Fermi-surface topology and the effects of intrinsic disorder in a class of charge-transfer salts containing magnetic ions: $\beta^\prime\prime-(\text{BEDT-TTF})_4[(\text{H}_3\text{O})M(\text{C}_2\text{O}_4)_3]Y$ ($M=$ Ga, Cr, Fe; $Y=$ C$_5$H$_5$N)

A. I. Coldea and A. F. Bangura
Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, United Kingdom

J. Singleton
National High Magnetic Field Laboratory, Los Alamos National Laboratory, TA-35, MS-E536, Los Alamos, New Mexico 87545, USA

A. Ardavan
Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, United Kingdom

A. Akutsu-Sato, H. Akutsu, S. S. Turner, and P. Day
Davy-Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London W1S 4BS, United Kingdom

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We report high-field magnetotransport measurements on $\beta^\prime\prime-(\text{BEDT-TTF})_4[(\text{H}_3\text{O})M(\text{C}_2\text{O}_4)_3]Y$, where $M =$ Ga, Cr, and Fe and $Y =$ C$_5$H$_5$N. We observe similar Shubnikov–de Haas oscillations in all compounds, attributable to four quasi-two-dimensional Fermi-surface pockets, the largest of which corresponds to a cross-sectional area $\approx$ 8.5% of the Brillouin zone. The cross-sectional areas of the pockets are in agreement with the expectations for a compensated semimetal, and the corresponding effective masses are $\approx m_e$, rather small compared to those of other BEDT-TTF salts. Apart from the case of the smallest Fermi-surface pocket, varying the $M$ ion seems to have little effect on the overall Fermi-surface topology or on the effective masses. Despite the fact that all samples show quantum oscillations at low temperatures, indicative of Fermi liquid behavior, the sample and temperature dependence of the interlayer resistivity suggest that these systems are intrinsically inhomogeneous. It is thought that intrinsic tendency to disorder in the anions and/or the ethylene groups of the BEDT-TTF molecules leads to the coexistence of insulating and metallic states at low temperatures. A notional phase diagram is given for the general family of $\beta^\prime\prime-(\text{BEDT-TTF})_4[(\text{H}_3\text{O})M(\text{C}_2\text{O}_4)_3]Y$ salts.

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I. INTRODUCTION

Superconducting charge-transfer salts of the molecule BEDT-TTF have attracted considerable experimental and theoretical interest because of their complex pressure-temperature ($P, T$) phase diagrams, some of which are superphysically similar to those of the “high-$T_c$” cuprates superconductors. For example, the superconducting phase in the $\kappa-(\text{BEDT-TTF})_2X$ salts is in close proximity to an antiferromagnetic insulator and/or Mott insulator; it is also surrounded by other unusual states, including what has been termed a “bad metal.” Recent magnetization, thermal expansion, and resistivity experiments suggest that this “bad metal” may in fact represent the coexistence of Fermi-liquid-like and insulating phases. The presence of both metallic and insulating states at low temperatures is probably related to progressive freezing-in of disorder associated with the terminal ethylene-groups of BEDT-TTF (which can adopt either a “staggered” or “eclipsed” configuration) and/or with the anions, $X$. As yet there is no strong theoretical concurrence on the mechanism for superconductivity in the BEDT-TTF salts, with electron-electron interactions, spin fluctuations, charge fluctuations, and electron-phonon interactions under consideration. It is therefore unclear as to whether the mixed insulating/metallic phase referred to above is a prerequisite for or a hindrance to superconductivity. However, a recent paper has pointed out the sensitivity of the superconductivity in BEDT-TTF salts to nonmagnetic impurities and disorder, suggesting that this is evidence for $d$-wave superconductivity. In order to address some of these issues we have studied a new family of charge-transfer salts of the form $\beta^\prime\prime-(\text{BEDT-TTF})_4[(\text{H}_3\text{O})M(\text{C}_2\text{O}_4)_3]Y$, where $M$ is a magnetic [Cr$^{3+}$ ($S = 3/2$), Fe$^{3+}$ ($S = 5/2$)] or nonmagnetic [Ga$^{3+}$ ($S = 0$)] ion and $Y$ is a solvent molecule such as C$_5$H$_5$N (pyridine), C$_6$H$_5$CN (benzonitrile) or C$_6$H$_5$NO$_2$ (nitrobenzene). $Y$ essentially acts as a template molecule, helping to stabilize the structure; its size and electronegativity affect the unit cell volume, and the amount of disorder in the system. The unit-cell volume is also affected by changing the $M$ ion inside the tris(oxalate) structure. Furthermore, a subsidiary motive for varying $M$ is to search for potential role for magnetism in the mechanism for superconductivity. In this context, the magnetic charge-transfer salt $\lambda-(\text{BETS})_2\text{FeCl}_4$ (Refs. 27,28) has been found to exhibit a field-induced superconducting state in fields $\approx 17$ T. Whilst these data appear to be explicable by the Jaccarino-Peter compensation effect, others have suggested that the Fe ions play some role in the superconducting state. Although there are many detailed differences between individual samples, the $\beta^\prime\prime-(\text{BEDT-TTF})_4[(\text{H}_3\text{O})M(\text{C}_2\text{O}_4)_3]Y$ salts show two distinct classes of low-temperature behavior, superconducting and metallic as summarized in Fig. 1, which shows the interlayer magnetoresistivity $\rho_{22}$ (see Sec. II) of three samples at a temperature $T = 0.50$ K. Salts with $Y =$ C$_6$H$_5$CN (benzonitrile), C$_6$H$_5$NO$_2$ (nitrobenzene), and C$_6$H$_5$N (pyridine) show superconducting transitions at the fields 17.2 T, 15 T, and 11 T, respectively. Samples with C$_6$H$_5$CN (benzonitrile) show superconducting transitions at low fields $< 1$ T, and with C$_6$H$_5$NO$_2$ (nitrobenzene) at high fields $> 20$ T.
trile) or C₆H₅NO₂ (nitrobenzene) are superconductors.²¹,²⁴ At temperatures below the superconducting-to-normal transition, they tend to exhibit negative magnetoresistance, on which is superimposed one or two series of Shubnikov–de Haas oscillations. By contrast, the C₅H₅N (pyridine) salt shows no superconductivity, positive magnetoresistance and a complex series of Shubnikov–de Haas oscillations; this is entirely typical of the salts containing pyridine.

