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Slow quantum oscillations in the semimetallic spin-density-wave state of tetramethyltetraselenafulvalinium nitrate $(TMTSF)_2NO_3$

Neven Biškup
Laboratoire de Physique des Solides, Bâtiment 510, Université de Paris-Sud, 91405 Orsay, France and Institute of Physics of the University, P.O. Box 304, 41000 Zagreb, Croatia

Luis Balicas
Laboratoire de Physique des Solides, Bâtiment 510, Université de Paris-Sud, 91405 Orsay, France

Silvia Tomić
Institute of Physics of the University, P.O. Box 304, 41000 Zagreb, Croatia

Denis Jérome
Laboratoire de Physique des Solides, Bâtiment 510, Université de Paris-Sud, 91405 Orsay, France

Jean-Marc Fabre
Université de Montpellier II, Université des Sciences et Technique du Languedoc, F-34095 Montpellier, France
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We have observed a clear series of fine structures superposed on the angular dependence of the transverse magnetoresistance in the semimetallic spin-density-wave state of the organic conductor $(TMTSF)_2NO_3$. They appear at the positions defined by the strength of the field component parallel to the least-conduction direction ($B\cos\theta \simeq$ const). An observed asymmetry in the magnitude is due to the striking angular dependence of the oscillations amplitude. The frequency of the oscillations ($B_S = 63$ T) is close to the frequency of the field-induced spin-density-wave transitions found in the other Bechgaard salts. This oscillatory phenomenon is considered to result from the orbit quantization inside the closed parts of the Fermi surface which are due to the $2k_F$ anion ordering together with the imperfect spin-density-wave nesting.

The Bechgaard salts are a series of very anisotropic electrical conductors made up of large planar organic donor molecules [tetramethiltetraselenafulvalene (TMTSF)] and an inorganic acceptor X (PF_6, ClO_4, NO_3, etc.).[1] In addition to the strong molecular intrastack overlap along the highly conducting a axis, there are also relatively significant selenium-selenium contacts along the intermediate conductivity b axis. In contrast, only weak electron overlap exists along the least-conductivity c axis (molecule-anion-molecule direction). The electron transfer energies t_a, t_b, and t_c obtained in plasma-frequency measurements[2] and magnetoresistance measurements[3] are approximately 2900, 290, and 17 K, respectively. Band structure calculations have given consistent values and an open Fermi surface.[4] The latter was confirmed by magnetic anisotropy measurements which did not reveal any Landau diamagnetism associated with closed orbits.[5] Accordingly, one would not expect to see quantum oscillations of the susceptibility (de Haas–Van Alphen effect) and the resistivity (Shubnikov–de Haas effect) in magnetic fields.

However, it is now well established that in these materials magnetoresistance and magnetization exhibit three distinct types of oscillatory behavior,[1,6,7] The first one is known as slow oscillations and is associated with field-induced spin-density waves (FISDW's). Namely, the c^* component of magnetic field (B), above a threshold value ($B_{\rm th}$), restores the divergence of the spin susceptibility which was lost due to the bad nesting ($t_b > t_{b\rm cr}$). The divergence occurs at quantized values of the nesting wave vector $Q_n = (2k_F + ebBn, 2\pi/b)$. Thus, within a given FISDW phase, Q_n of the SDW's increases linearly with B in order to keep the Landau levels associated with the unnested electron pocket completely filled. This relation minimizes the diamagnetic energy at the expense of a slightly worse nesting. Once the nesting becomes too bad, the quantum number jumps to the value $n-1$ in order to assure a better nesting again. The separation between the inverse values of the fields at which phase transitions between the FISDW phases occur is nearly constant, similarly to the case of standard Shubnikov–de Haas oscillations. The experimentally observed values (B_S) range from 20 to 70 T and correspond to about 1% of the Brillouin zone in momentum space. The latter is about 3 times larger than the theoretically calculated area of the carrier pocket.[1]

