Pressure dependence of Shubnikov–de Haas oscillation spectra in the quasi-two-dimensional organic metal $\beta''(\text{BEDT-TTF})_4(\text{NH}_4)[\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{DMF}$

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The pressure dependence of the interlayer magnetoresistance of the quasi-two dimensional organic metal β''-$(\text{BEDT-TTF})_4(\text{NH}_4)[\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{DMF}$ [where BEDT-TTF represents bis(ethylenedithio)tetrathiofulvalene and DMF is dimethylformamide] has been investigated up to 1 GPa in pulsed magnetic fields up to 55 T. The Shubnikov–de Haas oscillation spectra can be interpreted on the basis of three compensated orbits in the whole pressure range studied, suggesting that the Fermi surface topology remains qualitatively the same as the applied pressure varies. In addition, all the observed frequencies, normalized to their value at ambient pressure, exhibit the same sizable pressure dependence. Despite this behavior, which is at variance with that of numerous charge-transfer salts based on the BEDT-TTF molecule, nonmonotonic pressure-induced variations of parameters such as the scattering rate linked to the various detected orbits are observed.

The family of isostructural monoclinic charge-transfer salts β''-$(\text{BEDT-TTF})_4(A)[M(\text{C}_2\text{O}_4)_3]\cdot\text{solv}$ has received much attention since it yielded, more than ten years ago, the first organic superconductor at ambient pressure with magnetic ions.[1] In the above formula, BEDT-TTF stands for the bis(ethylenedithio)tetrathiafulvalene molecule, A is a monovalent cation ($A=\text{H}_3\text{O}^+$, K^+, NH_4^+, etc.), M is a trivalent cation ($M=\text{Cr}^{3+}$, Fe^{3+}, Ga^{3+}, etc.), and solv is a solvent molecule such as benzonitrile (BN), dimethylformamide (DMF), nitrobenzene (NB), and pyridine (P). In the following, these compounds are referred to as A-M·solv. Even though all these compounds exhibit a metallic conductivity around room temperature, their electronic properties strongly depend on subtle details of their molecular arrangement. In this respect, the disorder, which is strongly sensitive to the nature of the solvent molecules, likely plays a significant role.[2,3] As an example, whereas H_3O-Fe·BN is superconducting with $T_c=8.5$ K,[1] H_3O-Fe·P exhibits a metal-insulator transition at 116 K.[2]

According to band structure calculations, the Fermi surface (FS) of H_3O-Fe·BN (Ref. 4) and NH_4-Fe·DMF (Ref. 5) [see Fig. 1(a)] originates from one elliptic orbit, of which the cross-sectional area is equal to that of the first Brillouin zone (FBZ). These orbits overlap in the $\Gamma'M'$ direction and come into contact at the Y' point, which should yield one electron- and one hole-compensated orbit with cross-sectional area of a few percent of the FBZ area, located around the points X' and M' of the FBZ, respectively. Nevertheless, the Shubnikov–de Haas (SdH) oscillation spectra recorded[6] on NH_4-Fe·DMF can rather be interpreted by assuming, as suggested in Ref. 5, that overlapping also occurs in the $\Gamma'Y'$ direction, leading to two hole- and one electron-compensated orbits labeled a, $b-a$, and b, respectively, in Fig. 1(b). However, this picture cannot hold for several compounds of the considered family. Indeed, only two frequencies were observed[7] for H_3O-M·NB whereas four frequencies were re-

ported for the H_3O-M·P ($M=\text{Cr},\text{Ga},\text{Fe}$) salts.[8] In these two latter cases, a density wave state, responsible for the observed strongly nonmonotonic temperature dependence of the resistance, has been invoked in order to account for this discrepancy. The FS of NH_4-Cr·DMF is probably even more complex since the SdH oscillation spectra can be accounted for by up to six orbits[9] even though a metallic conductivity is observed down to low temperature. Nevertheless, applied hydrostatic pressure has a drastic effect on the FS of this last compound since the number of Fourier components involved in the SdH oscillation spectra progressively decreases down to 3 as the pressure increases up to 1 GPa. In addition, these three frequencies are linked by a linear relation of the form $F_b=F_{b-a}+F_a$. In other words, the FS of NH_4-Cr·DMF under pressure is qualitatively the same as that of NH_4-Fe·DMF at ambient pressure.

