Intermediate regime in Tetrathiafulvalene-Chloranil (TTF-CA) pressure-induced neutral-ionic transition

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We report a detailed spectroscopic study of the pressure induced neutral-ionic phase transition (NIT) of the mixed-stack charge-transfer (CT) crystal tetrathiafulvalene-chloranil (TTF-CA). We show that the pressure induced phase transition is still first-order and involves the presence of an intermediate disordered phase, defined by the coexistence of two species of different ionicity. Further application of pressure gradually converts this phase into an homogeneous ferroelectric phase with a single ionicity. In addition, we detect strong pretransitional phenomena which anticipate the intermediate phase and are indicative of a precursor dynamic regime dominated by fluctuations.

I. INTRODUCTION

Neutral-ionic phase transitions (NIT) are pressure or temperature induced valence instabilities occurring in mixed stack charge-transfer (CT) crystals, where π-electron donor (D) and acceptor (A) molecules alternate along the stack direction. NIT are known since long time, but the microscopic origin of the many intriguing phenomena accompanying the transition is still controversial. For instance, the dielectric constant and conductivity anomalies have been ascribed to the presence of nanoscopic, mobile objects, the lattice relaxed neutral-ionic domain walls (NIDW), also referred as lattice relaxed charge-transfer exciton strings (LRCT). On the other hand, the dielectric constant anomaly can be well accounted for by the charge oscillations induced by the Peierls mode since the ionic stack is subject to Peierls instability. Another intriguing aspect of NIT is indeed associated with the dimerization Peierls instability, since dimerized ionic stacks are potentially ferroelectric.

Tetrathiafulvalene-Chloranil (TTF-CA) NIT is by far the most widely studied, also because it can be induced both by temperature T and pressure p. The ambient pressure T-induced transition occurs at T_c = 81 K, is first order, and has been well characterized by a series of structural and spectroscopic studies, whose list is too long to be reported here.

At T_c, the average charge on the molecular sites (ionicity, ρ) jumps from about 0.3 to over 0.5, the latter value being considered the borderline between neutral (N) and ionic (I) phases. The ionicity jump is accompanied by the stack dimerization. The Peierls modes have been identified in both the N and I phases, but of course they do not reach zero frequency, as the first order valence instability takes over.

The TTF-CA p-induced transition has been comparatively less studied. Early infrared (IR) spectra of the powders showed that above ~ 1.1 GPa the phase is ionic and dimerized, similarly to the low-T phase. On the other hand, preliminary X-ray measurements, never published in complete form, suggested that the p-induced transition is different from the T-induced one, occurring through some sort of “intermediate transition region”, from about 0.65 to 1.1 GPa. This finding has been confirmed by several spectroscopic data, but without agreement about the nature of this intermediate transition region. Several authors suggested that species of different ionicity were present, but the degree of ionicity was highly uncertain. Also the pressure interval of the coexistence region varied depending on the type of measurement. The use of powdered samples is certainly one of the reasons of such uncertainties, as for instance IR spectra are more difficult to interpret in the lack of polarization information. Moreover, it is known that the NIT is affected by the presence of defects, and these certainly dominate in powdered samples. In any case, qualitative phase diagrams started to emerge based on measurements in which both T and p were simultaneously changed. According to these studies, both neutral and ionic species coexist in the intermediate regime.

The first detailed study of the phase diagram, performed through neutron diffraction and NQR on TTF-CA single crystals, definitely evidenced a bifurcation of the N-I crossing line at a triple point located around 210 K and 0.5 GPa. According to these authors, the intermediate regime arising above the triple point has to be interpreted as a paraelectric phase, separating the ionic and dimerized (ferroelectric) from the neutral and regular stack phase. In other words, the intermediate regime is interpreted as a true thermodynamic phase, where dynamically disordered LRCT are present. The condensation and ordering of LRCT, driven by interstack interactions, yields the ferroelectric phase.

