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Hyperbolic Plasmons Propagate through a Nodal Metal

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Abstract:

Metals are canonical plasmonic media at infrared and optical wavelengths allowing one to guide and manipulate light at sub-diffractive length scales. A special form of optical waveguiding is offered by highly anisotropic crystals revealing different signs of the dielectric function along orthogonal directions. These latter types of media are classified as hyperbolic and many crystalline insulators, semiconductors and artificial metal-based metamaterials belong to that class. Layered anisotropic metals are also anticipated to support hyperbolic waveguiding. Yet this behavior remains elusive primarily because interband processes introduce extreme losses and arrest light propagation. Here, we report on the observation of propagating hyperbolic waves in a prototypical layered nodal-line semimetal ZrSiSe. The unique electronic structure with touching energy bands at nodal points/lines suppresses losses and enables a hyperbolic regime at the telecommunications frequencies. The observed waveguiding in metallic ZrSiSe is a product of polaritonic hybridization between near-infrared light and long-lived nodal-line plasmons. By mapping the energy-momentum dispersion of the nodal-line hyperbolic modes in ZrSiSe we inquired into the role of additional screening associated with the surface states.

Main text:

The dielectric permittivity tensor ($\epsilon = \epsilon_1 + i\epsilon_2$) in layered materials exhibits strong anisotropy such that the real part ϵ_1 may display opposite signs along different crystal axes. In this so-called hyperbolic regime, the isofrequency surface of the electromagnetic wave is an open hyperbola instead of the usual closed sphere or ellipse^{1–6}. In the hyperbolic regime, the interaction of light with collective modes of the matter results in hyperbolic polaritons exhibiting exotic properties including ray-like waveguiding inside the crystals at deeply subdiffractional wavelength. Propagating hyperbolic polaritons were previously explored in polar insulators, including: hBN^{1,7}, MoO₃^{8,9}, V₂O₅¹⁰, calcite¹¹ and in semiconducting WSe₂¹². Layered anisotropic metals have been predicted to manifest hyperbolicity across a broad spectrum^{4,13–15}. The prerequisite anisotropy in a layered metal stems from suppressed interlayer hopping leading to a stark directional-dependence of the (screened) plasma frequency ω_p , which marks the zero-crossing of the dielectric function. Layered metals, in principle, could reveal a vast frequency range of hyperbolicity between $\omega_p^c < \omega < \omega_p^{ab}$, where ω_p^{ab} and ω_p^c are in-plane and out-of-plane (screened) plasma frequencies¹⁵. Yet, insofar propagating hyperbolic plasmon polaritons (HPP) in layered metals have eluded faithful detection by direct imaging. Even though preconditions for hyperbolic plasmons are satisfied in a wide variety of anisotropic conductors^{4,16–19}, the significant electronic losses in common metals have precluded waveguiding.

Here, we use scanning near-field optical microscopy (SNOM) to visualize both the principal and the higher-order HPP modes. We demonstrate that the nodal-line semimetal ZrSiSe hosts propagating hyperbolic plasmon polaritons across the entire telecommunication wavelength range ($\lambda \approx 1.3 - 1.7 \mu\text{m}$, or $\omega \approx 7700 - 5900 \text{ cm}^{-1}$). The unique nodal-line band structure leads to a strong suppression of interband optical absorption, enabling near-infrared (IR) waveguiding in the interior of a layered metallic slab.

To access hyperbolic modes in ZrSiSe we performed two types of near-field optical experiments (Fig. 1a). The first one involves placing thin crystals of ZrSiSe on patterned gold antennas, which serve as launchers of hyperbolic modes into the interior of the sample^{2,3,12}. The second approach utilizes the sharp sample edge to launch the HPPs and reveals characteristic higher-order hyperbolic modes^{2,7}. The two complementary experiments produce consistent results.

Figure 1| Excitation and detection of hyperbolic plasmon polaritons in ZrSiSe. **a**, Schematic of the experimental setup. The near-infrared laser illuminates the sample residing on a circular gold antenna. The antenna launches hyperbolic plasmon polaritons that travel along conical trajectories (red arrows) inside the sample with angle θ from the surface normal. The hyperbolic rays reaching the top surface of the sample are separated by a distance δ and are scattered back to the detector by the sharp tip producing two characteristic rings in raster scanned images. Besides the antenna, sharp edges can also launch polaritons as shown on the left. Inset: the layered lattice structure of ZrSiSe. **b**, Topography image of a thin crystal of ZrSiSe covering the right part of a gold disk antenna. The orange curve is the topography profile along the white dashed line. **c**, Near-field optical amplitude image $S_3(\omega)$ of the same region with incident laser frequency $\omega = 6667 \text{ cm}^{-1}$. Thin red dashed lines indicate the split center-peaks of hyperbolic polariton modes along the circumference. Inset shows the angular-averaged line profile across the red dashed lines. **d**, Simulated z-component electric field for a hyperbolic medium on top of a gold antenna. The red arrow indicates the direction of the in-plane electric field of the incident light. The white dashed line marks the boundary of the Au disk. **e**, Near-field amplitude data within the sector region indicated by black dashed lines in **c**, assembled for laser frequencies from $\omega = 7143 \text{ cm}^{-1}$ to 5556 cm^{-1} (within the hyperbolic region) and at 2222 cm^{-1} (outside of hyperbolic range). Dashed lines mark the “hot rings” associated with the hyperbolic polaritons modes for $\omega = 7143 \text{ cm}^{-1}$ ($\lambda = 1.4 \mu\text{m}$) and $\omega = 5556 \text{ cm}^{-1}$ ($\lambda = 1.8 \mu\text{m}$), respectively. Scale bars in panels **b-d** are 300 nm.

