Optical conductivity of multifold fermions: the case of RhSi

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We measured the reflectivity of the multifold semimetal RhSi in a frequency range from 80 to 20000 cm⁻¹ (10 meV – 2.5 eV) at temperatures down to 10 K. The optical conductivity, calculated from the reflectivity, is dominated by the free-carrier (Drude) contribution below 1000 cm⁻¹ (120 meV) and by interband transitions at higher frequencies. The temperature-induced changes in the spectra are generally weak – only the Drude bands narrow upon cooling with an unscreened plasma frequency being constant with temperature at approximately 1.4 eV, in agreement with a weak temperature dependence of the free-carrier concentration determined by Hall measurements. The interband portion of conductivity exhibits two linear-in-frequency regions below 5000 cm⁻¹ (∼600 meV), a broad flat maximum at around 6000 cm⁻¹ (750 meV), and a further increase starting around 10 000 cm⁻¹ (∼1.2 eV). We assign the linear behavior of the interband conductivity to transitions between the linear bands near the band crossing points. Our findings are in accord with the predictions for the low-energy conductivity behavior in multifold semimetals and with earlier computations based on band structure calculations for RhSi.

I. INTRODUCTION

Multifold fermions are quasiparticles described by higher-spin generalizations of the Weyl equation. They can be realized in the multifold semimetals – the materials, which possess the characteristic electronic band crossings with degeneracies higher than two [1, 2]. A number of such semimetals has recently been predicted and experimentally confirmed among the materials from the space group 198 (SG198), which symmetry is non-centrosymmetric and has no mirror planes, leading to a realization of “topological chiral crystals” [3–9]. In such semimetals, the quantized circular photogalvanic effect (QCPGE) has been forecasted in 2017 [10]. In this non-linear optical phenomenon the helical (i.e., circularly polarized) photons excite the chiral band carriers in such a way that the resultant photocurrent is quantized in units of material-independent fundamental constants. Recently, the observation of QCPGE has been reported in RhSi [11], a member of SG198 and an established multifold semimetal [4–6].

These remarkable theoretical results and experimental observations demand further optical characterizations of RhSi, in particular since the knowledge of frequency-dependent conductivity, \( \sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega) \), is essential for proper interpretation of QCPGE experiments. Because there is no characteristic energy scale, the quasi-particles near the linear-band crossings in three dimensions are expected to be characterized by the interband \( \sigma_1(\omega) \) proportional to the probing light frequency [12–14]. Indeed, such linear \( \sigma_1(\omega) \) has been observed in many Dirac and Weyl semimetals [15–18]. The optical conductivity of the multifold semimetals has also been predicted to demonstrate a linear \( \sigma_1(\omega) \) [12]. Most recently, optical conductivity has been specifically calculated for RhSi from its band structure [20]. In this paper, we experimentally examine these theoretical results.

II. EXPERIMENT

Single crystals of RhSi were grown in the same way as described in Ref. [11]. The vertical Bridgman crystal-growth technique was utilized to grow the crystals from the melt using a slightly off-stoichiometric composition (excess Si). First, a polycrystalline ingot was prepared using arc-melt technique by mixing the stoichiometric amount of constituent Rh and Si elements of 99.99% purity. Then the crushed powder was filled in a custom-designed sharp-edged alumina tube and finally sealed inside a tantalum tube with argon atmosphere. A critical composition with slightly excess Si was maintained to ensure a flux growth inside the Bridgman ampule. The whole assembly was heated to 1550 °C with a rate of 200 °C/h and halted for 12 h to ensure good mixing of the liquid. Then the crucible was slowly pulled to \( \sim 1100 \) °C with a rate of 0.8 mm/h and finally quenched to room temperature. The temperature profile was controlled by attaching a thermocouple at the bottom of the tantalum ampule containing the sample. Single crystals with average linear dimensions of a few millimeters were obtained. The crystals were first analyzed with a white beam backscattering Laue x-ray diffractometer at room temperature. The obtained single and sharp Laue spot could be indexed by a single pattern, revealing excellent quality of the grown crystals without any twinning or domains. The structural parameters were determined using a Rigaku AFC7 four-circle diffractometer with a Saturn 724+ CCD-detector applying graphite-monochromatized Mo-Kα radiation. The crystal structure was refined to be cubic \( P_2_1_3 \) (SG198) with the lattice parameter \( a=4.6858(9) \) Å.

