Probing lattice dynamics and electron-phonon coupling in the topological nodal-line semimetal ZrSiS

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Topological materials provide an exclusive platform to study the dynamics of relativistic particles in table-top experiments and offer the possibility of wide-scale technological applications. ZrSiS is a newly discovered topological nodal-line semimetal and has drawn enormous interests. In this paper, we have investigated the lattice dynamics and electron-phonon interaction in single-crystalline ZrSiS using Raman spectroscopy. Polarization and angle-resolved Raman data have been analyzed using crystal symmetries and theoretically calculated atomic vibrational patterns along with phonon dispersion spectra. Wavelength- and temperature-dependent measurements show the complex interplay of electron and phonon degrees of freedom, resulting in resonant phonon and quasielastic electron scattering through interband transition. Our high-pressure Raman studies reveal vibrational anomalies, which are the signature of structural phase transitions. Further investigations through high-pressure synchrotron x-ray diffraction clearly show pressure-induced structural transitions and coexistence of multiple phases, which also indicate possible electronic topological transitions in ZrSiS. This study not only provides the fundamental information on the phonon subsystem, but also sheds some light in understanding the topological nodal-line phase in ZrSiS and other isostructural systems.

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I. INTRODUCTION

Over the last few years, the condensed matter physics community has witnessed enormous advancement in band theory, which leads to the discovery of topological insulators (TIs) [1,2] and topological semimetals (TSMs) [3–7] and has triggered intense investigations to find materials with exotic topological phases of matter. While these systems are fascinating due to the intriguing physics of relativistic particles, they also appear to be promising candidates for technological applications [8,9]. Topological materials are characterized by unique surface and bulk states with topologically distinct electronic band structures. A TI possesses finite band gap in the bulk state, whereas its surface state hosts linear band crossings. On the other hand, in TSMs, bulk conduction and valence bands cross each other at either fourfold (Dirac node) [3,4] or twofold (Weyl node) degenerate points [5–7], depending on the inherent symmetries of the system. Near these nodes, the electronic bands obey linear dispersion relation and provide the exclusive platform to study the dynamics of long-sought Dirac/Weyl fermions. Presently, the primary objective in this field is not only to find new materials with such unique band structure, but also to look beyond the Dirac/Weyl-type excitations.

From band structure calculations, recently, the monolayers of WHM (W = Zr, Hf; H = Si, Ge, Sn; M = O, S, Se, Te) family of materials have been proposed to be two-dimensional TIs [10]. These isostructural compounds have identical electronic band structure. Although TI bands have been observed on the surface of bulk ZrSnTe crystal [11], ARPES and transport experiments have revealed topological nodal-line semimetal phase in several other members of this family [12-15]. In these systems, the bulk conduction band and valence band cross along a one-dimensional line in k space instead of discrete points, thus making them even more interesting from the perspective of fundamental physics. ZrSiS is the starting member of this group and hosts multiple linear band crossings at different energy values of bulk band structure, which form a nodal line [12]. Remarkably, in ZrSiS, the linear band crossing persists up to an energy range $\sim 2 \text{ eV}$ (largest reported so far) and, hence, can provide the robust topological system desired for industrial applications. Moreover, the quasi-two-dimensional Fermi surface, extremely large and anisotropic magnetoresistance, and multiband quantum oscillations in ZrSiS have already been the focus of a number of studies [12-14]. These reports inferred that the layered structure with square Si atom sublattice essentially controls the unique topological properties in ZrSiS and other isostructural systems. In fact, it is well established that the structural symmetries play a key role in protecting the accidental degeneracies and nontrivial topological electronic bands in a material. On the other hand, the system can be driven to electronic topological transitions by symmetry breaking. Raman scattering is a

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well-known nondestructive powerful tool for studying the structural symmetries of a material and to probe the impact of phonon on electronic energy bands [16–18]. Together with low-temperature measurements and high-pressure technique, this method enables us to draw an in-depth picture of the phonon dynamics, electron-phonon interaction, and possible structural and topological phase transitions. This information is crucial for understanding the structural, thermal, and electronic properties, and may help to comprehend the mechanism of the observed topological nodal-line semimetal phase in ZrSiS as well as in other members of the *WHM* family.

In this paper, we have done Raman spectroscopy measurements on single-crystalline ZrSiS. The Raman modes have been probed in the basal plane (crystallographic c axis is parallel to the wave vector k_i of the incident laser) and *edge plane* (k_i is perpendicular to the c axis) configurations. All the Raman active phonon modes at the Brillouin zone center and their vibrational patterns have been identified from the firstprinciples calculations as well as crystal symmetry analysis. While analyzing our data, we came across a recent paper by Zhou et al. [19] on the Raman study of ZrSiS. The authors have performed the Raman measurements at ambient conditions and presented the polarization dependent study only. On the other hand, we have performed and analyzed both polarizationresolved and crystal-angle-resolved Raman measurements in detail. From the wavelength- and temperature-dependent Raman studies, we have identified the complex interplay of phonons with electronic degree of freedom in ZrSiS. To further explore the phonon dynamics, Raman scattering experiments have been done under high pressure. To the best of our knowledge, there is no high-pressure study on ZrSiS so far. Pressure is an effective and clean way to tune the lattice as well as electronic states and is expected to have a significant impact on the layered structure of ZrSiS. Apart from the softening of the phonon modes, we have observed pressure-induced vibrational anomalies in the Raman spectra. To correlate the observed results, high-pressure synchrotron x-ray diffraction (HPXRD) measurements have been performed. HPXRD spectra reveal structural phase transitions along with the coexistence of multiple phases and also likely to be accompanied by the electronic topological transition in ZrSiS.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

