

Anomalous Nature of Neutral-to-Ionic Phase Transition in Tetrathiafulvalene-ChloranilJ. B. Torrance, A. Girlando,^(a) J. J. Mayerle, J. I. Crowley, V. Y. Lee, and P. Batail^(b)
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(Received 23 June 1981)

A phase transition starting at 84 K and indicated by a marked color change of the sample has been found in the organic insulator tetrathiafulvalene-chloranil. Optical, infrared, and Raman measurements indicate that this is a reversible transition from a nominally neutral (N) solid to a nominally ionic (I) salt. Surprisingly, the N-I transition is not first order, but occurs over a broad temperature region (~30 K), in which there is a coexistence of N and I molecules.

PACS numbers: 64.70.Kb, 78.30.Jw, 72.80.Le, 61.50.Lt

In most organic charge-transfer solids, the donors and acceptors stack alternately on top of each other in a mixed stack. For this reason, the materials are not highly conducting. These materials tend^{1,2} to contain either neutral donor D^0 and acceptor A^0 molecules, or cations D^+ and A^- . The overlap between D and A hybridizes these states,^{3,4} so that these solids are only *nominally* neutral (N) or *nominally* ionic (I). In a recent systematic study⁵ of a large number of these materials, it was shown how they range from being near the neutral-ionic boundary to being far from it. For ten of the neutral compounds near this boundary, it was discovered⁵ that applying pressure above a certain threshold results in a distinct change in color of the samples. This reversible change was interpreted as a phase transition from a neutral to ionic solid, driven by the increase in the electrostatic Madelung energy at high pressure. This was the first observation of such a transition in any kind of material.

Since detailed measurements at these high pressures (5–50 kbar) are quite difficult, it was hoped that one of the neutral compounds closest to the neutral-ionic boundary might undergo the same transition at low temperature, presumably driven by the increase in Madelung energy caused by the thermal contraction. Indeed, we report here finding such a transition in tetrathiafulvalene-chloranil (TTF-chl) below ~84 K. At 300 K, this compound is neutral with mixed stacks,⁶ but becomes⁵ ionic at pressures above ~8 kbar, one of the lowest transition pressures. The discovery that this compound becomes ionic at low temperatures is particularly significant, since it opens up the feasibility of investigating the N-I phase transition with a wide variety of experiments that

could not be easily performed at high pressures. For example, we report here preliminary optical, infrared, Raman, and x-ray unit-cell measurements that provide further evidence that the observed transition is between neutral and ionic states. Furthermore, they demonstrate that the phase transition at 84 K is not first order, as would have been expected. Rather, the sample goes from neutral to ionic over the broad temperature range from ~84 to ~50 K, within which *both* neutral and ionic molecules coexist.

On cooling a sublimed film of TTF-chl, the phase transition appears as a distinct, reversible change in color from yellow to red seen near 77 K. The optical-absorption spectrum at 300 K for such a sublimed film and a powdered sample dispersed in KBr are compared in Fig. 1 with that of a film at ~11 K. The spectra are seen to be very similar for the film and powdered samples. The low-temperature spectrum is also very similar to that found⁵ at high pressure. The change in color observed is caused primarily by the appearance of a new, intense absorption band in the visible near 2.9 eV. For comparison, we have examined the spectra of the isolated molecules and ions in solution: TTF⁰, chl⁰, TTF⁺, and chl⁻. Both of the neutral molecules, having closed shells, absorb strongly only in the ultraviolet near 4.1 eV, while each of the molecular ions has intramolecular transitions in the visible associated with excitations of its unpaired electron: 2.85 and 2.7–2.9 eV for TTF⁺ and chl⁻, respectively. The energy of this ionic absorption compares favorably with the energy of 2.9 eV for the extra absorption peak appearing at low temperatures, and thus provides strong evidence for the assignment as a transition from neutral to

