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The low-temperature phase of α-(BEDT-TTF)$_2$KHg(SCN)$_4$: II. Pressure dependence of the Shubnikov–de Haas oscillations

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Abstract. The magnetoresistance of α-(BEDT-TTF)$_2$MHg(SCN)$_4$ (where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene and M = NH_4 or K) has been studied under pressures of up to 14.8 kbar and for temperatures down to 0.7 K. The $\sim$671 T (α) and $\sim$4270 T (β) Shubnikov–de Haas oscillations observed in the ambient pressure magnetoresistance of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ persist to the highest pressure while the other quantum oscillatory frequencies are removed under pressure. A strong second-harmonic component of the α-frequency oscillations is observed on the raw data at 1 bar and is initially suppressed by pressure but returns above $\sim$9 kbar. Furthermore, in the salt α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ a similar pronounced second harmonic of the quantum oscillations has been observed at the highest pressures. The origins of these features of the data are discussed in the context of current models of the Fermi surfaces of these materials.

1. Introduction

This paper and the preceding one ([1] hereafter referred to as I) are concerned with the magnetotransport properties of the organic charge-transfer salts α-(BEDT-TTF)$_2$MHg(SCN)$_4$, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene and M = K or NH_4 [2]. Despite the similarity of the crystal structures of these salts they possess markedly different ground states; superconductivity in the case of M = NH_4 [3] and what is believed to be a spin-density-wave (SDW) state in M = K [4, 5]. The high quality of crystals that have been synthesized has allowed the Fermi surfaces of these materials to be studied in detail via the Shubnikov–de Haas (SdH) and de Haas–van Alphen (dHvA) effects ([6–9] and references therein).

These studies have shown that the magnetoresistance of the M = NH_4 salt is relatively simple, exhibiting a single series of SdH oscillations [6]. It is believed that in this case the Fermi surface consists of a single quasi-two-dimensional (Q2D) pocket and a pair of warped quasi-one-dimensional (Q1D) sheets. However, in, for example, the M = K salt the magnetoresistance contains multiple SdH frequencies and also exhibits phenomena such as negative magnetoresistance and hysteresis between rising and falling field sweeps [8, 9]. In this case it is proposed that the Q1D sheets of the simple Fermi surface that exists for M = NH_4 have nested to give a complicated reconstructed Fermi surface with strongly

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corrugated Q1D sheets and further Q2D pockets [10]. By applying magnetic fields in excess of $B_K \sim 23$ T (the so-called 'kink field') or by raising the temperature above $T_N \sim 8$ K the M = K salt reverts to a behaviour similar to that of the M = NH_4 material [8, 11]. It is believed that this is due to destruction of the SDW state.

In this paper (paper II) we report measurements of the SdH effect in both α-(BEDT-TTF)$_2$KHg(SCN)$_4$ and α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ under hydrostatic pressures of up to 14.8 kbar and for temperatures in the range 0.7–4.2 K. A comprehensive description of recent high-pressure studies of the α-phase salts is to be found in [12]. It has been suggested that the application of pressure to α-(BEDT-TTF)$_2$KHg(SCN)$_4$ removes the SDW state at $P_c \sim 5$ kbar, leading to a reversion to the unnested normal metallic state [12–14] Fermi surface, similar to that found in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$. This proposed reconstruction of the Fermi surface at P_c has been associated with a number of changes observed in the magnetoresistive properties of the material, namely removal of the large hump in the background magnetoresistance of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ [13], the elimination of the large second-harmonic content from the waveform of the main SdH oscillation series [12] and a transition in the angle-dependent magnetoresistance oscillations (AMROs) from a Q1D character to a Q2D form [14]. Evidence, in this paper, leads us to suggest that P_c may not represent the destruction of the SDW at all. It has also been suggested that since α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ has a unit cell volume of 2010 Å^3 in contrast to 1997 Å^3 for α-(BEDT-TTF)$_2$KHg(SCN)$_4$ it might be possible to induce a density-wave state in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ by the application of pressure [12]. For these reasons detailed studies of the high-pressure states of these materials are desirable.

2. Experimental method

Single crystals of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ and α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ were prepared by standard electrochemical techniques [4]. Gold pads were evaporated to a depth of 100 nm upon the faces of the samples corresponding to the crystalline ac planes. Silver-loaded epoxy was then used to bond 25 μm diameter gold wires to these pads.

The samples were (successively) mounted in a non-magnetic clamp pressure cell so that their conducting ac planes were perpendicular to the magnetic field. Petroleum spirit was employed as the pressure medium and pressure was applied at room temperature using a hydraulic press. The pressure cell was then mounted in a custom built ^{3}He cryostat which allowed temperatures as low as $\sim$0.7 K to be reached. The cell was radiatively cooled from room temperature to 77 K over a 12 h period, in order to ensure that the pressure applied to the sample remained hydrostatic, after which the pressure in the cell was measured. This was achieved via a four-wire measurement of the resistance of a manganin pressure gauge adjacent to the sample within the cell that had a well characterized temperature and pressure dependence. Further cooling to 4.2 K then occurred, over a $\sim$3 h duration, after which the pressure was measured again. Throughout the experiment the pressure values measured at 77 K were found to be consistent with those measured at 4.2 K. The mechanical strength of the cell limited the maximum pressure attainable to 15 kbar at 4.2 K.

Measurements were made of the magnetoresistance of the samples in fields of up to 16 T using standard four-wire a.c. (131 Hz) techniques. Currents of 10 μA were directed in the (interplanar) crystalline b^*-axis direction (perpendicular to the ac planes). The ambient pressure measurements were carried out using the same apparatus, after the measurements under pressure, with the petroleum spirit removed from the cell.

