Observation of fast oscillations in the magnetoresistance of the Bechgaard salt (TMTSF)$_2$SbF$_6$

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We report on a low-temperature and high-field study of (TMTSF)$_2$SbF$_6$ at ambient pressure, where TMTSF stands for tetramethyltetraselenafulvalene. We observe in this salt a single series of fast oscillations in the magnetoresistance inside the spin-density-wave state, with oscillation frequency $F = 170$ T for $B\|c^*$. The angular and thermal behavior of these oscillations has been explored and seems rather similar to that of other salts having octahedral anions (PF$_6$: $F = 230$ T, AsF$_6$: $F = 206$ T). However, the frequency in SbF$_6$ is surprisingly much lower, a feature perhaps attributable to anion volume. [S0163-1829(98)06345-0]

The Bechgaard salts (TMTSF)$_2$X, where TMTSF stands for tetramethyltetraselenafulvalene and X is an inorganic anion (ClO$_4$, NO$_3$, PF$_6$, AsF$_6$, …) have been extensively studied during the past 18 years because of the very rich physics due to their quasi-one-dimensional character.[1] Different systems of fast oscillation (FO) depending on the nature of the anion have been observed in the magnetoresistance (MR) in the above salts.[2–4] The MR of the two brother salts PF$_6$ and AsF$_6$ exhibits a single series of Shubnikov–de Haas–like FO at 230 and 208 T, respectively.[5,6] Rather similar behavior has been evidenced: first, only the B component along c^* is involved (orbital effect), and second, a conventional increase of the FO amplitude when temperature is lowered is followed by an unconventional, sharp decrease around 3 K. For many years, the origin of the FO has remained an open and controversial subject. However, recent theories and experiments from Kishigi and Machida,[7] Uji *et al.*,[8] and Brooks *et al.*[9] bring in new ideas and approaches to this phenomenon.

It is known that the geometry (symmetry) and orientational ordering of the anions play roles in determining the low-temperature properties of the FO (number of series, frequency, etc.). After (TMTSF)$_2$PF$_6$ and (TMTSF)$_2$AsF$_6$, it seemed relevant if not pertinent to study the SbF$_6$ compound, in order to follow the FO properties when increasing the anion volume, without changing the octahedral symmetry. Here, we report the first observation of the FO in (TMTSF)$_2$SbF$_6$ as a single series of oscillations of frequency 170 T. The regular but significant decrease of this FO frequency, going from PF$_6$ ($F = 230$ T) to AsF$_6$ (206 T) to SbF$_6$ (170 T), is a strong indication of the influence of the anion. Moreover, it is worth mentioning that the SbF$_6$ salt has never been studied under high magnetic fields.

The experiments were carried out in pulsed magnetic fields at Toulouse, which are characterized by a long-time decrease (~ 1 s) and a maximum field close to 40 T. We have used the standard four-contact technique (gold paste and 17-μm gold wires) to mount the samples. The resistivity ρ_{xx} and the transverse MR were measured using a 20-kHz ac current (of low enough amplitude to avoid heating or non-Ohmic effects) flowing along the best conducting needle direction (a axis). A rotating sample holder that allows a 360° variation of the (B, c^*) angle, where B is tilted in the (c^*, b^*) plane, was employed for the study of the transverse magnetoresistance angular dependence. It is our experience that increasing the anion volume makes these salts more and more brittle. So, even using a very slow cooling rate (0.1 K min^{-1}), we observed many cracks during cooling between 200 and 70 K. Aside from these, metallic behavior is observed down to 12 K, where the dielectric, spin-density-wave (SDW) phase appears. The metal-insulator transition temperature $T_{SDW} = 12 \pm 0.5$ K was conventionally estimated from the extrema of $d \ln(R)/d(1/T)$ (see Fig. 1).[10]

The sample orientation was determined by the MR anisotropy when B is rotated in the (c^*, b^*) plane. As usual for the Bechgaard salts, a rather sharp minimum was assigned to the b' direction (with an accuracy of $\pm 1°$). This direction, the
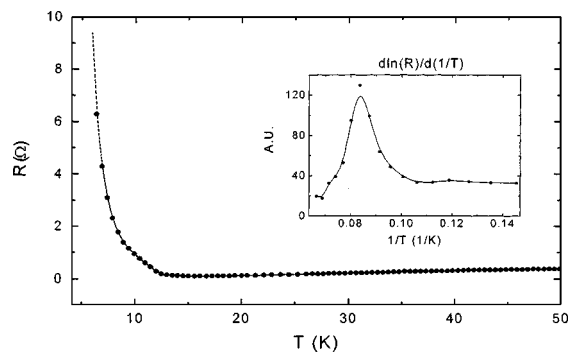

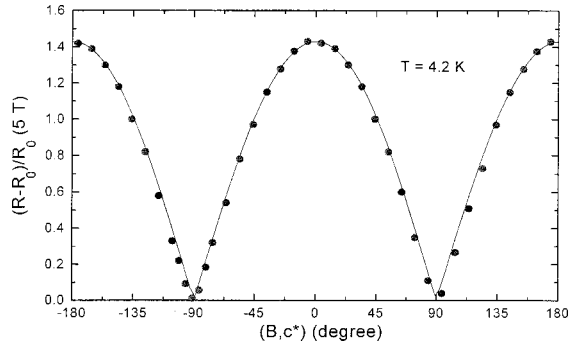FIG. 1. Resistance vs temperature, showing the SDW transition near 12 K. Inset: $d \ln(R)/d(1/T)$ plot.

