Landau spectrum and twin boundaries of bismuth in the extreme quantum limit

Zengwei Zhu, Benoît Fauquè, Liam Malone, Arlei Borba Antunes, Yuki Fuseya, and Kamran Behnia

The Landau spectrum of bismuth is complex and includes many angle-dependent lines in the extreme quantum limit. The adequacy of single-particle theory to describe this spectrum in detail has been an open issue. Here, we present a study of angle-resolved Nernst effect in bismuth, which maps the angle-resolved Landau spectrum for the entire solid angle up to 28°. The experimental map is in good agreement with the results of a theoretical model with parabolic dispersion for holes and an extended Dirac Hamiltonian for electrons. The angular dependence of additional lines in the Landau spectrum allows us to uncover the mystery of their origin. They correspond to the lines expected for the hole Landau levels in a secondary crystal tilted by 108°, the angle between twinned crystals in bismuth. According to our results, the electron reservoirs of the two identical tilted crystals have different chemical potentials, and carriers across the twin boundary have different concentrations. An exceptional feature of this junction is that it separates two electronic subsystems in bismuth. According to our results, the electron reservoirs of the two identical tilted crystals have different chemical potentials, and carriers across the twin boundary have different concentrations.

Semiclassically, the Landau spectrum of bismuth is a fascinating solid. Its average bulk diamagnetism is larger than in any nonsuperconducting solid, its magnetoresponse is huge, and it dwarfs any other solid with its Nernst coefficient. During the last century, the electronic properties of bismuth were subject to numerous studies (see refs. 1–3 for reviews). In particular, studies of de Haas–van Alphen effect and Shubnikov–de Haas effects led to a precise determination of the components of the Fermi surface (4, 5), which consists of a hole ellipsoid at T point and three identical electron ellipsoids at L point (6).

Recently, there has been a renewal of interest in the electronic spectrum of bismuth at very high magnetic fields in the vicinity of the quantum limit (7–11). The quantum limit is attained when the magnetic field is strong enough to confine electrons to their lowest Landau levels (LLLs). With a magnetic field of affordable magnitude, this limit can only be attained in low-density metals like bismuth or graphite. Emergence of collective effects in a three-dimensional electron gas in such a context has been a subject of theoretical speculation (12, 13).

The first measurements of the Nernst response in bismuth up to a magnetic field of 12 T led to the observation of giant quantum oscillations (14). The signal was found to sharply peak at each intersection of a Landau level and the chemical potential. Similar oscillations were also found in graphite (15), another bulk semimetal, leading to several theoretical studies offering explanations for the occurrence of these giant quantum oscillations (16–18).

The extension of the Nernst data up to 30 T led to the observation of additional Nernst peaks at magnetic fields exceeding the quantum limit (7). These peaks were unexpected and, given the known structure of the Fermi surface in bismuth, could not be attributed to any Landau level. Moreover, angle-resolved torque magnetometry measurements found a complex phase diagram for a magnetic field slightly tilted off the trigonal axis (8). These experimental findings raised the issue of collective effects in bismuth at high magnetic fields. In this context, the high-field phase diagram of bismuth became subject to a theoretical reinvestigation (19, 20). At high magnetic fields, the chemical potential continuously shifts to preserve charge neutrality. Therefore, quantum oscillations are no longer a periodical function of B−1. Further complexity arises due to an angle-dependent Zeeman energy and cyclotron mass for both electrons and holes (4). Very recently, a fair agreement was found between the results of a theoretical model treating the electrons with an extended Dirac Hamiltonian and the experimentally detected Landau spectrum up to 12 T (21). The results narrowed down the possible choice of theoretical parameters to describe the system in presence of moderate magnetic fields, but the origin of the additional lines remained an open question.

Several explanations for the origin of additional Nernst peaks have been proposed. It was suggested that they had been generated by misalignment (20). But this was ruled out by measurements of the Nernst effect in presence of a tilted magnetic field (11). It was speculated that surface states could give rise to these additional peaks (22). But both the amplitude and the profile of the Nernst peaks point to a bulk origin (23). Moreover, their complex angle dependence does not follow what is expected for a 2D state. Until now, the origin of these additional lines on top of the complex Landau spectrum has remained a mystery.

Previous angle-resolved Nernst measurements mapped the Landau spectrum in a limited angular window (11). Here, we present map of Landau spectrum extended up to 28° and across the whole solid angle. Comparing the experimental map with the results of the theoretical model for bulk bismuth allows us to find a solution to this mystery. All lines resolved by the experiment match the theoretical expectations. In particular, the additional lines follow an angular variation corresponding to a crystal tilted by 108°, as expected in case of a twinned bismuth crystal. The results suggest that the entire phase diagram of bismuth, at least up to 28 T, can be explained within the single-particle theory. Surprisingly, however, we find that the agreement between theory and experiment can be attained only if one assumes that the chemical potential in the tilted crystal is not set by the primary crystal and the two crystals have distinct chemical potentials and carrier densities. This implies that carriers cannot freely flow across the twinning plane, the interface between the two crystals.