We first focus on experiments involving an Au disk launcher underneath the crystal. As illustrated in Fig. 1a, the HPPs propagate as conical rays and emerge on the surface of the sample as “hot rings” with enhanced nano-optical contrast surrounding the edge of the Au antennas. The propagation angle θ (with respect to surface normal) is controlled by the anisotropic permittivities of the sample^{1-3,12}:

$$\tan(\theta) = \frac{i\sqrt{\epsilon_{ab}}}{\sqrt{\epsilon_c}} = \frac{\delta/2}{d}, \quad (1)$$

where δ is the separation of the rings on the top surface and d is the sample thickness. We examined the topography (Fig. 1b) and the corresponding near-field optical amplitude ($S_3(\omega)$, Fig. 1c) image of a thin ZrSiSe crystal partially covering the gold disk. At $\omega = 6667 \text{ cm}^{-1}$, a clear double-ring like pattern (red dashed lines) emerges along the Au antenna boundary. This double-ring pattern is distinct from a featureless response in the interior of the sample (away from the Au antenna) and also distinct from the internal resonances of the Au antenna at much larger length scales (Extended Data Fig.3). In Fig. 1d we plot the simulated z -component of the electric field for a 26 nm thick hyperbolic medium fully covering a 25 nm thick gold antenna (see Methods). A clear double-ring feature appears in the simulation, in agreement with the experiment (Fig. 1c). The separation of the hot rings on the sample surface is anticipated to systematically change with varying frequency of the illuminating beam in a fashion predicted by Eq. (1). The varying ring-separation is confirmed by the experimental near-field amplitude images taken as a function of frequency with selected images shown in Fig. 1e. The blue and red dashed lines mark the positions of the hot rings at $\omega = 7143 \text{ cm}^{-1}$ and $\omega = 5556 \text{ cm}^{-1}$, with gradually changing ring-separations for frequencies in between. In contrast, the double-ring feature is completely absent at $\omega = 2222 \text{ cm}^{-1}$ (outside of the hyperbolic range), showing instead a homogeneous near-field response (see also Extended Data Fig.2).

We now inquire into quantitative details of propagating HPPs in ZrSiSe. We averaged the radial line profiles within the sectors depicted in Fig. 1e and plot these in Fig. 2a. The experimental ring separation $\delta(\omega)$ is obtained by fitting the line profile with two Gaussian functions and a linear background, shown for $\omega = 7634 \text{ cm}^{-1}$ and 5556 cm^{-1} in Fig. 2a (See Methods for complete analysis taking into account the finite thickness of the Au antenna in Fig. 2a). With the ab -plane permittivity known from previous measurements on bulk crystals²⁰, the experimental ring-separation δ together with the sample thickness d allows for the extraction of the c -axis permittivity of ZrSiSe from Eq. (1). These latter data are displayed in Fig. 2b along with the experimental ab -plane permittivity (squares). The hyperbolic regime in ZrSiSe extends between $\approx 2837 - 9091 \text{ cm}^{-1}$ (see Supporting Information Sec. S1, S2). Finally, we observe yet another hallmark of the hyperbolic ray propagation which is the linear scaling of inter-peak separation δ with the increasing sample thickness (Fig. 2c). Broadband hyperbolic electrodynamics in layered nodal metal ZrSiSe is therefore firmly established.

Figure 2| Hyperbolic electrodynamics of ZrSiSe. **a**, Line profiles of the near-field scattering amplitude at several laser frequencies. Black dashed lines are fits using two Gaussian functions for the $\omega = 7634 \text{ cm}^{-1}$ and 5556 cm^{-1} line profiles. Green and yellow shaded areas indicate the individual Gaussian function representing the hyperbolic rays. The separation $\delta(\omega)$ increases with decreasing frequencies and reflects the dispersion of ϵ_{ab} and ϵ_c . Bottom panel shows the topography line profile (orange) near the edge of the Au disk (gold) in Fig. 1a. The downward slope (tan α) of the sample (blue) leads to a minor correction to the measured ring-separation δ (see Methods). **b**, In-plane dielectric function (ϵ_{ab} , red line) obtained from far-field optical measurements. The ϵ_{ab} values at selected frequencies (squares) together with $\delta(\omega)$ in **a** are used to extract ϵ_c (circles) according to Eq. (1). The black line is a Drude-Lorentz fit of the experimental out-of-plane dielectric function data. Inset is the isofrequency surface in momentum space inside the hyperbolic regime ($\epsilon_{ab} < 0, \epsilon_c > 0$). **c**, Hyperbolic ray separation $\delta(\omega)$ as a function of flake thickness d at $\omega = 6061 \text{ cm}^{-1}$ (red) and $\omega = 7143 \text{ cm}^{-1}$ (blue). The separations scale linearly (grey dashed line) with increasing flake thickness.

