Magnetoresistance Studies in the Low-Dimensional Organic Metal
α-(ET)$_2$TIHg(SeCN)$_4$ under Pressure: Experiments and
Simulation by Tight Binding Band Structure Calculations

P. Auban-Senzier (1), A. Audouard (2), V. N. Laukhin (2,3), R. Rousseau (4,5), E.
Canadell (4,6), L. Brossard (2), D. Jérome (1) and N. D. Kushch (3)

(1) Laboratoire de Physique des Solides(*), Université de Paris-Sud, 91405 Orsay Cedex, France
(2) Laboratoire de Physique des Solides(*** et Service National des Champs Magnétiques Pulsés(***),
INSA, Complexe Scientifique de Rangueil, 31077 Toulouse, France
(3) Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, Chernogolovka,
MD 142432, Russia
(4) Institut de Ciência de Materials de Barcelona, Campus de la U.A.B., 08193 Bellaterra, Spain
(5) Permanent address: Department of Chemistry, The University of Michigan, Ann Arbor,
Michigan 48109, USA
(6) Permanent address: Laboratoire de Chimie Théorique(****), Université de Paris-Sud, 91405
Orsay Cedex, France.

(Received 27 March 1995, revised 19 May 1995, accepted 4 July 1995)

Résumé. — Des mesures de magnétorésistance ont été effectuées dans le conducteur organique
bidimensionnel α-(ET)$_2$TIHg(SeCN)$_4$ jusqu'à la température de 0.4 K et sous pression hydrosta-
tique. Une seule série d'oscillations Shubnikov-de Haas est observée dans la gamme de pression
comprise entre 3.5 et 11 kbar. La masse cyclotron décroît lentement lorsque la pression augmente
et la fréquence des oscillations augmente rapidement depuis la valeur de (653 ± 3)$T$ à
pression ambiante jusqu'à (790 ± 3)$T$ à 11 kbar. Une modélisation basée sur la méthode des
liaisons fortes suggère que la dépendance en pression de l'aire de l'orbite fermée de la surface de
Fermi est due au glissement, induit par la pression, des molécules des chaînes ne contenant qu'un
type de donneurs. Au contraire de son composé frère α-(ET)$_2$NH$_4$Hg(SCN)$_4$, il présente des
oscillations lentes, de fréquence (47±3)$T$, à pression ambiante. Elles ne sont pas observées entre
3.5 et 11 kbar et pourraient être en relation avec un emboîtement des orbites ouvertes à pression
ambiante qui pourrait détruire la supraconductivité dans le composé à base de sélénium.

Abstract. — Magnetotransport measurements have been carried out in layered organic metal
α-(ET)$_2$TIHg(SeCN)$_4$ at temperatures down to 0.4 K and under hydrostatic pressure. Only one

(*) (URA CNRS 02)
(*** (ERS CNRS 111)
(***) (UMS CNRS 819)
(****) (URA CNRS 506)

© Les Editions de Physique 1995
series of Shubnikov-de Haas oscillations is observed in the applied pressure range from 3.5 to 11 kbar. The cyclotron mass decreases slowly with increasing pressure and the oscillation frequency increases rapidly from its ambient pressure value of (653 ± 3)T to (790 ± 3)T at 11 kbar. A model tight binding study suggests that the pressure dependence of the area of the closed part of the Fermi surface is consistent with a pressure induced sliding motion of the molecules in the donor chains containing only one type of donors. Slow oscillations with frequency (47 ± 3)T have also been observed at ambient pressure in contrast to its superconducting sister compound \( \alpha-(ET)_2NH_4Hg(SCN)_4 \). They are not observed in the applied pressure range and might be connected with some nesting of the open orbits at ambient pressure which may result in a destruction of superconductivity in the Se-containing compound.

