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Role of Solvent in Phase Transition of NMeQn(TCNQ)$_2$

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Differential thermal gravimetry and differential scanning calorimetry studies of the 390 K phase transition of NMeQn(TCNQ)$_2$ on samples containing different amounts of acetonitrile solvent are presented. It is shown that evaporation of the solvent is the driving force of a phase transition recently reported for this material. Transport properties—dc and ac conductivity and dielectric constant—of the phase containing the solvent are weakly dependent on solvent concentration.

The organic charge transfer salt *N*-Methyl-Quinolinium (Tetracyanoquinodimethane)$_2$ (NMeQn(TCNQ)$_2$) shows an irreversible phase transition around 390 K.[1,2] In phase A (the phase found before the transition), the conductivity is high ($\sigma(300\text{ K}) \sim 20\,\Omega^{-1}\,\text{cm}^{-1}$) and various physical properties can be described by a one dimensional model with structural disorder.[3] When heated to 390 K the material changes to phase B in which the conductivity is smaller by several orders of magnitude and shows a semiconducting temperature dependence with a well defined activation energy. The susceptibility of phase B follows a Curie–Weiss law down to 4.2 K indicating a weak coupling between the spins. These properties suggest that electrons are strongly localized in this phase.[1] An irreversible phase transition was reported by Flandrois *et al.*[4,5] in the charge transfer complex DECA(TCNQ)$_2$, the drastic changes in the physical properties in this case were related to structural differences.

In this paper we suggest that in NMeQn(TCNQ)$_2$ these changes are related to the evaporation of the solvent which gives rise to a structural disorder in phase A.

We present differential thermal gravimetry (DTG), and differential scanning calorimetry (DSC) results together with measurements of the dc and microwave conductivity and dielectric constant of $NMeQn(TCNQ)_2$ samples with various amounts of acetonitrile solvent and demonstrate that acetonitrile evaporation is the driving force of the irreversible phase transition. Furthermore we argue that the main effect of the weakly bound solvent molecules is to screen the coupling between the neighbouring chains and to stabilize a phase which is thermodynamically unstable without the solvent.

$NMeQn(TCNQ)_2$ crystals were obtained in the form of long needles with well defined crystal faces (typical dimensions 3–4 × 0.6 × 0.6 mm^3). The composition,[6] determined by the optical spectra of the acetonitrile solution, was found to be somewhat less (1 : 1.8) than the value corresponding to the formula $NMeQn(TCNQ)_2$ but X-ray data show a structure[1,7] having a close similarity to $Qn(TCNQ)_2$. The acetonitrile content was varied by appropriately choosing the rate of cooling of the acetonitrile solution from 350 K to room temperature. For a cooling rate longer than a day a modification with a lower TCNQ content in the form of small platelets was obtained. This modification was not studied. The results we present are on materials obtained using cooling rates of 2°/min and 0.2°/min.

The DTG results show the presence of 0.55 mole and 1.07 mole acetonitrile in the materials prepared with a higher and lower cooling rate respectively, evaluated from the weight loss during the transition. The DSC curves of the two types of samples containing different amounts of acetonitrile (Figure 1) are similar. In addition to the strong peak at 397 K, the sample with higher acetonitrile content shows a second, less intense, peak. DTG curves do not show this structure the acetonitrile evaporates continuously from the material in the temperature region where the anomalies in the DSC curves were obtained. The change in enthalpy is found to be proportional to the acetonitrile content (see insert of Figure 1), the contribution from sources other than solvent evaporation (e.g. structural and electronic rearrangements) is less than 2 cal/g.

This together with the X-ray results—which show only a small contraction ($\sim 10\%$) perpendicular to and a small expansion ($\sim 2\%$) along the chains[1,7]—demonstrates that the solvent evaporation is the dominant process responsible for the sharp changes in the various physical properties.