Temperature-dependent transport measurements (lon-
tical conductivity (b) and the dielectric permittivity (c) of RhSi at selected temperatures between T = 10 and 295 K. Note logarithmic x-scale. The insets show: the dc resistivity vs. T (d), the Hall electron concentration vs. T (e), and a zoom of the permittivity spectra near the zero crossings (f).

FIG. 2. Drude-Lorentz fits (lines) of the measured optical spectra (symbols) of σ₁ and ε₁ of RhSi at 10 and 295 K, as indicated. Note logarithmic x-scale.

Figure 1 displays the optical reflectivity R(ν) and the real parts of the optical conductivity and dielectric constant, ε₁(ν) = 1 − 2σ₂(ν)/ν, for the studied RhSi sample in the full measurement-frequency range at a number of temperatures. For frequencies higher than ∼8 000 cm⁻¹ (∼1 eV), the optical properties are independent of temperature. For the spectra analysis, we performed standard Drude-Lorentz fits [22], where the Drude terms describe the free-carrier response, while the Lorentzians mimic the interband optical transitions and phonons. Examples of such fits are presented in Fig. 2. Here we kept the zero-frequency limit of optical conductivity to be equal to the measured dc-conductivity value at every temperature. No other restrictions on the fit parameters were imposed. For best possible model description, the experimental spectra of R(ν), σ₁(ν) and ε₁(ν) were fitted simultaneously.

III. RESULTS AND DISCUSSION

Temperature-dependent (T = 10 – 295 K) optical reflectivity, R(ν), was measured on a polished surface of a RhSi single crystal (with roughly 1.5 × 1.5 mm² in lateral dimensions) over a broad frequency range from ν = ω/(2πc) = 80 to 20 000 cm⁻¹ (1 meV – 3 eV). The spectra in the far-infrared (below 700 cm⁻¹) were collected with a Bruker IFS 113v Fourier-transform spectrometer using in situ gold coating of the sample surface for reference measurements. At higher frequencies, a Bruker Hyperion infrared microscope attached to a Bruker Vertex 80v FTIR spectrometer was used. For these measurements, freshly evaporated gold mirrors served as reference. No sample anisotropy was detected in agreement with the cubic crystallographic structure.

For Kramers-Kronig analysis, zero-frequency extrapolations have been made using the Hagen-Rubens relation in accordance with the temperature-dependent longitudinal dc resistivity measurements. For high-frequency extrapolations, we utilized the x-ray atomic scattering functions [21] followed by the free-electron behavior, R(ω) ∝ 1/ω⁴, above 30 keV.

We found that the skin depth of the probing radiation exceeds 30 nm for all temperatures and frequencies (in the far-infrared range, it is above 200 nm). Hence, our optical measurements reflect the bulk properties of RhSi.
The screened plasma frequency, $\nu_{\text{pl}}$, corresponds to the zero crossing of the optical transitions to the plasma edge is observed in Ref. [11] and calculated (Ref. [20]) optical spectra of RhSi: optical conductivity (a) and dielectric function (b).

A. Electronic response

At low frequencies, RhSi demonstrates a typical (semi)metallic response. The intraband contribution to the spectra can be best fitted with two Drude components, which have different scattering rates. Such multicomponent Drude fits are often used to describe the optical response of multiband systems, particularly different semimetals [23, 24, 26]. In the case of RhSi, the two-Drude approach can be justified by the presence of a few bands crossing the the Fermi level [1, 5, 21, 22], see Fig. (a): one set of bands is around the $R$ point and the others are near the $\Gamma$ and $M$ points of the Brillouin zone. The first set provides the dominating contribution to the free-carrier response and is also responsible for the electron type of conduction. The second Drude term is necessary to describe the optical spectra accurately. Let us note that exact interpretation of such a two-Drude approach is arguable. The two components are not necessarily associated with two different bands, but might instead be related to the scattering processes within a band and between two different bands.

The scattering rates of the Drude terms are found to be $250$ cm$^{-1}$ (25 meV) and $800$ cm$^{-1}$ (100 meV) at 100 K. These values correspond to the mid-ranges for the spectra at all measurement temperatures. At $T$ different from 100 K, the scattering rates change only within $\pm 20\%$ of these values. The mid-range relaxation times are, hence, $21$ and $6.6$ fs. These values are somewhat larger than the value reported in another optical study of RhSi [11] indicating the improved quality of RhSi samples investigated in this work.

