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LETTER TO THE EDITOR

The electrodynamic response of single crystals of the quasi-two-dimensional organic metal α-(BEDT-TTF)$_2$NH$_4$Hg(NCS)$_4$ between 50 and 100 GHz: observation of cyclotron resonance and quantum oscillations

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Abstract. The electrodynamical response of single crystals of the quasi-two-dimensional organic metal α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ has been studied in the frequency range 50–100 GHz in magnetic fields of up to 15 T, and at temperatures down to 1.5 K. The experiments were carried out using the cavity perturbation technique; the cavity was rectangular, allowing the high-frequency currents in the sample to be excited in two different geometries. A prominent feature attributed to cyclotron resonance was observed, corresponding to a cyclotron mass of $(1.9 \pm 0.2)m_e$. The electrodynamical response of the samples also exhibited magnetic quantum oscillations and an ESR/EPR signal.

The α-(BEDT-TTF)$_2$MHg(SCN)$_4$ family of charge-transfer salts, where M can be NH$_4$, K, Tl or Rb, has been studied extensively during the last few years (see, e.g. [1, 2] and references therein), as they exhibit a variety of interesting behaviours at low temperatures. Whilst the salts with M = Tl, K and Rb undergo transitions at ~8–10 K into what are believed to be spin-density-wave ground states [2], the salt with M = NH$_4$ is a superconductor with $T_c \sim 1$ K [3]. Thus far these quasi-two-dimensional (Q2D) metals have been studied almost exclusively by conventional magnetotransport methods involving either direct currents (DC) or low-frequency ($\leqslant$100 Hz) alternating current (AC) [1]. However, AC measurements at frequencies exceeding the carrier scattering rate can potentially give additional information about the electronic structure and scattering processes in these systems [4, 5]. Motivated by this possibility, we have carried out measurements of the high-frequency (50–100 GHz) electrodynamical response of single crystals of α-(BEDT-TTF)$_2$NH$_4$Hg(NCS)$_4$ which are reported in this letter.

The cavity perturbation technique has been used to measure the millimetre-wave response of individual single crystals. Despite the fact that a cylindrical cavity is simpler to manufacture, a number of practical considerations led to the use of a rectangular cavity. Firstly, rectangular cavities can in general be made much smaller than cylindrical ones, and can thus be mounted in the bore of a superconducting magnet in a wide variety of orientations and positions. Secondly, placing the sample in the centre of a rectangular

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cavity makes it possible to measure its response at both electric and magnetic field maxima without remounting, simply by changing the cavity mode [6]. Moreover, as the spectrum of a rectangular cavity is very simple, the geometry of the microwave field at a particular frequency is easily inferred.

The cavity used in the present experiments was made from a standard copper waveguide with a 1 mm wall thickness, and had approximate dimensions $6 \times 3 \times 1.5$ mm^3. The fundamental frequency of the empty cavity was $\sim$55 GHz; the Q-factor in this mode was about 1200 at room temperature and 1700 at 4.2 K. The empty cavity could also be excited at 71, 90 and 105 GHz, corresponding to higher harmonics of the waveguide. The sample was mounted in a thin-walled quartz capillary, and could be placed in the centre of the cavity through a 1 mm diameter hole in the centre of one of the wider of the waveguide walls. The position of the holes and the comparatively thick walls minimized radiation losses. The sample was at the antinode of the millimetre-wave electric field (E) for the 55 and 90 GHz cavity modes and at the magnetic field strength (H) maximum for the 71 and 105 GHz modes [7].

The cavity was placed in ^{4}He exchange gas inside a variable-temperature insert which allows the sample temperature to be adjusted between 1.5 K and 300 K. The external, swept magnetic induction B was supplied by a 15 T superconducting magnet [7]. Normally the sample was oriented so that the Q2D highly conductive planes were perpendicular to the waveguide axis (i.e. perpendicular to $\boldsymbol{B}$). In this geometry, when the sample is positioned at the maximum of H, the $\boldsymbol{H}$-field is parallel to the Q2D planes, so the absorption is due almost entirely to induced interplane currents [6]. However, when the sample is positioned at the E-antinode, the response will be dominated by induced in-plane currents. Note that samples could also be mounted at an arbitrary angle to $\boldsymbol{B}$.

The cavity operated in transmission mode. It was weakly linked to oversized waveguides via 0.8 mm diameter holes. Attenuators were used to damp standing waves in the waveguides. At high frequencies, however, the standing-wave frequency becomes smaller then the cavity bandwidth, and so the impedance match becomes worse. In order to ensure that standing waves did not affect the results, a series of sweeps of the external magnetic field were carried out at different frequencies near the cavity resonance.

