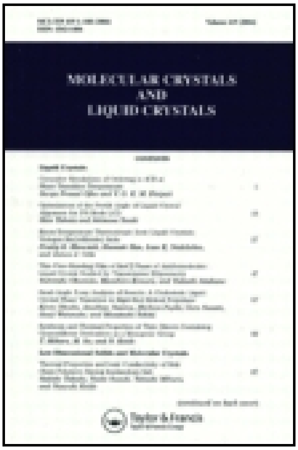

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Physical Properties of One Dimensional Conductors

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Physical Properties of One Dimensional Conductors

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In the course of investigations of organic metals we have investigated the cation-radical series $TMTTF_2$-X' with $X' = BF_4$, ClO_4, PF_6, SCN and Br. On this isomorphous series a large range of physical properties have been studied: electrical conductivity, magnetic susceptibility, EPR, optical reflectivity and specific heat. In correlation with crystallographic results, which indicate the existence of TMTTF diads, the dominant interactions are analyzed. It results that the metallic behavior at high temperatures and the occurrence of a Peierls distorsion below 100 K arise mainly from a competition between electron–electron and electron–phonon coupling inside the cation-radical chains.

1 INTRODUCTION

Since the discovery of high conductivity in organic charge transfer salts, namely TTF-TCNQ (tetrathiafulvalenium-tetracyanoquinodimethane) and derivatives, an extensive investigation of the physical properties of these new quasi one-dimensional materials has been carried out.

Ion-radical salts with only one type of efficient stacks should in principle, provide simple model systems in which a physical understanding can be gained by the allowance to apply theoretical results more easily.

In order to reach such a goal a series has to be synthetized the members of which should be isomorphous and isostoichiometric.[1] This is the case with tetramethylated-tetrathiafulvalenium (TMTTF) cation-radicals:[2]

$$(TMTTF)_2 - X' \quad \text{with} \quad X' = BF_4^-, ClO_4^-, SCN^-, PF_6^-, Br^-, \ldots$$

A first attempt has been done by WUDL[1] who indicated the synthesis of TTF and different methylated TTF salts; he indicated the presence of

$TMTTF^+$ complexed with tetrafluoroborate (BF_4^-) under another stoichiometry.

The cristallographic structure has been investigated on these salts.[3] They belong to the triclinic system with quasi-regular stacks of TMTTF units nearly perpendicular to the *c*-axis and a unit cell depending slightly on the counterion size. These cation-radicals present a metallic behavior around room-temperature, we have undertaken therefore the investigations of the physical properties.

2 PHYSICAL PROPERTIES

The synthesis of these compounds has been realized by two ways:

—$X' = BF_4^-$, ClO_4^- oxydation of acetonitrile solution of TMTTF with fluoboric and perchloric acids.

—$X' = SCN^-$, PF_6^-, Br^-: double exchange reaction between $TMTTF_2$-BF_4 and a quaternary ammonium salt.

For each compound the elemental chemical analysis has been performed and lead to the given stoichiometry 2-1. They appear stable under ambient conditions except for the bromine complex which evolves slowly. It seems that its composition is not exactly the 2:1 stoichiometry as already evidenced on other charge transfer salts with halides.[4]

On these cation-radical salts the physical properties have been investigated:

—electrical conductivity and EPR experiments have been carried out with single crystals.

—optical reflectivity, magnetic susceptibility and specific heat on polycrystalline samples.

2.1 Electrical conductivity

The low frequency ac conductivity has been measured on single crystals by using a four probe standard technique with aquadaq or platinium paint for contacts As already noticed by WUDL[1] these compounds are brittle and present practically uncurable defects; the thermal variation experiments are therefore venturous. The most reliable results are presented on Figure 1 and Table I. Below the maxima of conductivity, reported in the best cases in Table I, a semi-conducting behavior is observed. As suggested by the experiments, if we assume that the mean activation energy is not influenced by cracks generations an estimate can be done (Table I). A similar value is found for BF_4^-, ClO_4^- and PF_6^- salts; but the bromine compound presents a

