Pressure dependence of the magnetoresistance oscillations spectrum of beta"-(BEDT-TTF)4(NH4)[Fe(C2O4)3].DMF

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Pressure dependence of the magnetoresistance oscillations spectrum of β"-(BEDT-TTF)$_4$(NH$_4$)[Fe(C$_2$O$_4$)$_3$]·DMF

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Abstract

The pressure dependence of the interlayer magnetoresistance of the quasi-two dimensional organic metal β"-(BEDT-TTF)$_4$(NH$_4$)[Fe(C$_2$O$_4$)$_3$]·DMF has been investigated up to 1 GPa in pulsed magnetic fields up to 55 T. The Shubnikov-de Haas oscillations spectra can be interpreted on the basis of three compensated orbits in all the 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 sizeable pressure dependence. Despite this behavior, which is at variance with that of numerous charge transfer salts based on the BEDT-TTF molecule, non-monotonous pressure-induced variations of parameters such as the scattering rate linked to the various detected orbits are observed.
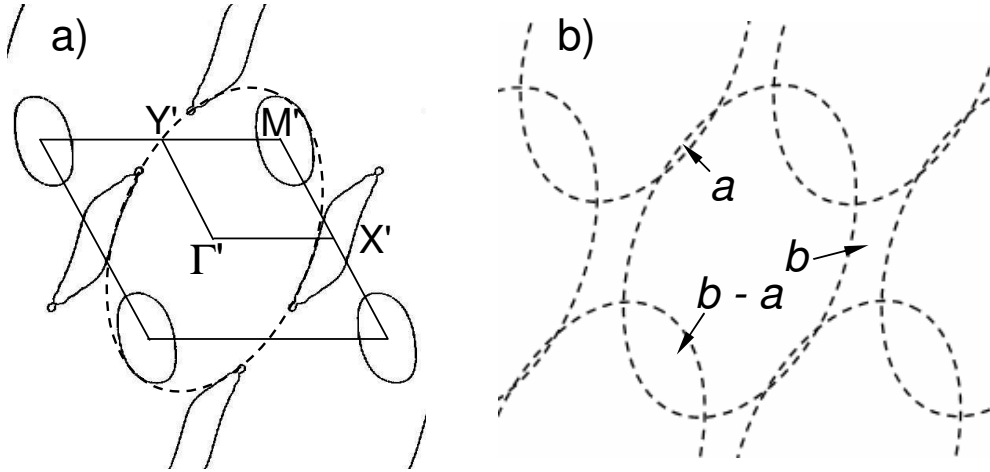
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FIG. 1: (a) Fermi surface of β''-(BEDT-TTF)$_4$(NH$_4$)[Fe(C$_2$O$_4$)$_3$]·DMF at ambient pressure according to band structure calculations [5]. (b) Representation of intersecting elliptic hole orbits (⊙ orbits in dashed lines) leading to three compensated electron (b) and hole (a and $b - a$) orbits. The area of the ⊙ orbits is equal to that of the first Brillouin zone (see text).

The family of isostructural monoclinic charge-transfer salts β''-(BEDT-TTF)$_4$(A)[M(C$_2$O$_4$)$_3$]·Solv have 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 = H$_3$O$^+$, K$^+$, NH$_4^+$, etc.), M is a trivalent cation (M = Cr^{3+}, Fe^{3+}, Ga^{3+}, etc.) and Solv is a solvent molecule such as benzonitrile, dimethylformamide, nitrobenzene and pyridine, labelled hereafter BN, DMF, NB and P, respectively. 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$_3$O-Fe·BN is superconducting with T$_c$ = 8.5 K [1], H$_3$O-Fe·P exhibits a metal-insulator transition at 116 K [2].

According to band structure calculations, the Fermi surface (FS) of H$_3$O-Fe·BN [4] and NH$_4$-Fe·DMF [5] [see Fig. 1(a)] originates from one elliptic orbit, of which the cross section area is equal to that of the first Brillouin zone (FBZ). These orbits overlap in the Γ'M' direction and come into contact at the Y' point which should yield one electron and one hole compensated orbits with cross section 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 on NH_4-Fe·DMF [6] can rather be interpreted assuming, as suggested in Ref. 5, that overlapping also occurs in the Γ'Y' direction leading to two hole and one electron compensated orbits labelled 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 for H_3O-M·NB [7] whereas, four frequencies were reported for the H_3O-M·P (M = Cr, Ga, Fe) salts [8]. In these two latter cases, a density wave state, responsible for the observed strongly non-monotonous 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 oscillations 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 latter compound since the number of Fourier components involved in the SdH oscillations spectra progressively decreases down to three 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 would be 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 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 K to 4.2 K. Quasi-hydrostatic 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 organic liquid GKZh-94 was used as pressure-transmitting medium. The quoted pressure values at low temperature are corrected taking into account the decrease of pressure on cooling. Experimental details for interlayer resistance measurements and Fourier analysis can be found in Refs. [6, 9].