The millimetre waves were produced and detected by an AB Millimetre MVNA 8-350 millimetre-wave vector network analyser (MVNA). This is based on the harmonics of tunable YIG oscillators and a superheterodyne receiver technique. The in- and out-of-phase components of the last intermediate frequency (500 Hz) from the MVNA were measured using a lock-in amplifier. At low frequencies the out-of-phase signal was used to lock the source to the cavity, and the transmission (proportional to the cavity Q-factor [6]) and the cavity frequency were recorded. At higher frequencies the two components were recorded simultaneously whilst the source frequency was stabilized using a quartz crystal oscillator (EIP 575). In the latter case, when the cavity frequency shifts during the field sweep were small, the in-phase signal was proportional to the Q-factor, whilst the out-of-phase signal was proportional to the frequency shift of the cavity [6, 8]. Since the Q-factor of the loaded cavity remains fairly large ($Q \geqslant 200$ even at room temperature), the changes in $1/Q$ and the resonant frequency are proportional to the changes in the real and imaginary parts of the sample response respectively [6, 8].

α-(BEDT-TTF)$_2$NH$_4$Hg(NCS)$_4$ was chosen for this preliminary study, as it is known to have the simplest low-temperature electronic bandstructure of the α-phase family of (BEDT-TTF) salts [2]. Its calculated Fermi surface consists of a quasi-two-dimensional (Q2D) warped cylinder (holes), with a cross-sectional area corresponding to a quantum oscillation (de Haas–van Alphen or Shubnikov–de Haas) frequency of about 570 T, and

two quasi-one-dimensional Fermi sheets (electrons), slightly warped in both the in-plane and interplane directions [9]. The cylinder is thought to be corrugated by $\lesssim$1% [10, 11]. The in-plane resistivity of this material is typically 10 mΩ cm at 4.2 K [12], with an in-plane anisotropy of around 3–5; the interplane resistivity is approximately 5–6 orders of magnitude larger [9, 12].

The single-crystal samples were grown by standard electrochemical techniques described elsewhere [9]. Typical crystals were platelets with dimensions $1.5 \times 0.7 \times 0.1$ mm^3; the large surfaces of the samples corresponded to the Q2D conducting planes. Samples of this size shifted the resonant frequency of the cavity by about 2.5 GHz in the fundamental mode; the Q-factor of the loaded cavity was about 250 at room temperature and about 1200 at 1.5 K in this mode. In the 70 GHz mode the frequency shift due to such samples was about 0.8 GHz; the Q-factor for this mode was about 400 at room temperature and about 1300 at 1.5 K.

Although the parameters of the empty cavity were almost field independent at high magnetic fields, they exhibited field-dependent structure in the low-field region (figure 1(a)). The largest, peak-like feature observed in the response of the empty cavity (figure 1(a)) is now known to be due to impurities in the solder used to mount the end faces of the cavity onto the waveguide [13]. Although in some cases the background response of the empty cavity could be subtracted from the total signal, only raw data will be presented in this preliminary study and the low-field region will not be treated in detail.

Figures 1(b) and 1(c) show the absorption of the loaded cavity (i.e. $1/Q$) versus applied magnetic induction B for the 68 and 105 GHz modes (i.e. with the sample in the H-antinode) [14]. A prominent maximum in the sample absorption can be seen in both figures. This feature broadened rapidly with increasing temperature and shifted to higher magnetic fields as $\sim 1/\cos(\theta)$ if the sample was tilted so that the normal to the Q2D planes made an angle of θ to $\boldsymbol{B}$. This behaviour is characteristic of cyclotron resonance of Q2D carriers; the cyclotron mass derived from the position of the maximum absorption is $m_c = (1.9 \pm 0.2)m_e$ at both frequencies.

Quantum oscillations can clearly be seen in the absorption when $B \geqslant 11$ T. The frequency of the oscillations is about 570 ± 10 T, in good agreement with the Shubnikov–de Haas oscillation frequency observed in conventional (DC or low-frequency AC) magnetotransport and magnetization experiments [3, 10, 12, 15, 16]. The limited temperature range of the apparatus ($T \geqslant 1.5$ K) leads to the effective mass derived from the temperature dependence of the quantum oscillations in this work being insufficiently accurate for meaningful comparisons with the other studies; however, over the limited range studied, the temperature dependence of the amplitude of the quantum oscillations appears similar to those observed in conventional experiments [3, 15, 16].

