an edge-sharing triangular arrangement, and Sb atoms are linked to the adjacent chains, resulting in the pseudo-1D crystal structure. As revealed in Fig. 1c, the bond distances between Cr and Se atoms in these octahedra range from 2.5301 to 2.5949 $\text{\AA}$, resulting in a

slightly distorted octahedron because of the asymmetric chemical bond lengths, and the Sb–Se1 and Sb–Se2 bond distances are 2.6486 and 2.6714 $\text{\AA}$, respectively. The synthesized SbCrSe_3 single crystal in Fig. 1d exhibits an ~ 10 -mm-long aciculiform along the b -axis. The inset graph in Fig. 1e depicts the surface morphology along the mirror side. The predominant (00l) diffraction peaks indicate that the c -axis is perpendicular to the mirror side, which is used to acquire other data in this work. Moreover, the XRD pattern in Fig. 1e of the SbCrSe_3 sample (crushed single crystal) agrees with that presented in a previous report (PDF#50-0853) [40], in which no distinct secondary phase is detected.

Furthermore, STEM-HAADF imaging, electron diffraction, and EDX mapping were utilized to gain in-depth insight into the structural characterization and the relative orientation of the cleaved (00l) crystal plane of the SbCrSe_3 crystal. As displayed in Fig. 1g, h, the clear lattice fringe, in conjunction with the distinguishable fast Fourier transformation image, implies the single crystal-line feature. Interestingly, the Miller index of the diffraction spot and the measured interplanar distance, marked in Fig. 1g, h, respectively, elucidate that the orientations of the long and short edges shown in Fig. 1g are [020] and [200], respectively, thus establishing that the preferred orientation of long edges for the cleaving plane of the SbCrSe_3 crystal is the b -axis. In addition, the EDX mapping for the synthetic SbCrSe_3 sample in Fig. 1i confirms the uniform distribution of Sb, Cr, and Se elements, which shows excellent consistency with the EPMA results, as displayed in Fig. S1.

Identifying Raman mode symmetries

The Raman spectrum not only contains rich information on phonon properties near the Brillouin zone, but is also closely correlated with crystal structures in terms of symmetry. The backscattering geometry ARPRS measurement was performed on the cleaved (00l) crystal plane of the SbCrSe_3 crystal at room temperature (the schematic of the experimental setup is exhibited in Fig. S2) to determine the phonon vibrational symmetries for the Raman modes and relevant anisotropy. The a -axis and b -axis of the SbCrSe_3 crystal were defined as the x' and y' directions, respectively, as shown in Fig. S2c. Fig. S2a, b separately display the two configurations for the ARPRS experiment, where the green rectangle symbolizes the sample, the red arrow indicates the polarization direction of the incident laser, and the blue arrow represents the original polarization of Raman back-scattered signal from the sample surface corresponding to

Figure 1 Structural analyses and characterizations of the SbCrSe_3 single crystal. (a) Crystal structure of SbCrSe_3 along the b -axis. (b) CrSe_6 double chains along the b -axis. (c) Bond lengths from Cr to Se and Sb to Se. (d) The SbCrSe_3 crystal, the b -axis, is along the long crystal dimension, which is about 10 mm in length. (e) XRD patterns for SbCrSe_3 compared with PDF#50-0853 and single-crystal SbCrSe_3 show predominantly (00l) peaks. The inset shows the image for single-crystal SbCrSe_3 used for powder XRD. (f) HRTEM image of SbCrSe_3 along [001] zone axis. The corresponding selected-area electron diffraction pattern and HRTEM image for (g) and (h), respectively. (i) The STEM-HAADF image and the corresponding EDX mapping demonstrating the chemical homogeneity of the SbCrSe_3 crystal.

the analyzer-selected vertical or horizontal direction (denoted as perpendicular [$\perp$] or parallel [$\parallel$] polarization configuration, respectively). Fig. 2a displays the Raman spectra of SbCrSe_3 single crystal measured in the cleaved (00l) crystal plane at an angle of 0° using unpolarized, parallel, and perpendicular polarization configurations. Fourteen Raman modes can be obviously observed under the unpolarized configuration. However, with regard to the under $\perp$ and $\parallel$ polarization configurations, the peak intensities of some vibrational modes can be enhanced, reduced, or even disappear periodically, indicating the existence of polarization-dependent behavior.