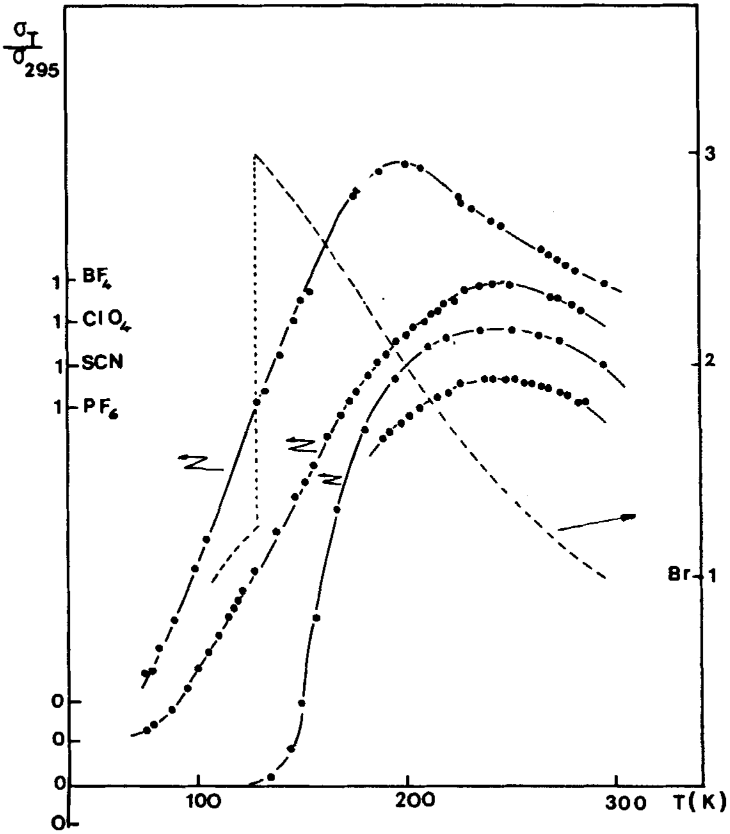

FIGURE 1 Thermal variations of electrical conductivity in reduced coordinates (σ_T/σ_{295}) for the different radical-cations investigated.

TABLE I

Compounds X' = / Physical characteristics	BF$_4$	ClO$_4$	PF^6	SCN	Br
$\sigma_{RT}(\Omega^{-1}\ \mathrm{cm}^{-1})$	50	30	20	60	260
$(\sigma_{\max}/\sigma_{RT})$	1.2	1.15	1.1	1.1	3.2
$T_{\max}$	190	230	245	240	100
ΔE(ev) (around 50 K)	$\sim 4.10^{-2}$	$\sim 4.10^{-2}$	$\sim 4.10^{-2}$	—	1,4 10^{-2}

lower activation energy whereas the thiocyanate salt has a too low conductivity below liquid nitrogen temperature to determine any figure.

It must be pointed out that the more spread results about the absolute value of the electrical conductivity are relative to this last material and related to its chemical stability.

2.2 Electron paramagnetic resonance

The EPR spectra have been examined on single crystals with a standard X-band spectrometer. In a first step a room temperature investigation has been done to determine the principal magnetic axes by studying rotation diagrams of line-width and line positions: there are the y-axis parallel to the stacking-axis b and the x and z orthogonal axes in the perpendicular rotation plane (y-axis corresponds to $H_0 \parallel b$ and $H_1 \perp b$; x-axis to $H_0 \parallel a$ and $H_1 \parallel b$, z-axis to $H_0 \parallel c$ and $H_1 \parallel b$, H_0 and H_1 are respectively the static and hyperfrequency magnetic fields).

The values observed at room temperature for the line-width (S in gauss) between inflexion points and the g-factor of the observed Lorentzian lines are presented on Table II together with the mean-values of these second order rank tensors $\bar{S}$ and $\bar{g}$. A few observations have to be done on these results:

—the observed resonance lines are narrow, with a slight anisotropy, very similar for each compound except the bromine salt.

TABLE II

Physical properties \ Compounds X' =	BF_4	ClO_4	PF_6	SCN	Br
Linewidth (in gauss)					
S_{yy}	2.86	3.00	2.90	3.20	5.43
S_{xx}	3.57	3.80	3.64	3.60	6.57
S_{zz}	4.57	5.00	4.64	4.70	7.43
$\bar{S} = \frac{1}{3}(S_{yy} + S_{xx} + S_{zz})$	3.70	3.95	3.68	3.83	6.40
g-factor					
g_{yy}	2.0021	2.0020	2.0020	2.0019	2.0020
g_{xx}	2.0089	2.0086	2.0086	2.0088	2.0088
g_{zz}	2.0107	2.0107	2.0107	2.0107	2.103
$\bar{g} = \frac{1}{3}(g_{yy} + g_{xx} + g_{zz})$	2.0072	2.0070	2.0071	2.0071	2.0070
Paramagnetism					
χ_p (10^4 emu CGS/mole) at 295 K	6.17	5.76	6.45	6.60	5.28

