

LETTER TO THE EDITOR

Large magnetic-field-induced Fermi surface changes in α -ET₂KHg(NCS)₄

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Abstract. We report angle-dependent magnetoresistance experiments on the charge-transfer salt α -ET₂KHg(NCS)₄ using fields of up to 30 T. The data indicate that the widely reported high-field ‘kink’ observed in the magnetoresistance of the α -ET₂MHg(NCS)₄ (M = K, Tl, Rb) family of charge-transfer salts represents a transition from an imperfectly nested spin-density wave ground state, characterized by a quasi-one-dimensional Fermi surface sheet tilted with respect to the b^*c plane, to a state with a cylindrical two-dimensional Fermi surface.

Charge-transfer salts of the molecule ET (bis(ethylenedithio)tetrathiafulvalene or BEDT-TTF) have been the subject of intense experimental study since high-quality crystals became available [1,2]. The simplicity of the band-structures of the ET salts, and the relative ease with which they may be calculated and measured makes the compounds attractive systems for studying many fundamental problems [3]. Within this family of materials, the α -ET₂MHg(NCS)₄ (M = NH₄, K, Tl, Rb) compounds have excited much interest, as they appear to represent a test of the prerequisites for superconductivity [2]. The salts are isostructural with a predicted Fermi surface (FS) consisting of a two-dimensional (2D) closed hole pocket and a one-dimensional (1D) open electron band [4]. However, whereas the M = NH₄ salt is a superconductor with $T_c \sim 1$ K, the salts with M = K, Tl or Rb are metallic down to $\lesssim 200$ mK [5]. Furthermore, α -ET₂NH₄Hg(NCS)₄ shows simple positive magnetoresistance (MR) and Shubnikov–de Haas oscillations (SdHo) with a periodicity close to that expected from the predicted 2D FS hole pocket [6], whereas the low-temperature MR of the M = K, Tl, Rb salts exhibits novel effects such as hysteresis [7–9] and apparent large spin-splitting [8–11]. However, perhaps the most celebrated features of the α -ET₂MHg(NCS)₄ (M = K, Tl, Rb) salts are the onset of antiferromagnetic order at temperatures $T_N \simeq 8 - 10$ K and the presence below this temperature of a region of sharp negative MR at fields $\simeq 22 - 30$ T, known as the ‘kink’ [7–12]. These phenomena have been linked to the possible presence of a spin-density wave (SDW) ground state [7–12], with the kink signalling the destruction of the SDW by the external field [8]. In spite of these ideas, the low-temperature band-structure and the field-induced changes giving rise to the kink have remained the subjects of speculation.

In this letter, angle-dependent MR oscillations (AMRO) [13, 14] in α -ET₂KHg(NCS)₄ have been used to investigate this problem. The AMRO indicate that the low-temperature, low-magnetic-field band-structure is dominated by a 1D open section of FS inclined at $\simeq 21^\circ$

to the crystallographic b^*c plane; qualitatively similar behaviour has also been recently observed in $\alpha\text{-ET}_2\text{TlHg}(\text{NCS})_4$ [10,14]. On raising the magnetic field through the kink, however, the AMRO change in character, indicating that the FS now possesses a 2D closed section in the form of a distorted warped cylinder. The data therefore give definitive proof that the kink is the signature of a magnetic-field-induced change in the Fermi surface.

$\alpha\text{-ET}_2\text{KHg}(\text{NCS})_4$ crystals of typical dimensions $1 \times 1 \times 0.1 \text{ mm}^3$ were prepared electrochemically [2,15], and gold wires were attached to both ac platelet faces using platinum paint. MR measurements were performed with the current in the b^* direction (b^* is perpendicular to the conducting ac planes) in ^3He and ^4He cryostats which allowed the sample to be rotated about two perpendicular axes *in situ*. The samples were initially oriented to $\pm 1^\circ$ by x-ray techniques and by measuring the polarized infrared reflectivity at room temperature [16]. Standard AC current techniques were used; to avoid sample heating, the current was kept between 0.1 and 100 μA and care was taken to ensure that the MR values were neither current- nor frequency-dependent. Steady fields were provided by the hybrid magnets at Nijmegen.