3. Experimental data

3.1. Magnetoresistance of α-(BEDT-TTF)$_2$KHg(SCN)$_4$

Measurements of the quantum oscillations occurring in the magnetoresistance of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ at ambient pressure were found to be the same as those reported in paper I, with the α, β, λ, μ and ν frequencies described in that paper all observable at appropriate temperatures. Figure 1 shows the effect on the magnetoresistance of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ of applying pressure. The large hump in the background magnetoresistance that occurs at ambient pressure is rapidly suppressed and the magnetoresistance tends towards linearity at the highest pressures.

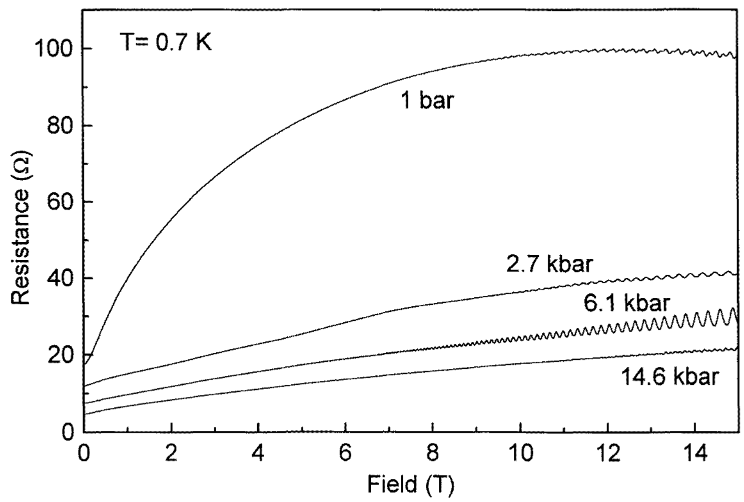

Figure 1. Pressure dependence of the magnetoresistance of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ at 0.7 K.

The development of the waveform of the quantum oscillations with pressure is shown in figure 2, where the non-oscillatory contribution to the magnetoresistance has been removed via division by a polynomial fit to the background magnetoresistance. The SdH oscillations at 1 bar are dominated by the α frequency ($\sim$671 T), which exhibits a large second-harmonic content that has been often been attributed to spin-splitting [8, 15]. Upon the application of 2.7 kbar of pressure this component of the waveform is removed. As the pressure is increased to 6.1 kbar it remains absent from the data but a marked increase in the fundamental amplitude of the α-frequency oscillations is evident. Further pressurization of the crystal causes a reduction in the amplitude of the oscillations and the progressive recovery of the second-harmonic content of the waveform.

Fourier transforms of the oscillations occurring between 10–15 T and at 0.7 K are presented in figure 3 for three pressures. The relative amplitudes of the second-harmonic (2α) peak to the fundamental (α) peak at the various pressures reflects the observations made in figure 2. Note that at 14.6 kbar the second-harmonic (2α) Fourier transform peak is twice the size of the fundamental (α) peak. In addition, Fourier analysis shows that the λ, μ and ν frequencies are all strongly suppressed by pressure and are only observed in the ambient pressure data. The β frequency, however, remains resolvable in all of our data with the exception of those recorded at 6.1 kbar.

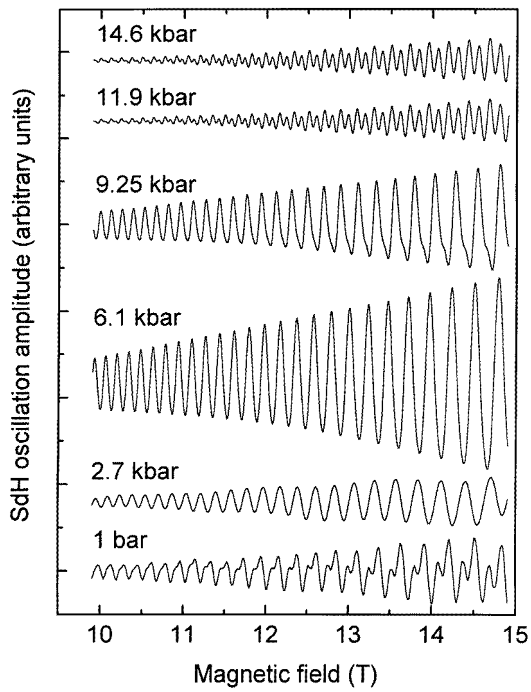

Figure 2. Pressure dependence of the SdH waveform at 0.7 K (the non-oscillatory background magnetoresistance has been removed).

Both the α and β frequencies were found to increase linearly with pressure. The α frequency changes from 671 T at ambient pressure to 856 T at 14.6 kbar (a mean rate of $\sim$12.7 T kbar^{-1}), while the β frequency increases from 4270 T to 4515 T over the same interval (a rate of $\sim$16.3 T kbar^{-1}).

The effective masses associated with the α frequency and its second harmonic were measured as a function of pressure by application of the Lifshitz–Kosevich (LK) formula [16] to the temperature dependence of the quantum oscillations. As mentioned in paper I, the precise physical significance of the effective mass obtained from LK analysis of the SdH oscillations in the α-phase BEDT-TTF salts is uncertain; however, they allow comparisons to be made between different experiments. The mass m_α^* associated with the α-frequency fundamental was found to decrease from $(2.0 \pm 0.1)m_e$ at ambient pressure to $(1.3 \pm 0.1)m_e$ at 14.6 kbar as shown in figure 4(a) (square data points) while the mass associated with the second harmonic was approximately pressure independent at $(2.8 \pm 0.4)m_e$ (triangular points). It is noted that the ambient pressure effective mass obtained from LK analysis of the α-frequency dHvA oscillations in this material was found to be $(1.46 \pm 0.1)m_e$. The difference between this mass and that derived from the SdH oscillations is commented upon in paper I, where it was implied that the value of m_α^* obtained in dHvA measurements is possibly more representative of the true effective mass in this material than that derived from SdH measurements.

