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Indications for electron localization effects in the strongly 2D organic metal κ-(BEDT-TTF)$_2$I$_3$ as observed by Shubnikov-de Haas experiments

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Abstract. – In the strongly two-dimensional (2D) organic metal κ-(BEDT-TTF)$_2$I$_3$ anomalous damping effects of the magneto-quantum oscillations are reported for the special conditions $\Theta = 0°$ (*i.e.*, $B \perp$ to the conducting planes), $B > 12$ T and $T < 1$ K. A new observed oscillation frequency $F_0 = 13.2$ T is found to control these effects at low Landau level filling factors ν of F_0. This is of special interest since the damping effects are attributed to a localization of electrons which may occur in 2D systems especially at low ν.

In extremely two-dimensional (2D) electronic systems electron localization effects may occur at high magnetic fields and low temperatures [1-3]. In this work we took up the possibility that such localization effects may not only influence the quantum Hall effect (QHE) [4] and the fractional quantum Hall effect (FQHE) [5, 6] but also magneto-quantum oscillation (QO) experiments. We performed Shubnikov-de Haas (SdH) experiments on the strongly 2D organic metal κ-(BEDT-TTF)$_2$I$_3$, where the observed strong damping of the QOs is shown to be connected with a newly found Landau level structure reaching very low filling factors.

The charge-transfer salt κ-(BEDT-TTF)$_2$I$_3$ based on the electron donor BEDT-TTF [**b**is (**e**thylene**d**i**t**hiolo)-**t**etra**t**hia**f**ulvalene] is an organic metal with a superconducting transition at around 4 K [7, 8]. κ-(BEDT-TTF)$_2$I$_3$ consists of 2D conducting BEDT-TTF-sheets, separated by I$_3$-layers. Tight-binding band structure calculations [7] indicate that the Fermi Surface (FS) consists of an elliptical and a circular hole orbit (see insert of fig. 1) corresponding

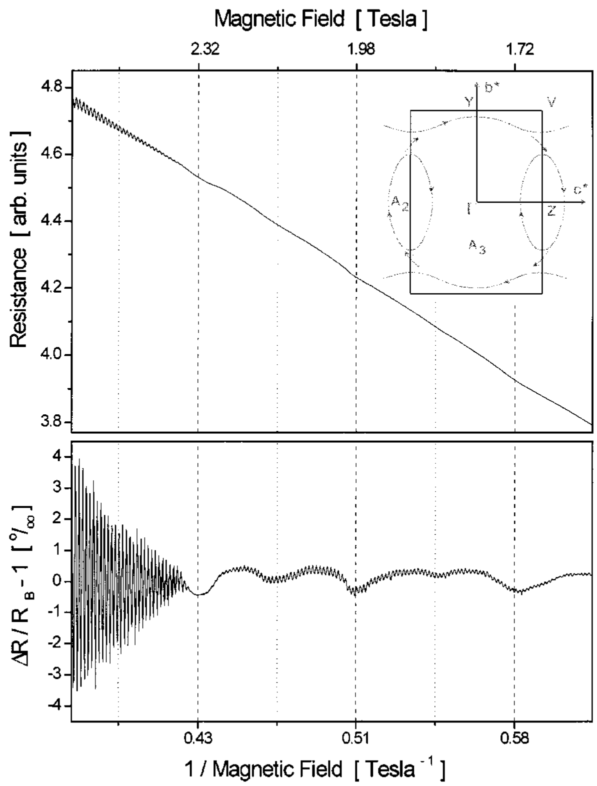

Fig. 1. – Top: SdH signal between 1.6 T and 2.7 T at 0.38 K and $\Theta = 0°$ *vs.* $1/B$. The oscillations with F_0 are observed as dips at the field positions marked by grid lines. Bottom: oscillatory part ΔR of the signal rescaled by the background magnetoresistance R_B. Insert: Fermi surface of κ-(BEDT-TTF)$_2$I$_3$.

to the observed de Haas-van Alphen (dHvA) frequencies $F_2 = 570$ T and $F_3 = 3883$ T, respectively [9].

