Weyl Nodes Close to the Fermi Energy in NbAs

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The noncentrosymmetric transition-metal monopnictides NbP, TaP, NbAs, and TaAs are a family of Weyl semimetals in which pairs of protected linear crossings of spin-resolved bands occur. These so-called Weyl nodes are characterized by integer topological charges of opposite sign associated with singular points of Berry curvature in momentum space. In such a system, anomalous magnetoelectric responses are predicted, which should only occur if the crossing points are close to the Fermi level and enclosed by Fermi surface pockets penetrated by an integer flux of Berry curvature, dubbed Weyl pockets. TaAs is shown to possess Weyl pockets, whereas TaP and NbP have trivial pockets enclosing zero net flux of Berry curvature. Herein, via measurements of the magnetic torque, resistivity, and magnetization, a comprehensive quantum-oscillation study of NbAs is presented, the last member of this family where the precise shape and nature of the Fermi surface pockets is still unknown. Seven distinct frequency branches, three of which have not been observed before, are detected. A comparison with density functional theory calculations suggests that the two largest pockets are topologically trivial, whereas the low frequencies might stem from tiny Weyl pockets. The enclosed Weyl nodes are within a few meV of the Fermi energy.

1. Introduction

In the past years extensive studies have been conducted to investigate and unveil the chiral massless Weyl fermions in the transition-metal monopnictides MX (M = Ta, Nb) (X = P, As) and other proposed Weyl-semimetal (WS) candidates.\cite{1,2} In the isostuctural MX compounds, four nodal rings related by C\textsubscript{4} symmetry are predicted in the first Brillouin zone (BZ) (blue rings in Figure 1). Upon inclusion of spin-orbit coupling (SOC), the nodal rings gap out and only three chiral pairs of Weyl points off the mirror planes remain gapless (red and green points in Figure 1). Early observations of the linear band crossings in the bulk and topological Fermi-arc surface states by angle-resolved photoemission spectroscopy were able to confirm the existence of Weyl fermions in all four materials of this family,\cite{3-6} setting the stage for investigations of their relevance for the materials’ electronic properties. Magnetotransport experiments tried to uncover the Adler–Bell–Jackiw anomaly, that is, a negative longitudinal magnetoresistance when the electric and magnetic field are applied in parallel.\cite{7,8} However, initial findings of negative magnetoresistance\cite{6,9-12} later turned out to be caused by a phenomenon known as current jetting, which is observed in materials with high charge carrier mobility.\cite{13,14} The intrinsic longitudinal magnetoresistance is found to be dominated by classical orbital effects and weak antilocalization,\cite{15} and the absence of the Adler–Bell–Jackiw magnetotransport might be explained by the distance of the Weyl nodes to the Fermi energy.\cite{16}

In all members of this family, small Fermi surface pockets evolve along the nodal ring and quantum-oscillation experiments are able to determine the precise shape and nature of the pockets. Depending on the distance of the Weyl nodes to the Fermi energy in the given electronic structure, either pockets enclosing zero total Berry flux or integer nonzero Berry flux occur. The latter situation occurs when separate Fermi surface pockets enclose each Weyl node of a pair, in which case we name them Weyl pockets. Combined quantum-oscillation and density functional theory studies were able to indirectly prove the existence of Weyl pockets in TaAs,\cite{17} whereas their existence was dismissed in TaP\cite{14} and NbP.\cite{18} NbAs, however, is the last compound in this series where the Fermi surface is not completely established and the existence of Weyl pockets is under debate.
Here, we present an experimental study of quantum oscillations in NbAs. Via magnetoresistance measurements, four quantum-oscillation frequency branches have been detected and assigned to C\textsubscript{4}v-related pairs of either a topologically trivial electron and a nontrivial hole pocket\cite{[19]} or to trivial nested electron and hole pockets\cite{[20]}. These two types of larger pockets were confirmed by magnetic torque measurements and a kink of the magnetization at the quantum limit was assigned to the zero-energy Landau-level characteristic for topological materials\cite{[21]}. Via magnetoresistance measurements, four quantum-oscillation frequency branches have been detected and assigned to C\textsubscript{4}v-related pairs of either a topologically trivial electron and a nontrivial hole pocket\cite{[19]} or to trivial nested electron and hole pockets\cite{[20]}. These two types of larger pockets were confirmed by magnetic torque measurements and a kink of the magnetization at the quantum limit was assigned to the zero-energy Landau-level characteristic for topological materials\cite{[21]}. Here, we present an experimental study of quantum oscillations in NbAs. Via magnetoresistance as well as magnetization and magnetic torque experiments in combination with density functional theory (DFT) calculations, we are able to draw a more detailed picture of its Fermi surface. The main findings are that it consists of at least one further type of small pocket, additionally to the two known larger ones, with frequencies down to $F \approx 0.7$ T. The two large pockets are crescent-shaped topologically trivial electron and hole pockets, whereas the small pocket represents a candidate for Weyl pockets with nodal points that are extremely close to the Fermi level.

