Kondo-semimetal to Fermi-liquid phase crossover in black phosphorus to pressure-induced orbital-nematic gray phosphorus

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We perform a comparative study of the electronic structures and electrical resistivity properties of black (A17) and of pressurized gray (A7) phosphorus, showing band-selective Kondo-esque electronic reconstruction in these layered p-band phosphorus allotropes. Based on density functional dynamical mean-field theory calculations, we show that gray phosphorus can host a three-dimensional Kondo semimetal to a Fermi liquid phase crossover under anisotropic compression, which lifts in-layer orbital degeneracy. Therein, the 3p spectrum is almost unaffected both in the semiconducting and semimetallic Kondo phases, however in the Fermi liquid regime strong electronic reconstruction is predicted to exist in the orbital nematic phase of compressed gray phosphorus. These findings contribute to the microscopic understanding of the role played by dynamical multiorbital electronic interactions in the low energy spectrum of correlated semiconductors and topological semimetals.

I. INTRODUCTION

Black phosphorus (BP, not to be misunderstood as boron phosphide) is the thermodynamic most stable allotrope of elemental phosphorus at normal conditions [1]. In its A17 orthorhombic crystal structure layers of six-membered rings with chair conformation are stacked along [010]. Alternatively, a single layer can be decomposed into sets of interconnected zigzag chains on two different planes. Therein, phosphorus atoms are threefold connected. The layers are held together by van der Waals forces into a three-dimensional crystal as shown in the left panel of Fig. 1. Despite its classic status as an element [2], phosphorus remains surprising due to fascinating structure/property relationships hosted by this layered p-band material [3]. Particularly interesting are strain-induced band gap modifications [4–6], which allows us to tune semiconductor BP into anisotropic Dirac semimetal [7], and a superconducting phase transition induced by pressure [8]. In the latter, selective low-energy electronic reconstruction suggests placing BP among correlated electron systems, like pointed out elsewhere [9].

The one-particle band gap of multilayer and bulk BP [10] as well as in BP films [11] remains an open problem of current interest. Ab initio density functional calculations of bulk BP yield a band gap in the range of 0.3 eV to 0.35 eV [12], a value compatible with scanning tunneling data [13]. However, this gap size appears to be in conflict with transport data by at least two groups [14,15], where the d c resistivity measurements at ambient pressures show a temperature-dependence behavior characteristic of narrow band semiconductors with very low activation energies. Band gap estimations for few-layer and bulk BP as well as different GW implementations BP show broad band gap variations in this p-band system [10].

Under moderate compression (∼5 GPa) BP transforms into the semimetallic rhombohedral α-As type structure (A7), as displayed in Fig. 1, right panel. While not group-subgroup related, A17 and A7 can be accommodated in a common monoclinic subgroup (P 2/c) with phosphorus atoms on general Wyckoff positions ([16]. Due to its peculiar electronic structure [17], narrow band gap [12] BP displays anisotropic particle-hole excitations [18], magnetoresistance [14,19], and ther-mal transport properties [20]. Under hydrostatic compression [15,21], electrical resistivity measurements reveal that the one-particle energy gap of orthorhombic BP can be continuously reduced down to zero, which is reached at a critical pressure $P_c \approx$ 1.25 GPa [15]. The characteristic low-temperature resistive divergence of semiconducting systems is gradually suppressed. Beyond $P_c$ the resistivity shows semimetallic behavior, which indicates a pressure-induced insulator to semimetal transition [15,22]. Under pressure, two consecutive reversible structural transitions occur: from orthorhombic BP to a rhombohedral phase (gray phosphorus) occurring at 5.5 GPa [23], followed by transformation into a simple-cubic phase at pressures about 11 GPa [24]. Near the semiconductor-to-semimetal transition, applied pressure pushes the valence and the conduction bands together [15], causing substantial changes in the topology of the Fermi surfaces [22]. Hall resistivity measurements of bulk BP close to $P_c$ show in fact evidence of Lifshitz transition.