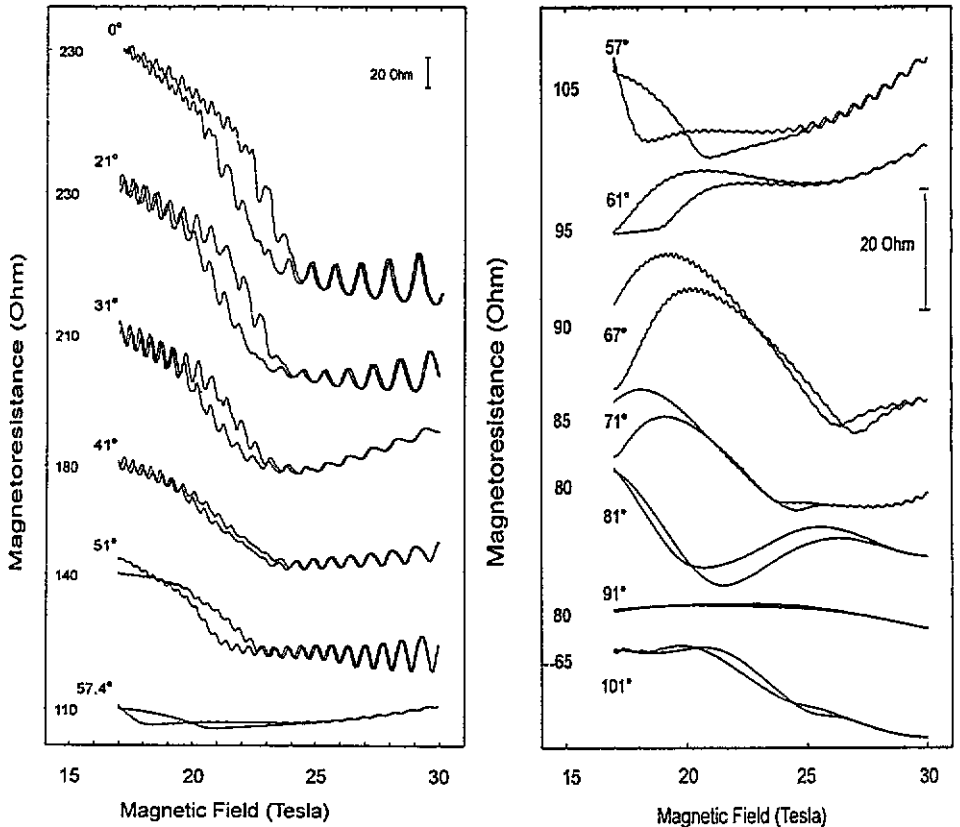


Figure 1. MR of an $\alpha\text{-ET}_2\text{KHg}(\text{NCS})_4$ crystal at 500 mK; data for both up- and down-sweeps of the field are shown (some of these data have been previously plotted in [8]). The field is applied in the b^*c plane; labels denote the angle between the field and the b^* axis. Data are offset for clarity; the resistance at the origin of each trace is marked on the left axes.

Figure 1 shows the MR of an $\alpha\text{-ET}_2\text{KHg}(\text{NCS})_4$ sample between 16 and 30 T; the field has been applied at several angles in the b^*c plane. The data illustrate many of the MR

features of the α -ET₂MHg(NCS)₄ (M = K, Tl, Rb) salts, which may be listed as follows.

(i) There is a region of strong negative MR (the 'kink') around 22 T when the field is parallel to b^* [7-11].

(ii) At fields around and below the kink, there is hysteresis in the MR [7-10].