This paper is organized as follows. Experimental details and the behavior of the ß″-(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]Y salts are given in Sec. II whereas the relevant structural details and the behavior of the ß″-(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]C₆H₅N salts are presented in Sec. III, which also outlines the mechanisms which introduce disorder. Magnetoresistance data analyzed in Sec. IV shows the Shubnikov–de Haas oscillations which suggest that there are four Fermi-surface pockets, the areas of which obey the additive relationship expected for a compensated semimetal. The results are discussed in Sec. V and a notional phase diagram for the ß″-(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]Y salts is proposed showing the influence of unit cell size and disorder. A summary is given in Sec. VI.

II. EXPERIMENTAL DETAILS

The ß″-(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]Y samples were grown using electrocrystallization techniques as described elsewhere:²¹–²³ they are generally ~1×1×0.2 mm³ hexagonal platelets or needles. It is possible to deduce the upper and lower faces that are parallel to the highly conducting quasi-two-dimensional planes by visual inspection. Electrical contacts were made to these surfaces by using graphite paint to attach 12 µm platinum wires. The interlayer (magneto)resistance Rₜₜ ≈ Rₜₛ (Ref. 3) was measured using standard four-terminal ac techniques. This involves driving the current and measuring the voltage between pairs of contacts on the upper and lower surfaces.³ Magnetoresistance experiments were carried out in quasistatic fields provided by a superconductive magnet in Oxford and a 33 T Bitter coil at NHMFL Tallahassee. The crystals were mounted in a ³He cryostat which allowed rotation to all possible orientations in magnetic field; sample orientation is defined by the angle θ between the direction of the magnetic field and the normal to the quasi-two-dimensional planes and the azimuthal angle φ. Sample currents between 1 and 25 µA were used at typical frequencies 18–300 Hz. Although around 20 crystals have been studied, in this paper we shall focus on two or three typical samples of each salt; samples are distinguished by the consistent use of a label (e.g., M = Cr, sample A).

III. STRUCTURAL CONSIDERATIONS AND DISORDER IN THE LOW-TEMPERATURE PHASE

A. Structure and bandfilling

Figure 2 shows a projection of the crystal structure along the a axis of the ß″-(BEDT-
TABLE I. Lattice parameters of β''-(BEDT-TTF)$_4$[(H$_2$O)M(C$_2$O$_4$)$_3$]Y salts (C2/c symmetry group) measured around 120 K.

<table>
<thead>
<tr>
<th>M/Y</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>β</th>
<th>V(Å$^3$)</th>
<th>T(K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga/C$_5$H$_7$NO$_2$</td>
<td>10.278</td>
<td>19.873</td>
<td>35.043</td>
<td>93.423</td>
<td>7145.2</td>
<td>100</td>
<td>22</td>
</tr>
<tr>
<td>Cr/C$_5$H$_7$NO$_2$</td>
<td>10.283</td>
<td>19.917</td>
<td>34.939</td>
<td>93.299</td>
<td>7144.4</td>
<td>150</td>
<td>26</td>
</tr>
<tr>
<td>Fe/C$_5$H$_7$NO$_2$</td>
<td>10.273</td>
<td>19.949</td>
<td>35.030</td>
<td>92.969</td>
<td>7169.6</td>
<td>120</td>
<td>26</td>
</tr>
<tr>
<td>Cr/C$_6$H$_7$CN</td>
<td>10.240</td>
<td>19.965</td>
<td>34.905</td>
<td>93.69</td>
<td>7121.6</td>
<td>120</td>
<td>25</td>
</tr>
<tr>
<td>Fe/C$_6$H$_7$CN</td>
<td>10.232</td>
<td>20.043</td>
<td>34.972</td>
<td>93.25</td>
<td>7157</td>
<td>120</td>
<td>21</td>
</tr>
<tr>
<td>Ga/C$_6$H$_7$N</td>
<td>10.258</td>
<td>19.701</td>
<td>34.951</td>
<td>93.366</td>
<td>7051.9</td>
<td>120</td>
<td>22</td>
</tr>
<tr>
<td>Fe/C$_6$H$_7$N</td>
<td>10.267</td>
<td>19.845</td>
<td>34.907</td>
<td>93.223</td>
<td>7101.0</td>
<td>150</td>
<td>23</td>
</tr>
</tbody>
</table>