The single crystals of ZrSiS were synthesized in the iodine vapor transport method [20]. The polycrystalline powder was prepared by solid-state reaction of elemental Zr (Alfa Aesar 99.9%), Si (Strem Chem. 99.999%), and S (Alfa Aesar 99.9995%) in two steps. Si and S (in stoichiometric ratio 1:1) were sealed in an evacuated quartz tube and heated at 1000 °C for 48 h. The resultant powder was mixed with Zr and again sealed in a quartz tube under vacuum and heated at 1100 °C for 48 h. The obtained polycrystalline powder together with iodine were finally sealed in another quartz tube under dynamic vacuum. This tube was placed in a gradient furnace for 72 h. During this period, the polycrystalline powder was kept at 1100 °C, whereas the temperature at other end of the tube was maintained at 1000 °C. Shiny, platelike single crystals were obtained at the cooler end. As grown crystals were characterized by high-resolution transmission electron microscopy (HRTEM) using an FEI, TECNAI G^2 F30, S-TWIN microscope operating at 300 kV and equipped with a GATAN Orius SC1000B CCD camera. The elemental compositions were checked by energy dispersive x-ray spectroscopy in the same microscope.

The ambient pressure and low-temperature Raman spectra were collected with a LABRAM HR 800 systems, which is equipped with a spectrometer of 80-cm focal length, 1800-gr/mm grating, and a Peltier cooled CCD. Lasers of wavelength 488, 633, and 785 nm were used to excite the sample. A $100 \times$ objective with NA 0.9 was used to focus the laser beam on the crystal.

A symmetric diamond-anvil cell (DAC) with culet size 300 μ m was prepared to generate high pressure up to 57 GPa (Fig. 7 in Appendix). A stainless steel or rhenium gasket was preindented with 36- μ m thickness, followed by laser drilling the central part to make a 170- μ m-diameter hole. We made sure that the sample thickness is about one-third of the gasket thickness to avoid damage of crystal and to maintain a good hydrostatic condition. Silicone oil was used as pressure transmitting media. The pressure calibration was carried out with ruby fluorescence method [21]. High-pressure Raman spectra were collected using inVia Renishaw Raman spectrometer with a 532-nm exciting laser and 2400-1/mm grating.

For HPXRD measurements, same DAC was used with Ne gas as a pressure-transmitting medium. Pressure was calibrated with equation of state of gold and platinum, which were loaded along with the sample inside the DAC. The experiments were carried out at Advanced Photon Source, GSECARS, 13IDD beamline with wavelength $\lambda = 0.3344$ Å. The two-dimensional (2D) diffraction images were integrated with FIT2D software and obtained intensity-2 θ patterns were analyzed using GSAS software to receive the information about the phases and lattice parameters.

All first-principles density functional theory (DFT) [22,23] based simulations have been performed using the plane-wave based Vienna ab initio simulation package (VASP) [24-26]. have used projector-augmented wave We (PAW) potentials [27,28], and the wave functions were expanded in the plane-wave basis with a kinetic energy cutoff of 350 eV. The exchange-correlation functional was chosen to be Perdew-Burke-Ernzerhof (PBE) [29] implementation of the generalized gradient approximation (GGA). Total energies were converged to less than 10^{-6} eV. In the case of structural relaxation, the positions of the ions were relaxed towards the equilibrium using conjugate gradient algorithm, until the Hellman-Feynman forces became less than 0.001 eV/Å. The phonon band structure has been calculated using the finite-difference method [30,31], as realized in the PHONOPYcode [32,33] in conjugation with DFT as executed in the VASP code. To cross-check our results, we have calculated the zone center phonon frequencies using density functional perturbation theory (DFPT) [34] as implemented in the VASP code.

III. RESULTS AND DISCUSSION

ZrSiS crystallizes in tetragonal structure with lattice symmetry P4/nmm (space group No. 129) and point group



FIG. 1. (a) Crystal structure of ZrSiS. (b) HRTEM image along the *ac* plane. Inset shows the magnified image along with the interlayer spacing. (c) Selected area electron diffraction (SAED) pattern obtained through HRTEM measurement. (d) Schematic representation of the Raman measurement for *basal plane* and *edge plane* configurations.

 D_{4h} [20,35]. Figure 1(a) shows the crystal structure of ZrSiS, where a, b, and c are crystallographic axes. Layers of Zr and S are sandwiched between the Si square nets located in the *ab* plane. Neighboring S atoms reside between two Zr layers. The high-resolution transmission electron microscopy (HRTEM) image of a typical ZrSiS single crystal is shown along *ac* plane in Fig. 1(b). High-quality crystalline nature of the samples can be clearly seen with an interlayer spacing ~ 8 Å [shown in the inset of Fig. 1(b)]. The electron diffraction pattern of the crystal is shown in Fig. 1(c) with the Miller indices of the corresponding lattice planes. We have also performed the x-ray diffraction measurements on the powdered sample (discussed later) and analyzed the spectra by Rietveld structural refinement using FULLPROF software package. The refined lattice parameters are a = b = 3.546(2)and c = 8.055(4) Å. The obtained lattice constant along c axis is in excellent agreement with the interlayer spacing in the HRTEM image. For theoretical calculations of the Raman modes, we have optimized the lattice constants. The calculated lattice parameters a = b = 3.677 and c = 7.947 Å are consistent with the x-ray diffraction results. The small difference between the theoretical and experimental values can appear due to the generalized gradient approximation of the first-principles calculations, which often overestimate the lattice parameters [36]. Additional characterization details can be found in our earlier paper [13]. Figure 1(d) schematically illustrates the experimental setups for basal plane and edge *plane* configurations. Here, θ is the angle of rotation for the polarization vector and has been discussed later.