The second type of oscillation is known as fast or high-frequency Shubnikov–de Haas-like oscillations. They have only been observed in magnetoresistance with fundamental frequency (B_F) between 230 and 550 T. B_F, as well as B_S, has a $\cos\theta$ (θ is the angle between the field direction and the c^* axis) dependence, revealing the orbital origin of both phenomena. The fast oscillations were observed well below B_{th} and retained the same frequency, as the threshold field for FISDW's was exceeded. Moreover, this type of oscillation was found in the ambient-pressure SDW state of $(TMTSF)_2PF_6$ in the temperature range between 10 and 4.2 K. The SDW vector was estimated to be close to the commensurate value $Q_{SDW}=(0.5a^*,0.24\pm0.03b^*)$ and $(0.5a^*,0.20\pm0.05b^*)$, by two different groups,[8,9] ignoring the third, weakly coupled c^* direction. This value is near the optimal nesting vector calculated at 4 K and at ambient pressure.[10] Therefore Q_{SDW} assures the best nesting of the Fermi surface and presumably does not leave pockets on the Fermi level. These results are also supported by a well-defined thermally activated resistivity behavior. Until now, proposed theoretical pictures were not able to explain this phenomenon.

The third type of oscillatory behavior is known as Lebed resonance. It appears at the magic angles (θ_M), which satisfy the commensurability condition between two periodicities in the electron motion along an open orbit on the Fermi surface in the b and c directions. The positions of the Lebed fine structure (i.e., θ_M) are independent of the field strength and temperature.

In this paper we report on detailed measurements of the angular and temperature dependence of the transverse magnetoresistance in the SDW state of the $(TMTSF)_2NO_3$ compound which contains ordered anions with periodicity $(2k_F,0,0)$. Kang *et al.* reported the observation of oscillations with the frequency 75±10 T and assigned them as the fast oscillations.[11] Audouard *et al.* observed two series of Shubnikov–de Haas–like oscillations for a field along the c^* axis with frequencies of 63 and 249 T.[12] Our work concentrates on the former series and reveals a novel type of oscillatory behavior. We find that the fundamental frequency displays $\cos\theta$ behavior, as expected for an anisotropic electronic system. On the other hand, the oscillation amplitude exhibits a striking angular behavior and an unusual temperature dependence, unexpected for the standard Shubnikov–de Haas oscillations. We argue that a semimetallic low-temperature Fermi-surface topology is at the origin for the observed phenomena.

The measurements were carried out with a conventional low-frequency lock-in technique using a typical current of 10 μA along the sample's a axis in magnetic fields up to 12 T. Three single crystals were studied from two different preparation batches and with typical dimensions $5\times0.15\times0.09$ mm^3. Four contacts were made by silver paint on preevaporated gold pads. Samples were mounted on a rotating holder, yielding rotations in the (b',c^*) plane perpendicular to the a axis.

The data presented here are from a sample with the best resistivity ratio rr≅200 (rr$=\rho_{RT}/\rho_{min}$, where ρ_{RT} and ρ_{min} are the resistivities measured at room temperature and 10.3 K, respectively) and with the SDW transition temperature $T_{SDW}=9.05$ K. The magnetoresistance $(\Delta R/R_0)$ behavior from 0 to 12 T for $\theta=0°$ and at 4.2 K is presented in Fig. 1. θ is the angle which gives a field

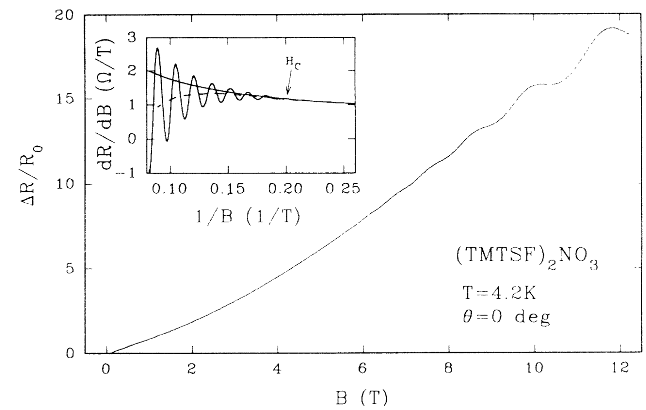


FIG. 1. Magnetoresistance $(\Delta R/R_0)$ at 4.2 K for a magnetic field (B) along the c^* direction. The inset shows the resistance derivative (dR/dB) vs the inverse field $(1/B)$. The solid line is a fit to the data below H_c. The dashed line is a guide for the eye.

direction from the c^* axis in the (b',c^*) plane. Large amplitude oscillations start to emerge from the nearly linear power-law behavior and become already visible at 5 T (see the inset of Fig. 1). The fundamental frequency (B_S) of the oscillations follows a $\cos\theta$ angular dependence, revealing the orbital origin of the phenomenon (Fig. 2). Absolute values of B_S were obtained following the standard procedure. Namely, as the oscillations are periodic in $1/B$ (see inset of Fig. 1), we can apply the Onsager relation $1/B_n=(n+\gamma)/B_S$, where γ is a phase fac-

