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Superconductivity in TTF[Ni(dmit)₂]₂ films

J.-P. SAVY¹, D. DE CARO¹, L. VALADE¹, J.-P. LEGROS¹, P. AUBAN-SENZIER², C. R. PASQUIER²,
J. FRAXEDAS³ and F. SENOCQ⁴

¹ *Laboratoire de Chimie de Coordination, UPR CNRS 8241 - 205 route de Narbonne, F-31077 Toulouse, France*

² *Laboratoire de Physique des Solides, Université Paris-Sud, UMR CNRS 8502 - Orsay, F-91405, France*

³ *Institut de Ciència de Materials de Barcelona (ICMAB-CSIC) - Campus de la UAB, E-08193 Bellaterra, Spain*

⁴ *ENSIACET-CIRIMAT, UMR CNRS 5085 - 118 route de Narbonne, F-31077 Toulouse, France*

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Abstract – We report on the observation of a superconducting transition in a fiber-like film of the TTF[Ni(dmit)₂]₂ phase electrodeposited on silicon substrates. Superconductivity is evidenced by a broad drop of the resistance below 0.8 K under the application of a hydrostatic pressure of 7.7 kbar. Zero resistance is not reached due to the contribution of inter-fiber resistance. Superconductivity is confirmed by the application of a magnetic field perpendicular to the plane of the film. The critical field determined on the film is in agreement with that obtained in bulk single crystals.

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Introduction. – After the discovery of superconductivity in the organic metal (TMTSF)₂PF₆ (TMTSF = tetramethyl-tetraselenafulvalene) [1], a long list of organic superconductors with transition temperatures T_c below 13 K have been synthesized in the form of single crystals using the well-known and widely applied electrocrystallization technique [2–5]. In these materials both the modification of the organic building blocks and of the associated anions were considered for reaching ambient pressure superconductors with high T_c values. Within the (TMTSF)₂X phases, known as Bechgaard salts, where X represents a monovalent ion, (TMTSF)₂ClO₄ was the first discovered ambient pressure superconductor with $T_c = 1.4$ K [6]. The highest T_c value achieved to date, $T_c = 12.8$ K, was obtained for κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl, where BEDT-TTF stands for bis(ethylenedithio)-tetrathiafulvalene [7]. TTF[Ni(dmit)₂]₂ (TTF = tetrathiafulvalene, dmit = dithiolthione-dithiolate) was the first superconductor including a transition metal complex with $T_c = 1.6$ K under $P = 7$ kbar [8,9]. Within this family, α -(EDT-TTF)[Ni(dmit)₂](EDT-TTF = ethylenedithiotetrathiafulvalene), exhibits ambient pressure superconductivity with $T_c = 1.3$ K [10].

The above-mentioned organic superconductors have been obtained and studied as single crystals. Other morphologies such as thin crystals (~ 10 μ m thick), have

been obtained for the κ -(BEDT-TTF)₂Cu[N(CN)₂]Br phase using confined electrocrystallization displaying the same superconducting transition as the bulk samples ($T_c = 11.6$ K at ambient pressure) [11]. Rare examples of thin films of organic superconductors have been reported, and superconductivity has been evidenced only in few cases. Most of the initial work was devoted to micrometer thick films of (BEDT-TTF)₂I₃, because one of its polymorphs, the β_H -phase, exhibits a relatively high transition temperature ($\simeq 8$ K) [12]. Laukhina and co-workers provided the first evidence of an *incomplete* superconducting transition in such films; *incomplete* referring to the fact that zero-resistance was not achieved [13]. Other investigations on (BEDT-TTF)₂I₃ films reported activated conductive behavior (no resistivity drop below the onset transition temperature), but evidenced either diamagnetism [14] or microwave absorption [15]. Thin films (~ 10 μ m) of (TMTSF)₂ClO₄ were grown on top of particular crystal faces of a (TMTSF)₂PF₆ single crystal used as a template [16]. The temperature dependence of the zero-field resistance of the film exhibits the properties of (TMTSF)₂ClO₄ alone since its resistivity decreases towards a sharp superconducting transition with an onset T_c of 1.4 K. Recently, superconductivity has been observed in ultra-thin films (20 nm) of K₃C₆₀ [17]. Partial evidences of superconductivity have also been given for Au(dmit)₂ Langmuir-Blodgett films [18].

