Charge-density waves in tetrathiafulvalene-tetracyanoquinodimethane

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The observed structural phase transitions in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) are analyzed using a Landau-Ginzburg-type free energy. It is shown that because of a coupling between the components q_a and q_c of the wave vector associated with the charge-density wave, the latter is expected to be nonzero for $38 < T < 47$°K, contrary to previous expectations.

The structural phase transitions occurring in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) have been a subject of extensive experimental and theoretical study in recent years.[1-6] Early x-ray[1] and neutron-diffraction[2] experiments revealed two distinct transitions occuring at $T_3 \simeq 38$ °K and $T_1 \simeq 54$ °K. Below 38 °K the charge-density wave is found to be associated with a reciprocal vector $\vec{q}_{CDW} = (0.25a^*, 0.29b^*, 0)$. As the temperature is raised above 38 °K the component of the reciprocal vector along the a^* direction q_a changes at first discontinuously, but then smoothly until it becomes $q_a = \frac{1}{2}a^*$. The satellite reflections disappear at 54 °K. In a most interesting recent paper,[3] Bak and Emery have analyzed these phase transitions using a Landau-Ginzburg approach. They conclude that a third transition should take place at some temperature T_2, between 38 and 54 °K, above which the component q_a of the charge-density wave is locked at $q_a = \frac{1}{2}a^*$. For $T_3 < T < T_2$ the q_a component is expected to vary continuously with T. It then changes discontinuously at 38 °K and becomes $q_a = \frac{1}{4}a^*$. A careful examination of the original experimental data seems to support these predictions with $T_2 \simeq 47$ °K. Further measurements[2] performed with higher resolution by Ellenson *et al.* show the transition T_2 occurs at 49 °K.

In the present paper, symmetry considerations[7] are used to construct the most general Landau-Ginzburg free-energy functional corresponding to the phase transitions in TTF-TCNQ. Two new terms arise which have not been considered previously. The first is linear in q_b (the component of the $\vec{q}$ vector along the b^* axis). As will be discussed later, it accounts for the temperature dependence of the Fermi momentum along the chains. The second term introduces a coupling between $q_a - \frac{1}{2}a^*$ and q_c. Because of this coupling, the q_c component associated with the charge-density wave is predicted to be nonzero for $T_3 < T < T_2$. Furthermore, for $T \lesssim T_2$ this component should vary linearly with $q_a - \frac{1}{2}a^*$. Experimental tests of these predictions should contribute significantly to our understanding of this interesting but complicated system.

To start, consider the symmetry properties of the order parameter associated with the $T_1 = 54$ °K transition. The symmetry group of the high-temperature phase of TTF-TCNQ is[1] $G_0 = P2_1/c$, where the twofold screw axis is parallel to the b axis. Following Landau, we assume that the order parameter belongs to one irreducible representation of the group G_0. Neutron-diffraction and x-ray experiments show that the charge-density wave associated with this transition is characterized by a wave vector $\vec{q}_{CDW}$ which is found to be equal to $\vec{q}_0 = (0.5a^*, 0.295b^*, 0)$. As will be discussed later, the component q_b of $\vec{q}_{CDW}$ is expected to vary slowly with temperature below T_1. This variation has not been observed experimentally. Consequently, the order parameter which describes the immediate vicinity of the transition transforms under translation as

$$\vec{t}: \ \psi_{\vec{q}_0} \Rightarrow e^{i\vec{q}_0 \cdot \vec{t}} \psi_{\vec{q}_0} \tag{1}$$