Assuming this to be the case, then it is interesting to compare the effective mass obtained in dHvA experiments to that which has been measured in cyclotron resonance experiments. A number of cyclotron resonance experiments have now been carried

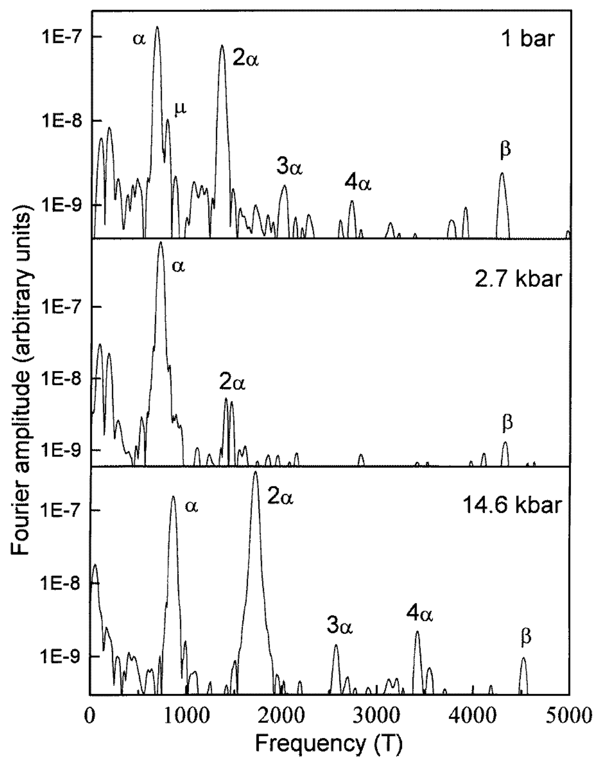

Figure 3. Fourier transforms of the data of figure 2 at 1 bar, 2.7 kbar and 14.6 kbar.

out on the α-(BEDT-TTF)$_2$MHg(SCN)$_4$ (M = K, Tl and NH$_4$) salts and have yielded dynamical masses close to a value of $m^*_{CR} \approx 1.35m_e$ [17–19]. The effective mass obtained in the dHvA measurements of paper I gives $m^*_\alpha = (1.4 \pm 0.1)m_e$ in the SDW regime of α-(BEDT-TTF)$_2$KHg(SCN)$_4$, with masses generally in the range 1.4–1.5m_e now having been obtained in dHvA and SdH experiments in the SDW wave states of the α-(BEDT-TTF)$_2$MHg(SCN)$_4$ salts with M = K [7, 14, 20, 21], Tl [22] and Rb [12]. The dynamical mass m^*_{CR} measured in cyclotron resonance experiments is, according to the theory of Kohn [23], independent of quasiparticle interactions and is representative of the band mass renormalized only by electron–phonon interactions. In contrast, the masses derived by LK analysis of SdH and dHvA oscillations should be additionally influenced by electron–electron interactions. It is seen that the mass m_α has almost the same value as m^*_{CR} and that a difference between these masses cannot be distinguished within the experimental errors of the measurements. Hence, it appears that the effective mass measured in the SDW states of the α-phase salts may not be significantly renormalized over the m^*_{CR} value. However, masses derived from the amplitude of the quantum oscillations in circumstances where SDW states are not thought to exist generally give larger values of m_α. The effective mass derived from dHvA oscillations above the field-induced kink transition in α-(BEDT-TTF)$_2$KHg(SCN)$_4$ has been measured as $m_\alpha = (2.7 \pm 0.1)m_e$ [7] while in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ m^*_α has been measured to have a value of ~2.5–2.7m_e ([6, 24] and this work). This may indicate that the effects of quasiparticle interactions are suppressed within the SDW state.

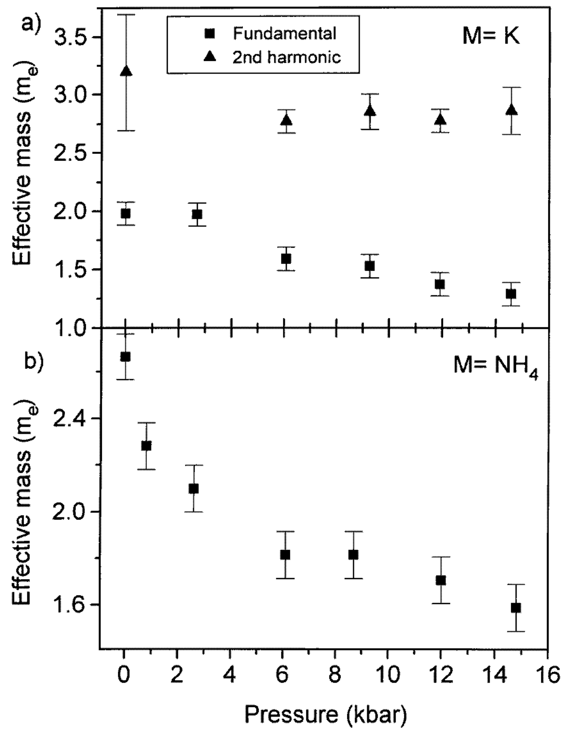

Figure 4. (*a*) Pressure dependence of the effective mass of the α frequency in α-(BEDT-TTF)$_2$KHg(SCN)$_4$ (square symbols) and its second harmonic (triangles). (*b*) Pressure dependence of the effective mass of the fundamental series of oscillations in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$.

3.2. Magnetoresistance of α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$

Figure 5 shows the field dependence at 0.7 K of the magnetoresistance of α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$, at a number of pressures. The superconducting transition is rapidly suppressed by pressure, with the transition to the superconducting state already incomplete at 0.8 kbar. As was the case in α-(BEDT-TTF)$_2$KHg(SCN)$_4$, the background magnetoresistance drops in magnitude and becomes progressively more linear as pressure is applied.

