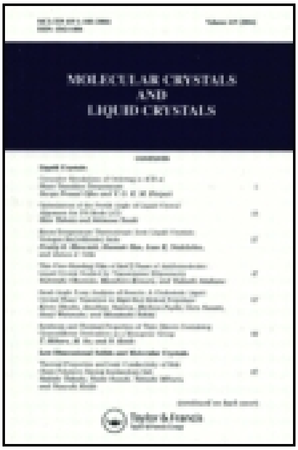

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NONLINEARITY AND HYSTERESIS IN TTF-TCNQ

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We show that the Landau theory for the transverse sliding in TTF-TCNQ reduces to two coupled nonlinear differential equations for the fields representing the modulation and the phase of the ordering. The problem is nonintegrable and, beside the erratic solutions, possesses also bands of periodic solutions. The band of most interesting solutions can be divided by separatrices into subbands of topologically compatible solutions. We argue that these separatrices are topological barriers which cannot be crossed, so that the system is confined to the subband of configurations bounded by two separatrices. This is the basis for the explanation of the hysteresis observed in the sliding temperature range.

INTRODUCTION

TTF-TCNQ is a well-known example of a periodically ordered system with temperature variation in the periodicity of the two observed superstructures. These superstructures appear below 49 K, as the so-called "$2k_F$" and "$4k_F$" Bragg spots. The corresponding wave rectors are $\vec{q}_{2kF}=(q,2k_F,0)$ and $\vec{q}_{4kF} = 2\vec{q}_{2kF}$[1]. The last connection indicates that the two orderings are correlated at low temperatures. Here, we start from the assumption which agrees with the experimental data, namely that the $2k_F$-ordering is dominant, and concentrate only on its temperature behavior. Its transverse component, q(T), varies from a*/2 towards a*/4 as T

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decreases from 49 K, and finally gets pinned at the latter commensurate value below 38 K[1,2]. The neutron scattering experiments[2] showed an additional peculiar feature of this ordering, sketched on Fig. 1:

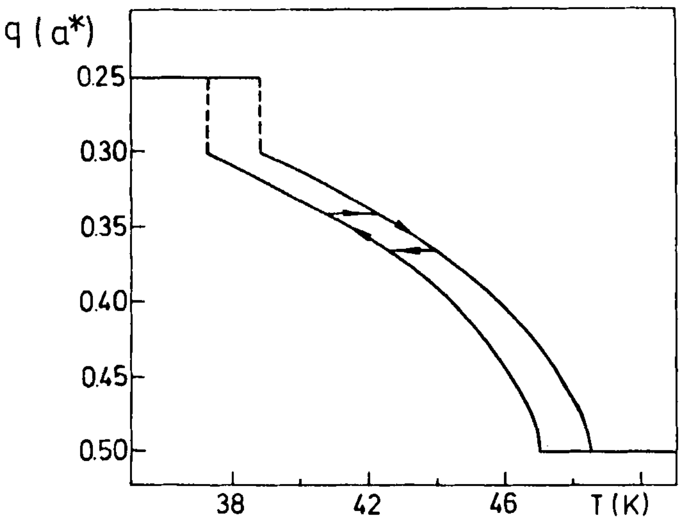

FIGURE 1. The hysteresis in the sliding temperature range (Based on data by Ellenson et al[2])

the heating and cooling q(T) curves are separated by about 1,5 K. By changing the direction of the temperature variation one always goes along the horizontal bridge q = const between the two lines, as indicated on the figure.

