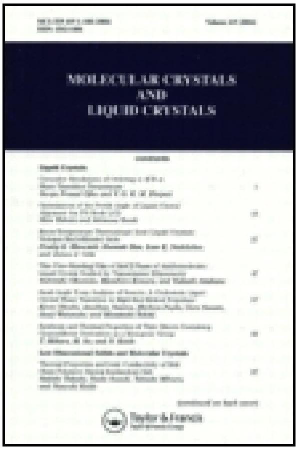

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CONDUCTING ORGANIC COMPOSITES OF TWO INSULATING REACTIVE SOLIDS : A THERMOPOWER STUDY

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Abstract The thermopower, S, of solid-solid donor acceptor TTF/TCNQ composites is investigated at room temperature. S is negative when acceptor TCNQ is in excess, positive when donor TTF is in excess and then just vanishing in equimolar mixtures.

During the last few years, we have devoted a number of papers [1,2,3,4] to the electronic properties of a particular kind of organic conducting composites simply produced through a direct, solid-solid, charge-transfer, reaction process.

A nice consequence is that, from two initially insulating reactants, one can produce quite easily a great variety of conducting composites. In fact, the only thing one has to do is to grind the two solid components together.

In this communication, we consider the most interesting case, solid-solid charge-transfer reaction between acceptor TCNQ (tetracyanoquinodimethane) and donor TTF (tetrathiafulvalene). We present various additional data on the transport properties of such composites, especially on the thermopower at room temperature.

The powdered TCNQ/TTF mixture, at first highly coloured yellow and orange, turns rapidly dark on grinding. It also gains intense infrared activity, intense E.P.R. spectra, and high electrical conductivity, after compaction under a moderate pressure, fixed once for all at P = 2.4 Kbars in this study[2,3].

The mixture is directly compacted inside a small, easily made, transparent plexiglass cell, designed for 4-probe measurements of electrical conductivity, σ, under pressure. A cyclindrical pellet is thus formed whose diameter and length are measured with binoculars after application of pressure[5].

The conductivity σ depends on four main parameters which are : temperature T, pressure P, molar fraction of donor x and grinding time t. Here, all measurements are made at fixed T (300 K) and P (2.4 K bars), so that only the variations of the last two parameters x and t are left in play : $\sigma = f(x,t)$.

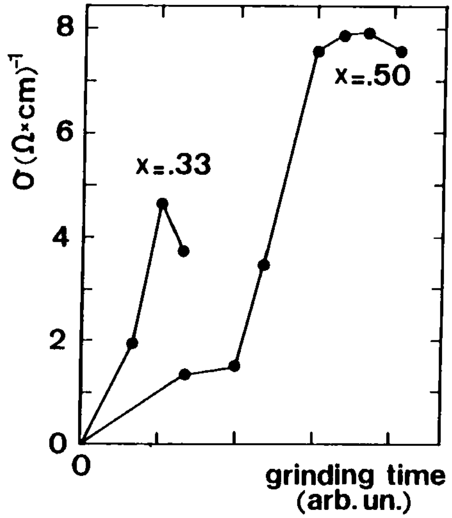

FIGURE 1 Dependence of electrical conductivity, σ, on grinding time t for : $x = 0.33$ and $x = 0.50$

Figure 1 shows, for $x = 0.33$ and $x = 0.50$ for example, that σ is a rather sensitive function of t. A well defined maximum $\sigma_M(x)$ is attained after a time t_M. This time t_M is found to be a rather sharp function of x^6.

In Figure 2 the conductivity σ_M so defined is reported, together with the corresponding conductivity-activation energy Ea, as a function of x. Ea is evaluated here from an Arrhenius plot of the T-dependence of σ_M around $T = 300$ K. The conductivity σ_M exhibits a high absolute maximum at x-value 0.5 which corresponds to equal proportions of donor TTF and acceptor TCNQ. The value of this maximum is close to 8 $(\Omega\,\mathrm{cm})^{-1}$, more than 10^{10} times the σ value measured in pure TCNQ crystals.

Ea increases slowly from 0.015 to 0.025 eV between $x = 0.1$ and 0.5. At $x = 0.5$, Ea starts to increase steeply, attaining 0.080 eV at $x = 0.8$.

Percolation thresholds occur on both sides, near $x = 0$ and $x = 1$. In particular[4], with only 3% molar of TTF, the conductivity of TCNQ is enhanced by more than 7 orders of magnitude and, correlatively, the activation energy Ea is lowered by a factor of 30.

Minor modifications of the cell device first utilized for conductivity measurements were subsequenly carried out, in order to also perform a thermopower study on the same samples[5].