Under cross-polarized configuration, the typical polarized Raman spectra and false-color diagram with a rotation angle from 0° to 360° are shown in Fig. S3a and Fig. 2b, respectively. Interestingly, in this configuration, peak intensities of all the modes varying with sample rotation have a periodicity of 90° to present a four-lobed

shape; some modes have maximum intensities corresponding to angles at 0° , 90° , 180° , and 270° (such as 49, 144, 172, and 238 cm^{-1}) and some at 45° , 135° , 225° , and 315° (e.g., 64, 125, 153, and 185 cm^{-1}). In contrast, in the parallel polarization configuration (Fig. S3b and Fig. 2c), some Raman mode intensities repeat after 180° , producing a two-lobed shape (e.g., 64, 125, 185, and 254 cm^{-1}), which could be used to estimate the crystalline orientation (along a - or b -direction) of the cleaved (00l) in-plane of SbCrSe_3 (as discussed later). Some modes have a 90° variation period, exhibiting a four-lobed shape (e.g., 49, 144, 172, and 238 cm^{-1}). These results show not only the anisotropic optical feature of the SbCrSe_3 crystal but also the dependence of the polarized Raman spectrum on crystalline orientation.

Based on the group theory calculation, the sample angle-dependent intensities of each Raman active mode in different crystal planes of the SbCrSe_3 sample were fully

Figure 2 ARPRS of SbCrSe₃. (a) Measuring Raman spectra at a 0° angle under ⊥, ||, and unpolarized configurations. False-color plots of polarized Raman intensities under (b) cross and (c) parallel polarization configurations, respectively.

evaluated, which is fundamentally important to identify the mode symmetries. The following calculations are suitable for analyzing the cleaved (00l) crystal plane, and the results of the remaining crystal faces are included in the Supplementary information (SI Section I). When the (00l) plane of the crystal in the x - y plane is rotated, an angle θ exists between laboratory coordinates (xyz) and crystal coordinates ($x'y'z'$). Raman tensors ($\bar{R}$) of a crystal are defined according to its crystal coordinates, and the laboratory coordinates can be converted to ($\bar{R}'$) by $\bar{R}' = \bar{M} \cdot \bar{R} \cdot \bar{M}^{-1}$, where $\bar{M}$ is defined as the orthogonal transform matrix to link the two coordinates.

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \bar{M} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}, \quad \bar{M} = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (1)$$

The intensity (I) of the observed Raman vibration modes can be expressed as

$$I \propto \left| \bar{e}_s \cdot \bar{M} \cdot \bar{R} \cdot \bar{M}^{-1} \cdot \bar{e}_i \right|, \quad (2)$$

where $\bar{e}_s$ and $\bar{e}_i$ are the unit polarization vectors of the scatter and incident lasers, respectively. The incident laser with unit polarization vector along the y -axis ($\bar{e}_i = (010)$) propagates along the z -direction to impinge on the sample. The scattered Raman signal is collected through the selectivity analyzer with unit polarization vector $\bar{e}_s^T =$

(100) defined as perpendicular configuration and $\bar{e}_s^T = (010)$ defined as parallel configuration. For an absorptive material, the Raman tensor elements are complex numbers, with real and imaginary parts [23,41]. Thus, the Raman tensors of A_g and B_{1g} (see SI Section I for other modes B_{2g} and B_{3g}) according to the D_{2h} point group can be expressed as [41]

$$\begin{aligned} \bar{R}(A_g) &= \begin{pmatrix} ae^{i\varphi_a} & 0 & 0 \\ 0 & be^{i\varphi_b} & 0 \\ 0 & 0 & ce^{i\varphi_c} \end{pmatrix}, \\ \bar{R}(B_{1g}) &= \begin{pmatrix} 0 & de^{i\varphi_d} & 0 \\ de^{i\varphi_d} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \end{aligned} \quad (3)$$

