Influence of disorder on the metal insulator phase transition in Di-(Tetramethyltetraselenafulvalene)-ium perbromate, (TMTSF)$_2$BrO$_4$

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Résumé. Nous présentons une étude expérimentale d'un nouveau sel (TMTSF)$_2$BrO$_4$ comprenant des mesures de conductivité électrique, de susceptibilité RPE et de diffusion diffuse des rayons X. Le désordre dû à des défauts statiques limite la mise en ordre des anions et détermine le comportement à basse température de la susceptibilité paramagnétique (loi en $T^{-\alpha}$ avec $\alpha \neq 1$).

Abstract. An experimental study including measurements of electrical conductivity, EPR susceptibility and X-ray diffuse scattering of a novel (TMTSF)$_2$ BrO$_4$ salt is presented. Disorder due to static defects inhibits a complete anion ordering phase transition and determines the activated behaviour of the electrical conductivity and the low temperature $T^{-\alpha}$ ($\alpha \neq 1$) behaviour of the paramagnetic susceptibility.

1. Introduction. — A novel member of the (TMTSF)$_2$X family, (TMTSF)$_2$BrO$_4$, contains a tetrahedral anion BrO$_4^-$ which is nearly the same size as ReO$_4^-$, and it is iso-structural with the other members of this family [1]. Nearly planar TMTSF molecules stack in columns extending along the high conductivity a-axis of the triclinic unit cell (space group P1). Non-centrosymmetric anions separate these stacks in the c direction and are statistically disordered at room temperature (RT). BrO$_4^-$ belongs to the group of tetrahedral anions together with ClO$_4^-$, ReO$_4^-$, BF$_4^-$, IO$_4^-$ and FSO$_4^-$This last anion has in contrast to the former a permanent dipole moment [2]. Among them (TMTSF)$_2$ClO$_4$ is at present the only solid which is metallic at ambient pressure down to low temperatures, and with a transition to a superconducting (SC) ground state at 1.2 K [3]. (TMTSF)$_2$ReO$_4$ [4], (TMTSF)$_2$FSO$_4$ [5] and (TMTSF)$_2$BF$_4$ [6] exhibit metallic behaviour down to 180 K, 86 K and 40 K respectively. At these temperatures the materials undergo a phase transition which involves an ordering of the anions [7] and a simultaneous distortion of the organic stack [8]. Below the transition temperature, the potential associated with the structural change opens a gap at the Fermi level which establishes a non-magnetic insulating ground state. The competition of these two ground states in tetrahedral anions complexes has been studied in (TMTSF)$_2$ReO$_4$ [4, 9]. In short, the application of pressure gradually changes the electrical behaviour from semiconducting to metallic and above 10 kbar SC is observed below 1.4 K. Besides SC and anion ordered (AO) ground states, there is a third spin density wave (SDW) antiferromagnetic insulating state found in materials with anions of octahedral symmetry: PF$_6^-$ and AsF$_6^-$ [10, 11].
In this paper we report an experimental study of (TMTSF)$_2$BrO$_4$ including transport and magnetic properties as well as X-ray measurements. We have performed measurements of the temperature dependence of the a-axis resistivity at two pressures: 1 bar and 2 kbar, and EPR and X-ray measurements at ambient pressure.

2. Experimental and results. — 2.1 Resistivity measurements. — Resistivity measurements were made using a low frequency (70 Hz) ac method with a measuring current of 10 µA. Four electrical contacts were made using silver paint diluted with butyl acetate on previously evaporated gold contacts. The dimensions of the samples measured in this work were typically $1 \times 0.15 \times 0.1$ mm$^3$. For the 2 kbar pressure run a small pressure clamp was constructed. Cyclohexane was used as the pressure fluid with a freezing point of 17°C at 2 kbar. The 2 kbar pressure run was done in order to prevent sample cracks. Figures 1 and 2 show the temperature dependence of the resistivity at 1 bar and 2 kbar pressure respectively. The RT conductivity was found to be approximately $200 (\Omega \text{cm})^{-1}$, a value close to the 300 $(\Omega \text{cm})^{-1}$ observed in (TMTSF)$_2$ReO$_4$ [4]. At ambient pressure, on cooling, the conductivity almost does not change down to 250 K, where it suddenly drops by more than one order of magnitude. Below this temperature it decreases more gradually down to helium temperature.