B. Disorder mechanisms

The β''-(BEDT-TTF)$_4$[(H$_2$O)M(C$_2$O$_4$)$_3$]Y salts are prone to structural disorder primarily because the terminal ethylene groups (−CH$_2$CH$_2$−) of the BEDT-TTF molecules are able to adopt different configurations (twisted/staggered or eclipsed) depending on how they interact with the anion layer.\cite{22,23} Moreover, since C$_5$H$_7$N is smaller than the other templating Y molecules, it does not fill the whole of the hexagonal cavity. Changing the solvent molecule from Y = C$_5$H$_7$NO$_2$ to Y = C$_6$H$_7$N induces additional structural freedom, leading to disorder in around one quarter of the terminal ethylene groups.\cite{23,24} As a result, the ethylene groups are the dominant cause of both static and dynamic disorder at high temperatures, and static disorder below 90 K, the temperature around which the two different configurations are "frozen in,"\cite{22} as found in the α-phase salts.\cite{11,12,13}

The C$_6$H$_7$N molecule can also introduce disorder by adopting two different orientations in the anion layer. By contrast, the other solvents, Y = C$_5$H$_7$NO$_2$ and Y = C$_6$H$_7$CN, lock into one ordered configuration.\cite{22}

Having discussed the various mechanisms for disorder, we shall now examine how disorder is manifested in the resistivity of the samples.

C. The temperature dependence of the resistivity

The temperature dependence of the normalized interplane resistance, $R_{zz}(T)/R_{zz}(286 K)$, for five typical β''-(BEDT-TTF)$_4$[(H$_2$O)M(C$_2$O$_4$)$_3$]C$_2$H$_7$N samples is shown in Fig. 3; for comparison, equivalent data for M = Ga, Y = C$_5$H$_7$NO$_2$ are displayed in the inset. Whilst many of the features in the data are quite sample or cooling-rate dependent, all of the samples (M = Ga, Cr, Fe) are consistent in displaying a transition from metallic-type behavior (positive $dR_{zz}/dT$) to insulating-type behavior (negative $dR_{zz}/dT$) at $T_{MI} \approx 150$ K. Values of $T_{MI}$ are listed in Table II.

The minimum in resistance at $T_{MI}$ may represent the onset of a possible form of density-wave state. Quasi-two-dimensional conductors in which the Fermi surface is completely gapped by a density wave exhibit a resistivity that rises by several orders of magnitude as the temperature falls, as found for (BEDT-TTF)$_3$Cl$_2$H$_2$O (Ref. 34). By contrast, the resistance of the β''-(BEDT-TTF)$_4$[(H$_2$O)M(C$_2$O$_4$)$_3$]C$_2$H$_7$N salts (shown in Fig. 3) only increases by a factor of −1.5–3. The latter behavior is similar to that of quasi-two-dimensional conductors in which a density wave only partially nests the Fermi surface, leaving residual Fermi-surface pockets as found for the Mo bronzes\cite{25} and α-(BEDT-TTF)$_2$KHg(SCN)$_4$.\cite{36} In such
cases, the conductivity is a convolution of a metallic component, typically varying as a power law in temperature (due to the unnested portions of the Fermi surface) and an insulating component with an activated temperature dependence (due to the energy gap of the density-wave state). The exact form of the resistivity depends on which component dominates. An alternative scenario that could potentially lead to similar resistivity behavior is the segregation of the sample into insulating and metallic domains, as also proposed for the \( k \)-\((\text{BEDT-TTF})_2X \) salts (see Ref. 9 and references therein).

In Sec. IV we shall see that the Fermi-surface topology is more complicated than that predicted by the band structure calculations, which may be additional evidence that the transition at \( T_{\text{MI}} \) is associated with the formation of a density wave.