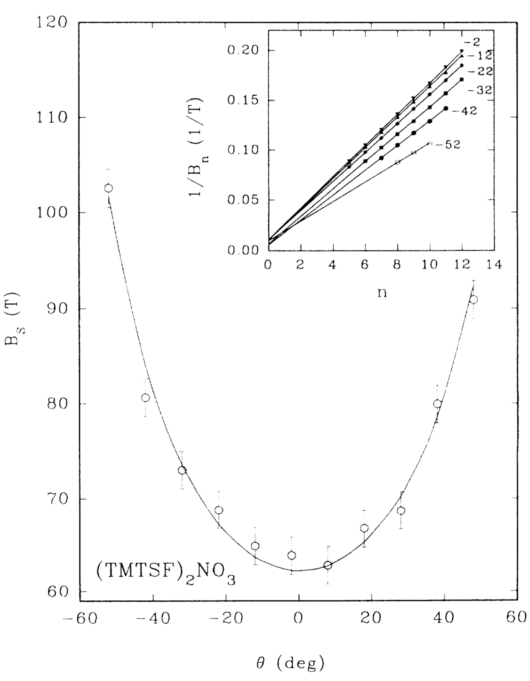
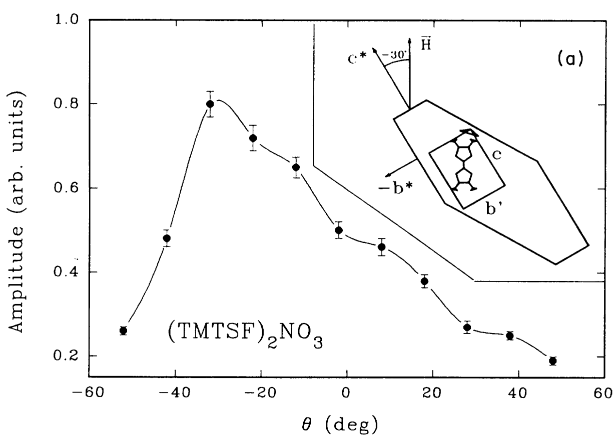


FIG. 2. Angular dependence of the oscillation fundamental frequency (B_S) at 4.2 K. The solid line is a fit to the $\cos\theta$ behavior. Inset: inverse field $(1/B_n)$ for several field orientations vs the index (n) of the oscillation maximum in the magnetoresistance.

tor, to get B_S. The inset of Fig. 2 shows inverse field values ($1/B_n$) versus corresponding integral numbers (n) assigned to an oscillation maximum for several field oscillations. The slope and segment provide a fundamental field $B_S(\theta=0°)=63\pm2$ T and $\gamma\cong0.7$, respectively. The former value is in excellent agreement with the one found by Audouard *et al.*[12] Figures 3(a) and 3(b) show the angular and temperature variation of the oscillations amplitude (for the fixed number n), respectively. The observed behavior is striking in that it reveals a maximum at a field angle $\theta=-30°$. The latter feature together with the $\cos\theta$ dependence of the fundamental frequency B_S define a novel magnetoresistance anisotropy (see Fig. 4). A rapid decrease of the amplitude below 4.2 K contrasts with the temperature behavior expected for the standard Shubnikov–de Haas oscillations. Finally, we point out that we did not observe any temperature dependence of the oscillation frequency B_S and of the field at which the oscillations become visible ($H_s\cong5$ T). We assigned H_c in the plots dR/dB vs $1/B$ (see the inset of Fig. 1) to a discontinuity in the low-field magnetoresistance variation (solid line). Once the oscillations start to appear, the slope of the magnetoresistance rise becomes smaller (dashed line). This feature is the most pronounced at 1.2 K (Fig. 5) because of the faster increase of the low-field magnetoresistance at lower temperatures.[13] Furthermore, the field H_c is angular dependent and roughly follows the $\cos\theta$ behavior (Fig. 6). The mere fact that it seems that there is a critical field for the appearance of the oscillations also contradicts the behavior expected for the standard Shubnikov–de Haas oscillations.