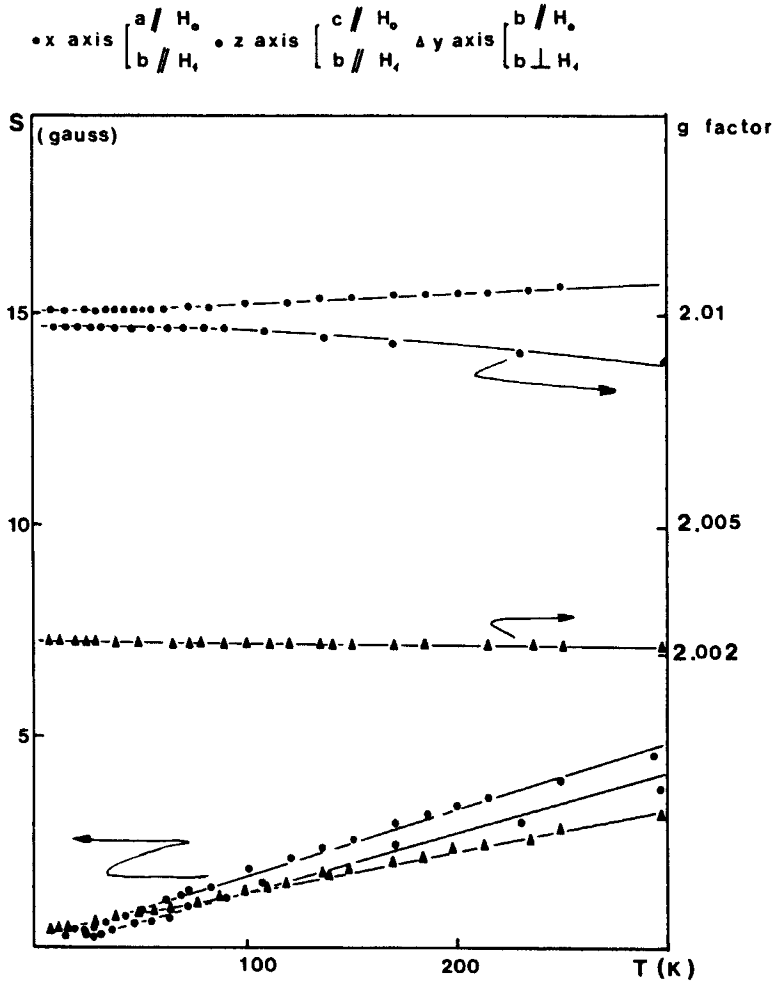

FIGURE 2 Thermal dependence of the diagonal terms of the g-factor and linewidth S tensors on a $TMTTF_2$-BF_4 single crystal.

—the g-factor exhibits a larger anisotropy than in charge transfer complexes with a mean value characteristic of the $TMTTF^-$ radical-cation: $\bar{g} = 2.0071 \pm 0.0001$ (the g-value in THF solution is 2.0079).

In a second step the temperature dependences of the g-factor and the linewidth were examined between 300 and 5 K. The results are very similar for all compounds except thiocyanate compound which presents a linewidth maximum around 60 K. We present therefore the thermal variations relative to one compound only: $(TMTTF)_2$-BF_4 (Figure 2).

Two facts are significant:

—the *g*-factor values are quasi-constant because of the existence of one kind of stacks; a slight variation is observed that we will explain later on;

—the line widths exhibit a linear temperature dependence down to 30 K with a constant slope for every principal position. At very low temperature around 20 K a bump is observed which might be due to the modulation of the tunnelling splitting through the transitions of CH_3 group between the ground and first excited torsional states as already evolved for TMTTF-TCNQ.[5]

2.3 Paramagnetic susceptibility

The magnetic susceptibility has been measured with a Faraday balance; after standard corrections for the core diamagnetism by using PASCAL's constants, the absolute values of paramagnetism have been calculated (see Table II). The thermal variations between 300 and 3 K have been investigated, they are presented on Figure 3.

Two kinds of behavior occur:

—for the tetrafluoroborate and perchlorate salts a strong change of paramagnetism is observed at respectively 41 and 70 K which indicates the possibility of a phase transition.

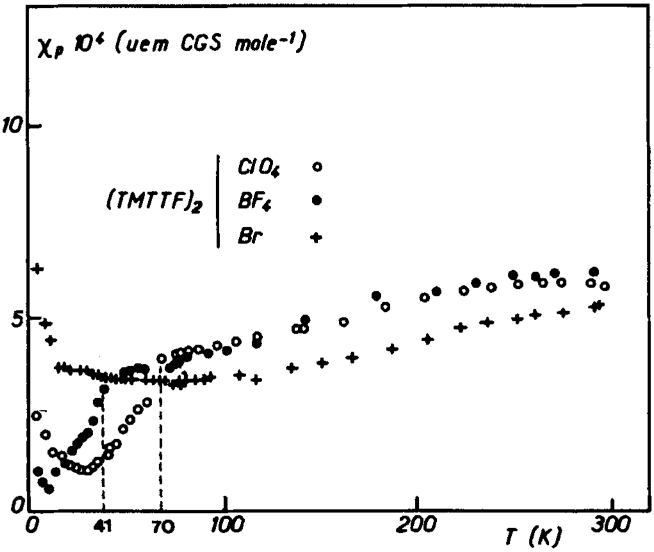

FIGURE 3 Thermal variations of static paramagnetic susceptibility for three different materials; only tetrafluorate and perchlorate salts present a transition temperature.