The ratio between the conductivity at ambient temperature ($\sigma_{RT}$) and at helium temperature ($\sigma_{4.2}$) is $\sigma_{RT}/\sigma_{4.2} \approx 4 \times 10^5$. When a low pressure (2 kbar) is applied, the conductivity remains constant down to about 200 K and a peak anomaly in resistivity appears at about 180 K. Similar conductivity behaviour was observed in the parent compound (TMTSF)$_2$ReO$_4$. At ambient pressure the ReO$_4$ salt displays even sharper resistivity increase below 180 K reaching a value of $4 \times 10^5$ of $\rho_{RT}$ already at 80 K [4] (note this is a value the BrO$_4$ salt reaches at 4.2 K). When 8 kbar pressure is applied to (TMTSF)$_2$ReO$_4$ the resistivity increase starts at lower temperature (~ 130 K) and is more gradual as in the BrO$_4$ salt [9]. The nature of a resistivity peak is not clear. It was obtained in both cooling and warming cycles which might be argument for that it is a real effect.

The main result of the conductivity measurement is that (TMTSF)$_2$ BrO$_4$ displays semiconducting behaviour below about 250 K (at ambient pressure) with an effective value of the activation energy of about 150 K in the temperature range $40 K \leq T \leq 140 K$ and of about 50 K below 40 K.

2. 2 EPR measurements. — Electron paramagnetic resonance (EPR) experiments were performed at 9.4 GHz using a standard EPR spectrometer [12]. The maximum power which could be delivered to the...
sample cavity was of the order of 100 mW. Normal operating levels were −15 dB and −10 dB from the maximum and care was taken to avoid saturation.

Cooling and temperature control were achieved using an Oxford Instruments continuous flow helium system and the temperature was measured by an iron:gold/chromel thermocouple. The temperature stability was about 0.1 K and the accuracy is estimated to be within 0.5 K. Samples were mounted together with a DPPH marker on a plexiglass holder inside a standard quartz EPR tube. Two runs were performed on two different single crystals with masses of 0.07 and 0.11 mg, respectively. The EPR signal at RT was obtained only in the third run, which was performed on several aligned single crystals with a total mass of 0.45 mg. In all runs the crystals were mounted with the highly conducting a-axis perpendicular to the static magnetic field ($H_0$). Field sweeps were from 100 G at low temperatures to 2.5 kG at high temperatures, always being about 10 times larger than the linewidth. For the single Lorentzian EPR signal, the paramagnetic susceptibility in arbitrary units was calculated as the product $A_0 \times LW^2$. $A_0$ is peak to peak amplitude and $LW$ is peak to peak width of the absorption signal. To determine the EPR susceptibility ($\chi_{EPR}$) in magnetic units we have performed an independent run on a single crystal of copper sulfate pentahydrate CuSO$_4 \times$ 5 H$_2$O, a well defined standard which is known to obey a Curie law behaviour down to helium temperature. The results of the EPR measurements are shown in figure 3 and figure 5. In the temperature region below 100 K down to 4.2 K, the EPR signal was found to be within the noise, Lorentzian. The linewidth (Fig. 3b) is decreasing with temperature being about 7 G at 4.2 K. The EPR susceptibility (Fig. 3a) is nearly constant (about $3 \times 10^{-4}$ emu/mole) down to about 50 K. Below this temperature the signal gradually evolves into a Curie-like tail, but with a different exponent $\chi_{EPR} \sim T^{-}\alpha$, where $\alpha = 0.72 \pm 0.07$ (Fig. 6). The concentration of the spins responsible for such
A behaviour is small about 1-2 % at 4.2 K and about 3-4 % at 50 K. The obtained values are rather close to the values found for Qn(TCNQ)₂, which belongs to the TCNQ group of salts, where a $T^{-1}$ law was first found. According to reference [12] $\chi_{\text{EPR}} (50 \text{ K}) \sim 5 \times 10^{-4} \text{ emu/mole}$ and $\chi_{\text{EPR}} (4.2 \text{ K}) \sim 20 \times 10^{-4} \text{ emu/mole}$.