From the group-symmetry analysis, the zone center optical phonon modes of ZrSiS can be expressed as $\Gamma_{ZrSiS} = 2E_u + 2A_{1g} + 2A_{2u} + 3E_g + B_{1g}$ [37]. Among them, A_{2u} and E_u



FIG. 2. (a) Room-temperature Raman spectra for *basal plane* (black curve) and *edge plane* (red curve) configurations. The shaded region in the lower panel represents the calculated phonon density of states for ZrSiS. (b) Vibration patterns corresponding to the Raman active modes.

modes are IR active, whereas the other six modes $(2A_{1g}, B_{1g}, B_{1g})$ and $3E_g$) are Raman active. In Fig. 2(a), the results of Raman measurements at room temperature $(297 \pm 1 \text{ K})$ for the two configurations of the ZrSiS crystal are presented along with the calculated phonon density of states (PDOS), shown by the filled area. In the *basal plane* configuration, the incident laser beam excites the *ab* plane of the crystal and shows three Raman active modes. On the other hand, for the edge plane measurements, the crystal is rotated by 90° around b axis so that the laser now falls on the bc plane of the crystal. In this configuration, all the six Raman active modes have been observed. A comparison of the theoretical PDOS and experimental Raman spectra shows that not all the peaks in theoretical PDOS appear in the experimental spectra. This is expected as other theoretically obtained modes do not satisfy the selection rules for Raman spectra. To identify the observed modes, we have calculated phonon dispersion for ZrSiS (Fig. 10 in Appendix) and estimated all Raman active frequencies at the Brillouin zone center using first-principles calculations. As shown in Table I, the calculated frequencies are in excellent agreement with the experimental results. Note that the E_g modes are absent in the *basal plane* measurements, which can be explained from the lattice symmetry analysis, discussed later. In Fig. 2(b), the vibrational patterns of all six Raman active modes have been illustrated. The A_{1g} optical modes at 212 and 303 cm⁻¹ belong to the antisymmetric vibration of Zr and S atoms along the c axis. The vibration of Si

TABLE I. Comparison of the calculated and experimental Raman active phonon frequencies at room temperature (297 ± 1 K).

| Mode | Calc. Freq. (cm ⁻¹) | Expt. Freq. (cm ⁻¹) |
|-----------------------|------------------------------------|------------------------------------|
| $\overline{A_{1g}^1}$ | 212 | 210 ± 0.5 |
| $A_{1g}^{2^{8}}$ | 303 | 303 ± 0.5 |
| B_{1g} | 312 | 312 ± 0.7 |
| E_{q}^{1} | 132 | 134 ± 0.5 |
| E_a^{\diamond} | 323 | 321 ± 0.5 |
| E_g^{3} | 347 | 347 ± 0.5 |



FIG. 3. Polarized Raman spectra of (a) *edge plane* and (b) *basal plane* configurations.

atoms along the *c* axis with frequency 312 cm^{-1} corresponds to B_{1g} . The E_g modes at 132, 323, and 347 cm⁻¹ come from the in-plane vibrations of Zr, Si, and S atoms. The observed results are consistent with the earlier paper by Zhou *et al.* [19].

To verify the symmetry of the observed modes, we have measured the polarized Raman spectra in the backscattering configurations with light polarization along certain crystallographic directions. We use Porto's notation for parallel $[z(xx)\overline{z} \text{ and } z(yy)\overline{z}]$ and perpendicular $[z(xy)\overline{z} \text{ and } z(yx)\overline{z}]$ configurations. Here, the z axis is along the crystallographic c axis for basal plane configuration and antiparallel to the a axis for edge plane configuration [see Fig. 1(d)]. The observed polarized Raman spectra of ZrSiS for both configurations are shown in Fig. 3. Only A_{1g} modes have been detected when the measurement was conducted in the parallel channels, i.e., $z(xx)\overline{z}$ or $z(yy)\overline{z}$. On the other hand, B_{1g} and E_g modes are present for $z(xy)\overline{z}$ or $z(yx)\overline{z}$ polarization configurations. The observed small intensity of the forbidden modes at a particular configuration is due to the small misalignment of the laser polarization with crystallographic axis.

The intensity (*I*) of different Raman active modes obeys a fundamental relation [38]

$$I \propto |\hat{e}_i \cdot \operatorname{Re} \cdot \hat{e}_s|^2 , \qquad (1)$$

where \hat{e}_i and \hat{e}_s are the unit polarization vectors of the incident and the scattered light, respectively. Re represents the rank-2 Raman scattering tensor for a particular mode and is determined by the point-group symmetry of the material. For ZrSiS, with respect to the principal axes of the crystal, the scattering tensors in the *bc* plane have the forms

$$\operatorname{Re}(A_{1g}) = \begin{bmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{bmatrix}, \quad \operatorname{Re}(B_{1g}) = \begin{bmatrix} \delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & 0 \end{bmatrix},$$
$$\operatorname{Re}(E_g) = \begin{bmatrix} 0 & 0 & -\rho \\ 0 & 0 & \rho \\ -\rho & \rho & 0 \end{bmatrix}.$$

Here, α , β , δ , and ρ are Raman scattering components, which can be extracted by fitting the experimental data. When the polarization vectors of the incident and scattered light are parallel, say along the *y* axis in an orthogonal *xyz* coordinate system, the unit vectors are given by

$$\hat{e}_{i,xyz} = \begin{bmatrix} 0 & 1 & 0 \end{bmatrix}; \quad \hat{e}_{s,xyz} = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}.$$

To get the *basal plane* configuration, one has to rotate the crystal by 90° around the *b* axis. This operation introduces a rotational matrix, which modifies the scattering tensors in the following forms:

$$Re(A_{1g})(basal) = \begin{bmatrix} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \alpha \end{bmatrix},$$
$$Re(B_{1g})(basal) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & \delta \end{bmatrix},$$
$$Re(E_g)(basal) = \begin{bmatrix} 0 & \rho & \rho \\ \rho & 0 & 0 \\ -\rho & 0 & 0 \end{bmatrix}$$

Using these matrices in Eq. (1), one can find that in *basal plane* configuration A_{1g} and B_{1g} modes should be present, whereas the intensity of the E_g modes is always zero. The obtained results from crystallographic symmetries are consistent with our experimental observations, as shown in Fig. 2(a).