Experimental Procedures

We measured the Nernst effect with a standard one heater–two thermometer setup. The Nernst voltage was measured with two
pairs of electrodes. As the magnetic field rotates, we switched from one pair of electrodes to another in order to measure the component of electric field in the plane perpendicular to the magnetic field. For each rotating plane, the experiment was performed in a dilution refrigerator inserted into a superconducting magnet for fields below 12 T and in a He\(^4\) cryostat inserted in a resistive water-cooled magnet for fields between 12 and 28 T.

Fig. 1 presents the raw Nernst data as a magnetic field is swept in the (trigonal, binary plane). The data for the two other planes are shown in SI Text. Each Nernst peak is associated with the intersection of a Landau level and the chemical potential. As seen in the lower panel of Fig. 1, different sets of data obtained at low and high magnetic field and with different pairs of electrodes match with each other. The peaks associated with the hole pocket can be clearly identified and are represented by red solid circles in Fig. 1. But other peaks remain, whose origin is harder to pin down.

Fig. 1. (Upper) Nernst signal in a tilted magnetic field in the (trigonal, binary) plane for different tilt angles. (Lower) Nernst peaks superposed on a color plot of the same data. The angle \(\theta\) represents the angle between the magnetic field and the trigonal axis. Those Nernst peaks that are clearly associated with holes are represented by solid red circles and others by white triangles. The high- (low-)field data was obtained at 1.5 (0.49) K. Digits represent orbital indexes for hole Landau levels. They become spin-split (\(\pm\)) when \(\theta \neq 90^\circ\).
Model
For electrons at \( L \) points, we employed the extended Dirac Hamiltonian introduced in ref. 21. The parameters used here are also the same as those in ref. 21, where the fitting is carried out below 12 T.

At high field, however, we have to take into account the interband coupling between the LLLs of the conduction and valence bands (24), while it is negligible below 12 T. At zero field, the conduction and valence bands will not be coupled because they have opposite parity. On the other hand, at a finite field, the coupling should be proportional to the field. Such an effect of a magnetic field (25), which can couple the two LLLs.

Here, two new parameters are introduced:

\[
E_{\text{inter}}^{\text{new}} = \pm \sqrt{\left( e \left| k_z \right| g \beta B \right)^2 + \left( V \beta_0 B \right)^2},
\]

and \( e(k_z) = \sqrt{\Delta^2 + h^2 k_z^2 \Delta/m_z} \), which are obtained by simplifying the model used in ref. 24. \( \beta_0 = |e|/\hbar m_z c = 0.1158 \text{ meV/T} \)

Here, two new parameters are introduced: \( V \) expresses the magnitude of the interband coupling, and \( V' \) is the correction to the additional g-factor \( g' \), both of which give contributions proportional to \( B \). Both \( V \) and \( V' \) are scalars and dimensionless, whereas the longitudinal mass \( m_z \) and \( g' \) are tensors as is given in ref. 21.

The separation between the two LLLs decreases with increasing magnetic field in the low-field region; the separation takes its minimum value at \( B_{\text{min}} \) and then increases in the high-field region. We set the parameters as \( V = 0.15 \) and \( V' = -0.0625 \). With these parameters, \( B_{\text{min}} \sim 30 \text{ T} \), and the minimum value of the separation is about 1 meV (see SI Text for a discussion of the different parameters used here and in ref. 24).

Results
Crystal Structure and Twins. The key point in elucidating the mystery of additional lines in the Landau spectrum resides in the rather exotic rhombohedral crystal structure of bismuth. The unit cell is obtained by pulling a cube along its body diagonal. This departure from higher symmetry is believed to be triggered by a Peierls transition (26). The distortion can be visualized by considering a symmetry-lowering operation on a tetrahedron. In absence of distortion, each atom would be at a vertex of a tetrahedron. At each of these vertices, the angle between two adjacent edges is 60° (Fig. 2A). The tetrahedron remains invariant by a \( 2\pi/3 \) rotation around any of the four equivalent trigonal axes. The structural distortion corresponds to a displacement of one of the four vertices, which reduces the angle between the three adjacent edges at that particular vertex to less than 60°. In this distorted structure, out of four original trigonal axes, only one survives and the structure keeps its threefold rotational symmetry around this trigonal symmetry.