Above 100 K up to RT the signal is asymmetric. Computer analysis of the line shape shows that the signal is not single Lorentzian as in the lower temperature region, but a superposition of two Lorentzian lines separated by about 80 G (Fig. 4). Besides a rather narrow low temperature single EPR line, there is a broad component emerging above 100 K. The results are shown in figure 5. Not so good signal to noise ratio and in particular the broadness of the second line ($LW₂ \sim 225 \text{ G at 115 K and } LW₁ \sim 380 \text{ G at RT}$) prevent better quantitative calculation of its intensity. The estimated error is about 25 %. However there is no doubt that the narrow low temperature line is diminishing with increasing temperature, in contrast to the broad line whose intensity is gradually increasing up to about 250 K with no appreciable further change up to RT. The RT paramagnetic susceptibility is roughly estimated to be about $8 \times 10^{-4} \text{ emu/mole}$. This value is not so far from values estimated for some other (TMTSF)$_2$X compounds like the SbF₆ salt ($\chi_{\text{EPR}} (\text{RT}) \sim (6.0 \pm 0.5) \times 10^{-4} \text{ emu/mole}$) or the BF₄ salt ($\chi_{\text{EPR}} (\text{RT}) \sim (6 \pm 2) \times 10^{-4} \text{ emu/mole}$) [10]. Furthermore, estimated RT value for $\chi_{\text{EPR}}$ in Qn(TCNQ)₂ is also about $6 \times 10^{-4} \text{ emu/mole}$ [13] and thus we infer that our estimate of $\chi_{\text{EPR}} (\text{RT})$ in (TMTSF)$_2$BrO₄ is rather reliable.

The composite structure of the EPR signal might correspond to two different electron systems. The condition for resolving different absorption lines is that the difference between the Larmor frequencies of these two systems is larger than the exchange rate of the electrons between them. Then, it is rather natural to ascribe broad component to the conduction electrons and the narrow component to the localized ones. We interpret the gradual intensity decrease of the « broad » component below 250 K as due to a decrease in the number of free electrons which then become localized. The localized electrons contribute to a « narrow » component and their exchange interaction leads to the $T^{-\alpha}$ ($\alpha \neq 1$) behaviour of the paramagnetic susceptibility below 50 K.

2.3 X-RAY DIFFUSE SCATTERING MEASUREMENTS. — As in other investigations of one-dimensional organic conductors, measurements were performed with the fixed-film, fixed-crystal method, using monochromatized CuKα (1.54 Å) X-ray radiation. The temperature change from 10 K to 300 K was achieved with a standard cryocooler and was regulated within few tenths of degree. Three samples were used during this study, all have given the same result. The most surprising result of this investigation is that no true structural phase transition could be detected in (TMTSF)$_2$BrO₄ in contrast to other salts containing tetrahedral anions like (TMTSF)$_2$ReO₄ and (TMTTF)$_2$ClO₄ [7]. This situation is well illustrated by the X-ray pattern taken at 10 K and presented in figure 7. It shows, between layers of main Bragg reflections, broad diffuse spots characteristic of a short range order at a reduced wave vector $\frac{1}{2} a^*$, which corresponds to 2 $k_F$. At this temperature, measurements of the satellite linewidths lead to the correlation lengths of 25 Å (about 3 lattice spacings) in the chain direction and 10 Å (about 1 lattice spacing) in the transverse directions. However these broad reflections are comparable in intensity to that of precursor effects of the same linewidth observed in (TMTSF)$_2$ReO₄ few degrees above its metal-insulator phase transition at 176 K, indicating that (TMTSF)$_2$BrO₄ experiences the same kind of structural transformation as the former compound. The temperature dependence of the satellite peak intensity.