The ambient pressure quantum oscillations in this sample consisted of a single frequency measured as 576 ± 2 T, which we associate with the hole pocket of the Fermi surface predicted by band-structure calculations. No frequencies analogous to the β, λ, μ or ν frequencies seen in α-(BEDT-TTF)$_2$KHg(SCN)$_4$ were detected and no large second-harmonic component of the α frequency was present in the ambient pressure data. It has been established [6] that the fundamental frequency of the SdH oscillations in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ is (567 ± 1) T, implying that the crystalline ac planes of our sample may have been tilted by as much as $\sim 10^\circ$ relative to the magnetic field. In what follows, we have not introduced any correction factor into the analysis of our α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ data in order to compensate for this difference; in any case such a correction will only be very small and probably similar in size to the experimental errors.

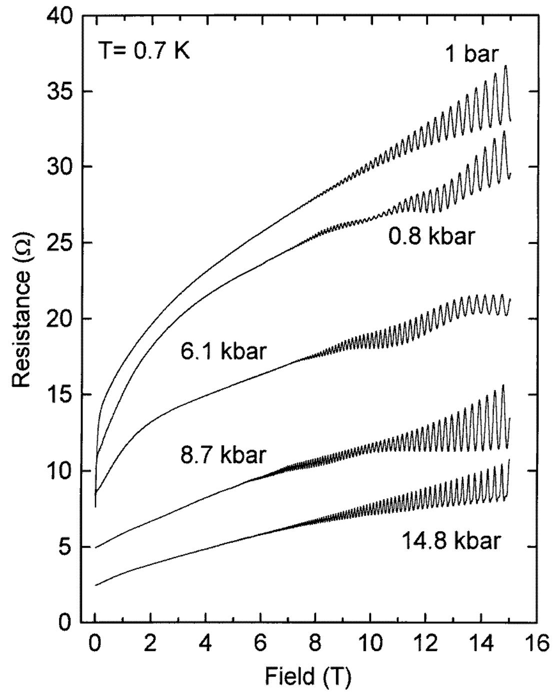

Figure 5. Pressure dependence of the magnetoresistance of α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ at 0.7 K.

The application of pressure to the sample caused the frequency of the α oscillations to increase at a rate of $\sim$17.8 T kbar^{-1} reaching 840 T at 14.8 kbar. In addition, in the pressure range 0.8–8.7 kbar the magnetoresistance exhibited a low-frequency oscillation, a feature shared by the data of Klepper *et al* [25]. Due to the weak amplitude and long period of these oscillations it could not be determined whether or not they were periodic in reciprocal field. However, if it is assumed that they are quantum oscillations, their frequency would be $\sim$20–30 T.

However, perhaps the most remarkable feature of these data is the observation of a double-peak structure in the waveform in the SdH oscillations at 14.8 kbar and 0.7 K (figure 6(*a*)). This phenomenon has not previously been observed in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ and has always rather been associated with the presence of the SDW state in α-(BEDT-TTF)$_2$KHg(SCN)$_4$.

The effective mass of the α-frequency SdH oscillations was measured to be $(2.7\pm0.1)m_e$ at ambient pressure. This undergoes a sharp drop to $(2.3 \pm 0.1)m_e$ by 0.8 kbar, coincident with the suppression by pressure of the superconducting state, and then gradually decreases with applied pressure, reaching $(1.6 \pm 0.1)m_e$ at 14.8 kbar (figure 4(*b*)). An earlier experiment [12] found a similar rapid decrease in the effective mass of α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ with pressure as the superconductivity was simultaneously suppressed. This type of correlation between the effective mass and the superconducting critical temperature, T_c, as a function of hydrostatic pressure has also been observed in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [26]. In that case the larger effective masses measured when superconductivity was present in the sample were proposed to result from strong quasiparticle interactions within the material. These interactions tend to be strongly

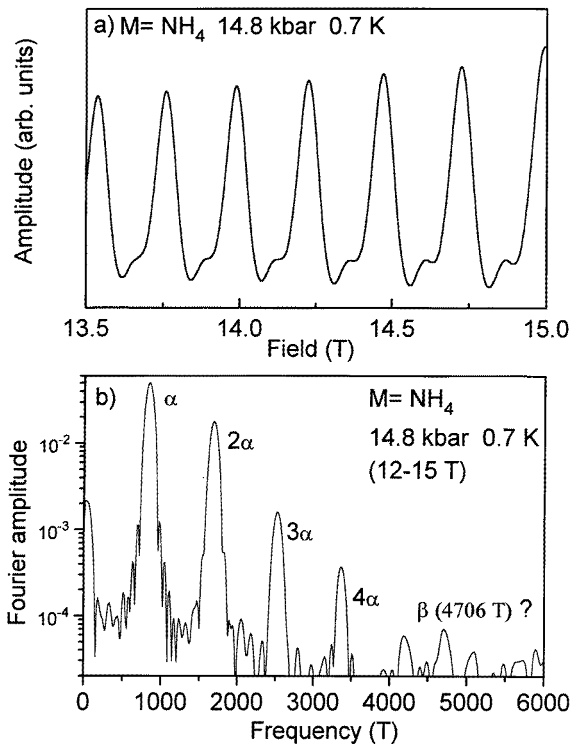

Figure 6. (*a*) Spin-splitting on the SdH waveform of α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ at 14.8 kbar and 0.7 K (the non-oscillatory background magnetoresistance has been removed). (*b*) Fourier transform of the SdH waveform from 12–15 T.

dependent upon bandwidth and so are suppressed when applied pressure forces the BEDT-TTF molecules closer together, hence broadening the bands. An experiment employing the use of uniaxial stress rather than hydrostatic pressure [27] has shown that superconductivity can be induced in α-(BEDT-TTF)$_2$KHg(SCN)$_4$. In that case the uniaxial stress causes the spacing of the molecules within the BEDT-TTF layer to increase via Poisson's effect and an increase in the effective mass is observed as superconductivity is induced.