for any lattice vector $\vec{t} = (n_1 a, n_2 b, n_3 c)$, with n_1, n_2, and n_3 integers. By applying the symmetry operators of G_0 to $\psi_{\vec{q}_0}$ one obtains two linearly independent order parameters, $\psi_{\vec{q}_0}$ and $\psi_{-\vec{q}_0}$, which form a basis for an irreducible representation of G_0. To completely specify the symmetry properties of the order parameter one must determine how $\psi_{\vec{q}_0}$ transforms under the symmetry operators of the group of $\vec{q}_0$, namely, $G_{\vec{q}_0}$ (the subgroup of G_0 which leaves $\vec{q}_0$ invariant). We have $G_{\vec{q}_0} = 2_1$. Since the order parameter $(\psi_{\vec{q}_0}, \psi_{-\vec{q}_0})$ forms a basis for an irreducible representation of G_0, the component $\psi_{\vec{q}_0}$ should transform into itself as a basis of an irreducible representation of the group $G_{\vec{q}_0}$. Therefore, $\psi_{\vec{q}_0}$ transforms under the twofold screw axis, either as

$$2_1: \ \psi_{\vec{q}_0} \Rightarrow +e^{0.295\pi i} \psi_{\vec{q}_0}, \tag{2a}$$

or as

$$2_1: \ \psi_{\vec{q}_0} \Rightarrow -e^{0.295\pi i} \psi_{\vec{q}_0}. \tag{2b}$$

In Eq. (2a) the charge-density waves on the two TCNQ (or TTF) chains which belong to the same

unit cell have the same phase (and the mode is acoustic), while in Eq. (2b) they are out of phase (and the mode is optic). The actual distortion mode has not yet been determined experimentally. For our purposes, the exact nature of the order parameter (whether it is acoustic or optic) is not important since we obtain the same free-energy functional in both cases. It is, however, assumed that the order parameter belongs to only one irreducible representation of G_0 and hence it is not a linear combination of the two modes. The appropriate Landau-Ginzburg functional associated with the order parameter $(\psi_{\vec{q}_0}, \psi_{-\vec{q}_0})$ is the most general form invariant under the symmetry group G_0. Define two real order parameters ϕ_1 and ϕ_2 by

$$\psi_{\pm\vec{q}_0} \equiv \phi_1 \pm i\phi_2 . \tag{3}$$

To second order in ϕ_j, the free-energy functional then takes the form

$$f(\phi_{1,\vec{q}}, \phi_{2,\vec{q}}) = \frac{1}{2}\int d^3q\,[(r + \alpha q_1^2 + \beta q_2^2 + \gamma q_3^2 + \delta q_1 q_3)(\phi_{1,\vec{q}}\phi_{1,-\vec{q}} + \phi_{2,\vec{q}}\phi_{2,-\vec{q}}) + \eta q_2(\phi_{1,\vec{q}}\phi_{2,-\vec{q}} - \phi_{1,-\vec{q}}\phi_{2,\vec{q}})] + \cdots , \tag{4}$$

where $\phi_{j,\vec{q}}$ are the Fourier components of ϕ_j and q_1, q_2, q_3 are the components of $\vec{q}$ along the a^*, b^*, and c^* axes, respectively. The fluctuating field $\phi_{1,\vec{q}} + i\phi_{2,\vec{q}}$ corresponds to a charge-density wave with wave vector $\vec{q}_0 + \vec{q}$. The expression (4) includes two terms not previously considered:

$$\eta q_2(\phi_{1,\vec{q}}\phi_{2,-\vec{q}} - \phi_{1,-\vec{q}}\phi_{2,\vec{q}}) , \tag{5a}$$

$$\delta q_1 q_3(\phi_{1,\vec{q}}\phi_{1,-\vec{q}} + \phi_{2,\vec{q}}\phi_{2,-\vec{q}}) . \tag{5b}$$