Thin films of conducting materials have been grown on flat electrodes as gold, platinum and silicon, replacing the anode platinum wires of conventional electrocrystallization by such substrates. To our knowledge, Zhu and co-workers were the first to prepare a thin film of a metal dithiolate-based conductor [19]. This team also prepared nanowire arrays of the $\text{NMe}_4[\text{Ni}(\text{dmit})_2]_2$ superconductor by electrodeposition [20]. Wang and co-workers have grown the $(\text{BEDT-TTF})_2\text{PF}_6$ phase on gold electrodes [21]. Fine patterned electrodes have been used by Tanaka and co-workers to grow small crystals of Bechgaard salts. In this work, the electrode lines appear as covered by a film [22].

We have focused on the use of silicon wafers for electrodepositing numerous molecular conductors, which exhibit various morphologies and electrical behaviors [23–26]. Among them, films of the $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$ [25] and $\text{Ni}(\text{tmdt})_2$ [26] phases show metallic behavior down to low temperatures (tmdt = trimethylenetetrafulvalenedithiolate). As $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$ crystals are known to show superconductivity under pressure, the electrical properties of films of this material were investigated and the results are reported in this paper.

Experimental details. – $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$ films were electrodeposited on intrinsic (001)-oriented silicon plates at a $6.25 \mu\text{A cm}^{-2}$ current density from a 3 : 1 molar ratio of the TTF and $\text{NBu}_4[\text{Ni}(\text{dmit})_2]$ starting materials in acetonitrile, following the procedure described in ref. [25].

X-ray diffraction data were collected with a Seifert XRD 3000 TT diffractometer working in the Bragg-Brentano configuration (θ/θ), using $\text{Cu } K_\alpha$ radiation (0.15418 nm), and fitted with a diffracted beam monochromator. Scanning electron micrographs were obtained with a JEOL JSM 6700F scanning electron microscope (SEM) equipped with a field-effect gun.

We have performed resistivity (ρ) measurements using gold wires and a standard low frequency ac lock-in technique with applied currents of 1 to $10 \mu\text{A}$. Hydrostatic pressure was applied in a CuBe clamp using silicone oil as the transmitting medium. The pressure, at ambient temperature, is deduced from the resistance of a manganese gauge located close to the sample in the pressure cell. Below 40 K and down to the lowest temperature, 80 mK, the temperature of the sample was given by a RuO_2 thermometer located in the pressure cell. This thermometer is carefully calibrated at each pressure with respect to another RuO_2 thermometer glued on the outside of the pressure cell.

Results and discussion. – Previously reported $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$ films were deposited on silicon substrates at low current density ($1.5 \mu\text{A cm}^{-2}$) from a 3 : 1 $\text{TTF}:\text{NBu}_4[\text{Ni}(\text{dmit})_2]$ molar ratio of the starting materials in acetonitrile [25]. In these conditions, deposits showed a grain-like morphology and exhibited a metallic behavior down to 12 K. We could not study further these samples, because they developed cracks due to