Sizable electronic reconstruction qualifies therefore pressurized phosphorus as an orbital-selective p-band system, hosting renormalized electronic states at low energies. Here, we extend our earlier density functional dynamical mean-field theory study of bulk BP [9] to predict the appearance of intrinsic many-body correlation effects in the electronic structure of A7 gray phosphorus (GP), the high pressure layered polymorph of BP. Careful comparison of the multiorbital (MO) spectral functions of black and gray phosphorus provides insights into the MO correlated electronic behavior of GP. Additionally, we explore the role played by an orbital nematic state, which could be induced via anisotropic compression,
showing the emergence of a Fermi liquid electronic state at low temperatures.

MO physics is inherently complex due to lattice, charge, and spin degrees of freedom [25]. These coupled correlations have hampered theoretical studies to treat them in a fully realistic way. Density functional plus dynamical mean-field theory (DFT + DMFT) [26] allows for a systematic approach to MO electronic correlation. In MO systems, external perturbations like pressure, lattice distortions, and chemical doping can cause spectacular electronic effects. As an illustration thereof, here we study correlation- and nematic-induced electronic reconstructions using the DFT + DMFT method, which self-consistently takes into account these effects in real materials.

Since electronic correlation is ubiquitous, an interesting question in the context of correlated semiconductors [27,28] is whether many-body correlation effects, characteristic of narrow band materials [25], can also be hosted in $p$-band semimetals. Based on a realistic model, in this paper we provide a comparative many-particle description of the correlated electronic structure of black and high-pressure gray phosphorus and of its impact on electrical transport. Our results, which are derived from reconstructed spectral functions, reveal that bulk GP hosts a MO Kondo state [29,30], which undergoes to a metallic Fermi liquid state upon lifting the in-plane orbital degeneracy in the high-pressure phase.

The Kondo effect is known as one of the most interesting phenomena in conventional metals [31]. Historically, the Kondo effect occurs in the presence of dilute concentration of localized spins coupled to the Fermi sea of metals [32]. The many-body interaction between the localized spin and conduction electron screens the impurity spin leading to a weak divergent resistance, as one approaches zero temperature. It also results in sharp Kondo resonances in the electron spectral functions of narrow band, Fermi liquid metals [33]. Here, we are particularly interested in emergent Kondo physics in $p$-band semimetals [34–37], which is expected to be distinct from impurity-induced Kondo effect in conventional metals due to the specific electronic structure of the gapped, semimetallic electron gas at low energies. To date, there are only few theoretical studies and experimental evidences for Kondo-esque-like physics in graphene [34,35,38], graphite [37], and elemental bismuth [36]. The reason is that the Kondo effect is not easily accessible by experiments on $p$-band systems. In $V$-shaped, Dirac-fermion $p$ band materials like graphene and graphite, the low-electron density of states (DOS) near the Dirac point prevents the appearance of correlation-induced Kondo and Fermi liquid fingerprints. The Kondo temperatures, for example, are expected to be extremely small [39]. Therefore, this many-particle effect may be shifted to temperatures, which would be experimentally inaccessible. In transport experiments the Kondo effect is usually manifested by the logarithmic increase of the electrical resistivity at low temperatures [35,40]. The low temperature upturn in resistivity is seen in a variety of systems [41] and can originate from many-particle corrections to resistivity due to weak electron localization, canonical Kondo effect (or the scattering of conduction electrons by localized impurities) or as discussed in the context of carbon nanotubes [30], the Kondo effect in $p$-band materials can also occur in the absence of spin impurity or orbital degeneracy is present in the system. In such a case, the role of spin is replaced by other degrees of freedom, such as an orbital quantum number, and the leading logarithmic corrections in the electrical resistivity are thus due to the local interactions between electrons on different orbitals [29].