The natural edges of thin hyperbolic materials can also launch polaritons (Fig. 1a), albeit with weaker launching efficiencies²¹. In order to explore HPPs near the edges, we focused on the phase contrast images. The enhanced sensitivity of the phase contrast identified the weak higher-order HPP modes: yet another electrodynamics signature of a hyperbolic medium^{2,7}. In Figures 3a-3c, we present near-field phase contrast images obtained for a triangular-shaped 20 nm thin ZrSiSe crystal on Si/SiO₂ substrate for a few representative laser frequencies. At $\omega = 8333 \text{ cm}^{-1}$ (Fig. 3a), the phase contrast reveals a strong fringe localized very close to the right edge, which gradually extends into the interior of the sample as the laser frequency decreases. Multiple fringes of different periodicity are particularly apparent at $\omega = 6250 \text{ cm}^{-1}$ (Fig. 3c), analogous to the principle and higher-order polariton modes on the edge of hBN^{2,7}. In order to

accurately extract the HPP wavelength, we utilized a previously developed electromagnetic solver²² (See Methods) to simulate the phase contrast with the complex polariton momentum $q_p = \frac{2\pi}{\lambda_p}(1 + i\gamma)$ as input. Here, λ_p is the polariton wavelength and γ accounts for damping of the polariton wave.

Figure 3| Hyperbolic plasmon polaritons in crystals of ZrSiSe. Near-field phase (4th harmonic) image of a 20 nm thin crystal of ZrSiSe at **a**, $\omega = 8333 \text{ cm}^{-1}$, **b**, $\omega = 7143 \text{ cm}^{-1}$ and **c**, $\omega = 6250 \text{ cm}^{-1}$, scalebars are 500 nm. **d**, Line profile of the phase contrast (blue dotted line) at $\omega = 6250 \text{ cm}^{-1}$ along the dashed line in **c**. Orange dotted line corresponds to the derivative of the phase line profile, revealing features at multiple spatial periodicities. Dashed line is the simulation of the derivative profile with two periodicities, corresponding to the principal (red arrow) and higher-order (black arrow) HPPs. **e**, (Left) Experimental derivative line profiles ($d\phi_4/dr$) at multiple laser frequencies between $\omega = 8333 \text{ cm}^{-1}$ and $\omega = 5000 \text{ cm}^{-1}$. The grey shaded region indicates the boundary of the crystal. The higher-order polariton mode near the boundary develops at frequencies below 6944 cm^{-1} . (Right) Simulated derivative line profiles (see Methods) at each frequency using either a single or two polariton modes, each with a distinct polariton wavelength λ_p and damping γ . Circular and triangular symbols mark the peaks related to the principal and higher-order HPPs.

The experimental and simulation results for hyperbolic modes probed at $\omega = 6250 \text{ cm}^{-1}$ are displayed in Fig. 3d, where the blue dotted line is the phase contrast line profile along the line indicated in Fig. 3c. A weaker peak (q_1) is visible around 70 nm from the edge of the crystal (grey shaded area), followed by a longer wavelength oscillation (q_0). To better resolve the shorter wavelength oscillations (q_1), we inspected the derivative of the phase line profile (orange dotted line). Both weaker and stronger peaks in the derivative line profiles are well described by the simulation (black dashed line) involving two polariton modes. As we show below, the two modes correspond to the principal and higher-order HPPs in ZrSiSe. Importantly, the location of

higher-order polariton modes with shorter wavelengths is uniquely determined by the location of the weaker peak in the phase derivative line profile.

To map the dispersion of HPP modes, we simulated the phase derivative profiles for multiple frequencies. In Fig. 3e, we show the experimental and simulated phase derivative traces for frequencies between $\omega = 8333 \text{ cm}^{-1}$, and 5000 cm^{-1} . The phase derivative line profile obtained at $\omega = 8333 \text{ cm}^{-1}$ can be adequately reproduced with a single damped polariton of wavelength λ_{p0} . However, for laser frequencies smaller than $\omega = 6944 \text{ cm}^{-1}$ an additional mode with much shorter wavelength λ_{p1} is needed to fully account for the experimental data. The polariton momentum can then be extracted from the simulated polariton wavelength using $\text{Re } q_p = \frac{2\pi}{\lambda_p}$, allowing a direct comparison with predictions based on full experimental dielectric tensors in Fig. 2b.

