Extremely large magnetoresistance from electron-hole compensation in the nodal loop semimetal ZrP$_2$

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Several early transition metal dipnictides have been found to host topological semimetal states and exhibit large magnetoresistance. In this study, we use angle-resolved photoemission spectroscopy (ARPES) and magneto-transport to study the electronic properties of a new transition metal dipnictide ZrP$_2$. We find that ZrP$_2$ exhibits an extremely large and unsaturated magnetoresistance of up to 40,000 % at 2 K, which originates from an almost perfect electron-hole compensation. Our band structure calculations further show that ZrP$_2$ hosts a topological nodal loop in proximity to the Fermi level. Based on the ARPES measurements, we confirm the results of our calculations and determine the surface band structure. Our study establishes ZrP$_2$ as a new platform to investigate near-perfect electron-hole compensation and its interplay with topological band structures.

Topological semimetals have attracted considerable scientific interest owing to their unique electronic structure and unconventional transport properties, such as extremely large magnetoresistance (XMR) [1–6] and planar Hall effect [7, 8], as well as their deep connection with the high-energy particle physics [9]. These unusual properties not only pave the way for future electronic and spintronic devices, but also provide a test-bed for our current models of transport theories [10]. The characteristic dispersion feature of most topological semimetals is a linear intersection of quasiparticle bands near the Fermi energy. In the most well studied examples, i.e. Dirac [11, 12] and Weyl semimetals [1, 13, 14], the energy bands intersect each other on a single point in $k$-space with four- and two-fold degeneracies, respectively. Nodal line semimetals, on the other hand, exhibit band crossings that extend on a one-dimensional path in $k$-space [15], which can be either an open line, a closed loop, and even loops with complex connectivity [16–19]. Examples of nodal line semimetals have been found in ZrSiS-type materials [20–23], and early transition metal dipnictides MX$_2$ (M = Nb, Ta, Mo, W; X = P, As, Sb) in the absence of spin-orbit coupling (SOC) [24–27].

In early transition metal dipnictides (TMDPs), non-trivial topology is often accompanied by unsaturated XMR [1, 3, 28–31]. Elements highlighted in Fig. 1(a) all exhibit XMR in TMDPs. While XMR has been found for TMDPs made of group V and VI metals, as highlighted in Fig. 1(a), no group IV TMDP has been studied. Here, we investigate ZrP$_2$ as a case study that demonstrates the ubiquity of these properties in early TMDPs. We propose that two factors are key for understanding the relation between topology and XMR in these compounds: non-symmorphic crystal symmetry, and partial charge transfer in the bonding.

Most of known early TMDPs crystallize either in an OsGe$_2$ type (space group C$2$/m, No. 12) or MoP$_2$ type structure (space group Cmc2$_1$, No. 36), as shown in Fig. 1(b,c) [32]. In the MoP$_2$ structure, the four TM sites are related by three glide planes ($b$, $c$, and $n$ glide planes) whereas in the OsGe$_2$ structure two pairs of TM sites are related by one glide plane ($a$ glide plane). In both cases, the conventional unit cell therefore contains four and the primitive unit cell two formula units. The non-symmorphic symmetry thus indirectly guarantees an even number of valence electrons, regardless of the atomic number of the TM. Moreover, the effective doublings of the unit cell cause band back-folding, facilitating the occurrence of band crossings such as nodal lines.

Considering that the $d$ electrons of early transition metals are relatively weakly bound and easily transferable to the pnictogen [33], we would expect to see fully filled valence bands and empty conduction bands, consistent with a band insulator with no charge carriers. However, early TMDPs consistently show metallic conductivity in experiments [32, 33]. This inconsistency is resolved by assuming that the charge transfer is incomplete, resulting in semimetallic Fermi surfaces. The electron- and hole-like charge carriers’ density are hence naturally close to compensated, leading to an unsaturated XMR within the semiclassical approximation (Fig. 1(d)) [34, 35]. We note that the above statements should generally hold true for all early TMDPs. However, to the best of our knowledge, no group IV TMDP has ever been reported to dis-
play nonsaturating XMR, leaving an open question to the generality of the above simple arguments based on non-symmorphic symmetry and incomplete charge transfer.