Next, we have studied the complete crystal orientationdependent Raman spectrum for ZrSiS. We chose the *edge plane* configuration because all the modes can be identified in this setup and rotated the polarization vector in the crystallographic *bc* plane by rotating the single crystal (Fig. 11 in Appendix). The intensity variation of different modes (Fig. 12 in Appendix) can be fitted well using the following equations:

$$I(A_{1g}) \propto |\alpha \cos^2 \theta + \beta \sin^2 \theta|^2$$

= $C_1 + C_2 \cos 2\theta + C_3 \cos 4\theta$, (2)

 $I(B_{1g}) \propto |-\delta \cos^2 \theta|^2 = C_4 + C_5 \cos 2\theta + C_6 \cos 4\theta$, (3)

$$I(E_g) \propto |2\rho \sin\theta \cos\theta|^2 = C_7 - C_8 \cos 4\theta.$$
 (4)

These relations have been derived from Eq. (1) using the scattering matrices for the *edge plane* (details are provided in the Appendix). Here, the parameters C_i (i = 1, 2, ..., 8) are the functions of the components of Raman scattering tensors and θ is the angle between the polarization vector and crystallographic *b* axis. All the modes show fourfold symmetry patterns. The observed results are in contrast to the report by Zhou *et al.* [19], where the Raman modes generate twofold symmetry. This is due to their experimental setup, where the measurements were performed by changing the light polarization. As discussed by Ma *et al.* [39], to obtain the complete structural symmetry, instead of changing the light polarization, one has to rotate the single crystal, which has been done in the present case (details are provided in the Appendix).



FIG. 4. Raman spectra of ZrSiS with different incident laser excitations in *basal plane* configuration. The black dashed lines correspond to the background. The yellow shaded area represents the fitting of the QE scattering using Lorentzian line shape and the orange shaded Gaussian peak is the plasmon maximum at 703 cm⁻¹ for 785 nm laser. Insets show the integrated intensity of the QE and phonon scattering (A_{1g}^2) as function of excitation energy.

We have also performed the wavelength-dependent Raman measurements for both basal plane and edge plane configurations. In Fig. 4, the result for basal plane configuration is shown as a representative. A definite dependency of the Raman scattering intensity on the energy of the incident laser is observed. The integrated intensity of the most intense peak (A_{1g}^2) shows the highest value at low excitation energy $(\lambda = 785^{\circ} \text{ nm}, E = 1.58 \text{ eV})$ as displayed in the inset of Fig. 4. This enhancement is due to the coincidence of the laser energy with an intrinsic electronic transition of ZrSiS. Calculated bulk electronic band structure of ZrSiS [12] shows that at Γ point the energy gap is around 1.4 eV, which is consistent with the reflectivity measurement [40]. Here, the enhancement of the intensity for A_{1g}^2 mode with decreasing excitation energy from 2.54 to 1.58 eV, can be due to the fact that the laser energy is approaching towards the energy gap at Γ point. In topological semimetals, the complex interplay of electronic and phonon degrees of freedom results in a quasielastic (QE) scattering [41]. In the excitation energy-dependent Raman spectra, in contrast to the narrow phonon features, we have observed a broad and well-defined peak close to the laser energy (yellow shaded area in Fig. 4) instead of a flat background. Such feature is reproducible over multiple measurement cycles on different single crystals of ZrSiS. This peak can be attributed to the QE electronic scattering. The presence of such scattering in Dirac semimetal Cd_3As_2 has been reported recently [41]. The line shape of the QE electronic scattering can be fitted well with the Lorentzian function. In semimetals, the Lorentzian shape of QE scattering appears due to the electronic energy density fluctuations [42]. The intensity of QE scattering peak is highly photon energy dependent (inset of Fig. 4). This behavior can be explained as a resonant enhancement of the phonon and it occurs, when the energy of the scattered photon matches with one of the excitonic transition energies [43,44]. The occurrence of resonant enhancement and QE scattering at the same excitation energy implies that both the processes involve same intermediate state. A peak with Gaussian line shape (orange shaded area in Fig. 4) has been observed at 703 cm^{-1} ,



FIG. 5. (a) Raman spectra of ZrSiS at different representative temperatures. (b) Raman frequency and (c) FWHM of characteristic Raman modes as a function of temperature. The solid lines are drawn as guide to eyes.

which may be a direct evidence for the single-particle or collective excitations (plasmonlike) [41].