In this work we shall interpret this unusual hysteresis as related to the particular domain pattern which follows from the Landau model for the commensurate-incommensurate transition at 38 K.[3] The corresponding wave vector star has four points ($\pm q$, $\pm 2k_F$, 0) and two legs

$$\psi_{\pm} = \rho_{\pm} \exp (i\theta_{\pm}),$$

so that the only possible fourth order Umklapp term is given by[3]

$$\rho_+^2 \rho_-^2 \cos \left(2(\theta_+ + \theta_-) + 4qna\right), \qquad (1)$$

where a is the interchain lattice constant. Its activation below 38 K (q = a*/4) leads to the stable homogeneous configuration with $\rho_+=\rho_-$ (amplitude modulation) and the fixed value of the relative phase $\theta_+ + \theta_-$. On the contrary, the homogeneous configurations for incommensurate values of q have only one or another leg activated ($\rho_+ = 0$ or $\rho_- = 0$) which corresponds to the phase modulation. Being degenerate, these two configurations are expected to form domains with the domain walls in which the relative weight of two legs i.e. the modulation and the relative phase change continuously. The Umklapp term (1) again contributes to the free energy, but now only locally within domain walls. Thus the consideration of domain patterns in the sliding temperature range reduces to the determination of (meta)stable configurations for the fields non-linearly coupled in the expression (1).

MODEL

The full free energy functional follows straightforwardly from the initial Landau expansion for TTF-TCNQ chain structure. After concentrating on the transverse direction in which TCNQ and TTF chains alternate (which corresponds to the wave number q(T) from eq.1), and approximating this scale by the continuous one (na $\rightarrow$ x) after retaining the Umklapp term (1), the free energy has the form

$$F = \frac{\sqrt{2CB|\Delta|}R^3}{4a\lambda}\int dy \left\{ \left(\frac{d\phi}{dy}\right)^2 + \sin^2\frac{\phi}{2}\cdot \right.$$
$$\left. \cdot\left(\left(\frac{d\beta}{dy} - \frac{\lambda^2}{\sqrt{|\Delta|}}\right)^2 + \frac{4\lambda^2}{|\Delta|}\left(\sin^2\frac{\beta}{2} - \frac{\lambda^2}{4} + \Delta\right)\right)\right\} . \qquad (2)$$

The two field variables introduced here represent just the relative phase

$$\beta \equiv 4\delta x + 2(\theta_+ + \theta_-) - \pi , \qquad (3)$$

and the modulation

$$\tan\frac{\phi}{4} \equiv \frac{\rho_-}{\rho_+} , \quad 0<\phi<2\pi . \qquad (4)$$

The two other fields are

$$\frac{1}{2}(\theta_+ - \theta_-) \text{ and } R^2=\rho_+^2 + \rho_-^2 . \qquad (5)$$

The first one is minimized out from the free energy (2), while R, the temperature dependent absolute amplitude, can be taken as approximately space independent. The convenient space scale chosen in eq.2,

$$y = \frac{2R\sqrt{B|\Delta|}}{\lambda\sqrt{C}}\ x \qquad (6)$$

is temperature dependent due to the presence of parameters R and $\lambda^2=4C\delta^2/BR^2$, where $\delta=q-a^*/4$, and C and B are constant parameters from the Landau expansion. The remaining parameter Δ is defined as

$$\Delta = \lambda^2/4 - b ,$$

where b is the ratio of the interchain and intrachain anharmonic coupling parameters. The existence of the first-order transition at 38 K is consistent only with b>0[3,4].

ANALOGY WITH CLASSICAL MECHANICS

The thermodynamical problem (2) has a very direct classical mechanical analogue. With y interpreted as a time variable, F is just the action integral for a particle moving on the spherical surface, with β and ϕ representing two angular coordinates. Since the "Lagrangian" in eq.(1) does not depend explicitly on y, there is obviously one "constant of motion", which represents the energy in the mechanical sense, but has no direct thermodynamic meaning. We could not find the other "constant of motion", in agreement with the numerical calculations which indicate that it does not exist. The system of Hamilton-Jacobi equations which corresponds to eq.(2) thus appears to be nonintegrable.

