ESRF	**Experiment title:** **Condensation and ordering of charge-transfer excitations at the neutral-to-ionic transition**	**Experiment number:** HS-941
Beamline: BM2/CRG	**Date of experiment:** from: 15 09 1999 to: 20 09 1999	**Date of report:** 29 09 1999
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Report:

The neutral-to-ionic transition is an unusual type of phase transition since it is associated with a cooperative electron tranfer at solid state. It results from the condensation and the ordering (crystallization) of charge-transfer (CT) excitations [1]. It has been observed in several organic CT complexes with a mixed-stack packing[2], where electron donor (D) and acceptor (A) molecules alternate (semiconductor compounds). This phase transition is characterized by both a cooperative change of the electronic state of molecules (ionicity), with a large increase of the degree of CT between the neutral (N) and the ionic (I) states, and a dimerization process which takes place in the I state, i.e. the creation of (D^+A^-) pairs along the stack (symmetry breaking) :

N phase ... $D^\circ\ A^\circ\ D^\circ\ A^\circ\ D^\circ\ A^\circ$ ... I phase ...$(D^+A^-)(D^+A^-)(D^+A^-)$...

Electronic and structural aspects are strongly coupled : changes of the electronic state only exist with structural distorsions, affecting both intra- and inter-molecular geometries.

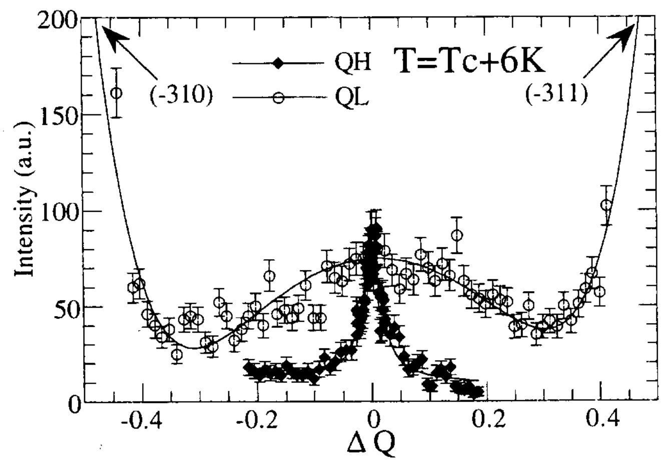
The prototype compound, tetrathiafulvalene-chloranil (TTF-CA), possesses a singular solid-liquid-gas like (P,T) phase diagram [1] associated with the condensation of CT excitations which can next crystallize with a ferroelectric arrangement between the dimerized ionic chains [3]. Thermal activation of lattice-relaxed CT excitations plays a central role in the phase transition process:

....$D^\circ A^\circ D^\circ A^\circ (D^+A^-)(D^+A^-)(D^+A^-) D^\circ A^\circ D^\circ A^\circ$...

Such non-linear excitations, specific of quasi-one-dimensional systems with strong electron-phonon coupling, can also be discussed in terms of self-trapped CT excitons which self-multiply. Intriguing physical properties, such as photo-induced phase transformations where one photon can transform a few hundred of DA pairs [4], are governed by these CT excitons

Recently, we have discovered a new type of N-I ordering in a derivative of TTF-CA : 2,6-dimethylTTF-CA. This ordering corresponds to the establishment of a long range order between N and I planes which regularly alternate in the low temperature phase. It manifests itself by the appearance of superstructure reflections at $c^*/2$. This phenomenon, due to Coulomb frustration effects, had been predicted a long time ago by theoreticians [5] but never observed until now. This observation has been realized on a single crystal set on a high-resolution 4-circle diffractometer with a conventional X-ray source, but no diffuse scattering associated with lattice relaxed CT excitations had been observed at that time. Using D2AM/CRG beamline (May 98) and after the set-up of the best experimental conditions we were able to show that this transition is second order (for the first time for a temperature-induced N-I transition) and to observe critical diffuse scattering just above Tc (see report CRG 02-02-96), i.e. the first direct experimental evidence of the lattice-relaxed CT excitations.

In this present experiment, we have observed the temperature behaviour of this critical diffuse scattering around the superstructure reflection (-3 1 0.5) in the three directions of the reciprocal space. Below Tc, the shape of the reflection corresponds to long range order, while above Tc it becomes broader and broader in $\mathbf{b}^*$ and $\mathbf{c}^*$ directions but it remains very thin along $\mathbf{a}^*$, forming only diffuse ($\mathbf{b}^*\mathbf{c}^*$) planes (Figure). It is associated with the existence of quasi uncorrelated unidimensional condensed ionic exciton-strings. Technical problems in the optic hutch prevent us from studying the whole shape of the diffuse scattering.



Q scans around (-3 1 0.5) showing diffuse (b*,c*) planes at Tc+6 K (ESRF, D2AM, λ=1.04 Å). The diffuse scattering along b*, similar to the one observed along c*, is not shown for clarity. Lines are guides for the eyes.

References

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