At around $1500$ cm$^{-1}$ ($\sim 200$ meV), a characteristic plasma edge is observed in $R(\nu)$. This edge correlates with the zero crossing of $\varepsilon(\nu)$, which corresponds to the screened plasma frequency, $\nu_{\text{pl}}^\text{scr} = \nu_{\text{pl}}/\sqrt{\varepsilon_{\text{inf}}}$. Here, $\varepsilon_{\text{inf}} = 65 \pm 5$, is the cumulative contribution of the higher-frequency optical transitions to $\varepsilon_1$ as obtained from the fits and $\nu_{\text{pl}}$ is the unscreened plasma frequency. As best seen from Fig. (f), the screened plasma frequency is $\nu_{\text{pl}}^\text{scr} = (1470 \pm 30)$ cm$^{-1}$ [h$\omega_{\text{pl}}^\text{scr} = (182 \pm 4)$ meV] and independent of temperature, the corresponding unscreened plasma frequency being $\nu_{\text{pl}} = (11.90 \pm 700)$ cm$^{-1}$ [h$\omega_{\text{pl}} = (1470 \pm 90)$ meV]. This value of plasma frequency coincides within the experimental uncertainty with the value obtained from the Drude fits, $\nu_{\text{pl}} = (11.200 \pm 600)$ cm$^{-1}$ [h$\omega_{\text{pl}} = (1390 \pm 80)$ meV], which includes contributions...
from both Drude terms and also shows no $T$-dependence.

The absence of any detectable temperature dependence of $\omega_p$ is in qualitative agreement with the very modest temperature-induced change of the carrier concentration: $n(T)$ increases by only 20% as $T$ goes from 2 to 300 K, see Fig. (1e).

The unscreened plasma frequency is related to the free-carrier concentration $n$ and either to the effective mass $m^*$ in the case of parabolic bands: $\omega^2_{pl} = 4\pi e^2 n/m^*$, or to the Fermi velocity $v_F$ for linear bands: $\omega^2_{pl} = A e^2 v_F^2/21/\hbar$, where $A$ is a numerical constant proportional to the band degeneracy [27]. Having the measured $n(T)$ and $\omega_{pl} \approx \text{const}(T)$, we can estimate that $m^*$ and $v_F$ vary by 20 and 13%, respectively, as $T$ goes from room temperature down 10 K. This modest variation of the effective band parameters at the Fermi-level position must be related to a slight temperature-induced uprise of the Fermi level, which crosses the non-parabolic and not perfectly linear bands in RhSi (e.g., the almost flat bands near the $\Gamma$ point), see Fig. (1a). A change of the Fermi-level position in such bands leads to variations in the effective mass and Fermi velocity of free carriers. [Note, that if we go further away from the Fermi level in RhSi, the linear approximation for the bands in the vicinity of the $\Gamma$ point works better].

The relatively large value of $\omega_{pl}$ (cf. the results for other nodal semimetals [15, 18, 28]) and the fairly high ($\sim 10^{21}$ cm$^{-3}$) free-electron density of RhSi, see Fig. (1d), are consistent with the results of band structure calculations [4, 5, 20, 25], which show that the Fermi level in RhSi is quite deep in the conduction band for the electron momenta near the corners ($R$ points) of the Brillouin zone (Fig. (1a)). This situation makes the optical response of RhSi similar to the one observed in the Dirac semimetal Au$_2$Pb [29]: free carriers dominate the low-frequency ($\nu < 2000$ cm$^{-1}$, $\hbar \nu < 250$ meV) region of $\sigma_1(\nu)$ and $\varepsilon(\nu)$. Still, unlike the situation in Au$_2$Pb, the optical transitions between the linearly dispersing bands can be resolved in RhSi.

In Fig. (3) our optical findings at $T = 10$ K are plotted together with the results of band-structure-based calculations from Ref. [20] and with the previously reported measurements of Ref. [11]. The experimental curves follow each other quite well. The deviations between the curves can be explained by different free-carrier contributions (cf. the difference in the scattering times discussed above) and probably by a somewhat more accurate Kramers-Kronig analysis utilized in the present work: our reflectivity measurements are performed in a broader frequency range as compared to the measurements from Ref. [11].

Despite some discrepancy between the calculations and both experimental curves in Fig. (3a), the match can be considered as satisfactory. One has to keep in mind that calculations of the optical conductivity from the electronic band structure are rather challenging, particularly for semimetals: a survey of the available literature reveals only a qualitative match between the calculated optical conductivity and experimental results for a wide range of nodal semimetals studied recently [18, 24, 30, 32]. Nevertheless, both the low-energy features of the interband experimental $\sigma(\nu)$ – the initial (i.e., for the frequencies just above the Drude roll-off) linear increase and the further flattening – are reproduced by theory.

