Anomalous dispersion of optical phonons at the neutral-ionic transition: Evidence from diffuse X-ray scattering

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Diffuse X-ray data for mixed stack organic charge-transfer crystals approaching the neutral-ionic phase transition can be quantitatively explained as due to the softening of the optical phonon branch. The interpretation is fully consistent with vibrational spectra, and underlines the importance of electron-phonon coupling in low-dimensional systems with delocalized electrons.

The physics of low-dimensional materials is governed by the complex interplay between electron-electron (e-e) and electron-phonon (e-ph) interactions. The resulting phenomenology is very rich and includes complex phase diagrams, competing phases, quantum phase transitions and multistability. Solitons and domain boundaries are intriguing low-energy excitations in 1-dimensional (1D) systems such as polyacetylene [1] or organic charge-transfer (CT) salts [2]. The neutral-ionic phase transition (NIT) observed in CT crystals with mixed stacks [3] offers unique opportunities for investigating this rich physics. NIT is an electronic quantum phase transition, driven by the volume compression on cooling or under pressure, in which a stack of largely neutral molecules with regular spacing \( \ldots D^\rho A^\rho D^\rho A^\rho \ldots \) switches to a dimerized stack of more ionic molecules, \( \ldots (D^\rho A^-)(D^\rho A^-) \ldots \) or \( \ldots (A^\rho D^\rho)^- (A^\rho D^\rho)^- \ldots \) \( \rho < 0.5 \). Dimerization is a structural or Peierls transition driven by e-p interactions. NIT with discontinuous changes in \( \rho \) and in the dimerization amplitude \( \delta \) are observed in some CT crystals, while others show continuous variations of \( \rho \) and \( \delta \) [2].

In addition to domain walls or topological solitons [1] that separate regions with opposite dimerization, CT crystals with mixed stacks have neutral-ionic domain walls (NIDWs) that separate neutral and ionic regions along the 1D stack. Nagaosa [2] introduced the concept of NIDW and the corresponding excitations or domains, called lattice-relaxed exciton strings, LR-CT. These concepts were subsequently used to discuss the anomalies observed at NITs including the appearance of unassigned bands in infrared (IR) spectra [4], orders-of-magnitude enhancements of dielectric constants [3, 6], and diffuse X-ray (DXR) signals [2, 8]. However, NIDWs were originally restricted [2] to the immediate vicinity of a discontinuous NIT, and the energy of domains is in most cases too large to allow for appreciable thermal population [5]. Here we demonstrate that soft modes and e-ph coupling provide alternative explanations of all anomalies observed at NIT, without the restriction to a discontinuous NIT and without invoking either NIDWs or LR-CTs.

The first observation of a soft mode associated with NIT was in the mid-IR spectra of tetrathiafulvalene-chloranil (TTF-CA) [10]. TTF-CA is the prototypical and best characterized CT salt, with a discontinuous NIT at \( T_c = 81 \text{K} \) from a regular neutral \( (\rho \sim 0.3) \) stack to a dimerized ionic \( (\rho \sim 0.6) \) stack. For \( T > T_c \) weak IR bands polarized along the stack axis appear close to the frequency of Raman-active \( A_g \) molecular modes. These bands, originally assigned to the NIDWs dynamics [3], are combinations of the \( A_g \) modes with the IR-active dimerization phonon. A careful analysis of IR and Raman spectra allowed for a reliable estimate of the frequency of the soft mode [10]. Similar results have been obtained recently for dimethyl-TTF-CA (DMTTF-CA) [11], in which almost complete softening is observed. The circles in Fig. 1 show the frequency of the soft mode in both crystals for \( T > T_c \).

The dielectric peak at NIT was assigned to NIDW fluctuations [3, 6], but its magnitude can be quantitatively modeled as due to the soft dimerization mode that acquires a huge IR intensity near the transition [12, 13]. DXR data [2, 8] have been interpreted in terms of long LR-CTs in DMTTF-CA and short ones in TTF-CA: so far they offer the only unchallenged evidence for NIDWs.