Figure 4| Dispersion relations of the hyperbolic plasmon polaritons for ZrSiSe. **a**, Momenta of the principal polaritons (circles) and higher-order polaritons (triangles) are extracted via $q_p(\omega) = 2\pi/\lambda_p$ from data in Fig. 3. The data points are superimposed on the calculated imaginary part of the reflection coefficient, $\text{Im}(r_p)$, using experimental dielectric functions (Fig. 2b). The grey dashed line represents the free-space light cone. Green and black dashed lines indicate analytical solutions for the divergence of $\text{Im}(r_p)$ for the higher-order HPP branches, with and without surface state metallicity, respectively. Red dashed line is a guide for the dispersion of the principal branch. **b**, The band structure of ZrSiSe: bulk (blue) and 5-layer slab (red). Compared to the bulk bands, additional interband transitions (green arrow) associated with the surface states contribute to the plasmonic response. Inset shows the nodal-line structure (red lines) in the Brillouin zone of ZrSiSe. **c**, Schematic band structure E vs k_{ab} , k_c away from the high-symmetry plane (grey-shaded plane in the top inset of **b**). In partially gapped nodal metals, interband optical transitions at energies above the van Hove energy (Δ') are suppressed. **d**, Schematic of the real optical conductivity (blue) and the joint density-of-states (gray) for bulk ZrSiSe. Optical losses quantified by the conductivity are likewise rapidly suppressed at energies above Δ' .

The extracted HPP momenta are organized in a frequency-momentum (ω, q) dispersion plot in Figure 4. It is customary to identify HPPs via the divergences of the reflection coefficient $r_p(\omega, q)^{1,23}$. A colormap of $\text{Im}(r_p)$ provides an instructive way to visualize both the dispersion and the damping of the HPP modes. The colormap in Fig. 4a is calculated for a 20 nm thick crystal of ZrSiSe residing on SiO_2/Si substrate using experimental dielectric functions in Fig. 2b. As expected, multiple dispersive branches develop in the hyperbolic frequency range,

corresponding to the principal and higher-order modes that are propagating within the bulk. The calculated hyperbolic dispersions agree with the experimental momenta (colored circles and triangles), unequivocally corroborating the notion of hyperbolic plasmon polaritons in ZrSiSe.

We remark that the dispersion of the higher-order branch (triangles) in Fig.4 slightly deviates from the predicted maximum of $\text{Im}(r_p)$ (black dashed lines). These latter deviations are more apparent in the $\omega(q)$ -dispersion at $\omega > 6400 \text{ cm}^{-1}$ ($\approx 0.8 \text{ eV}$), marked by a green dot in Fig. 4a. We recall that ZrSiSe shows a significant degree of electronic correlations^{20,24,25} revealed through the reduction of the Drude spectral weight. Such interaction effects are expected to renormalize the plasmon dispersions at finite momenta and to slower the group velocity^{26,27}. However, the observed dispersion anomalies Fig.4a reveal an opposite trend, implying an enhanced group velocity.

Searching for the root cause of the dispersion anomaly in Fig.4a, we focus on the possible role of surface states. ZrSiX (X=Se, S, Te) family along with other topological semimetals are known to host various forms of conducting surface states^{28–31}. In ZrSiSe, these surface states produce enhanced metallicity attested by band structure calculations for a thin slab (Fig.4b) and therefore could modify the polaritonic dispersion. Indeed, the HPP mode dispersion admits a modified dispersion prompted by the surface state metallicity (see Methods). By adding surface state layers with a (screened) plasma frequency $\omega_{p,s} = 1 \text{ eV}$ ³⁰ and an interband transition term at $\omega_0 = 0.78 \text{ eV}$, the agreement between the data (triangles) and prediction (green dashed lines) is much improved (Fig. 4a).

We now comment on the preeminent role that the nodal-line structure of the ZrSiSe family of materials^{31,33} plays in both broadband hyperbolicity and reduced interband loss. Dirac nodal-line semimetals possess band-touching points extended through lines or loops in the Brillouin zone^{34–36}. In ZrSiSe, the unique cage-like nodal-lines (Fig. 4b inset) imply that the bands are essentially “flat” along the c -axis while remaining highly dispersive in the ab -plane^{20,31,37}, thus giving rise to $\omega_p^{ab} \gg \omega_p^c$. More importantly, the combination of quasi-2D joint density-of-states (JDOS) and the abundance of van Hove singularities suppress the interband loss in ZrSiSe. Specifically, the optical conductivity of ZrSiSe follows $\sigma_1(\omega) \sim \text{const.}$ across a broad range of frequencies^{20,36,38,39}; this latter behavior is a product of linear-in-frequency JDOS that resembles graphene. Van Hove singularities exist between the nodal-lines^{20,37} and the saddle-point structure (Fig. 4c) leads to a decrease in JDOS above the van Hove energy (Δ'). As a result, the corresponding $\sigma_1(\omega)$ is suppressed above 0.4 eV (Fig. 4d, Fig. S1). The dip in the dissipative part of the optical conductivity σ_1 for ZrSiSe leads to the regime of high $\sigma_2/\sigma_1 \approx 3$ (Extended Data Fig.1) ultimately enabling propagation of only moderately damped plasmon polaritons in near-IR (Extended Data Fig.5). In contrast, the σ_2/σ_1 is less than 1 for other hyperbolic materials candidates in the near-IR range^{4,16}. The net effect is that nodal metals represent a unique type of hyperbolic conductors with losses low enough to support propagating HPPs at near-IR frequencies, as we have demonstrated by direct nano-imaging for ZrSiSe.