As shown in refs. [10-12], crystals of this material represent a strongly 2D electronic system with the "warping" or corrugation of the cylindrical FS smaller than $0.35°/_{\circ\circ}$. This corresponds to an anisotropy given by the ratio of the transfer integrals t perpendicular and parallel to the conducting planes of $t_\perp/t_\parallel < 1 \times 10^{-4}$. In spite of the strong two-dimensionality the Lifshitz-Kosevich (LK) theory for QO in 3D systems (cf., *e.g.*, [13]) remains well applicable as long as the magnetic field is *declined* from the orientation normal to the conducting (b, c)-planes, *i.e.*, $\Theta \neq 0°$ (minor deviations can be explained by the oscillation of the chemical potential [14]). However in the special field orientation $B \perp (b, c)$ (*i.e.*, $\Theta = 0°$) strong anomalous damping effects of the QOs with the frequencies F_2 and F_3 are observed for $B > 12$ T and $T < 1$ K, so that the LK theory is not applicable any more [11, 15, 16].

In order to investigate the origin of the damping effects, SdH experiments on high-quality single crystals (Dingle temperature $T_\mathrm{D} < 0.1$ K, see below) were performed at 380 mK $\leq$ T $\leq$ 1.3 K and $B \leq 20$ T for the field orientation $\Theta = 0°$. Besides the well-known frequencies F_2 and F_3 [17] a new QO frequency F_0 is observed above 1.25 T. Figure 1 (top) shows the resistance signal between 1.6 T and 2.7 T. The ratio between the oscillatory part ΔR of the signal and the background magnetoresistance R_B (obtained by a quadratic curve fit) is shown

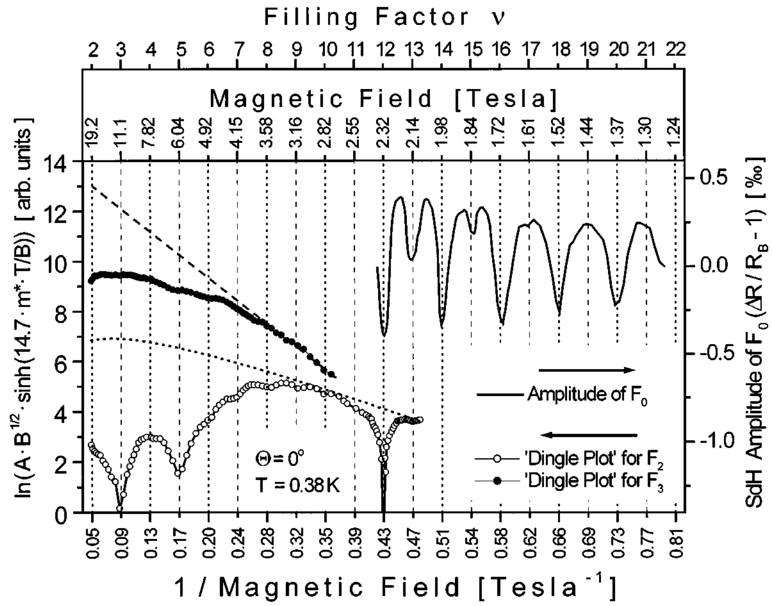

Fig. 2. – Right: SdH oscillations of F_0, indicated by the filling factor ν of F_0 on the top axis. Left: "Dingle plots" of F_2 and F_3, where A are the respective FFT amplitudes (taken from neighbouring narrow field windows and considering $m^*_{F_2} = 1.9 m_\mathrm{e}$ and $m^*_{F_3} = 3.9 m_\mathrm{e}$). Compared to the estimated dashed and dotted curve (taking account for the magnetic breakdown effect) the experimental data show strong damping effects at high fields.