2. Experimental and Computational Methods

Crystals of NbAs were grown by chemical vapor transport (CVT) using iodine as transport agent. The polycrystalline material was synthesized in a first step by a direct reaction of microcrystalline powders of the elements niobium (Alfa Aesar 99.99%) and arsenic (Alfa Aesar 99.9999%). Starting from this microcrystalline powder, NbAs crystallized in a temperature gradient from $940^\circ$C (source) to $1060^\circ$C (sink) and a transport-agent concentration of 13.5 mg cm\textsuperscript{-3} iodine (Alfa Aesar 99.998%). Crystals obtained by CVT were characterized by electron-probe microanalysis and using X-ray diffraction technique. Laue spectroscopy was used to confirm the single-crystalline structure and orientation.

Magnetization measurements were conducted on a Quantum Design SQUID vibrating sample magnetometer between $T = 2$ K and $20$ K in magnetic fields up to $B = 7$ T. For each angle, the sample was glued in the required orientation with an angular accuracy of $\pm 5^\circ$.

Transport measurements were carried out in an Oxford Instruments dilution refrigerator at $T = 0.035$ K in fields up to 15 T using a rotation stage. Data acquisition via National Instruments PXI cards and digital lock-in procedures were used in this setup. The magnetic torque $\tau = m \times B$ was measured using CuBe foil cantilevers with a capacitive readout similar to the design in previous studies\cite{[22,23]} in an Oxford Instruments $^3$He insert at $T = 0.25$ K in magnetic fields up to 15 T, and using TqMag piezoelectric torque cantilevers\cite{[24]} in a PPMS down to 2 K and in magnetic fields up to 14 T. The magnetic field was rotated in the (001), (100), and (110) planes. The field angles are defined with respect to the high-symmetry axis, as shown in Figure 7c.

The electronic structure of NbAs was calculated using the Vienna ab initio simulation package\cite{[25]} NbAs crystallizes in the space group \textit{I}4\textit{md} (#109). Experimental lattice parameters were used where $a = b = 3.4517$ Å and $c = 11.680$ Å.\cite{[26]} The 4a Wyckoff positions of both Nb and As were allowed to relax in the calculations leading to (0,0,0) for Nb and (0,0,0.417) for As, respectively. The exchange correlation energy was considered on the level of the generalized gradient approximation (GGA), following the Perdew–Burke–Ernzerhof parametrization scheme.\cite{[27]} The energy cutoff of the plane waves was set to 450 eV. The resulting band structure is in general consistent with the results published earlier.\cite{[28]} For accurate Fermi surfaces, the bands were interpolated using maximally localized Wannier functions\cite{[29]} in dense $k$-grids of 300 $\times$ 300 $\times$ 300 points in the full BZ. Quantum oscillations appear, when electron energy levels are quantized in the presence of a magnetic field. With changing magnetic field, they pass through the Fermi energy and cause oscillations in the density of states, which themselves lead to oscillations of resistivity or magnetization. The oscillations are analyzed using the standard Lifshitz–Kosevitch theory.\cite{[30,31]} The quantum-oscillation frequencies $F$ correspond to extremal Fermi-surface cross sections $A$ perpendicular to the applied magnetic field direction via $F = (\hbar/2\pi e)A$. Thus, by rotating the magnetic field and comparing the angular dependence of the oscillation frequencies to those from band structure calculations, the Fermi-surface topography can be obtained.\cite{[32,33]} The effective mass averaged over such extremal orbits is given by the temperature dependence of the oscillation amplitude $A \propto \chi/\sinh(\chi)$, where $\chi = 14.69 m^* T / B$\cite{[31]} Here, $B$ is either a fixed field or the average reciprocal field of the analyzed data window. In the second case, the field range was chosen to be as small as possible and the amplitude change with field was taken into account.\cite{[34]} For the quantum-oscillation analysis, a background was subtracted from the measured data and a Fast Fourier transform (FFT) was conducted on the residual oscillatory part.