PERIODIC SOLUTIONS

Among the solutions of the Hamilton-Jacobi equations, let us first mention the "equilibrium points", i.e. the configurations which are homogeneous in y. These are (i) $\phi=\pi$, $\beta=0$, and (ii) $\phi=0$ or 2π, β arbitrary. The first solution is stable for $\Delta<0$, and represents the commensurate ordering below 38 K. Further, there are periodic domain solutions in which ϕ oscillates around π [$\phi(m\ell/2)=\pi$, ℓ-periodicity, m=0, 1, 2, ...], with β being equal to $2mn\pi$ (n=0, 1,2 ...) at these points. Numerically, such trajectories are obtained only for two particular continuous sets of pairs of initial slopes $d\phi/dy|_{y=0}$, $d\beta/dy|_{y=0}$. The two bands which correspond to these sets contain trajectories with even and odd values of n. For pairs of initial conditions close to the above sets the trajectories appear to be erratic. The presence of the erratic solutions is related to the nonintegrability of the Hamilton-Jacobi equations.

The free energy of the erratic solutions averaged per unit length is much larger than that of the nearby periodic solutions which have the free energies comparable to those of the homogeneous solutions. Some other bands of periodic solutions are also possible, but their free energies are considerably higher. We thus conclude that the two bands of periodic solutions are the best candidates for metastable states. They also suit well the intuitive picture of the domain patterns in the sliding temperature range mentioned before.

The closer examination of the two bands shows that the continuous change in the initial conditions within the given set (band) is associated with the continuous variation in the periodicity ℓ and the corresponding value of free energy. However, providing that[5]

$$\Delta > |1-\lambda|^2, \qquad (7)$$

each band of solutions is divided in subbands by separatrices. From one subband to another n changes by two (e.g. from 0 to 2, etc. or from 1 to 3 etc) together with increasing ℓ. The separatrices by themselves are trajectories in which ϕ "rotates" $\phi(\ell/2)=2\pi$, $\phi(\ell)=3\pi$, etc ; they cannot be realized physically, due to the restriction on ϕ in eq.(4). When the condition (7) is not fulfilled, the bands contain only n=0 and n=1 solutions respectively.

Rough estimates suggest that the condition (7) might be easily fulfilled in TTF-TCNQ above 38 K. We thus meet an interesting question: how do the separatrices appearing in the band of periodic configurations influence the incommensurate transverse ordering?

SEPARATRICES - TOPOLOGICAL BARRIERS

The direct insight into the form of the solutions in the real space shows that two energetically close configurations separated by a separatrix, are topologically quite different. In order to pass from one to another, one has to shift locally (in every second domain wall) CDWs along chains by a finite amount equal to the half of Peierls wavelength ($\pi/2k_F$). Presumably, the corresponding intermediate states are too high in free energy to be attained. Thus, being once in a given subband, the system is not able to leave it through the separatrix ends.

Regarding the change of configurations due to the variation of temperature (i.e. of the parameter λ in eq.(2)), we note that every change of periodicty (of both, basic CDW periodicity and the periodicity of domain walls) involves the "friction" to the underlying discrete lattice. The system can avoid this friction by properly changing states in its energetically almost degenerate subband, as long as it is somewhere inside the subband. However, when it comes to one of the subband ends, it looses this freedom since it cannot pass through the separatrix. Instead, it continues by following the separatrix temperature variation, and consequently the lattice friction effects appear. By reversing the temperature variation, the system again keeps constant periodicities by going back inside the subband.

CONCLUSION

The above discussion has brought up all the elements for the explanation of the hysteresis in TTF-TCNQ above 38K. We identify heating and cooling curves of Fig.1, with the temperature variation of the two extremal states in some physically preferable subband of metastable states. The horizontal lines which appear by reversing the temperature change, correspond to the "frictionless" change of states in this subband.

Furthermore, the above model may perhaps explain the observed broadening of the $2k_F$-spots in the a*-direction with the increase of temperature along both, sliding and horizontal q(T) curves. The broadening along the sliding curves comes from the decrease of the separation between domain walls due to the increase of λ (i.e. temperature). Concerning the horizontal lines, the functions ϕ and β change along these lines so that the width of domain walls increases at the expense of the domains. This leads again to the broadening of the Bragg spots.

Let us finally point out that in the present model the sliding of the wave vector occurs due to the presence of the separatrices (i.e. topological barriers) in the set of the thermodynamically stable configurations. Otherwise the system would prefer to keep to periodicity constant in order to avoid the "friction" with the discrete lattice. This picture contributes to a better understanding of the wave vector sliding.

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