The temperature-dependent Raman spectra for ZrSiS are presented in Fig. 5(a). The spectra show changes in frequency and full-width at half-maximum (FWHM) of the modes in the temperature range 80-320 K. We have fitted all the Raman spectra using Lorentzian functions to estimate the frequency shift as well as the linewidth of the observed Raman modes in the studied temperature range. Figures 5(b) and 5(c) show the temperature dependence of frequency and linewidth of the observed Raman modes, except for B_{1g} because the intensity of this mode is very small. Variations of peak positions and FWHMs with temperature show two different regions roughly below and above 150 K. Although the feature is weak for some modes, it is still detectable and is beyond the experimental error bars. The Raman frequencies of the modes remain almost the same in the low-temperature region but monotonically redshifted with the rise of temperature. Such behavior cannot be fitted assuming a linear dependence throughout the measured temperature range. The factors, which cause the temperature dependence of Raman shifts, are phonon-phonon interaction and thermal expansion. Thermal expansion of the material leads to decrease in frequency of the modes. The temperature

TABLE II. Estimated thermal expansion coefficient (α), isobaric (γ_{iP}) and isothermal (γ_{iT}) mode-Grüneisen parameters, and Fermi velocity from the measured Raman spectra.

| $\omega_{ph} \ { m cm}^{-1}$ | a_i (cm ⁻¹ /GPa) | $\alpha (10^{-5} \mathrm{K}^{-1})$ | γiP | γiT | v_F (10 ⁵ m/s) |
|------------------------------|-------------------------------|------------------------------------|------|------|--------------------------------|
| 134 | 1.44 | 1.39 | 2.77 | 1.23 | 1.1 |
| | | (up to 15 GPa) | | | |
| 210 | 2.71 | 1.48 | 2.96 | 1.88 | 0.9 |
| 303 | 2.04 | 1.43 | 2.84 | 0.97 | 1.7 |
| 321 | 3.36 | 0.98 | 1.94 | 1.51 | 0.6 |
| 347 | 4.99 | 1.20 | 2.48 | 2.07 | 2.6 |
| | | | | | |

dependence of *i*th phonon energy can be written as [45]

$$\omega_{ph,i}(T) = \omega_i(0) + \Delta_i^1(T) + \Delta_i^2(T), \tag{5}$$

where $\Delta_i^1(T)$ is due to thermal expansion and $\Delta_i^2(T)$ is related to the phonon-phonon interaction. $\omega_i(0)$ is the phonon frequency at zero temperature, which is obtained by extrapolating the temperature-dependent Raman shift. As $\omega_i(0)$ is higher than $\Gamma_i(0)$ (FWHM at zero temperature), the contribution of phonon-phonon coupling in ZrSiS must be small compared to the shift due to thermal expansion [45]. To analyze the red-shift of the modes at higher-temperature region, we have used a linear dependency $\omega_i(T) = \omega_i(0) + \chi_i T$ [blue line in Fig. 5(b)], where χ_i is the first-order temperature coefficient [46,47]. Using χ_i values, we have estimated the thermal expansion coefficient and isobaric mode-Grüneisen parameter (γ_{iP}) for all the modes, which are shown in Table II. The FWHM of the peaks show two different slopes with temperature. Except for A_{1g}^2 , all other modes show a constant FWHM at low temperature and an abrupt change near 150 K, above which it increases with increasing temperature. In a perfect crystal, the linewidth of the phonon (Γ) is governed by its interaction with other elementary excitations and can be expressed as $\Gamma = \Gamma^{an} + \Gamma^{\text{EPC}}$. Γ^{an} is the phonon-phonon coupling term, which describes the anharmonic coupling between phonons and Γ^{EPC} represents the electron-phonon coupling [48]. Γ^{an} is always present in a system, but Γ^{EPC} comes into play only when the electronic band gap is zero. Here, the FWHM values at lower temperatures indicate that the contribution from thermal anharmonicity is lower than the spectrometer resolution (1 cm^{-1}) . The increase in FWHM with temperature may be a sign of increased electron-phonon interaction and, thus, an increase in phonon energy dissipation [49]. This would lead to increased electron scattering rate and hence a change in the nature of temperature dependence of resistivity around 150 K, as observed in the transport measurements [13]. We can also calculate the Fermi velocity (v_F) of the electrons using the relation [48]

$$v_F = \frac{2 \operatorname{Slope}(\Gamma)\omega_{\Gamma}}{\Gamma^{\operatorname{EPC}}},\tag{6}$$

where Slope(Γ) is the slope of phonon dispersion curve, obtained from the quadratic fit to the data presented in Fig. 10 in the Appendix and ω_{Γ} is the measured phonon frequency at zone center. Γ^{EPC} has been calculated by deducing maximum possible anharmonicity contribution (spectrometer resolution 1 cm⁻¹) from the measured FWHM at low temperature. The estimated v_F for all the modes (see Table II) are in excellent agreement with that calculated from quantum oscillation measurements (~10⁵ m/s) [13]. From the wavelength- and temperature-dependent Raman studies, it is evident that the lattice dynamics in ZrSiS possesses a strong correlation with the changes in the electronic properties.

