Excitonic Instability and Pseudogap Formation in Nodal Line Semimetal ZrSiS

A. N. Rudenko1,2, E. A. Stepanov2,4, A. I. Lichtenstein3,4, and M. I. Katsnelson2,4

1School of Physics and Technology, Wuhan University, Wuhan 430072, China
2Institute for Molecules and Materials, Radboud University, Heijendaalseweg 135, 6525 AJ Nijmegen, The Netherlands
3Institute for Theoretical Physics, University of Hamburg, Jungiusstrasse 9, D-20355 Hamburg, Germany
4Theoretical Physics and Applied Mathematics Department, Ural Federal University, Mira Street 19, 620002 Ekaterinburg, Russia

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Electron correlation effects are studied in ZrSiS using a combination of first-principles and model approaches. We show that basic electronic properties of ZrSiS can be described within a two-dimensional lattice model of two nested square lattices. A high degree of electron-hole symmetry characteristic for ZrSiS is one of the key features of this model. Having determined model parameters from first-principles calculations, we then explicitly take electron-electron interactions into account and show that, at moderately low temperatures, ZrSiS exhibits excitonic instability, leading to the formation of a pseudogap in the electronic spectrum. The results can be understood in terms of Coulomb-interaction-assisted pairing of electrons and holes reminiscent of that of an excitonic insulator. Our finding allows us to provide a physical interpretation of the unusual mass enhancement of charge carriers in ZrSiS recently observed experimentally.

ZrSiS belongs to a class of three-dimensional materials that feature a low-energy tight-binding (TB) model. To this end, we exploit the formalism of maximally localized Wannier functions (WFs) [17–19], which allows us to find a unitary transformation that projects the DFT eigenstates onto the set of Bloch functions that are supposed to describe bands in the relevant energy region. Having done this, one can construct the TB Hamiltonian defined in the optimal WF basis. A minimal model that would describe the nodal line structure of ZrSiS requires two orbitals. Taking this into account, we utilize the criterion of maximal localization in order to find two relevant WFs for ZrSiS [20], whose resulting real-space representation is shown in Fig. 1. One orbital $w_B^{A(r)}(r)$ is localized on the Zr atom and resembles a cubic harmonic of $d_{xy}$ symmetry, whereas the other orbital $w_B^{B(r)}(r)$ is more delocalized and is situated in a region between one Zr and two Si atoms. The corresponding linear spreads amount to 3.1 and 3.8 Å, respectively. The energy bands being the eigenvalues of the Wannier Hamiltonian are shown in Fig. 1 from which one can see a good match between the DFT and Wannier projected bands in the vicinity of the Fermi energy. Importantly, by projecting the Bloch states $\psi_k^{AB}(r)$ onto the resulting WF, one can see that $|\psi_k^{A}\rangle \approx |w_k^A\rangle$ and $|\psi_k^{B}\rangle \approx |w_k^B\rangle$, meaning that each Bloch band is primarily composed of a single WF, and that the overlap between different Bloch bands $\langle \psi_k^{A}\psi_{k'}^{B}\rangle$ is essentially zero at any k point, as depicted by the color of the bands in Fig. 1.

The resulting lattice model for ZrSiS is schematically shown in Fig. 2. The model is given by two nested square sublattices (A and B) in two dimensions. The corresponding Hamiltonian reads

$$H = \sum_{ij \in A} (t_{ij} + \Delta \delta_{ij}) a_i^\dagger a_j + \sum_{ij \in B} (t_{ij} - \Delta \delta_{ij}) a_i^\dagger a_j,$$

where $a_i^\dagger$ ($a_i$) is the creation (annihilation) operator, $\Delta = 0.835$ eV is the on-site energy shift originating from the difference between the sublattices, and $t_{ij}$ are the dominant hoppings parameters, which are restricted to the next-nearest-neighbor interactions within each of the sublattice: $t_{AA}$ and $t_{BB}$. Remarkably, $t_{AA} \approx -t_{BB} \approx 0.74$ eV, while the intersublattice hopping amplitude is considerably smaller, $t_{AB} \sim 0.1$ eV $\ll t_{AA}$, and, therefore, it is not considered here, which significantly simpli-
Formally speaking, this instability is similar to formation of Berry phase for the superconductors. It is not easy, however, to find hole symmetry is playing the same role as time-reversal symmetry. Cooper pairs in superconductors in the sense that electron-excitonic instabilities, widely discussed in the literature [28–31]. Bi-layer graphene is another example for the realization of the excitonic instabilities, widely discussed in the literature [28–32].

Within our model for ZrSiS, the dispersion of electrons [Eq. (2)] is diagonal in the sublattice space, and it exhibits a high degree of electron-hole symmetry \( \varepsilon_A(k) = -\varepsilon_B(k) \). Furthermore, the nodal line band topology ensures a finite density of states at the Fermi energy, which makes ZrSiS a natural candidate for the excitonic insulator or, at least, for a system in the vicinity of a quantum phase transition to the excitonic insulator phase (“virtual” excitonic insulator). Therefore, it is instructive to consider electron-electron interactions explicitly, which is done in this Letter at the level of the two-orbital Hubbard model.