(iii) Above the kink there is one series of SdHo of frequency $B_F = 656 \pm 10$ T; below it, the SdHo are of a similar frequency ($B_F = 670 \pm 5$ T) but more complex, exhibiting a strong second harmonic component at certain angles [7-11]. The frequency of the SdHo is within a few percent of that expected from the 2D hole pocket predicted by band-structure calculations. In addition, depending on the sample quality and/or cooling method, an apparent second series of SdHo has been observed below the kink in α -ET₂KHg(NCS)₄ and α -ET₂TlHg(NCS)₄ [8,10].

(iv) The background MR oscillates in size as the sample is tilted in the field [8].

The angular dependence of the MR of α -ET₂KHg(NCS)₄ at 12 T and 24 T is shown in detail in figure 2; MR data were recorded whilst the crystal was rotated in the field. The horizontal axis represents the angle between the field and the b^* axis (θ), whilst each trace is labelled with an azimuthal angle ϕ describing the plane of rotation; $\phi = 0^\circ$ represents rotation about the a axis and increasing values of ϕ represent angular displacement of the rotation axis in the ac plane towards the c axis; rotation about the c axis corresponds to $\phi \simeq 90^\circ$. The experiment was performed by first setting ϕ ; the sample was then rotated at 12 T and 24 T (figures 2(a) and (b)).

In the 12 T data in figure 2(a), a series of AMRO are observed as θ is varied; the minima in the MR are very sharp and are periodic in $\tan(\theta)$ at each azimuthal angle. However, this periodicity varies as a function of ϕ , as does the amplitude of the AMRO, which almost vanish at $\phi = 70^\circ$. If the periodicity of the minima, deduced from a plot of minimum index versus $\tan(\theta)$ (figure 3(a), inset) is plotted as a function of the azimuthal angle ϕ , it is seen to vary as $(1.25 \pm 0.05)/\cos(\phi - \phi_0)$, where $\phi_0 = -21 \pm 3^\circ$ (figure 3(a)); i.e. the maximum amplitude and minimum periodicity in $\tan(\theta)$ ($=1.25 \pm 0.05$) of the AMRO occurs when the field rotation plane forms an angle $21 \pm 3^\circ$ with the b^*c plane.

Qualitatively similar behaviour has been observed in α -ET₂TlHg(NCS)₄, which has been studied in steady fields of up to 14 T [10,14]; however, in that instance the characteristic plane of maximum AMRO amplitude was at an angle of $24 \pm 1^\circ$ with the b^*c plane. The authors of [10] and [14] argued that the inverse cosine dependence of the AMRO period was evidence for the existence of a characteristic plane in the electron system, due to a 1D FS sheet. AMRO in substances containing a 1D FS sheet have been modelled by a number of authors [10,17], who calculate the velocities of quasi-1D electrons subjected to a magnetic field. If the field is applied in a general direction, the velocity components perpendicular to the 1D direction sweep out all possible values and average to zero. However, if the field is oriented so that the electron's k vector is along a reciprocal lattice vector, the transverse velocity takes only a limited set of values [10,17]. Thus, its time-averaged velocity is non-zero, leading to dips in the MR periodic in $\tan(\theta)$. The periodicity is proportional to $1/\cos(\phi - \phi_0)$, ϕ_0 being the azimuthal angle at which the plane of rotation of the field is perpendicular to the 1D axis. The FS of α -ET₂KHg(NCS)₄ calculated using the room temperature crystal parameters does contain a 1D sheet in the b^*c plane; however the 1D FS section indicated by the AMRO is tilted by $21 \pm 3^\circ$ with respect to this.