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**Figure 6.** Logarithm of the EPR susceptibility versus logarithm of temperature below 50 K. Fitting to $\ln \chi = - \alpha \ln T$ gives $\alpha = 0.72 \pm 0.07$. The solid line is a guide for the eye.

**Figure 7.** X-ray pattern of (TMTSF)$_2$BrO₄ at 11.5 K showing midway between layers of main Bragg reflections broad superlattice spots (arrow). Note very strong diffuse scattering surrounding main Bragg reflections. On this pattern the a direction is horizontal.
Fig. 8. — Temperature dependence of the superlattice peak intensity and its half width at half maximum (H.W.H.M.) along a. Note the saturation of both quantities below 100 K. Above this temperature the superlattice peak intensity decreases almost linearly with the temperature with a slope whose extrapolation gives a zero intensity at about 250 K.

and its half width at half maximum (H.W.H.M.) is shown in figure 8. This figure clearly shows that both quantities saturate to a constant value below 100 K. Above this temperature the peak intensity decreases almost linearly with temperature with a slope which extrapolates to zero intensity around 250 K. However, above 225 K there is a rounding in its temperature dependence and a weak diffuse intensity can still be detected at RT. Above 100 K, the satellite width along a begin to increase, leading to a correlation length of about one lattice spacing at 250 K.

The observation of the saturation of the peak intensity and satellite width, greater than the experimental resolution, shows that the superstructure remains frozen in a short range ordered state below 100 K. At first, it is possible that the complete long range order (LRO) is not achieved because the cooling rate was too rapid with respect to the kinetic effects associated with the ordering of counterions, which might be specially low for the BrO₄ anion. However, a further inspection of the X-ray pattern taken at 10 K (Fig. 7) shows that the main Bragg reflections are surrounded by diffuse scattering of intensity unusually high at such a low temperature (10 K). Furthermore, this intensity does not change appreciably with temperature, which means that it does not come from X-rays scattered by thermally populated phonons. Thus the diffuse intensity represents more likely a scattering by static defects (which might come from displaced molecules in the structure). The structural disorder may be responsible for the absence of LRO in the anion ordering process down to 10 K.

Such an amount of low temperature diffuse scattering around Bragg reflections has not been observed in any of the pure (TMTSF)₂X salts investigated so far. It has, however, been observed in TMTSF-DMTCNQ and (TMTSF)₂PF₆ [14] that about 1% of irradiation induced defects can give rise to a similar scattering. However, our investigation of (TMTSF)₂BrO₄ cannot give any information on the exact nature of defects present in the structure. Debye-Waller factor refinement of the structure might give informations on possible displacement of molecules.

3. Discussion. — The important and decisive role of disorder in one-dimensional (1d) systems was predicted by Mott and Twose in 1961 [15]. Thereafter this subject has been in a focus of interest of many authors (see ref. [16] and references therein). Namely, a simple qualitative argument given by Mott and Twose shows that in 1d all electron states are localized by static defects. But at finite temperature and in quasi-1d compounds, where coherent motion of charge carriers between chains can take place, the above argument might be substantially reduced. However, one can easily understand that if, by some reasons which shall be developed later, a pseudo-gap is created at the Fermi level, disorder might localize electronic states in its vicinity, as it is well known in three-dimensional materials [17]. The presence of localized states changes dramatically the mechanism of the electrical conductivity and the creation of magnetically uncompensated spins leads to an additional low temperature contribution to the paramagnetic susceptibility.