Now, any of the four vertices of the tetrahedron can be subject to such a distortion (Fig. 2A). Therefore, bismuth crystals can
have up to four domains. When at least two of such domains are simultaneously present in a crystal, the crystal is twinned. The atomic positions near a twin boundary in bismuth, originally documented by Hall (27), is illustrated in Fig. 2B. A typical bismuth single crystal has many of such twin boundaries. Their presence can be used to establish a direction for trigonal and bisectrix axes and thus determine the sign of the tilt angle of the electron ellipsoid (28). Twin boundaries have been directly detected by Scanning Tunneling Microscopy measurements (29). When a sample is twinned, in addition to the principal crystal, there is a secondary

Fig. 3. The Landau spectrum for holes and electrons according to theory (solid lines) and experiment (symbols). The three panels correspond to the three rotating planes. Peaks resolved by experiment and identified as arising from holes (red open circles) or electrons (green open triangles) are displayed.
crystal, which has its trigonal axis tilted by 108° respective to the original crystal. The two crystals share one binary axis (Fig. 2C).

**Landau Spectrum.** Fig. 3 compares the theoretical prediction with experimental results for three planes of rotation. For each plane of rotation, a panel shows both the Nernst peaks resolved by the experiment and the expected theoretical lines for holes and electrons. There is no ambiguity for hole peaks. As for electron peaks, we have selected Nernst peaks displaying an angular dependence close to what is theoretically expected. As seen in Fig. 3, the agreement is excellent for holes and rough for electrons. In the case of binary-bisectrix plane (Fig. 3C), the experimentally resolved hole peaks are sometimes split because of a small residual misalignment. When the field is oriented perpendicular to the trigonal axis, the Zeeman splitting of holes is extremely sensitive to the orientation and suddenly vanishes when the field is perpendicular to the trigonal axis (see Fig. 3A and B).

Given the quality of the agreement between theory and experiment in case of holes, it is natural to wonder about the origin and significance of the discrepancy observed in the case of electrons. The discrepancy is particularly visible at high fields. The theoretical lines for electrons tend to occur in magnetic fields significantly lower than the experimental ones. This is particularly the case for the angular window around the trigonal axis. We failed to find adequate theoretical parameters to close this gap between theory and experiment.

**The Additional Lines.** In Fig. 3, only those peaks that could be attributed either to electron or holes are shown. Fig. 4 displays additional peaks (i.e., those that are clearly not associated with electrons) together with the hole peaks. The experimental peaks are compared with what is theoretically expected for holes of a secondary tilted crystal. This secondary crystal shares one binary axis with the original crystal, but has its trigonal axis tilted 108° off, as depicted in Fig. 2C. As seen in Fig. 4, the agreement is good. A careful examination of Fig. 4C indicates that the additional lines merge with the hole lines when the field is aligned along one of the three binary axes. This is the binary axis common to the two twinned crystals. When the magnetic field is oriented along this binary axis, the spectrum does not show any additional features. In this configuration, the two crystals have the same crystal axis along the magnetic field and share an identical Landau spectrum.

Previous studies of the high-field phase diagram of bismuth focused on the angular window close to the trigonal axis (8, 11). As seen in Fig. 5, in this range, the results obtained here are quite similar to those found in a previous study of angle-resolved...
Nernst effect (11) on another bismuth crystal. In both cases, experiment detects several lines and in particular three unexpected high-field peaks when the field is oriented along the trigonal axis as originally reported back in 2007 (7). The additional peaks are not fractional peaks as initially assumed (7), but can be indexed as $2\gamma\text{i}$, $1\gamma\text{i}$, and $3\gamma\text{i}$ of a secondary tilted crystal as expected in the twinning scenario.

As seen in Figs. 4 and 5, in the case of hole lines, the agreement between theory and experiment is impressive, both for the primary and the tilted crystal. This agreement has been obtained by assuming that the chemical potential continuously shifts with increasing magnetic field to preserve charge neutrality. Now, this field-induced shift in chemical potential strongly depends on the relative orientation of the magnetic field and the crystal axes (21).

One can think of two possibilities in presence of a strong magnetic field: (i) the twinned crystals share a common chemical potential as they do at zero field. (ii) The twinned crystals do not share a common chemical potential and as the magnetic field is applied, a difference between their Fermi energies and their carrier densities gradually builds up.

According to our results, the second scenario clearly prevails. If one assumes that the twinned crystals share a common chemical potential set by the primary crystal, then theory fails to reproduce the experimentally resolved spectrum (see SI Text). On the other hand, the agreement between theory and experiment is satisfactory, if one assumes that each of the two crystals keeps its own chemical potential set by its local environment with respect to the orientation of the magnetic field. As seen in Fig. 5 C and D, this means that when the field is near the trigonal axis, there is a significant discontinuity both in chemical potential and in carrier density across the twin boundary.

