NQR Investigation of the Temperature-Induced Neutral-to-Ionic Phase Transition in the Mixed-Stack Charge-Transfer Complex TTF-CA*

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Z. Naturforsch. **47a,** 257–260 (1992); received August 3, 1991

The chlorine-35 NQR has been investigated in the mixed-stack charge-transfer complex tetrathiafluvalene-chloranil. The neutral-to-ionic (N-I) phase transition is clearly seen on the NQR spectrum. Among several features of the spectra recorded and their counterpart in the sample behaviour, the evidence for the change in the crystal symmetry and the quite likely existence of neutral domains in the ionic phase below the N-I transition temperature are the most striking ones.

Key words: TTF-CA, TINIT, Neutral-to-ionic phase transition, Mixed-stack charge transfer complex, NQR, ^{35}Cl.

Introduction

TTF-CA (tetrathiafluvalene-choranil, Fig. 1) is a molecular charge-transfer compound undergoing a neutral-to-ionic transition (NIT) when it is cooled down to about 80 K. Several compounds, including TFF-CA, showing such a transition, but pressure induced (PINIT), were reported by Torrance et al. [1] in 1981. TTF-CA was the first compound to present also a temperature-induced neutral-to-ionic transition (TINIT) [2, 3]. Since that time, another TINIT has been reported by Iwasa et al. (TMB-TCNQ) [4]. The behaviour of TTF-CA near the NIT is different when the transition is approached by increasing the pressure or lowering the temperature.

Experimental results from optical, infrared and Raman spectroscopy, X-ray or neutron diffraction, specific heat, dielectric constant, electric conductivity, RPE and RMN measurements are available. Tentative interpretations of physical facts and theoretical developments have been proposed.

The system is rather complex as seen from the different behaviour when the transition is temperature or pressure induced and from the fact that the mixed-stack chains are usually considered as 1D systems while the electrostatic interactions in the Madelung term is three dimensional.

Schematically, the NIT appears as an increase in the low charge transfer (0.3 electron) in the quasi-neutral, high temperature phase to a higher one (0.7 electron) in the quasi-ionic, low temperature phase [3]. The increase in the charge transfer is accompanied by a shift in the position of the donor and acceptor

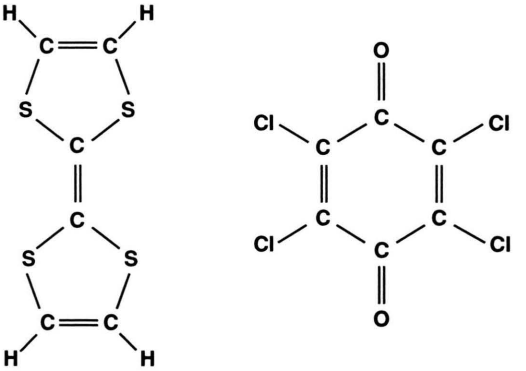

Fig. 1. The tetrathiafluvalene and chloranil molecules.

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* Presented at the XIth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, London, U.K., July 15–19, 1991

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molecules in the crystal, leading to a dimerization forming D^+A^- pairs along the chains in the crystal "a" direction.

It seemed worthwhile to start an NQR investigation on the chlorine atoms of the chloranil molecule in the compound, as this can bring new information at the microscopic level.

Experimental

The sample, in powder state, was prepared by co-sublimation of the basic compounds. The spectrometer is of the pulsed type with signal accumulation. The echo signal was usually recorded and, for T_1 studies, the recovery of the signal after a saturating pulse was monitored.

Previous NQR Results

The first results of the investigation were published in early 1991 by Gourdji et al. [5]. The main features then reported are:

The transition at 79 K is clearly evidenced by a strong change in the chlorine NQR spectrum.

Above the transition the spectrum is composed by two narrow lines of equal intensity and about 500 kHz apart from each other (Fig. 2); the temperature dependence of their frequencies is roughly as expected from standard thermal motion averaging. The linewidth, about 10 kHz at room temperature, increases as the sample is cooled down up to 30 kHz near 79 K.

Below the transition (Fig. 3), the lines are broad (30 to 50 kHz) and their frequencies are lowered by about 200 kHz. More precisely, the high frequency resonance clearly appears as a doublet while the low frequency one does not show any structure; however, as its integral intensity is the same as that of the doublet, it can be considered as formed of two components with almost the same frequencies.

The change observed in the line number follows from a change in the crystal structure produced by the shift in the molecule position tending to form donor-acceptor pairs; the shift also destroys some of the symmetry elements in the crystals, as shown by neutron diffraction [6]. From the structure of the neutral phase (monoclinic, $P2_1/n$ [7]), two crystallographically inequivalent chlorine sites exist, yielding two NQR lines as observed and, in the ionic phase below the transition, up to eight inequivalent sites may be expected from the reduction of the number of symmetry elements. Unfortunately, the lack of resolution resulting from the large width of the resonances has prevented the observation of the expected structure in the chlorine resonance.

Another feature worthy of mention is the presence in the spectrum, on the high frequency side of the resonances below 79 K, of small lines, precisely at the frequencies of the lines in the neutral phase. More strikingly, their relaxation times ($\simeq 0.15$ s) are also the same and differ from that of the ionic phase lines ($\simeq 1$ s). Their presence below 79 K indicates the coexistence of the neutral and ionic phases in this temperature range.