3. Results

3.1. Theoretical Prediction

In our calculations, the W1 Weyl points in the $k_z = 0$-plane are located at $(\pm0.0026, 0.4817, 0)$ in units of the conventional
Figure 2. Band structure of NbAs near the Weyl nodes. The band structure of NbAs in the GGA with SOC along the lines connecting pairs of Weyl nodes a) for W1 Weyl nodes located at (±0.0026, 0.4817, 0) in units of the conventional reciprocal lattice vectors and b) for W2 Weyl nodes located at (±0.0198, 0.2811, 0.5847) (and symmetry-related) positions. The dashed lines indicate the Fermi energy (black) and the energy level of the Weyl nodes (blue), respectively.

3.2. Magnetization Along High-Symmetry Directions

Let us start by looking at the magnetization at $T = 2\,\text{K}$ along the main crystallographic high-symmetry directions in Figure 3a. In all directions, strong quantum oscillations are visible on top of a background signal consisting of two main contributions. The strong diamagnetic contribution $M_{\text{dia}}$, as expected for a semimetal, and a paramagnetic contribution $M_{\text{para}}$ from a small amount of magnetic impurities are discussed. We model those contributions using the following fit for the data for $B  \parallel [001]$

$$M = M_{\text{para}} + M_{\text{dia}}$$

(1)

$$M_{\text{para}} = N g J \mu_B B f (x), \quad x = g J \mu_B B / k_B T$$

(2)

$$B f (x) = \frac{2 J + 1}{2 J} \coth \left( \frac{(2 J + 1) x}{2 J} \right) - \frac{1}{2 J} \coth \left( \frac{x}{2 J} \right)$$

(3)

$$M_{\text{dia}} = \chi B$$

(4)

This yields a total magnetic moment of $J = 3.5$, an impurity concentration $N = 80\,\text{ppm}$, and the diamagnetic susceptibility $\chi = -2.1\,\text{emu/mol}$.

The strong quantum oscillations of high frequency are analyzed by subtracting the background signal and taking the FFT of the oscillatory part in inverse fields (see Figure 3b). These frequency branches at $F = 15.8\,\text{T}$ and $F = 21.8\,\text{T}$ for $B  \parallel [001]$ have been observed before and have been associated with trivial electron pockets and nontrivial hole pockets based on the effective mass and a phase shift\(^\text{[29]}\) or with trivial electron and hole pockets.\(^\text{[29]}\) As we will show below, we come to the conclusion that both stem from trivial electron and hole pockets, as in the study by Komodo et al.\(^\text{[29]}\)

In addition, our measurements reveal a smaller frequency in all directions that appears clearly at fields of $F \approx 1\,\text{T}$. A zoom on this field range is shown in Figure 3c, where we normalized the inverse field range by the oscillation frequencies.

A small quantum-oscillation frequency indicates a very small Fermi surface pocket, which will reach its quantum limit at a
magnetic field of the order of the quantum-oscillation frequency. Above this field, the Fermi surface pocket is depleted and the charge carriers redistribute to other pockets in a multiband system. In accordance with this, the oscillation with the small frequency stops after a final kink in the data.