DXR scattering was widely used in the 80’s to study soft modes that drive structural transitions, including the Peierls transition in CT salts with a segregated stack [14]. The Peierls transition in mixed (DA) stacks is however different: the soft mode or incipient soft mode is an optical phonon instead of an acoustic phonon as in segregated stacks. The sharp Lorentzian-shaped DXR signal collected in one spatial direction implies a strong dispersion of the relevant phonons and is unusual for the optical branch of a molecular crystal. This was the basis for rejecting a soft mode interpretation in favor of LR-CTs.
But e-ph coupling is extremely effective in 1D and anomalous dispersion of optical phonons is well known in polyacetylene [15].

Here we demonstrate that DXR data can be quantitatively understood as due to the progressive softening of the zone-center optical phonons as the system is driven towards the NIT. A sharp anomaly develops in the optical phonon branch that, although occurring in non-metallic systems, is analogous to the Kohn anomaly in 1D metals, and shares the same origin, namely, e-ph coupling. Peierls transitions were similarly proposed for 1D metals and later generalized to transitions driven by e-ph coupling in insulators and spin chains.

The DXR intensity, $I$, is related to the frequency $\omega$ of the soft mode by a simple relation [14]:

$$I(q) \propto \frac{k_B T}{\omega^2(q)}$$

where $q$ is the wavevector. Reliable estimates of $\omega(0)$ were obtained from the analysis of combination bands in IR spectra of both TTF-CA and DMTTF-CA [10, 11]. Since DXR scattering is in arbitrary units, Eq. (1) yields the temperature dependence of $\omega(0)$ to within a scale factor. The diamonds in Fig. 1 are scaled $\omega(0)$ from DXR. The striking coincidence of DXR and IR estimates of $\omega(0)$ for $T > T_c$ in both salts provides strong motivation for a soft-mode analysis. But several issues must be addressed for such an interpretation, starting with the strong dispersion of the optical branch.

To confirm the soft-mode picture, we consider the dispersion of optical phonons in a 1D stack with equal spacing, harmonic force constant $K$ for nearest-neighbor lattice displacements, molecular masses for D and A, and linear e-ph coupling. For simplicity, we describe the electronic structure of the mixed stack using a spinless-fermion (SF) model, an uncorrelated model [4] that can readily be solved for long chains. The electronic Hamiltonian describes $N/2$ spinless fermions on $N$ molecular sites with periodic boundary conditions, as follows:

$$H_{SF} = \Gamma \sum_p (-1)^p \hat{n}_p - \sum_p t_p \hat{b}_p$$

where $p$ runs on the sites, $\hat{n}_p$ counts the fermions on $p$ site, $t_p$ is a transfer integral, and $\hat{b}_p = (a_p^\dagger a_p + H.c.)$ is the bond-order operator. In the SF model, a single fermion moves from an odd (D) to an even (A) site to describe electron transfer between DA and D$^+$A$. $2\Gamma$ then represents the energy required to ionize a DA pair and implicitly includes all contributions from e-e interactions and from the coupling of electrons with molecular vibrations [9]. The hopping integrals are modulated by lattice phonons: $t_p = t_0 + \alpha(x_p - x_{p+1})$ where $x_p$ is the displacement of the $p$ site, and $t_0$ will be used as the energy unit. The e-ph coupling constant $\alpha$ enters the definition of the vibrational relaxation energy: $\epsilon_d = \alpha^2/K$. Aside from a spin factor, the model was discussed by Rice and Mele [16], and at $\Gamma = 0$ it reduces to the SSH model [1].