We note that the solvent is only weakly bound in the solid. This is supported by the nearly identical solvent evaporation temperatures obtained on a number of TCNQ salts[2] and also by the relatively low temperature at which evaporation occurs. Nevertheless, this temperature is higher than the boiling point of acetonitrile (377 K). The heat of evaporation of CH_3CN from the salt (12 cal/g) is also higher than that of vaporization of liquid acetonitrile (5.4 cal/g). The binding energy between acetonitrile and $NMeQn(TCNQ)_2$ is therefore considerably weaker than the binding forces in the crystal but is nevertheless greater than that of the liquid acetonitrile itself.

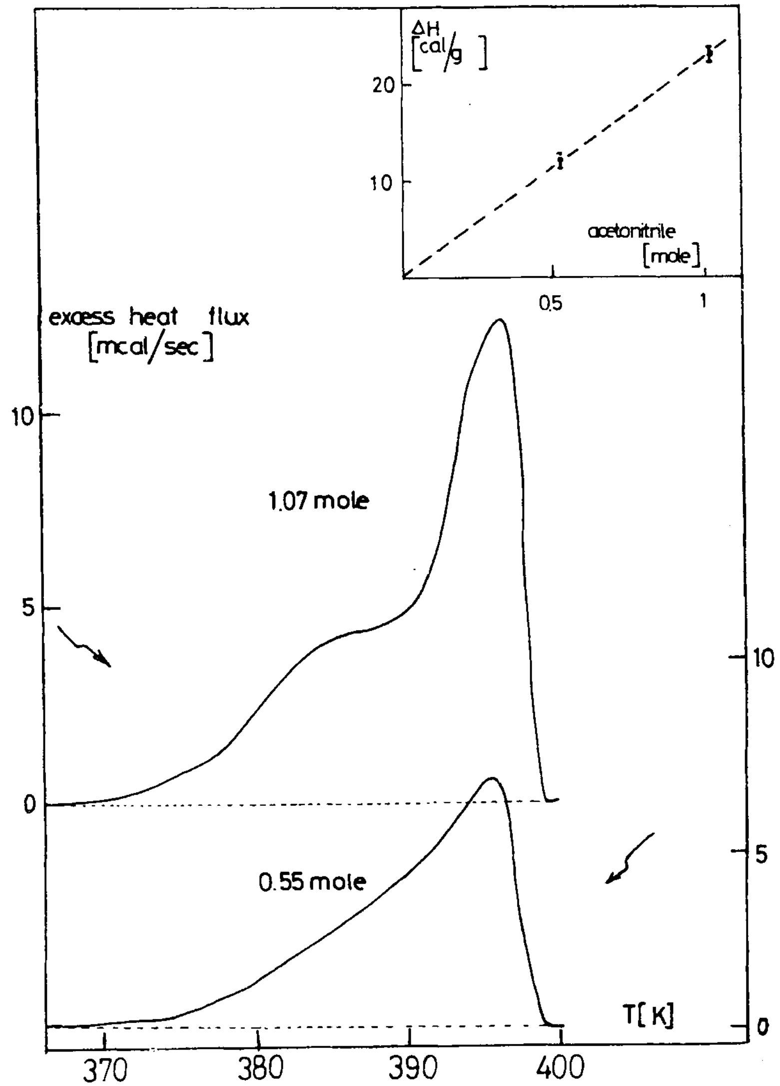

FIGURE 1 DSC curves of the two NMeQn(TCNQ)$_2$ samples with different acetonitrile contents. The enthalpy change versus the acetonitrile content obtained by integrating the DTG curves is shown in the insert.