—for the bromine compound, as for the two other ones (SCN and PF_6) the results of which are not given on Figure 3, a smooth thermal variation is enregistered on a freshly crystallized material.

Besides, this salt is not chemically stable: after a few months, a decrease of paramagnetism is observed which could be correlated to a bromine departure. Concerning $(TMTTF)_2$, PF_6 and SCN, samples which are chemically stable, some compaction effect seems to occur as detected for TCNQ quaternary ammonium salts and attributed to spurious surface effects.[6]

2.4 Optical reflectivity

The optical reflectivity has been examined at room temperature on polycristalline compacted samples in the visible and near infrared spectrum.[7] The mean value $\bar{R}$ of the reflectivity coefficient versus the energy of the incident light is given on Figure 4 for the three considered samples: they exhibit a similar behavior which is characteristic of a metallic compound with a plasma edge around 1 ev. The plasma frequency can be evaluated by using DRUDE theory[8] as we will present in the discussion.

2.5 Specific heat

The specific heat thermal variation has been done between 5 and 300 K with an automatic adiabatic calorimeter.[9] Because about one gramm of compound is necessary just one compound, namely $TMTTF_2$-BF_4, has been examined. At low temperature the thermal variation is classical and furnishes the Debye temperature $\theta_D \simeq 51$ K.

But a sharp anomaly has been evidenced which confirms the presence of a phase transition at 41 K (Figure 5).

2.6 Discussion of the experimental results

The cation radical salts are metallic organic compounds which might undergo a metal-insulator transition at lower temperature than the temperature of the conductivity maximum. This transition has not been detected by electrical conductivity measurements (Figure 1) however magnetic and heat capacity experiments allow us to detect such a phase transition. Two classes of compound appear according to this argument:

—the BF_4 and ClO_4 salts which present a reproducible phenomenon at respectively $T_c = 41$ and 70 K

—the bromine, SCN and PF_6 salts on which experimental difficulties arised and precluded actually to detect such a transition which must occur at least for SCN and PF_6 according to conductivity measurements.