The Raman scattering intensities of different modes can further be expressed as

$$I(A_g, \perp) \propto \frac{1}{4} \sin^2 2\theta \cdot (|a|^2 - 2|a||b| \cdot \cos\varphi_{ab} + |b|^2), \quad (4)$$

$$I(A_g, ||) \propto |a|^2 \cdot \sin^4 \theta + |b|^2 \cdot \cos^4 \theta + 2|a||b| \cdot \cos\varphi_{ab} \cdot \sin^2 \theta \cdot \cos^2 \theta, \quad (5)$$

$$I(B_{1g}, \perp) \propto d^2 \cdot \cos^2 2\theta, \quad (6)$$

$$I(B_{1g}, ||) \propto d^2 \cdot \sin^2 2\theta, \quad (7)$$

where || and ⊥ represent parallel and perpendicular po-

larizations, respectively, and $\varphi_{ab} = \varphi_a - \varphi_b$ is the phase difference. The relations between I and θ based on group theory analysis for all Raman active modes of SbCrSe₃ are summarized in Table S2. Notably, the calculated Raman scattering intensities of the B_{yg} ($x = 1-3$) modes, independent of the phase difference φ , are determined by the real parts only. Moreover, when the direction of the incident laser is perpendicular to the (001) surface, only Raman-active A_g and B_{1g} modes can be detected.

An interesting detail to note in the parallel polarization configuration is that the angular dependence of the A_g intensity with a periodicity of 180° differs from that of B_{1g} modes with a 90° periodicity out of the 2θ dependence. In the perpendicular polarization configuration, although both A_g and B_{1g} modes have a similar 90° variation period, the A_g mode intensity as a function of 2θ shows a sine-like feature, and the relation of B_{1g} mode intensity as a function of 2θ exhibits a cosine-like behavior. Thus, the distinguished difference in periodicity or functional relationship (I versus 2θ) in these modes is highly beneficial for assigning experimental Raman-active modes symmetry. As can be observed from Table S3, the fitting curves according to Equations (4–7) show excellent consistency with the experimental data. All B_{1g} modes

marked by the red lines in both configuration and A_g modes (the blue lines) under cross-polarized geometry show the expected four-lobed shape, and significantly, A_g modes under the parallel polarization configuration exhibit two-lobed shapes. Unambiguously, the symmetry of experimentally observed vibrational modes can be well confirmed, which results from the reliable fitting and complementary results for both configurations. Furthermore, in the parallel polarization configuration, the intensities of some modes (e.g., ~64 and ~185 cm⁻¹) with a periodicity of 180° reach the maximum values at 0° or 180° along the b -axis and obtain their minimums at 90° and 270° along the a -axis. Such characteristics could be used as a guide to verify the desirable crystalline orientation of small crystals or films [20,21].

For a better understanding and further verification of these modes assigned to corresponding vibrational symmetry, the phonon dispersion curves along the high symmetry point directions and the vibrational symmetry of phonons vertically intersected with the phonon bands at the Γ point in the Brillouin zone were calculated. As shown in Fig. 3a, the calculated phonon dispersion of SbCrSe₃ along the high symmetry path is in the absence of imaginary frequency, which suggests that the calculated

Figure 3 Phonon properties of SbCrSe₃. (a) The calculated phonon dispersion and density of states for SbCrSe₃ in left and right panels, respectively. The atomic vibrations of some Raman modes (b) $B_{1g}^1 \sim 47$ cm⁻¹, (c) $A_g^2 \sim 58$ cm⁻¹, and (d) $B_{1g}^3 \sim 163$ cm⁻¹, respectively.

lattice structure is thermodynamically stable. With a large number of atoms (20) in the primitive cell of SbCrSe_3 , 60 phonon bands composed of three acoustic branches and 57 optical branches can be obtained, in which the expected 30 Raman active modes with four inequivalent irreducibles ($10A_g + 5B_{1g} + 10B_{2g} + 5B_{3g}$) are predicted. These active Raman modes are in agreement with the group theory analysis, as listed in Table S4. Compared with the DFT calculation results, the experimentally determined vibrational modes exhibit excellent consistency. Some modes, which are not experimentally observed, are also predicted. The visualization of the atomic vibrations of some Raman modes (such as $B_{1g}^1 \sim 47 \text{ cm}^{-1}$, $A_g^2 \sim 58 \text{ cm}^{-1}$, and $B_{1g}^3 \sim 163 \text{ cm}^{-1}$) is displayed in Fig. 3b–d, respectively. The atomic displacement of B_{1g}^1 and B_{1g}^3 modes is along the b -axis (out of the $[010]$ plane), whereas that of A_g^2 mode belongs to in-plane (010) vibration.