The authors of [10] and [14] proposed a SDW ground state for α -ET₂TlHg(NCS)₄ with a wavevector

$$Q = \frac{\zeta A}{6} + \frac{C}{6} + \left(\frac{\eta}{3} - \frac{1}{6}\right) B \quad (1)$$

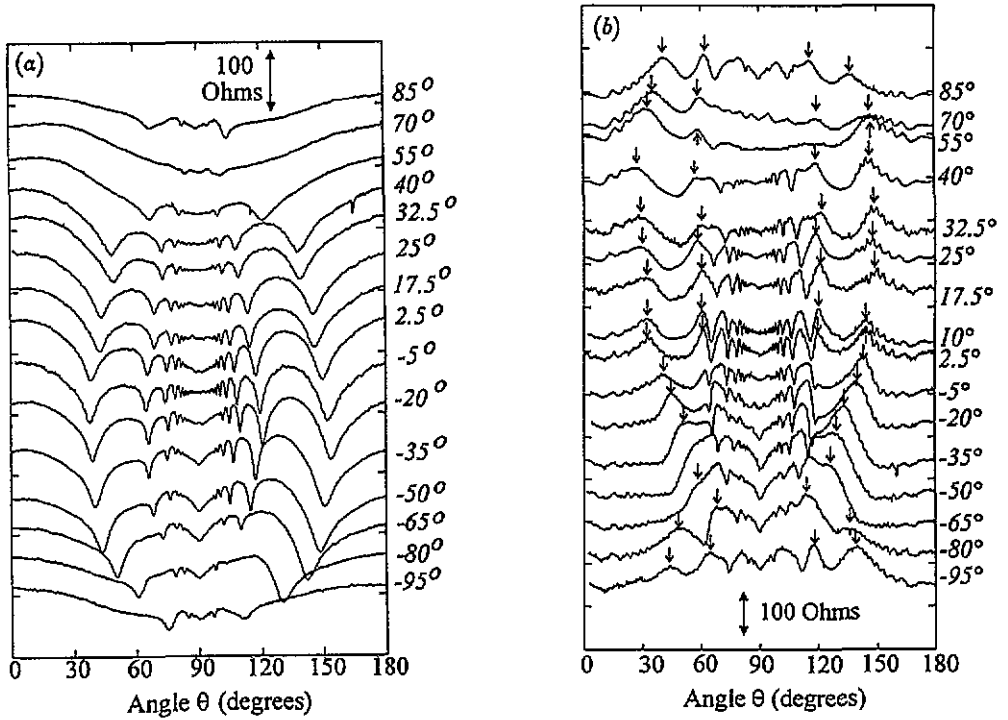


Figure 2. AMRO of an α -ET₂KHg(NCS)₄ crystal at 1.5 K for several values of the angle ϕ (see text). Data for 12 T and 24 T are shown in figures 2(a) and (b) respectively. The traces are offset for clarity. The arrows in figure 2(b) indicate the 2D MR peaks associated with the high-field phase.

where A, B and C are the reciprocal lattice vectors of the room temperature crystal structure and η and ζ are ± 1 [10,14], in order to fit their 14 T AMRO data. The action of the proposed SDW state on the calculated band-structure results in a warped quasi-1D FS tilted by 26° with respect to the b^*c plane, plus small 2D pockets [14]. It was also suggested that breakdown orbits between these pockets and the 1D sheets could explain the various SdHo frequencies observed below the kink [10,14]. In view of the very similar low-field AMRO of the K and Tl α -phase salts, it is likely that such a SDW state may also be used to explain the low-temperature, low-field behaviour of α -ET₂KHg(NCS)₄.

Turning to the AMRO in α -ET₂KHg(NCS)₄ at 24 T (figure 2(b)), at first sight the data appear rather similar to those observed at 12 T; indeed, the oscillations for $60^\circ \lesssim \theta \lesssim 120^\circ$ may be fitted by a minimum period in $\tan(\theta)$ of 1.25 ± 0.05 (as at 12 T) and an offset angle of $\phi_0 = -14 \pm 4^\circ$ (figure 3(b)). However, outside this range of θ the behaviour at 24 T is decidedly different from that at 12 T. Figure 4 shows the evolution of the AMRO at constant ϕ for various fixed fields from 17 T to 25 T. As the field is raised, the sharp MR minima observed in the angular ranges $0 < \theta < 60^\circ$ and $120^\circ < \theta < 180^\circ$ at low fields vanish and new extra *peaks* in the MR appear.