in fig. 1 (bottom). At 2 T the oscillations with F_0 reach a magnitude of $\Delta R/R_\mathrm{B} \approx 0.4^\circ/_{\circ\circ}$. The oscillation period of $\Delta[1/B] = 0.0756\ \mathrm{T}^{-1}$ corresponds to $F_0 = 13.23$ T (note that in this field region spin splitting is observed). Exactly the same value for F_0 is obtained from the slope of a plot of Landau level filling factor ν *vs.* $1/B$ between 1.2 T and 2.35 T (not shown here). The value of F_0 corresponds to an orbit in k-space with an extremal area $A_{\mathrm{ext},F_0} = 0.126\ \mathrm{nm}^{-2}$ which represents a small pocket of about $3.4^\circ/_{\circ\circ}$ of the first Brillouin zone. Up to now such an orbit is neither observed in QO experiments on a κ-phase material of the BEDT-TTF family, nor deduced from tight-binding band structure calculations obtained with unit cell parameters at 300 K [7] as well as at 10 K [18].

In the right part of fig. 2 the SdH amplitudes of F_0 are plotted *vs.* $1/B$ from 1.25 T to 2.5 T. In this field region only a weak field dependence of the amplitudes of F_0 is observed. The so-called "Dingle temperature" T_D was not estimated from this field dependence since the underlying LK theory is known to be not applicable on this compound at $\Theta = 0^\circ$. Only a rough estimation of T_D could be performed via the scattering time τ using the formalism for the SdH effect given in [19]. By this an upper limit $T_\mathrm{D} < 0.1$ K can be obtained which is in agreement with the observation of QO already at such low fields.

Above about 2.4 T F_0 could not be observed directly since the amplitudes of F_2 and F_3 strongly increase with field and dominate over those of F_0. However, the *action* of F_0 onto the amplitudes of F_2 and F_3 can be unambiguously observed up to high fields. Before illustrating this, we recall some pecularities of the anomalous damping effects. Besides their restriction to $\Theta = 0^\circ$, they are found to be strongly field and temperature dependent so that they influence the estimation of the effective mass m^* leading to an apparent field dependence of m^* [11,15].

While up to now these damping effects were illustrated by their temperature dependence, we will focus here on their field dependence. This is done by means of the so-called "Dingle plots" (DPs) of the implicit values of the FFT amplitudes of F_2 and F_3 (see y-axis in fig. 2, left) *vs.* $1/B$. In the standard LK theory the slope of a linear DP is a measure for the $T_{\mathrm{D}} = \hbar/2\pi k_{\mathrm{B}}\tau$. In the present case of magnetic breakdown (MB) the LK theory has to be extended by the so-called "coupled network description" (CND) to take account for the magnetic-field dependence of the MB probabilities (see [13] and refs. therein). According to the LK theory and the CND the DP of F_2 should be sublinear while that of the MB orbit F_3 is expected to be a straight line (the curves are determined by T_{D} and the magnetic breakdown field B_{MB}). The low-field region, which is least influenced by the anomalous damping effects, can only be fitted taking a rather high $B_{\mathrm{MB}} \approx 4$ T and a by far too high $T_{\mathrm{D}} \approx 0.4$ K (see dotted curve in fig. 2 for F_2 and dashed line for F_3). This indicates that already at low fields the behaviour of the QO amplitudes can be only hardly described by the LK theory and the CND. At higher fields the discrepancy becomes much stronger. Above 2 T the DP of F_2 strongly deviates from the estimated curve (note the logarithmic scale). The DP of F_3 shows strong deviations from linearity above about 4 T. By this both DPs indicate strong damping effects at high fields, which cannot be explained by MB effects.

The most important features in the DPs of both F_2 and F_3 are discontinuities in their curvature at high fields. For their understanding the field positions of the minima in the SdH signal of F_0 (where the Fermi energy E_{F} lies just between two successive spin-splitted Landau levels) are marked by grid lines. The discontinuities and minima in the DP of F_2 show the same oscillatory structure as the oscillations with F_0. They occur at the field values where the resistance minima of the oscillations of F_0 are expected (*i.e.*, where E_{F} lies between two successive spin levels of F_0). The same behaviour (however weaker in magnitude) is observed in the DP of F_3. This behaviour is observed in SdH experiments at $\Theta = 0°$ on several crystals. By this F_0 is identified to be directly involved in the damping of the amplitudes of F_2 and F_3. The filling factor ν of F_0, as indicated at the top axis of fig. 2, turns out to be a controlling parameter for these effects. While the amplitude of F_2 is already damped at $\nu < 13$, that of F_3 is first demonstrably damped in the MB regime for $\nu < 7$. The magnitude of the damping effects increases strongly with decreasing ν of F_0. Note that at the highest applied field $\nu = 2$ is reached with only two spin levels of the lowest Landau level of F_0 being occupied below the FS. While F_2 and F_3 are at fairly high filling factors when the damping effects in their amplitudes occur [10, 15, 16], F_0 is already close to the quantum limit (QL), *i.e.* at low ν.