In agreement with data of Ref. 6, the interlayer zero-field resistance exhibits a pronounced
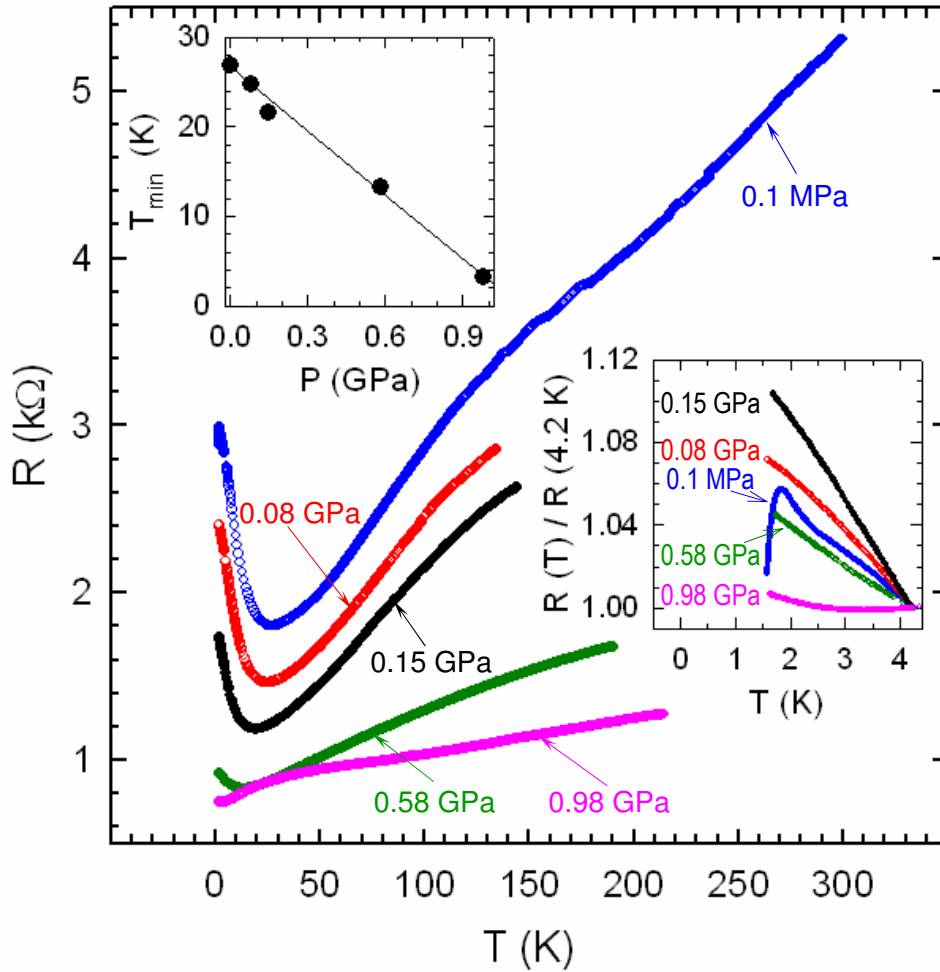
FIG. 2: (Color online) Temperature dependence of the zero-field interlayer resistance for the various pressures applied. The lower inset displays the low temperature part of the data. The pressure dependence of the temperature at which the resistance goes to a minimum (T_{min}) is displayed in the upper inset. The pressures applied at low temperature are indicated in the figure.