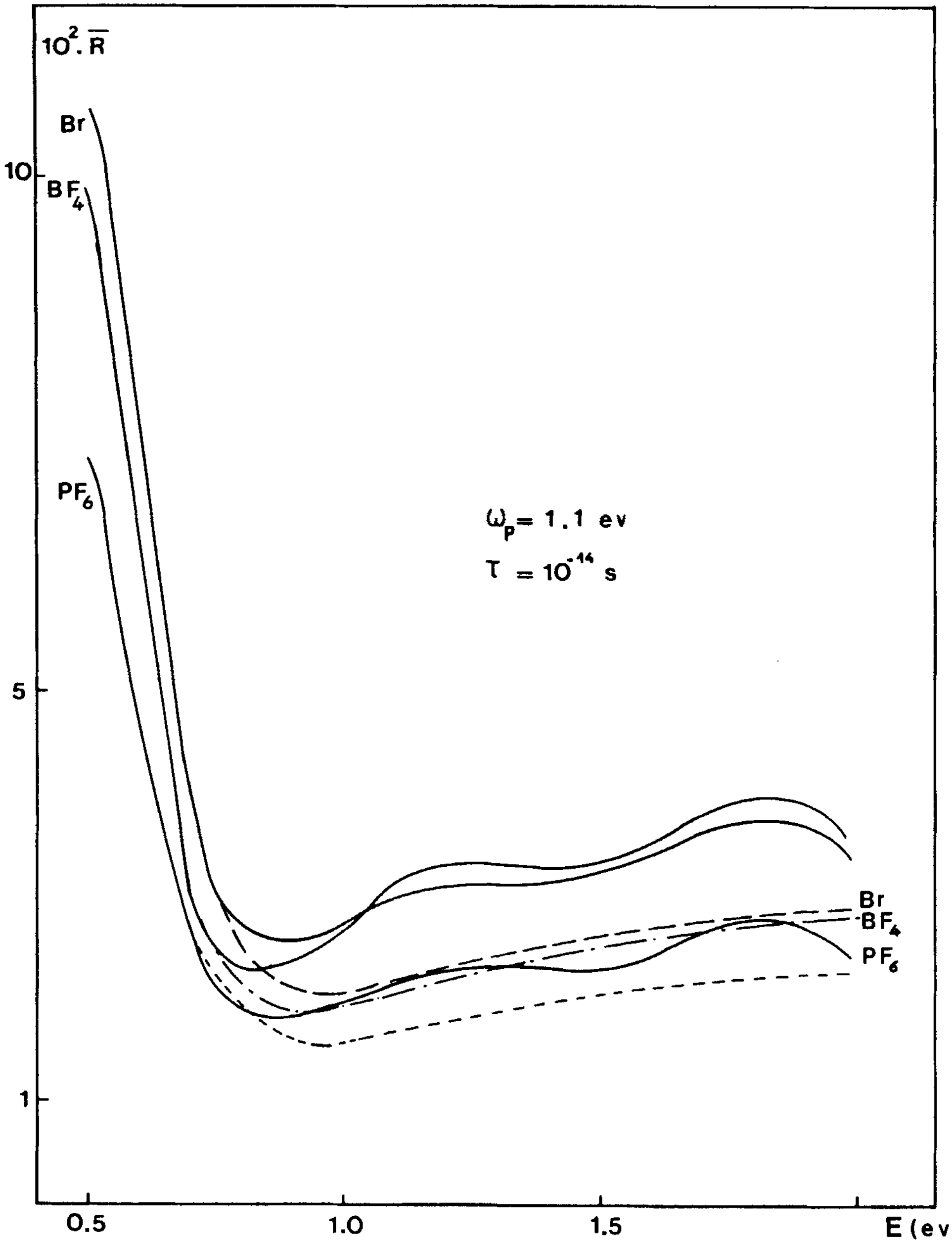

FIGURE 4 Optical resistivity measurements on powders at room temperature for different samples; mean values of the optical resistivity ($\bar{R}$) versus energy (E).

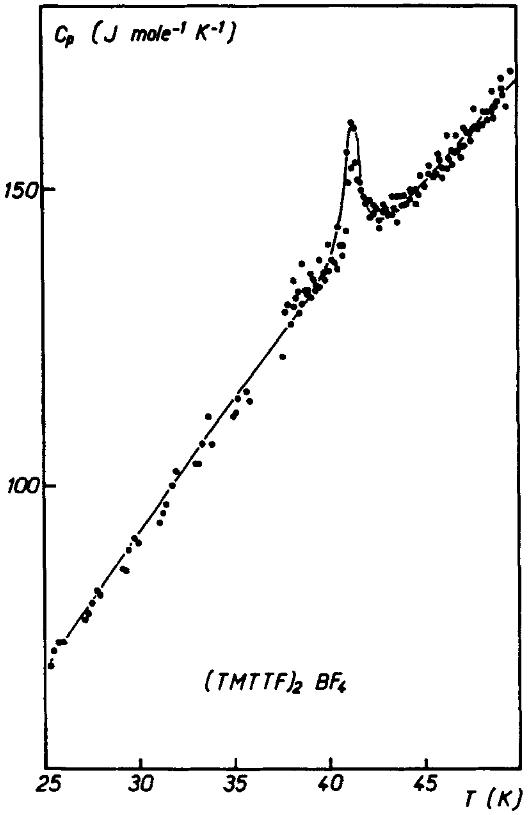

FIGURE 5 Specific heat anomaly observed on TMTTF$_2$-BF$_4$ around T_c = 41 K

We will discuss these aspects in the last part of this work by looking what are the different informations gained from each physical property investigated.

3 ANALYSIS OF THE DOMINANT INTERACTIONS

These cation-radicals are metallic: they are therefore mixed valency compounds, i.e. with less than one electron per site.

Two solutions are currently offered to reach such a result either the charge transfer amount is fractional as currently observed in charge transfer complexes with stoichiometry 1–1[1] or a complex composition occurs. This last case occurs for cation-radicals as already observed with TTF series where the fractional composition is explained in terms of qualitative Madelung energy arguments.[4] Here we have observed a classical stoichiometry $TMTTF_2$-X' (which is just doubtful for the bromine derivative) which allow us to assume one unpaired electron for two TMTTF by assuming a full charge transfer.