1. Introduction

The members of the isostructural \( \alpha-(ET)_2MHg(XCN)_4 \) family (ET=bis(ethylenedithio)tetra-thiafulvalene; M=K, Tl, Rb or NH4; X=S or Se) are quasi two-dimensional (2D) organic conductors of great interest due to the variety of their low-temperature properties. At room temperature their Fermi surface (FS), which is composed of both slightly warped quasi-2D cylinder (closed hole orbits) and quasi-1D sheets (open electron orbits) [1], is expected to be very similar for all of them [2]. Nevertheless, \( \alpha-(ET)_2MHg(SCN)_4 \) compounds with M = K, Tl, Rb undergo a magnetic field- and temperature-dependent phase transition at low \( T_p = 8\pm10 \) K temperature [3–5] into a ground state with i) anisotropic magnetic susceptibility [6] typical of magnetic ordering system with formation of spin density wave (SDW), ii) complex magneto-oscillatory behaviour and iii) anomalies in the semiclassical and angular-dependent magnetoresistance (MR) [3, 4, 7–13]. They even exhibit the so called weak superconductivity at \( T < 300 \) mK [14, 15]. On the other hand the compound with M = NH4 does not undergo the phase transition at \( T_p \) and becomes a superconductor below 1.4 K [16, 17], whereas the selenium-containing salt \( \alpha-(ET)_2TlHg(SeCN)_4 \) is a stable organic metal without any phase transition down to at least 80 mK [18, 19].

Hydrostatic pressure \( (P > 3 \text{ kbar}) \) suppresses the low-temperature phase transition at \( T_p \) associated with the nesting of the open orbits in \( \alpha-(ET)_2MHg(SCN)_4 \) with M = K, Tl, Rb restoring the high-temperature metallic state [17, 20]. In contrast, a moderate pressure \( (P > 2 \text{ kbar}) \) destroys superconductivity in \( \alpha-(ET)_2NH_4Hg(SCN)_4 \) and improves the nesting of the quasi-1D open sheets thus producing small closed orbits which give rise to slow magnetoresistance oscillations with frequency around 45T at 2 kbar [21].

An important problem to solve is to understand why the \( \alpha-(ET)_2TlHg(SeCN)_4 \) salt does not exhibit superconductivity in contrast to its sister compound \( \alpha-(ET)_2NH_4Hg(SCN)_4 \). In order to bring some enlightments about this question, we have studied the effect of pressure on the magnetotransport properties and FS of Se-containing salt \( \alpha-(ET)_2TlHg(SeCN)_4 \) in connection with tight binding FS calculations.

2. Experimental

The details of the electrochemical synthesis as well as the crystal structure and some of the zero-field properties of the \( \alpha-(ET)_2TlHg(SeCN)_4 \) compound have been published elsewhere [18]. The samples were mounted using the standard four-contact method with annealed platinum wires (20 \( \mu \text{m} \) in diameter) which were glued to sample by graphite paste. Both alternating current (10 or 20 \( \mu \text{A}, 77 \text{ Hz} \)) and magnetic field were applied along the \( b^* \)-direction (i.e., per-
3. Experimental Results and Discussion

Both the room temperature conductivity \([\frac{d\ln(\sigma)}{dP} = 0.12 \text{kbar}^{-1}; \, \sigma(P = 0) = 1000 \div 2000 \, \Omega^{-1} \, \text{cm}^{-1}]\) and the residual resistivity ratio (from 40 at 3.5 kbar up to 60 at 11 kbar) of the sample increase with increasing pressure. The low temperature magnetic field dependence of the magnetoresistance at 0.4 K is displayed in Figure 1 for three different hydrostatic pressures. Only one series of Shubnikov-de Haas (SdH) oscillations is observed. The semiclassical magnetoresistance \([R_{SC} - R_0]/R_0\) (where \(R_{SC}\) and \(R_0\) are the field-dependent semiclassical part of the resistance and the zero-field resistance, respectively, at the given pressure) increases with increasing pressure while the SdH oscillation amplitude clearly decreases. The oscillatory part of the magnetoresistance have been calculated as \([R - R_{SC}]/R_{SC}\), where \(R\) is the sample resistance. The data deduced from Figure 1 above 5 T is shown in Figure 2. Clear SdH oscillations become visible starting from \(\sim 5 \, \text{T}\) at \(T < 1 \, \text{K}\), as it is the case at ambient pressure [18,19].