Pressure-dependent Raman spectra for ZrSiS have been recorded inside a DAC in the *edge plane* configuration for the compression as well as decompression cycles up to 57 GPa as shown in Figs. 6(a) and 6(b), respectively. During compression, all the predominant Raman modes other than E^1_{σ} have been observed to shift towards higher frequencies with increasing pressure as depicted in Fig. 6(c). E_g^1 mode shows a softening $(\sim 1 \text{ cm}^{-1})$ at around ~ 17 GPa and then starts to harden monotonically with pressure [Fig. 6(c) inset]. At ~17 GPa, a new band, labeled "1," emerges at $\sim 148 \text{ cm}^{-1}$. Another two new bands, labeled "2" and "3," appear by splitting of A_{1g}^1 and E_g^2 at ~5 and ~10 GPa, respectively. The bands 2 and 3 are almost inseparable from the parent modes $(A_{1g}^1$ and E_{g}^{2}) up to the highest applied pressure during compression. For all the new bands, with increasing pressure, the frequency increases, intensity reduces, and pressure-induced broadening has been observed. All these observed changes are almost reversible during decompression [Fig. 6(b)]. The existence of all the parent phase modes, along with the new modes and their smooth dependencies on pressure, suggest the coexistence of the new phase with the parent tetragonal phase. It is possible that the new high-pressure phases have been resulted from the lattice distortion and stacking faults, which occur due to the destabilization of the weakly bonded S bilayers as reported in layered PbFCl [50] and BaFCl systems [51]. During pressure release, a small peak, marked as "*" in Fig. 6(b), emerges at ~ 16 GPa. By comparing the peak positions at ambient conditions, we have concluded that it may be the signature of B_{1g} mode, which is not clearly visible during compression. The pressure dependencies of the high-frequency modes (E_q^2) and E_a^3) are almost linear. For other modes, it can be fitted with quadratic function and the fitted curves are shown as solid lines in Fig. 6(c). E_g^1 mode increases monotonically with pressure after softening, whereas the mode 1 starts to separate faster above ~ 31 GPa. The pressure derivative (a_i) and the isothermal mode-Grüneisen parameter (γ_{iT}) have been calculated for all modes using the theoretically estimated bulk-modulus value [37] as shown in Table II. The difference between γ_{iP} and γ_{iT} is mainly due to the electron-phonon coupling effect, which was not excluded for the calculation of γ_{iP} . We have calculated FWHM for E_g^1 mode and observed an interesting behavior as shown in Fig. 6(d). For E_g^1 , FWHM is maximum at ~ 15 GPa and it decreases on either side asymmetrically, followed by a steep rise for higher pressures. At around this pressure range, we have noticed that (i) a new mode 1 starts to appear (at \sim 17 GPa) and (ii) the softening of E_g^1 occurs.

To correlate our results, let us discuss the geometric structure of tetragonal ZrSiS, isopuntal with PbFCl [52,53] and built up by stacking five 4⁴ square nets into layers of [...Si₂-Zr-S-S-Zr-Si₂...] along the fourfold axis. Zr atoms form a part of the double layer of S atoms and build up sheets of square pyramids $[Zr_{5/5}S]_n$, which alternate along the *c* axis with



FIG. 6. Variation of Raman modes with pressure during (a) compression and (b) decompression up to 57 GPa. (c) Pressure dependencies of parent phase Raman modes along with new modes. Inset shows the softening of E_g^1 mode at around ~17 GPa. (d) Variation of FWHM for E_g^1 mode as a function of pressure during compression. The dashed green line is drawn as guide to eyes.

planer Si_{2n} layers [52,53]. Si atoms are packed into layers that are twice denser than S layers, resulting in appreciable Si-Si bonding and modest S-S bonding into the unit-cell structure. All the E_g modes correspond to the vibrations, which are confined in the *ab* plane. As our first-principles calculations show, the lowest-frequency E_g^1 mode corresponds to relative motion of the two adjacent S layers with each Zr layer moving in phase with its nearest-neighbor S layer, i.e., lacks c-axis vibrations. On the other hand, the A_{1g}^1 mode corresponds to the asymmetric vibrations related to Zr and S atoms and describes the in-phase motion of S bilayers with Zr layers on either side. The calculations on phonon density of states also predict that the contribution to the highest optical phonon branches, which correspond to the lowest-frequency Raman active modes, comes only from Si and S atoms. Hence, it is expected that E_g^1 and A_{1g}^1 modes (related to S atoms), which describe the relative motion between the two weakly bonded Si₂-Zr-S units, can be quite sensitive to interlayer interactions under any external perturbations such as high pressure. The S bilayers, involving the stabilizations of the interlayer arrangements, contribute significantly to E_g^1 and A_{1g}^1 modes in the *ab* plane. We also found that under high pressure, low-frequency E_g^1 mode is more susceptible to change than any other Raman active modes.

The sublinear pressure dependency of Raman modes indicates that the coupling between the layers increases under external pressure [Fig. 6(d)]. In contrast to PbFCl, the nonlinearity in ZrSiS exists up to the highest applied pressure 57 GPa, suggesting a more rigid structure. This is also supported by their differences in the bulk modulii, 51 and 144 GPa for PbFCl and ZrSiS, respectively [37,50]. The decrease of FWHM followed by the softening of E_g^1 mode at ~17 GPa is a clear indication of change in the interlayer bonding nature, i.e., from layer type to more isotropic structure. A similar kind of asymmetric decrease in FWHM for a low-frequency phonon mode was reported earlier in a topological insulator system Sb_2Se_3 [54]. The authors inferred the phenomenon as pressure-induced electronic topological transition (ETT) from band to topological insulating state. We found that multiple electronic bands are present at the zone center of ZrSiS with energy separations comparable to excitations of laser energies to the interband transitions. Some topological insulators like BiTeI and Bi₂Se₃ [55,56] also show similar results. Gradual splitting of the A_{1a}^1 mode and the appearance of modes labeled 1, 2, and 3 can be the indication of isostructural symmetry lowering due to the instability occurring in the S bilayers.