The vibrational problem in the absence of e-ph coupling ($\epsilon_d = 0$) describes a 1D harmonic chain with two masses. It has a well known solution, and the red continuous line in Fig. 2 shows the dispersion curve for the optical branch, $\omega_0(q)$, calculated for the molecular masses of DMTTF-CA and with $K$ fixed as to get $\omega_0(0) = 110$ cm$^{-1}$. In the presence of e-ph coupling, $\epsilon_d > 0$, new harmonic force constants add to $K$, corresponding to the second derivatives of the ground state (GS) electronic energy $E$ vs the site displacements:

$$\left(\frac{\partial^2 E}{\partial x_p \partial x_{p+r}}\right)_{eq} = \alpha^2 (\Pi_{r-1} + \Pi_{r+1} - 2\Pi_r)$$

where $\Pi_r = -\left(\frac{\partial^2 E}{\partial t_p \partial t_{p+r}}\right)_{eq}$, the bond-bond polarizabilities, are electronic quantities. In the SF model:

$$\Pi_r = 2 \sum_{k,l} \frac{(GS|\hat{b}_p|kl)(kl|\hat{b}_{p+r}|GS)}{\epsilon_l - \epsilon_k}$$

where $|kl\rangle$ is the excited state of $H_{SF}$ with a fermion promoted from the $k$-th filled orbital to the $l$-th empty orbital, and $\epsilon_k$ is the $k$-orbital energy. Much as in polyacetylene [17], the electronic delocalization leads to long-range bond-bond polarizabilities, and hence to long-
range force constants that are responsible for an anomalous dispersion of the optical phonon branch. The acoustic branch is only marginally affected by e-ph coupling.

In momentum space, the squared vibrational frequencies $\omega(q)^2$ are obtained, as usual, by diagonalizing the $2 \times 2$ force constant matrices, whose elements contain sums over $\Pi_r$ as well as $K$ and the molecular masses. The largest softening occurs at $q = 0$, where a simple expression holds for the optical branch frequency $[18]$: 

$$\omega(0) = \omega_0(0) \sqrt{1 - \epsilon_d \chi(\Gamma)}$$

where $\chi = -\frac{\partial^2 E(\Gamma, \delta)}{\partial \delta^2} |_{\delta = 0}$, the curvature of the electronic GS energy along the dimerization coordinate, $\delta$, only depends on $\Gamma$. The divergence of $\chi$ at $\Gamma = 0$ marks the unconditional Peierls instability of a half-filled 1D metal. For finite $\epsilon_d$ CT stacks are stable against dimerization for $\Gamma > \Gamma_P$, where $\Gamma_P$ is defined by $\epsilon_d \chi(\Gamma_P) = 1$. Peierls transitions have been extensively studied and there are analytical expressions for $\chi(\Gamma)$ for uncorrelated models $[19]$ and numerical results for correlated models $[18, 20]$. 

Figure 2 shows the evolution of $\omega(q)$ as function of $\Gamma > \Gamma_P$. For the chosen parameters, the Peierls transition occurs at $\Gamma_P$ = 0.05, where the softening is complete, $\omega(0) = 0$, and a giant anomaly develops in the dispersion of optical phonons. The softening of the optical branch follows directly from linear e-ph coupling. An important new result in Fig. 2 is the explicit expression for the phonon dispersion as the dimerization transition is approached. With $\omega(q)$ in hand, we can model the DXR profile $I(q)$ using Eq. 5.

DXR profiles $I(q)$ are measured as a function of $T$, while the phonons in the SF model are computed as a function of $\Gamma$. The profile in either case is characterized by the peak height $I(0)$ and by the half-width at half-maximum, $q_{1/2}$. The calculated $I(q)$ in Fig. 3 are based on Eq. 1 with $\omega(0)$ taken from vibrational data, and the best-fit parameters, $\epsilon_d$ and $\omega_0(0)$, in the caption. Insets $b$ and $c$ specify $\Gamma(T)$ for DMTTF-CA and TTF-CA, respectively, and an almost linear relation is extracted in each case. The measured and calculated values of $q_{1/2}$ are seen in insets $c$ and $f$ to be in excellent agreement, especially close to the transition. DXR profiles in mixed-stack CT salts close to the NIT can be quantitatively explained by the softening of the dimerization mode and the related anomaly in the optical phonon branch.