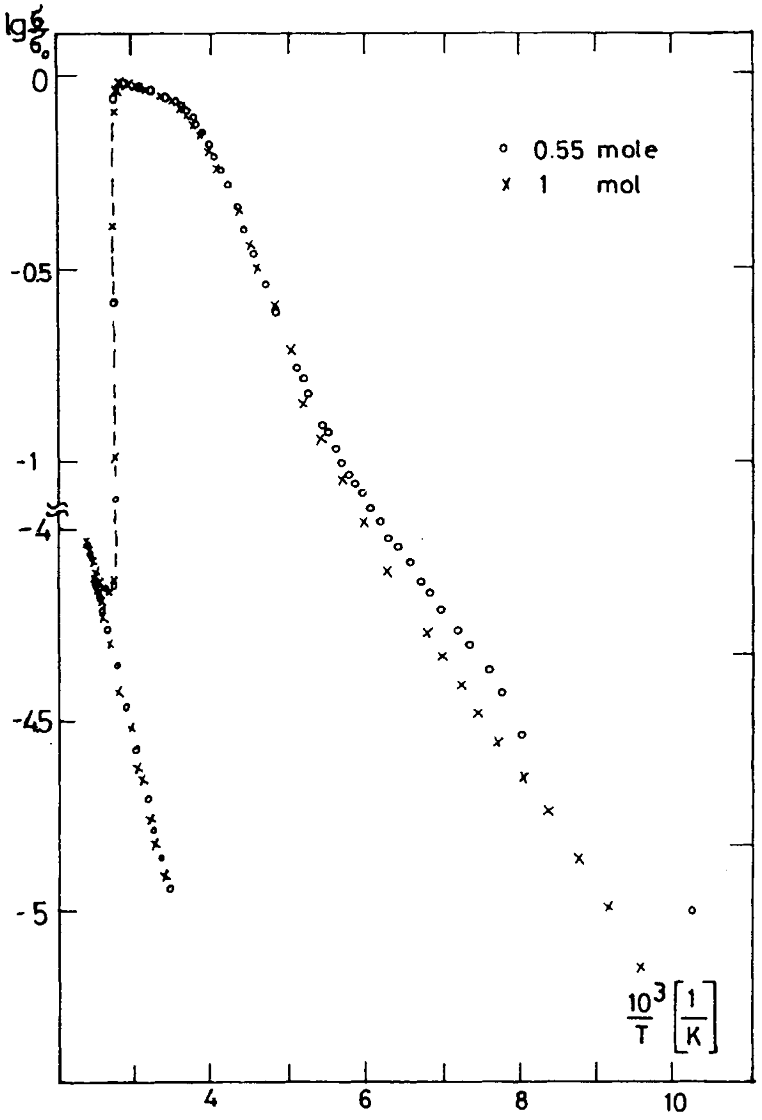

FIGURE 2 dc conductivity of single crystals of different acetonitrile contamination.

The behaviour of the dc conductivity above 100 K is shown in Figure 2 for both solvent concentrations. In phase A it does not follow a simple exponential law, but begin to flatten around room temperature. Before reaching a maximum the transition to the B phase takes place and the conductivity drops by four orders of magnitude. In the B phase the simple $\sigma \sim \exp(-\Delta E/kT)$ formula describes well the temperature dependence with

$\Delta E = 0.3$ eV. The characteristics of the conductivity of phase A (and also other properties such as the magnetic susceptibility)[1,3] are very similar to those of a well known class of TCNQ salts of which Qn(TCNQ)$_2$ and Ad(TCNQ)$_2$ are typical examples.[8] In these materials the donor molecules are asymmetric and their orientations are randomly distributed between two possible orientations per site. Therefore the permanent dipole moments of the donors in the charge transfer state give rise to a random potential felt by the electrons moving along the TCNQ chains. This inherent disorder is claimed to be responsible for their unusual physical properties.[9]

This similarity between the A phase and the "disordered 1d" materials,[3] the conductivity of which shows a characteristic frequency dependence below the maximum and which have large dielectric constants, is further demonstrated in Figure 3. A well observable dispersion develops at lower temperatures and the dielectric constant is large for the A phase (see the insert of Figure 3). The dispersion of the conductivity and the dielectric constant increases with the acetonitrile content. The microwave conductivity follows the jump found for dc at the transition to the B phase but in this phase the temperature dependence could not be measured. The dielectric constant in the B phase is small: $\varepsilon = 4.4 \pm 0.5$, indicating a well defined, large gap for the single particle excitations.

The observed properties of phase B show no trace of disorder and we believe the donors are ordered in this material.[10,11] Since no lattice distortion (i.e. doubling of the primitive cell) was observed it is argued[1,12] that the sharp gap in the single particle and collective excitation spectrum is a consequence of the interchain and intrachain Coulomb interactions.