A transition to a low temperature ground state at finite temperature is obtained as a consequence of 3d coupling between chains. And it is well-known that in many quasi-1d salts (e.g. salts belonging to the TCNQ family), a dielectric transition of the Peierls type takes place [18]. As stated in the introduction some compounds belonging to the (TMTSF)₂X family display also a dielectric transition caused by anion ordering or by stabilization of a magnetic SDW phase. On the other hand, in some TCNQ salts (e.g. Qn(TCNQ)₂, Adz(TCNQ)₂) the dielectric transition is absent, even although for Qn(TCNQ)₂ 1d structural instabilities at 2 kₚ and 4 kₚ wave vectors have been observed [20]. These compounds were found to have some disorder in their structure caused either by randomly oriented asymmetric cations or by impurities. The same behaviour occurs also under irradiation, where small amounts of irradiation induced defects suppress the Peierls charge density wave (TMTSF-DMTCNQ [21]) and the SDW ((TMTSF)₂PF₆ [22]) insulating states. Larkin and Mel'nikov [23] have shown that impurities suppress both dielectric and SC phase transitions.
Indeed a current investigation of \( (\text{TMTSF})_2X_n Y_{1-n} \) alloy \((X = \text{ClO}_4, Y = \text{ReO}_4)\) show that even a slight doping of \((\text{TMTSF})_2\text{ClO}_4\) with \text{ReO}_4 suppresses the SC transition temperature at least to below 50 mK [24]. A similar result has been obtained with a small amount of irradiation induced defects on the high pressure SC phase in \((\text{TMTSF})_2\text{PF}_6\) [25]. In the case of the AO phase transition, which involves also the organic stacks, the results obtained for \((\text{TMTSF})_2\text{BrO}_4\) show that a large amount of disorder does not suppress the coupling itself but rather its spatial extent. One possible difference might be that this kind of phase transition, which does not present 1d structural precursors, is not so sensitive to the 1d nature of the electronic gas, as for the phase transitions considered above. However, the establishment of a 2\( k_F \) periodicity, even on a limited correlation length still lead, probably with the help of disorder, to a change in electrical (Fig. 1) and magnetic (Fig. 3, Fig. 5) properties below 250 K. At RT disorder has no dramatic effect on the electronic gas and the metallic like state is observed. As shown earlier the electronic conductivity \((\sim 200 \, (\Omega \cdot \text{cm})^{-1})\) is comparable to that of \((\text{TMTSF})_2\text{ReO}_4\) [4]. At low temperature both compounds display semiconducting behaviour but the electrical conductivity of \((\text{TMTSF})_2\text{BrO}_4\) is roughly two orders of magnitude larger than in \((\text{TMTSF})_2\text{ReO}_4\). Also, the estimated activation energy in the \text{ReO}_4 salt [4] of about 1000 K is roughly 10 times larger than the estimated effective activation energy in the \text{BrO}_4 salt \((\sim 100 \, \text{K})\). Furthermore, they display qualitatively similar decrease of the EPR susceptibility, although the sudden drop found in the \text{ReO}_4 salt below \( T_e = 180 \, \text{K} \) is rather smeared out in the \text{BrO}_4 salt. Moreover, the EPR susceptibility in \((\text{TMTSF})_2\text{BrO}_4\) does not go to zero at low temperatures, as in \((\text{TMTSF})_2\text{ReO}_4\), but develops a Curie-like tail below 50 K. A suitable explanation might be that a true electronic gap does not exist in the density of states, but that a formation of the short range order with the 2\( k_F \) periodicity opens a pseudo-gap at the Fermi level. Disorder localizes electronic states in the 2\( k_F \) pseudo-gap that leads to the low temperature semiconducting behaviour and \( T - \alpha \) behaviour of the paramagnetic susceptibility. In the following we shall develop this explanation according to theoretical models in references [16] and [17]. Disorder creates a random potential along the highly conductive chains and so affects the form of the 1d electron wave functions responsible for the electrical conductivity. In real space, the electron mean free path is thus restricted to \( l_q \) (in 1d systems mainly defined by backward scattering) so that the characteristic time is \( \tau_q = l_q/v_F \), where \( v_F \) is the Fermi velocity. At RT it is reasonable to assume that \( \tau_q \gtrsim \tau_{\text{ph}} \) which implies that the scattering by phonons defines the conduction mechanism \( \sigma = \sigma_0 \sim \tau_{\text{ph}} \). Below 250 K, the short range order with 2\( k_F \) periodicity starts to develop signifying the beginning of the \text{BrO}_4 ordering.