4. Discussion

4.1. Pressure dependence of the phase boundary of the SDW state in α-(BEDT-TTF)$_2$KHg(SCN)$_4$

Many of the proposals [8, 9, 15, 29] made to account for the large second-harmonic content of the α-frequency SdH oscillation series observed in the low-field, low-temperature phase of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ have explained it as a direct consequence of the presence of an SDW which is thought to exist in that region of the phase diagram. The observation of this characteristic waveform in our α-(BEDT-TTF)$_2$KHg(SCN)$_4$ data at pressures higher than $P_c \sim 5$ kbar (the pressure at which it has been suggested that the SDW state is destroyed [12–14]) and also in our α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ data (where no SDW state is thought to be present) at 14.8 kbar suggests that this assertion may be incorrect.

The origins of the second-harmonic component of the SdH oscillations will be discussed further in the next section but first it is useful to review the other features observed in the magnetoresistance of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ that have led to the proposal that the SDW state is suppressed at $P_c \sim 5$ kbar.

This evidence includes the observations that: (1) the large hump in the background magnetoresistance is suppressed by pressure and the magnetoresistance becomes linear [13]; (2) the point of inflection in zero-field cooling curves, which has been proposed to represent the onset of the SDW state at temperature T_N, decreases with increasing pressure [13, 31]; (3) the AMROs change in character from the Q1D form, commonly associated with the reconstructed Fermi surface, to the Q2D form found above the kink transition [14]; (4) the λ, μ and ν series of quantum oscillations are not observable at high pressures ($P > \sim 2.5$ kbar).

This collection of observations clearly demonstrates that a significant change in the Fermi surface topology of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ is taking place as the pressure applied to it is increased through P_c. However, it is not obvious that this changing behaviour represents the removal of the SDW state. We note that, according to the recent theory of Blundell and Singleton [32], the features listed above can be explained as due to the presence of the *strongly* corrugated Q1D sections of Fermi surface that are proposed to form in the reconstructed Fermi surface of the SDW state from the remnants of the Q2D hole pocket of the unnested Fermi surface [10]. In [32] it has been shown that Fermi surface sheets that possess high harmonic components of their warping give rise to the deep resistivity minima seen in the AMROs of the low-field, low-temperature phase of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ and also account for the change in the form of the magnetoresistance between being 'sublinear' in the AMRO minima to having a 'superlinear' form in the AMRO maxima, in the field region below the kink transition [29]. For this reason it is possible that the suppression of features such as (1) and (3) listed above may not be reliable indicators of the point at which the SDW is removed in this material. Instead they may only indicate that the strongly warped sections of Q1D Fermi surface are being destroyed by the application of pressure. This latter suggestion does not necessitate a phase transition out of the SDW state but merely an improvement in the nesting of this state such that the strongly warped Q1D Fermi surface sheets disappear leaving a Fermi surface topology that is instead dominated by the Q2D closed sections. Point (2) mentioned above might be accounted for on this basis if it is assumed that it corresponds to a change in the nesting vector within the SDW state rather than the boundary of that phase. Also, as explained in paper I, the λ and ν oscillations in the magnetoresistance are interpreted as arising from the Stark quantum interference mechanism [16], involving the Q1D Fermi surface sections while the μ series of oscillations has been interpreted as originating from a closed Fermi surface section that occurs due to imperfect nesting of the Q1D sections of the unreconstructed Fermi surface. The observation (point (4) above) that these frequencies are removed by the application of pressure is thus consistent with the suggestion that pressure removes the Q1D Fermi surface sections.

The change at high pressure ($P \gtrsim 5$ kbar) to a Fermi surface characterized by the closed Q2D Fermi surface sections is most clearly exhibited by the high-pressure AMRO experiment of Hanasaki *et al* [14] in which the shape of the closed pocket that exists at high pressure has been derived and found to be similar in shape and orientation to that which has been observed in the high-field and high-temperature regions of the α-(BEDT-TTF)$_2$KHg(SCN)$_4$ phase diagram [11]. In addition to the AMROs associated with this closed Fermi surface pocket, Hanasaki *et al* [14] have also observed weak features in the AMROs, for $P > P_c$, which they have attributed to the presence of Q1D sections of Fermi surface aligned along the c^*-axis direction. This is the direction in which the Q1D

Fermi sheets of the unnested Fermi surface run [4] and if the interpretation of these features were correct this might constitute good evidence for the removal of the SDW state at P_c. However, any such Q1D minima occurring in AMROs associated with the unreconstructed Fermi surface of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ should have a periodicity in the tangent of the tilt angle of approximately b/c when the AMRO is measured with the rotation of the magnetic field in the plane of the sheets, where b and c are the magnitudes of the real space crystal lattice vectors $\boldsymbol{b}$ and $\boldsymbol{c}$ in the absence of any magnetic superlattice [32]. The ratio b/c is thus expected to take the value $\sim$2.1 while the features in the data of Hanasaki *et al* [14] yield a value of 0.48, implying that these minima are not a result of Fermi surface sheets of the unreconstructed Fermi surface. Furthermore, the theory of Blundell and Singleton [32] predicts that the Q1D Fermi surface sheets of the unreconstructed Fermi surface, even if they are present, should not be observable in the AMROs since they are only *weakly* warped. In the semiclassical model of the Q1D AMROs [32] it is essential that the Q1D Fermi surface sections must have a high harmonic content to their warping in order to exhibit a significant AMRO effect. In the reconstructed Fermi surface this requirement is fulfilled because the Q1D sheets are the remnants of the cylindrical hole pockets of the unnested Fermi surface and thus contain strong cusps [10]. If, however, nesting has not occurred then the Q1D sections should be too smooth to give measurable minima in the AMRO. This explains the absence of any observable Q1D AMRO in the α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ salt which has a similar Fermi surface to the unreconstructed α-(BEDT-TTF)$_2$KHg(SCN)$_4$ salt [11].