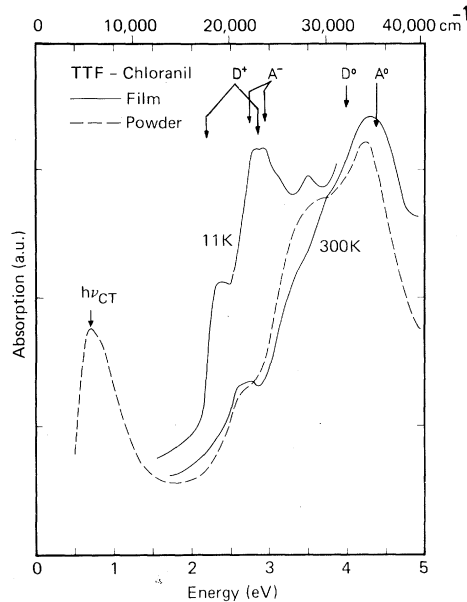


FIG. 1. Absorption of sublimed film above and below the N-I phase transition. Arrows represent absorption peaks of neutral and ionized molecules in solution.

ionic.

Two other probes often useful for studying the ground-state charge density of organic solids are infrared and Raman spectroscopy.⁷ Their utility is based upon the changes in strength of the intramolecular bonds caused by changes in the charge density. In fact, the vibrational spectra generally present quite appreciable frequency shifts of the intramolecular modes upon ionization; these are well known for TTF and chloranil since the vibrational spectra of both the neutral and fully ionized species have been extensively studied.⁸ Figure 2 shows how dramatically the Raman spectrum of TTF-chl changes upon the phase transition; a similar kind of variation is also observed in the infrared spectrum. As will be shown in detail elsewhere,⁹ the room-temperature spectra can be reasonably well interpreted as the superposition of the spectra of quasineutral (ca. 70%–80%) TTF and chl units, whereas the low-temperature ones indicate the presence of quasi-ionic (ca. 60%–70%) species. As just one example, the TTF $A_g \nu_2$ mode located at 1555 and 1505 cm^{-1} in neutral and fully ionic TTF,⁸ respectively, is found at 1540 at room temperature, but shifts to 1521 cm^{-1} at low temperature (Fig. 2). The vibrational data are then consistent with the optical data, providing strong evidence that the transition observed in TTF-chl is from neutral to ionic.

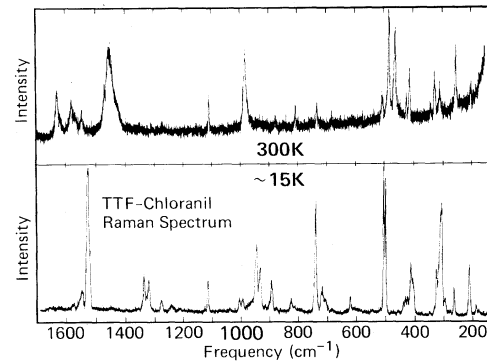


FIG. 2. Raman spectra of unoriented film on Cu substrate above and below neutral-ionic phase transition. Exciting line was 568.2 nm.

Both simple¹ and detailed^{3,4} theoretical studies of this transition suggest that it should be first order, i.e., that the material should change discontinuously from neutral to ionic.¹⁰ In order to examine how TTF-chl transforms from neutral to ionic, we have made x-ray powder diffraction measurements¹¹ of the unit-cell parameters through the phase transition. The temperature dependence of the stacking, or a -axis, lattice constant is shown in Fig. 3. The large thermal contraction between 300 and 84 K is typical of a stacked organic solid (and is presumably responsible for driving the phase transition in this case). The transition itself is seen by the additional contraction beginning near 84 K. Note that this additional contraction is not discontinuous, but increases gradually between 84 and ~ 50 K. It is not clear *a priori* what is physically varying continuously over ~ 30 K between neutral and ionic, nor is it clear what the order parameter of a N-I transition is.