The introduction of the sample into the cavity also causes an ESR/EPR line to appear; this is superimposed on the shoulder of the peak-like feature due to the background response (figures 1(b) and 1(c)). The field resolution of the present apparatus is insufficient for us to determine the g-factor precisely, but it is within 0.2% of 2; the linewidth is about 7 mT at 68 GHz. The ESR in the α-phase (BEDT-TTF) salts has been analysed in detail using traditional resonant-cavity techniques to reveal a g-factor of 2.01 [17]; the present result therefore agrees with this value to the limit of experimental accuracy.

When the sample was placed at a maximum of E, the results were quite different (figures 2(a) and 2(b)). A large increase in the microwave absorption of the sample is observed at the high fields. Despite this, the quantum oscillations are much less visible than in figures 1(b) and 1(c). Figures 2(a) and 2(b) show that a small, broad maximum in the sample absorption is clearly visible; assuming again that the maximum corresponds to a cyclotron resonance,

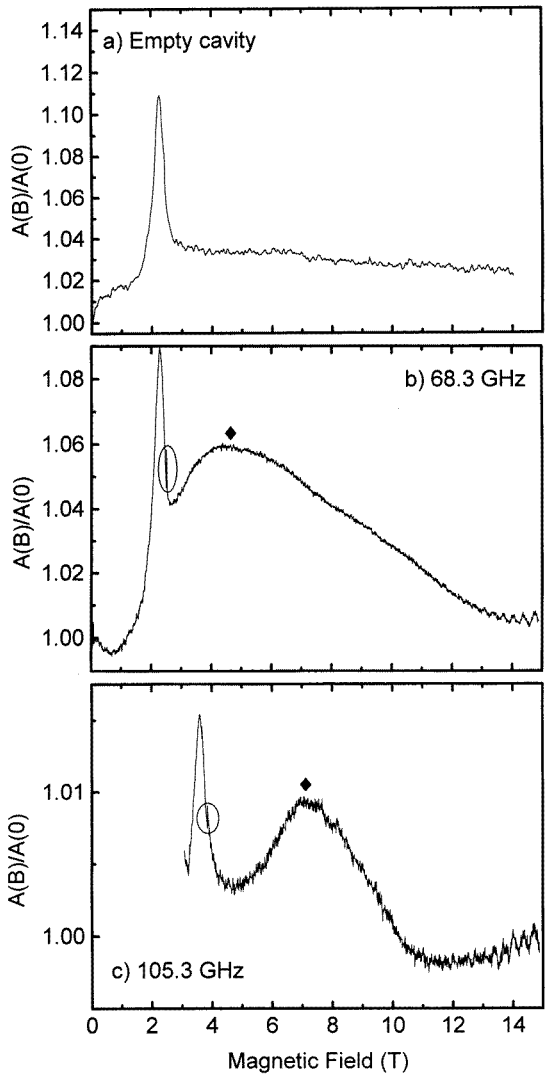

Figure 1. (a) shows the normalized absorption $A(B)/A(0)$ (proportional to $1/Q$) versus magnetic field for the millimetre-wave cavity and empty sample holder. The peak at low fields is thought to be due to the solder used to construct the cavity [13]; at higher fields the cavity is almost field independent. (b) and (c) show the normalized absorption of the loaded cavity versus magnetic field at frequencies of 68.3 and 105.3 GHz respectively. In both cases the sample is placed at the millimetre-wave H-field maximum (temperature 1.5 K) and the large peak on the left is due to the background response of the cavity (see (a)). The diamonds indicate the theoretical positions of cyclotron resonances corresponding to a cyclotron mass of $1.9m_e$ and the rings mark the ESR/EPR line due to the sample. Quantum oscillations can be clearly seen at high fields at both frequencies.

cyclotron masses of $m_c = (1.8 \pm 0.2)m_e$ and $m_c = (2.0 \pm 0.2)m_e$ are obtained at 50 GHz and 81 GHz respectively.