One further point of consideration regarding the possibility of a phase transition at P_c is the behaviour of the effective mass associated with the α-frequency SdH oscillations, m_α. As has been commented upon in section 3.1, this parameter seems to take a value close to that of the cyclotron mass m^*_{CR} in the presence of an SDW while having a much higher mass upon removal of this state. It is noted that m^*_α does not increase at P_c but remains close to the value of m^*_{CR}, possibly indicating that the SDW state has not been destroyed.

In conclusion then we suggest that on the grounds of the experimental data which we have reviewed in this section the question of whether the SDW state is destroyed at P_c or not remains an open one. What can, however, be stated with certainty is that the strongly corrugated Q1D Fermi surface sections that exist within the low-field, low-temperature phase of this salt are removed above P_c either by destruction of the SDW state or by a change in the nesting properties of that state. We shall now continue by discussing features of our data such as the strong second-harmonic content of the α-frequency SdH oscillations and the observation of the β frequency within this context.

4.2. Second-harmonic content of the α frequency in α-(BEDT-TTF)$_2$KHg(SCN)$_4$

The origin of the large second-harmonic component of the waveform of the α-frequency SdH oscillations in α-(BEDT-TTF)$_2$KHg(SCN)$_4$ has been the subject of some controversy in recent years. The proposals that have been made to explain this phenomenon fall broadly into two categories, one of which is that the waveform is actually due to the superposition of two series of oscillations from different extremal orbits on the Fermi surface [28, 29] and the other being that only a single extremal Fermi surface orbit is involved but that the SdH oscillations from this orbit exhibit (exchange-enhanced) Zeeman spin-splitting [8, 9, 15, 21, 30].

Prior to the present work a double-peak structure in the waveform of the raw data of the α SdH frequency had only been observed to occur in the ambient pressure SDW state of the α-(BEDT-TTF)$_2$MHg(SCN)$_4$ salts with M = K, Rb and Tl. If it is supposed that this large second-harmonic component of the oscillations is caused by spin-splitting then in general it should become progressively better resolved with increasing field. However, in the case of these salts the splitting of the oscillations is removed when they are driven through their kink transitions into their 'normal' metallic high-field states ($B > B_K$) [7–9]. For this reason most explanations of the splitting effect have postulated that a SDW state is essential for its observation [8, 9, 15, 29]. The observation of strong splitting of the α-frequency SdH at pressures in excess of ~9.25 kbar (well above the pressure at which it has been proposed that the SDW state is destroyed, $P_c \sim 5$ kbar [12–14]) therefore implies that this cannot, however, be the case. If the SDW state is removed for pressures in excess of P_c then obviously the splitting of the α frequency cannot be accounted for as a feature of the SDW state. If instead it is assumed that the SDW state persists to the highest pressures that we have measured (~15 kbar) then the splitting effect must be varying within that state such that it disappears around 5 kbar, only to return upon application of higher pressures. In either of these two scenarios it is clear that the presence of a strong second-harmonic content of the α-frequency SdH is not due to the existence of the SDW. Bearing this in mind we shall now discuss some of the findings of the previous descriptions of this splitting phenomenon.

One of the most detailed treatments of this effect is that of Sasaki and Toyota who studied the ratio, δ/Δ, of the separations of adjacent peaks in the SdH and dHvA oscillations, in a reciprocal field, which they assigned to spin-splitting (δ) and alternate dips which they attributed to Landau level splitting (Δ), as a function of both field and tilt angle [15]. This led them to propose that the large second-harmonic content of the oscillations was due to exchange-enhanced spin-splitting which could be described by introducing a field-dependent effective g factor. This method relies upon the assumption that minima in the quantum oscillations (as measured in reciprocal field) correspond directly to the positions of levels in the energy spectrum.

We have attempted to apply this analysis method to our ambient pressure SdH and dHvA data of paper I but have found that it is flawed in a number of respects. Firstly, such analysis should not be attempted on data where the separate peak positions are not well resolved. In particular, oscillations where the spin-splitting appears as a point of inflection in the waveform rather than as two separate peaks cannot be analysed by this method. We note that in the dHvA trace and the SdH data taken at tilt angles greater than $\sim 10^\circ$, in [15], the peak positions are not well resolved, resulting in large scatter of the δ/Δ values. Secondly, if there are quantum oscillatory frequencies present in the data other than the series responsible for the spin-splitting then this will lead to additional modifications of the peak positions.

Attempts at analysis of our data using the method of [15] clearly confirm this last point. Our SdH data recorded at $\theta = 0^\circ$ shows that δ/Δ oscillates between values of ~0.47–0.53, with a period of (105 ± 7) T. It is clear that this corresponds to the difference between the μ and α SdH oscillation frequencies. This behaviour is clearly seen on the raw data of figure 1(a) of paper I where it is seen that the spin-splitting effect appears to be largest in the beat minima of the oscillations but substantially reduced in the beat maxima. Thus the presence of any significant amount of μ frequency in the data will render this analysis method useless.

Sasaki and Toyota [15] also studied δ/Δ as a function of tilt angle, θ, to the magnetic field. Assuming an exchange field, $H_{ex} = 5.19$ T (defined as $H_{ex} = \Delta E/m_B$, where ΔE is the energy by which the Zeeman spin-splitting is enhanced via the exchange interaction and μ_B is the Bohr magneton), a g factor of $g = 1.83$ and writing the effective mass as $m^* = 1.4 m_e/\cos\theta$ (so as to take account of the fact that the Landau level separation is determined only by the component of field directed along the b^* direction), they obtained the equation $\delta/\Delta = 1 - (1.56/\cos\theta)$ to describe the angular dependence of the ratio of the spin to Landau level splitting. If instead it is assumed that there is no exchange enhancement of the spin-splitting and a field-independent g factor then equation (3) of [15] gives $\delta/\Delta = 2 - (m^* g\mu_B/e\hbar\cos\theta)$. Inserting in this equation the value of $m^*g = 3.07$ obtained from the harmonic ratio experiment of Pratt *et al* [9] then it becomes $\delta/\Delta = 1 - (1.535/\cos\theta)$ which is similar to that derived by Sasaki and Toyota and in good agreement with the angle-dependent data of [15]. We thus conclude that at present there is not sufficient experimental evidence to substantiate the claims made for a field-dependent g factor in α-(BEDT-TTF)$_2$KHg(SCN)$_4$.