Some of us have already suggested that the SDW ground state in the NO_3 compound might be semimetallic, rather than semiconducting as in the model systems $(TMTSF)_2PF_6$ and AsF_6.[14] Figure 7 shows one piece of evidence more for that statement. Namely, the magnetoresistance ($\Delta R/R_0$) for two samples with different resistivity ratio rr behave in two distinct ways. We recall that rr is widely used as a measure of the sample purity. A larger rr means less impurities. At a fixed temperature, $\Delta R/R_0$ for the rr$\cong$200 sample obeys a power-law behavior (until H_c is reached) with the exponent n is close to 2.5 at 1.2 K.[13] On the other hand, $\Delta R/R_0$ for the rr$\cong$42 sample starts to saturate already at low fields.



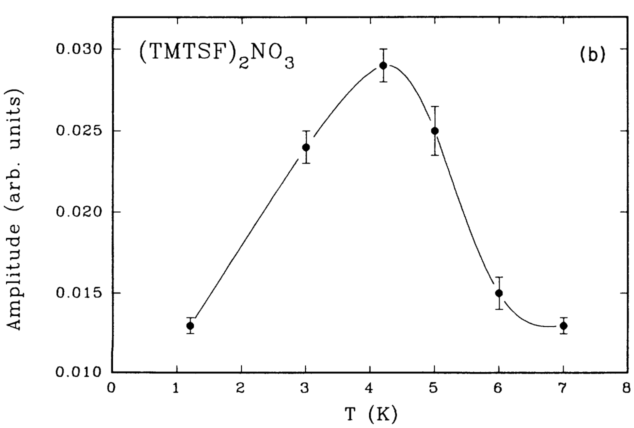


FIG. 3. (a) Angular dependence of the oscillation amplitude at 4.2 K. The solid line is a guide to the eye. Inset: sample geometry. (b) Temperature dependence of the oscillation amplitude at 4.2 K.

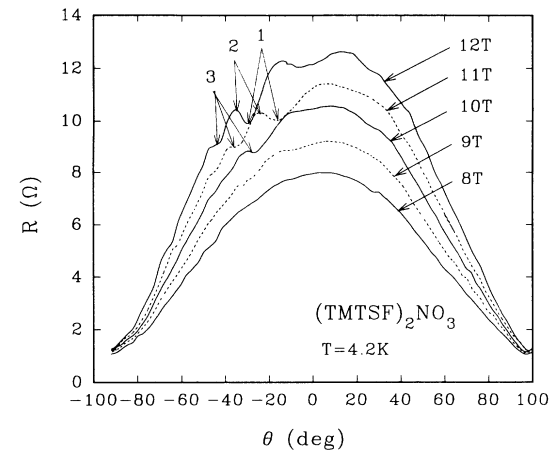


FIG. 4. Angular dependence of the resistance for five values of the magnetic field. Arrows with corresponding numbers represent points with the same $B\cos\theta$ values.

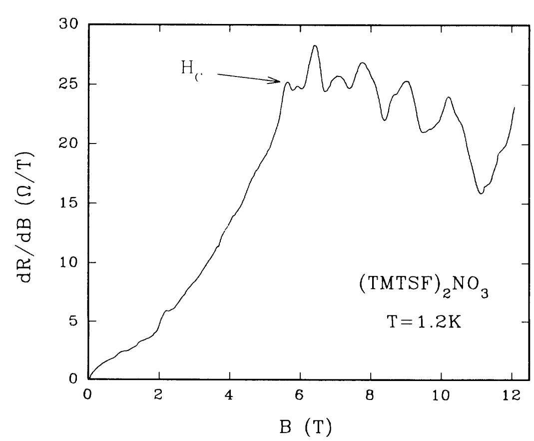


FIG. 5. Resistance derivative (dR/dB) vs the field (B) at 1.2 K. The arrow indicates the point where the slope changes and the oscillations begin.

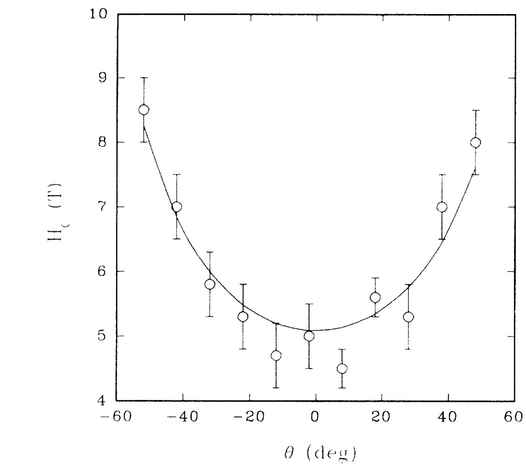


FIG. 6. Angular dependence of the critical field (H_c) above which the oscillations appear. The solid line is a fit to the $\cos\theta$ behavior.