The sharp DXR peaks observed in DMTTF-CA were previously assigned to the presence of long LR-CT excitations $[7]$, whereas the broader signals in TTF-CA were ascribed to shorter domains $[8]$. Here the difference between the two systems is quite naturally related to their different transitions. DMTTF-CA undergoes a continuous (or almost continuous) dimerization transition $[11]$: $\rho(T)$ is continuous, the phonon frequency $\omega(0)$ softens to zero (or almost so), and the dip in the phonon dispersion fully develops leading to sharp DXR peaks. On the other hand, only incipient soft-mode behavior is observed in TTF-CA, whose discontinuous NIT at 81 K interrupts the softening $[3]$. As a result, the dispersion anomaly does not fully develop and comparatively broad DXR peaks are observed.

The non-interacting model, $H_{SF}$ in Eq. 2, can be solved for very long chains, as needed to get enough resolution in the dispersion curves. To show that the anomalous dispersion in the optical phonon branch survives correlations, we now turn attention to the standard correlated model for NIT, the modified Hubbard (MH) model $[4]$ with linear e-ph coupling. MH describes $N$ electrons on $N$ sites, and, as in SF, $2\Gamma$ is the energy required to ionize a DA pair. Correlations are taken into account by a restricted basis that excludes $D^{2+}$ and $A^{2-}$ sites. Intersite e-e interactions $V$ can be introduced in addition to linear e-ph coupling.

MH bond-bond polarizabilities $\Pi_r$ are calculated as numerical derivatives of the exact GS energy of finite chains (up to 20 sites) with periodic boundary conditions. We compare results for SF and MH chains with the same $\rho$,
and in the left panels in Fig. 4 we show the $r$-dependence of the $\Pi_r$ for two systems with $\rho = 0.22$ and 0.46, far and close to NIT, respectively. For both systems, apart from a scale factor, the $\Pi_r$ calculated in SF and MH models have similar behavior and oscillate between positive and negative values, much as found in polyacetylene [17]. The right panel of Fig. 4 compares the MH and SF phonon dispersion curves calculated for the same $\rho$ values. For the SF case we set the parameters relevant for DMTTF-CA. In the MH model, to account for the stronger e-ph coupling in correlated systems, we rescale $\epsilon_d$ to obtain the same $\omega(0)$ as in SF.

Far from NIT, at $\rho = 0.22$, the effect of e-ph coupling is mild; $\Pi_r$ decays rapidly with $r$, well within distances achievable in a periodic 20 site chain. As a result, the discrete MH points for $\omega(q)$ fall exactly on top of the SF curve in Fig. 4, right panel. On the contrary, near the transition ($\rho = 0.46$), $\Pi_r$ acquires a long-range tail that cannot be appreciated in a 20-site system. Nevertheless, the MH points of the dispersion curves approximately fall on the SF curve. We conclude that the sharp anomaly in the optical phonon branch is a characteristic feature of NIT, and that its basic physics is well captured by models without e-e correlation.

In conclusion, we ascribe DXR scattering in DMTTF-CA and TTF-CA crystals on approaching the NIT to the evolution of a Kohn-like anomaly in the optical phonon branch, related to the softening of the dimerization phonon. The anomaly is due to amplified e-ph coupling near an electronic transition. Our interpretation, quantitatively consistent with vibrational frequencies as extracted from mid-IR data, is supported by the calculation of phonon dispersion curves in SF and MH models for electronic systems with linear (Peierls) e-ph coupling. Linear e-ph coupling has enormous effects in systems with delocalized electrons in 1D, as best demonstrated by polyacetylene [19]. In CT salts the amount of delocalization increases when moving towards NIT from the N side, giving rise to several anomalous features that have often been interpreted as evidences for exotic excitations like NIDW or LR-CT. Such excitations are, however, only expected in the immediate vicinity of a first-order transition [20]. The soft mode interpretation of anomalous mid-IR bands in CT salts appearing on approaching NIT, as well as the huge peak in the dielectric constant measured at NIT has already been discussed [10, 11, 12, 13]. Here we showed that DXR scattering is another manifestation of e-ph coupling in 1D.

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