The reason for this apparently complex behaviour may be seen in figure 1; it is due to the angle dependence of the kink transition. It has been argued that the kink represents a phase boundary between two different states of the α -ET₂MHg(NCS)₄ salts, and that the true position of the boundary is marked by the field at which the hysteresis disappears,

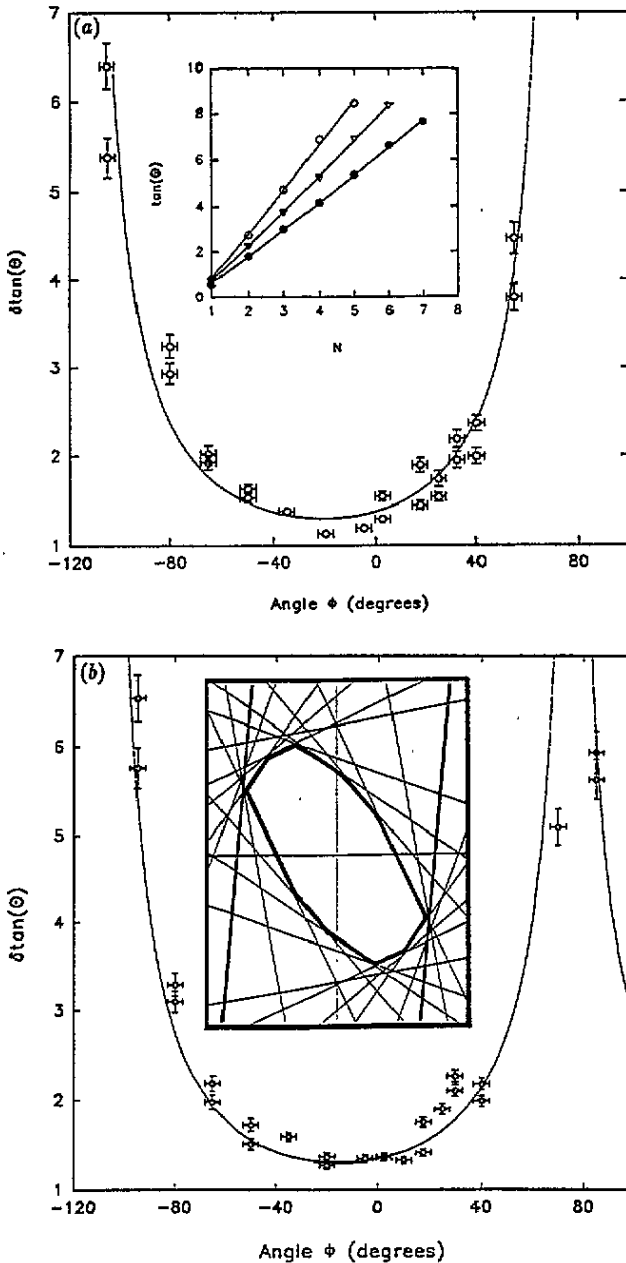


Figure 3. ϕ dependence of the periodicity of the AMRO in figure 2. The inset in figure 3(a) is a plot of MR minimum index versus $\tan(\theta)$ for three values of ϕ . The main figures show fits of $1.25/\cos(\phi - \phi_0)$ to the gradients obtained for 12 T data (part (a)) and 24 T data (part (b)); gradients are points. The bold curve in the inset in part (b) is the 2D FS shape deduced for the high-field phase (see text: horizontal axis parallel to a and $3.6 \times 10^9 \text{ m}^{-1}$ long); the fine lines indicate the tangents derived from the 2D AMRO.