The fact that the damping of the amplitudes of F_2 and F_3 are found to be equidistant in $1/B$ gives rise to the question, whether so-called "warping nodes" caused by a corrugation of the Fermi surface (FS) can be the origin. In fact there are several arguments which contradict this possibility. For shortness only one of them will be discussed here. An assumed corrugation which influences amplitudes of both F_2 and F_3 could only be realized in the part of the FS covered by both orbits in k-space, which is the part enclosing **Z** (see insert of fig. 1). Assuming a certain absolute value of corrugation, this would modify the extremal areas A_{ext,F_2} as well as A_{ext,F_3} by a different percentage. This would result in different field intercepts for the damping of the amplitudes of F_2 and F_3. In contrast to that, the observed field intercepts of the damping effects are identical for both F_2 and F_3 (see fig. 2 left). This shows that the damping effects cannot be attributed to a "warping" of the FS but that they are connected with the new fundamental frequency F_0.

Besides a possible "warping" of the FS a number of other possibilities have been investigated in order to find an origin for the observed damping effects [10, 15]. It was found that magnetic interactions (MI) do not play a considerable role in the field range covered by the experiments and that the FS is stable up to high fields. Moreover, no additional MB is found up to 60 T [14].

Finally also the consideration of spin splitting cannot explain these strong damping effects, especially in view of the very narrow angular range around $\Theta = 0°$ of their occurrence [12, 14, 16, 20]. The oscillatory structure in the damping effects is observed on a number of samples from different batches. A possible twinning of the crystals can be excluded, since a twinning would not restrict the damping effects to $\Theta = 0°$.

Considering the strong 2D character of this compound these damping effects were alternatively interpreted as an indication for a localization of electrons [10, 12, 15]. Such localization effects are a result of electron correlations in 2D systems and can be described in terms of the occurrence of localized so-called quasiparticle excitations with fractional statistics (QPFS), which are generated at magnetic-field values not corresponding to fractional ν [1-3]. They define an (unoccupied) position of a fractional charge in real space. Such excitations are preferably attached to impurities or crystal defects and thus they are *localized* there. It was shown that the electronic system minimizes its energy by screening the quasiparticles by means of an accumulation of electrons in their vicinity. With this the *screening electrons* themselves turn to be *localized*. For sufficiently low disorder, high fields and low temperatures this localization plays a role in the FQHE [5,6]. It may be plausible that the localized screening electrons may not contribute to quantum oscillations in transport any more. This would result in damping effects of the QOs, *e.g.*, as observed.

The central features discussed in connection with the occurrence of electron localization are two-dimensionality, high magnetic fields, low temperatures and the filling factor ν. Two-dimensionality is required since localization effects are shown to be a result of electron correlations, which are present as soon as the electron motion perpendicular to the conducting layers is suppressed by two-dimensionality and their in-plane motion is limited by Landau quantization. Since the strength of such correlations increases with field, electron localization may only occur at high magnetic fields and low temperatures, so that $\hbar\omega_{\mathrm{c}} \gg k_{\mathrm{B}}\mathrm{T}$ becomes an important controlling parameter for these effects. First theoretical publications on QPFS describe electron localization only at low ν or even in the extreme QL, *i.e.*, for $\nu < 1$ (see, *e.g.*, ref. [1]). However later publications present different hierarchial models describing QPFS even at arbitrary ν (see, *e.g.*, ref. [2]). This corroborates with later experiments which show the FQHE already considerably above QL (*e.g.*, in ref. [6] for $\nu < 4$). By this, theory as well as experiments indicate that electron localization is not necessarily restricted to QL.