Although Kondo-like physics has been studied in the context of $p$-band materials [34–38], there has been no theoretical attempt to describe the emergence of orbital Kondo effect [29,30] and its crossover to a Fermi regime in phosphorus allotropes. In this paper we present a comprehensive DFT + DMFT analysis for the correlated MO problem of $A7$ GP to show that an emergent orbital Kondo effect in a $p$-band system can be tuned towards a Fermi liquid state via distortion induced orbital-nematic order with lifting twofold orbital degeneracy. Within local density approximation plus dynamical mean-field theory (LDA + DMFT) [26] framework we show that the concomitant interplay between MO electronic interactions and twofold orbital degeneracy in the $p_{x,y}$ orbitals of GP gives rise to an orbital Kondo effect, implying the formation of orbital singlets at low temperatures as in carbon orbitals [30]. Additionally we show that the twofold orbital degeneracy of $A7$ phosphorus can be lifted by an orbital field which can be tuned via uniaxial compression in the bulk. We demonstrate the presence of distinct low-energy frequency dependence behavior of the electronic self-energies and their relation to electrical transport across the orbital Kondo to Fermi liquid phase crossover.

II. RESULTS AND DISCUSSION

BP (space group $Cmca$) is a narrow band gap semiconductor under ambient pressure conditions [15]. Its orthorhombic crystal structure consists of corrugated layers of six-membered rings stacked along the [010] direction (see Fig. 1, left panel). As in the case of bulk BP, the individual layers of $A7$ phosphorus are also connected by van der Waals forces. GP has a rhombohedral structure (space group $R3m$) [24], similar to elemental bismuth [36]. Being a homologue of Bi and As, $A7$ phosphorus is characterized by extended puckered layers of three-connected phosphorus atoms, with shorter distances within each layer than between (111) layers. Upon
\[
\begin{align*}
H_{\text{int}} &= U \sum_{i} n_{ia} n_{ib} - J_{H} \sum_{ia=ib} S_{ia} \cdot S_{ib}.
\end{align*}
\]

Here, \( a = x,y,z \) label the diagonalized 3p bands and \( a(k) \) is the one-electron band dispersion, which encodes details of the one-electron (LDA) band structure. To label the \( x,y,z \) orbitals of GP we have used the same reference system as in the work by Y. Hayasi \textit{et al.} \cite{17} and in Ref. \cite{9}. \( U \equiv U - 2J_{H} \), with \( U,U \) being the intra- and interorbital Coulomb repulsion and \( J_{H} \) is Hund’s rule coupling. Within LDA the one-band dispersions are read off from \( a(k) \); these are inputs for MO LDA + DMFT which generates, respectively, Kondo insulat-

FIG. 2. Comparison between the LDA orbital resolved density of states (DOS) for bulk BP (dashed line) and GP (solid line), showing sizable one-particle band narrowing of the conduction band states of bulk GP. Notice as well the (narrow gap) insulating and semimetallic nature of BP and GP, respectively.

rhombohedral distortion, semiconducting \( A17 \) phosphorus becomes a \( p \)-band semimetal with a small number of valence band states at the Fermi energy (\( E_{F} \)), as shown in Fig. 2. Here, LDA calculations for the crystal structure at real conditions were performed using the linear muffin-tin orbitals (LMTO) \cite{42,43} scheme in the atomic sphere approximation. More precisely, calculations were performed using the scalar relativistic version of the PY-LMTO \cite{43}. Similar to BP \cite{9}, the total density was converged on a grid of 301 irreducible \( k \) points, and the radii of the atomic spheres were chosen as \( r = 2.74 \text{ a.u.} \) in order to minimize their overlap. The corresponding orbital resolved LDA DOS is shown in Fig. 2. As seen, BP shows a marked anisotropy near \( E_{F} \), which reflects structural differences within the layers (\( x,y \) directions) and along the stacking (\( z \) direction). This anisotropy is of top importance in understanding transport properties consistent with a narrow gap scenario, like demonstrated elsewhere \cite{9}.