Conclusions

In a typical bismuth crystal, twin boundaries abound but minority domains occupy a small fraction of the total volume of the sample. According to our preliminary neutron diffraction measurements on the crystals used in this study, the volume occupied by the major domain is an order of magnitude larger than each of the three minority domains. It is therefore quite a surprise that the contribution of one of these domains is such that the magnitude of the Nernst peaks caused by their Landau levels is comparable to those of the primary crystal. What sets the magnitude of the Nernst quantum oscillations remains an open question. If the field-induced wrapping states [the 3D equivalent of the edge states of the quantum Hall effect (30)], happen to play a role, then a twinned crystal with sufficient depth can generate a signal that weighs much larger than the volume it occupies.

The origin and the fine structure of the barrier between the crystals with different chemical potential emerges as a new subject. Such barriers are common in semiconducting heterostructures. But the one under study has a number of intriguing peculiarities: The two crystals share the same structure and an identical chemical potential in zero magnetic field. Moreover, while the carrier density is different across the junction, the two systems are compensated and charge neutrality is locally preserved. Finally, the discontinuity in the chemical potential is a consequence of Landau quantification in a very anisotropic context. The wrapping states discussed by Koshino et al. (30) have different Landau indexes across the twin boundary. Their length scale is set by the magnetic length. On the other hand, the length scale associated with charge reorganization at the interface is the Fermi wavelength. In our context of investigation, these two length scales are comparable in size.

One conclusion of this study is that the one-particle theory can successfully reproduce the experimentally resolved phase diagram of bismuth in a magnetic field as strong as 28 T. The fate of the three-dimensional electron gas in bismuth and in graphite diverges (31). In graphite, the system undergoes a field-induced thermodynamic phase transition (32). This phase transition is believed to be a nesting-driven density-wave transition (33), which is expected to occur due to the instability of the quasi-one-dimensional conductor emerging beyond the quantum limit. The absence of a phase transition in bismuth raises the following question: What protects bismuth from a similar instability?

ACKNOWLEDGMENTS. We are grateful to J. Alicea, G. Mikitik, A.J. Mills, Y. Sharlai, and V. Oganseyan for fruitful discussions. This work is supported by Agence Nationale de Recherche as a part of QUANTHERM project and by EuroMagNET II under the European Union Contract 228043. Y.F. is supported by Multidisciplinary Research Laboratory System of Osaka University and also by Young Scientists (B) (23740269) from Japan Society for the Promotion of Science and by a Grant-in-Aid for Scientific Research (A) on “Dirc Electrons in Solids” (No. 24244053) of The Ministry of Education, Culture, Sports, Science, and Technology, Japan.

1. Edelman VS (1976) Electrons in bismuth. Adv Phys 25:555–613.
2. Issi JP (1979) Low temperature transport properties of the group V semimetals. Aust J Phys 32:585–628.
3. Dresselhaus MS (1971) Electronic properties of the group V semimetals. J Phys Chem Solids 32:Suppl 1:3–33.
4. Smith GE, Baraff GA, Rosell JM (1964) Effective g factor of electrons and holes in bismuth. Phys Rev 135:A1118–A1124.
5. Bhatta VN (1967) De Haas-van Alphen and galvanometric effects in Bi and Pb alloys. Phys Rev 156:785–797.
6. Liu Y, Allen RE (1995) Electronic structure of the semimetals Bi and Sb. Phys Rev B 52:1566–1577.
7. Behnia K, Balicas L, Kopelevich Y (2007) Signatures of electron fractionalization in ultraquantum bismuth. Science 317:1729–1731.
8. Li U, et al. (2008) Phase transitions of Dirac electrons in bismuth. Science 321:547–550.
9. Faupé B, et al. (2009) Hall plateaux at magic angles in bismuth quantum limit. Phys Rev B 79:245124.
10. Faupé B, Vignolles B, Proust C, Issi JP, Behnia K (2009) Electronic instability in bismuth far beyond the quantum limit. New J Phys 11:13012.
11. Yang H, et al. (2010) Phase diagram of bismuth in the extreme quantum limit. Nat Commun 1:47.
12. Halperin BI (1987) Possible states for a three dimensional electron gas in a magnetic field. J Phys C 20:1913–1915.
13. MacDonald AH, Bryant GW (1987) Strong magnetic-field states of the pure electron plasma. Phys Rev Lett 58:515–518.
14. Behnia K, Meašon MA, Kopelevich Y (2007) Oscillating Nernst-Ettingshausen effect in bismuth across the quantum limit. Phys Rev Lett 98:166602.
15. Zhu Z, Yang H, Faupé B, Kopelevich Y, Behnia K (2010) Nernst effect and dimensionality in the quantum limit. Nat Phys 6:26–29.
16. Bergmann D, Oganseyan V (2010) Theory of dissipationless Nernst effects. Phys Rev Lett 104:066601.
17. Sharlai YV, Mikitik GP (2011) Oscillations of the Nernst coefficient in bismuth. Phys Rev B 83:085103.