Such a behavior is well known in compensated semimetals such as bismuth where already a small number of impurities make the compensation not perfect and therefore the quadratic rise to saturate.[15]

Furthermore, the NO_3 SDW is imperfectly nested as indicated by the smaller activation energy and lower transition temperature.[14] Recently, Osada *et al.* calculated that the anion ordering with the wave vector $(2k_F,0,0)$, which occurs below 45 K in the NO_3, generates an electron and a hole pocket and makes the electronic system semimetallic[16] (here we recall that Grant was the first to point that out[4]). That would further imply that the imperfectly nested SDW ordering $(2k_F,\pi/b)$ splits the large pocket into four small ones (two electron and two hole pockets) below $T_c \cong 9$ K. Maki has analyzed these quasiparticle orbits in a magnetic field.[17] Each pair of the orbits gives the identical quantized levels which differs mutually only in the sign and are situated in the energy range $\Delta-\varepsilon_0<\pm E<\Delta+\varepsilon_0$. Δ is the SDW order parameter, and $\varepsilon_0=[t_b^2\cos(ap_F)/2t_a\sin^2(ap_F)]$ is the measure of the imperfect nesting. The highest quantum number $n_{\max}$ is estimated by a semiclassical analysis, and the fundamental period B_S of the oscillations is identified with the change of $n_{\max}$ to $n_{\max}-1$. B_S is then given by

$$B_S=(\sqrt{2}\Phi_0/\pi^2ab't_a)$$

$$\times\{[\Delta(T)\varepsilon_0]^{1/2}+[\Delta(T)+\varepsilon_0]\tan^{-1}[\varepsilon_0/\Delta(T)]^{1/2}\}\ ,$$

where $b'=b\cos\gamma$ and $\Phi=hc/2e$ is the quantized flux. Using $T_c\cong 9$ K, we can estimate $\varepsilon_0/\Delta_0\cong 0.8$ from the SDW phase diagram,[18] where $\Delta_0\cong 21$ K, for the perfectly nested SDW. Taking therefore $\varepsilon_0\cong 17$ K and $t_a\cong 2900$ K, we obtain $B_S\cong 18$ T, which is smaller than the experimentally observed value by a factor of 3.5. Note that a similar quantitative disagreement is still actual for FISDW's. Further, the magnetic field breaks through the SDW gap Δ, which implies that the beginning of the disappearance of the slow oscillations takes place for $\omega_b\geq(\Delta\varepsilon_0)^{1/2}$. This corresponds to a threshold field of about $H_{\text{th}}\cong 11$ T. It is important to note that the magnetic breakthrough opens a novel trajectory along the large closed orbit and therefore enables concomitant growing up of the fast oscillations. In addition, Maki's model also predicts the suppression of the slow oscillations above 18 T, since for $B>B_S$ there is no Landau level left in the pocket. Recent experiments of Audouard *et al.*[12] verify the predictions of this model and identify the field range of the simultaneous existence of both oscillations between 14 and 25 T. The theoretical value of $B_B\cong 220$ T is also in fairly good agreement with the experimentally observed value of 249 T.

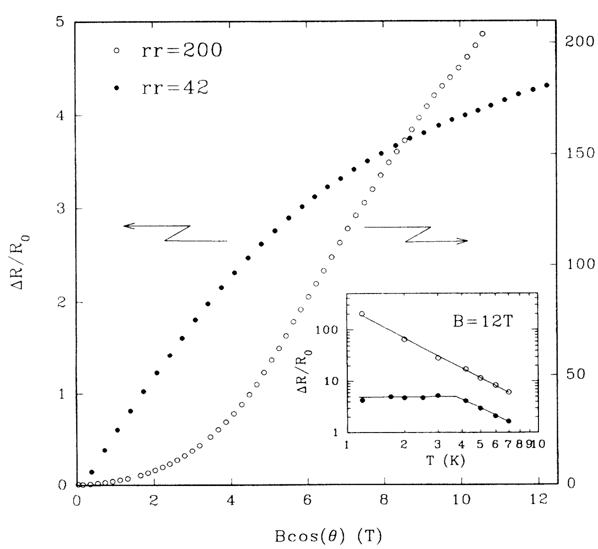


FIG. 7. Magnetoresistance ($\Delta R/R_0$) at 1.2 K for the sample rr≅200 (open points) and rr≅42 (solid points). Inset: $\Delta R/R_0$ at 12 T vs temperature. The solid line is a fit to the power-law behavior (see text).

