It has been known for a long time that doping elemental bismuth with antimony decreases the carrier density and eventually leads to a semimetal to semiconductor transition. Bi$_x$Sb$_{1-x}$ alloys are remarkable n-type thermoelectric material operating near 100 K. The evolution of their Fermi surface, notably under pressure, as well as their transport coefficients above 4.2 K have been intensively studied. They are attracting new attention in the context of research on "topological insulator", which was first proposed and then reported to be detected in this family on the semiconductor side (i.e. for $x > 0.08$). The metallic side of this semimetallic-semiconductor phase boundary permits to explore the instabilities of an ambipolar three-dimensional electron gas as the carrier density is continuously pushed to zero. Moreover, the small size of the Fermi surface pulls down the quantum limit. This limit is attained when all carriers are at the lowest Landau level. The barely-screened Coulomb repulsion of the semimetal at zero-field is expected to become even stronger beyond this limit. In the case of pure bismuth, the quantum limit was found to occur at a field as low as 3T. An ultraquantum anomaly at twice this field was detected in both charge transport and Nernst response. Its origin appears to lie beyond the one-particle picture and linked to unidentified many-body effects.

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thermopower to linear specific heat (\(q = \frac{S\times N}{\mu J\text{ mol}^{-1}K^{-1}}\)), where \(e\) is the electron charge and \(N_A\), the Avogadro number) is more than four orders of magnitude larger than unity, the typical ratio found in metals with conventional carrier density\(^{24}\). Since \(q\) is expected to inversely scale with carrier density\(^{25}\), this is not surprising. It is instructive to compare the low-temperature thermoelectric responses of Bi\(_{0.96}\)Sb\(_{0.04}\) and Bi. In pure bismuth\(^{26}\), it is non-monotonous and very small below 1K indicating that contributions by electrons and holes to thermopower are comparable and cancel out at very low temperatures. On the other hand, the frankly negative and \(T\)-linear Seebeck coefficient in Bi\(_{0.96}\)Sb\(_{0.04}\) implies the domination of electron-like carriers. Since the system remains compensated the contraction of the volume of the electron and hole pockets should be strictly equal. Therefore, this predominance cannot be simply explained by the difference in the evolution of the hole and electron Fermi energies with Sb doping. On the other hand, close to \(x=0.04\), the energy spectrum of the electron pocket, which is only partly linear in momentum in the case of pure bismuth becomes strictly linear. Thus, the negative sign of the thermopower reflects the enhanced thermoelectric response of Dirac fermions compared to conventional quasi-particles.

We also measured the thermal conductivity of the sample in zero field (not shown) and found that it is dominated by lattice thermal conductivity as in pure bismuth with an almost undetectable electron contribution\(^{27}\).

To probe the Fermi surface quantitatively, we studied the quantum oscillations of various transport properties. As seen in Fig. 2, in presence of a quantizing magnetic field along the trigonal, both resistivity and the Hall effect show visible oscillations. Panel c of the same figure, a semi logarithmic plot of resistivity vs. inverse of the magnetic field, reveals an oscillation period of 0.45\(T^{-1}\), three times larger than in pure bismuth (0.15\(T^{-1}\))\(^{11,12}\). This means that the equatorial cross section of the hole ellipsoid has become three times smaller. The quantum limit, the passage to the \(n = 0\) Landau level, occurs at field of about 3T. Note also the additional anomaly in both \(\rho_{xx}\) and \(\rho_{xy}\) at a yet higher field (∼6T).

As seen in the main panel of Fig. 3, quantum oscillations of the Nernst response are easily detectable. Their large amplitude is reminiscent of (but less pronounced than) the case of pure bismuth\(^{12}\). The period of these oscillations matches the period of Shubnikov-de Haas oscillations of Fig. 2. Each Nernst maximum is concomitant with a resistivity minimum. One remarkable feature is the emergence of new peaks at the lowest temperature linked to the large Zeeman splitting. In bismuth for a field along trigonal, the Zeeman energy, \(E_Z\), of holes is such that \(E_Z = 2.17\hbar\omega\)\(^{11}\). In other words, the Zeeman splitting is so large that the field corresponding to the \(0^+\) peak is lower than the one associated with \(2^+\). This was detected in both resistivity\(^{11}\) and Nernst\(^{12}\) data. Thus, the occurrence of the same feature in our data on Bi\(_{0.96}\)Sb\(_{0.04}\) indicates that here also \(E_Z > 2\hbar\omega\).