The aim of this paper is to investigate the pressure dependence of the interlayer magnetoresistance of the NH_4-Fe·DMF salt. A behavior strongly different from that of the
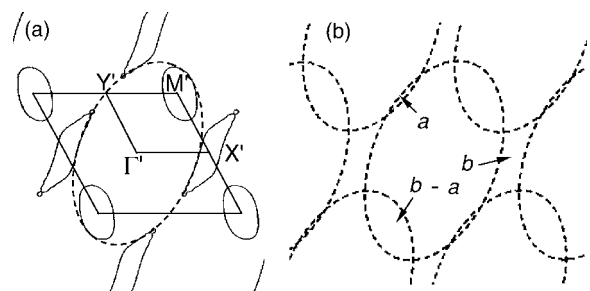

FIG. 1. (a) Fermi surface of β''-$(\text{BEDT-TTF})_4(\text{NH}_4)$ $[\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{DMF}$ at ambient pressure according to band structure calculations. (Ref. 5). (b) Representation of intersecting elliptic hole orbits ($\odot$ orbits in dashed lines) leading to three compensated electron (b) and hole (a and $b-a$) orbits. The area of the $\odot$ orbits is equal to that of the first Brillouin zone (see text).
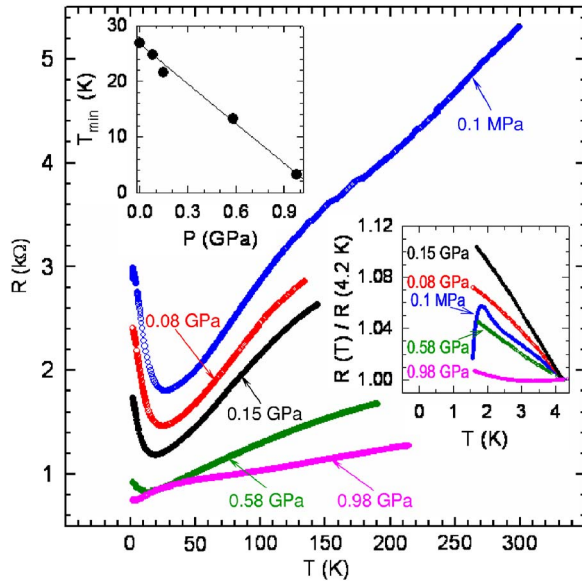
FIG. 2. (Color online) Temperature dependence of the zero-field interlayer resistance for the various pressures applied. The lower inset displays the low-temperature part of the data. The pressure dependence of the temperature at which the resistance goes to a minimum (T_{min}) is displayed in the upper inset. The pressures applied at low temperature are indicated in the figure.

related compound NH_4-Cr·DMF and numerous salts based on the BEDT-TTF molecule is observed.

The studied crystal was an elongated hexagonal platelet with approximate dimensions $0.4 \times 0.2 \times 0.1$ mm^3, the largest faces being parallel to the conducting ab plane. Magnetoresistance experiments were performed in pulsed magnetic field up to 55 T with a pulse decay duration of 0.32 s, in the temperature range from 1.6 to 4.2 K. Quasihydrostatic pressure was applied in an anvil cell designed for isothermal measurements in pulsed magnetic fields,[10] up to 0.98 ± 0.05 GPa at low temperature. The silicon oil GKZh-94 was used as pressure-transmitting medium. The quoted pressure values at low temperature are corrected by taking into account the decrease of pressure on cooling. Experimental details for interlayer resistance measurements and Fourier analysis can be found in Refs. 6 and 9.