Now if we refer to the crystallographic study, the x-ray resolved structure of $TMTTF_2$-Br[3] shows that with the triclinic system the TMTTF units are not symmetrically equivalent and the calculated consecutive distances along the *a*-axis inside one unit cell are 3.50 Å and 3.53 Å. The same result is generalized to every salt of this series which is isomorphous.[2] Therefore we

$$\varepsilon(k) = \pm\, t_{/\!/} \sqrt{1 + \frac{t_{/\!/}'^{2}}{t_{/\!/}^{2}} + 2\,\frac{t_{/\!/}'}{t_{/\!/}} \cos kb}$$

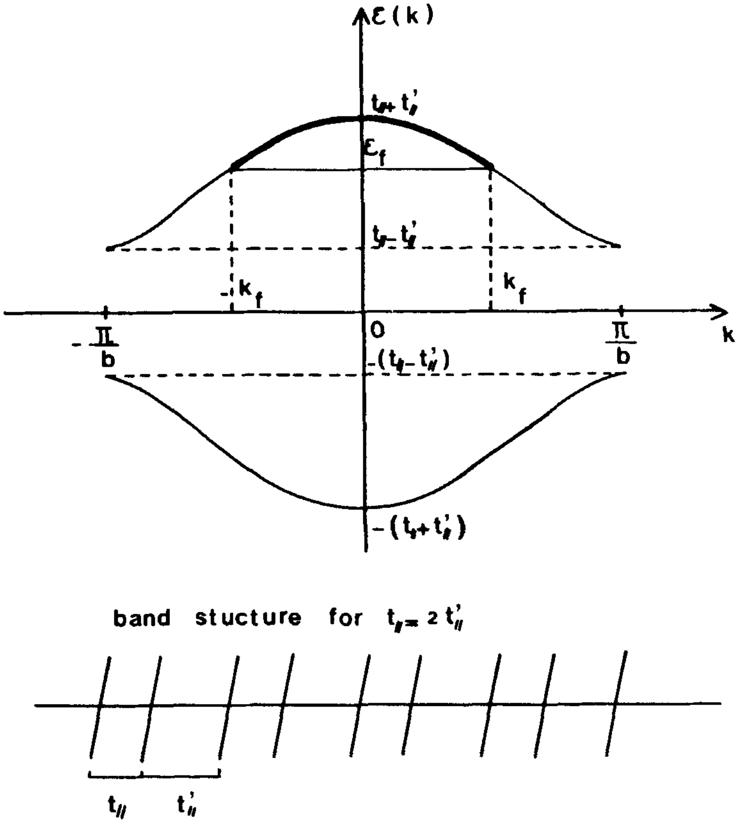

FIGURE 6 Energy-wavevector relation [$\varepsilon = f(k)$] in the tight binding approximation for the case of a dimerized chain occupied with an average of one-half electron per site as represented schematically below.

are in presence of TMTTF diads each of them containing one electron and the electronic band to be considered is half-filled. This is the first reported example where organic compounds with a metallic behavior don't present a regular segregated stack of ion-radicals. It must be pointed out however that to observe this kind of stacking it should be necessary to assume that these compounds crystallize in a monoclinic system; under this assumption the electronic band should be one quarter empty which is slightly different to explain the physical properties.

According to PINCUS[13] we can represent the 1*D* electronic energy-wavevector relation in the tight binding approximation (Figure 6). It is necessary to define the transfer integral between molecules of a given dimer $t_{\parallel}$ and between molecules on adjacent dimers $t'_{\parallel}$. Two energy bands exist, they are separated by an energy gap $\Delta E = 2(t_{\parallel} - t'_{\parallel})$ and with a width egal to $2t'_{\parallel}$. If the alteration factor decreases for a regular stack $t_{\parallel} = t'_{\parallel}$, the energy gap disappears and the bandwidth reaches its usual value $4t'_{\parallel}$.

Now, we will examine how the different interactions, which are known to exist in these quasi one dimensional systems, are estimated from the given experimental results.

—*interactions inside one chain*: there are the electron-phonon interaction as initially proposed by Peierls[10] and improved for the fluctuation effects by Lee Rice and Anderson[11] and the electron–electron interaction which is taken into account in Hubbard model (*U* is the parameter for the coulombic repulsion).

—*interactions between chains*: they stabilize the 1*D* system as shown by Rice and Strassler[12] with a phenomenological 3*D* coupling. The nature of the coupling has to be discussed, it can be an electronic hopping process characterized by $t_{\perp}$ or an electrostatic interaction.

—*effects of disorder*: it must be discussed in connection with the structural investigation and specifically the nature of the counterion.

3.1 Electron–electron interaction: plasmon edge and paramagnetism

As pointed out by Tomkiewicz *et al.*[4] the paramagnetic susceptibility and the optical reflectivity data in the metallic regime are able to give the electronic bandwidth value for a given model. By using the tight binding model of non-interacting electrons it is possible to appreciate if an enhanced paramagnetism due to strong Coulomb interactions occurs.