All of the \( Y = \text{C}_6\text{H}_5\text{N} \) crystals also consistently exhibit a feature at a lower temperature, \( T_p \approx 60-80 \) K (shown in Fig. 3). However, depending on the sample, this is manifested either as a change from insulating- to metallic-type behavior (\( M = \text{Ga} \), all samples; \( M = \text{Cr} \), sample B; \( M = \text{Fe} \) sample A), or as merely a shoulder on a resistivity that continues to increase with decreasing temperature (\( M = \text{Cr} \), sample A; \( M = \text{Fe} \), sample B). Such a feature is also indicative of a number of contributions to the conductivity acting in parallel. For example, it is possible to reproduce the behavior of \( M = \text{Cr} \), sample B, between 60 K and \( T_{\text{MI}} \) using a resistor network model that combines metallic (resistivity \( \propto T^n \), with \( n \approx 1-2 \)) and thermally-activated components \( \propto \exp(E_A/k_B T) \) (see also Ref. 38). Although the exact values obtained depend on the details of the resistor network model used, the values of \( E_A \) obtained from fitting data between \( T_p \) and \( T_{\text{MI}} \) show a consistent increase from \( M = \text{Fe} \) \( (E_A \approx 170-220 \) K) through \( M = \text{Ga} \) \( (E_A \approx 300 \) K) to \( M = \text{Cr} \) \( (E_A \approx 400-500 \) K), i.e., the activation energy \( E_A \) increases with decreasing unit cell volume (see Table I).

The features discussed thus far do not seem to depend on sample cooling rate. By contrast, in all five \( M = \text{Cr} \) samples studied, there is an additional peak in the resistivity at \( 400-500 \) K, \( T_{\text{MI}} \) and the temperature of which both depend on the sample cooling rate. By contrast, samples with \( M = \text{Ga} \), \( Fe \) only exhibit a small inflection at \( T_{\text{MI}} \). At the lowest temperatures, \( R_{zz}(T)/R_{zz}(286 \) K) values ranging from around 0.5 (\( M = \text{Fe} \), sample A) to 7 (\( M = \text{Cr} \), sample A) are obtained (Fig. 3); the actual value reached seems more dependent on the sample batch rather than the identity of the \( M \) ion (e.g., compare \( M = \text{Cr} \), samples A and B). This points to a prominent role for disorder in determining the low-temperature resistive behavior of the \( \beta''-\text{(BEDT-TTF)}_4[(\text{H}_2\text{O})\text{M(C}_2\text{O}_4)_3]_2\text{C}_6\text{H}_5\text{N} \) salts.

As \( T \) tends to zero, the resistivity of \( M = \text{Cr} \) sample B drops quite sharply, although zero resistance is never attained. A similar drop in resistance for \( M = \text{Ga} \) below 2 K, which was destroyed by an applied field of 0.16 T, was previously reported as evidence for superconductivity. However, none of the \( M = \text{Ga} \) samples studied in the present work exhibited such a feature. This is possibly related to the recent observation that superconductivity in the \( \text{BEDT-TTF} \) salts is very sensitive to disorder and nonmagnetic impurities.

On the other hand, a robust superconducting state is stabilized below \( T_c = 7 \) K for \( M = \text{Ga} \) and \( Y = \text{C}_6\text{H}_5\text{NO}_2 \) [as shown in the inset of Fig. 3(a)] and for \( M = \text{Fe} \) and \( Y = \text{C}_6\text{H}_5\text{CN} \) [Fig. 1(b) and Ref. 21]. For completeness, note that both of the latter superconducting salts show a single metal-insulator transition [see inset of Fig. 3(a)] similar to that observed at \( T_{\text{MI}} \) in the \( Y = \text{C}_6\text{H}_5\text{N} \) salts. However, for the superconducting salts \( T_{\text{MI}} \) seems somewhat sample dependent; values ranging from \( T_{\text{MI}} = 68 \) K (Ref. 24) to \( T_{\text{MI}} \approx 160-180 \) K (Ref. 22) have been reported for the \( M = \text{Ga} \), \( Y = \text{C}_6\text{H}_5\text{NO}_2 \) salt.

To summarize this section, the resistivities of the \( \beta''-\text{(BEDT-TTF)}_4[(\text{H}_2\text{O})\text{M(C}_2\text{O}_4)_3]_2\text{C}_6\text{H}_5\text{N} \) salts exhibit a complex temperature and sample dependence (Fig. 3). The minimum in \( R_{zz} \) at \( T_{\text{MI}} \) is an intrinsic feature of all samples,