In order to examine this behavior microscopi-

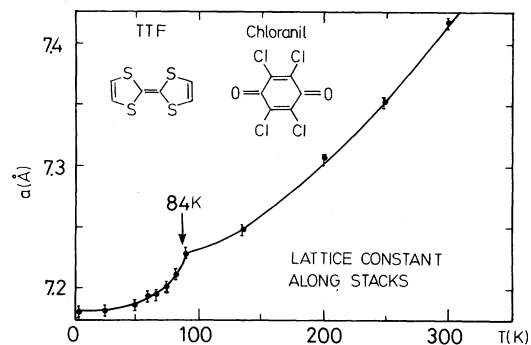


FIG. 3. $a(T)$ showing a continuous, broad transition starting below ~ 84 K.

cally, we have measured the intramolecular vibrational spectra through the transition. The infrared spectra in the $1500\text{--}1700\text{-cm}^{-1}$ range shown in Fig. 4 illustrate most clearly and dramatically the behavior also found⁹ for the other infrared and Raman modes. These absorption spectra were obtained on an oriented film, with the polarizer perpendicular to the stacking axis, so that only the intramolecular in-plane modes can be observed. The mode shown in Fig. 4 primarily involves⁹ a C=O stretching of the chloranil molecule. This mode is particularly sensitive because the extra electron on chl⁻ is largely localized in an antibonding orbital on the C=O moiety, decreasing⁸ its stretching frequency by 160 cm^{-1} , from 1685 cm^{-1} in chl⁰ to 1525 cm^{-1} in chl⁻. In Fig. 4, we identify⁹ the C=O stretching mode at 300 K as the band at 1658 cm^{-1} and at 15 K the band at 1586 cm^{-1} . The change in frequency indicates a change from neutral to ionic. The frequencies also emphasize the fact that these states are only quasineutral and quasi-ionic. This point is further indicated by the continuous frequency decrease of this mode (labeled *N* in Fig. 4) from 300 to 90 K, indicating that the solid is gradually becoming more ionic. These effects are presumably due to hybridization of the purely

neutral and ionic molecules caused by the appreciable molecular overlap along the stack. The presence of vibronic effects⁷ and other solid-state interactions makes it difficult to analyze these shifts quantitatively.

Insight into the nature of the intermediate state between ~ 90 and ~ 60 K is evident from the spectra at ~ 83 and ~ 73 K: These clearly show the superposition of neutral and ionic spectra (as also found in the other infrared and Raman modes). Thus, the vibrational spectra unambiguously indicate the *coexistence* of both neutral and ionic TTF and chloranil molecules over a rather broad (~ 30 K) temperature range. The variation of the optical spectrum (Fig. 1) through the intermediate temperature region is also consistent with the coexistence of neutral and ionic molecules.

It is important to consider over what time scale these neutral and ionic molecules would appear distinct and when they would appear averaged. Electrons are transferred back and forth between TTF and chl molecules at a frequency related to the transfer integral or bandwidth. *Along the stacks*, the overlap is large and this frequency is probably of the order of 2000 cm^{-1} . Since the 2000 cm^{-1} is much faster than the difference between the vibrational frequencies of a neutral and an ionic molecule, a *single*, averaged vibration is expected, whose frequency depends on the fraction of neutral and ionic molecules in the stack. Hence, in the neutral phase, we observe a single band, shifted somewhat from the neutral frequency toward the ionic. Similarly, below ~ 50 K, we see a single line in the ionic phase. Between ~ 90 and ~ 60 K, the observation of a superposition of *two* lines separated by as little as 2 cm^{-1} in some cases indicates that these two species must be on different stacks, since only then could the electronic overlap be less than 2 cm^{-1} . Thus, the data in Fig. 4 show the coexistence of stacks of neutral and stacks of ionic molecules over a ~ 30 K range in temperature. The data also suggest that the number of ionic stacks is possibly the relevant order parameter for the transition.