Anharmonic phonon decay and thermal properties

The temperature-dependent Raman spectrum was measured from 78 to 310 K in the cleaved (001) plane, as shown in Fig. 4a and Fig. S4, to further elucidate the mechanisms of phonon scattering in SbCrSe_3 crystal. Based on the above discussion, the vibrational symmetry of each experimentally observed Raman mode can be explicitly identified, as marked in Fig. S4. All Raman peaks obviously show a redshift, and the corresponding linewidths broaden with increasing temperature

throughout the measured temperature range (Fig. 4a), which is mainly attributed to anharmonic interactions between phonons [42,43]. Here, the Raman modes B_{1g}^1 ($\sim 49 \text{ cm}^{-1}$) and B_{1g}^3 ($\sim 172 \text{ cm}^{-1}$), with the characteristics of the atomic vibration along the b -axis, are selected to investigate the inherent phonon scattering processes. The temperature variation of peak frequencies and FWHMs of these Raman modes are depicted in Fig. 4b, c, respectively. The conventional model assuming the decay of an optical phonon into two (representing three-phonon process) or/and three phonons (four-phonon process) is applied to illustrate the temperature-dependent behaviors for peak position and FWHM. Therefore, the temperature-dependent phonon frequency and linewidth are commonly expressed as [44]

$$\omega = \omega_0 + A \left[1 + \frac{2}{e^{\hbar\omega_0/2k_B T} - 1} \right] + B \left[1 + \frac{3}{e^{\hbar\omega_0/3k_B T} - 1} + \frac{3}{(e^{\hbar\omega_0/3k_B T} - 1)^2} \right], \quad (8)$$

$$\Gamma = \Gamma_0 + C \left[1 + \frac{2}{e^{\hbar\omega_0/2k_B T} - 1} \right] + D \left[1 + \frac{3}{e^{\hbar\omega_0/3k_B T} - 1} + \frac{3}{(e^{\hbar\omega_0/3k_B T} - 1)^2} \right], \quad (9)$$

where ω_0 is the intrinsic frequency, Γ_0 is the broadening at 0 K, k_B is the Boltzmann constant, $\hbar$ is the reduced Planck's constant, and the coefficients (A , B , C , and D) are the anharmonic constants.

Figure 4 In-situ Raman spectra of SbCrSe_3 . (a) Raman scattering spectrum of SbCrSe_3 at a temperature range from 78 to 310 K. Temperature dependence of the peak positions and linewidth for (b) B_{1g}^1 and (c) B_{1g}^3 , respectively. The red and black solid lines are the corresponding fitted lines.

As indicated by Fig. 4b, the fitted lines on the basis of Equations (8) and (9) match well with the experimental results of B_{lg}^1 modes, and the relevant fitting parameters are summarized in Table 1. Notably, compared with the obtained value of the anharmonic coefficients (A and C) with reference to the three-phonon process, the coefficients (B and D) involved in the four-phonon process can be neglected owing to their small magnitudes, which indicates that the three-phonon interactions are dominant. Similar to the conclusion of B_{lg}^1 mode, the temperature variation of the peak position and FWHM of B_{lg}^3 mode can be well characterized by the three-phonon scattering process, as listed in Table 1. Therefore, one can conclude that the three-order anharmonicity in lattice potential is more accurate for describing the temperature-dependent evolution of frequency and linewidth for SbCrSe₃ crystal. Intriguingly, in contrast to the B_{lg}^1 mode, fitting parameters A and C shown in Table 1 for B_{lg}^3 mode exhibit relatively large values, thereby implying that the B_{lg}^3 mode ($\sim 172 \text{ cm}^{-1}$) contributed by the vibrations of Se atoms has stronger anharmonic phonon–phonon coupling and thus plays a vital role in the reduction of the κ_{L} . In addition, the relaxation time τ for the decay process (the phonon lifetime), which is closely associated with κ_{L} , can be estimated by the simple relation [45], $\tau = \frac{1}{\pi c \Gamma}$, where c represents the light velocity and Γ is the FWHM of Raman modes. As shown in Fig. 4b, c, the FWHMs for both modes broaden with the increasing temperature, suggesting that the phonon lifetimes decrease, thereby decreasing κ_{L} with the elevated temperature. Simultaneously, it is evident that the change in the FWHM of B_{lg}^3 mode is significantly greater than that of B_{lg}^1 mode, which suggests the phonon lifetime of B_{lg}^3 mode drops faster as the temperature rises. Thus, B_{lg}^3 mode is again verified to play a more important role in reducing κ_{L} .