FIG. 3. Temperature dependence of the normalized interplane resistance \( R_{zz}(T)/R_{zz}(286 \) K) in zero magnetic field for different samples of \( \beta''-\text{(BEDT-TTF)}_4[(\text{H}_2\text{O})\text{M(C}_2\text{O}_4)_3]_2\text{C}_6\text{H}_5\text{N} \) with (a) \( M = \text{Ga} \) (sample A) (the inset shows \( \beta''-\text{(BEDT-TTF)}_4[(\text{H}_2\text{O})\text{M(C}_2\text{O}_4)_3]_2\text{Y} \) with \( M = \text{Ga} \), \( Y = \text{C}_6\text{H}_5\text{NO}_2 \) for comparison), (b) \( M = \text{Cr} \) (sample B) [the inset shows \( M = \text{Cr} \) (sample A)] and (c) \( M = \text{Fe} \) (samples A and B). The arrows indicate the temperatures described in the text.
and, by analogy with resistivity data from other quasi-two-dimensional systems, probably indicates the onset of a density-wave state. The form of the resistivity at temperatures just below this suggests metallicity and thermally-activated contributions to the conductivity acting in parallel. At lower temperatures, the behavior of the samples is much more divergent, with \( R_{\perp}(T)/R_{\perp}(286 \text{ K}) \) values spread between 0.5 and 7 indicating an additional thermally-activated process (or processes) which is (are) probably dependent on the degree of disorder within the samples. By contrast, the temperature-dependent resistivity is rather simpler for the \( \beta^\alpha-(\text{BEDT-TTF})_2[(\text{H}_2\text{O})\text{M}(\text{C}_2\text{O}_4)_3]Y \) salts with \( Y=\text{C}_6\text{H}_5\text{NO}_2 \) and \( Y=\text{C}_6\text{H}_5\text{CN} \). The difference may be attributable to the higher degree of structural disorder possible in the \( Y=\text{C}_6\text{H}_5\text{N} \) salts, resulting from the less constrained ethylene groups and greater rotational freedom of the \( Y \) molecule.\(^{22}\) Similar electronic properties determined by the disordered anions (that lock into two different configurations) were found for \( \beta^\alpha-(\text{BEDT-TTF})_2\text{SF}_2\text{CHFCF}_2\text{SO}_3 \) for which resistivity shows a metal-insulating transition near 190 K, compared with the superconducting compound, \( \beta^\alpha-(\text{BEDT-TTF})_2\text{SF}_2\text{CF}_2\text{CF}_2\text{SO}_3 \) (\( T_c=5.4 \text{ K} \), which has ordered anions.\(^{40}\)

### IV. LOW-TEMPERATURE MAGNETORESISTANCE

#### A. Shubnikov–de Haas frequencies and Fermi-surface pockets

Figure 4 shows the field dependence of \( R_{zz} \) for several samples of \( \beta^\alpha-(\text{BEDT-TTF})_2[(\text{H}_2\text{O})\text{M}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{N} \) with \( M=\text{Ga} \), \( \text{Cr} \), and \( \text{Fe} \) measured at several temperatures between 0.50 K and 4.2 K. All samples exhibit Shubnikov–de Haas oscillations superimposed on a positive background magnetoresistance. Several frequencies are visible in varying proportions. For example, the dominant series of oscillations for \( M=\text{Cr} \) is of relatively low frequency, whereas the dominant oscillations for \( M=\text{Ga} \), \( \text{Fe} \) are of a higher frequency. The amplitude of the oscillations varies slowly with temperature, suggesting the corresponding effective masses are not very large.\(^{41}\)

No clear signature of superconductivity was observed either in the field, angle or temperature dependence of \( R_{zz} \). The field, angle or temperature dependence of \( R_{zz} \) shows a metal-insulating transition near 190 K, compared with the superconducting compound, \( \beta^\alpha-(\text{BEDT-TTF})_2\text{SF}_2\text{CF}_2\text{CF}_2\text{SO}_3 \) (\( T_c=5.4 \text{ K} \), which has ordered anions.\(^{40}\)

\[
\frac{\Delta R_{zz}}{R_{zz}} = \frac{R_{zz} - R_{bg}}{R_{zz}}.
\]

Here \( R_{bg} \) is the slowly-varying background magnetoresistance approximated by a polynomial in \( B \). As long as \( \Delta R_{zz}/R_{zz} \ll 1 \), \( \Delta R_{zz}/R_{zz} \approx -\Delta \sigma_{zz}/\sigma_{bg} \) where the \( \sigma \) are equivalent terms in the conductivity\(^{41,42}\) [\( \Delta \sigma_{zz}/\sigma_{bg} \) is the quantity dealt with in the Lifshitz-Kosevich (LK) treatment of Shubnikov–de Haas oscillations\(^{43}\) used to extract effective masses and the scattering time of the quasiparticles]. The \( \Delta R_{zz}/R_{zz} \) values were processed using both the maximum entropy method (MEM) (filter size=200) (Ref. 43) and the fast Fourier transform (FFT) usually over the field range 7–32 T. The two methods give similar representations of the frequencies present, as shown in the right panel of Fig. 4.