When the sample is placed at a maximum of E (figures 2(a) and 2(b)), the in-plane conductivity is responsible for its electrodynamical response. Since its value is relatively

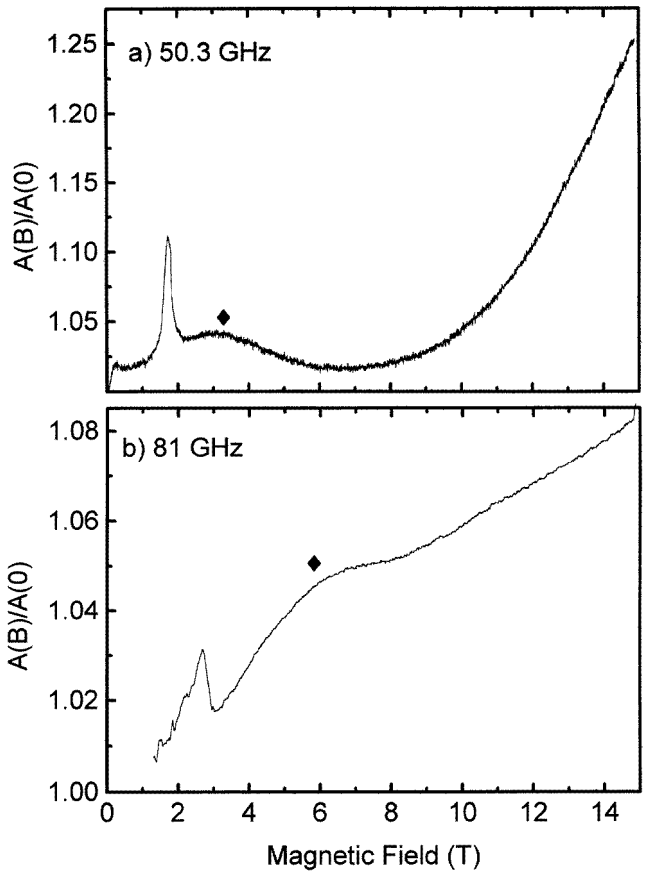

Figure 2. Normalized absorption of the loaded cavity versus magnetic field at frequencies of 50.3 GHz (a) and 81 GHz (b), with the sample placed at the millimetre-wave E-field maximum (temperature 1.5 K). At both frequencies the large peak on the left is due to the background response of the cavity (see figure 1(a)). The diamonds indicate the positions of cyclotron resonances corresponding to cyclotron masses of $1.8m_e$ (a) and $2.0m_e$ (b). Note that the impedance increases at fields higher than the cyclotron resonance field and that the quantum oscillations become extremely weak in this geometry.

large (see earlier), the skin depth is smaller than the sample thickness. Furthermore, the wave vector of the electromagnetic wave inside the sample is parallel to the external magnetic field. Cyclotron resonance has been studied under these conditions in Bi and other metallic elements [8]. In general, it was found that no resonance peak should be observed in the millimetre-wave absorption of a simple metal; instead, the absorption should increase rapidly in B-fields higher than that of the cyclotron resonance [8]. However, if the sample thickness is comparable to the skin depth, a small broad resonant peak corresponding to the cyclotron resonance position can appear on the background rapid impedance growth; the height of the peak and its width depend in a complicated way on the sample thickness and carrier scattering time, whilst its position corresponds to that calculated from the carrier cyclotron mass [8] (compare figures 2(a) and 2(b)).

When the sample is placed at a maximum of H (figures 1(b) and 1(c)), the millimetre-wave $\boldsymbol{H}$-field is parallel to the sample planes. High-frequency currents therefore circulate

through the sample, resulting in millimetre-wave losses due to the interplane resistivity. These losses are much larger than those caused by in-plane conductivity because of the very large anisotropy in the α-phase (BEDT-TTF) salts (see earlier). Furthermore, the size of the interplane resistivity leads to estimates of the skin depth of a few millimetres, i.e. larger than the sample width [9].

Cyclotron absorption (figures 1(b) and 1(c)) associated with interplane currents might at first appear surprising in a Q2D material. However, the Q2D Fermi cylinders in BEDT-TTF salts are known to be warped [18, 19] such that the interplane velocity component varies during the course of a cyclotron orbit around the cylinder [20]. The field-induced interplane velocity variation is cyclical; therefore, if a high-frequency $\boldsymbol{E}$-field oscillating at the cyclotron frequency is directed parallel to the $\boldsymbol{B}$-field, resonant absorption may occur.

It appears that the data in figures 1 and 2 are in qualitative agreement with these considerations. The microwave absorption in the sample grows rapidly as B is increased when the sample is placed at an E-field maximum (figures 2(a) and 2(b)). Conversely the absorption goes down almost to the zero-field value when the sample is at an H-field maximum (figures 1(b) and 1(c)).