FIG. 2. Magnetoresistance anisotropy for $B = 5$ T rotated in the (c^*, b') plane.

projection of the b axis onto the plane perpendicular to a, is more relevant than b^* for magnetotransport, as it lies in the conducting a-b plane (unlike b^*), and is normal to the interlayer c^* direction. This sample orienting was done at 4.2 K for a field of 5 T (Fig. 2). We can notice a very important anisotropy ratio, the MR being almost zero ($<1\%$) for $B \| b'$ at $\pm 90°$ and around 140% for $B \| c^*$. Moreover, this MR follows very well a cosine law, indicating its orbital origin. In order to search for possible FO's, which are known to appear in the SDW state in the other salts, we have done a first set of experiments at different temperatures, from 2 to 10 K. The MR up to 36 T is displayed in Fig. 3. As for the PF_6 and AsF_6 salts, the ambient, background MR has a monotonic B dependence and exhibits a maximum near 3 K (see Fig. 4). A single series of oscillations is clearly and directly visible on the MR. They qualitatively contain the two well-known characteristics of FO: $1/B$ periodicity and a restricted existence range, from ~ 2 to 8 K with a maximum around 3.5 K (also in Fig. 4). The fundamental frequency, obtained from either an Onsager plot or Fourier transforms, is $F = 170 \pm 4$ T, the lowest frequency yet observed in the Bechgaard salts. Here, we exclude from the discussion the 64-T series found in the NO_3 salt, and the field-induced SDW (FISDW) resistance oscillations of nominally ~ 35-T frequency seen in ClO_4 and PF_6. In NO_3, it is thought that bona fide closed orbits develop after the anions order, while the "slow" frequency of the FISDW gives the FO its name. For completeness, we explored the angular dependence of the SbF_6 fundamental frequency and the oscillation amplitude when B is rotated in the (c^*, b') plane (Fig. 5). The usual cosine law (within the experimental error) has been found.
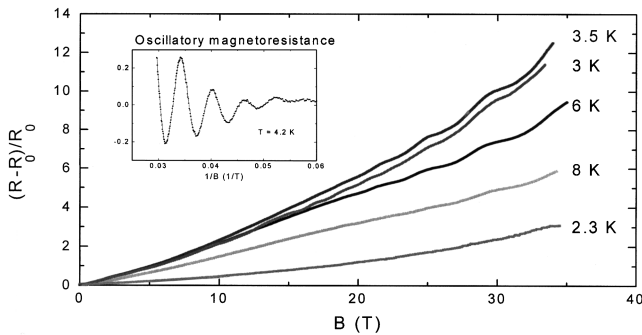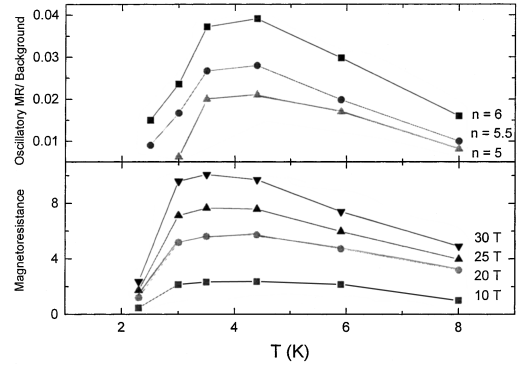

FIG. 4. Magnetoresistance amplitude and FO amplitude vs T, showing that both decrease below ~ 3 K, similar to all the other TMTSF salts studied.

The clear dependence of the FO frequency on the anion species has to be explained. The anion mass should not be involved in any case, so the frequency is more likely linked to the anion size (respectively, 94, 102, 118 $Å^3$ for PF_6, AsF_6, and SbF_6 at room temperature[11]), which modifies both the cell parameters and the Fermi-surface (FS) topology. This trend, which starts with the ClO_4 salt (77 $Å^3$) where the FO frequency is about 260 T,[2,12] is shown in Fig. 6 (note the inverted y scale). We also depict in Fig. 6 a corresponding relationship between the FO frequency and the momentum-space area of the pre-SDW, metallic-phase first Brillouin zone, here defined as $(\pi/a) \times (\pi/b)$. This linear dependence may become important when one attempts to attribute the FO to closed orbits on the nested Fermi surface in the SDW state.