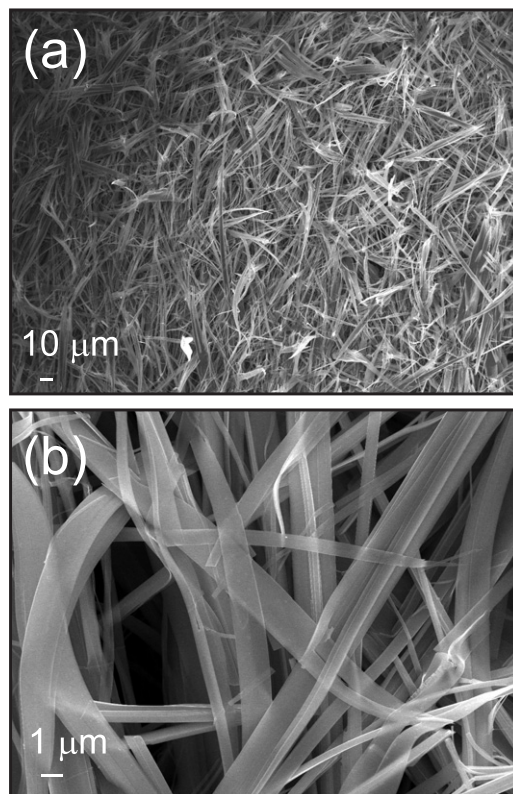


Fig. 1: SEM images of thin films of $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$ grown on silicon substrates.

mechanical stresses at cryogenic temperatures. In order to solve this problem, other deposits were obtained at higher current densities, $6.25 \mu\text{A cm}^{-2}$, using the same molar ratio. In these conditions, the films show a fiber-like morphology, as illustrated in fig. 1(a). Typically, the $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$ fibers, arranged as bundles, are $1\text{--}2 \mu\text{m}$ wide and $20\text{--}60 \mu\text{m}$ long (see fig. 1(b)). The change in morphology of deposits upon variation of the current density during electrochemical growth has been previously observed in the case of $\text{Ni}(\text{tmdt})_2$ films [26]. XPS and Raman studies performed on the fiber-like films (not shown) give similar results as those obtained on grain-like films [25]. The fiber-like morphology of the films mimics the needle-like morphology of the $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$ single crystals: the SEM images from fig. 1 suggest that the crystallographic b axis (longer dimension of the fibers) is mostly oriented in the plane of the film while both a and c axes are randomly oriented.

In order to perform further characterizations, the films had to be separated from the silicon substrate. After peeling it off the substrate surface, the films preserve their integrity and can be cut into pieces and further used as samples. Each sample is nearly planar with a surface of a few mm^2 and an average thickness of $50 \mu\text{m}$.

Several such pieces have been used to obtain the experimental XRD pattern shown in fig. 2. This pattern is in good agreement with the simulation calculated using single crystal data for $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$ as indicated in

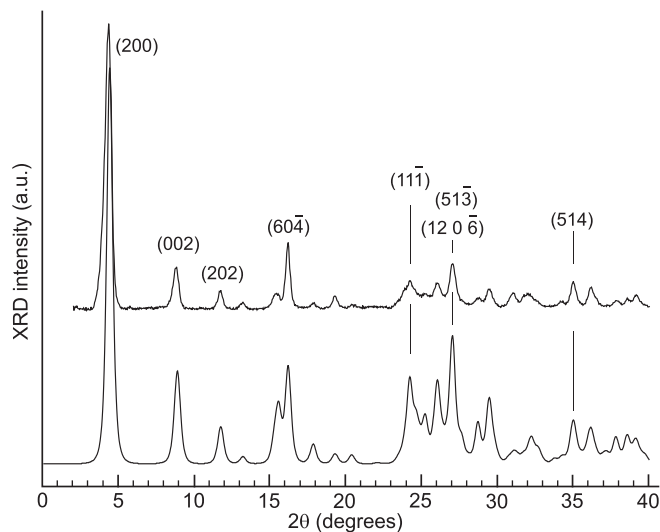


Fig. 2: X-ray powder diffraction of TTF[Ni(dmit)₂]₂. The upper curve shows the experimental pattern of a film while the lower curve displays the simulated diffraction pattern obtained using the single-crystal data from ref. [27].

the appendix. The important broadening and overlapping of the experimental peaks, due to the small crystallite size, prevented from performing accurate data reduction. However, this broadening allows to estimate, via the Scherrer equation, the crystallite size to ca. 16 nm, at least for the (200) reflection.

