THREE-DIMENSIONAL ORDERING IN TTF-TCNQ

A. Bjeliš and S. Barišić
Institute of Physics of the University,Zagreb

The three-dimensional ordering of Peierls type in the chain system TTF-TCNQ below 54K is characterized by the temperature dependent star of wave vectors[1]: The wave-number in the chain direction (b) has the same incommensurate value (q_b=0.295b*) at all temperatures. The transverse wavenumber in the direction of alternating chains (a) is equal to a*/2 for 54K>T>49K, decreases continuously for 49K>T>38K, and finally jumps to a commensurate value a*/4 at 38K. The continuous variation of q_a is explained within the model of the bilinear interchain coupling in the two-chain system[2,3]. The lock-in of q_a at a*/4 below 38K is interpreted in terms of the activation of a fourth-order Umklapp term in the Ginzburg-Landau expansion[4]. This necessarily leads to an amplitude modulated ordering. On the other hand, in the interval 49K>T>38K the phase modulated ordering has been suggested[4] using a phenomenological argument for the 49K transition. Here we use a simple model of anharmonic coupling for TCNQ chains to demonstrate the physical criterion which makes such a behavior possible.

The terms in GL expansion describing respectively a purely local, intrachain and interchain coupling per one molecule are given by

$$\frac{1}{N}\sum_{nj}\{B_0u_{nj}^4 + \frac{1}{8}B_1\sum_{\delta}(u_{nj+\delta}-u_{nj})^4 + \frac{1}{8}B_2\sum_{\delta}(u_{n+\delta j}-u_{nj})^4\}. \quad (1)$$

Here n,j,δ go over the chains, the sites in a chain, and the nearest neighbors respectively. u_{nj} is the TCNQ Peierls deformation, which in the mean-field approximation is given by the linear combination of four waves ($\pm q_a,\pm q_b$) defining the star. Expressed in terms of complex amplitudes $\psi(q_a,q_b)=\psi^*(-q_a,-q_b)=\rho_1\exp(i\theta_1)$, $\psi(q_a,-q_b)=\psi^*(-q_a,q_b)=\rho_2\exp(i\theta_2)$, eq.1 reduces to

$$b_1(\rho_1^4+\rho_2^4) + b_2'\rho_1^2\,\rho_2^2 \,, \tag{2}$$

where

$$b_1 = B_\parallel + B_\perp \,, \tag{3}$$

$$b_2' = 4b_1 + (B_\parallel - B_\perp)\,\delta_{q_a,a^*/4}\cos 2(\theta_1+\theta_2) \tag{4}$$

and $B_\perp \equiv B_2(1-\cos q_a a)^2$. Both the local and the intrachain coupling enter uniquely as an effective "along the chain" coupling, $B_\parallel \equiv B_0 + B_1(1-\cos q_b b)^2$, into the new coefficients b_1, b_2'.

The system comprising the fourth-order invariants (2) is stable provided $b_1>0$, $|b_2'|/2b_1>-1$. With these conditions satisfied, the ordering is phase modulated ($\rho_1\neq 0$, $\rho_2=0$ or vice versa) if $b_2'/2b_1>1$, and amplitude modulated ($\rho_1=\rho_2\neq 0$) if $|b_2'|/2b_1<1$ [4].

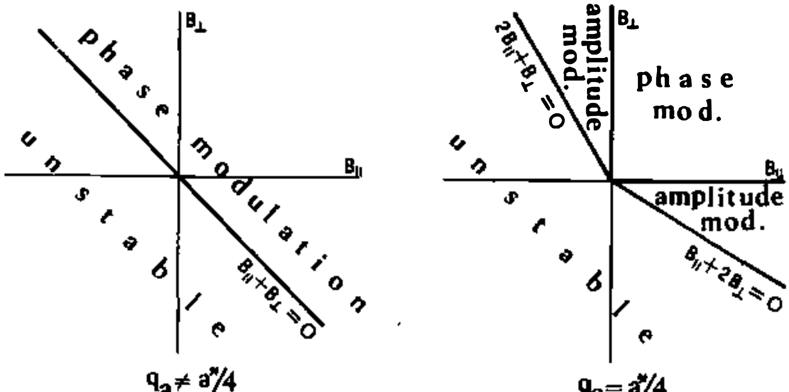

Fig.1

In Fig.1 these conditions are sketched in terms of coefficients $B_\parallel$, $B_\perp$. It is seen that for $q_a\neq a^*/4$ only the phase modulation is stable (for $B_\parallel+B_\perp>0$), in agreement with our previous conclusion [4]. With the Umklapp term activated ($q_a=a^*/4$), the amplitude modulation occurs when $B_\perp<0$, $B_\parallel+2B_\perp>0$ or when $B_\parallel<0$, $2B_\parallel+B_\perp>0$. The commensurate lock-in is thus feasible provided either the "along the chain" or the interchain anharmonic coupling is attractive. If both are repulsive the ordering is phase modulated and the second term in the expression (2) containing the Umklapp contribution remains equal to zero.

As regards the chain system TTF-TCNQ, it is reasonable to expect that the interchain anharmonic coupling is much weaker than the coupling along the chain, i.e. $|B_{\perp}| << |B_{\parallel}|$. Hence the model (1) suggests that the commensurate lock-in at 38K as described in Ref.(4), accounts for the anharmonic coupling which is repulsive along chains and attractive in the transverse a-direction.

References

1) R.Comés et al., Phys.Rev. Lett. 35 (1975) 1518.
2) K.Šaub, S.Barišić and I.Friedel, Phys.Lett. 56A(1976)302; A.Bjeliš and S.Barišić, Proceedings of the Siofok Conference, August, 1976, to be published.
3) Per Bak and V.J.Emery, Phys.Rev.Lett. 36 (1976) 978.
4) A.Bjeliš and S.Barišić, Phys. Rev. Lett. 37 (1976) 1517.