denoting the destruction of domain structure due to internal fields [7,9]. Applying this criterion to the data of figure 1, it will be seen that the end of the hysteretic behaviour

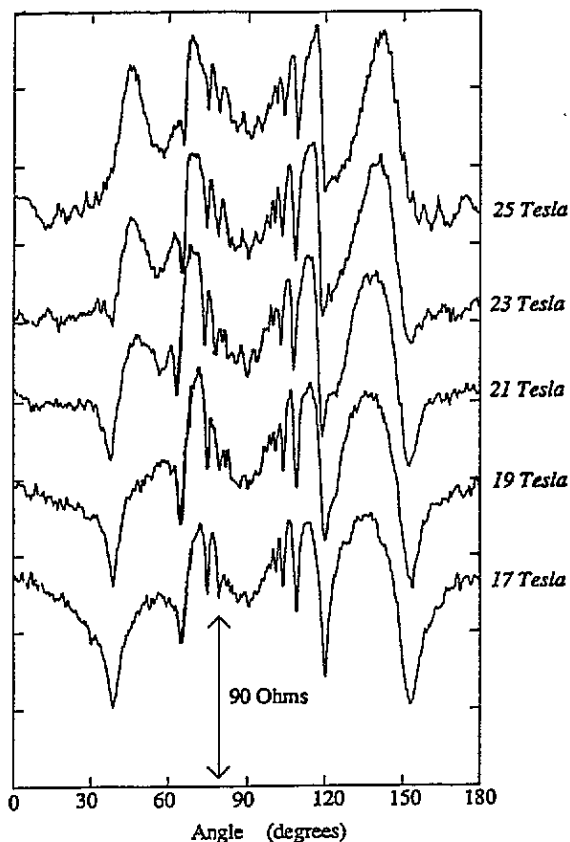


Figure 4. The evolution of the peaks in the angle-dependent MR of $\alpha\text{-ET}_2\text{KHg(NCS)}_4$ with increasing magnetic field. The azimuthal angle is -20° . Note that the sharp MR minima between $60^\circ < \theta < 120^\circ$ persist to 25 T, but that they gradually disappear with increasing field to be replaced by peaks outside this angular range. The temperature is 1.5 K.

occurs just below 24 T for angles up to $\theta \simeq 57^\circ$ and then moves to higher fields. It may therefore be said that the peaks in the MR at 24 T observed in the range $0 < \theta < 60^\circ$ and $120^\circ < \theta < 180^\circ$ (figure 2(b)) represent phenomena characteristic of the high-field phase of $\alpha\text{-ET}_2\text{KHg(NCS)}_4$ whilst the sharp dips in the MR remaining outside this angular range (i.e. $60^\circ < \theta < 120^\circ$) are characteristic of the low-field 'below the kink' phase. As the field increases further, the peaks associated with the high-field phase persist to higher θ . This is seen in the data in figure 1, where the MR at 30 T peaks at $\theta = 33 \pm 1^\circ$, $59 \pm 1^\circ$ and $70 \pm 1^\circ$ [8].

Whereas the MR minima observed at 12 T for all angles and at 24 T for $60^\circ < \theta < 120^\circ$ exhibit a periodicity in $\tan(\theta)$ with a very marked ϕ dependence ($1/\cos(\phi - \phi_0)$), the positions of the extra peaks in the MR at 24 T have a much weaker dependence on ϕ , and are observable at all azimuthal angles (the peaks are marked by arrows in figure 2(b)). This suggests that the mechanism responsible for the peaks is quasi-2D and therefore that the conductivity of the high-field phase of $\alpha\text{-ET}_2\text{KHg(NCS)}_4$ is dominated by a section of the FS which is 2D in nature. Peaks in the AMRO of quasi-2D materials have been treated in several theoretical works (see [13] and [18] and references therein) and are connected with the vanishing of the electronic group velocity perpendicular to the 2D layers. The angles θ_i