The low-loss hyperbolic plasmons in the near-IR range benefit from the combination of the high density of Dirac fermions and the unique nodal band structure in Fig.4. Remarkably, the suppression of interband optical transition offers a concrete example to the hypothesis of the

“band structure engineering” approach to low-loss hyperbolic plasmonics^{40,41}. The propagating hyperbolic plasmon polaritons reported here demonstrate yet untapped potential of nodal-line semimetals as low-loss natural hyperbolic media. We anticipate similar effects in the closely related ZrSiS⁴² and other nodal semi-metals⁴³. We envision future band structure engineering based on these nodal-line semimetals could lead to further increase of the polariton quality factor and propagation length in the technologically important near-IR wavelength. Beyond applications, the multiple hyperbolic branches reported here constitute a crucial first step in exploring the intertwined bulk and surface states effects in topological semimetals with polaritonic observables.

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Methods

Single crystal growth and device fabrication. The ZrSiSe single crystals were synthesized using a chemical vapor transport method as described previously^{20,33}. For Au antenna patterned devices, Au/Cr (25 nm/1 nm) disks were e-beam deposited on SiO₂/Si substrates following standard e-beam lithography processes using a lift-off resist. ZrSiSe flakes were then directly exfoliated on Au/Cr disks in a glovebox filled with inert gas (O₂ < 1 ppm, H₂O < 0.1 ppm). Prior to exfoliation, the substrates were annealed in glovebox at 250 °C for 1 hr to remove any residual moisture on the surface.

Near-infrared nano-optical measurements. We used a scattering-type scanning near-field optical microscope (s-SNOM, Neaspec) based on an atomic force microscope (AFM) operating in tapping mode. The tapping frequency of the AFM tip is around 70 kHz and near-field data are collected at higher harmonic ($n = 3$ or 4) of the tapping frequency to suppress the far-field background. For the gold antenna launcher experiment the difference frequency generation outputs of a pulsed laser source (Pharos, Light Conversion) were used. For the edge-launching experiments, we used a continuous-wave tunable laser from M Squared. Tunable outputs between 1140 nm – 2200 nm are generated by frequency mixing of a high-power 532 nm diode laser (EQUINOX) and a Ti:Sapphire laser tunable between 700 nm – 1000 nm (SolsTiS).

Geometrical correction considering finite antenna thickness. Due to the finite thickness of the underlying Au antenna, the sample exhibits a downward slope outside the antenna boundary (Fig. 1b). This small slope ($\tan \alpha$) leads to a finite asymmetry ($\frac{\delta}{2} > \frac{\delta'}{2}$) in the propagation distance of the two rays (Fig. 2a bottom), which we corrected in the extraction of $\delta(\omega)$ as following. The two distances δ and δ' are related by $\frac{\delta}{\delta'} = 1 + \tan \alpha \cdot \tan \theta$, where $\tan \theta = \frac{\delta}{2d}$ and d is the sample thickness. The measured double-ring distance is denoted as $\Delta = \frac{\delta}{2} + \frac{\delta'}{2}$. Substituting δ' in terms of Δ and δ , we obtained $\delta = \Delta - \frac{2d}{\tan \alpha} + \sqrt{\Delta^2 + \frac{4d^2}{\tan^2 \alpha}}$. At the limit of $\alpha \rightarrow 0$ (no downward slope) or $d \rightarrow \infty$ (infinitely thick sample), $\delta \rightarrow \Delta$.

Simulation of plasmonic fringes near the sample edge. The input parameter into the model is a complex wavevector $Q = q_p(1 + i\gamma)$, where $q_p = \frac{2\pi}{\lambda_p}$ and γ represents the dimensionless damping coefficient of the polariton mode. For very thin layers ($d \ll \lambda_p$), one can approximate the sample by a two-dimensional conducting layer with an effective sheet conductivity

$$\sigma_{eff} = \frac{i\omega\kappa}{2\pi Q}, \quad (S1)$$

with $\kappa = \frac{\epsilon_0 + \epsilon_2}{2}$ being the average permittivity of the surrounding media. The sample is modeled by a two-dimensional strip of width L at the boundary of two half-spaces with permittivities $\epsilon_0 = 1$ (air) and $\epsilon_2 = 1.94$ (SiO₂). The SNOM signal is taken to be proportional to the induced dipole moment on the probe. The scanning probe is modeled by a spheroid, with radius of curvature $a = 40$ nm and length $L = 1400$ nm. We compute the charge distribution n_i in the sample induced by

the probe. This quantity can be found by combining Gauss's law with the charge continuity equation, giving

$$\Phi(\mathbf{r}) - V(\mathbf{r}) * n_i(\mathbf{r}) = \Phi_{ext}(\mathbf{r}), \quad (S2)$$

with the operation $A * B$ denoting convolution, $\Phi(\mathbf{r})$ being the full potential, and $V(\mathbf{r})$ being the in-plane Coulomb potential. The external field is taken to be constant with an incidence angle $\theta = 60^\circ$ from the surface normal. Using the translation symmetry of the problem in the lateral direction, Eq. (S2) is reduced to a one-dimensional integral equation. Replacing the derivatives by finite differences further simplifies Eq. (S2) to a matrix inversion. The SNOM signal is then found by computing the dipole moment induced on the probe by the distribution $n_i(\mathbf{r})$. The complex signal (S) is calculated for a range of tip positions from each quantity $n_i(\mathbf{r})$ and then demodulated to the 4th harmonic in order to compare with the experimental line profiles shown in Fig. 3e.