Here, we demonstrate that ZrP$_2$ is the first group IV dipnictide to exhibit nonsaturating XMR. The electron and hole carrier densities determined from magnetotransport measurements are almost perfectly compensated, which quantitatively agrees with the observed XMR [34]. The electron-hole (e-h) compensation is further confirmed by density functional theory (DFT) calculations, which also reveal the existence of a nodal loop below the Fermi level in the k-space. Our band structure calculations are verified by angle-resolved photoemission spectroscopy (ARPES).

Crystals of ZrP$_2$ were grown by a two-step process. Stoichiometric mixtures of zirconium (Alfa Aesar, 99.7 %, foil) and red phosphorus (Alfa Aesar, 99.995 %, pieces) with an addition of iodine were pre-reacted at 800 °C for seven days. Subsequently, crystals were grown by horizontal chemical vapor transport using a temperature gradient from 760 °C (source) to 810 °C (sink) with 7.5 mg/ml iodine as transport agent. After ten days, needle-like crystals of typical dimensions 0.3x0.3x5 mm$^3$ were obtained in the sink. Details of the crystal characterization are given in the Supplementary Materials [36].

The electrical transport and Hall measurements were performed with a conventional five-probe geometry on a 9 T PPMS (Quantum Design). The Hall data was anti-symmetrized to remove contributions from the transverse magnetoresistance.

ARPES measurements were performed at the micro-ARPES endstation of the MAESTRO beamline 7.0.2 at Advanced Light Source (ALS) and the I$^2$ endstation of beamline UE112 PGM at BESSY. Samples were cleaved and measured at 15 K (20 K) and pressures lower than 4×10$^{-11}$ torr (1×10$^{-10}$ torr) at ALS (BESSY). Energy and angular resolution at both endstations are better than 20 meV and 0.2 °, respectively.

Electronic structure calculations were performed within the framework of density functional theory as implemented in the package Wien2k [37]. The generalized gradient approximation with the PBE parametrization [38] was used. Due to the semimetallicity of ZrP$_2$, calculations were also performed with the mBJ functional [39]. The basis set size was set to R$_{mt}$K$_{max}$=7. For bulk calculations, the irreducible Brillouin zone (BZ) was sampled with 1440 k points. Surface band structures were obtained from slab calculations. Slabs were constructed by stacking 5 unit cells along c separated by 20 Å vacuum. The BZ was sampled with a 16x30x3 k mesh.

ZrP$_2$ crystallizes in a distorted PbCl$_2$ type structure (Fig. 1(f)) belonging to the non-symmorphic space group $Pnma$ (No. 62, $D_{4h}^{16}$) [40]. Half of the P$^+$ atoms form chains with short P-P bonds (2.34 Å) along the b axis in-
Fig. 2(b), the MR, which is defined as MR = ρ(B)/ρ(0) – 1, remains unsaturated in fields up to 9 T and reaches 40,000% at 2 K and 9 T. The field dependence of the MR is close to parabolic and can be fitted to a power law MR = a + b · B^n with c = 1.92.

To investigate the origin of the large and unsaturated MR in detail, we performed Hall measurements where the resistivity ρxy(B) is perpendicular to both the field and electric current. The ρxy(B) curves (Fig. 2(c)) feature a distinct non-linearity that can be fitted with a semiclassical two-band model [34]. We note that the noise level of these curves is inherent to ZrP_2 due to the narrow width of the crystals. By simultaneously fitting MR and Hall resistivity to the two-band model, we obtained carrier densities n_e,h and mobilities μ_e,h as shown in Fig. 2(d). At room temperature, electrons are the dominant charge carriers. Upon cooling, the ratio n_e/n_h decreases and the charge carriers become almost completely compensated below 50 K, with n_e/n_h = 0.999(2) at 2 K. The mobilities of electrons and holes also show similar values for all temperatures and reach high values up to 2.3 × 10^5 cm^2/Vs at 2 K, which further confirms the good crystal quality. Together, our magneto-transport measurements strongly suggest that e-h compensation is the origin for the unsaturated XMR in the semimetal ZrP_2.

