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Fermi-surface topology of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br at ambient pressure

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Ambient pressure Fermi-surface measurements are reported for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. The single Shubnikov–de Haas frequency that is detected (3798±5 T) corresponds to 100% of the Brillouin zone and can be attributed to the β orbit that results from magnetic breakdown. From the temperature dependence of the oscillations, it appears that κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$)Br possesses a conventional Fermi-liquid ground state, although with a short mean free path, possibly due to the presence of Cu(II) ions. The effective mass as determined from the β-orbit oscillations is $m^* = 5.4 \pm 0.1 m_e$. [S0163-1829(97)52632-4]

The radical cation-based organic superconductor with the highest ambient pressure superconducting transition temperature (T_c) is κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (Ref. 1) ($T_c = 11.6$ K, inductive onset; $T_c = 12.5$ K, resistive onset), where BEDT-TTF stands for bis(ethylenedithio)tetrathiafulvalene. This charge-transfer salt has a layered structure (*Pnma*, $Z=4$) consisting of alternating layers (*ac* plane) of conducting BEDT-TTF cations and insulating polymeric dicyanimide bromide anions. Recent ^{13}C-nuclear magnetic resonance[2–4] (NMR) and low-temperature specific heat measurements[5] have aroused considerable interest in the possibility that κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br has an unconventional Fermi-liquid ground state.[6] In this connection, it has been pointed out that several of the organic superconductors with transition temperatures over 10 K have features in common with the cuprate superconductors, such as quasi-two-dimensional (Q2D) electronic structures, negligible or inverse isotope effects on T_c,[7] spin fluctuations,[4,8] a non-s-wave character of the superconducting condensate,[9–11] and the close proximity to an antiferromagnetic ground state. For example, the isostructural compound κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl possesses an antiferromagnetic ground state, but undergoes a conversion to a superconducting state with the application of minimal pressure ($T_c = 12.5$ K, inductive onset at 0.3 kbar pressure).[12]

Theoretical and experimental Fermi-surface studies have provided valuable insights into the conducting and superconducting properties of organic metals. The Fermi surface of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br obtained from tight-binding band calculations[1] consists of overlapping distorted cylinders split into quasi-one-dimensional (Q1D) electron sheets and closed Q2D elliptical hole pockets accounting for approximately 12% of the Brillouin zone[13] (BZ).

Although quantum oscillatory effects are commonly observed in organic metals, repeated attempts to obtain Shubnikov–de Haas (SdH) or de Haas–van Alphen oscillations in high magnetic fields at ambient pressure have been unsuccessful. Oscillations attributed to the SdH effect have been observed in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br at a pressure of ≈9 kbar.[14] The oscillation frequency corresponds to a clyindrical Fermi surface in the *ac* plane, but represents only 4.4% of the BZ. Possible reasons for the lack of quantum oscillations at ambient pressure have been discussed,[14] and include crystal quality, a distortive structural transition,[15,16] or a low-temperature magnetic ordering transition.[17] By the implementation of pulsed high magnetic fields extending to 60 T, we present ambient pressure measurements of the SdH effect in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br.

Single crystals of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br were synthesized electrochemically[18] on platinum electrodes at a constant current of 2×10^{-3} A m^{-2} employing 10.4 mg of BEDT-TTF (TCI) and Ph$_4$PN(CN)$_2$ (Ref. 19) (164.8 mg)/CuBr (Aldrich 99.999%, 67.2 mg) in 5 ml and 10 ml of 95% 1,1,2-trichloroethane:5% ethanol (v/v), respectively. The reaction was carried out at 25 °C under dry nitrogen in a vibration-isolated environment, and the crystals were harvested after 25 days. The samples were mounted with the *ac* plane perpendicular to the applied field ($ac \perp \mathbf{H}$). Four wire techniques were employed using 25.4 μm gold wires attached with graphite paint. Contacts were placed on opposite faces of the sample, so as to maximize the longitudinal (interplane) component of the magnetoresistivity. Magnetotransport measurements employed the high-frequency lock-in detection technique (≈500 kHz). The crystal was held in place with a small amount of epoxy to prevent it from moving during the field pulse. Care was taken to ensure that only a single surface of the sample was in contact with the epoxy, in order to avoid additional strain. Temperatures down to 380 mK were achieved using a plastic ^{3}He refrigerator with the capacitor driven pulsed magnetic fields provided by the National High Magnetic-Field Laboratory, Los Alamos.