To summarize, the phase diagram for TTF-chl is schematically shown in Fig. 5. At room temperature, this material is neutral, but so close to the neutral-ionic boundary that a slight increase in the Madelung energy favors the ionic ground state. The increase can be achieved either by applying pressure or by the thermal contraction associated with lowering the temperature, as we have shown here. The transition between neutral and ionic is not first order and not simple, but

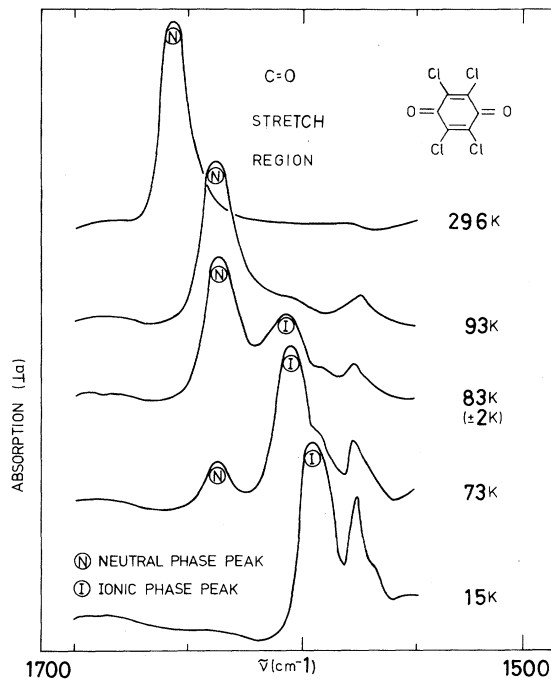


FIG. 4. Temperature variation (accuracy ± 2 K) of the polarized infrared absorption spectra of an oriented film.

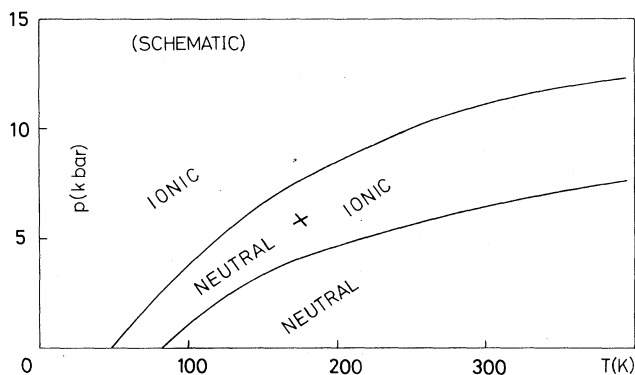


FIG. 5. Schematic phase diagram for TTF-chl.

appears to involve an intermediate region in which both neutral and ionic stacks coexist. A possible explanation for the existence of this anomalous intermediate region is offered in the following paper.¹²

Two of us (A.G. and P.B.) acknowledge receipt of an IBM Worldtrade Fellowship. We also thank M. Philpott (IBM, San Jose) and C. Pecile (Padova University) for the use of Raman and infrared spectrometers.

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Model of the Neutral-Ionic Phase Transformation

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(Received 23 June 1981)

A model is presented describing how an organic solid transforms between a neutral and an ionic ground state. Whereas for a one-dimensional stack this transition is expected to be first order, the Coulomb interactions between stacks can cause the phase transition to occur over a broad temperature range by stabilizing an *intermediate* region in between the neutral and ionic phases, in which both neutral and ionized species coexist, as observed in tetrathiafulvalene-chloranil.

PACS numbers: 64.70.Kb, 71.45.Nt, 72.80.Le, 61.50.Lt

The organic charge-transfer solid tetrathiafulvalene (TTF)-chloranil has mixed stacks, with the donor (TTF) and acceptor (chloranil) alternating along the *a* axis.¹ Between 50 and 84 K, this compound appears^{2,3} to undergo some sort of phase transformation, above which the TTF and chloranil molecules are present as nominally neutral species,^{1,2} but below which TTF⁺ and

chloranil⁻ ions appear. At 300 K a similar transformation⁴ appears under high pressure between ~6.5 and ~11 kbar and in other compounds at other pressures.⁴ These transitions have been identified^{2,4} as N-I⁵ phase transitions. Here we will focus on the low-temperature transition in TTF-chloranil where more data are available, but the results will be readily applicable to the