![Fig. 1: (a) The zero-field resistivity Bi\(_{0.96}\)Sb\(_{0.04}\) as a function of \(T^2\) for a current along the binary axis. The inset shows the data over a wider temperature range. (b) The temperature-dependence of the Seebeck coefficient at low temperatures for a temperature gradient along the binary axis.](image-url)
As the system cools, the $0^+$ anomaly gradually dominates the $2^-$ peak. We note that this temperature evolution is more radical here than in the case of pure bismuth [12].

The period of quantum oscillations varies as a function of magnetic field. This can be seen in the lower panels of Fig. 3 which presents the $B^{-1}$ position of successive Landau levels for both orientations of magnetic field. If the period was constant, the data would fall on a straight line. The upward curvature is reminiscent of the case of pure bismuth [11] and is a signature of a field-induced modification of the carrier density and Fermi surface volume. According to a picture proposed many years ago [28], charge neutrality in this compensated system implies a continuous adjustment in carrier density of both holes and electrons. This leads to a steady increase in the size of the Fermi surface, in particular in the vicinity of the quantum limit. As seen in the lower panels, the upward curvature is much stronger for a field along the bisectrix, which was also the case in pure bismuth [28].

Table 1 compares the period of quantum oscillations in Bi (according to one authoritative study [29]) with what is found here for Bi$_{0.96}$Sb$_{0.04}$ at the low field. For each field orientation, the frequency of oscillations directly yields the projected area of the Fermi surface. Hence, the volume of the hole ellipsoid can be unambiguously determined. It is smaller by a factor of 8 in the alloy. Even though the electron pockets have remained invisible, their overall volume is expected to contract identically. Indeed, the system is expected to remain compensated during the smooth evolution towards the insulator. Thus, we conclude that the carrier density for both electrons and holes in Bi$_{0.96}$Sb$_{0.04}$ is $4 \times 10^{16} \text{cm}^{-3}$. This is in fair agreement with the estimation by Brandt and co-workers [6]. It is remarkable to find that a Fermi liquid behavior persists at such a low level of carrier concentration. A residual resistivity of $32 \mu \Omega \text{cm}$ for such carrier density (assuming an equal mobility for electrons and holes) would imply a mobility of $2.4 \times 10^6 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$, significantly lower than bismuth [12], but remarkably high for an alloy.

In order to investigate the transport properties of the system deep in the ultraquantum regime, the Bi$_{0.96}$Sb$_{0.04}$ crystal was put in a 28 T resistive magnet of Grenoble.
As seen in the figure, in both cases the most prominent peak among the Nernst anomalies occurs at the quantum limit (9T in bismuth and 3T in the alloy). Note also the broadening of the Nernst anomalies in the alloy. As for the ultraquantum regime, as seen in the figure, three sharp anomalies were resolved in bismuth [16]. They occurred at fields corresponding to 3/2, 5/2 and 7/2 times the quantum limit. Here, in Bi₀.₉₆Sb₀.₀₄, we resolve at least one ultraquantum anomaly at twice the quantum limit. We recall that this field scale has very visible signatures in charge transport (See Fig. 2).

Can this anomaly be caused by the electron pockets? Since the latter remain undetected, this question cannot be answered with certainty. However, as seen in Fig. 2 the sign of the jump at 6 T in the Hall resistivity is the same as the 3T anomaly: It is positive. A similar feature was seen in the Seebeck data. Both these suggest that this anomaly is linked to the hole-like carriers. In the case of pure bismuth, the electron pockets, which are elusive in transport measurements, dominate the magnetization response and torque magnetometry has emerged as a powerful probe of the electron pockets across the quantum limit [30, 31]. Future angular torque magnetometry studies should shed more light on the origin of the ultraquantum anomalies detected here.