In support for these findings, we performed DFT calculations and the resulting band structure is presented in Fig. 3(a). ZrP_2 shows semimetallicity with both electron and hole-like bands crossing the Fermi level. The corresponding Fermi surface is formed by two hole-like bands, α and β sheets in Fig. 3(b,c), and one electron-like band γ, see Fig. 3(c). However, the volume of the α hole pocket is very small compared to the other pockets and can be neglected without losing soundness of the model. The description by an effective two-band model remains valid and in accordance with transport experiments. The calculated ratio of the carrier densities n_e/n_h equals 1.02, demonstrating almost perfect e-h compensation in line with the electrical transport experiments.

A close look to the low energy band structure reveals a nodal loop in the k_x = 0 plane, with energy slightly below the Fermi level, as shown in Fig. 3(e). The stability of the nodal loop against opening a gap is guaranteed by the n-glide plane (Fig. 1(f)), i.e., the bands have eigenvalues of opposite sign with respect to the glide reflection symmetry, as indicated in Fig 3(d). Upon inclusion of SOC, the nodal loop opens a small gap, which varies between 7 to 20 meV.

In order to get a conclusive picture on the electronic structure of ZrP_2, we employed ARPES as a tool to directly map the band structure. The experimental bulk Fermi surface shown in Fig. 4(a) was measured with 40 eV photons at BESSY. This photon energy was chosen to correspond to k_z = 0, as determined by photon-energy dependent measurements (see SM [36]). The data confirms the presence of both the β hole pocket and the γ electron pocket, in good agreement with theory and transport experiments. The α hole pocket is too small to be identified, given the resolution of our ARPES data.

We further confirm the agreement between theory and ARPES by investigating the high-symmetry paths Y-Y and M-M in a large binding energy window, as illustrated in Fig. 4(b,c). At the low photon energy used in our experiment, k_z is ill-defined, as a consequence of the short mean free path of the photoemitted electron, and the relatively small size of the Brillouin zone along k_z [41].
We find that the uncertainty of $k_z$ is ca. 0.6 π/c (see SM [36] for details). Therefore, we compare the spectra with the projected bulk band structure within the $k_z \in [0, 0.6\pi/c]$ range, and find good agreement in the entire binding energy range. We note that the band crossing point of the nodal loop along $\bar{Y}-\Gamma-Y$ could not be identified owing to two possibly concomitant reasons: i) at any measured photon energy only one of the two crossing bands is seen, due to unfavorable photoemission cross section [42]; ii) broadening from surface disorder and $k_z$ integration smears out the band crossing.

In addition to the bulk band structure, we have studied the surface states of ZrP$_2$. Generally speaking, the appearance of surface states in ARPES depends on experimental conditions such as the quality and topography of the cleaved surface. This is of particular importance for 3D materials like ZrP$_2$, where cleaving may reveal different surface terminations [36]. Here, a small beam spot size can help to probe a single termination in the ARPES experiment. For this reason, we conducted additional ARPES studies using microARPES, the results of which are shown in Fig. 4(d-f). The spectra are dominated by surface states, in contrast to the data shown in Fig. 4(a-c). The projected bulk Fermi surface is enclosed by intense surface states, which disperse over more than 1 eV. Along $\bar{M}-X-\bar{M}$, the surface states are well separated from the projected bulk band structure, whereas they partly hybridize with the bulk along $\bar{Y}-\Gamma-Y$. Altogether, we find excellent agreement between the measured spectra and the slab calculations considering a surface termination that exposes the phosphorus chains without breaking them [36].