In agreement with the data of Ref. 6, the interlayer zero-field resistance exhibits a pronounced minimum at T_{min} =27 K at ambient pressure (see Fig. 2). This behavior is at variance with that reported for the in-plane resistance which is metallic down to low temperature.[5] Even though the temperature dependence of the interlayer resistance of NH_4-Cr·DMF remains qualitatively the same in the studied pressure range (up to 1 GPa),[9] the resistance minimum of NH_4-Fe·DMF is linearly shifted toward low temperatures as the applied pressure increases (see the upper inset of Fig. 2). At 0.98 GPa, T_{min} is decreased down to 3 K and a strongly negative curvature is even observed around 40 K at this applied pressure. In addition, the pressure dependence of the interlayer resistance measured at room temperature is $d(\ln R)/dP = -1.35 \pm 0.15$ GPa^{-1}. This is close to the value reported for NH_4-Cr·DMF $[d(\ln R)/dP = -1$ GPa$^{-1}]$.[9] Otherwise, the resistance drop observed below 1.8 K at ambient pressure, possibly connected with the onset of a superconducting transition,[6] is suppressed from 0.08 GPa, as evidenced in the lower inset of Fig. 2.

Magnetoresistance data collected at 1.6 K are displayed in Fig. 3(a). It can be remarked that the background magnetoresistance, which is slightly negative at low pressure, is positive at 0.98 GPa while it exhibits a nonmonotonic behavior at 0.58 GPa; namely, a bump is observed around 12 T at this applied pressure, in the studied temperature range from 1.6 to 4.2 K. The Fourier analysis of the oscillatory part of the magnetoresistance data is displayed in Fig. 3(b). In agreement with data of Ref. 6, five frequencies are observed at ambient pressure, namely, $F_a = 49 \pm 2$ T, $F_{b-a} = 193 \pm 2$ T, $F_b = 241 \pm 5$ T, $F_{b+a} = 287 \pm 5$ T, and $F_{2b} = 482 \pm 20$ T. At first sight, the only noticeable feature regarding Fourier analysis of Fig. 3(b) is the pressure-induced vanishing of the amplitude of the components at F_{b+a} and F_{2b}. Recall that, owing to the temperature and field dependencies of their small amplitudes, these two components were attributed[6] to frequency combinations typical of networks of coupled orbits[11–13] rather than SdH oscillations linked to either individual or magnetic breakdown (MB) orbits. As previously reported, the relationship $F_a + F_{b-a} = F_b$, which accounts for the compensation of these orbits, is observed since $F_a + F_{b-a} = 242 \pm 4$ T.

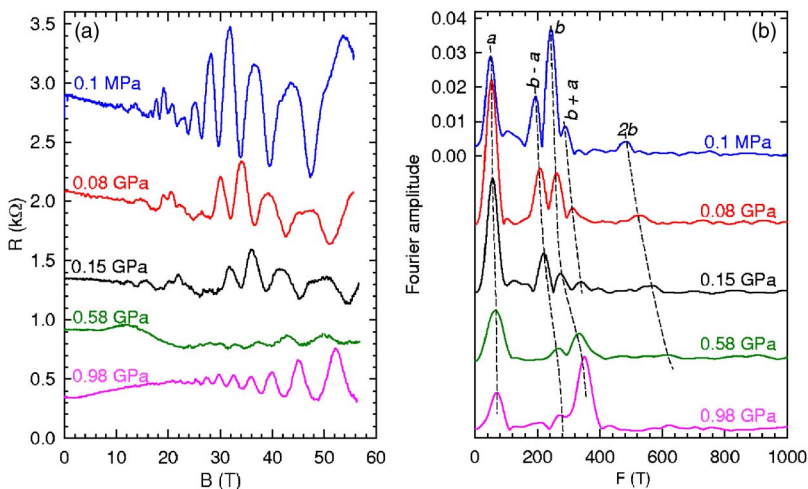As the applied pressure increases, the Fourier spectra re-