The synchrotron XRD patterns, recorded as a function of pressure ranging from 2.2 to 30.2 GPa, are shown in Fig. 7. To index the strongest peaks of the pure tetragonal crystal lattice (ICSD File No. 1527641), a theoretically calculated pattern for 1 atm has also been plotted, using the refined lattice parameters a = b = 3.546(2) and c = 8.055(4) Å, from our ambient condition XRD data. At 2.2 GPa, our analysis of HPXRD data assuming the parent P4/nmm crystal structure



FIG. 7. The x-ray diffraction patterns with varying pressure. The calculated diffraction pattern for the parent tetragonal phase has been plotted to index the high-pressure phases. The slanted arrows (red, blue, and black) show the emergence of new peaks, whereas solid Δ shows the intensity enhancement of a new peak (020) associated with the monoclinic phase. S is the impurity peak from sulfur and tracked throughout the pressure region (dashed line). The letters T, O, and M stand for the tetragonal, orthorhombic, and monoclinic phases, respectively. The braces on the right side show approximate phase coexistence of the respective phases during compression.

resulted in successful indexing of almost all the diffraction peaks in the x-ray pattern other than a weak peak marked as S. This peak has been tracked throughout the measured pressure range (0-30.2 GPa). By careful analysis, we have identified that the peak S originates from a small amount of unreacted sulfur on the surface of the single crystals, which were crushed to get the powdered sample. With the application of pressure, a number of significant changes have been observed, which are marked with arrows in Fig. 7. Some of these changes can be discernible at and below 5 GPa. However, the major parent tetragonal phase is present even at highest pressure 30 GPa in significant amount as supported by our pressure-induced Raman spectra. The extensive studies on the high-pressure structural evolution of the ionic-layered matlokite [50], alkaline-earth halo fluorides [51,57], metaloxide hallides [58], and hydride halides composed of sequence of layers, showed the series of symmetry-lowering structural transitions from tetragonal to monoclinic phase via the intermediate orthorhombic phase. These results helped us to narrow down the search for the lower-symmetry phases in our layered ZrSiS sample. The structure at 3.7 GPa is closely related to tetragonal phase as it can produce all the peaks except the new peaks. Due to large *c*-axis compressibility, the phase must receive a smaller c/a ratio than that at ambient conditions as well as the a or b axis should be longer than the ambient value. Considering these conditions, we have found the presence of an orthorhombic phase (space group: *Pnma*) with lattice parameters a = 4.23523, b = 4.9869, and c = 8.31257 Å at 3.7 GPa, coexisting with the tetragonal lattice a = 3.52026 and c = 7.97655 Å. We have performed LeBail



FIG. 8. (a) Variation of lattice parameter *c* for the tetragonal phase with pressure. The discontinuity in the same appeared at 18.7 GPa marked with arrow. (b) Variation of lattice parameter *a* and (c) the normalized volume of the tetragonal phase (V/V_0) with pressure. The solid line in (c) shows EOS where the values of $B_0 = 141 \pm 4.5$ GPa and $B'_0 = 5.1 \pm 0.5$ are shown. The letters T, O, and M stand for the tetragonal, orthorhombic, and monoclinic phases, respectively.

fitting for the XRD patterns to index the coexisting phases considering the refinements of lattice parameters without any refinements of atomic positions at high pressures. For the orthorhombic phase, the atom positions of the BaBr₂-type structures (ICSD File No. 1527183) have been taken as an initial guess considering the fact that ZrSiS crystallizes in this type at high pressure [59]. The peaks corresponding to the orthorhombic phase are indexed in Fig. 7, whereas all the other intense peaks are reproduced by the parent P4/nmm structure. The pressure-induced lattice compression and coexistence of phases can be the reasons for the changes observed in the Raman modes $(A_{1g}^1 \text{ and } E_g^2)$ at around 5 GPa. A small shoulder peak to the left of $(020)_T - (212)_O$ (marked with blue arrow in Fig. 7) appeared at \sim 8.7 GPa. As the pressure is increased, the peak can be clearly identified until 30 GPa. At around 16 GPa, a new peak appeared just right to the $(004)_T$ peak. The intensity of this new peak is seen to increase with increasing pressure. All the peaks from the tetragonal and orthorhombic phases are clearly visible, whereas the new peaks can not be indexed with either of these two phases. An analysis at ~ 16 GPa shows the mixture of three phases: a tetragonal parent phase with coexisting orthorhombic and monoclinic phases. Our XRD data analysis shows that the coexistence of the three phases persists up to the highest applied pressure 30 GPa. The newly emerged peak can be indexed as $(020)_M$ of monoclinic phase (space group: $P2_1/m$) with lattice parameters a = 7.81417, b = 3.56305, and c =3.56305 Å with $\beta = 107.045^{\circ}$. This monoclinic structure is identical to the one reported for BaFCl [51]. A similar type of gradual increase in intensity with increasing pressure has also been observed for BaFBr and BaFCl systems starting from 22 to 60 GPa [51,60]. The authors inferred that the phase transition corresponds to the gradual distortion of the tetragonal phase to a monoclinic phase through an intermediate orthorhombic phase. In layered transition-metal dichalcogenides [61,62], the structural phase transition with an increase of intensity for a particular peak can be explained by the changes in Wyckoff's positions of the atoms, corresponding c/a ratio, and the variation in chalcogen-metal-chalcogen bond angles. Our XRD results highly correlate the observed softening of the E_{a}^{1} phonon mode in Raman spectra at around 17 GPa. As we have already discussed, the interlayer arrangements of S bilayers contribute to the E_g^1 mode in the *ab* plane. We infer that due to high *c*-axis compressibility, there can be a large compression of the electron charge density of the S ions between the adjacent weakly bonded S layers along the c axis. Therefore, the anisotropic distribution of such charge density in the ab plane started to distort the lattice during compression. At high pressure above 16 GPa, the tilting of either orthorhombic lattice in the *ab* plane or tilting of the tetragonal lattice in the ab plane with respect to c axis may cause the orthorhombic to monoclinic phase transition. The effect of such lattice distortions clearly supports our results on pressure-induced Raman spectra. In Fig. 8(a) we have plotted the variation of the lattice parameter c of the parent tetragonal lattice with pressure. The discontinuity of ~ 0.3 Å is a clear indication of the growing instability in the parent lattice at around ~ 18.7 GPa. Although the signature of the monoclinic phase appears below 18.7 GPa, it is possible that when a sufficient amount of monoclinic phase sets in, we can observe the measurable discontinuity in the lattice parameters. As shown in Figs. 8(b) and 8(c), we have not found any discontinuity in the lattice parameter a and the calculated normalized unit-cell volume (V/V_0) for the tetragonal phase as a function of pressure. The unit-cell volume gradually decreases with pressure without showing any volume collapse. The observed sluggish and smooth nature of the phase transition is due to the small difference in the Gibbs free energy among these three phases [50,63]. Assuming the tetragonal phase for whole pressure range 0-30 GPa, a third-order Birch-Murnaghan equation of state (EOS) has been used to fit V/V_0 with pressure. The obtained bulk modulus is $B_0 = 141 \pm 4.5$ GPa with pressure derivative $B'_0 = 5.1 \pm 0.5$ and agrees very well with the theoretically calculated value 144 GPa [37]. The system appears hard to compress with respect to ZrSiTe and ZrSiSe [37].