As displayed in Figure 3, Fourier transforms reveal a fundamental frequency and a well-pronounced second harmonic. We would like to emphasize the strong pressure dependence of the fundamental amplitude, while the amplitude of the second harmonic is roughly independent

### Figure 1

- Low-temperature magnetic field dependence of the longitudinal magnetoresistance \((I//B//b^*)\) of \(\alpha-(ET)_2\)Hg(SeCN)_4 for different pressures.
T = 0.4 K

\[
\frac{R_{\text{sc}}}{R_{\text{sc}}} \sim 0.05
\]

\[
\frac{R_{\text{sc}}}{R_{\text{sc}}} \sim 0.12
\]

\[
\frac{R_{\text{sc}}}{R_{\text{sc}}} \sim 0.2
\]

\[
1/B (T^{-1})
\]

Fig. 2. — Oscillatory part of the magnetoresistance deduced from Figure 1. \( R_{\text{sc}} \) is the semiclassical part of the resistance (see text).

on pressure.

The measured SdH fundamental frequency, \( F \), increases linearly from the ambient pressure value of \( (653 \pm 3)T \) [19] to \( (790 \pm 3)T \) at 11 kbar (Fig. 4a). As \( F \) is directly proportional to the extremal cross-section area of the closed orbit in \( k \)-space, this indicates that the area of the quasi-2D part of FS has increased by 21% at 11 kbar. Same \( (\text{d}(\ln(F))/\text{d}P = 0.02 \text{ kbar}^{-1}) \) and slightly higher \( (\text{d}(\ln(F))/\text{d}P = 0.03 \text{ kbar}^{-1}) \) pressure dependences have been observed in the sulphur-analog compounds \( \alpha-(\text{ET})_2\text{Kg(SCN)}_4 \) [20] and \( \alpha-(\text{ET})_2\text{NH}_4\text{Hg(SCN)}_4 \) [21], respectively. It is worthwhile noticing that the phase factor \( \gamma \) entering the Onsager relation \( 1/B_{\gamma} = (n + \gamma)/F \) (where \( B_{\gamma} \) is the field value at the maximum of the oscillation corresponding to the Landau level \( n \)) is close to 0 up to 3.5 kbar and increases under higher pressure (\( \gamma \sim 0.2 \) and 0.3 for 5 and 7.5 kbar, respectively). At 11 kbar, \( \gamma \) is difficult to estimate due to the relative increase in the anharmonicity of the oscillations (see Fig. 3). The cyclotron mass associated with this orbit was derived by fitting the temperature dependence of the Fourier transform amplitude, measured in the temperature range 0.4 ± 3.5 K at each pressure value, to the Lifschitz-Kosevich (L-K) formula [23]. The cyclotron mass slowly decreases with increasing pressure from \( m_c = (1.8 \pm 0.05) m_0 \) (for \( B < 12 \text{ T} \) [19] (where \( m_0 \) is the bare electron mass) or \( m_c = (2.05 \pm 0.05) m_0 \) [24] at ambient pressure down to \( m_c = (1.6 \pm 0.05) m_0 \) at 11 kbar (Fig. 4b). The Dingle temperature is in the range 1 ± 1.6 K. It can be noticed that much larger pressure-induced decrease of the cyclotron mass related to closed orbits have been reported in both \( \kappa-(\text{ET})_2\text{Cu(SCN)}_2 \) [26] and \( \alpha-(\text{ET})_2\text{MHg(SCN)}_4 \) (where \( M = \text{K}, \text{Tl}, \text{NH}_4 \) and \( \text{Rb} \)) [27], while no pressure-dependence has been observed for \( \alpha-(\text{ET})_2\text{NH}_4\text{Hg(SCN)}_4 \) [21]. The generally large measured values of the cyclotron mass \( m_c = 3.5 m_0 \) and \( m_c = 2.1 m_0 \) for
Fig. 3. — Fourier spectrum of the Shubnikov-de Haas oscillations displayed in Figure 2.