Hyperbolic plasmon polariton dispersion with surface states. The momentum of the hyperbolic plasmon polariton (HPP) modes with surface conductivity σ_{2D} obeys the following Fabry-Perot quantization condition:

$$q_l(\omega) = \frac{i\sqrt{\varepsilon_c}}{d\sqrt{\varepsilon_{ab}}} \left[\pi l + \arctan \left[i \frac{\varepsilon_0}{\varepsilon_1} \left(1 - \frac{2q}{q_{2D}} \right) \right] + \arctan \left[i \frac{\varepsilon_2}{\varepsilon_1} \left(1 - \frac{2q}{q_{2D}} \right) \right] \right] \quad (S3)$$

where $l = 0, 1, 2$ is the mode index, d is the sample thickness, ε_0 (ε_2) is the dielectric function of the top (bottom) medium, and $\varepsilon_1 = \sqrt{\varepsilon_{ab}}\sqrt{\varepsilon_c}$ is the mean dielectric function of the hyperbolic material with the in-plane ($\varepsilon_{ab} < 0$) and out-of-plane ($\varepsilon_c > 0$) components having opposite signs. Here, q_{2D} is related to the (complex) surface state conductivity σ_{2D} of the hyperbolic metal via $\sigma_{2D} = \frac{i\omega(\varepsilon_0 + \varepsilon_2)/2}{2\pi q_{2D}} = \frac{i\omega\kappa}{2\pi q_{2D}}$. Inside the hyperbolic regime of ZrSiSe, ε_1 is much larger than the dielectric function of the environment ($\varepsilon_0 = 1$ and $\varepsilon_2 = 1.94$). At $\omega = 6250 \text{ cm}^{-1}$ and considering only the real part, $\varepsilon_1 = \sqrt{\varepsilon_{ab}}\sqrt{\varepsilon_c} \approx 8.6i$ and therefore $i \frac{\varepsilon_j}{\varepsilon_1} \ll 1$ for $j = 0, 1$.

Assuming $q_{2D} \ll q$, we can then approximate $\arctan \left[i \frac{\varepsilon_j}{\varepsilon_1} \left(1 - \frac{2q}{q_{2D}} \right) \right] \approx i \frac{\varepsilon_j}{\varepsilon_1} \left(1 - \frac{2q}{q_{2D}} \right)$ for $j = 0, 1$. Equation (S3) can then be simplified as:

$$q_l(\omega) = \frac{i\sqrt{\varepsilon_c}}{d\sqrt{\varepsilon_{ab}}} \left[\pi l + i \frac{\varepsilon_0 + \varepsilon_2}{\sqrt{\varepsilon_{ab}}\sqrt{\varepsilon_c}} \left(1 - \frac{2q}{q_{2D}} \right) \right] \quad (S4)$$

and in the lossless limit ($\text{Re } \sigma_{2D} = 0$) we obtain:

$$q_l(\omega) = \frac{\pi l \sqrt{\varepsilon_c} \sqrt{|\varepsilon_{ab}|} + 2\kappa}{d|\varepsilon_{ab}| + 8\pi \text{Im}(\sigma_{2D})/\omega} \quad (S5)$$

The influence of the surface state metallicity will be parameterized by its complex sheet conductivity σ_{2D} . If the imaginary part of σ_{2D} at a given frequency is negative (positive), it will modify the HPP momentum to a larger (smaller) value, corresponding to enhanced (reduced) screening on the HPP dispersion.

Extended Data Figures

Extended Data Fig.1|In-plane optical conductivity ($\tilde{\sigma} = \sigma_1 + i\sigma_2$) ratio for several layered semimetals. The ratio of σ_2/σ_1 for ZrSiSe (solid lines) and other layered metallic systems with screened plasma frequency around 1 eV. Higher σ_2/σ_1 indicates lower electronic loss and higher plasmonic quality factor. The minimum in the dissipative part of the optical conductivity σ_1 for ZrSiSe improves its plasmonic quality factor dramatically in the near-IR wavelengths.

Extended Data Fig.2|Hyperbolic ray launching experiment for fully covered Au antenna. **a**, Topography image of a 28 nm ZrSiSe crystal on top of a 2 μm wide Au circular antenna. The normalized near-field amplitudes (S_3/S_2) outside ($\omega = 2222 \text{ cm}^{-1}$) and inside ($\omega = 6250 \text{ cm}^{-1}$) the hyperbolic regime are shown in panel **b** and **c**, respectively. Insets in panels **b** and **c** are the schematic of the isofrequency surfaces. Dashed lines in **a** and **b** indicate the boundary of the underlying Au antenna. Scale bars in all panels are 200 nm.