In contrast with BP, the orbital resolved spectral functions of GP show an appreciable one-particle band narrowing (\( \approx 2.15 \text{ eV} \)) of the conduction band states at high energies and a suppression of the one-electron band gap centered near \( E_{F} \). Similar to bismuth \cite{36}, elemental phosphorus has a formal +3 oxidation state, which implies half occupation in the \( p \) sector. Upon \( A17 \) to \( A7 \) phase transformation all electronic

\( 3p \) carriers acquire some itinerance, which provides valence and conduction band states in all active \( 3p-(x,y,z) \) orbitals near \( E_{F} \). This situation of three half-filled semimetallic bands and twofold (\( x,y \)) orbital degeneracy provides the underlying microscopic one-band seeds of an orbital Kondo scenario \cite{30} in \( A7 \) phosphorus.

The many-body MO Hamiltonian relevant for bulk phosphorus is \( H = H_{0} + H_{\text{int}} \) \cite{9} with
We use MO DMFT for the three-orbital model of bulk phosphorus with the MO iterated-perturbation theory (MO-IPT) as an impurity solver of the many-particle problem in DMFT. This method has been benchmarked by comparison with numerically exact quantum Monte Carlo results in the limit of large lattice dimensions (DMFT) [46], where very good accord between IPT and CTQMC for both one-band and multiband Hubbard models was found.

The MO LDA + DMFT scheme [26] adequately describes the effect of local dynamical interactions in the limit of large lattice dimensions (DMFT) [33], so we do not repeat the equations here. It is worth mentioning, however, that the IPT is an interpolative ansatz that connects the two exactly soluble limits of the one-band Hubbard model [47], namely,
effects in GP compared to BP. Sizable correlation effects manifest themselves above the gap (BP) and pseudogap (GP) scales as negative bump structures, as is apparent from the orbital-resolved self-energies. This unveils an underlying Kondesque physics as in graphite [37]. Stronger electronic correlations imply a reduction of the vanishing region in the GP MO self-energies (Fig. 4). Proximity to an anisotropic Kondo semimetallic state is indicated by the narrowing of the negative bump structures lying above and below the Fermi energy, $E_F (\omega = 0)$. Spectral redistribution in response to additional small perturbations (like external anisotropic compression) can drive it into a true metallic state, which hosts quadratic $\omega$ dependence in $Im \sigma (\omega)$ at low temperatures, as shown below. This is a manifestation of the intrinsically correlated nature of the system of interest.

Additionally, to elucidate close similarities between the semiconducting and semimetallic states found for BP and GP at $U = 10$ eV as well as the crucial role played by MO interactions on electrical transport in layered phosphorus-based $p$-band materials the temperature ($T$) dependence of the $dc$ resistivity is computed using the orbital resolved LDA + DMFT spectral functions. Within the Kubo formalism [50], the $dc$ conductivity can be expressed as

$$\sigma_{dc} (T) = \frac{2\pi e^2}{h} \sum_a \rho_a (\omega) a |f(\omega)|$$

where $\rho_a^{(0)} (\omega)$ is the LDA DOS.

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in pressurized A7 phosphorus with concomitant reduction of the Kondo temperature \( T_K = 16 \) K for GP with \( U = 10 \) eV), or the temperature below which \( \rho(T) \) displays an insulating upturn. Particularly interesting is the Kondo resistivity (see the right inset) [35,40], which according to our description arises from the interplay between \( x,y \)-orbital degeneracy [30] and U-induced MO Kondo effect within DMFT [29]. Moreover, in the right inset of Fig. 5 we display the changes in the \( \ln(T) \) corrections for different values of the on-site Coulomb repulsion \( U \). Interestingly, the \( T \) dependence in the left inset of Fig. 5 resembles the one seen in experiments of pressurized phosphorus, [15] showing significant changes in the low-\( T \) resistivity upturn. This might be the precursor for the pressure-induced insulator-metal transition in elemental phosphorus. Based on our results in Fig. 4 it can plausibly be assumed that noticeable electronic reconstruction occurs in pressurized GP at low pressures. Taken together, these results support a description of bulk GP as correlated semimetal, proximate to a low-\( T \) Fermi liquid metal as shown below.