We identify four frequencies which occur consistently in all of the transforms over the complete temperature range (see Figs. 4 and 5), and are similar in all \( \beta^\alpha-(\text{BEDT-TTF})_2[(\text{H}_2\text{O})\text{M}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{N} \) samples with \( M=\text{Ga} \), \( \text{Cr} \), and \( \text{Fe} \). These frequencies are \( F_a \approx 38–50 \text{ T} \), \( F_{\beta} \approx 86–98 \text{ T} \), \( F_{\gamma} \approx 293–308 \text{ T} \), and \( F_{\delta} \approx 345–353 \text{ T} \); the ranges cover the values observed in the different samples (see Table II). In addition, two other peaks, with frequencies \( F' \approx 190–206 \text{ T} \) and \( F'' \approx 236–248 \text{ T} \), were observed less consistently in the transforms. The peak at very low frequencies (\( \approx 20 \text{ T} \)) is an artifact of the subtraction of the background magnetoresistance; its position and amplitude depends on whether \( R_{bg} \) was approximated by a second or
regions of magnetic field pinned to relatively sharp Landau levels over restricted re-
turns, we attribute the complex mixed harmonics are generated. Another possibility is that the chemical potential becomes 
likely explanation. The peak seen occasionally in the transforms at a fre-
corresponds to the maximum entropy method (top solid lines) and fast Fourier transform 
where a plethora of small Fermi surface pockets results 
oscillations due to the two “parent” orbits. The fact that, 
stimulated with increasing temperature than any of the 
likely to result from frequency-mixing effects in quasi-two-dimensional metals 
likely to be a second harmonic of the oscillations due to the 
reduce the oscillations at \( F'' \) are suppressed much more rapidly with increasing temperature than any of the possible parent frequencies suggests that CPOE is the more likely explanation.

At this point, it is worth recalling that the band structure calculations predict only two Fermi-surface pockets, of equal area, whereas the experimental data suggest four pockets. There are several potential reasons for this difference. First, although extended-Hückel calculations often give a reasonable qualitative description of the Fermi surfaces of many BEDT-TTF salts, the \( \beta'' \) phases have proved problematic; slight differences in input parameters seem to result in differing predicted topologies [as in the case of \( \beta''-(BEDT-TTF)_2AuBr_2 \) (Ref. 50)]. Secondly, the band structure calculations are based on structural measurements carried out at relatively high temperatures; contraction of the lattice could result in changes in the relative sizes of the various transfer integrals, leading to shifts in the bands with respect to the chemical potential. Finally, the presence of a series of pockets could be a consequence of a Fermi surface reconstruction determined by a possible change-density wave at \( T_{Mi} \) of the \( \beta''-(BEDT-TTF)_2(H_2O)M(C_2O_4)_3 \) salts.

Similar Fermi-surface reconstructions have been suggested for other \( \beta'' \) salts, including \( \beta''-(BEDT-TTF)_2AuBr_2 \) (where a plethora of small Fermi surface pockets results), \( \beta''-(BEDO-TTF)_2ReO_4H_2O \) (Ref. 33) and \( \beta''-(BEDT-TTF)_2SP_3CH_2CF_2SO_3 \), where it appears that the Fermi-surface nesting is more efficient.
Although the Shubnikov–de Haas oscillation frequencies are generally similar for the three $\beta''-(\text{BEDT-TTF})_4[(\text{H}_2\text{O})\text{M(C}_2\text{O}_4)_3]\text{C}_5\text{H}_5\text{N}$ salts, there are detail differences depending on the ion $M$. For example, the $F_\alpha$ frequency of the $M=\text{Cr}$ salts is consistently lower than that of the $M=\text{Ga}$ and $\text{Fe}$ compounds. The appearance of the Shubnikov–de Haas oscillations is also affected by the $M$ ion; the highest frequency oscillations ($F_\delta$) dominate the spectra of the compounds with $M=\text{Ga}$ and $\text{Fe}$, whereas that of the compounds with $M=\text{Cr}$ is dominated by the low frequency, $F_\alpha$ (see Figs. 4 and 5). This may be related to relatively small differences in the scattering mechanisms, rather than some intrinsic effect of the $\text{Cr}^{3+}$ ion. Examples of similar effects were observed in magnetoresistance data for the low-field, low-temperature phases of $\alpha-(\text{BEDT-TTF})_2\text{Cr}(\text{H}_3\text{O})_3$ and $\alpha-(\text{BEDT-TTF})_2\text{TlHg( SCN)}_4$.\footnote{53}

The relative amplitudes of the various Shubnikov–de Haas oscillation series vary from sample to sample, and batch to batch, with some series being undetectable in what is presumed to be the lower-quality samples, whilst being relatively strong in other crystals (see Secs. 1 and 5 of Ref. 53 and references cited therein). A second example is $\beta''-(\text{BEDT-TTF})_2\text{AuBr}_2$ for which comparison of the magnetic-quantum oscillation data from Refs. 50, 54–56 shows that the relative amplitudes of the lower and higher-frequency oscillation series varies considerably from sample to sample.

For completeness, we mention that the superconducting salts, $Y=\text{C}_6\text{H}_5\text{NO}_2$ with $M=\text{Ga}$ and $\text{Cr}$ and $Y=\text{C}_6\text{H}_5\text{CN}$ with $M=\text{Fe}$ show only two frequencies, with the low frequency, in the range 47–55 T and the high frequency in the range 190–238 T.\footnote{54}

**B. Effective masses**

A two-dimensional Lifshitz-Kosevich formula\footnote{57} has been used to extract the effective masses $m^*$ of the various Fermi-surface pockets, where possible. The Fourier amplitude of each series of quantum oscillations is given by

\[ A_{2D} \propto R_T R_D R_S, \]  

where $R_T = X/\sinh(X)$ is the temperature damping term, $R_D = \exp(-X(T_D/T))$ is the Dingle term ($T_D$ is the Dingle temperature) due to the broadening of the Landau levels caused by internal inhomogeneities, and $X = 14.694(T/B)(m^*/m_e)$.\footnote{58, 59}