An example of the high field magnetotransport data is shown in Fig. 1; the data clearly indicate the crossover transition (H_{c2}) from the superconducting to the normal metallic state at ≈10 T. An unusual aspect of these data is the negative slope of the magnetoresistance, persisting up to the highest magnetic fields available. We will return to a discussion of the slope of the magnetoresistance later in this paper. However, not until fields of ≈38 T do quantum oscillations appear. Fourier transformation reveals that the SdH frequency of 3798±5 T is very near to the area of the BZ (3795

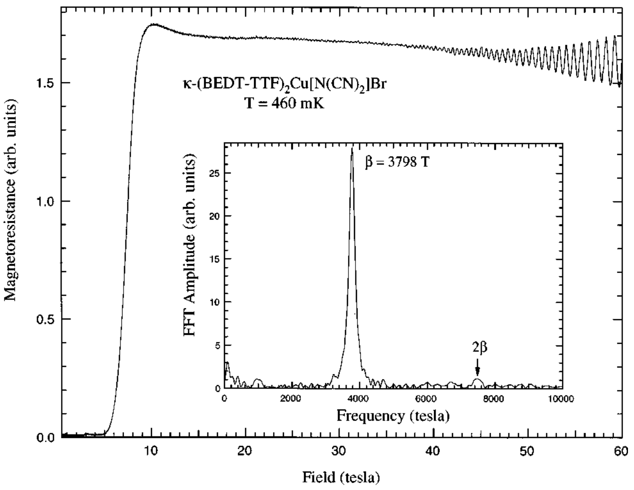

FIG. 1. The magnetoresistance of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br at 460 mK. Clear Shubnikov–de Haas oscillations are shown at fields above 38 T. The frequency of the oscillations is 3798±5 T which corresponds to 100% of the BZ, i.e., the magnetic breakdown orbit.

T) determined by means of low-temperature (20 K) x-ray crystallography.[7,20] While band-structure calculations[1] for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br yield a Fermi surface composed of a closed hole pocket (α orbit) bounded by Q1D sheets, a frequency equal to the BZ is generally observed at high fields in the κ-phase salts[21,22] due to magnetic breakdown.[23] The absence of other frequencies, such as the α pocket, implies that κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br is in the complete magnetic breakdown regime at the high magnetic fields at which the quantum oscillations are observed. A similar result was found for the BEDT-TSF analogue salt[24] [where BEDT-TSF stands for bis(ethylenedithio)tetraselenafulvalene], where the probability of the quasiparticles tunneling across the gap at the BZ boundary is close to unity. This contrasts with the results in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ ($T_c = 10.6$ K), in which the α frequency still persists at high magnetic fields.[25,26] Evidently, the gap in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br is much smaller than in the latter compound, as predicted by band-structure calculations.[1]

The SdH frequency obtained in this work differs greatly from that reported by Kartsovnik *et al.*[14] under hydrostatic pressure (9 kbar). While the frequency we have observed is undoubtedly due to the β orbit, the origin of the frequency reported in Kartsovnik *et al.* remains unclear. It is plausible that their measured frequency of ≈156 T (with an effective mass of $\approx 0.95 m_e$) could correspond to the α pocket of the calculated Fermi surface.[1,13] However, their measured frequency differs from the band-structure calculations by approximately a factor of 3. Such a large disagreement with tight-binding band theory is uncommon in charge-transfer salts. Hydrostatic pressure increases the size of the α pocket in κ-phase salts,[27] so it is unlikely that this could account for such a large discrepancy in the wrong direction. An alternative possibility is that the lower frequency originates from a density-wave, magnetic ordering[17] or a superstructural transition[15] at lower magnetic fields.