at which the maxima occur are given by $b'k_{\parallel}\tan(\theta_i) = \pi(i \mp 1/4) + A(\phi)$, where the signs $-$ and $+$ correspond to positive and negative θ_i respectively, b' is the effective interplane spacing, k_{\parallel} is the maximum Fermi wavevector projection on the plane of rotation of the field and $i = \pm 1, \pm 2 \dots$ [13]. Here positive i correspond to $\theta_i > 0$ and negative i to $\theta_i < 0$ [13]. The gradient of a plot of $\tan(\theta_i)$ against i may thus be used to find one of the dimensions of the FS, and, if the process is repeated for several planes of rotation, the complete FS shape may be mapped out. $A(\phi)$ is a function of the plane of rotation of the field, determined by the inclination of the plane of warping; hence this may also be found [13].

These procedures have been applied to the data shown in figure 2(b), and used to deduce the FS shape shown in the inset in figure 3(b). The errors in the various radii of the FS are liable to be quite large ($\approx 15\%$), as only two or four MR peaks are observable at each ϕ , corresponding to $i = \pm 1, \pm 2$; at such small values of i the above formula is least accurate [13]. However, the inset in figure 3(b) does show that the FS derived from the raw data is of roughly the correct area to account for the frequency of the sdHo above the kink (figure 1). As mentioned above, a 2D hole pocket of approximately this size is also predicted by the band-structure calculations [4]; however, the calculated hole pocket is almost circular in cross-section, whereas the FS derived from the data in this work appears to be elongated in the c direction, and tilted away from the c axis.

In summary, the AMRO data presented in this paper indicate unambiguously that a profound change in band-structure occurs at the MR kink in the α -ET₂MHg(NCS)₄ ($M = K, Tl, Rb$) family of charge-transfer salts. The low-field phase of α -ET₂KHg(NCS)₄ appears to have a FS which is quasi-1D in character and tilted at an angle $\approx 21^\circ$ to the b^*c plane; this is almost certainly due to the existence of a SDW ground state. The high-field phase is characterized by AMRO which are quasi-2D in nature, and which indicate a closed cylindrical FS.

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Note added in proof. A very recent paper supporting the conclusions in this letter has just come to our notice [19]. The authors observe AMRO at fields ≈ 14 T as a sample of α -ET₂KHg(NCS)₄ is raised in temperature through the magnetic ordering transition at 8 K. As the sample passes from the low-temperature to the high-temperature phase, the AMRO change in character, indicating that the Fermi surface has changed from predominantly one dimensional to predominantly two dimensional in form. This supports our suggestion that the low-temperature Fermi surface of α -ET₂KHg(NCS)₄ at fields above the 'kink' is similar to that at temperatures above the magnetic ordering transition.

References

- [1] Ishiguro T and Yamaji K 1990 *Organic Superconductors* (Berlin: Springer)
- [2] Kresin V Z and Little W A (ed) 1990 *Organic Superconductivity* (New York: Plenum)
- [3] For a recent review, see
1993 *Proc. Int. Conf. on Science and Technology of Synthetic Metals* (Göteborg, Sweden, 1992); *Synth. Met.*
56-8
- [4] Mori H, Tanaka S, Oshima M, Saito G, Mori T, Maruyama Y and Inokuchi H 1990 *Bull. Chem. Soc. Japan*
63 2183