3.3. Temperature Dependence and Effective Masses

In a second step, we analyze the temperature dependence and determine the effective masses in Figure 4. The oscillatory part of the magnetization as a function of inverse field for different temperatures is shown for $B || [001]$ and the magnetization at different temperatures is shown as a function of $B$ for $B || [100]$ and $[110]$ in Figure 4a. The FFTs of the oscillations are depicted in Figure 4b. The resulting temperature dependence of the amplitudes and the Lifshitz–Kosevich fits with corresponding effective masses are given in Figure 4c. The uncertainty of the effective masses is of the order of 10%. The effective mass values are in agreement with those obtained before\cite{19} within the error bars. For the low frequencies, we were not able to determine the effective masses, because the signal is very small and the background changes strongly with temperature.

3.4. Angular Dependence

Figure 5 shows the field dependence of resistivity and torque in NbAs taken at various angles for a rotation of the magnetic field, as indicated. The resistivity in Figure 5a shows metallic behavior as reported before.\cite{35} The magnetoresistance in 15T is around 100. This is large compared with normal metals but smaller than what was previously reported on NbAs, pointing to a slightly lower crystal quality.\cite{35} Superimposed on the magnetoresistive background are pronounced quantum oscillations starting at around 0.8T. In the torque data shown in Figure 5c and Figure 6, quantum oscillations are observable down to fields as low as 0.2T. Torque curves between 70 and 80° in Figure 5c exhibit torque interaction.\cite{31} Care has been taken that this does not influence the frequency determination. The FFT spectra of the resistivity and torque measurements at the accordant angles are shown in Figure 5b,d. The frequencies found here for $B || [001]$ agree with those observed in the magnetization ($F = 15.5T$ and $F = 21.5T$). Higher harmonics are also visible. For example, the third-highest observed peak corresponds to the second harmonic of the 21.5T component for the resistivity and the 15.5T component for the torque, each corresponding to the oscillation with largest amplitude. With increasing angle, we observe a shift of the two main FFT peaks to higher frequencies and a characteristic splitting within the (001) tilting plane (downward triangles in Figure 5d and upper dashed lines in Figure 7c). This behavior is in agreement with previous observations.\cite{20} The splitting reflects extremal orbits from two equivalent pockets in nodal rings that are turned by an angle of 90° with respect to each other in the BZ.

Figure 6 shows a zoom-in at low fields of the torque data from Figure 5c. The small frequency observed in magnetization also appears (oscillations below roughly 0.8T). In addition, a second, slightly higher, frequency clearly emerges for magnetic fields close to the [100] direction as visible in the raw data (e.g., in the 90° data in Figure 5c, the oscillation with maxima at roughly 4.5T, 6.5T, and 9.5T or in the 80° data in Figure 6 for $B > 0.6T$). When this frequency is larger than 3T, this oscillation and a third one also appear as peaks in the FFT (upward triangles in Figure 5d). The small oscillation frequencies were extracted from the raw data by taking the position of maxima and minima, as well as the FFT, where possible. Note that we do not observe the small frequency or a signature of its quantum limit in the resistivity data or the FFTs in Figure 5a,b.

The resulting angle-dependent frequencies are shown in Figure 7c. In addition to the dots showing frequencies obtained

![Figure 4](image1.png)

Figure 4. Temperature dependence of quantum oscillations. a) Magnetization for different temperatures for the field directions as indicated. b) FFT of the oscillatory part of the data in (a). c) Temperature dependence of the oscillation amplitude obtained from the FFTs (dots) and the Lifshitz–Kosevich fit (dashed lines) with the resulting effective masses as indicated.
from torque measurements and triangles from resistivity, stars denote frequencies determined from magnetization.