In order to establish a better connection between the features observed in the most interesting, low-energy part, of the experimental conductivity and the interband optical transitions, we show our $\sigma(\nu)$ together with the low-energy band structure of RhSi in Fig. (3). Additionally, we plot the interband contribution to the optical conductivity, $\sigma^\text{inter}_1(\nu)$, obtained by subtracting the Drude fits and the sharp phonon peaks (discussed below) from the measured spectra.

At the lowest frequencies (below approximately 2500 cm$^{-1}$ or 0.3 eV), the interband conductivity is entirely due to transitions in the vicinity of the $\Gamma$ point. No other interband optical transitions are possible (either the direct gap between the bands is too large, or the transitions are Pauli blocked). The bands near the $\Gamma$ point are all roughly linear (two of them are basically flat), thus a linear-in-frequency interband conductivity is expected [19]. Indeed, $\sigma^\text{inter}_1(\nu)$ is proportional to frequency in this range (marked with the orange arrows). At somewhat higher $\nu$ ($\sim 3000 – 4000$ cm$^{-1}$, 0.4 – 0.5 eV), the flat bands start to disperse downward, thus the linearity of $\sigma^\text{inter}_1(\nu)$ is not expected anymore. However, the interband contributions in the vicinity of the $R$ points become relevant at roughly the same energy (cf. the two grey arrows in panel (a)). These transitions provide a dominating contribution to conductivity, and the linear-in-frequency increase of $\sigma^\text{inter}_1(\nu)$ is restored with a larger slope (the grey arrow in panel (b)). At $\nu \geq 6000$ cm$^{-1}$ (0.8 eV), the optical conductivity flattens out, forming a broad flat maximum. We attribute it to the transitions between the almost parallel bands along the $M–R$ line, shown as the dotted green arrows. After the relatively flat region, $\sigma^\text{inter}_1(\nu)$ continues to rise (see Fig. (1b)), as more and more bands get involved in optical transitions.

In Fig. (3b) we also compare our results with the effective-Hamiltonian calculations [19] for the contributions near the $\Gamma$ point. An extrapolation of these calculations, originally performed for $\nu < 320$ cm$^{-1}$ (40 meV), to higher frequencies is shown as a solid purple line. The experimental $\sigma^\text{inter}_1(\nu)$ is generally steeper than the results of these calculations. A very similar behavior of the experimental conductivity versus such effective-Hamiltonian calculations has also been reported in Ref. [11]. Perhaps, at the lowest frequencies the match between the experiment and the model is better, but our signal-to-noise ratio is not sufficient for final conclusions (one should also remember that the $\sigma^\text{inter}_1(\nu)$ spectrum is obtained utilizing a Drude-terms subtracting procedure). In any case, the mismatch can be related to deviations of the bands from linearity even at low energies [4, 5, 20, 25]. Particularity, the spin-orbit coupling, neglected in Ref. [19], might be relevant. This can be
clarified in more advanced band-structure-based optical-conductivity calculations, which are beyond the scope of this paper.

Having established the connection between the features in the experimental low-energy interband conductivity and the band structure, we would like to add another note on the intraband response. The exact shape of the free-carrier contribution is obviously sample dependent, because, e.g., the impurity scattering rate differ from sample to sample. However, if the total amount of doping is low enough, the plasma frequency is fixed by the position of the Fermi level, which, in turn, can be found within the band structure calculation procedure. Such calculations produced \( \hbar \omega_{pl} = 1.344 \) eV, in excellent agreement with our result obtained above, \( 1.39 \pm 0.08 \) eV. Furthermore, the calculated and the observed spectral positions of the screened plasma frequency (the zero-crossing points of \( \varepsilon_1 \)) also match very well each other, as can be seen in Fig. 5b. This agreement of the plasma frequencies also indicates a good quality of our sample in terms of low defect and impurity concentration.

### B. Phonons

Based on its crystallographic symmetry, RhSi is supposed to show five infrared-active phonon modes; however, we can clearly identify only two of them in our spectra. The other modes are likely too weak to be resolved on top of the electronic background within the available experimental accuracy. The two sharp phonon modes fall in the spectral range from 200 to 400 cm\(^{-1} \) (25 – 50 meV), see Fig. 5c. The positions of these modes at \( T = 10 \) K are marked with thin vertical lines.