The positions of the absorption maxima measured at all frequencies appear to correspond to the same cyclotron mass value $m_c = 1.9m_e$ to within experimental errors. The effective mass in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ has been estimated from the temperature dependence of Shubnikov–de Haas and de Haas–van Alphen oscillations by a number of groups [3, 15, 16]; values obtained range from $2.2m_e$ [3] to $2.7m_e$ [15], with an average of around $2.5m_e$ [16]. Therefore the cyclotron mass observed in the present experiments is somewhat lower than the effective masses obtained in the quantum oscillation studies [3, 15, 16]. This observation is in qualitative agreement with theoretical work on the effects of many-body interactions [4].

Finally, we note that quantum oscillations have been observed for the first time in an organic material using conductivity measurements of a frequency comparable to the carrier scattering rate. The reason for these oscillations being much weaker in in-plane conductivity than in the interplane conductivity is as yet unclear. However, we note that almost all DC conductivity measurements have been done using the interplane geometry; the in-plane conductivity of this material has been little studied.

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References

[1] For a recent review see, e.g.,
1995 *Proc. Int. Conf. on Science and Technology of Synthetic Metals (Seoul, Korea, 1994)*; *Synth. Met.* **69–71**

[2] See, e.g.,
Harrison N, House A, Deckers I, Caulfield J, Singleton J, Herlach F, Hayes W, Kurmoo M and Day P 1995 *Phys. Rev.* B **52** 5584 and references therein

[3] Osada T, Kawasumi A, Yagi R, Kogoshima S, Miura N, Oshima M, Mori H, Nakamura T and Saito G 1990 *Solid State Commun.* **75** 901

[4] Quader K F, Bedell K S and Brown G E 1987 *Phys. Rev.* B **36** 156

[5] Singleton J, Pratt F L, Doporto M, Hayes W, Janssen T J B M, Perenboom J A A J, Kurmoo M and Day P 1992 *Phys. Rev. Lett.* **68** 2500

[6] See, e.g.,
Poole C P 1967 *Electron Spin Resonance* (New York: Interscience/Wiley)

Baden Fuller A J 1969 *Microwaves* (Oxford: Pergamon)
[7] Throughout this work we shall use H to denote the oscillating magnetic field strength due to the millimetre-wave radiation in the cavity and B to represent the quasi-static magnetic induction provided by the superconducting magnet.
[8] Galt J K, Yager W A, Merrit F R, Cetlin B B and Brailsford A D 1959 *Phys. Rev.* **114** 1396
Galt J K, Yager W A, Merrit F R, Cetlin B B and Dail H W 1955 *Phys. Rev.* **100** 748
[9] Mori H, Tanaka S, Oshima K, Saito G, T. Mori, Maruyama Y and Inokuchi H 1991 *Synth. Met.* **41–43** 2013
[10] Brooks J S, Uji S, Aoki H, Terashima T, Tokumoto M, Kinoshita N, Tanaka Y and Anzai H 1995 *Proc. Int. Conf. on Science and Technology of Synthetic Metals (Seoul, Korea, 1994)*; *Synth. Met.* **69–71** 839
[11] Howarth C 1995 *PhD Thesis* University of Bristol
[12] Sato H, Taniguchi H, Nakazawa Y, Kawamoto A, Kato K and Kanoda K 1995 *Proc. Int. Conf. on Science and Technology of Synthetic Metals (Seoul, Korea, 1994)*; *Synth. Met.* **69–71** 915
[13] Ardavan A 1995 private communication
[14] All of the samples studied exhibited very similar features and behaviour; for ease of comparison, figures 1 and 2 show data fom the same sample.
[15] Wosnitza J, Crabtree G W, Wang H H, Geiser U, Williams J M and Carlton K D 1992 *Phys. Rev.* B **45** 3018
[16] Doporto M, Pratt F L, Singleton J, Kurmoo M and Hayes W 1992 *Phys. Rev. Lett.* **69** 991
[17] Kinoshita N, Tokumoto M and Anzai H 1990 *J. Phys. Soc. Japan* **59** 3410
[18] Ishiguro T and Yamaji K 1990 *Organic Superconductors* (Berlin: Springer)
[19] Kartsovnik M V, Laukhin V N, Pesotskii S I, Schegolev I F and Yakovenko V M 1993 *J. Physique* **2** 89
Yamaji K 1989 *J. Phys. Soc. Japan* **58** 1520
[20] This is the mechanism which leads to the observation of significant magnetoresistance in conventional magnetotransport experiments employing interplane currents; see e.g. [3, 19].