Further, we address the angular and temperature behavior of the oscillation amplitude [see Figs. 3(a) and 3(b)]. First, we note that the orientation of the magnetic field $\theta(H,c^*)=-30°$ (which is the [013]* direction) at which the amplitude attains its maximum value is very close (inside a few degrees) to the direction of the anion-molecule-anion short link, i.e., the [011] direction [see the inset of Fig. 3(a)]. In the framework of the quasiclassical approach, that would imply that along this direction the extremal area (S_{ext}), which defines the fundamental frequency ($B_S\cong S_{\text{ext}}$), varies most smoothly; i.e., d^2S_{ext}/dk_z^2 is minimal for the $z=[001]$ direction.[19]

As far as the temperature behavior below 4 K is concerned, it certainly deviates from the standard expectation defined by the term $\exp(-2\pi^2Tm^*/B)$. We note that if we take the impurity scattering into account, the quantized levels have a finite width and this would lead to the same effect as a finite temperature. Indeed, we get larger amplitudes for the sample with rr≅200 than for the other with rr≅42. However, we would still expect to get an amplitude rise below 4 K. The inset of Fig. 7 shows that the rise of $\Delta R/R_0$ below T_c for the rr≅42 sample ($\Delta R/R_0\cong T^{1.3}$) completely saturates below 4 K, while $\Delta R/R_0$ for the rr≅200 sample continues to increase as $\Delta R/R_0 \cong T^2$ down to 1.2 K. In contrast, we observe a similar (power-law) decrease of the amplitude below 4 K for both samples. We recall that there are two other features showing the change in the behavior below 4 K. The activation energy strongly saturates (less than 5 K), and the power-law exponent of $\Delta R/R_0$, which is constant ($n \cong 1$) below T_c, starts to increase.[13]

Finally, we would like to comment on a common choice for the SDW wave vector $(2k_F,\pi/b)$ used also in Maki's theoretical model.[17] This is the optimal nesting vector resulting from the room-temperature band structure.[4] However, Ducasse, Abderrabba, and Gallois[10] have shown that the low-temperature variation of the Fermi-surface topology might be related only to the variation of the b component of the optimal nesting vector (Q_b). This variation leads in the case of the $(TMTSF)_2PF_6$ to $Q_b \cong \pi/2b$, in agreement with the NMR measurements (see the Introduction). We are tempted to propose that a similar change in the low-temperature band structure should be expected in the case of the NO_3 compound. Then the modified dispersion relation will lead to a different shape and size of the electron and hole pockets and consequently to the value of B_S which might be closer to the one found experimentally. The related theoretical calculation is in progress and will be published elsewhere.[20]

In conclusion, we have observed an oscillatory behavior of the magnetoresistance in the spin-density-wave state of $(TMTSF)_2NO_3$. Magnetoresistance is extremely sensitive to the sample purity, suggesting that the SDW ground state is semimetallic as expected from the band calculations. The $\cos\theta$ dependence of the fundamental frequency B_S of the oscillations (and the critical field H_c) and the magnitude $B_S \cong 63$ T itself are features reminiscent of the FISDW's. The angular dependence of the oscillation amplitude reveals the importance of the [011] direction in the unit cell, while its strong decrease below 4 K remains mysterious. The recent model by Maki identifies the quantization of the small orbits due to $(2k_F,0,0)$ anion ordering and $(2k_F,\pi/b)$ imperfectly nested SDW order as the origin of the observed oscillations. We propose that the theoretically underestimated value of B_S might be due to a low-temperature dispersion with the optimal nesting vector different than $(2k_F,\pi/b)$.

Since this paper was submitted, we have learned about similar work performed by Audouard *et al.*[21] Their work has also demonstrated the main features of the magnetoresistance oscillations in fields up to 12 T: the value of the fundamental frequency and the angular and temperature behavior of the oscillation amplitude. However, they do not discuss the possible existence of the critical field. In addition, they claim that measured samples of different parity (different residual resistivity ratio) showed the same behavior. The latter contradicts our findings.

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