Extended Data Fig.3|Hyperbolic ray launching data and fitting for a 25 nm ZrSiSe crystal on Au antenna. Near-field amplitude (top) and topography (bottom) data of ZrSiSe crystal on circular gold antenna collected at (a) $\omega = 7143 \text{ cm}^{-1}$ and (b) $\omega = 6061 \text{ cm}^{-1}$. The white dotted line indicates the boundary of gold. Blue and red dashed lines indicate the double-ring features at 7143 cm^{-1} and 6061 cm^{-1} , respectively. Inset in b is a topography linecut along the orange dashed line. Scalebars are 500 nm. The averaged line profiles of the near-field amplitude along the perimeter of the circular antenna are shown for (c) $\omega = 7143 \text{ cm}^{-1}$ and (d) $\omega = 6061 \text{ cm}^{-1}$. The line profiles are fitted with two Gaussian profiles (green and yellow dotted lines) and a linear background (gray dotted line).

Extended Data Fig.4|Hyperbolic ray launching data and fitting for a 40 nm ZrSiSe crystal on Au antenna. Near-field amplitude (bottom) and topography (top) data of ZrSiSe crystal on circular gold antenna collected at (a) $\omega = 7143 \text{ cm}^{-1}$ and (b) $\omega = 6061 \text{ cm}^{-1}$. The white dotted line indicates the boundary of gold. Blue and red dashed lines indicate the double-ring features at 7143 cm^{-1} and 6061 cm^{-1} , respectively. Inset in b is a topography linecut along the orange dashed line. Scalebars are 500 nm. The averaged line profiles of the near-field amplitude along the perimeter of the circular antenna are shown for (c) $\omega = 7143 \text{ cm}^{-1}$ and (d) $\omega = 6061 \text{ cm}^{-1}$. The line profiles are fitted with two Gaussian profiles (green and yellow dotted lines) and a linear background (gray dotted line).

Extended Data Fig.5|Hyperbolic plasmon propagation in a larger ZrSiSe crystal. a, Topography image of a 27 nm ZrSiSe flake sitting on SiO_2/Si substrate. b, The corresponding near-field phase images at $\omega = 5882 \text{ cm}^{-1}$, scalebar in panels a and b are 500 nm. c, Linecuts of the near-field phase (blue line) and topography (black line) obtained from a and b. d, Fast Fourier transform (FFT) amplitude of the near-field phase trace shown in c, showing several distinct modes that are color-coded. e, Inverse FFT of the different modes in d is plotted, with the center momentum labeled as q_0 , q_1 and q_2 . The blue dashed line is the sum of the different modes, showing good agreement with the experimental near-field phase in c.

References

1. Dai, S. *et al.* Tunable Phonon Polaritons in Atomically Thin van der Waals Crystals of Boron Nitride. *Science* **343**, 1125–1129 (2014).
2. Dai, S. *et al.* Subdiffractional focusing and guiding of polaritonic rays in a natural hyperbolic material. *Nat. Commun.* **6**, 6963 (2015).
3. Li, P. *et al.* Hyperbolic phonon-polaritons in boron nitride for near-field optical imaging and focusing. *Nat. Commun.* **6**, 7507 (2015).
4. Narimanov, E. E. & Kildishev, A. V. Metamaterials: Naturally hyperbolic. *Nat. Photon.* **9**, 214–216 (2015).
5. Zhang, Q. *et al.* Interface nano-optics with van der Waals polaritons. *Nature* **597**, 187–195 (2021).
6. Krishnamoorthy, H. N. S., Jacob, Z., Narimanov, E., Kretzschmar, I. & Menon, V. M. Topological Transitions in Metamaterials. *Science* **336**, 205–209 (2012).
7. Giles, A. J. *et al.* Ultralow-loss polaritons in isotopically pure boron nitride. *Nat. Mater.* **17**, 134–139 (2018).
8. Ma, W. *et al.* In-plane anisotropic and ultra-low-loss polaritons in a natural van der Waals crystal. *Nature* **562**, 557 (2018).
9. Zheng, Z. *et al.* A mid-infrared biaxial hyperbolic van der Waals crystal. *Sci. Adv.* **5**, eaav8690 (2019).
10. Taboada-Gutiérrez, J. *et al.* Broad spectral tuning of ultra-low-loss polaritons in a van der Waals crystal by intercalation. *Nat. Mater.* **19**, 964–968 (2020).
11. Ma, W. *et al.* Ghost hyperbolic surface polaritons in bulk anisotropic crystals. *Nature* **596**, 362–366 (2021).