4. Discussion

Before comparing the experimental angle dependence with the DFT predictions, we start by discussing the limitations of the DFT calculations. Comparing the band structure obtained with different functionals allows us to estimate the error bar of the DFT: We find that the bands near the Fermi energy can be shifted in energy by a few meV with respect to each other for different functionals. Because some of the Fermi surface pockets are so small, this can result not only in different Fermi surface shapes or a relative change in size but also in Lifshitz transitions, that is, the appearance or disappearance of entire small pockets. Fermi surfaces with cross sections of the order of 1 T in certain field directions are therefore at the limit of resolution.

In principle, all members of the TaAs family should be compensated systems and have an equal number of electrons and holes. Previous work claimed the materials to have small intrinsic doping (probably from impurities), as the best fit of the angular-dependent quantum oscillations and the Hall effect corresponded consistently to a shift of the Fermi energy to the electron-doped side for both TaP and TaAs. However, the DFT was unable to give the experimental angular dependence for some of the pockets in those works and therefore is of limited value for giving the correct electron count. A major argument, that a better compensation might actually be present in the real materials, is the insensitivity of the quantum-oscillation frequencies to different growth conditions. Many independent experimental quantum-oscillation studies on TaP, TaAs, and NbAs show very similar quantum-oscillation frequencies, although differences seem to be higher for Nb compounds compared with Ta compounds and quite strong differences were found for NbP. Having the above points in mind, we find a relatively good agreement of the calculated and the experimental angular dependence for GGA without shifting the Fermi energy away from the compensated level. The theoretical frequency branches are plotted together with the experimental data in Figure 7c. Note that each type of pocket is represented by one color and can have several frequency branches depending...
The agreement of the calculated H1 and E1 pockets with the experiment is rather good (Figure 7c). The experimental oscillations with small frequency of \( \approx 1 \) T near \( B||[001] \) up to \( \approx 15 \) T for \( B||[100] \) are extracted from the raw data by taking directly the positions of the minima and maxima (shown as full dots) and separately by identifying peaks in the FFT (given by the upward triangles in Figure 5d and shown as empty dots in Figure 7c). Their angular dependence seems to follow some branches of the W2 pocket (or the H1’ pocket that has a very similar shape). In particular, one frequency branch stays almost constant with angle, and one branch increases when going from \( B||[001] \) to \( B||[100] \). It is important to keep in mind that the experiment cannot distinguish oscillations with very close frequencies and would show a single oscillation with average frequency and modulated amplitude. Such an interference from different branches might explain the small difference in angular dependence from magnetization and magnetic torque for angles >45°. However, several small pockets from the calculation give branches that are qualitatively similar to the observed ones, leaving room for interpretation. The observation of two branches above 3 T near \( B||[100] \) actually suggests contributions from two types of pockets, but this relies only on three data points. Nevertheless, the prediction for W2 remains the closest to the experimental points of all pockets with low oscillation frequencies. Moreover, Fermi-volume changes for the W2 pocket needed to get a better quantitative agreement with the experiment are within the uncertainty of the calculations. The overall agreement of the calculation with the experiment suggests that NbAs has separate Fermi surface pockets around the W2 Weyl nodes with nontrivial topology and a Fermi energy that is only \( \approx 4 \) meV above the W2 Weyl nodes. This distance is the smallest one reported for this class of Weyl semimetals and less than half the energy distance of the Weyl nodes to the Fermi energy in TaAs and TaP. Although it was predicted for TaAs that the chiral contribution to the conductivity should dominate the transport when the Fermi energy is less than 5 meV away from the Weyl nodes,\[16\] this does not seem to be a guarantee for the observation of a chiral anomaly in NbAs, as a clear negative longitudinal magnetoresistance from the chiral anomaly could not be identified.\[15\]

It would be interesting to investigate further the quantum limit of the smallest Weyl pocket compared with the other pockets in light of the differences expected for the quantum limit magnetization of trivial and Weyl electrons.\[21,38\] However, discussing the sign of a signal in torque requires taking the different anisotropies of the Fermi surface pockets into account.