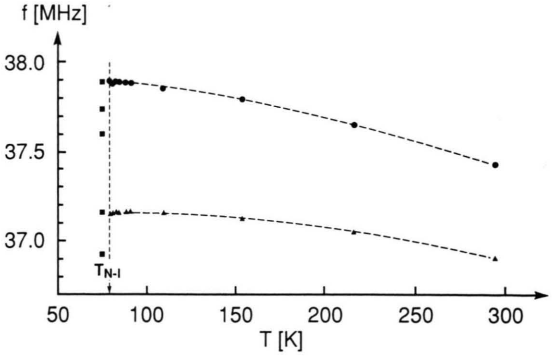

Fig. 2. Temperature dependence of the chlorine-35 NQR frequencies in the TTF-CA above the N-I transition temperature (dots and triangles) and at 77 K (squares).

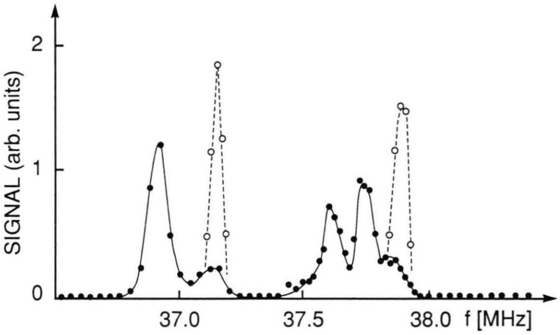

Fig. 3. The chlorine-35 spectrum in TTF-CA at 77 K (solid line) and at 83 K, i.e. above the N-I transition temperature (dashed line).

New NQR Results

Further investigation of chlorine NQR in TTF-CA has brought some new results concerning two major points:

One is the behavior of the "neutral phase" lines (NP lines) below 79 K.

The second is the relaxation above the transition temperature.

1. The NP lines in the ionic phase. They are reproducible; in particular, when the sample is cooled below 70 K, the lines disappear completely and when the sample is brought again to 77 K, i.e. still below the transition temperature, the lines reappear. The reversible behaviour of the NP lines below the transition temperature rules out the possibility of some hysteresis effect that would that delay the transformation, upon cooling, of some part of the sample into the ionic phase. It also strongly suggests a model of neutral domains existing in an essentially ionic phase.

2. Relaxation above the transition temperature. As far as the relaxation time is concerned, two temperature regions should be considered: the high temperature region, well above (more than 20 K), and the region just above the transition temperature, $T_{\text{N-I}} \simeq 79$ K.

a) In the high temperature region, the relaxation rate increases with temperature but proportional to $T^{3.5}$ showing that the simple two phonon Raman mechanism yielding a T^2 law should be refined.

b) Near the transition, the relaxation rate increases as temperature is decreased towards the transition with a $T_1 \propto (T - T_0)$ law (Fig. 4); $T_0 = 67$ or 70 K according to whether the correction for the still present high temperature contribution is neglected or taken into account. Such a linear dependence of T_1 on temperature has already been observed above the incommensurate phase transition in ThBr$_4$ [8], buth with the difference that in the latter T_0 is equal to the transition temperature while, in the case of TTF-CA, T_0 is some ten degrees below the transition. The increase of the relaxation rate when the transition is approached from above indicates the presence of some pretransitional mechanism detectable from about 20 K above $T_{\text{N-I}}$. A more extended analysis of the spin-lattice relaxation will be published later.

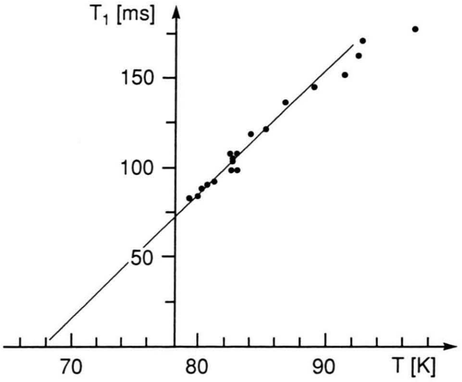

Fig. 4. The chlorine-35 relaxation time T_1 in TTF-CA in the temperature region just above the N-I transition, with linear temperature and relaxation time scales.

In addition to the two points just presented, it can be emphasized that a pretransitional effect is observable on the $\nu(T)$ curve corresponding to the low frequency line in the spectrum recorded at temperatures above the transition: if the behaviour of $\nu(T)$ is roughly as expected from standard thermal motion averaging in molecular crystals, more careful inspection shows an inflexion of the curve when the temperature is lowered near $T_{\text{N-I}}$ (Figure 2). In other words, the pretransitional mechanism also affects the NQR frequency.

Conclusion

So far, and to summarize, an NQR investigation of TTF-CA and the neutral-to-ionic transition at $T_{\text{N-I}}$ has shown that:

- the N-I transition is first order and no hysteresis was observed,
- the crystal symmetry is lowered at the transition, in accordance with neutron diffraction measurements,
- pretransitional mechanisms take place when the transition is approached from above,
- neutral domains exist in the ionic phase below $T_{\text{N-I}}$, and this point seems to be very important for a precise description of the N-I transition in TFF-CA.

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