**Coulomb interaction.**—Before considering many-body effects in ZrSiS, we estimate the strength of the Coulomb interactions in this material. As we are aiming at solving the two-orbital Hubbard model, we are interested in the partially screened Coulomb interaction \( U = (1 - VP)^{-1}V \), where \( V_{ij} = \langle i j | \hat{\mathbf{r}} - \hat{\mathbf{r}}' | i j \rangle \) is the bare interaction, and \( P \) is the static polarizability calculated here within the constrained random phase approximation [33,34]. The resulting on-site and inter-site Coulomb-interaction parameters estimated to \( U_{AA} \approx 2.00 \), \( U_{BB} \approx 1.22 \), and \( U_{AB} = 0.97 \) eV, respectively, which are deter-
minded in the WF basis defined above. As expected, the on-site interactions are different for the two sublattices, which is attributed to different orbital localization. In contrast to typical transition metal compounds, where interstite Coulomb interaction within the d shell is essentially screened by conduction electrons \[33\], interstite coupling in ZrSiS is not more than two times smaller than the on-site interaction, i.e., \(U_{ii}/U_{ij} \lesssim 2\), typical to p-electron systems \[34\]-\[38\]. The presence of a non-negligible interaction between the sublattices will result in a Coulomb mixing of the relevant low-energy states in ZrSiS.

Consideration of Coulomb interactions leads to the following action of the two-orbital Hubbard model written in momentum space

\[
S = -\sum_{k,\alpha} a_{k\alpha}^\dagger [iv + \mu_\alpha - \epsilon_\nu(k)] a_{k\alpha} + \sum_{q,\alpha} U_{\alpha\alpha} n_{q\alpha \uparrow} n_{-q\alpha \downarrow} + \frac{1}{2} \sum_{q,\alpha,\beta} U_{\alpha\beta} n_{q\alpha \uparrow} n_{-q\beta \downarrow}.
\]

Here, variables \(a_{k\alpha}^\dagger\) (\(a_{k\alpha}\)) correspond to creation (annihilation) of an electron with momentum \(k\) and fermionic Matsubara frequency \(\nu\) on a sublattice \(\alpha = \{A, B\}\), \(n_{q\alpha} = \sum_k a_{k\alpha}^\dagger a_{k\alpha}\) is an electronic density for the momentum \(q\) and bosonic Matsubara frequency \(\omega\). For simplicity, we use the combined notations for momentum and frequency \(k = (k, \nu)\) and \(q = (q, \omega)\) for electronic and bosonic variables, respectively. Then, the bare Green’s function of the model is diagonal in the sublattice \(\alpha = \{A, B\}\) space and reads \(G_{\nu}(k) = [iv + \mu_\alpha - \epsilon_\nu(k)]^{-1}\).

**Formation of a pseudogap.**—Similar to the case of superconductivity, the electron-hole instability \[23\]-\[24\] takes place at decreasing temperatures. At the critical temperature \(T_c\), the system may undergo the second-order phase transition toward the symmetry broken phase, characterized by anomalous averages; for the case of superconductivity, they describe Cooper pairing, while in the case under consideration, they couple electron and hole states. The ordered phase is characterized by the formation of the bound electron-hole pairs, which leads to a (pseudo)gap opening in the electronic spectrum. From the symmetry point of view, this works like an effective spin-orbit coupling, yet without the relativistic smallness parameter (i.e., can yield a much larger gap) and being strongly temperature dependent. Above the critical temperature, a pseudogap can arise due to fluctuation effects, similar to the antiferromagnetic pseudogap in the quantum two-dimensional antiferromagnet at finite temperatures \[39\]. Unlike the case of a superconductor, where the fluctuation effects are small due to the long-range character of the Cooper pairing, the situation may be different for the case of excitonic pairing since there are no reasons to a priori assume a very large exciton radius.

To capture the relevant fluctuation effects in ZrSiS, let us introduce the electronic self-energy \(\Sigma_\mu(k)\) that takes correlation effects in the particle-hole (excitonic) channel into account. In order to describe the main contribution that leads to the instability, the self-energy is taken in the following form

\[
\Sigma_\mu(k) = u_\mu a_{\mu}^\dagger + u_\mu^* a_{\mu},
\]

or

\[
\Sigma_\mu(k) = \sum_{q,\beta} W_{\mu\beta}(q) G_{\beta}(k + q),
\]

where the renormalized interaction

\[
W_{\mu\beta}(q) = U_{\mu\beta} \left[1 - X_{\mu\beta}^0(q)U_{\mu\beta}\right]^{-1}
\]

contains the two-particle ladder diagrams that couple electrons of different sublattices

\[
X_{\mu\beta}^0(q) = \sum_{k,\alpha} G_{\alpha}(k') G_{\beta}(k' + q)
\]

via the Coulomb interaction. The calculation of the self-energy [Eqs. (5) - (7)] is performed on a 128\times128 \(k\) mesh with 512 Matsubara frequencies using the fast Fourier transform scheme, similar to Ref. [44]. Then, the renormalized Green’s function is given by the usual Dyson equation

\[
G_{\mu}^{-1}(k) = G_{\mu}^{-1}(k) - \Sigma_\mu(k).
\]