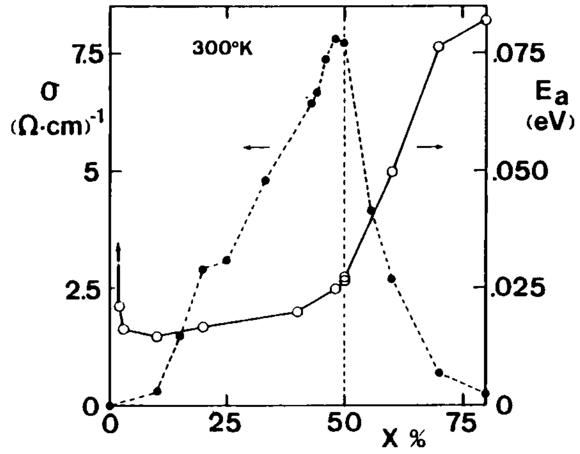

FIGURE 2 Dependence of conductivity σ_M and activation energy E_a on molar fraction x of donor TTF.

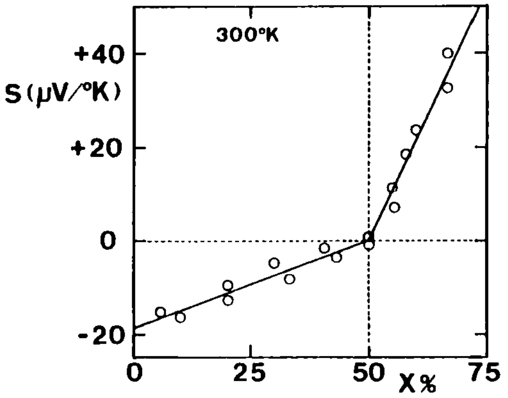

FIGURE 3 Dependence of thermopower S on molar fraction x of donor TTF.

The thermopower S of two independent series of samples, at T = 300 K, P = 2.4 K bars, and $t = t_M$, has been reported as a function of x in Figure 3.

S is shown to exhibit a rather remarkable behaviour, with two distinct regimes : S is negative when acceptor TCNQ is in excess, and it turns positive when donor TTF is in excess. Consequently, the thermopower of an equimolar mixture is just vanishing. In both regimes, a simple approximation to linear plots is acceptable within the limit of accuracy of the data, with however a slope which is about 5 times higher for $x > 0.5$ than for $x < 0.5$.

Application of elementary solid-state theory is certainly not fully justified in the present context. However, it provides, at least qualitatively, a rather good account of these results. Some comments will be devoted to this point further on.,

Let us call "Q" and "F" bands, the "effective" electron bands associated with TCNQ and TTF grains, respectively, in the composites. Formally, empty bands consist of $TCNQ^{o}$ (or TTF^{++}), full bands, of TTF^{o} (or $TCNQ^{--}$), and half-filled bands, of $TCNQ^{-}$ or TTF^{+}. Of course, either empty or full bands correspond to non-conducting systems.

The charge-transfer reaction is, in its simplest forms :

$$TCNQ^{o} + TTF^{o} \longrightarrow TCNQ^{-} + TTF^{+}$$

The reaction occurs randomly in the composite between pairs of grains, one of TCNQ and one of TTF, and not between individual molecules as in a solution. The reaction yield is supposed to be optimal, for any x, after a grinding time t_M.

Let us now assume that the thermopower of the composites can be quite generally expressed according to the form :

$$S(x) = a(x)\, S_Q(x) + b(x)\, S_F(x)$$

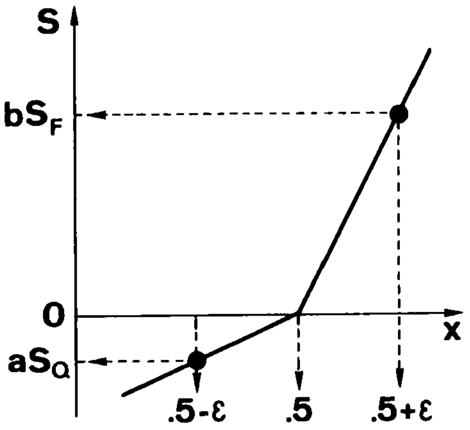

FIGURE 4 Schematic reproduction of Figure 3 showing that $bS_F(0.5+\varepsilon) > |aS_Q(0.5-\varepsilon)|$

in which, a and b are some weight functions such that : $a,b > 0$ and $a+b = 1$ (for instance, in the case of a classical two-band model[7] : $a = \sigma_Q/\sigma$ and $b = \sigma_F/\sigma$, with $\sigma = \sigma_Q + \sigma_F$).