Fig. 4. — Pressure dependence of a) the Shubnikov-de Haas oscillation frequency and b) cyclotron mass. Ambient pressure points are taken from [19] (diamond) and [24] (square). $m_0$ is the bare electron mass.
\(\kappa-(\text{ET})_2\text{Cu(SCN)}_2\) [26] and \(\alpha-(\text{ET})_2\text{MHg(SCN)}_4\) [27], respectively, at ambient pressure) have been ascribed to strong electron-phonon interactions [27] or electron correlations [26]. A more detailed knowledge of the pressure dependence of these interactions is required to interpret the pressure dependence of the cyclotron mass.

In order to provide some understanding of the above reported pressure dependence of the FS area, the following theoretical study of the FS was carried out. Since the crystal structure of \(\alpha-(\text{ET})_2\text{TlHg(SeCN)}_4\) (like any of the \(\alpha-(\text{ET})_2\text{MHg(XCN)}_4\) phases) has not been determined under pressure, a direct calculation of the FS under pressure is not yet possible. Under such circumstances the easiest way to tackle this problem is by using the well known tight-binding equations for the energy vs. \(k\)-dependence as a function of the different transfer integrals of the lattice [25]. The pressure effect can then be modeled by systematically changing the different transfer integrals. Once determined what changes are consistent with the observed increase of the closed portion of the FS, one can look at what structural changes can lead to these variations of the individual transfer integrals and discuss their likeliness.

According to different magnetoresistance studies the area of the closed portion of the FS is remarkably similar (~16%) for all of the \(\alpha-(\text{ET})_2\text{MHg(XCN)}_4\) phases. Except for some subtle differences, the calculated FS [2] for the salts with \(M = K, \text{NH}_4, \text{Tl} / X = S\) and \(M = \text{Tl} / X = \text{Se}\) are also very similar. However, for the salt with \(M = K / X = S\) the crystal structures at both 298 K and 104 K are known [1]. In view of these two observations the transfer integrals calculated for the low temperature structure of \(\alpha-(\text{ET})_2\text{KHg(SCN)}_4\) should provide the best starting point for our model study (i.e., the best approximation to the low temperature and ambient pressure structure). In addition, this salt offers also the possibility of studying the effect of thermal contraction on the FS which, in principle, could be related to the effect of pressure. Thus we carried out i) a complete extended Hückel tight binding calculation [28] of the FS’s of \(\alpha-(\text{ET})_2\text{KHg(SCN)}_4\) at 298 K and 104 K and then ii) the model tight binding study, on the basis of the transfer integrals calculated for the 104 K structure. Double-\(\zeta\) type orbitals for C and S were used everywhere. The \(H_{\mu\nu}\) values, as well as the exponents and weighting coefficients of the double \(\zeta\) orbitals, were taken from previous work [29]. A modified Wolfsberg-Helmholz formula was used to calculate the nondiagonal \(H_{\mu\nu}\) values [30] in the complete calculations. The different transfer integrals are defined in Figure 5, which is a representation of the slab where the donor molecules are viewed approximately along their long axis. Three of these transfer integrals (\(c_1\) to \(c_3\)) will be referred to as "intrachain transfer integrals" and the remaining four (\(p_1\) to \(p_4\)) as "interchain transfer integrals" [31]. As can be seen in Figure 5, the donor lattice contains two different types of donor chains (I and II). Chain type I contains only one type of donors (A) whereas chain II contains two different ones (B and C).