Evidence of LRCT was thought to be provided by IR spectra. However, by using combined single crystal IR and Raman data, some of us have shown that the
apparent signatures of LRCT in the $T$-induced NIT are actually due to the Peierls mode. For this reason we have decided to re-investigate the $p$-induced transition of TTF-CA by the same methods, namely, combined single crystal Raman and polarized IR data. A first set of experiments, focalized on the IR spectra polarized perpendicular to the stack, have clearly shown that two species of different ionicity are present in the intermediate transition region. In pressure experiments particular care has to be paid to pressure homogeneity on the sample, and before publishing a full paper we have carefully repeated the experiment, adding also measurements with polarization parallel to the stack. In the meantime, an independent paper has appeared, reporting single crystal optical spectra as a function of pressure. The reported IR spectra confirm our earlier experiment, but the interpretation is quite different from ours.

In the present paper we report the complete IR absorption spectra of TTF-CA single crystal, together with Raman spectra collected at the same pressures. We confirm that between 0.86 and 1.24 GPa species with different ionicity are simultaneously present. However, both species are on the $I$ side. In addition, a precursor regime, probably dominated by fluctuations, is present between $\sim 0.6$ and $\sim 0.86$ GPa. Possible scenarios emerging from the present measurements are discussed.

II. EXPERIMENTAL

TTF-CA has been prepared by mixing hot saturated acetonitrile solutions of commercial grade TTF and CA. Very thin single crystals suitable for infrared (IR) absorption have been obtained by subliming TTF-CA under reduced pressure. Thicker samples have been used for the Raman measurements. The crystals present significant dichroism in white light transmission: they appear green when light is polarized parallel to the stack axis $a$, and yellow for light polarized perpendicular to the stack.

The IR absorption spectra have been measured with a Bruker FTIR spectrometer (model IFS 66), equipped with a microscope. The Raman spectra were recorded with a Renishaw System 1000 micro-spectrometer (20X magnification objective) and using the 568.2 nm excitation line from a Kr ion laser. The laser power has been adjusted to 1 mW in order to reduce the risks of sample heating especially in proximity of the phase transition. The spectral resolution of both IR and Raman spectra is 2 cm$^{-1}$. High pressure measurements up to 3.2 GPa have been performed with a custom designed diamond anvil cell (DAC) able to fit under both IR and Raman microscopes. The samples have been inserted in either stainless-steel or copper gaskets, the latter allowing finer tuning at low to moderate pressures (up to 1.5 GPa). Pressure calibration has been done with the ruby luminescence technique. Estimated error bar in the pressure reading is $\pm 0.05$ GPa. Liquid paraffin (Nujol oil) has been used as the pressure transmitting medium both in IR and Raman. In IR, the spectral regions between 1360-1390 cm$^{-1}$ and 1430-1480 cm$^{-1}$ are obscured by the Nujol bands.

III. RESULTS

A. Valence instability: Ionicity

In Fig. 1 we show the IR absorption spectra polarized perpendicular to the stack axis in the 1500-1700 cm$^{-1}$ spectral region as a function of pressure. Here two bands at 1655 and at 1542 cm$^{-1}$ (spectrum at 0.05 GPa) are clearly observed, and can be safely assigned to the $b_{1u}$ C=O stretching mode in the coexistence regime. Solid circles indicate the band due to the $b_{2u}$ C=C stretching mode of CA molecules.

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stability, and can be used to accurately probe ionicity in view of its large frequency shift in going from the fully neutral CA\(^0\) (\(\omega = 1685 \text{ cm}^{-1}\)) to the fully ionic CA\(^-\) molecule (\(\omega = 1525 \text{ cm}^{-1}\)).\(^{23}\)

From Fig. 1 it is evident that the \(b_{1u}\), C=O band displays an anomalous behavior with increasing pressure. After a smooth softening accompanied by a sizeable broadening, it splits giving rise to two bands, marked A and B in the figure. The B band starts to appear around 0.86 GPa, at 1580 cm\(^{-1}\), on the low frequency side of the A band at 1610 cm\(^{-1}\). With increasing pressure the B band develops, gaining intensity at the expenses of the A band. Then above 1.24 GPa the intensity inversion is completed, the A band disappears, while the B band is observed at 1570 cm\(^{-1}\) and remains nearly unchanged up to the maximum experimental pressure we have reached (3.2 GPa).