In summary, we studied the transport properties of Bi₀.₀₄Sb₀.₉₆ across the quantum limit and quantified the carrier density and mobility of this semimetal. Even at such low level of carrier concentration, the zero-field ground state is a Fermi liquid. In the extreme quantum limit, at least one anomaly possibly emanating from unknown many-body effects was detected. We thank G. Lapertot for precious technical assistance. This work was supported by the Agence Nationale de la Recherche.

[1] A. L. Jain, Phys. Rev. 114, 1518 (1959)
[2] L. S. Lerner, K. F. Cutt and L. R. Williams, Rev. Mod. Phys. 40, 770 (1968)
[3] G. E. Smith and R. Wolfe, J. Appl. Phys. 33, 841 (1962)
[4] N. B. Brandt, L. G. Lyubutina and N. A. Kryukova, Sov. Phys. JETP 26, 93 (1968)
[5] N. B. Brandt and S. M. Chudinov, Sov. Phys. JETP 32, 815 (1971)
[6] N. B. Brandt, Kh. Dittmann and Ya. G. Ponomarev, Sov. Phys. Solid State, 13, 2408 (1972)
[7] B. Lenoir et al., J. Phys. Chem. Solids 57, 89 (1996)
[8] L. Fu and C. L. Kane, Phys. Rev. B 76, 045302 (2007)
[9] D. Hsieh et al., Nature 452, 970 (2008)
[10] B. I. Halperin and T. M. Rice, Rev. Mod. Phys. 40, 755 (1968)
[11] S. G. Bompadre et al., Phys. Rev. B 64, 073103 (2001)
[12] K. Behnia, M. -A. Méasson and Y. Kopelevich, Phys. Rev. Lett. 98, 166602 (2007)
[13] B. I. Halperin, Jpn. J. Appl. Phys. 26, 1913 (1987)
[14] K. Hiruma, G. Kido and N. Miura, J. Phys. Soc. Jpn, 51, 3278 (1982)
[15] K. Hiruma and N. Miura, J. Phys. Soc. Jpn, 52, 2118 (1983)
[16] K. Behnia, L. Balicas, Y. Kopelevich, Science 317, 1729 (2007)
[17] G. P. Mikitik and Yu. V. Sharlai, Low Temp. Phys. 26, 39 (2000)
[18] A. Ghosal, P. Goswami and S. Chakravarty, Phys. Rev. B 75, 115123 (2007)
[19] R. Hartman, Phys. Rev. 181, 1070 (1969)
[20] C. Uher and W. P. Pratt, Phys. Rev. Lett. 8, 491 (1977)
[21] H. K. Collan, M. Krusius and G. R. Pickett, Phys. Rev. B 1, 2888 (1970)
[22] K. Kadawaki and S. B. Woods, Solid State Commun. 58, 507 (1986)
[23] H. Kontani, J. Phys. Soc. Jpn. 73, 518 (2004)
[24] N. E. Hussey, J. Phys. Soc. Jpn. 74, 1107 (2005)
[25] K. Behnia, D. Jaccard and J. Flouquet, J. Phys.: Condens. Matter 16, 5187 (2004)
[26] C. Uher and W. P. Pratt, J. Phys. Rev. F, Metal Phys.
8, 1979 (1978)

[27] K. Behnia, M. -A. Méasson and Y. Kopelevich, Phys. Rev. Lett. 98, 076603 (2007)

[28] G. E. Smith, G. A. Baraff and J. M. Rowell, Phys. Rev. 135, A1118 (1964)

[29] R. N. Bhargava, Phys. Rev. 156, 785 (1967)

[30] L. Li, J. G. Checkelsky, Y. S. Hor, C. Uher, A. F. Hebard, R. J. Cava and N. P. Ong, Science 321, 547 (2008)

[31] B. Fauqué et al., to be published.