Finally, we perform a Padé continuation [41] of the renormalized Green’s function \(G_{\mu}(k, \nu)\) from the Matsubara axis to the real frequencies \(G(k, E)\) and calculate the spectral function \(A(k, E) = -(1/\pi) \text{Im} G(k, E)\) for different temperatures. At high enough temperatures, no significant changes of the spectral function are observed.

In Fig. 3 we show the resulting spectral function, as well as the density of states, calculated in the vicinity of the phase transition. One can see that at \(T_c \approx 135\ \text{K}\) the band crossing between the \(\Gamma\) and \(X\) points disappears, accompanied by a pronounced dip in the density of states. Therefore, one can see that there is a phase transition induced by many-body effects. Indeed, similar to \[39\], the renormalized interaction \[5\] that couples electrons from two different sublattices \(W_{AB}(q \to 0)\) depends on the temperature and diverges in the region close to the phase transition. This dependence follows from the logarithmic divergence of \(X_{\mu\beta}^0(q \to 0) \propto -N(0) \ln(\Delta/T)\) for zero doping, where \(N(0)\) is the density of states at zero Fermi energy, and \(\Delta\) is a cutoff of the order of bandwidth \[23\]-\[24\]. As a result, \(W_{AB}(q \to 0) \approx 1/\ln(T/T_c)\). In Ref. [10], the effect of a band renormalization was observed in strong magnetic fields. According to the experiment, the effective mass in ZrSiS depends not only on \(T\), but also on \(B\), which is the magnitude of the magnetic field. It can be shown that the magnetic field cuts off the logarithmic divergence responsible for the excitonic instability at energies on the order of the cyclotron frequency, \(\hbar\omega_c \sim B\). It means that in the expression for \(X^0\) given above, \(T\) is to be replaced by \(\max(T, \hbar\omega_c)\). Similar behavior was recently theoretically predicted and experimentally observed for the Fermi velocity renormalization in graphene \[42\].
The calculated temperature dependence of $1/X_{AB}^0(q \to 0)$ relative to the intrasublattice Coulomb interaction $U_{AB}$ is shown in Fig. 4. The condition $U_{AB}X_{AB}^0(q \to 0) = 1$ in Eq. (6) ensures a large contribution to the self-energy [5]. At zero doping it results in the formation of the pseudogap in a narrow region of temperatures close to $T_c \approx 135$ K, as shown in Fig. 3. As one can also see from Fig. 4 the critical temperature $T_c$ strongly depends on doping, which breaks the particle-hole symmetry and suppresses the instability. Even a small shift of the Fermi energy by $\varepsilon_F = 10$ meV results in a considerable decrease of $T_c$, whereas at higher values of $\varepsilon_F$, the phase transition becomes fully suppressed. This behavior is similar to suppression of singlet superconductivity by the magnetic field.

It is worth noting that the resulting phase diagram is very sensitive to detailed values of the parameters and especially to the intersublattice coupling parameter $U_{AB}$. Given that long-wavelength correlations are not considered explicitly in the model [5], one may expect that the properly defined parameter $U_{AB}$ can be further reduced by screening due to nonlocal interactions neglected in our formalism [43]. In turn, the reduction of $U_{AB}$ can lead to a considerable lowering of the transition temperature $T_c$, what immediately follows from Fig. 4. However, we note that the transition to the phase of excitonic pairing cannot be fully suppressed as long as particle-hole symmetry is strictly preserved. Probably only experiment can decide whether this condition is achievable in practice, and whether ZrSiS becomes a truly excitonic insulator at low enough temperatures or just close enough to the instability. The existence of an excitonic pseudogap cannot be conclusively supported by the reported angle-resolved photoemission spectroscopy data (e.g., Refs. 1 and 2), which might be related to the limited resolution, not sufficiently low temperatures, or external factors breaking the electron-hole symmetry (e.g., doping). Nevertheless, our results appear sufficient to explain qualitatively a strong renormalization of the effective mass observed in Ref. [2]. Further experiments, such as infrared optical measurements or scanning tunneling microscopy, may be needed to provide more consistent information on the many-body effects in ZrSiS.

**Conclusion.**—To conclude, we have demonstrated that ZrSiS is a system with moderately strong electron-electron interactions and a very high degree of electron-hole symmetry near the Fermi energy, which makes it close to excitonic instability. We predict a pseudogap formation in its electronic spectrum at low enough temperatures. Therefore, ZrSiS is a good example of the system where both nontrivial topology and correlation effects are important, which should motivate further experimental and theoretical studies.

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\[ \text{a.rudenko@science.ru.nl} \]

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