As mentioned earlier, some workers have attempted to account for the splitting of the ambient pressure α-frequency oscillations as the superposition of two separate series of oscillations resulting from different extremal Fermi surface orbits rather than a single spin-split series [28, 29]. One such model was described in detail by Kang [28] who proposed that the two components of the oscillations arose from the extremal maximum and minimum orbits of the warped Fermi surface cylinder from which the α frequency originates. This model does not account for the removal of the spin-splitting at the kink transition (since the warped Q2D Fermi cylinder giving α oscillations certainly still exists in the high-field ($B > B_K$) state). As first pointed out by Sasaki and Toyota [15], this model fails to explain the angular dependence of δ/Δ since the two separate frequencies must simultaneously increase as $1/\cos\theta$ with increasing tilt angle, θ.

A further model of the splitting in terms of the superposition of separate series of oscillations is that proposed by Athas *et al* [29], in which it is suggested that domains exist within the low-temperature, low-field state of the α-(BEDT-TTF)$_2$MHg(SCN)$_4$ salts with some domains characterized by the nested Fermi surface while others remain in the unreconstructed form. In this case the splitting is explained as arising from the superposition of oscillations from the α Fermi surface cylinders of the two types of domain. The criticism made of the model of Kang applies also to this description of the splitting effect which in particular cannot account for the suppression and subsequent recovery of the splitting effect as the pressure on the sample is increased.

In the light of the above discussion, we suggest that the existence of a SDW state is not a prerequisite for the presence of spin-splitting in the SdH waveform. Instead we suggest that the size of the spin-splitting is purely dependent upon the values of the effective mass, m^* and the g factor, g, both of which will in general have a pressure dependence. High-field studies of the quantum oscillations in α-(BEDT-TTF)$_2$KHg(SCN)$_4$ have shown that there is a pronounced change in the effective mass and scattering processes at the field-induced kink transition [7]. This could account for the removal of the large second-harmonic content of the α-frequency oscillations in the high-field ($B > B_K$) state of the ambient pressure data. The progressive recovery of the spin-splitting on our high-pressure SdH data, observed above ∼9 kbar, is explained by the gradual change in the product m^*g as a function of pressure. The observation of Athas *et al* [29] that the spin-splitting appears to vanish in minima in the Q1D AMROs of the SDW state can also be explained by the spin-splitting reduction factor in the LK formula changing as a function of tilt angle, θ. This factor has the form

$$\frac{M_1(\theta)}{M_2(\theta)} \approx \frac{\cos[\pi g^* m^*(\theta)/2]}{\cos[\pi g^* m^*(\theta)]} \tag{1}$$

where $M_1(\theta)$ and $M_2(\theta)$ are the magnitudes of the fundamental and second harmonic respectively, g^* is the effective g factor and $m^*(\theta)$ is the effective mass, assumed to vary with θ as $m^*(\theta) = m^*(0)/\cos\theta$. This leads to a minimum in the ratio of the amplitude of the second-harmonic amplitude to the first-harmonic amplitude at $\theta \approx 35°$ [9]. It was suggested that this observation constituted strong evidence for an explanation of the AMRO effect as resulting from a domain structure within the crystal [29]. We note that the second-harmonic content of the SdH oscillations in the AMRO minimum presented in [29] is smaller than in the AMRO maxima but is still obviously present on the raw data trace and its Fourier transform. Neither is any evidence presented for suppression of the spin-splitting in AMRO minima other than the first minimum. As such this observation cannot be used as justification for a domain-based model.

It was noted in paper I that the (ambient pressure) μ frequency, although, like the α oscillations, originating from a closed Q2D Fermi surface pocket, does not exhibit spin-splitting of its waveform. This observation can be accounted for on the basis that this pocket is characterized by a different effective mass to the α frequency (see table 1 of paper I).

4.3. The β frequency

The high-frequency (∼4270 T at ambient pressure) β oscillations are the only series other than the α frequency that are observed in the data up to the highest pressures. The origin of this frequency is uncertain. In paper I we have suggested that it is a characteristic of the SDW state. The observation of the β frequency at high pressures ($P > P_c$) thus supports the suggestion made earlier in this paper that the SDW may persist to the highest pressure that we have measured (∼15 kbar).

As mentioned in section 4.1, many of the features observed in the background magnetoresistance and the AMROs cannot be correlated with the existence of the SDW state, since they are only symptomatic of the presence of strongly warped Q1D Fermi surface sheets. In section 4.2 it has also been shown that the observation of a strong second-harmonic content in the α-frequency SdH oscillations cannot be linked to the presence of a SDW either. In contrast, since the existence of the β frequency is a feature that must arise from a quite specific Fermi surface configuration, it may well be the case that the presence/absence of this series of quantum oscillations in the data may be a more reliable indicator of whether or not the material has adopted a nested Fermi surface.

The first explanation of the β frequency that was proposed was that of Uji *et al* [33] who attributed it to complete breakdown of the unnested Fermi surface and took the observation of the β frequency at fields of ∼10 T as an indication that the SDW state was completely removed by this field. Thus, in this case the β frequency is considered to be a characteristic of the 'normal' metallic state. The absence of any change in the field-dependent ambient pressure AMROs at ∼10 T [8, 11], in contrast to the rather dramatic change at ∼23 T suggests, however, that it is instead at the higher field that the SDW state is removed. As mentioned in paper I, a recent pulsed field measurement [7] of the dHvA oscillations in α-(BEDT-TTF)$_2$KHg(SCN)$_4$ that was particularly sensitive to high-frequency oscillations showed no evidence for a β oscillation series above the kink field. It thus appears that it is incorrect to associate the β frequency with the high-field phase of this salt; rather it is a product of the reconstructed Fermi surface.

