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Report:

The neutral-ionic phase transition (NIT), observed in quasi-1D molecular charge-transfer (CT) crystals, is a strongly coupled *electronic* and *structural* phase transition in which stacks of uniformly spaced neutral molecules switch to dimerized stacks of ionic molecules. The dimerization is driven by the Peierls mechanism: The e-ph coupling which is extremely effective in 1D and enhanced in proximity of an electronic instability is expected to drive the structural phase transition, and the system should develop a soft *optical* phonon mode at $q=0$ with a large dispersion law, analogous to the Kohn anomaly in 1D metals [1].

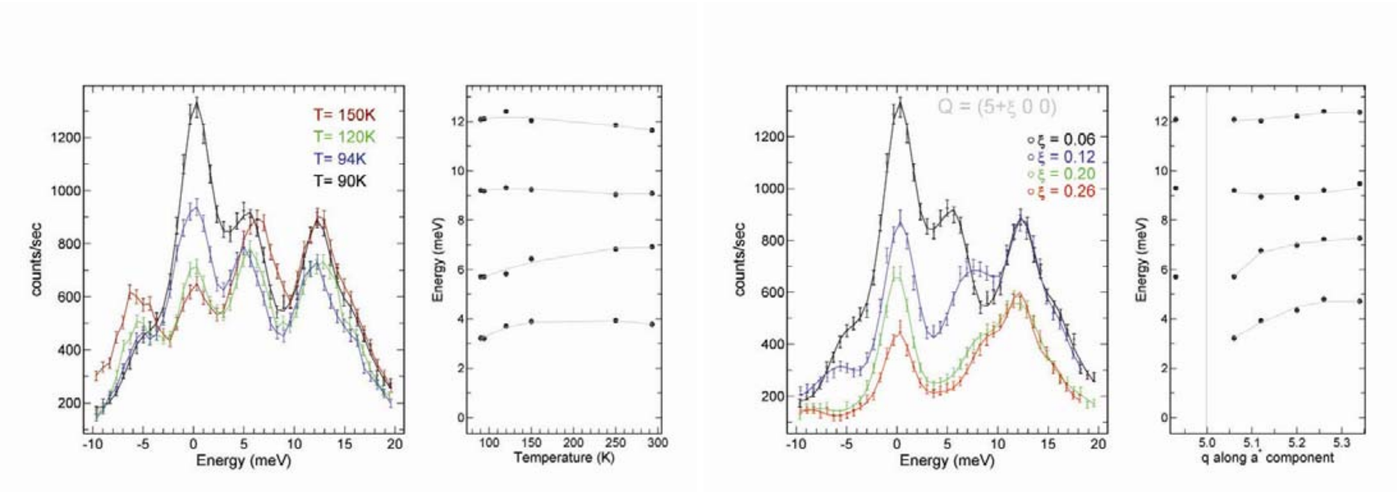
We studied NIT in Tetrathiafulvalene-Chloranil (TTF-CA), the prototypical and best characterized CT system with a discontinuous phase transition at T=81K. We have investigated the temperature dependent phonon frequencies around $q=0$ by inelastic x-ray scattering (IXS) close to (610), (600) and (500) Bragg spot reflections, in order to get an almost complete picture of the low frequency phonon dynamics with a^*-polarization.

The (610) reflection is absent in the neutral phase, therefore its intensity in the ionic one should dominantly come from the soft mode contribution, (600) was chosen as a reference for the acoustic phonons contribution and (500), always absent due to systematic absence, was also followed because of its large q component parallel to the soft mode polarization.

Unfortunately, experimental data collected close to (610) Bragg spot (not shown in the present report) do not evidence any softening on cooling. However we should keep in mind here that we were limited, due to a failure in the cryogenic environment, only in the range [300K-90K] of the neutral phase whereas the most dramatic effects should occur below 90K [2].

Experimental data close to (500) reflection are reported in Fig.1. Here, A_u and B_g symmetry modes with large projection along the stack axis (a^*-direction) can be observed, while A_g, B_u (the symmetry of the order parameter [3]) and acoustic modes are silent.

A weak softening on lowering temperature, marked only for the lowest frequency phonons, can be observed (Fig.1 left panel). The fitting parameters of the two lowest frequency modes are strongly correlated and not perfectly reproducible, however an overall red-shift of the spectral weight is clear. Moreover, quite recently low frequency IR spectra have shown that actually the phonons involved are more than one, with a complex mode-mixing as a function of temperature [2].



<u>Fig.1:</u> (Left) *Energy scans at (5.06 0 0) versus temperature and plot of the the energy of the modes as extracted from data fitting (the grey-line is a guide for the eye).* ***(Right)*** *Energy scans along the a*-direction close to (500) and relative dispersion curves at T=90K*

Slightly more evident is the large longitudinal dispersion along the a*-direction present at low temperature (Fig.1 right panels), which can be an indication of the strong e-ph coupling and of the Kohn anomaly. Here, the presence of acoustic phonons can be ruled out due to symmetry arguments, also supported by the comparison of fitted data extracted from scans close to the (600) reflection.

These anomalous features (high dispersion around the Brillouin zone center and the incipient softening) for the lowest energy A_u symmetry modes can be rationalize if we realize that these phonons are related to the effective B_u soft mode in a situation where the two chains of the unit cell are uncorrelated, and the system can be treated as strictly one-dimensional which actually occurs for high temperatures regime down to T_c+10K = 90K [4].

Results from the data analysis therefore seem to indicate the presence of an incipient softening and anomalous dispersion for some coupled phonons on approaching the transition temperature, which can be a weak manifestation of the effective soft mode behaviour. Unfortunately, we were not in the condition to safely confirm the Kohn anomaly and the soft mode behavior because we were not positioned in the correct Bragg spot to detect the B_u symmetry distortion of the order parameter, and because we could not reach the transition temperature.

<u>References</u>

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[3] M. Buron-Le Cointe et al., Phys.Rev.B **68**, 064103 (2003); Phys.Rev.B **51**, 3374 (1995)
[4] M. Buron-Le Cointe et al., Phys. Rev. Lett. **96**, 205503 (2006)