### B. Role of lifting twofold orbital degeneracy

Under external perturbations like pressure or lattice strain, the hopping elements and the crystal field splittings are renormalized in nontrivial ways. In practice however, it is very difficult to separate the effects of the hopping from those induced by crystal field splittings, even more so if lattice instabilities under pressure or negative pressure are not known a priori. Accordingly, since a semimetal-to-metal crossover which is likely to exist in the metastable phases [3] of phosphorus at low pressures, we adopt the following strategy to derive this crossover. Instead of actually lifting orbital degeneracy by uniaxial compression, we search for an instability of the semimetal phase to the paramagnetic Fermi liquid metal. Here, we follow the methodology used in earlier studies addressing the effect of orbital splittings on the correlated many-body states of transition metal oxides [51] and more recently to pressurized FeS [52] and solid oxygen [53]. We consider the orbital-dependent on-site energy term,

\[
H = \sum_{\sigma} \epsilon_n a_{\sigma n}^\dagger a_{\sigma n} - H_{\text{int}} + H_{\text{soc}} + H_{\text{augeon}}.
\]

To simulate the structural (and hence, electronic) changes upon uniaxial compression. This choice in \( H \) directly leads to \( n_y > n_x \) by itself, implying a ferro-orbital order along with a finite orbital nematicity,

\[
N \equiv n_x + n_y = \binom{ny - nx}{nx + ny} = 0.
\]

as discussed in the context of iron arsenide superconductors [54]. In our theory, \( a \) acts like an external field in the orbital sector (orbital fields), sensitively controlling the occupations of each orbital in much the same way as the magnetization of a paramagnet as function of an external magnetic, Zeeman field.

Figure 6 shows that small variations of with fixed \( U \) and \( J_H \) drive appreciable spectral weight transfer, producing orbital polarization and selective electronic reconstruction of the one-particle spectral functions. While the correlated DOS of the \( px \) orbital remains similar to the undistorted \( A7 \) phosphorus, \( px \) and \( py \) are clearly affected by the orbital field \( H \), showing large transfer of spectral weight with increasing \( \Delta \). As seen the
$p_z$ DOS remains semimetallic, while the $p_{x,y}$ bands undergo a semimetal-to-metal phase crossover with emergence of coherent Kondo peaks at $EF$. The underlying theoretical reason for this is as follows: With increasing scattering between the effectively semilocalized ($p_z$) and itinerant components ($p_{x,y}$) of the matrix DMFT propagators produces a Fermi liquid metal because of strong interband scattering operates in an orbitally polarized metallic system. Our results thus suggest that in broad band systems small changes in crystal field splittings might promote local orbital fluctuations which cuts off the Kondo scattering of the semimetallic channels. From our results, the orbital-selective Kondo semimetallic phase is thereby suppressed in distorted GP with broken twofold rotation symmetry, leading to continuous evolution of the coherent, semimetal to a correlated Fermi liquid like metal as shown below.