The presence of both covalent and ionic bonding features in ZrP$_2$, namely the phosphorus chains along the $b$-axis, indicates a significant degree of charge transfer from zirconium to phosphorus. However, in contrast to the insulating behaviour favored by complete charge transfer, our transport and spectroscopic measurements clearly evidence a charge compensated semimetallic ground state in ZrP$_2$. The e-h compensation at low temperatures is further confirmed by band structure calculations and accounts for the unsaturated XMR [34]. In this regard, ZrP$_2$ resembles the behavior of other early TMDPs such as NbAs$_2$ [2, 5] and WP$_2$ [1, 43, 44]. With the finding of XMR in ZrP$_2$, we are able to establish XMR as a general feature in early TMDPs. The underlying reason for this ubiquity is the combination of non-symmorphic symmetry and incomplete charge transfer.

Strictly speaking, semimetallicity alone is not sufficient to explain the unsaturated XMR in all of the reported materials. Within the semi-classical two-band model, unsaturated MR is only possible if the e-h densities are exactly compensated [34]. In the more realistic cases, XMR is associated with the combination of moderate to perfect e-h compensation and sufficiently high carrier mobility. Such conditions are commonly fulfilled in topological semimetals, where the band crossings close to the Fermi energy give rise to very high carrier mobilities (Fig. 1(e)). It has also been shown in several cases that an imbalanced e-h compensation can be offset by the very high carrier mobility, such that XMR is still observed [45–47]. Many of the early TMDPs were predicted and, in some cases, verified to host topologically non-trivial phases [1, 25, 27, 43, 48]. However, the coexistence of e-h compensation and non-trivial topology naturally complicates the disentanglement of their influence on transport, which has caused difficulties interpreting the origin of the XMR [29]. Based on our DFT calculations and ARPES measurements, we argue that ZrP$_2$ is a clean case where the unsaturated XMR can be fully ac-

![Figure 3](https://example.com/figure3.png)

**FIG. 3.** Electronic structure of ZrP$_2$ from DFT calculations without SOC. (a) Band structure with the three bands crossing $E_F$ colored. (b,c) 3D Fermi surface of ZrP$_2$ exhibiting two hole pockets ($\alpha$ and $\beta$) and an electron pocket ($\gamma$). Color coding according to panel a. (d) Close-up of the low-energy band structure in the $k_z = 0$ plane. Eigenvalues $\eta_{\pi}$ with respect to the $n$-glide plane are indicated (closed line $\eta_+$, dashed line $\eta_-$). (e) 3D visualization $E(k_x, k_y)$ of the $\beta$ and $\gamma$ bands forming the nodal loop (black line) in the $k_z = 0$ plane. Only one quadrant of the $k_x = 0$ plane is shown.
FIG. 4. Bulk and surface band structure of ZrP$_2$ measured by ARPES (both hν = 40 eV, linear horizontal polarization) and comparison with DFT calculations. (a) Bulk Fermi surface from ARPES (left) and calculations (right) both at $k_z = 0$. (b,c) Cuts along $\bar{Y}$-$\bar{\Gamma}$-$\bar{Y}$ and $\bar{M}$-$\bar{X}$-$\bar{M}$ showing bulk bands, respectively. Calculations show the projected band structures for $k_z \in [0, 0.6\pi/c]$ where bands with $k_z = 0$ are highlighted in black. (d-f) Data acquired at ALS, where the small spot size allowed us to focus on an area with a single termination, emphasizing the surface band structures [36]. Note that the calculated surface band structure was shifted by 50 meV with respect to the theoretical Fermi level to match the experimental dispersion. Experimental Fermi surfaces were integrated within ±10 meV of the Fermi level.

counted for by trivial e-h compensation. Contributions from the non-trivial nodal loop can be excluded as it lies ca. 70-230 meV below the Fermi level. Additionally, open-orbit Fermi surface topology as in MoAs$_2$ [3, 49] can be ruled out as the origin. A similar situation was found for the type-II Weyl semimetal WP$_2$ for which the XMR was attributed to e-h compensation despite the existence of Weyl nodes [43].