The resistivity measurements of the TTF[Ni(dmit)₂]₂ films were performed on three different samples, denoted as #1, which was extracted from a first film and measured at ambient pressure, and #2 and #3, both measured under pressure and extracted from a second film. In order to improve the quality of the contacts, four gold pads were evaporated on the surface of the samples before attaching the gold wires with silver paste. The gold pads were about 100 μm wide and 500 μm spaced from each other. However, the brittleness of the films due to weak inter-fiber contacts led us to measure #2 and #3 with four contacts but with only two gold pads. The two contacts without gold pads allowed us to measure the samples in four points during the pressurisation but were rapidly deteriorated during the cooling process, implying to perform two points measurements at low temperature. To get rid of the resistance of the wires, two gold wires were attached on each gold pad on #3. The measured resistance was then significantly decreased compared to a two points configuration.

The normalised four-point resistance of #1 *vs.* temperature at ambient pressure is shown in fig. 3. Down to about 100 K the normalised resistance is nearly constant, with some discontinuities due to the formation of cracks in the film. Below 100 K, the resistance increases. The temperature dependence of the resistance under 7.7 kbar, as shown in fig. 3 for sample #3, is similar to the ambient pressure one. Note the absence of jumps in the metallic regime and

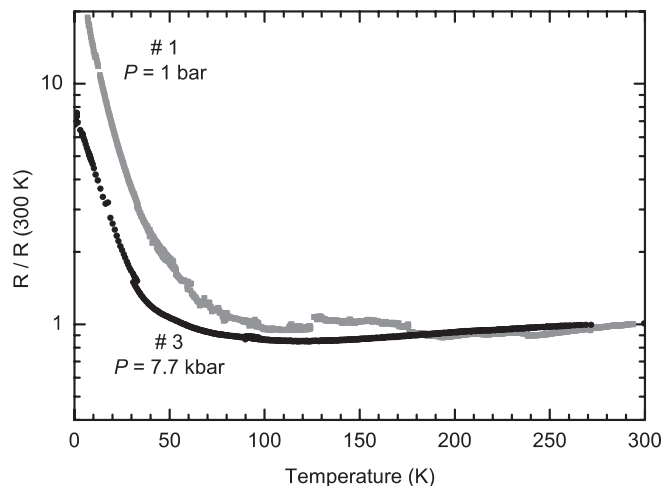


Fig. 3: Temperature dependence of the normalised resistance of TTF[Ni(dmit)₂]₂ films: #1 at ambient pressure (full grey squares) and #3 at $P = 7.7$ kbar (full black dots).

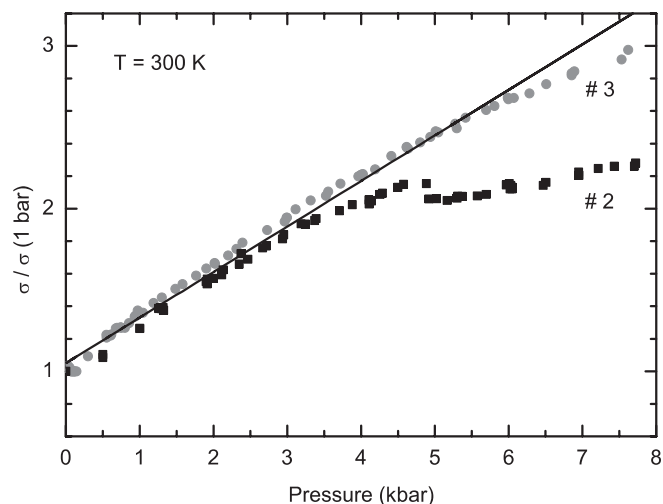


Fig. 4: Variation of the room temperature conductivities of TTF[Ni(dmit)₂]₂ films, normalised to their values at 1 bar, *vs.* hydrostatic pressure: #2 (full black squares) and #3 (full grey dots).

a weaker localisation at low temperature. Actually, the activation energy between 30 and 100 K, obtained from the $\log \rho$ *vs.* $1/T$ plot, is divided by 2.5 between 1 bar and 7.7 kbar. The behavior below 100 K, not observed in bulk single crystals, is the signature of grain boundaries, as was observed for TTF[Ni(dmit)₂]₂ deposits obtained by an adsorption technique [28].