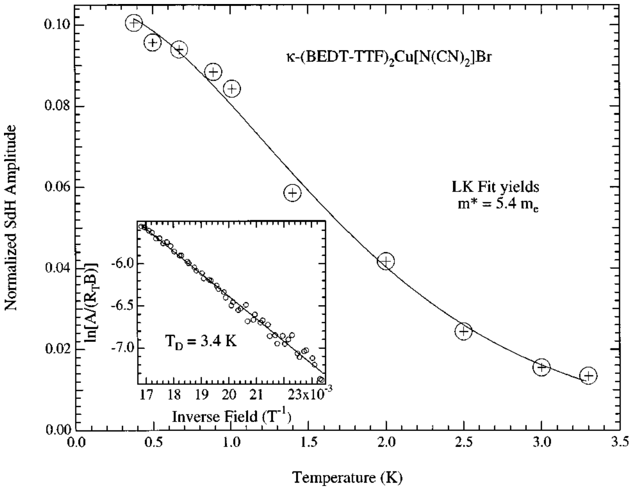

FIG. 2. The effective mass of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br is determined to be $5.4 \pm 0.1 m_e$ by fits of the amplitude of the SdH oscillations. The inset shows the Dingle plot resulting in $T_D = 3.4$ K.

A fit of the temperature dependence of the SdH oscillations to the function $R_T = X/\sinh(X)$ (Ref. 28) (where $X = 14.69\ m^*T/B$) is shown in Fig. 2. Fitting to the Lifshitz-Kosevich (LK) temperature reduction factor in a Q2D metal is warranted in the case where the amplitude of the oscillations is small compared to the background magnetoresistance.[26] It should be noted that the fit to the LK temperature reduction factor is consistent with conventional Fermi-liquid behavior. In contrast to the low effective mass obtained by Kartsovnik *et al.*, the effective mass we obtain in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br ($m^*_\beta = 5.4 \pm 0.1 m_e$ for the β frequency) is found to be comparable with other BEDT-TTF κ-phase salts.[21,22,25,26] Table I shows a comparison of various Fermi-surface parameters for several organic conductors. The effective mass of $5.4 m_e$ is nevertheless lighter than m^*_β in the lower T_c superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.[26] However, recent calculations[13] predict m^*_β for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br to be significantly lighter than in the latter salt, although our results indicate a difference of only ≈23%.

In quasi-two-dimensional conductors, the Dingle temperature is obtained from the slope γ (where $\gamma = 14.69 m^* T_D$) of a plot of the function $\ln[A/(R_T B)]$ versus $1/B$, where A is the amplitude of the resistance oscillations, divided by the background magnetoresistance (inset to Fig. 2). A study of the field dependence of the amplitude of the SdH oscillations reveals that the Dingle temperature $T_D \approx 3.4$ K is relatively

TABLE I. A comparison of fermiological properties affecting sample purity of various organic salts.

Compound	$m^*(m_e)$	T_D (K)	Frequency (T)	ℓ (Å)
κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br	5.4	3.4	3798 (β)	261
κ-(BEDT-TSF)$_2$Cu[N(CN)$_2$]Br[24]	2.7	2.4	3799 (β)	738
κ-(BEDT-TTF)$_2$Cu(NCS)$_2$[26]	7.0		3900 (β)	
κ-(BEDT-TTF)$_2$Cu(NCS)$_2$[22]	3.2	0.25	600 (α)	2366
κ-(BEDT-TTF)$_2$I$_3$[21]	3.9	0.4	3883 (β)	3102
α-(BEDT-TTF)$_2$KHg(SCN)$_4$[29]	2.0	0.4	570 (α)	2306
β-(BEDT-TTF)$_2$I$_3$[31]	4.7	0.53	3730 (β)	1902

high compared to other charge-transfer salts (Table I). The Dingle temperature of 3.4 K is equivalent to a scattering rate $\tau^{-1} \approx 2.8 \times 10^{12}$ s^{-1} or a mean free path of $\ell \approx 261$ Å. The Dingle temperature, alone, can be a misleading parameter, since it is renormalized by the cyclotron energy. We are comparing systems with different effective quasiparticle masses; it makes sense to compare the mean free paths (ℓ) in order to get a quantitative estimate of the purity of the respective systems. Table I indicates that ℓ in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br is approximately an order of magnitude smaller than in most other salts in which quantum oscillations are readily observed. The shorter mean free path therefore suggests that κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br has a higher impurity concentration.