Both modes can be accurately described by Lorentzians at any temperature. No asymmetric (Fano-like) models are necessary. This is in contrast to the situation in FeSi – an isostructural analogue of RhSi with presumably important role of electron correlations – where strong phonon-line asymmetry was reported in the optical spectra and related to electron-phonon coupling \( [33] \). The absence of detectable electron-phonon coupling indicates that electron-correlation effects are of no relevance in RhSi.

Let us finally mention that the phonon modes observed in RhSi demonstrate a usual broadening as temperature rises. Additionally, the low-frequency mode shows a small softening of its central frequency with increasing \( T \), which can be explained by usual thermal expansion (possible softening of another mode might be not resolved because of a larger width of this mode).

### IV. CONCLUSIONS

We have measured the broadband optical response of the multifold semimetal RhSi. Infrared-active phonons and electronic transitions are revealed in this study. The phonon modes demonstrate a trivial temperature dependence with no indications of strong electron-phonon coupling. The intraband electronic contribution (Drude) is relatively strong with the (unscreened) plasma frequency of approximately 1.4 eV. The interband optical conductivity demonstrates a linear increase at low frequencies (below 300 meV). We interpret this increase as a signature of the transitions between the linear bands crossing around the \( \Gamma \) point. At somewhat higher frequencies (400 – 600 meV), contributions from the linear bands near the \( R \) point (Pauli-blocked at lower frequencies) manifest themselves as an increased slope of \( \sigma_1 (\omega) \). These observations confirm the predictions for the optical-conductivity behavior in multifold semimetals.

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1. J. L. Mañes, Phys. Rev. B 85, 155118 (2012).
2. B. Bradlyn et al., Science 353, aa5037 (2016).
3. G. Chang et al., Nat. Mater. 17, 978 (2018).
4. G. Chang et al., Phys. Rev. Lett. 119, 206401 (2017).
5. P. Tang et al., Phys. Rev. Lett. 119, 206402 (2017).
6. D. S. Sanchez et al., Nature 567, 500 (2019).
7. Z. Rao et al., Nature 567, 496 (2019).
8. N. B. M. Schröter et al., Nat. Phys. 15, 759 (2019).
[9] D. Takane et al., Phys. Rev. Lett. 122, 076402 (2019).
[10] F. de Juan et al., Nat. Commun. 8, 15995 (2017).
[11] D. Rees et al., arXiv:1902.03230.
[12] P. Hosur et al., Phys. Rev. Lett. 108, 046602 (2012).
[13] Á. Bácsi and A. Virosztek, Phys. Rev. B 87, 125425 (2013).
[14] P. E. C. Ashby and J. P. Carbotte, Phys. Rev. B 89, 245121 (2014).
[15] R. Y. Chen et al., Phys. Rev. B 92, 075107 (2015).
[16] B. Xu et al., Phys. Rev. B 93, 121110 (2016).
[17] D. Neubauer et al., Phys. Rev. B 93, 121202 (2016).
[18] S. Kimura et al., Phys. Rev. B 96, 075119 (2017).
[19] M.-Á. Sánchez-Martínez et al., Phys. Rev. B 99, 155145 (2019).
[20] Z. Li et al., Phys. Rev. B 100, 155201 (2019).
[21] D. B. Tanner, Phys. Rev. B 91, 035123 (2015).
[22] M. Dressel and G. Grüner, Electrodynamics of Solids (Cambridge University Press, Cambridge, 2002).
[23] M. B. Schilling et al., Phys. Rev. B 95, 155201 (2017).
[24] D. Neubauer et al., Phys. Rev. B 98, 195203 (2018).
[25] https://www.topologicalquantumchemistry.com; http://www.cryst.ehu.es; B. Bradlyn et al., Nature 547, 298 (2017); M. G. Vergniory et al., Nature 566, 480 (2019).
[26] Z. Qiu et al., Phys. Rev. B 100, 125136 (2019).
[27] S. Das Sarma and E. H. Hwang, Phys. Rev. Lett. 102, 206412 (2009).
[28] F. Hütt et al., Phys. Rev. Lett. 121, 176601 (2018).
[29] R. Kemmler et al., J. Phys.: Condens. Matter 30, 485403 (2018).
[30] A. J. Frenzel et al., Phys. Rev. B 95, 245140 (2017).
[31] D. Chaudhuri et al., Phys. Rev. B 96, 075151 (2017).
[32] D. Grassano et al., Sci. Rep. 8, 3534 (2018).
[33] A. Damascelli et al., Phys. Rev. B 55, R4863 (1997).