![Graph showing ionicity vs pressure](image)

**FIG. 2:** (color online). (a): Pressure evolution of TTF-CA ionicity, \(\rho\), as estimated by the frequency of the \(b_{1u}\), C=O antisymmetric stretching mode. The yellow region marks the pressure range of the coexistence regime. (b): Relative concentration of the \(I_2\) species as estimated from the intensity ratio of the “B band” component. The dashed line is a guide for the eye. (c): Bandwidth (FWHM) of the \(b_{1u}\), C=O band as a function of pressure.

Ionicity values deduced from the experimental frequencies of the \(b_{1u}\), C=O band by assuming a linear frequency dependence are plotted in Fig. 2. Ionicity increases gradually from \(\rho = 0.19\) up to \(\rho = 0.47\) at 0.86 GPa. Applying pressure further a small discontinuity occurs. The TTF-CA system crosses the N-I borderline, conventionally located at \(\rho = 0.5\). An intermediate regime develops, where molecular species with two different ionicity, \(\rho(I_1)\) and \(\rho(I_2)\), coexist. \(\rho(I_1)\) slightly increases from \(0.55\) up to \(0.60\), while \(\rho(I_2)\) is almost constant.

These two different ionicities correspond to the two components, A and B, of the splitted band structure in Fig. 1 and the evolution of their relative intensities allows one to follow the concentrations, \(c(I_1)\) and \(c(I_2)\), of the two molecular species \((c(I_1) + c(I_2) = 1)\). The two species have variable concentration as demonstrated by Fig. 2(b), where \(c(I_2)\), estimated from the relative intensity of the B band, is plotted as a function of pressure. The concentration \(c(I_2)\) increases from 0.86 up to 1.24 GPa, and above this pressure only \(I_2\) molecules with \(\rho \sim 0.7\) are present.

In Fig. 2(b) we report the pressure evolution of the bandwidth of the \(b_{1u}\), C=O band. Here the discontinuity between 0.86 and 0.90 GPa in crossing the N-I borderline, is much clearer. Also notice the steep increase of bandwidth when approaching the coexistence region, indicative of a precursor regime with strong dynamic disorder.

We remark that the pressure dependence of the \(b_{2u}\), C=C band at 1542 cm\(^{-1}\), marked with solid circles in Fig. 1 is perfectly consistent with that of the \(b_{1u}\), C=O band. The frequency softening, followed by a gradual loss of intensity, indicates that ionicity smoothly increases up to 0.86 GPa. Above this pressure, when the system has shifted to the ionic side (\(\rho > 0.5\)), this band cannot be detected anymore in our spectra. This behavior is a consequence of the fact that in CA\(^-\) the description of this vibrational mode in terms of C=C stretching changes drastically, and its IR intensity falls down almost completely.\(^{24}\)

The above arguments validate our analysis of the 1500 - 1700 cm\(^{-1}\) spectral region and rule out the alternative interpretation proposed by Matsuzaki et al.\(^{22}\) based on the incorrect assignment of the B band in Fig. 1 to the \(b_{2u}\), C=C stretching band of the CA molecular units.

Finally we notice that the occurrence of the coexistence phase has been carefully checked by repeated pressure cycling on different TTF-CA samples. We can also rule out pressure inhomogeneity across the sample, since we have checked that Raman micro-spectroscopy, with a spatial resolution of about 5 µm, gives identical spectra throughout the whole sample. Moreover open circles in Fig. 2, representing experimental points taken on releasing pressure from 3.2 GPa, indicate that this phase is fully reversible and that hysteresis effects have not been detected.