3.2 Electronic 3D interactions: EPR linewidths and *g*-factors

The linewidths are anisotropic. As *y* is a privileged direction this anisotropy can be described by the ratio (S_{xx}/S_{yy}) or (S_{zz}/S_{yy}) (see Table II). These values are smaller than two whatever the temperature is. This result is in agreement with Yafet's theory for free charge carriers in anisotropic conductors when the motional averaging is effective.[16]

The temperature dependences of linewidth show a monotonous decrease at least in the metallic range (Figure 2). These results can be interpreted assuming a spin lattice relaxation rate mainly due to the modulation of spin-orbit coupling by lattice vibrations. Following Bloch[17] in the high temperature range:

$$\bar{S}^{-1} \sim T_2 \simeq T_1 \sim (\delta g)^{-2} \tau_{e-ph} \left(\frac{t_{\parallel}}{t_{\perp}}\right)^2$$

where:

T_2 and T_1 are the spin–spin and the spin–lattice relaxation times.

δg is the average g-shift ($\bar{g}$—2.0023). This is a constant for the series characteristic of the cation radical TMTTF$^+$ (Table II). Furthermore in this series with one kind of conducting stacks the g-factor is almost temperature independent. The slight variation which is observed (Figure 2) is correlated to the anisotropic thermal dilatation which changes the spin-orbit coupling strength through a mixing of the highest occupied atomic orbitals.

τ_{e-ph} is the scattering time characterizing the phonon part of the resistivity.

$(t_{\parallel}/t_{\perp})$ characterizes the effective electronic dimensionality; the $3D$ interactions are more and more efficient when this ratio decreases.

This relation shows that $S^{-1} \sim \tau_{e-ph} \sim \sigma$ if the electrical conductivity σ is governed by electron-phonon scattering. In the high temperature regime ($T \gg \theta_D$), with a supposed one-phonon process, a linear temperature dependence of linewidth is observed (Figure 2). There is a qualitative agreement at temperatures higher than $T_{\max}$ as defined from conductivity measurements (see Table I) but at lower temperatures the thermal dependence is not presently understood.

As usually done the plasma frequency in the conduction parallel to the conducting axis has been determined by fitting the observed optical reflectivity (Figure 4) to the Drude expression for the dielectric constant $\varepsilon(\omega)$:

$$\varepsilon(\omega) = \varepsilon_{\text{core}} - \frac{\omega_p^2}{\omega^2 + i\omega/\tau}$$

where:

$\varepsilon_{\text{core}}$ is the residual dielectric constant at high frequency,

τ is the electronic relaxation time,

ω_p is the plasma frequency: $\omega_p^2 = 4\pi Ne^2/m^*$ with N is the electron density and m^* is the optical effective mass.

By using the standard relation between the optical reflectivity R and the dielectric constant[8] it is possible to fit the experimental results in the vicinity of the plasma edge. The three parameters are ω_p, τ^{-1} and $\varepsilon_{\text{core}}$ which is quasi-constant about 2, for the considered molecular polarisability,[4] are given on Figure 4. The plasma frequency ω_p is about 1 ev with $\tau \simeq 10^{-14}$ s for each sample. In this $1D$ tight binding approximation with half filled-band this value leads to the bandwidth $2t'_{\parallel} = 1700$ K with an effective mass $m^* = 1.6\ m_0$ (m_0 is the free electron mass).

Now if we examine the paramagnetic susceptibility from the absolute value given at room temperature (Table I) we can estimate the transfer integral for the relevant model (Figure 6) by using usual Pauli paramagnetism calculation.[15] For $TMTTF_2$-BF_4 we get $2t'_{\parallel} = 400$ K.

Comparing these two results we conclude that the enhancement factor on the energy band is about 4.

We must conclude that the electron–electron interactions are not negligible for these compounds. The Hubbard model however has not been solved in this case of weakly dimerized chains. Therefore, a quantitative analysis of paramagnetism is not allowed.

Similar results have been observed on TTF-halides compounds[18] with a larger linewidth than in this series. The narrowness of the observed lines (Table II) indicates that the $3D$ electronic coupling characterized by $(t_\perp/t_\parallel)$ is weak. The largest linewidth observed for the bromine salt is not due to a more effective interchain coupling than in other isomorphous compounds but to a stronger spin-orbit coupling caused by the interaction of bromine with $TMTTF^{+}$.

3.3 Occurence of a periodic lattice distorsion

A phase transition has been clearly evidenced by the specific heat anomaly observed on $TMTTF_2$-BF_4 (Figure 5). Together with paramagnetism investigations (Figure 3) these results suggest a metal-insulator transition. Without large electron–electron interactions the Peierls theory for such a transition is well known.