The thermal conductivity of the SbCrSe₃ single crystal

along the b -axis was measured to further explore the thermal transport mechanisms. The calculated value was also determined by solving the phonon Boltzmann transport equation (BTE). The SbCrSe₃ crystal possesses high electrical resistivity (ρ) (Fig. S5), which is why the electronic thermal conductivity (κ_{e}) is negligible; this condition is also found in previously reported polycrystalline samples [15]. As displayed in Fig. 5a, with increasing temperature, the experimental thermal conductivity first sharply rises to a peak value of $\sim 15 \text{ W m}^{-1} \text{ K}^{-1}$ at 20 K and then slowly decreases to $\sim 2 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, suggesting the obtained SbCrSe₃ bulk crystal is a normal crystalline material and has intrinsically low κ_{L} . Unambiguously, the calculated κ_{L} from first principles agrees reasonably well with the measured results of a single crystal in the temperature range from 50 to 300 K, and is slightly higher than that of the polycrystalline samples at elevated temperatures because of the absence of grain boundary and van der Waals layer interface for phonon scattering. This result substantiates that three-order anharmonicity in lattice vibration potential can well describe the thermal transport in SbCrSe₃, which is consistent with the conclusions obtained by the *in-situ* Raman experiment. As shown in Fig. 5b, the anharmonic scattering rates (SRs), which are inversely proportional to the phonon lifetime, are remarkably enlarged with the rising temperature, which is responsible for the temperature-dependent evolution of κ_{L} . At frequencies below 200 cm^{-1} , the anharmonic SRs display a globally enhanced tendency, implying that the high frequency phonons have a relatively short lifetime. The cumulative κ_{L} at 100 and 300 K with regard to the phonon frequency is plotted in Fig. 5c. The inset of Fig. 5c shows that the contribution from optical branches for κ_{L} is larger than that from acoustic branches, which indicates the importance of optical branches in the thermal transport of SbCrSe₃ crystal. As shown in Fig. 5d, the thermal conductivities are dominated by the phonons with short mean free paths (MFPs), and the MFPs with a 50% accumulation of κ_{L} are only ~ 18 and 5 nm at 100 and 300 K, respectively, thereby indicating that multiscale structural engineering should

Table 1 Calculated anharmonic parameters for B_{lg}^1 and B_{lg}^3 modes of SbCrSe₃ according to Equations (8) and (9), and the corresponding fitting line shown in Fig. 4b, c

Mode	$\omega_0 \text{ (cm}^{-1}\text{)}$	$A \text{ (cm}^{-1}\text{)}$	$B \text{ (cm}^{-1}\text{)}$	$\Gamma_0 \text{ (cm}^{-1}\text{)}$	$C \text{ (cm}^{-1}\text{)}$	$D \text{ (cm}^{-1}\text{)}$
B_{lg}^1	51.48	−0.041	0.00006	2.31	0.015	0.00003
B_{lg}^3	175.92	−0.191	0.00022	2.53	0.131	−0.00061

Figure 5 Thermal transport properties of SbCrSe₃. (a) Lattice thermal conductivity κ_L for the SbCrSe₃ single crystal, calculated results, and polycrystalline SbCrSe₃ samples [15]. (b) Anharmonic SRs of SbCrSe₃ at 100 and 300 K. (c) κ_L integration for 100 and 300 K with respect to frequency along the b -axis, where the inset is the κ_L contribution percentage from the acoustic and optical branches. (d) Cumulative κ_L for 100 and 300 K with regard to the phonon MFP frequency along the b -axis.

be effective to reduce κ_L [46–49].