IV. CONCLUSIONS

In conclusion, we have performed a systematic Raman spectroscopy study on single crystals of ZrSiS. To probe all the Raman active modes, the measurements have been done along two crystallographic planes. The first-principles calculations have been conducted to identify the observed modes as well as the corresponding atomic vibrational patterns. The polarization and crystal rotation-dependent Raman studies further verify the mode identification and provide fundamental information about the structural symmetries of the system. The temperature and excitation energy variation measurements reveal resonant enhancement of phonon and quasielastic electronic scatterings, which are the signatures of complex electron-phonon interaction in ZrSiS. Furthermore, the high-pressure Raman spectra show vibrational anomalies and the appearance of new modes, suggesting possible structural transitions. From the structural analysis, we conclude that such modification in crystal structure may also lead to electronic topological transition, as observed in several topological materials. Our highpressure synchrotron x-ray diffraction measurements show very interesting pressure-induced structural transition from tetragonal to monoclinic phase via an intermediate orthorhombic phase with the absence of any volume collapse. The coexistence of three phases up to the highest applied pressure (30 GPa) and the structural transformations agree well with the high-pressure Raman spectroscopy results. Therefore, this paper presents a detailed study on the lattice dynamics and electron-phonon interaction in ZrSiS and may also provide the grounds for subsequent investigations in the present system as well as other isostructural compounds.

APPENDIX

1. High-pressure measurements

In Fig. 9, we have shown the setup of DAC for high-pressure Raman measurements.

2. Calculation of phonon dispersion

The theoretically calculated phonon dispersion spectra for ZrSiS are shown in Fig. 10.

3. Crystal orientation-dependent Raman spectroscopy

To describe the Raman spectrum for different crystal orientations and polarization geometry, let us introduce a Cartesian coordinate system, where the x' direction coincides with the crystallographic *a* axis. Whereas the y' and z' directions make an arbitrary angle (θ) with the crystallographic *b* and *c* axes, respectively (Fig. 11). In this representation, the scattering tensors are transformed as

$$\operatorname{Re}_{x'y'z'} = \Phi_{x'y'z'}\operatorname{Re}\tilde{\Phi}_{x'y'z'}, \qquad (A1)$$

where $\Phi_{x'y'z'}$ is the orthogonal transformation matrix

$$\Phi_{x'y'z'} = \begin{bmatrix} 1 & 0 & 0\\ 0 & \cos\theta & \sin\theta\\ 0 & -\sin\theta & \cos\theta \end{bmatrix}$$

and $\Phi_{x'y'z'}$ is its inverse. Using these transformed matrices in Eq. (1) of the main text, we have derived the intensity relations



FIG. 9. ZrSiS single-crystal sample and ruby inside DAC for high-pressure Raman measurements.



FIG. 10. Calculated phonon dispersion spectra for ZrSiS.

[Eqs. (2), (3), and (4) in the main text] for different Raman active modes.

To measure the crystal orientation-dependent Raman scattering of ZrSiS, we chose the *edge plane*, as all modes can be identified in this configuration. Initially, we have fixed the polarization vectors of the incident and scattered lights parallel to each other and along the crystallographic *b* axis. Note that at this point all the axes of the Cartesian coordinate system coincide with the crystallographic axes, i.e., $\theta = 0$. Now, we start to rotate the single crystal in the y'z' plane



FIG. 11. Schematic of the experimental setup for crystal orientation-dependent Raman spectroscopy. The crystal is rotated around the a axis, which is equivalent to rotation of the laser polarization vector in the bc plane.



FIG. 12. Angle dependence of Raman mode intensities in parallel configuration ($\hat{e}_i \parallel \hat{e}_s$) on *edge plane*.

in small steps and note the intensity variation of different modes. Although this method is equivalent to the rotation of the polarization vector along crystallographic bc plane, rotation of the sample has certain advantages. To change the polarization direction of both incident and scattered lights, one has to use additional optical pieces in the light path and adjust their polarization angles at each step. Such setup unavoidably

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introduces experimental uncertainties in the polarization angle and also can modulate the intensity of different modes [39]. The obtained angular dependence of the normalized intensity profile is shown in Fig. 12 (scattered points) for different modes as polar plots. The experimental data have been fitted well using Eqs. (2), (3), and (4) (solid red lines in Fig. 12), which have been derived from the crystal symmetry of ZrSiS.

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