The complete calculation of the FS’s for \(\alpha-(\text{ET})_2\text{KHg(SCN)}_4\) at 298 K and 104 K lead to surfaces which contain the usual warped 1D and closed 2D features [1, 2, 32]. The striking result however is that the area of the closed portion almost does not change. Since the transfer integrals increase with temperature lowering, this result is at first sight surprising when compared with the present experimental data. Obviously, pressure and thermal contraction must bring in different structural changes to the lattice.

Let us now turn to the model tight binding calculations. For this study the FS was recalculated for changes of up to 20% of the initial values of i) every individual transfer integral and ii) selected groups of these integrals. The main results are the following:

a) An increase of all both intrachain and interchain transfer integrals by the same amount leaves the area of the closed part of the FS unchanged.

b) An increase of all the interchain transfer integrals (\(p\)-type) leads to an increase of the closed part of the FS. For instance, increases of 10% and 20% of these transfer integrals lead
to increases of 10.4% and 18.8% of the area, respectively. The transfer integrals \( p_1 \) and \( p_4 \) (see Fig. 5) play the dominant role on this increase.

c) An increase of all the intrachain transfer integrals (c-type) leads to a decrease of the closed part of the FS. For instance, increases of 10% and 20% of these transfer integrals lead to decreases of 9.9% and 17.8% of the area, respectively. Such decreases are mostly imposed by the transfer integral \( c_2 \) alone.

With these results in mind it is easy to understand the almost nil effect of thermal contraction on the area of the closed part of the FS. As mentioned, thermal contraction leads to an increase of both interchain and intrachain transfer integrals so that the two contributions cancel each other. More important, these results also suggest how such an area increase as that reported here under pressure (21% at 11 kbar) can be reached. According to the results in (c) a decrease of \( c_2 \) should lead to an increase of the area of the closed portion of the FS. This is actually the case: a decrease of 10% in \( c_2 \) leads to an increase of 10.1% in the area. A decrease of \( a \) and \( c \) crystallographic parameters leads to interchain transfer integrals increase. Thus, if the intrachain transfer integrals can be kept almost constant, increases of around 20% of the interchain transfer integrals will lead to the observed 21% area increase at 11 kbar. In fact, it is quite easy to see how \( c_2 \) can be kept almost constant. Indeed, the calculations for a pair of \( A \) molecules involved in interaction \( c_2 \) (see Fig. 5) show that:

a) If the distance between planes of the two \( A \) donors decreases then \( c_2 \) increases. For instance, a decrease of the interplanar distance of 0.05 Å leads to an increase of \( c_2 \) of about 7%.

b) If there is a sliding of one donor towards the other along the short axis of the molecules then \( c_2 \) decreases. A sliding of about 0.08 Å leads to a decrease in \( c_2 \) of about 7%. In fact,
Fig. 6. — Oscillatory part of the ambient pressure longitudinal magnetoresistance versus inverse magnetic field. The insert displays the inverse magnetic field at the slow oscillations extremum versus Landau level index n at \( T = 0.8 \) K. Black and white dots which refers to the arrows, depict maxima and minima of the slow oscillations, respectively.

the large difference between the two transfer integrals along chain I \((c_1 = -0.011 \text{ eV and } c_2 = 0.140 \text{ eV})\) in the 104 K structure of \( \alpha \)-(ET)\(_2\) KHg(SCN)\(_4\)) is largely due to the different degree of sliding associated with the two pairs of A molecules. The sliding of the donors towards each other along the short molecular axis is around 0.7 Å larger in \( c_1 \) than in \( c_2 \) [32].

Thus, even if pressure increases \( c_2 \) by decreasing the intermolecular spacing, a compensation of this increase may be provided quite easily by small sliding motions of the donors. It seems quite likely that the increase of 21% of the area of the closed portion of the FS can simply arise from an increase of around 20% of the interchain transfer integrals (and mainly \( p_1 \) and \( p_4 \)). Such an increase under 11 kbar seems to be quite possible in view of the increases of 12% and 8%, respectively in \( p_1 \) and \( p_4 \) brought about by just the thermal contraction between 298 K and 104 K in \( \alpha \)-(ET)\(_2\)KHg(SCN)\(_4\)). In addition, 20% is probably an upper limit for the increase in the interchain transfer integrals because for not very large slidings of the pairs of molecules in \( c_2 \) the transfer integral can effectively decrease and thus contribute to the increase of the area. Therefore, the pressure dependence of the area of the closed part of the FS seems to be reasonable and consistent with a pressure induced sliding motion of the molecules in the donor chains (type I) containing only one type of molecules (A). Structural work under pressure is highly desirable to test this suggestion.