Different authors have examined the perturbation of the Peierls distorsion by electron–electron coupling. For example, Chan and Heine[19] have presented a microscopic model in which they define a criterion for the formation of a periodic lattice distorsion associated with a charge density wave. They have shown the intrasite coulombic interaction must not be too large to allow such combined effect.

McMillan[20] has proposed a phenomenological Landau theory based on the existence of charged density waves to interpret the phase transitions in low dimensional electronic systems. Two cases have to be considered either the CDW is commensurable or not with the lattice.

With the given stoichiometry and a full charge transfer we deal with the first case, a weakly first order transition with a "lock in" energy, this phase transition occurs at a higher temperature than for a second order transition with an incommensurable superstructure (such a case could exist with the bromide derivative but has not been already detected).

To prove the occurrence of a periodic lattice distorsion a structural investigation at low temperatures by x-rays diffuse scattering has to be done.

We have shown the weakness of 3*D* interactions. Then pretransitional effects, associated with large fluctuations must be important (see for example, Lee, Rice and Anderson).[11]

The thermal variation of paramagnetism must be sensitive to such effects. However, because of the existence of electron–electron interactions, it is not actually possible to take quantitatively account of them.

3.4 Disorder and coulombic effects

Up to now we have just considered the influence of cation-radicals but it is not possible to neglect the counterions shape and their structural positions: the considered anions are centrosymetric (Br^-, BF_4^-, ClO_4^-, PF_6^-) except SCN^- which presents a dipolar moment; its particular behavior even not well elucidated might be connected with this characteristic.

From crystallographic studies it appears that the bromide ions are distributed regularly along the *a*-axis; but for BF_4^-, as probably for ClO_4^-, and PF_6^-, each anion occupy statistically two positions on each side of a center of symmetry of the cell.[3] However, their motion could be stopped at lower temperatures giving rise to the phase transition as in Wuster's blue perchlorate.[21]

These counterions act on the TMTTF chains through electrostatic interactions. They are important for calculating the Madelung energy which explains the stabilization of the mixed valence state.[4] Actually, the effect of a dynamic disorder induced through Coulomb interactions on the electronic properties of the $TMTTF^{+}$ chain is not evaluated.

4 DISCUSSION AND CONCLUSION

The experimental investigations have shown that this series of isomorphic and isostoichiometric compounds present a similar behavior.

However some differences have been pointed out. On one side the cation-radicals formed with BF_4^-, ClO_4^- and probably PF_6^- exhibit a phase transition which has been presented as an electronic Peierls distortion. On the other side bromine and thiocyanate derivatives exhibit a particular behavior. Concerning $TMTTF_2$-Br, the most conductive compound, it seems that non-standard composition and chemical instability occur as already known with other halide systems. For $TMTTF_2$-SCN the situation has to be clarified in particular with the problem of stability compound versus pressure or some other factor.

The analysis of the dominant interactions is instructive; by comparison with TTF-halides and pseudohalide compounds the introduction of methyl group is significantly deduced. Two points we have shown warrant particular discussion:

—steric effect with a unit-cell expansion
—chemical effect because the CH_3 group is electron repelling.

4.1 The steric effect

The steric effect causes the lowering of transitions temperatures because the interchain couplings are smaller than in TTF series.[1] This point has been confirmed by the narrowness of the EPR linewidth. Large fluctuations must exist as in complex charge transfer TMTTF-TCNQ which appears to be the most 1*D* of the two-chains systems.[17]

4.2 The chemical effect

The chemical effect produce a charge and spin redistribution on $TMTTF^{+}$ rings with a large electron–electron effect for the dication.

This is evaluated by the enhanced paramagnetic susceptibility as we have deduced by comparison with plasmon frequency. The observed paramagnetism is indeed about five times larger than for TTF^{+} radical cations.[1] Besides, the electrical conductivity confirms this electron–electron coupling. Compared to TTF^{+} series the observed figures (Table I) are about one order of magnitude smaller[1] and in disagreement with the calculation from optical measurements.[8]

In conclusion, we can say that these cation-radical salts with only one type of efficient stacks do not provide a simple model system. From the crystallographic structure we have to consider the presence of diads with one electron on each. We are therefore in presence of a dimerized structure which present a metallic behavior but with a smaller electronic bandwidth than usually (Figure 6). The analysis of the dominant interactions shows that inside a chain the electron–electron and electron–phonon couplings are competitive and that the 3*D* interactions are relatively weak.

In such a frame the allowance to apply theoretical models which favor one kind of interaction is not possible. The physics of this series results from a subtle balance of these different interactions which could be evidenced by playing on the chemical structure variations, namely steroalloys, selenium analog or asymetric radical cations.

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