The spin-splitting term $R_S = \cos((\pi/2) [(g^* m^*/m_e) / \cos(\theta)])$, where $g^*$ is the effective $g$ factor, is not considered here and it will be the subject of a future publication.\footnote{60}

The Fourier amplitudes obtained over a field window 7–32 T were fitted to the $R_T$ term of Eq. (2) using around 8 different temperatures covering the range 0.5–4.2 K (for consistency, a polynomial of the same order was used to subtract the background magnetoresistance for each sample). Figure 6 shows typical amplitudes and corresponding fits for the $F_\gamma$ series. All of the $m^*$ values obtained for the different Fermi-surface pockets are listed in Table II.

To the limit of experimental error the effective masses for the $\gamma$ and $\delta$ pockets of the three salts are close to the free-electron mass, $m_e$. Whilst such values are light compared to...
BEDT-TTF salts, they are not without precedent in charge-M
whereas in the case of the TTF)\_2\ SF\_5\ CH\_2\ CF\_2\ SO\_3
different somewhat smaller for the other hand, the effective mass in
fluctuation effects enhanced the effective mass. On the
transfer salts. The effective masses of the
d that the magnetic moment on the 3
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any effect on the effective masses. This is in contrast to the
typical masses observed in (BEDT-TTF)\_4\ Cr
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FIG. 6. (a) Temperature dependence of the Fourier amplitude of the F\_x frequency in \beta'^-(BEDT-TTF)\_4\{\(H\_2O\)M(C\_2O\_4\)_3\}C\_5\ H\_5\ N for different M. The solid line is a fit to the data (points) using the R\_f term of Eq. (2) (solid line). The field window was \(\Delta B=7–32\ T\) for the samples with M = Cr (sample A) and M = Fe (sample A) and \(\Delta B=12–32\ T\) for the sample with M = Ga (sample A). Data for different M are offset for clarity. (b) The corresponding Dingle plots (ln[A\_2D sinh(X)/X] versus 1/B, where X = 14.695 m\_e T/B) for the F\_x frequency at T~0.5 K. The solid line is a linear fit to the data (points). The field windows overlapped by less than ~30%.
the typical masses observed in \beta'^-(BEDT-
TTF)\_2\ SF\_2\ CH\_3\ CF\_2\ SO\_3 (Ref. 52) or the \kappa- and \alpha-phase
BEDT-TTF salts,\textsuperscript{42} they are not without precedent in charge-
transfer salts.\textsuperscript{33,34} The effective masses of the
alpha pocket are somewhat smaller for the M = Cr and Fe salts (m\_e ~ m\_e/2) whereas in the case of the M = Ga salt, the \alpha effective mass seems rather larger. Apart from this, there is yet no evidence that the magnetic moment on the \(3d\) ions M = Cr and Fe has any effect on the effective masses. This is in contrast to the study on \kappa-(BETS)\_2\FeCl\_4, where it was proposed that spin fluctuation effects enhanced the effective mass.\textsuperscript{58} On the other hand, the effective mass in \lambda-(BETS)\_2\Fe\_2\Ga\_1\_x\Cl\_x is not very much affected by the presence of the magnetic ions but it is much larger than that in our compounds [~4m\_e (Ref. 30)].