### B. Structural instability: Dimerization

At room temperature and at ambient pressure TTF-CA crystallizes in the \(P2_1/n\) space group with two formula units per cell.\(^{25}\) The TTF and CA molecules alternate with uniform distance along the crystallographic a axis, each molecule residing on inversion symmetry center. The temperature induced NIT is accompanied by a dimerization instability, and at low temperature the space group is \(P_4\), with two dimerized stack per unit
It is well known that IR spectroscopy with light polarized parallel to the stack direction is a powerful method to study the dimerization instabilities in CT crystals. The loss of the inversion symmetry associated with the stack dimerization makes the Raman active totally-symmetric molecular vibrations also IR active. The totally-symmetric modes are coupled to CT electrons (e-mv coupling), and in IR they borrow huge intensity from the nearby electronic CT transition, with polarization parallel to the stacks. One can therefore discriminate between dimerized and uniform stack structure on the basis of the presence or absence of these characteristic IR bands (“vibronic bands”).

![Image](image_url)

**FIG. 3:** Polarized IR absorption spectra of TTF-CA as a function of pressure. Light polarized parallel to the stack direction (E || a). The spectral regions between 1360-1390 cm⁻¹ and 1430-1480 cm⁻¹ is not accessible due to absorption of the pressure medium. Inset: Normalized IR intensity of the CA a₃ ν₃ band.

In addition, it has been recently demonstrated that IR spectra parallel to the stack also yield useful information on pretransitional dynamics driving the dimerization instability. TTF-CA spectra in the neutral, uniform stack phase are indeed characterized by the presence of two-phonon excitations (IR “side-bands”), whose temperature evolution probes the energy of the soft mode involved in the stack distortion.

To investigate these structural and pretransitional phenomena of pressure induced NIT of TTF-CA, we have collected IR spectra polarized parallel to the stack axis as a function of pressure (Fig. 3). Three strong bands, marked by a triangle, square and circle in the figure, clearly develop above ~ 0.6 GPa. These vibronic bands are assigned to the most strongly e-mv coupled totally-symmetric modes, namely the CA a₃ ν₃ around 980 cm⁻¹, and the TTF a₃ ν₂ and ν₃ modes around 1350 and 1540 cm⁻¹, respectively. Their presence reflects the fact that dimerization is taking place on increasing pressure.

In the inset of Fig. 3 we report the pressure dependence of the normalized IR intensity of the CA a₃ ν₃ mode. This mode starts to appear as a broad weak band above 0.6 GPa and rapidly gain intensity reaching its maximum value around 1.0 GPa. A slight intensity decrease follows on increasing pressure further. The behavior of the other vibronic bands is qualitatively similar to this one, although it is not possible to carefully follow their intensity evolution, because the TTF a₃ ν₂ band is partially covered by absorption of the pressure transmitting medium, while the a₃ ν₂ band at 1540 cm⁻¹ occurs in a region overlapped by other fundamental vibrational bands.

The comparison between the inset of Fig. 3 with Fig. 2a seems to indicate that the dimerization and valence instability are not correlated in the pressure induced NIT of TTF-CA. The onset of dimerization appears to be around 0.6 GPa, reaching saturation at 1.0 GPa, whereas the double ionicity region starts at 0.86 and extends to about 1.24 GPa. However, in addition to the IR intensity of the CA a₃ ν₃ mode, one has to consider its bandshape, and make a proper comparison with the corresponding Raman band. To such aim, we report in Fig. 3 the pressure evolution of an enlarged portion of the IR spectrum polarized parallel to the stack, together with Raman spectra collected at the same pressures.

We analyze Fig. 3 starting from low pressures. Below 0.68 GPa we can easily identify the so-called side-bands, namely IR bands occurring above and below the a₃ ν₃ Raman band. The side-bands are clearly due to sum and difference two-phonon excitations between the Raman active molecular vibration and a low frequency lattice mode also coupled with the CT electrons. In the temperature induced transition of TTF-CA, the side-bands provide useful information on the soft mode which drives the dimerization instability, namely, the Peierls mode. At ambient conditions the side-bands are separated by about 70 cm⁻¹ from the central Raman band. At 0.39 GPa, the distance is about 50 cm⁻¹, approximately as in the 150 K spectrum at ambient pressure. In our experiments IR side bands can be clearly identified up to about 0.52 GPa, and disappear, merging in an unique broad band on further increasing pressure.