Besides the above discussed fast SdH oscillations, slow frequency oscillations have been observed at ambient pressure, as it was already noted in [19]. They can be more clearly evidenced in the field range between 5 and 14 T below 1.5 K and manifest as some amplitude modulation of the fast oscillations (Fig. 6). The inverse magnetic fields corresponding to their extrema (cf. arrows in Fig. 6) are plotted versus \( n \) in the insert of Figure 6 for the 0.8 K experiment. An estimation of the frequency of the slow oscillations from the slope in the insert
of Figure 6 gives the value of $(47 \pm 3) T$ that corresponds to 1.1% of the area of the first Brillouin zone [33]. On the contrary, we have not observed any slow oscillations on the samples measured under pressure in the range 3.5-11 kbar.

Assuming these slow frequency oscillations may be described, at ambient pressure, within the SdH model, they could be associated with a small closed orbit due to some nesting of quasi-1D sheets of FS in the $\alpha-(ET)_2 \text{TIHg(SeCN)}_4$. In contrast, the sister compound $\alpha-(ET)_2 \text{NH}_4 \text{Hg(SCN)}_4$ as noted above, displays very similar slow oscillations which appear only under moderate pressure ($P > 2$ kbar), the superconducting state vanishes as well. The fact that pressure can change the nesting conditions in organic conductors is known to occur in both quasi-1D [34] and quasi-2D [17, 20] organic conductors. We may believe now that superconductivity occurs in $\alpha-(ET)_2 \text{NH}_4 \text{Hg(SCN)}_4$ since no density wave state occurs at low temperature and ambient pressure [21]. Although no sign of density wave condensation appears in either the temperature dependence of the resistivity or the angle-dependent magnetoresistance oscillations data [24, 35], it has been found that no superconductivity is observed at ambient pressure down to 80 mK, which may be due to some nesting of the quasi-1D sheets of the FS in $\alpha-(ET)_2 \text{TIHg(SeCN)}_4$. Experiments at temperatures lower than 0.4 K and in the pressure range below 3.5 kbar are needed in order (i) to determine the electronic ground state and (ii) to study the pressure-induced disappearance of the slow oscillations.

Acknowledgments

We would like to thank Prof. S. Askenazy and Prof. E.B. Yagubskii for their interest and encouragements. We also acknowledge J. M. Broto, H. Rakoto and F. Goze for experimental help and P. Pari and G. Coffee for their contribution to the low-temperature experimental device at ambient pressure. VNL is grateful to CNRS for the provision of his stay in Toulouse by Contract No. ID 41/31. E.C. would like to thank the CNRS for a sabbatical which made the stay at ICMAB possible. R.R. would like to thank the NSERC of Canada for a postgraduate research fellowship.

References

[31] Although the authors of references [1] and [32] use eight different integrals, two of them (c3 and c4 in their reports) should be identical because of the existence of inversion centers in molecules B and C. The differences in the numerical values used for such integrals in references [1] and [32] should be due to some small numerical inaccuracy.
[32] Ducasse L., Fritsch A., Solid State Commun. 91 (1994) 201. The transfer integrals c1 and c2 in this reference are interchanged with respect to those used in reference [1], as well as in the present work.
[33] The slow oscillation frequency (45 T) measured at 2kbar in α-(ET)2NH4Hg(SCN)4 corresponds also to 1.1 percent of the room temperature BZ instead of 0.5 percent, as stated in reference [21].