This objection applies equally to the proposal of Athas *et al* [29] who also assumed that the β frequency results from the mechanism put forward by Uji *et al* but accounted for the presence of it below the kink transition by proposing the coexistence of domains of the material in both the nested and unreconstructed states below the kink transition. As described in both paper I and the present work, the extension of this model to explain the AMRO effect and features in the magnetoresistance such as the large second-harmonic content of the SdH oscillation waveform appears to be inappropriate.

An alternative suggestion that has been made is that the β orbit might be a mixture of harmonics due to orbits in a breakdown network within the SDW state [8]. The absence of frequencies other than the α and β at high ($P > P_c$) pressures shows that this cannot be the case.

As described in paper I, no β frequency has been observed in α-(BEDT-TTF)$_2$NH$_4$-Hg(SCN)$_4$ despite the lack of Fermi surface nesting in this salt. If the β frequency is a product of breakdown of the unreconstructed Fermi surface then it may be the case that α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$, which has a smaller α pocket than the other salts in the α-(BEDT-TTF)$_2$MHg(SCN)$_4$ family, may possess too large an energy gap between the Q1D Fermi surface sheets and the α pocket for breakdown to occur.

In the salt κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ it was found that an analogous energy gap was reduced in size as pressure was applied, leading to dominance of the SdH by the breakdown orbit at high pressures [26]. It might be hoped that breakdown of the Fermi surface of α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ might be induced similarly by pressure. Also, since in our α-(BEDT-TTF)$_2$KHg(SCN)$_4$ data the presence of the β orbit appears to be correlated to the presence of the spin-split SdH oscillation waveform (we note that the one pressure at which we could not observe the β frequency, 6.1 kbar, is also in the region where the spin-splitting is not apparent on the raw data) it might be hoped that a β frequency might show up on the 14.8 kbar α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ data where spin-splitting has also appeared. Figure 6(*b*) shows a Fourier transform of the 14.8 kbar data of figure 6(*a*). It is seen that there are frequency peaks that might be candidates for a β frequency. These peaks are, however, too small in amplitude to be confirmed to be SdH peaks and so we attribute them to background noise in the Fourier transform.

4.4. Low-frequency pressure-induced quantum oscillations

As mentioned in section 3, the magnetoresistance of α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ exhibits a low-frequency oscillation in the pressure range $\sim$0.8–8.9 kbar, similar to that observed by Klepper *et al* [25]. This slow oscillation was originally taken to be an indication of pressure-induced Fermi surface nesting within α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ but more recently has been interpreted as arising from the warping of the α-frequency Fermi surface cylinder [12]. However, there is as yet no other experimental evidence to suggest that pressure-induced nesting occurs in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$. It is not clear either whether this low-frequency oscillation can be attributed to warping of the α-frequency Fermi surface cylinder. If this were the case it might be expected that the Fourier transform peak of the α frequency might be split in the manner seen for the μ and β frequencies on the dHvA data of figure 3(*b*) of paper I. Additionally, it would be expected to become progressively more pronounced with pressure as the warping increases, rather than being removed above $\sim$10 kbar as is observed to be the case. One explanation might be that it could arise from a small section of the band structure being raised above the Fermi energy over this pressure range although there is no obvious feature of the calculated band structure that would lead to this happening [3]. At present a satisfying explanation of this series of oscillations is not forthcoming.

5. Conclusion

We have observed the persistence of the splitting of the waveform of the SdH oscillations in α-(BEDT-TTF)$_2$KHg(SCN)$_4$ up to pressures of 14.6 kbar. Evidence for the suggestion that the SDW state, which is thought to exist at low pressures in this material, is removed at a critical pressure of $P_c \sim 5$ kbar has been discussed in the context of these data. From this it has been concluded that the possibility of destruction of the SDW at P_c remains an open question. It is, however, clear that some degree of Fermi surface rearrangement takes place close to P_c, resulting in the removal of the strongly corrugated Q1D Fermi surface sheets that dominate the character of the magnetoresistance of this salt in the low-temperature, low-field region of its phase diagram. The removal of these sheets may only be due to an improvement in the nesting of the SDW state at P_c rather than its complete suppression.

We have suggested that the splitting of the SdH oscillation waveform is not intrinsically linked to the existence of a SDW state and instead results from spin-splitting of the Landau levels rather than from the superposition of two series of oscillations of equal frequency. The λ ($\sim$181 T), μ ($\sim$775 T) and ν ($\sim$856 T) frequencies that are observed at ambient pressure (paper I) are removed upon application of pressure. It is believed that these frequencies result from imperfect nesting of the Q1D Fermi surface sheets of the calculated Fermi surface and are thus destroyed by the Fermi surface rearrangement that occurs as P_c is approached. The only other frequency to persist to the highest pressures is the β ($\sim$4270 T, at ambient pressure) frequency, the origins of which remain unclear. This frequency does, however, appear to be a feature of the nested Fermi surface and along with the effective mass may provide the most reliable indication of the existence of a SDW.

Pressures of up to 14.8 kbar have also been applied to the isostructural salt α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$, which exhibits only a single SdH oscillation series. At 14.8 kbar the onset of spin-splitting in the waveform of the raw data has been observed for the first time in this material. No frequency analogous to the β frequency of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ is observed in the α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ salt.

It is clear that high-pressure studies of the quantum oscillations occurring in the α-(BEDT-TTF)$_2$MHg(SCN)$_4$ (where M = K, Rb, Tl or NH$_4$) family of salts is an area of research where further experimental investigation is necessary. In particular more experiments addressing the nature of the β frequency in α-(BEDT-TTF)$_2$KHg(SCN)$_4$ are desirable along with studies of the pressure dependence of the magnetic properties of this salt, in the hope of resolving the doubts surrounding the changes that take place in the Fermi surface of this material close to P_c.

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