Indeed, above ~ 0.6 we observe the development of a single vibronic IR band due to the CA a₃ ν₃. This band is initially very broad (almost 100 cm⁻¹), with the maximum occurring at a frequency lower than the cor-
As the pressure increases, the vibronic band sharpens and its frequency moves upwards, approaching the value of the Raman band. Around \( \rho \approx 0.9 \) GPa (but it is difficult to set a precise pressure, as we are comparing IR and Raman bandshapes) we start to see coincidence between the IR vibronic and the Raman band, perfect matching occurring at 1.0 GPa and above. The lack of IR and Raman frequency coincidence proves that the loss of the inversion symmetry is not complete along the stack, although some kind of local stack distortion has already taken place. This phenomenon is indicative of a new regime established between \( \rho \approx 0.6 \) GPa and \( \rho \approx 0.9 \) GPa and dominated by dynamic disorder. Notice that in this pressure range also the IR spectra polarized parallel to the stack direction (\( \mathbf{E} \parallel a \)). Red line: unpolarized Raman spectra.

The IR spectra polarized perpendicular to the stack show evident of strong dynamic disorder (Fig. 2c).

The IR spectra polarized perpendicular to the stack show that above \( \rho \approx 0.86 \) GPa we enter in a regime characterized by a double ionicity. This pressure is approximately the same in which we start to see coincidence between Raman and IR vibronic bands, both of which display a clear doublet structure. This regime is then characterized by comparable domains of different ionicity, and around 1.0 GPa we can affirm that the stacks are in any case fully dimerized, since the intensity of the vibronic bands saturates (inset of Fig. 3). As we have seen in the previous section, the double ionicity regime gradually evolves towards a single ionicity, which is finally reached above \( \rho \sim 1.24 \) GPa.

IV. DISCUSSION AND CONCLUSIONS

As already stated, TTF-CA \( T \)-induced NIT at ambient pressure is well characterized. It is a first order transition with a discontinuous \( \rho \) jump from \( \rho \sim 0.3 \) to just over 0.5, and a simultaneous dimerization of the stacks. The dimerization is anticipated by a critical softening of an effective Peierls mode which proves the displacive nature of the structural phase transition. On the other hand, the evolution of TTF-CA \( \rho \)-induced NIT is more complex, actually more than it has been thought so far.

The \( \rho \)-induced NIT is less discontinuous than the \( T \)-induced one, but is still first order since a weak discontinuity in the \( \rho(p) \) curve is observed between 0.86 and 0.9 GPa (Fig. 2b). Actually, if we follow the pressure evolution of the ionicity \( \rho \), three different regimes are identified. A neutral phase \( \rho < 0.5 \) at low pressure, a coexistence phase between 0.86 and 1.24 GPa, characterized by species of two different ionicities, and an ionic phase \( \rho \approx 0.7 \) at high pressures.

In the neutral phase the ionicity grows continuously with pressure, and reaches \( \rho = 0.47 \) at 0.86 GPa, the transition pressure. However, strong pretransitional phenomena related to both the valence and the structural instability start already above \( \rho \sim 0.6 \) GPa, when the ionicity is about 0.3. First, the bandwidth of the modes most sensitive to \( \rho \) shows a sharp increase with \( p \), starting above 0.6 GPa and reaching the maximum at the critical pressure \( p_c = 0.86 \) GPa (Fig. 2b). Second, approximately in the same pressure interval, the IR spectra polarized parallel to the stack are characterized by vibronic bands, corresponding to the activation in IR of intramolecular totally-symmetric modes. The activation, with appreciable intensity due to the coupling to the CT electrons, is the signature of a dimerization distortion. However, completely dimerized stacks would lead to IR-Raman frequency coincidence, due to the loss of the inversion symmetry along the stacks. IR-Raman frequency coincidence is not observed in the pressure interval we are considering (Figs. 3 and 4). This finding can be rationalized in terms of localized distortions, most likely fluctuating in time and space, on the average preserving the inversion symmetry. In other words, the \( \rho \)-induced phase transition at room \( T \) is preceded by a precursor regime characterized by fluctuating dimerized domains with variable \( \rho \) in the predominantly neutral and regular stack phase.