FIG. 3. (Color online) (a) Magnetoresistance at 1.6 K for the various pressures studied. Data at 0.15 and 0.98 GPa have been shifted down by 0.4 kΩ for clarity. (b) Fourier analysis of the oscillatory magnetoresistance data deduced from (a).
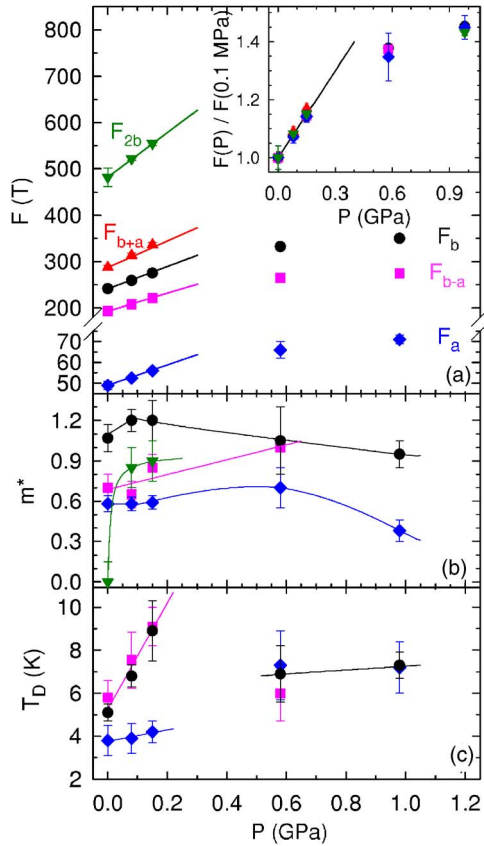
FIG. 4. (Color online) Pressure dependence of (a) the various Fourier components observed in the oscillatory magnetoresistance, (b) the effective masses, and (c) the Dingle temperatures (see text). The inset of (a) displays the pressure dependence of the frequencies normalized to their ambient pressure value. Solid straight lines in (a) correspond to $F(P)/F(0.1 \text{ MPa}) = 1 + \kappa P$ with $\kappa = 1$ GPa^{-1}. Solid lines in (b) and (c) are guides to the eye.

main similar. In particular, the above-mentioned linear relation is still valid at high pressure since, e.g., at 0.98 GPa, $F_a = 71 \pm 2$ T, $F_{b-a} = 274 \pm 6$ T (which yields $F_a + F_{b-a} = 345 \pm 8$ T), and $F_b = 350 \pm 1$ T. To be more exact, the pressure dependence of the relative value of the frequencies $F(P)/F(P=0.1 \text{ MPa})$ is the same for all the Fourier components observed, as evidenced in the inset of Fig. 4(a). This result is at variance not only with the behavior of NH$_4$-Cr·DMF, of which the FS topology is strongly modified under pressure,[9] but also with the data for compounds that illustrate the linear chain of coupled orbits model.[14–16] Indeed, the area of the closed α orbit of all these compounds is significantly more sensitive to the applied pressure than that of the MB-induced β orbit, although the FS topology remains qualitatively the same as the applied pressure varies. In this respect, it can be noticed that the area of the β orbit is equal to that of the FBZ, just as is the case of the $\odot$ orbit (see Fig. 1). Unfortunately, it was not possible to observe SdH oscillations linked to this latter orbit in the present case. Nevertheless, it is unlikely that the pressure dependence of the observed FS piece area follows that of the FBZ. Indeed the observed huge increase of frequency, namely, about 45% at 0.98 GPa, as reported in the inset of Fig. 4(a), cannot reflect

that of the FBZ area in view of the compressibility values reported for organic compounds. The influence of the applied pressure on the FS topology of some organic metals were successfully modeled by a modification of selected molecular orbital interactions.[14,17,18] In order to reproduce the pressure effect observed in the present case, simulations of the FS were carried out in which selected transfer integrals were varied. However, any attempt at such a tight-binding band structure calculation, which in most cases induces a slight rotation of the $\odot$ orbit,[19] fails to reproduce the experimental data. More precisely, the cross section of the electron and of one of the two hole tubes can significantly increase but, in any case, the cross section of the other hole tube decreases. In none of the simulations was a significant and simultaneous increase of the three cross sections observed even though electron-hole orbit compensation always holds.