This suggests to see that the two central conditions, two-dimensionality and $\hbar\omega_{\mathrm{c}} \gg k_{\mathrm{B}}T$ (rather than QL), may be the required conditions for electron localization. In this case localization effects would not be restricted to the filling factor range where the FQHE is directly observed.

In the following it is discussed whether the above-mentioned conditions for electron localization may be fulfilled in the experiments on κ-(BEDT-TTF)$_2$I$_3$. As mentioned above (see also [21, 14]), this compound is one of the strongest 2D systems within the quasi-2D organic charge-transfer salts, so that the required two-dimensionality may be given. However just concerning this aspect it should be stressed that the strong damping effects are restricted to $\Theta = 0°$, *i.e.*, $B \perp (b, c)$, while for angles $\Theta \neq 0°$ nearly normal 3D LK behaviour is observed (see above). For the strong damping at $\Theta = 0°$, we consider that this is the exclusive field orientation where the cyclotron orbits of the electrons lie completely within the conducting (b, c)-planes, so that only at this angle the 2D character can take full effect. For all other angles $\Theta > 0°$ the perpendicular component of Lorentz force compels the electrons to leave the (b, c)-planes. One may doubt whether the electrons of such a strong 2D system may leave their individual planes. However, the temperature dependence of both the resistivity with $I \perp (b, c)$ and the bulk thermopower with $\nabla T \perp (b, c)$, show metallic properties below 300 K (at $B = 0$ T) [8]. This indicates an electron motion perpendicular to the (b, c)-planes regardless of strong two-dimensionality. Now, if an electrical field or even a low temperature gradient may generate such a motion, it is plausible that Lorentz force may do the same at $\Theta \neq 0°$. This means that for a tilted magnetic field the electrons of this 2D layered system are forced to leave the conducting planes for a motion into the third dimension. Thus the intrinsic two-dimensionality with electron localization is hindered on taking full effect at $\Theta \neq 0°$. This would explain the restriction of the strong anomalous damping effects to $\Theta = 0°$.

Focusing onto the role of $\hbar\omega_c/k_B T$ in QO experiments on κ-(BEDT-TTF)$_2$I$_3$, the connection between this ratio and the magnitude of the damping effects was investigated. In ref. [10] it was shown that the damping effects are neither connected with a certain critical field nor with a certain temperature, but indeed determined just by $\hbar\omega_c/k_B T$. For F_3 they typically occur above about $\hbar\omega_c/k_B T > 8$–10, while for F_2 this ratio is about 20. This supports the argument that $\hbar\omega_c/k_B T$ rather than low filling factors may be the controlling parameter for localization effects.

These effects are observed already in field regions with fairly high ν of both frequencies, F_2 and F_3 (*e.g.*, at 12 T there are still about 45 Landau levels of F_2 below the FS). Despite the theoretical possibility of arbitrary ν, it may be questionable whether electron localization can occur at such high ν in the case of κ-(BEDT-TTF)$_2$I$_3$. Just in this context the observation of the new QO frequency F_0 and its connection with the damping effects in the amplitudes of F_2 and F_3 is of special importance. It is plausible to see that a strongly 2D system close to its QL may generate localized states as soon as the Fermi level is situated between its Landau bands. But it is much more surprising that a frequency as F_0 influences the damping effects in the amplitudes of F_2 and F_3 and finally F_0 controls the other oscillations at fields when its own filling factor ν is below 7-8. F_0 forces proximity to quantum limit onto the amplitudes of F_2 and F_3 *despite* the fact that F_2 and F_3 themselves are at fairly high ν.

The presented SdH experiments on the strongly 2D organic metal κ-(BEDT-TTF)$_2$I$_3$ indicate that possible localization effects generated by a low frequency as F_0 close to its QL may take over onto electrons of other parts of the FS, which themselves are far away from QL conditions. This result certainly might give an answer to the question, why damping effects in the amplitudes of F_2 and F_3 are observed at such high ν. Further experiments are necessary concerning the origin of F_0, which at the moment cannot be explained by tight-binding band structure calculations.

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