The fluctuating behavior fades around \( p_c = 0.86 \) GPa, as evidenced by Fig. 2, and TTF-CA develops an intermediate phase which persists up to 1.24 GPa.
pressure range the $b_{1u}$ C=O band, which probes the ionicity, shows a well resolved doublet structure (Fig. 1), the IR intensity of the vibronic bands reaches the maximum value and frequency matching between IR and Raman bands is definitely established (Figs. 3 and 4). These experimental findings indicate that the intermediate phase is characterized from the structural point of view by the lack of inversion symmetry, and from the electronic point of view by the coexistence of species with different ionicity, $\rho(I_1) \sim 0.6$ and $\rho(I_2) \sim 0.7$. The intensity evolution of the C=O doublet shows that the $\rho(I_1)$ component gradually converts into the more ionic one, $\rho(I_2)$ (Fig. 2). We then argue that this phase is not a well defined, ordered phase with a spatially modulated ionicity parameter, but is properly described in terms of a static disordered phase where species with two different ionicity coexist.

On increasing pressure further, coexistence is smoothly suppressed and, above 1.24 GPa, TTF-CA is ionic ($\rho \sim 0.7$) and dimerized similarly to the low-$T$ ferroelectric phase. We do not detect discontinuities or significant spectral changes, besides the vanishing of the $\rho(I_1)$ species in favor of the more ionic $\rho(I_2)$. Accordingly, we suggest that the phase transformation from the intermediate to the final ionic phase occurs continuously through a disorder-order type mechanism.

![FIG. 5: TTF-CA phase diagram at $T = 293K$, variable $p$.](image)

Fig. 5 reports a sketch of the just described TTF-CA phase evolution on increasing $p$ at ambient temperature. Several hypotheses have been formulated about the nature of the intermediate regime between the neutral, regular and the ionic dimerized stack phase. Up to now, the most credited idea has been that of a “paraelectric” phase, dominated by fluctuating, disordered LRCT, which precede and induce the tridimensional ordering to the ferroelectric (ionic and dimerized) phase. Our results suggest that we have a precursor regime, with fluctuations (shaded area in Fig. 5), and a new phase, characterized by the simultaneous presence of two different ionicities, which precedes the ferroelectric phase.

We believe that thermally accessible low-lying excitations such as LRCT, are present in the precursor regime between $\sim 0.6$ and $\sim 0.86$ GPa. Other experimental data are in support of this idea. Single crystal reflectivity data show coexistence of neutral and ionic species between $\sim 0.3 - 0.4$ GPa and $\sim 0.9 - 1.0$ GPa. In the electronic spectra the boundaries of the precursor regime appear slightly wider than those reported in Fig. 5. On the other hand, such boundaries cannot be sharp, and electronic data are more sensitive than vibrational ones. Dielectric response as a function of pressure shows anomalies in the relaxation frequency, starting at about 0.5 GPa (the data extend only to 0.7 GPa). Furthermore, the dc conductivity increases exponentially with $p$, the maximum value being reached at about 0.87 GPa, the critical pressure for the insurgence of the $I_1 + I_2$ phase. All these data have been explained in terms of the presence of LRCT, and our data in the precursor regime can be interpreted in the same way.