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 towards low temperatures as the applied pressure increases (see the upper inset of Fig 2). At 0.98 GPa, T_{min} is decreased down to
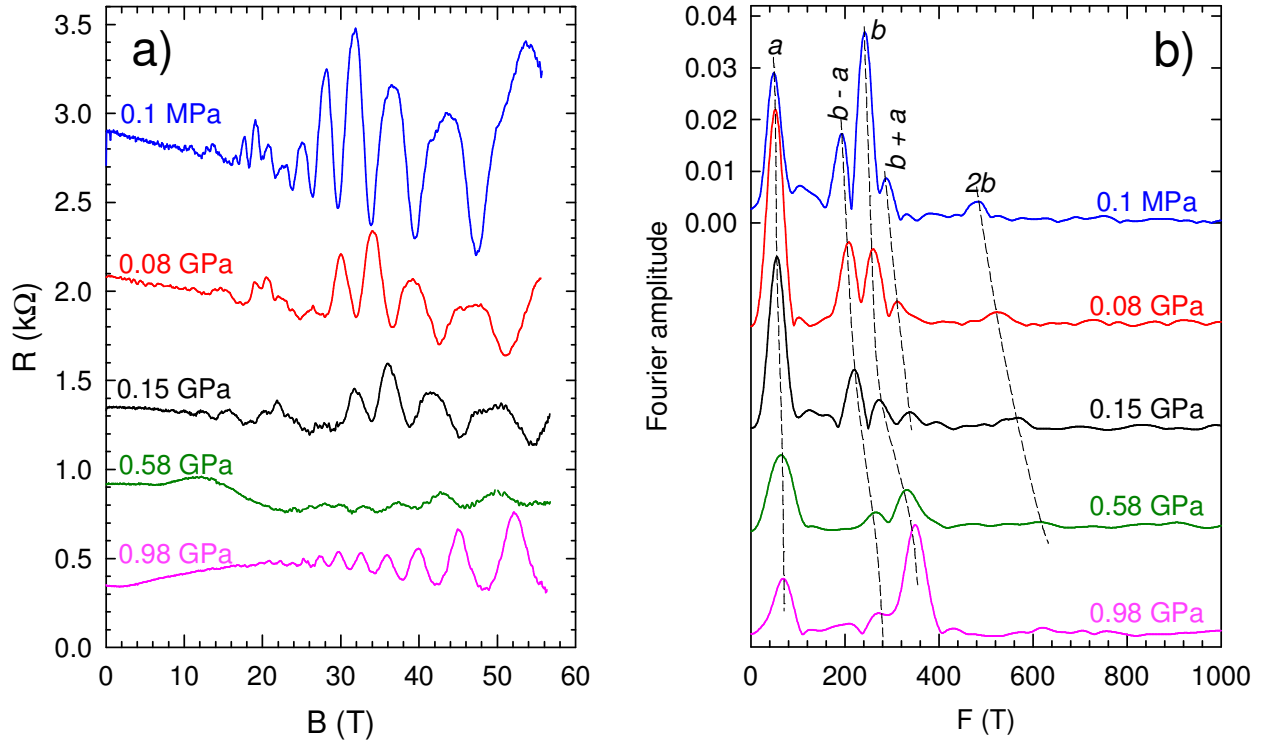
FIG. 3: (Color online) (a) Magnetoresistance at 1.6 K for the various pressures studied. Data at 0.15 GPa and 0.98 GPa have been shifted down by 0.4 kΩ for clarity. (b) Fourier analysis of the oscillatory magnetoresistance data deduced from Fig. 3(a).