12. Sternbach, A. J. *et al.* Programmable hyperbolic polaritons in van der Waals semiconductors. *Science* **371**, 617–620 (2021).
13. Gjerding, M. N., Petersen, R., Pedersen, T. G., Mortensen, N. A. & Thygesen, K. S. Layered van der Waals crystals with hyperbolic light dispersion. *Nat. Commun.* **8**, 320 (2017).
14. Berkowitz, M. E. *et al.* Hyperbolic Cooper-Pair Polaritons in Planar Graphene/Cuprate Plasmonic Cavities. *Nano Lett.* **21**, 308–316 (2021).
15. Low, T. *et al.* Polaritons in layered two-dimensional materials. *Nat. Mater.* **16**, 182–194 (2017).
16. Esslinger, M. *et al.* Tetradymites as Natural Hyperbolic Materials for the Near-Infrared to Visible. *ACS Photonics* **1**, 1285–1289 (2014).
17. Frenzel, A. J. *et al.* Anisotropic electrodynamics of type-II Weyl semimetal candidate WTe₂. *Phys. Rev. B* **95**, 245140 (2017).
18. Wang, C. *et al.* Van der Waals thin films of WTe₂ for natural hyperbolic plasmonic surfaces. *Nat. Comm.* **11**, 1158 (2020).
19. Shao, Y. *et al.* Nonlinear nanoelectrodynamics of a Weyl metal. *PNAS* **118**, e2116366118 (2021).
20. Shao, Y. *et al.* Electronic correlations in nodal-line semimetals. *Nat. Phys.* **16**, 636–641 (2020).
21. Dai, S. *et al.* Efficiency of Launching Highly Confined Polaritons by Infrared Light Incident on a Hyperbolic Material. *Nano Lett.* **17**, 5285–5290 (2017).
22. Fei, Z. *et al.* Gate-tuning of graphene plasmons revealed by infrared nano-imaging. *Nature* **487**, 82–85 (2012).
23. Novotny, L. & Hecht, B. *Principles of Nano-Optics*. (Cambridge University Press, 2012).

24. Gatti, G. *et al.* Light-Induced Renormalization of the Dirac Quasiparticles in the Nodal-Line Semimetal ZrSiSe. *Phys. Rev. Lett.* **125**, 076401 (2020).
25. Paschen, S. & Si, Q. Quantum phases driven by strong correlations. *Nat. Rev. Phys.* **3**, 9–26 (2021).
26. van Loon, E. G. C. P., Hafermann, H., Lichtenstein, A. I., Rubtsov, A. N. & Katsnelson, M. I. Plasmons in Strongly Correlated Systems: Spectral Weight Transfer and Renormalized Dispersion. *Phys. Rev. Lett.* **113**, 246407 (2014).
27. Lundeberg, M. B. *et al.* Tuning quantum nonlocal effects in graphene plasmonics. *Science* eaan2735 (2017) doi:10.1126/science.aan2735.
28. Zhu, Z. *et al.* Quasiparticle interference and nonsymmorphic effect on a floating band surface state of ZrSiSe. *Nat. Commun.* **9**, 4153 (2018).
29. Topp, A. *et al.* Surface Floating 2D Bands in Layered Nonsymmorphic Semimetals: ZrSiS and Related Compounds. *Phys. Rev. X* **7**, 041073 (2017).
30. Xue, S. *et al.* Observation of Nodal-Line Plasmons in ZrSiS. *Phys. Rev. Lett.* **127**, 186802 (2021).
31. Schoop, L. M. *et al.* Dirac cone protected by non-symmorphic symmetry and three-dimensional Dirac line node in ZrSiS. *Nat. Commun.* **7**, 11696 (2016).
32. Chi, S. *et al.* Surface Nonlinear Optics on Centrosymmetric Dirac Nodal-Line Semimetal ZrSiS. *Adv. Mater.* **32**, 1904498 (2020).
33. Hu, J. *et al.* Evidence of Topological Nodal-Line Fermions in ZrSiSe and ZrSiTe. *Phys. Rev. Lett.* **117**, 016602 (2016).
34. Burkov, A. A., Hook, M. D. & Balents, L. Topological nodal semimetals. *Phys. Rev. B* **84**, 235126 (2011).

35. Fang, C., Chen, Y., Kee, H.-Y. & Fu, L. Topological nodal line semimetals with and without spin-orbital coupling. *Phys. Rev. B* **92**, 081201 (2015).
36. Shao, Y. *et al.* Optical signatures of Dirac nodal lines in NbAs₂. *PNAS* **116**, 1168–1173 (2019).
37. Habe, T. & Koshino, M. Dynamical conductivity in the topological nodal-line semimetal ZrSiS. *Phys. Rev. B* **98**, 125201 (2018).
38. Schilling, M. B., Schoop, L. M., Lotsch, B. V., Dressel, M. & Pronin, A. V. Flat Optical Conductivity in ZrSiS due to Two-Dimensional Dirac Bands. *Phys. Rev. Lett.* **119**, 187401 (2017).
39. Carbotte, J. P. Optical response of a line node semimetal. *J. Phys.: Condens. Matter* **29**, 045301 (2017).
40. Gjerding, M. N., Pandey, M. & Thygesen, K. S. Band structure engineered layered metals for low-loss plasmonics. *Nat. Commun.* **8**, 15133 (2017).
41. Lewandowski, C. & Levitov, L. Intrinsically undamped plasmon modes in narrow electron bands. *PNAS* **116**, 20869–20874 (2019).
42. Ebad-Allah, J. *et al.* Pressure-Induced Excitations in the Out-of-Plane Optical Response of the Nodal-Line Semimetal ZrSiS. *Phys. Rev. Lett.* **127**, 076402 (2021).
43. Narang, P., Garcia, C. A. C. & Felser, C. The topology of electronic band structures. *Nat. Mater.* **20**, 293–300 (2021).

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