C. Dingle temperatures
A further insight into the properties of our samples is
given by the Dingle temperature, T\_D, which can be used to
parametrize the scattering rate\textsuperscript{20,41} the spatial potential fluctuations or a combination of the two.\textsuperscript{3,20} The T\_D values for the \delta pocket are listed in Table II; typical fits are shown in Fig. 6(b). Note that T\_D is consistently larger for the compounds with M = Fe (T\_D~4 K, corresponding to a scattering time of \(\tau \approx 0.3\ ps\) and is smaller for the salts with M = Cr (T\_D~1.5 K, corresponding to \(\tau \approx 0.8\ ps\). This difference is visible even in the raw data, with fewer oscillations being visible for the M = Fe salt. As both compounds contain mag-
netic ions some form of magnetic scattering (such as spin-
disorder scattering\textsuperscript{39}) may be excluded as the reason for
these differences and the degree of nonmagnetic disorder
present, determined by the anions and the solvent is more likely to be the determining factor.
Interestingly, there is no apparent correlation between the values of R\_zz(T)/R\_zz(286 K) (see Fig. 3) and the Dingle
temperatures for each sample (Table II). For example, the sample with the largest R\_zz(T)/R\_zz(286 K) (\(T \approx 7\)) (M = Cr, sample A) has a T\_D which is a factor 2.2 smaller than that of the sample with the smallest R\_zz(T)/R\_zz(286 K) (\(T \approx 0.5\)) (M = Fe, sample A). The Dingle temperatures extracted from Shubnikov–de Haas oscillations suggest that M = Cr, sample A is of higher quality, whereas M = Fe, sample A has the lower resistivity ratio. This strongly suggests that the samples are not of a uniform single phase at the lowest tem-
peratures but their overall properties probably represent a mixture of metallic and insulating domains. Within this
mixture, the metallic domains may well be of quite high quality, as evidenced by the observation of Shubnikov–de Haas os-
cillations with a reasonably small Dingle temperature.
Further support for such an idea is given by comparing the values of R\_zz(10 K)/R\_zz(286 K) ~ 0.5–7 seen in
Fig. 3 with R\_zz(10 K)/R\_zz(286 K) ~ 0.001 obtained for the unambiguously metallic salt \beta'-(BEDT-TTF)\_2\Fe.\textsuperscript{60} This great disparity is an indication that a large fraction of the quasiparticles in the \beta'^-(BEDT-
TTF)\_4\{\(H\_2O\)M(C\_2O\_4\)_3\}C\_5\ H\_5\ N salts that are mobile at room temperature do not contribute to the bulk conductivity at low temperatures. This loss of charge carriers is presum-
ably related to the suggested density-wave transition at T\_Ml (which perhaps gaps part of the Fermi surface) and to the
subsequent “freezing out” of further quasiparticles (sug-
gested by the negative dR\_zz/dT values seen for several of the samples as shown in Fig. 3) caused by disorder at lower temperatures.
In summary, it is most likely that the Dingle temperature
gives a gauge of only the quality of the metallic regions of
the samples, whereas the R\_zz(T)/R\_zz(286 K) values are indi-
cative of the relative proportion of insulating and metallic
domains within the crystals.
V. DISCUSSION: PROPOSED PHASE DIAGRAM

In the previous sections we have described the transport properties of $\beta''$-(BEDT-TTF)$_4$[(H$_3$O)M(C$_2$O$_4$)$_3$]$_Y$ salts exhibiting a metal-insulator transition at $T_{MI}$, as well as the coexistence of metallic and density-wave-like states, such as Shubnikov–de Haas oscillations, indicative of reasonably long scattering times and mean-free paths $\sim$ 300 Å and hence low disorder. This suggests that the Shubnikov–de Haas and cyclotron-resonance data are only informative about the disorder in the metallic regions of a sample.

VI. SUMMARY

In conclusion we have studied the Fermi-surface topology of $\beta''$-(BEDT-TTF)$_4$[(H$_3$O)M(C$_2$O$_4$)$_3$]$_Y$, with $M = $ Ga, Cr, Fe and $Y = $ C$_6$H$_5$N. All of the studied salts exhibit similar Shubnikov–de Haas–oscillation spectra, which we attribute to four quasi-two-dimensional Fermi-surface pockets. The cross-sectional areas of the pockets are in agreement with the expectations for a compensated semimetal, and the corresponding effective masses are $\sim m_e$, rather small compared to...
to those of other BEDT-TTF salts. Apart from the case of the smallest Fermi-surface pocket, varying the $M$ ion seems to have little effect on the overall Fermi-surface topology or on the effective masses.

Despite the fact that all samples show quantum oscillations at low temperatures, indicative of Fermi liquid behavior, the sample and temperature dependence of the interlayer resistivity lead us to suggest that these systems are intrinsically inhomogeneous. It is possible that the intrinsic tendency to disorder in the anions and/or the ethylene groups of the BEDT-TTF molecules leads to phase separation of the samples into insulating and metallic states.

Based on the data in this paper, and those from Ref. 24, we have constructed a notional phase diagram for the $\beta''$-(BEDT-TTF)$_2$[(H$_3$O)M(C$_2$O$_4$)$_2$]Y salts which exhibits some similarities with that of the $\kappa$-(BEDT-TTF)$_2$X superconductors.

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\*Present address: Department of Material Science, Graduate School and Faculty of Science, Himeji Institute of Technology, Hyogo 678-1297, Japan.
†Present address: Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo 152-8552, Japan.
\* Present address: Department of Material Science, Graduate School and Faculty of Science, Himeji Institute of Technology, Hyogo 678-1297, Japan.

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37 V. Dobrosavljevic, D. Tanaskovic, and A.A. Pastor, cond-mat/0206529 (unpublished).

38 An additional activated component must be introduced to reproduce the data for $M=\text{Cr}$ sample A over the same temperature region.


44 A.I. Coldea et al. (unpublished).


49 Note that Shoenberg’s mechanism for frequency-mixing effects due to the oscillatory magnetic field within the sample (Ref. 42) is not generally feasible in BEDT-TTF salts, because the low quasiparticle density results in a rather small oscillatory magnetization (Ref. 50). In this context, the $M$ ion is also unimportant; our compounds do not show any long range magnetic order down to 0.5 K (Ref. 51).


61 V. Laukhin and A.-K. Klehe (private communication).


65 For instance there are no $\beta$-compounds available with a large enough unit cell to check whether the low-pressure, low-temperature state from which superconductivity emerges is a Mott insulator, as in the case in the $\kappa$-phase salts.