- [5] Ito H, Kaneko H, Ishiguro T, Ishimoto H, Kono K, Horiuchi S, Komatsu T and Saito G 1993 *Solid State Commun.* **85** 1005
- [6] Singleton J, Pratt F L, Doporto M, Caulfield J, Hayes W, Deckers I, Pitsi G, Herlach F, Janssen T J B M, Perenboom J A A J, Kurmoo M and Day P 1993 *Synth. Met.* **56** 2198
Wosnitza J, Crabtree G W, Wang H H, Carlson K D, Vashon M D and Williams J M 1991 *Phys. Rev. Lett.* **67** 263
- [7] Sasaki T and Toyota N 1992 *Solid State Commun.* **82** 447
Sasaki T, Sato H and Toyota N 1991 *Synth. Met.* **42** 2211
- [8] Pratt F L, Singleton J, Doporto M, Fisher A J, Janssen T J B M, Perenboom J A A J, Kurmoo M, Hayes W and Day P 1992 *Phys. Rev. B* **45** 13904
- [9] Brooks J S, Agosta C C, Klepper S J, Tokumoto M, Kinoshita N, Anzai H, Uji S, Aoki H, Perel A S, Athas G J and Howe D A 1992 *Phys. Rev. Lett.* **69** 156
- [10] Kartsovnik M V, Kovalev A E and Kusch N D 1993 *J. Physique I* **3** 1187
- [11] Sasaki T, Toyota N, Tokumoto M, Kinoshita N and Anzai H 1990 *Solid State Commun.* **75** 93, 97
Tokumoto M, Swanson A G, Brooks J S, Agosta C C, Hannahs S T, Kinoshita N, Anzai H, and Anderson J R 1990 *J. Phys. Soc. Japan* **59** 2324
Osada T, Yagi R, Kawasumi A, Kagoshima S, Miura N, Oshima M, Mori H, Nakamura T and Saito G 1991 *Synth. Met.* **42** 2171
Osada T, Yagi R, Kagoshima S, Miura N, Oshima M, and Saito G 1990 *Phys. Rev. B* **41** 5428
- [12] Klepper S J, Brooks J S, Athas G J, Chen X, Tokumoto M, Kinoshita N and Tanaka Y 1994 *Proc. Tenth Int. Conf. on the Electronic Properties of Two Dimensional Systems (Newport, RI, 1993)*; 1994 *Surf. Sci.* at press
- [13] Kartsovnik M V, Laukhin V N, Pesotskii S I, Schegolev I F and Yakovenko V M 1992 *J. Physique I* **2** 89
- [14] Kartsovnik M V, Kovalev A E, Laukhin V N, and Pesotskii S I 1992 *J. Physique I* **2** 223
- [15] Oshima M, Mori H, Saito G and Oshima K 1989 *Chem. Lett.* **1989** 1159
Saito G and Kagoshima S (ed) 1990 *The Physics and Chemistry of Organic Superconductors (Springer Proc. in Physics 51)* (Berlin: Springer) p 257
Kurmoo M, Talham D R, Day P, Parker I D, Friend R H, Stringer A M and Howard J A K 1987 *Solid State Commun.* **61** 459
- [16] Pratt F L, Hayes W, Fisher A J, Singleton J, Spermon S J R M, Kurmoo M and Day P 1989 *Synth. Met.* **29** F667
Kuroda H, Yakushi K, Tajima H, Ugawa A, Tamura M, Okawa Y, Kobayashi A, Kato R, Kobayashi H and Saito G 1988 *Synth. Met.* **27** A491
- [17] Lebed A G' and Bak P 1989 *Phys. Rev. Lett.* **63** 1315
Montambaux G and Littlewood P B 1989 *Phys. Rev. Lett.* **62** 953
Yakovenko V M 1992 *Phys. Rev. Lett.* **68** 3607
Naughton M J, Chung O H, Chaparaba M, Bu X and Coppens P 1991 *Phys. Rev. Lett.* **67** 3712
Osada T, Kagoshima S and Miura N 1992 *Phys. Rev. B* **46** 1812
- [18] Yamaji K 1989 *J. Phys. Soc. Japan* **58** 1520
- [19] Kovalev A E, Kartsovnik M V, Shibaeva R P, Rozenberg L P, Schegolev I F and Kusch N D 1994 *Solid State Commun.* **89** 575