The proportionality of the integrated DSC and DTG curves excludes the possibility of a rearrangement of the donors during the phase transition and we believe that the large differences in the physical properties are related mainly to the presence of the solvent in phase A. Indeed in this phase some properties are dependent on solvent concentration. As originally suggested,[1] the highly polarizable CH$_3$CN molecules act as a randomly distributed screening medium which decreases the Coulomb coupling between the chains and gives rise to random potential .This disorder makes phase A of NMeQn(TCNQ)$_2$ similar to those materials in which the disorder is due to the randomly oriented donors. A change in the random potential, i.e. a change in the concentration of the incorporated solvent, is expected to alter significantly the dc conductivity at lower temperatures only (a somewhat similar problem for Qn(TCNQ)$_2$ is studied in Ref. 13), while the microwave properties—which are much more sensitive to polarization effects—are more affected in the studied temperature range.

Finally we note that the difference between properties of the two phases demonstrate that the electronic states in organic charge transfer salts are

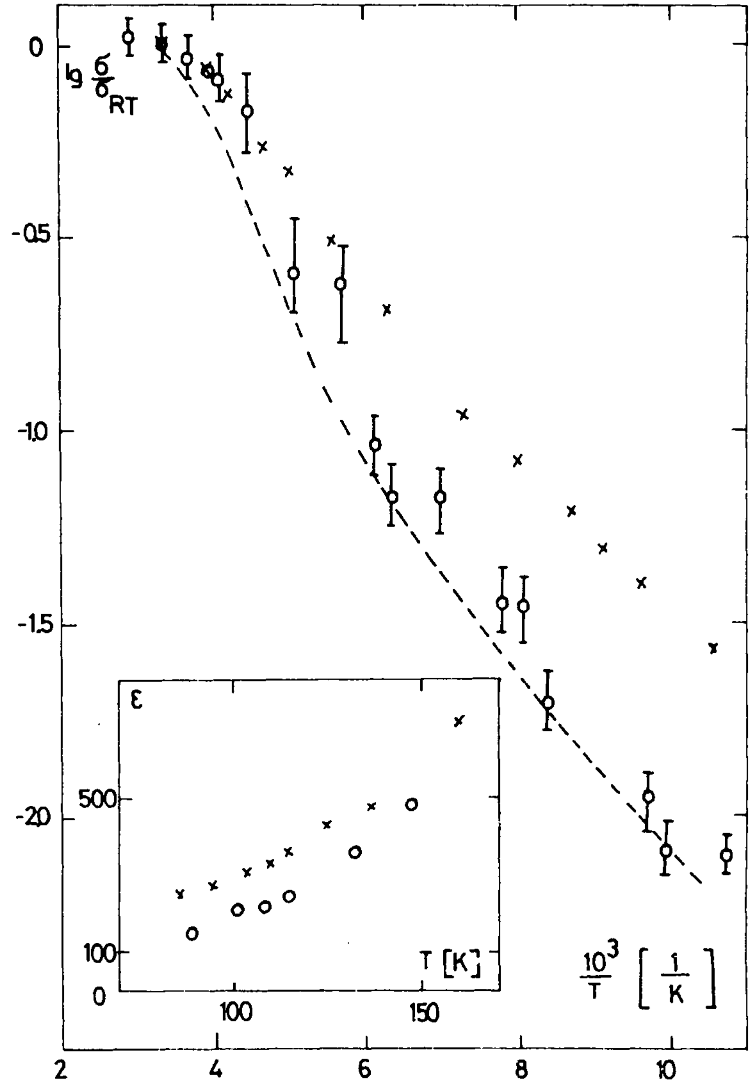

FIGURE 3 ac conductivity and dielectric constant of single crystals of different acetonitrile contamination. The dc curve of the 1.07 mole acetonitrile sample is shown by the dotted line.

strongly influenced by factors which have not usually been considered in recent treatments.[14] In this case in particular differences in band filling and in the structure can be excluded, and only the coupling between the chains is affected. The high conductivity in complex TCNQ salts therefore appears to be due to the lack of three dimensional long range order[11] with partial band filling being only a necessary condition.

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