5. Conclusion

We investigated quantum oscillations appearing in the magnetization, magnetic torque, and resistivity in NbAs. Summarizing the earlier findings, the Fermi surface of NbAs consists of at least three pockets, one of which was not experimentally observed before. Comparing the angular dependence of the quantum-oscillation frequencies with the calculated electronic structure reveals a reasonably good agreement without shifting the Fermi energy. The smallest pocket showing quantum oscillations of the order of 1 T most probably stems from Weyl pockets around the

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**Figure 7.** Fermi surface and angular dependence of the quantum-oscillation frequencies. a) Bird-eye’s view on the Fermi surface pockets aligned along one nodal ring, where the E1 pocket is oriented toward the \( \Gamma \) point. b) Nested Fermi surface pockets in side view; \( H_2 \) is located inside \( H_1 \) and \( E_2 \) inside \( E_1 \). c) Angular dependence of quantum-oscillation frequencies from torque (dots, see text), resistivity (triangles), and magnetization (stars) and from the DFT band structure (lines). Different full lines correspond to the Fermi surface pockets as indicated in (a) and (b), where reddish colors represent hole-like surfaces \( H_1 \), \( H_2 \), and \( H_1' \) and blueish represents electron-like Fermi pockets \( E_1 \), \( E_2 \), \( E_1' \) and \( W_2 \). All frequency branches of one type of pocket are represented with one color. The black dashed lines are guides to the eye.
W2 Weyl nodes which are only 4 meV below the Fermi energy. Hence, NbAs likely hosts topological Weyl pockets.

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Conflict of Interest
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[1] B. Yan, C. Felser, Annu. Rev. Condens. Matter Phys. 2017, 8, 337.
[2] N. P. Armitage, E. J. Mele, A. Vishwanath, Rev. Mod. Phys. 2018, 90, 015001.
[3] X. Wan, A. M. Turner, A. Vishwanath, S. Y. Savrasov, Phys. Rev. B 2011, 83, 205101.
[4] B. Lv, H. Weng, B. Fu, X. Wang, H. Miao, J. Ma, P. Richard, X. Huang, L. Zhao, G. Chen, Z. Fang, X. Dai, T. Qian, H. Ding, Phys. Rev. X 2015, 5, 031013.
[5] S.-Y. Xu, I. Belopolski, N. Alidoust, M. Neupane, G. Bian, C. Zhang, R. Sankar, G. Chang, Z. Yuan, C.-C. Lee, S.-M. Huang, H. Zheng, J. Ma, D. S. Sanchez, B. Wang, A. Bansil, F. Chou, P. P. Shibayev, H. Lin, S. Jia, M. Z. Hasan, Science 2015, 349, 613.
[6] L. X. Yang, Z. K. Liu, Y. Sun, H. Peng, H. F. Yang, T. Zhang, B. Zhou, Y. Zhang, Y. F. Guo, M. Rahn, D. Prabhakaran, Z. Hussain, S.-K. Mo, C. Felser, B. Yan, Y. L. Chen, Nat. Phys. 2015, 11, 728.
[7] S. L. Adler, Phys. Rev. 1969, 177, 2426.
[8] J. S. Bell, R. Jackiw, Il Nuovo Cimento A 1969, 60, 47.
[9] S.-M. Huang, S.-Y. Xu, I. Belopolski, C.-C. Lee, G. Chang, B. Wang, N. Alidoust, G. Bian, M. Neupane, C. Zhang, S. Jia, A. Bansil, H. Lin, M. Z. Hasan, Nat. Commun. 2015, 6, 7373.
[10] C.-L. Zhang, S.-Y. Xu, I. Belopolski, Z. Yuan, Z. Lin, B. Tong, G. Bian, N. Alidoust, C.-C. Lee, S.-M. Huang, T.-R. Chang, G. Chang, C.-H. Hsu, H.-T. Jeng, M. Neupane, D. S. Sanchez, H. Zheng, J. Wang, H. Lin, C. Zhang, H.-Z. Lu, S.-Q. Shen, T. Us, Neupert, M. Zahid Hasan, S. Jia, Nat. Commun. 2016, 7, 10735.