In general, polycrystalline thin films of metallic molecular organic materials exhibit an activated electron transport evidencing the limiting effect caused by grain boundaries between metallic single crystals [15,29–32]. The conduction mechanism can be modeled as resistive networks with metallic samples and non-metallic resistors connected in series and in parallel. The critical influence of grain boundaries on superconducting films can be best exemplified for the inorganic high- T_c superconductors, for

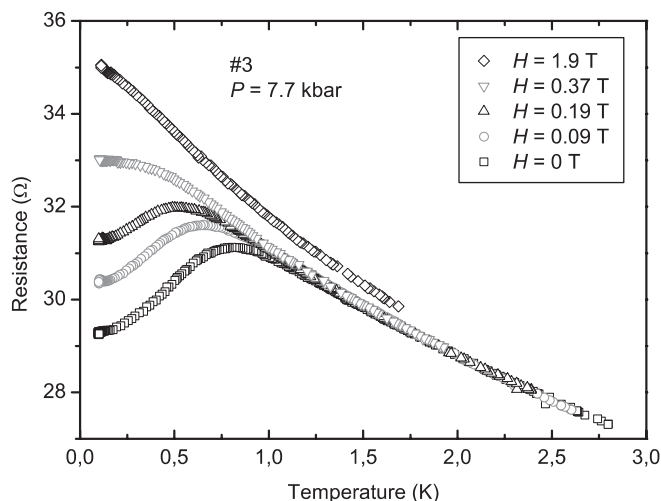


Fig. 5: Temperature dependence of the resistance of #3 TTF[Ni(dmit)₂]₂ film at $P = 7.7$ kbar, in the superconducting temperature domain, for different applied magnetic fields ranging from 0 to 1.9 T.

which the low critical current densities of the polycrystalline samples limit large-scale applications [33–35].

As shown in fig. 4, the variation of the room temperature conductance, normalised to its value at ambient pressure, *vs.* hydrostatic pressure for #2 and #3 is quasilinear at low pressure. The slope, $d\sigma/\sigma(1 \text{ bar})dP \simeq 0.28 \text{ kbar}^{-1}$, is remarkably similar to the value, 0.33 kbar^{-1} , measured in bulk single crystals [36]. This demonstrates that the influence of the inter-grain resistance is not a limiting factor to probe the intrinsic properties of the compound. The difference in the variation of the conductivity with pressure between #2 and #3 is attributed to a larger number of cracks occurring in #2 at high pressure.

Superconductivity manifests by a broad drop of the resistance in the localised regime below 0.8 K, as illustrated in fig. 5. The decrease of the resistance reaches, at 80 mK, only 6.5% of the resistance at the critical temperature. This small decrease is due to the contributions of grain boundaries and of the two contacts to the measured resistance. The effective presence of superconductivity has been confirmed by the application of a magnetic field perpendicular to the plane of the film. This incomplete superconducting transition is shifted to lower temperatures by increasing the magnetic field (see fig. 5). At 1.9 T, the transition is no more observed above 80 mK, in agreement with the critical field obtained in bulk single crystals [8,9].

Conclusions. – A superconducting transition has been evidenced in a film of the TTF[Ni(dmit)₂]₂ phase showing fiber-like morphology. This result shows that the electrodeposition technique affords a promising way to produce films exhibiting the properties known on single crystals. Moreover, this technique uses milder conditions as compared to vapour phase methods, and its use can be envisioned for all molecular conductors.

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APPENDIX

Room temperature XRD single-crystal data of TTF[Ni(dmit)₂]₂ were published in ref. [37] with agreement factors $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.097$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.117$. More accurate data ($R = 0.026$, $R_w = 0.019$) were obtained at 295 K by D. Chasseau and S. Hebrard-Brachetti [27]. These last data were used in the present work for the simulation of the powder diffraction pattern and taking into account the experimental broadening of the diffraction lines.

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