At this point, it is interesting to compare the precursor regime of the $p$-induced NIT with that of the $T$-induced NIT. LRCT have been invoked in both cases, but actually the experimental results are different, and can be interpreted in a different way. For instance, by lowering the temperature the dielectric constant shows a dramatic increase as $T_c = 81$ K is approached, whereas the $p$ variation is less remarkable, and evidenced by looking at the relaxation frequency change. The $T$-dependence of the dielectric anomaly can be quantitatively explained as due to the charge oscillations induced by the Peierls soft mode and evidence of the soft mode has been achieved by looking at the IR side-bands formerly considered as experimental proofs of LRCT. Finally, if the conductivity increase in the $p$-induced NIT is due to current carrying LRCT their presence and role is only marginal in driving the $T$-induced NIT, as the conductivity shows an increase only within a few degrees before $T_c$. Recent model calculations have indeed shown that LRCT are thermally accessible at ambient temperature, whereas their concentration is very small at $T_c$. Metastable domains are then important in TTF-CA $p$-induced NIT, but not in the $T$-induced one.

According to the above description, LRCT characterize the precursor regime of TTF-CA $p$-induced NIT. However, they do not anticipate and build the ionic, ferroelectric phase, but a double ionicity phase, $I_1 + I_2$, whose nature we shall now address. First of all, it is not the paraelectric phase described in Ref. since domains of different ionicity have comparable concentrations, and well defined ionicity (Figs. 1 and 2a). It is therefore difficult to imagine that the phase between 0.86 and 1.24 GPa is a dynamic phase, characterized by mobile nanoscopic domains of different nature. Also, a mixed phase containing both $N$ and $I$ stacks has been proposed several times, both from the standpoint of theory and of experiment. However, our data strongly suggest that the two species with different ionicity are both on the ionic side, $\rho(I_1) \sim 0.6$ and $\rho(I_2) \sim 0.7$. We have several hints in this direction. We remind only that at 1.0 GPa the intensity of the vibronic bands saturates (inset of Fig. 3), indicating completely dimerized stacks, with ionicity values well above the conventional $\rho = 0.5$ borderline. Thus the intermediate phase is likely a statically disordered mixed phase, defined by randomly oriented polar domains of different ionicity, which gradually
polarize evolving towards the ordered ferroelectric phase above 1.24 GPa.

The characterization of the precursor regime and the found coexistence of two different ionic domains in the intermediate phase are the most novel results of this work. From this perspective, we may also envision a mechanism of TTF-CA $p$-induced NIT involving a competition between nucleation and a sort of solid state spinodal decomposition. In this picture the precursor regime is the nucleation regime, characterized by large amplitude local fluctuations (droplets). Rather than evolving in the new stable phase when the droplets size reaches a critical value, we may have the insurgence of small amplitude large scale fluctuations of the order parameter, so that the system is globally unstable, and immediately develops the mixed $I_1 + I_2$ phase, with strongly intermixed mesoscopic domains. Further application of pressure converts this phase into the ferroelectric phase with a single ionicity. However, additional measurements, and in particular high resolution structural analysis, are needed before we can give credit to the just sketched appealing but highly speculative scenario.