S_Q and S_F stand for the respective contributions of the "Q" and "F" subsystems and so, they should rather be viewed as statistical averages. In this oversimplified picture (which ignores both dimerizations and Coulomb correlations), one then gets:

S_Q (S_F) = 0, or <0, or >0, according to whether, on the average, the "Q" ("F") band is half-filled, or less than half-filled, or more, respectively.

On this basis, the following experimental features can be simply accounted for :

a) $x = 0.5$: "Q" and "F" bands are half-filled : $S_Q = S_F = 0$
and, then : $S = 0$.

b) $x < 0.5$: the "Q" band is less than half-filled : $S_Q < 0$
the "F" band is half-filled : $S_F = 0$
then : $S = aS_Q < 0$.

c) $x > 0.5$: the "Q" band is half-filled : $S_Q = 0$
the "F" band is more than half-filled : $S_F > 0$
then : $S = b\,S_F > 0$

d) The occurence of different mechanisms for $x < 0.5$ and $x > 0.5$ also accounts for the change in slope dS/dx at $x = 0.5$

e) $x = 0.5$, but $t < t_M$: reaction still incomplete :
the "Q" band is less than half-filled :
$S_Q < 0$, as if $x = 0.5 - \varepsilon$ (cf. Figure 4)
and the "F" band is more than half-filled :
$S_F > 0$, as if $x = 0.5 + \varepsilon$ (cf. Figure 4)
then : $S = a\,S_Q + b\,S_F > 0$
because $bS_F > |aS_Q|$ (cf. Figure 4)

This last point also receives experimental confirmation : Figure 5 illustrates, for $x= 0.5$, the dependence of S on grinding time t. As long as $t < t_M$, S has a positive value. As $t \rightarrow t_M$, S is regularly decreasing, so that $S = 0$ for $t > t_M$, as in a).

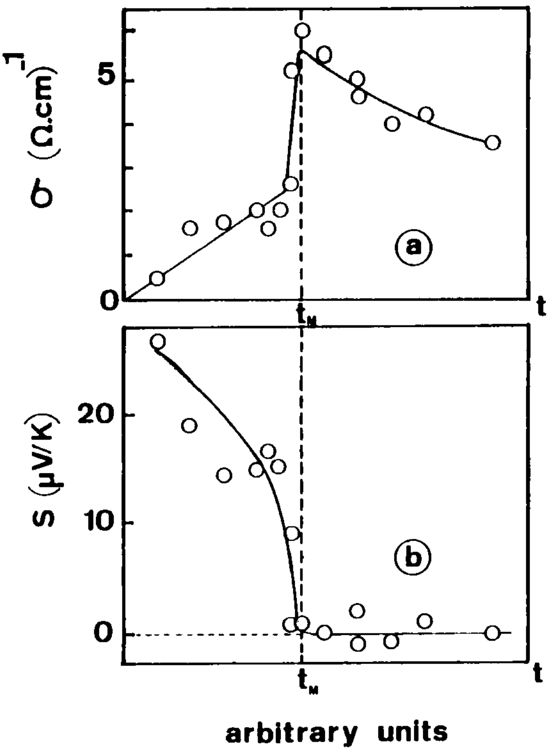

FIGURE 5 Comparative behaviour of conductivity σ and thermopower S versus grinding time t, for equimolar composites.
Note the positive sign of S for $t < t_M$.

Some final comments on the reliability of the preceding approach come from the transport properties of TTFTCNQ and $TEATCNQ_2$ (TEA = triethylaminomium), two crystalline systems which, although belonging to the same class of TCNQ salts, are in fact basically different[8,9]. The first is essentially a simple uncorrelated metal, whereas the second is a strongly correlated semiconductor.

The thermopower of the two salts has been reviewed by Chaikin[10]. In TTFTCNQ, S is proportionnal to T, as in a metal with no Coulomb correlations. In $TEATCNQ_2$, S saturates to a high-T limit of -60 μV/°K,which is characteristic of the spin contribution in correlated systems.

A remarkable fact is that the same kind of distinction is still roughly maintened in the corresponding composites, namely equimolar TCNQ/TTF and TCNQ/TEATCNQ mixtures. In particular, one gets, at 300 K and under 2.4 Kbars :

$\sigma = 8\ (\Omega\ \mathrm{cm})^{-1}$, Ea = 0.025 eV and S = 0, in this first case [3,4], and

$\sigma = 0.06\ (\Omega\ \mathrm{cm})^{-1}$, Ea = 0.15 eV and S = - 66 µV/ °K, in the second case[3,4].

This provides some ground to believe that the neglect of correlations in the preceding approach might be, at least in part, justified. Ultimately, none of the various correlated models developped by Chaikin [10] were able to account for such a simple result :

$$S\ (\ x = 0.5\ ) = 0.$$

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