Expanding on our previous discussion, in what follows we provide a microscopic interpretation for the semimetallic-to-metallic crossover in GP and its implication to anisotropic electronic mobilities in the nematic state in depth. Specifically, in addition to the orbital-selective electronic reconstruction revealed in Fig. 6, we show that the imaginary parts of the electronic self-energies are reshaped as well and correlate with the evolution of the LDA + DMFT spectral functions with $\omega$. This in our opinion reinforces the basic hypothesis about the interplay between structural distortions (inducing changes in crystal field splittings) and sizable MO many-body correlations between the effectively semilocalized ($p_z$) and itinerant orbitals of the one-particle $p_z$-DOS as shown in Fig. 6, the frequency dependence of $\Im \Sigma_{\omega}(\omega)$ does show $-\omega^2$ Fermi liquid dependence as increases toward to larger values. This in turn suggests that in broad band electron systems correlation effects might not be directly probed by spectroscopy experiments but they might be hidden in the correlated self-energies as recently shown for bulk BP [53]. Also interesting in Fig. 7 is the clear Fermi liquid energy dependence of $\Im \Sigma_{\omega}(\omega)$, implying that this is the most correlated $3p$ orbital sector due to enhanced electronic states near $EF$ in the distorted bulk. This prediction could be corroborated by future spectroscopy and transport experiments probing anisotropic (in-plane and out-of-plane) spectral functions and electronic mobilities in the orbital nematic state of bulk GP.

To gain insights on the interplay between electron-electron interactions and orbital nematicity on the multiple structure of the GP, in Fig. 8 we display the temperature dependence of the electrical resistivity showing its evolution from a Kondo semimetal to a metallic Fermi liquid behavior on increasing the orbital field. As visible in the inset of Fig. 8 at $\Delta = 0.75 \text{ eV}$ the temperature dependence of resistivity follows Fermi liquid behavior with a quadratic dependence at low temperatures. Meanwhile, the $\ln(T)$ dependence observed in Kondo systems is still found at values below 0.3 eV. Interesting as well is the fact that for $0.35 < \Delta < 0.5 \text{ eV}$ we obtain an almost linear $T$ dependence, usually referred to as non-Fermi liquid behavior. Even though the nature of non-Fermi liquid state is in debate and the variation from the $T$ to $T^2$ dependence

![FIG. 7. Orbital-resolved self-energies (imaginary part, $\Im \Sigma_{\omega}(\omega)$) across the Kondo insulating to Fermi liquid crossover of orbital nematic GP. Notice the substantial reduction of the near zero constant value of $\Im \Sigma_{\omega}(\omega)$ near $EF$ in all channels upon increasing the orbital field and the smooth crossover to a $-\omega^2$ dependence characteristic of correlated Fermi liquid metals.](Image)

![FIG. 8. $T$ dependence of electrical resistivities for the Kondo semimetallic and metallic state of orbital nematic GP. Particularly interesting is the suppression of the $\ln(T)$ behavior and the resistivity upturn with increasing $\Delta$. The inset displays resistivity curves of GP for the different values on a linear scale, showing the changes in $\rho(T)$ towards a $T^2$ dependence characteristic of Fermi liquid metals.](Image)
with doping, pressure, and “chemical pressure” are considered as common characteristics in the cuprates and iron-based superconductors, to the best of our knowledge it has never been considered in the context of Kondo to Fermi liquid crossover of broad band $p$ band systems. Taken together, our results in Figs. 7 and 8 indicate that enhancement of electronic correlations upon uniaxial compression could promote higher-$T_c$ superconductivity hitherto not probed yet in pressurized phosphorus allotropes and related $p$ band systems.

### III. CONCLUSION

In this work we have studied the role of multiorbital electronic correlations in bulk BP and GP allotropes, showing the existence of semimetallic Kondo-like behavior in the electronic and transport properties of bulk GP. We have also explored the interplay between sizable electronic correlations and in-plane rotational symmetry breaking in bulk GP and the emergence of an orbital nematic phase, which is likely to exist in compressed GP. The unusual anisotropic character of electronic and charge transport induced by an orbital nematic state with lifted twofold orbital degeneracy reveals an orbital-selective Kondo to Fermi liquid crossover. This arises from low-energy scatterings having their origin in the competition between pressure induced semimetallicity and orbital nematicity within the LDA + DMFT approximation. Taken together, many-particle electron-electron correlation effects are predicted to be important for the occurrence of emergent orbital Kondo and Fermi liquid behavior in topological Dirac and Weyl semimetals [55] without embedded impurities [56].

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