High-pressure optical study of the neutral–ionic phase transition in TTF-CA

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We have studied the pressure-induced neutral–ionic phase transition of tetrathiafulvalene-chloranil (TTF-CA) with polarized infrared absorption spectra of single crystals inside a diamond anvil cell (DAC). The evolution of the phase transition is complex, implying at least two steps. The nature of the intermediate regime is briefly discussed.

Key words: charge transfer crystals; phase transitions; organic semiconductors; high-pressure optical spectroscopy

1. Introduction

Neutral–ionic phase transitions (NIT) in mixed stack charge-transfer (CT) crystals were discovered nearly 25 years ago [1, 2], but continue to attract considerable attention [3] in view of the intriguing properties exhibited at the transition, such as unusual dielectric responses [4] or negative resistance effects [5]. NITs are characterized by a change in the degree of ionicity, $\rho$, the average charge on the electron-donor (D) and electron-acceptor (A) molecules that alternate along the stack. In the ionic phase ($\rho \geq 0.5$), the stack dimerises due to Peierl instability [3]. Therefore, there is a complex interplay between electronic valence instability (order parameter – $\rho$) and the structural phase transition (order parameter – the extent of dimerisation $\delta$).

Among CT salts undergoing NIT, the prototype tetrathiafulvalene-chloranil (TTF-CA) occupies a special place, because it is almost unique in undergoing both temperature- [2] and pressure-induced [1] neutral–ionic phase transitions. On the other hand, most experimental studies have been devoted to the $T$-induced phase transitions.

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Studies on the \( p \)-induced transitions [6–10] showed that it occurs through some sort of “intermediate phase”, whose nature has remained elusive. The issue is important for a proper construction of the TTF-CA pressure–temperature \((p-T)\) phase diagram [11, 12] and for the understanding of the NIT mechanism in general.

2. Experimental

TTF-CA single crystals were prepared by vacuum sublimation (75° C) of crystals obtained by mixing saturated acetonitrile solutions of commercial grade TTF and CA. In this way, very thin single crystals, suitable for absorption spectroscopy, were grown. The crystals exhibit significant dichroism in white light transmission: they appear green when the light is polarized parallel to the stack axis \( a \), and yellow when polarized perpendicular to the stack.

The infrared (IR) absorption spectra were measured with a Bruker FTIR spectrometer (model IFS66), equipped with an A590 microscope. The spectral resolution was 2 cm\(^{-1}\). High-pressure measurements up to 3.2 GPa were performed with a custom designed gasketed diamond anvil cell (DAC), able to fit under the IR microscope. Nujol or perfluorocarbon oil was used as the pressure-transmitting medium. Nujol oil, which is hydrostatic up to 5 GPa, gave good results in terms of pressure homogeneity inside the DAC. On the other hand, the pressure appeared to be inhomogeneous throughout the sample when perfluorocarbon oil was used, so these measurements were disregarded. Pressure calibrations were done with the ruby luminescence technique [13]. Error bars in pressure readings were \( \pm 0.05 \) GPa.

3. Results

Figure 1 shows a portion of the absorption spectra polarized perpendicular to the stack axis (i.e. roughly parallel to the molecular planes) as a function of pressure. The reported spectral region (1525–1685 cm\(^{-1}\)) shows the pressure evolution of the CA \( b_{1u} \nu_{10} \) normal mode, corresponding to carbonyl antisymmetric stretching. The frequency of this mode is generally used to estimate \( \rho \) by assuming a linear frequency dependence: \( \nu(\rho) = \nu(0) - \Delta_{\text{ion}} \rho \), where \( \Delta_{\text{ion}} = 160 \) cm\(^{-1}\) is the ionicity frequency shift from the fully neutral (CA\(^0\), 1685 cm\(^{-1}\)) to the fully ionic molecule (CA\(^-1\), 1525 cm\(^{-1}\)).

Figure 2 compares the pressure evolution of ionicity, as estimated from the frequency of the CA \( b_{1u} \nu_{10} \) mode, with the corresponding temperature evolution [14]. In the temperature induced NIT, \( \rho \) jumps discontinuously from 0.3 to 0.5 at \( T_{N-I} = 81 \) K, evidencing the first-order character of the phase transition. The evolution of the pressure-induced phase transition is much more complex. The ionicity increases smoothly on increasing pressure up to \( \rho \approx 0.45 \) at 0.85 GPa. Above this pressure, two bands corresponding to the CA \( b_{1u} \nu_{10} \) mode are clearly seen, which indicates the coexis-
Fig. 1. Pressure dependence of the TTF-CA absorption spectra polarized perpendicular to the stack axis in the 1525–1685 cm$^{-1}$ spectral region. Continuous-line spectra refer to the intermediate phase.