CONCLUSIONS

In this study, bulk SbCrSe₃ single crystal was successfully synthesized by self-fluxing and annealing. Advanced SCXRD and HRTEM techniques confirmed that the long edge of the fabricated needlelike crystal is along the b -axis. The combination of the ARPRS measurement and group theory calculation was used to identify the Raman mode symmetries for the cleaved (001) crystal plane of SbCrSe₃, which is further corroborated *via* DFT calculations. Interestingly, some modes (e.g., $A_g^2 \sim 64$ cm⁻¹ and $A_g^7 \sim 185$ cm⁻¹) using the ARPRS measurement can be used to verify the crystalline orientation of small crystals or films. In addition, a finding facilitated by the *in-situ* Raman experiment is that the three-phonon interactions dominate the thermal transport of the SbCrSe₃ crystal. Furthermore, the theoretically calculated κ_L exhibits ex-

cellent agreement with the measured results, confirming that the approximation considering the three-order term in lattice vibrational potential is reasonable. This work not only provides a fundamental understanding of vibrational modes and lattice anharmonicity in the quasi-1D crystal of SbCrSe₃, but also describes a fast and facile method to explore the thermal transport properties of other novel low-dimensional materials.

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Author contributions Wu H, Gong X, Lu X, Wang G, and Zhou X designed the experiment and wrote the paper. Wu H, Gong X, Peng Y, Zhang L, Wang A, and He M conducted the experimental testing and crystal growth. Zhang B and Liu J carried out the microstructure characterization. Peng K, Gu H, Han G, Chai Y, and Guilmeau E participated in data analyses. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

Hong Wu is a PhD candidate in experimental condensed matter physics at Chongqing University. His main research is focused on the synthesis and physical properties of single crystal-based thermoelectric materials and novel thermoelectric materials with low thermal conductivity.

Xiangnan Gong received his master's degree from Wenzhou University (2011). Subsequently, he joined HORIBA as a senior technical engineer for Raman spectrometer. Currently, he is an engineer at the Analytical and Testing Center of Chongqing University. His work and research interests mainly focus on the Raman spectroscopy of crystal structures caused by various external fields, including temperature, stress, and polarization.

in 3D printing technologies for metals.

Guoyu Wang received his PhD degree in condensed matter physics from the University of Science and Technology of China (2007). After working as a postdoc researcher at The Hong Kong Polytechnic University (2007–2009) and University of Michigan (2009–2012), he accepted a faculty position at Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences in 2013. His current research is focused on thermoelectric materials and strongly correlated systems. He is also interested

Xu Lu obtained his PhD in experimental condensed matter physics from Michigan State University in 2014. Afterward, he stayed in the same group, working as a postdoc fellow until August 2015. Then, he joined the Department of Applied Physics, Chongqing University, China, as a “100 Talented Researchers of Chongqing University.” His research interest is thermal energy conversion materials, including thermoelectric materials and low-thermal-conductivity materials for thermal barriers.

Xiaoyuan Zhou received her PhD from the Department of Applied Physics, The Hong Kong Polytechnic University (2008). She worked as a postdoc research associate at the University of Washington (2008–2010) and University of Michigan (2010–2013). In 2013, she joined Chongqing University as a professor. Her current research is focused on thermoelectric materials and their applications.

拉曼光谱定义SbCrSe₃单晶的振动模式对称性和声子非谐性

吴宏^{1,2†}, 公祥南^{3†}, 彭义⁴, 张龙¹, 张斌³, 彭坤玲¹, 刘杰³, 韩广⁵, 王爱峰¹, 柴一晟¹, 何明全¹, 顾豪爽⁴, Emmanuel Guilmeau⁶, 王国玉^{2*}, 卢旭^{1*}, 周小元^{1,3*}

摘要 本文报道了SbCrSe₃单晶的合成方法及其在2–300 K温度范围内的热输运性能。通过角分辨偏振拉曼光谱技术、群论和理论计算分析,我们首次定义了该晶体沿(001)解理面的拉曼振动模式对称性,并可利用其某些模式确定晶体轴向。另外,通过原位变温拉曼光谱和理论计算相结合的方式,分析得出三声子散射过程即可准确地描述晶格热导率对温度的依赖关系。本文从一个全新的角度揭示了SbCrSe₃的热输运性质,为研究其他低维材料热性能提供了有力借鉴。