The electronic states localized by disorder are now starting to be situated in a pseudo-gap gradually opening in the density of states at the Fermi level. As the temperature decreases \( \tau_{\text{ph}} \) increases and \( \tau_q \) becomes much less than \( \tau_{\text{ph}} \). If we assume that \( T \gg 1/\tau_{\text{ph}} \), conduction is obtained by thermally activated hopping with a rate \( \tau_{\text{ph}}^{-1} \). In other words, the electron jumps from one localized state to another with energy \( \Delta E \) above with the probability \( e^{-\Delta E/T} \). Gradual opening of the pseudo-gap below 250 K implies an increase of the density of localized states at the Fermi level. This is reflected in a small and temperature dependent activation energy being about 150 K in the higher temperature region and about 50 K below 40 K.

The gradual localization of electron states down to 100 K is also reflected in the EPR signal (Fig. 5). Its composite structure signifies that there are two different electron systems. The « broad » component might be interpreted as due to the electrons from the conduction band and is most important at RT. The narrow component comes from localized electrons and represents the main and the only relevant contribution to the EPR signal below 100 K. The gradual intensity decrease of the broad component below 250 K then correspond to the loss of free charge carriers being localized in the pseudo-gap opened at the Fermi level. Below 50 K the EPR susceptibility follows a \( T^{-\alpha} \) law with \( \alpha \neq 1 \) (Fig. 6). The fact that \( \chi_{\text{EPR}}(T) \) increases more slowly than \( T^{-1} \) means that the localized spins are interacting with each other. The \( T^{-\alpha} \) law behaviour (together with the absence of the dielectric transition) has been observed earlier in quasi-1d compounds mentioned above (\( \text{Qn(TNCQ)}_2 \) and \( \text{TTT}_2\text{I}_{3.4}, \text{etc...} \)) [26]. Several theoretical interpretations were proposed almost all being based on the random 1d Heisenberg model [27, 28]. The main assumption is a random distribution of spins with probability \( p \) of spacing between unpaired spins \( l_{sd} = l_0 \, p^{-1/2} \). The existing disorder in \((\text{TMTSF})_2\text{BrO}_4\) leads to localization of electron states in the pseudo-gap opened at the Fermi level. Then a small Coulomb repulsion is enough to cause these states to be singly occupied which leads to the interaction among them and to \( T^{-\alpha} \) low temperature behaviour. In other words, defects break the chains into segments \( l_q \) but not all of them are magnetically « active » i.e. only those with an odd number of spins behave as an entity with spin 1/2. Thus, the number of spins estimated from the \( T^{-\alpha} \) law \((\sim 3 \% \)) gives a measure of the average magnetic segment length \( l_{sd} \approx 30 \, a' \approx 100 \, \text{A} \) (\( a' \) is the average distance between TMTSF molecules along the a-axis).

4. Summary. — To summarize, we have presented transport, magnetic and structural properties of a novel perbromate salt \((\text{TMTSF})_2\text{BrO}_4\). It is the first member of the \((\text{TMTSF})_2\) \( X \) family with tetrahedral anions in which a complete transition to the low
temperature dielectric ground state is suppressed by disorder in the structure. The X-ray results show that the anion ordering phase transition gradually develops below about 250 K, but the material never displays long range order. The results indicate correlation length of about 25 Å at low temperatures. This is in contrast to one-dimensional instabilities of Peierls type (CDW or SDW) where disorder does not allow transversal coherence to develop and therefore the transition temperature is decreased. The conductivity is almost constant between room temperature and 250 K (σ_RT ~ 200 (Ωcm)^{-1}) below which it is decreasing down to 4.2 K.

The activation energy is small and temperature dependent and is estimated to be about 50 K below 40 K. The paramagnetic susceptibility due to free electrons is gradually diminishing below 250 K, while the component due to localized electrons is increasing. We have interpreted this behaviour as an evidence of one-dimensional localization of electronic states due to disorder in a pseudo-gap opened at the Fermi level. Localization also determines the low temperature behaviour of the paramagnetic susceptibility which displays a T^{-α} (α = 0.72) low behaviour below 50 K. We infer that this is due to the exchange interaction between spins situated about 15 lattice spacing (~ 100 Å) apart from each other.

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