Let us consider now the temperature and field dependence of the amplitude of the oscillations as the pressure varies. This can be achieved in the framework of the Lifshits-Kosevich formula[20] which has been reported to satisfactorily account for the data of SdH oscillations linked to closed orbits in quasi-2D networks of compensated electron and hole orbits, even in the case of crystals with low scattering rate.[11] Effective masses (m_i^*), deduced from the temperature dependence of the amplitudes are given in Fig. 4(b). Since magnetoresistance data at ambient pressure, which are in agreement with those of Ref. 6, were only recorded at 1.6 and 4.2 K, the effective masses given in Fig. 4(b) are taken from Ref. 6. Despite the large error bars obtained for the data at 0.58 GPa (at this pressure, the amplitude of the oscillations is rather small, as displayed in Fig. 3) it can be concluded that large variations of the effective masses occur as the applied pressure varies. It can also be noticed that m_{2b}^* has finite values under pressure, even though they are significantly lower than expected within the semiclassical picture (which predicts $m_{2b}^* = 2m_b^*$) as already observed in many 2D organic conductors.[21] This is at variance with data at ambient pressure for which a temperature-independent amplitude has been reported, which is therefore compatible with a zero effective mass.[6] This feature, which can be considered in connection with the above-mentioned pressure-induced decrease of the amplitude of the Fourier component with the frequency F_{b+a}, indicates that the nonsemiclassical features of the oscillatory spectra vanish as the applied pressure increases. Since nothing is known regarding the value of the MB gaps between the orbits, MB was not considered in the analysis of the field-dependent amplitude of the oscillations. The deduced Dingle temperatures are given in Fig. 4(c). As already reported for the salts of this family with the unsymmetrical DMF solvent,[6,9] large Dingle temperatures are observed. In the low pressure range, up to 0.15 GPa, different values of the Dingle temperature are obtained for a, on the one hand, and $b-a$ and b orbits, on the other hand. A jump of T_D is observed between 0.15 and 0.58 GPa and, contrary to the data at low pressure, the same Dingle temperatures are observed, within the error bars, for a and b at 0.58 and 0.98 GPa. Even though the pressure dependence of the observed frequencies indicates that the FS topology remains qualitatively unchanged as the pressure varies, the large pressure dependence of the effective masses, the nonmonotonic

behavior of the Dingle temperatures, as well as the behavior of the magnetoresistance under pressure [see Fig. 3(a)] suggest variations of the electronic structure as the applied pressure varies.

In summary, the most striking feature regarding the SdH oscillatory spectrum of NH_4-Fe·DMF under pressure is the very strong pressure sensitivity of the observed frequencies, which increase by 45% at 0.98 GPa. In line with this result, a sizable pressure dependence of the zero-field interlayer resistance is observed. Nevertheless, the pressure dependence of the normalized value of the various frequencies is the same, within the error bars, for all of them, which suggests that the FS topology remains qualitatively the same in the applied pressure range studied. Even more, it is consistent with the preservation of the orbit compensation as the applied pressure varies. This behavior is at variance with that of both the related compound NH_4-Cr·DMF (Ref. 9) and the organic compounds that illustrate the model of linear chains of orbits.[14–16] Oppositely, the behavior of the zero-field resistance as the temperature varies is significantly modified by applied pressure. In addition, significant variations of the effective masses and nonmonotonic behaviors of the scattering rates linked to the various Fourier components are observed under pressure. These features suggest that, despite the above-discussed pressure dependence of the frequencies, some variations of the electronic structure occur under pressure. The present results clearly demonstrate that we are still far from completely understanding the subtle details of the electronic structure of this remarkable family of organic compounds.

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