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1. S. Horiuchi, T. Hasegawa, Y. Tokura, J. Phys. Soc. Jap. 75 051016 (2006).
2. A. Girlando, A. Painelli, S.A. Bewick, Z.G. Soos, Synth. Metals 141 129 (2004).
3. J.B. Torrance, J.E. Vazquez, J.J. Mayerle, V.I. Lee, Phys. Rev. Lett. 46 253 (1981).
4. J.B. Torrance, A. Girlando, J.J. Mayerle, J. I. Crowley, V.I. Lee, P. Batail, S. J. LaPlaca, Phys. Rev. Lett. 47 1747 (1981).
5. N. Nagaosa, J. Phys. Soc. Japan, 55, 3488 (1986).
6. M.H. Lemée-Cailleau, M. Le Cointe, H. Cailleau, T. Luty, F. Moussa, J. Roos, D. Brinkmann, B. Toudic, C. Ayache, N. Karl, Phys. Rev. Lett., 79, 1690 (1997). An extension of the $p, T$ phase diagram to include room temperature data is given in: E. Collet, M. Buron-Le Cointe, M. H. Lemée-Cailleau, H. Cailleau, and F. Moussa, www-lib.cea.fr/activ99-00/pp18-49.pdf.
7. T. Luty, H. Cailleau, S. Koshihara, E. Collet, M. Takesada, M.H. Lemée-Cailleau, M. Buron-Le Cointe, N. Nagaosa, Y. Tokura, E. Zienkiewicz, B. Ouladdiaf, Europhys. Lett., 59, 619 (2002).
8. L. Del Freo, A. Painelli, and Z. G. Soos, Phys. Rev. Lett. 89 (2002) 027401/1–4.
9. Z.G. Soos, S.A. Bewick, A. Peri, and A. Painelli, J. Chem. Phys. 120 (2004) 6712.
10. M. Masino, A. Girlando, A. Brillante, R.G. Della Valle, E. Venuti, N. Drichko, M. Dressel, Chem. Phys. 325, 71 (2006).
11. M. Masino, A. Girlando, Z.G. Soos, Chem. Phys. Lett. 369, 428 (2003).
12. A. Girlando, C. Pecile, A. Brillante, K. Syassen, Solid State Comm. 57, 891 (1986).
13. Y. Tokura, H. Okamoto, T. Koda, T. Mitani, G. Saito, Solid State Comm. 57, 607 (1986).
14. R.M. Metzger, J.B. Torrance, J. Am. Chem. Soc. 107, 117 (1985), and J. B. Torrance, private communication.
15. Y. Kaneko, S. Tanuma, Y. Tokura, T. Koda, T. Mitani, G. Saito, Phys. Rev. B 35 8024 (1987).
16. H. Okamoto, T. Koda, Y. Tokura, T. Mitani, G. Saito, Phys. Rev. B 39 10693 (1989).
17. M. Hanfland, A. Brillante, A. Girlando, K. Syassen, Phys. Rev. B 38 1456 (1988).
18. K. Takaoa, Y. Kaneo, H. Okamoto, Y. Tokura, T. Koda, T. Mitani, G. Saito, Phys. Rev. B 36 3884 (1987).
19. T. Mitani, Y. Kaneo, S. Tanuma, Y. Tokura, T. Koda, G. Saito, Phys. Rev. B. 35, 427 (1987).
20. M. Masino, A. Girlando, A. Brillante, R. Della Valle, E. Venuti, Material Science-Poland 22, 333 (2004).
21. H. Matsuzaki, H. Takamatsu, H. Kishida and H. Okamoto; J. Phys. Soc. Jap. 74 2925 (2005).
22. G. J. Piermarini, S. Block, J. P. Barnett and R. A. Forman; J. Appl. Phys. 46 2774 (1975).
23. A. Girlando, F. Marzola, C.Pecile, J.B. Torrance, J. Chem. Phys. 79 1075 (1983).
24. P. Ranzieri, M. Masino, A. Girlando, in preparation.
25. M. Le Cointe, M.H. Lemée-Cailleau, H. Cailleau, B. Toudic, L. Toupet, G. Heger, F. Moussa, P. Schweiss, K. H. Kraft, N. Karl, Phys. Rev. B, 51, 3374 (1995).
26. E. Collet, M. H. Lemée-Cailleau, M. Buron-Le Cointe, H. Cailleau, S. Ravy, T. Luty, J. F. Bérrar, P. Czarnecki, N. Karl, Europhys. Lett., 57, 67 (2002).
27. H. Okamoto, T. Mitani, Y. Tokura, S. Koshihara, T. Komatsu, Y. Iwasa, T. Koda, and G. Saito, Phys. Rev. B 43, 8224 (1991).
28. Z. G. Soos and A. Painelli, private communication.
29. J. Hubbard and J. B. Torrance, Phys. Rev. Lett. 47, 1750 (1981).
30. The $p$ value marking the borderline between $N$ and $I$ stacks is ill defined, since NITs imply both valence and dimerization instability, and the borderline $p$ is different for regular and dimerized stacks. Cf. A. Girlando and A. Painelli, Phys. Rev. B 34, 2131 (1986).
31. P. M. Chaikin and T. C. Lubensky, Principles of condensed matter physics, Cambridge Univ. Press, Cambridge (U.K.), pp. 479-491.