Fig. 2. Temperature (left panel) [14] and pressure (right panel) evolution of the ionicity $\rho$, as estimated from the CA $b_{1u}$ mode (see text). The vertical lines indicate the pressure range stability of the intermediate phase.

tence of two CA species of different ionicities, namely $\rho_1 \approx 0.5–0.6$ and $\rho_2 \approx 0.7$. The relative amount of the two species varies with pressure: The band corresponding to the more ionic $\rho_2$ species, present in the 0.9 GPa IR spectra only as a shoulder, gradu-
ally gains intensity and dominates over the $\rho_1$ band above 1.1 GPa (Fig. 1). In addition, while the ionicity of the $\rho_2$ species is nearly constant around 0.7, the ionicity of the $\rho_1$ species slightly increases from 0.5 to 0.6 on increasing the pressure (right panel of Fig. 2). We point out that the doublet structure in the IR spectra is hardly due to any macroscopic inhomogeneity, such as a non-uniform strain in the crystal, as we have checked for pressure homogeneity by means of micro-Raman mapping of the crystal sample. Moreover, the spectral changes are well reproducible for various cycles on different crystal samples. The doublet structure disappears above 1.2 GPa, and we observe a single CA $b_{1u} \nu_{10}$ band. Above this pressure, the ionicity is unique again, and increases from $\rho \approx 0.70$ to $\rho \approx 0.78$ at 2 GPa.

4. Discussion

We will now review previous studies on the pressure-induced NIT of TTF-CA and compare them with the data presented above. A generally accepted picture emerging from previous spectroscopic studies is that the $p$-induced NIT in TTF-CA occurs through some sort of intermediate state, in which quasi-ionic and quasi-neutral molecular species ($I + N$) coexist. Indeed, evidence of a doublet structure for bands mostly sensitive to ionicity has been found in vibrational IR [6, 8], Raman spectra [9], and in UV-VIS optical reflectivity measurements [7]. At room temperature, this intermediate mixed ($I + N$) state starts at a pressure around 0.7 GPa and ends up at 1.1 GPa, when the system undergoes the transition towards a single ionicity ionic phase [6, 8].

More recently, the $p$-$T$ phase diagram of TTF-CA has been investigated by means of neutron diffraction and nuclear quadrupole resonance in a remarkable work by Lemée-Cailleau et al. [11]. They postulate the existence of a triple point, located approximately at 0.5 GPa and 205 K, above which the $N$-$I$ first order phase transition line splits into two. Such an observation agrees with the picture described above, implying an intermediate phase in the $p$-induced NIT above 205 K. The nature of this unusual solid-state $p$-$T$ phase diagram has been described in terms of the condensation and ordering of CT excitations [11, 12]. In other words, at relatively high temperatures, the neutral phase should be considered to be composed of neutral and ionic dynamic domains, thermally fluctuating in time and space. When the concentration of the ionic domains is high enough, a first order phase transition occurs: the ionic domains condense in 1-D strings, forming the intermediate phase. The first order line ends up at a critical point, when the difference between the neutral and intermediate phases disappears. By further increasing pressure, a 3-D ordering phase transition of the 1-D ionic strings drives the intermediate phase to the ionic phase.

Our data (Fig. 1) confirm the presence of an intermediate phase, which now appears well established even at room temperature. As a consequence, the neutral phase-to-intermediate phase transition line should be extended up to at least 300 K, shifting...
the critical point, if any, to a higher temperature. At variance with previous studies, we observe the starting of the intermediate state at a pressure around 0.85 GPa, slightly higher than the previously reported values. Both species ($\rho_1 + \rho_2$) seem to be already on the ionic side. We remark, however, that the IR spectra polarized parallel to the stack axis, which are not reported here and currently under analysis, show significant changes already at 0.7 GPa. In addition, we point out that the neutral–ionic borderline changes with the stack structure: if the stack is regular, theory puts the crossover at $\rho \approx 0.68$ [15], whereas for a chain of DA dimers the crossover is at $\rho \approx 0.5$. Further studies, both experimental and theoretical, are therefore needed, and are in progress, to understand the complex nature of the pressure-induced NIT in TTF-CA.

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References


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