In one such model proposed by Uji et al.,[8] the FO are said to be explained by magnetic breakdown (MB) orbits arising from a reconstructed Brillouin zone and reconstructed Fermi surface, after the nesting at the spin-density-wave formation. Using a simple model for the FS, one would expect that the resulting orbit area is linked to the area of the first Brillouin zone (precisely to $\sin \gamma/ab$, where γ is the angle between the a and b crystal axes) and to the transfer integral ratio t_b/t_a. Then, it would be interesting to know if an increase of the anion volume modifies those two parameters in such a way as to decrease the orbit area. In the conventional Shubnikov–de Haas (SdH) effect, the frequency $F = 1/\Delta(1/B)$ is directly proportional to the k-spaced orbit area. If the SDW transition is characterized by a nesting
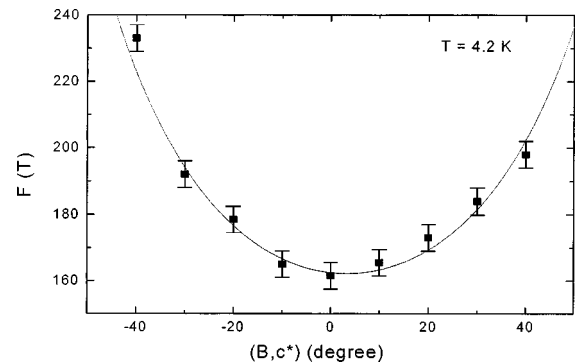

FIG. 3. Magnetoresistance at high field for different temperatures and $B \| c^*$. Inset: Oscillations at 4.2 K.

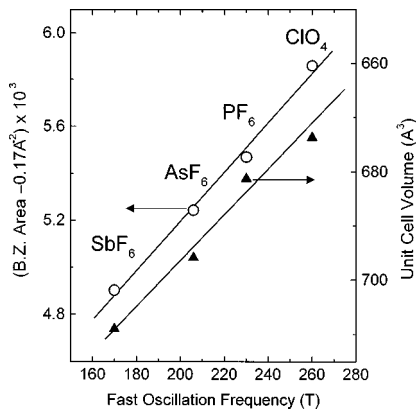FIG. 5. Anisotropy in the fundamental frequency when B is rotated in the (c^*, b') plane.

FIG. 6. Variation of the fast oscillation frequency in $(TMTSF)_2X$ salts with anion X, as seen in unit-cell volume (right) and Brillouin-zone area (left).

vector $Q_{SDW} = (Q_x, Q_y, Q_z)$ which is less than ''optimal,'' it will leave behind finite-area electron/hole pockets, rather than completely destroying the metallic FS. If the nesting is perfect, no FS remains, and we are left with an insulator. Charge carriers in these imperfectly nested pockets can undergo Landau quantization in a strong field. However, the orbit areas predicted by all band-structure calculations are much too small to explain the observed frequencies. In a strong enough field, significantly larger orbits may form after magnetic breakdown, amounting to a few percent of the first Brillouin zone. This is comparable to the observed frequencies, thereby lending credence to the MB model of Machida, as pointed out by Uji et al.

Some puzzles and contradictions remain, however. One relates to the lack of corresponding magnetization oscillations in these materials. If the FO are due to real Landau quantized electronic orbits, one would certainly expect de Haas–van Alphen (dHvA) oscillations to accompany the

SdH-like FO. To date, magnetization oscillations have only been observed in the NO_3 salt, and these are not thought to be related to the FO.[13] No magnetic oscillations have been detected in the AsF_6 or PF_6 salts up to 30 T, in the temperature range 0.4 to 20 K, to a sensitivity level of $\sim 10^{-12}$ A m^2.[14] If the postnesting, post-MB FS consists of electron and hole orbits of exactly equal area, it is entirely possible that dHvA oscillations will be averaged out by this compensation. Magnetic oscillations have been observed in the ClO_4 salt in the FISDW state, but not in the ambient SDW or metallic states. No data are available on magnetic measurements in the FISDW state in PF_6 or AsF_6.

A second problem lies in the temperature dependence at low temperature. Conventional SdH and dHvA oscillations are damped at high temperature by phase smearing, but saturate to a constant value at low temperature. The precipitous decay of the FO amplitude below ~ 3 K in Fig. 4, common to all the TMTSF salts, was attributed by Uji et al. to a gradual change in the SDW nesting vector, causing the compensated, MB-formed orbits to shrink in size. As the nesting improves, the orbit areas go to zero, eliminating the FO. Our problem with this argument is that the FO frequency, intimately tied to the orbit areas, is constant for all temperatures where the FO's are observed, including below 3 K. The model of Ref. 8 cannot be correct as it stands.

In conclusion, we have studied the high-field behavior of the MR of $(TMTSF)_2SbF_6$. The observation of a single series of FO's having a fundamental frequency of 170 T confirms that (i) this type of oscillatory phenomenon is a common property of the Bechgaard salts, (ii) the conditions of appearance of the FO are destroyed at low temperature ($T < 3$ K), and (iii) the anion nature has a strong influence on the FO frequency (even keeping the octahedral symmetry).

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