The direct observation of the nodal loop in the $k_x = 0$ plane by ARPES was prevented by experimental limitations. Nevertheless, the excellent agreement between our calculations and the ARPES spectra provides a strong support for its presence in the low energy band structure of ZrP$_2$. Inclusion of soft X-ray ARPES in future investigations might be a powerful tool to reduce the $k_z$ broadening and resolve the nodal loop along $k_z$.

One might wonder about the topological nature of the surface states seen by ARPES and DFT. Nodal line semimetals are expected to host the so called drumhead topological surface states [15]. However, the presence of a drumhead surface state is only guaranteed on the (100) surface of ZrP$_2$, whereas ZrP$_2$ naturally cleaves on the (001) surface. Together with the strongly termination dependent connectivity of the (001) surface states found in our calculations, we conclude that the observed surface states are trivial in nature. This contrasts a recent report on HfP$_2$ [50], a heavier homologue of ZrP$_2$, where similar (001) surface states were interpreted as topological. Minor differences in the bulk band structures of ZrP$_2$ and HfP$_2$ may account for this contrast.

The structural similarity between ZrP$_2$ and HfP$_2$ can be further exploited. ZrP$_2$ has three heavier homologues: ZrAs$_2$, HfP$_2$ and HfAs$_2$ belonging to the same structure type [33, 52]. The band structures are therefore very similar to ZrP$_2$. In particular, all these materials feature a nodal loop in the $k_x = 0$ plane (see Fig. 5). The
eral consequence of non-symmorphic symmetry and in-
non-trivial topology can be excluded as the origin of the
by ARPES experiments. However, contributions from
compensation. Our band structure calculations, show-
40,000 % at 2 K and 9 T is explained by trivial e-h
consistent picture of the electronic structure and the result-
experimental and theoretical methods, we derived a con-
Hence, we cannot directly compare their band structures.

In summary, we demonstrated that ZrP$_2$ is an e-h com-
Compensated nodal loop semimetal. By applying combined
oretical methods, we derived a consistent picture of the elec-
t of ZrP$_2$ and ZrAs$_2$ were used, respectively.

FIG. 5. Gap opening along the nodal loop through increased
Band structures along Y-Γ-Z for (a) ZrP$_2$, (b) ZrAs$_2$,
(c) HfP$_2$, and (d) HfAs$_2$. Black lines: without SOC, red lines: 
SOC. Experimentally determined crystal structures were 
used for calculations on ZrP$_2$ [40] and ZrAs$_2$ [51]. For HfP$_2$
and HfAs$_2$, the crystal structures of ZrP$_2$ and ZrAs$_2$ were 
used, respectively.

strength of SOC, however, increases significantly between
ZrP$_2$ (lightest) and HfAs$_2$ (heaviest). Accordingly, the
gap opened along the nodal loop by SOC increases from
20 meV in ZrP$_2$ to 120 meV in HfAs$_2$. The ZrP$_2$ family of 
materials thus provides a good platform to study the evolu-
tion of nodal loops with increasing SOC, an aspect of 
nodal loops that has received little attention so far. Fur-
thermore, substitution of the pnictide with Ge, Si and Se
has been demonstrated [51, 53, 54], which opens the pos-
sibility of shifting the chemical potential by doping and 
access the topological crossings. We note that the cor-
responding diantimonides ZrSb$_2$ and HfSb$_2$ exist as well 
but have been shown to exhibit rather metallic behavior [55], 
presumably due to a lesser degree of charge transfer 
from zirconium/hafnium to antimony. In addition, the 
diantimonides crystallize in a different structure and 
space group than the diphosphides and diarsenides [56]. 
Hence, we cannot directly compare their band structures.

In summary, we demonstrated that ZrP$_2$ is an e-h com-
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