Since the quantum oscillatory effects observed in this material are consistent with a conventional Fermi liquid, an alternative explanation must be sought for the anomalous behavior of the NMR (Refs. 2–4 and 8) relaxation rate. One possibility is that a small amount of Cu(II) is incorporated into the copper(I) dicyanamide bromide chains of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, and is coupled to the cation layers. In contrast to Cu(I), Cu(II) is magnetic with angular momentum $J = 1/2$ and, therefore, has the potential to act as an effective electron-scattering center. Convincing evidence has been provided for the existence of trace quantities of Cu(II) trapped in the predominantly Cu(I) anion network of κ'-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, profoundly affecting its normal state and superconducting properties.[32] Reasonable mechanisms exist for the introduction of a limited number of Cu(II) sites into κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br by way of the Cu(I)Br starting material, the electrocrystallization procedure, or subsequent crystal storage. For example, light and water are known to facilitate the conversion of Cu(I) to Cu(II).[30] It is important to point out that reasonable procedures were employed in the preparation of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br to ensure its purity, but it is difficult to rule out or, for that matter, detect the presence of traces of Cu(II). The negative slope of the magnetoresistance presented in Fig. 1, shown more clearly in Fig. 3(a), can be interpreted as *negative magnetoresistance* if we extrapolate the zero-field magnetoresistance to $T = 0$, excluding the superconducting transition [Fig. 3(b)]. The apparent presence of *negative magnetoresistance* is also consistent with a magnetic scattering mechanism. Low-frequency (17 Hz) resistivity measurements [Fig. 3(c)] performed in a 20 T superconducting magnet verify this feature in transport measurements performed at higher frequencies. Magnetic scattering centers could account for the large Dingle temperature in this material as well as the existence of spin fluctuations.[4,8] The hypothesis of Cu(II) inclusion in the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br salt is certainly worthy of further investigation.

In summary, Shubnikov–de Haas measurements reveal that κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br appears to possess a conventional Fermi-liquid ground state, with a short mean free path, possibly due to the presence of Cu(II) ions. The predicted breakdown orbit agrees to within 0.1% of the measured β frequency. The obtained effective mass of $m^* = 5.4 \pm 0.1 m_e$ is not exceptionally large, but is comparable to that found in other κ-phase BEDT-TTF salts. Experiments are in progress to prepare Cu(II)-free samples of the Cu[N(CN)$_2$]Br charge-transfer salt and to correlate magnetoresistance profiles with quantitative estimates of Cu(II) concentration. The synthesis of higher purity samples will hopefully enable the detection of quantum oscillations at lower magnetic fields. This would afford the particularly exciting possibility of observing the de Haas–van Alphen effect within the vortex state which has the potential to finally resolve the symmetry of the order parameter.[33]

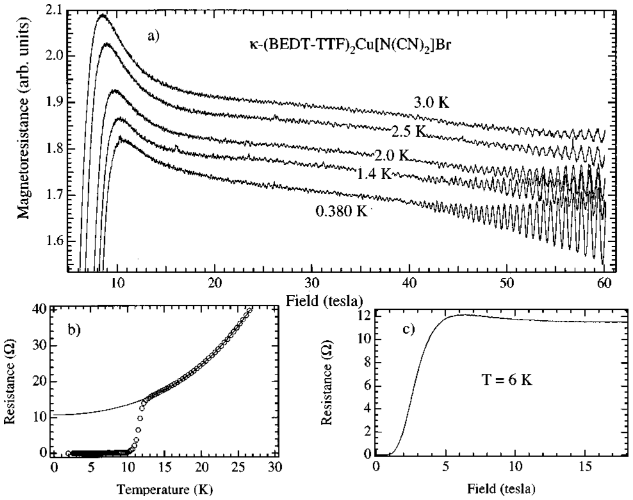

FIG. 3. (a) The magnetoresistance of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br measured at 511 kHz shows a negative slope of the magnetoresistance at fields above H_{c2} for different temperatures. (b) An extrapolation of the resistance to $T = 0$, neglecting the superconducting transition. (c) Low-frequency resistivity measurements also show a negative slope of the magnetoresistance, measured in a 20 T superconducting magnet.

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Note added in proof. It has recently come to our attention that SdH oscillations originating from the β orbit have been observed under a hydrostatic pressure of 7.7 kbar.[34] We would like to thank Dr. M. V. Kartsovnik for bringing this to our attention.

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