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 non-monotonic 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 K 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 amplitude, these two latter components were attributed [6] to frequency combinations typical of networks of coupled orbits [11, 12, 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 remain 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 $F(P)/F(P = 0.1$ MPa$)$ is the same for all the Fourier components observed, as evidenced in the inset of Fig. 4(a). This result is not only at variance with the behavior of NH_4-$Cr \cdot DMF$, 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, 15, 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 it 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 pieces area follows that of the FBZ. Indeed the observed huge increase of frequency, namely about 45 percent 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 modelled 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 of such tight binding band structure calculations, 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 a significant and simultaneous increase of the three cross sections was observed even though electron-hole orbits 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 (LK) formula[21] which has been reported to satisfactorily account for the data of SdH oscillations linked to closed orbits in q-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 K 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 [22]. 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 non-semiclassical 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 GPa 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 GPa 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
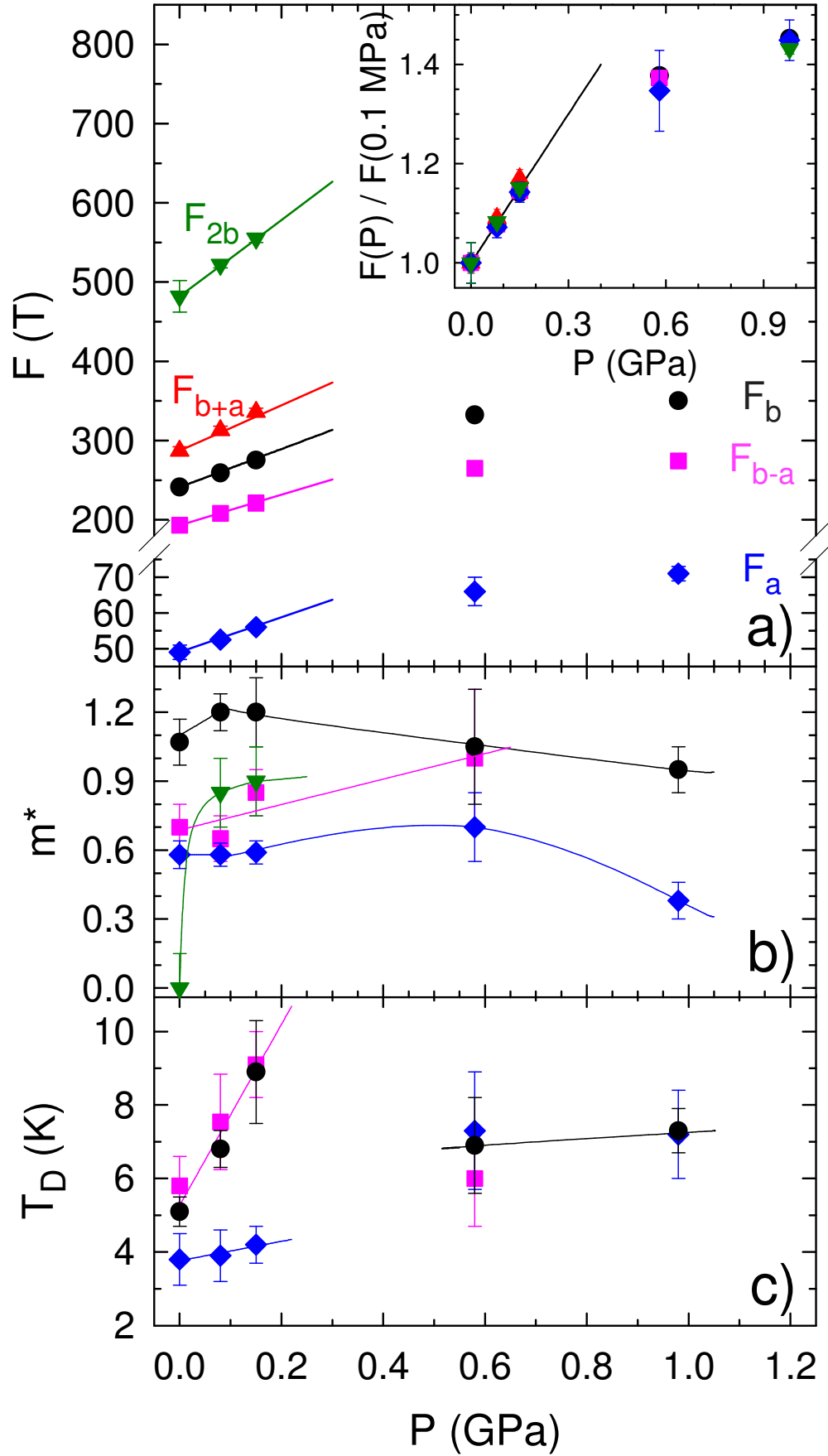
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FIG. 4: (Color online) Pressure dependence of (a) the various Fourier components observed in the oscillatory magnetoresistance, (b) the effective masses and (c) the Dingle temperatures (see text). The inset of (a) displays the pressure dependence of 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 $\kappa = 1$

pressure dependence of the effective masses, the non-monotonous 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 percent at 0.98 GPa. In line with this result, a sizeable 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 orbits compensation as the applied pressure varies. This behavior is at variance with that of both the related compound NH_4-Cr·DMF [9] and the organic compounds that illustrate the model of linear chains of orbits [14, 15, 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 non-monotonous 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 understand the subtle details of the electronic structure of this remarkable family of organic compounds.

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