To discuss the effect of these terms recall that the free energy of the system is given by

$$F = \min_{\{\phi_{j,\vec{q}}\}} f(\phi_{j,\vec{q}}) . \tag{6}$$

As usual, we may assume $r \sim T - T_1$. For stability we require $\beta > 0$ and the quadratic form $Q = \alpha q_1^2 + \gamma q_3^2 + \delta q_1 q_3$ must be positive definite (i.e., α, $\gamma > 0$, $\alpha\gamma - \delta^2 > 0$) for $T \simeq T_1$. Then the order parameter which minimizes the free energy (4) for $T_2 < T < T_1$ is $\phi_{j\vec{q}'}$ with $\vec{q}' = [0, (\eta/2\beta)\,b^*, 0]$. The charge-density wave is therefore associated with $\vec{q}_{\mathrm{CDW}}(T) = \vec{q}_0 + \vec{q}'$. Since, by observation, the order parameter which becomes critical at T_1 is associated with $\vec{q}_{\mathrm{CDW}}\ (T = T_1) = \vec{q}_0$, the vector $\vec{q}'$ should vanish at $T = T_1$ and hence $\eta\ (T = T_1) = 0$. We therefore assume $\eta \sim T - T_1$. For $T < T_1$ the vector $\vec{q}'$ does not vanish, and the component q_b of $\vec{q}_{\mathrm{CDW}}$ should become different from[8] $0.295b^*$. The component q_b is associated with the Fermi momentum of the electrons along the b axis,[9] and therefore the η term represents the temperature variation for the Fermi momentum. This variation is very slow, and has not so far been detected experimentally. However, in a recent x-ray study by Kagoshima, Ishiguro, and Anzai,[1] it has been reported that the wave number of the phonon anomaly at $0.41b^*$ does vary with temperature. The η term can be used to explain this variation. At the temperature $T_2 < T_1$ the quadratic form Q becomes unstable in a certain direction in the (q_1, q_3) plane, and another transition takes place. This transition occurs for $\alpha\gamma - \delta^2 = 0$. Below T_2 (i.e., for $\alpha\gamma - \delta^2 < 0$) *both* components q_1' and q_3' associated with the order parameter should become nonzero, and $\vec{q}_{\mathrm{CDW}}(T) = \vec{q}_0 + (q_1', 0, q_3')$. By minimizing (4) for $T < T_2$ we find

$$q_3'/q_1' = \delta/2\gamma , \quad q_1^2 \sim \delta^2 - \alpha\gamma . \tag{7}$$

Therefore q_3' is proportional to q_1' for $T \lesssim T_2$, and both vary as $(\delta^2 - \alpha\gamma)^{1/2} \sim (T_2 - T)^{1/2}$. A model calculation, which takes into account the Coulomb forces between the charge-density waves, suggests that the ratio $q_3' c/q_1' a$ is of the order of 0.1.[10] It would be of great interest to study the q_c component experimentally and test these predictions.

As pointed out by Bak and Emery,[3] one can understand the nature of the T_2 transition from a more microscopic viewpoint as follows: TTF-TCNQ is composed of linear chains of TTF and TCNQ molecules. For $T_2 < T < T_1$ only one set of molecules (apparently[11] the TCNQ) exhibits charge-density waves. Coulomb interaction between the chains favors $q_a = \frac{1}{2}a^*$ and therefore $q_1' = 0$. At $T = T_2$ the other set of chains orders. Coulomb interaction between nearest-neighbor chains of different types favors $q_a = 0$. Because of these competing interactions, the q_a component starts deviating from $\frac{1}{2}a^*$ at T_2. However, if one recognizes that *the a and c axes are not perpendicular* (the angle between a and c is 104°) and considers Coulomb interaction between *next*-nearest chains one finds that the component q_c should deviate from zero below T_2 as predicted phenomenologically.

At $T = 38$ °K, $\tilde{q}_{CDW}$ changes discontinuously owing to fourth- and higher-order terms in the free-energy functional (4). Below 38 °K it is expected that the component q_c, like q_a, should become locked and hence be commensurate with the lattice. The numerical value of q_c depends on the exact mechanism which drives the transition and therefore cannot be uniquely predicted from the free-energy functional (4). There are, however, experimental indications[1] that $q_c = 0$ for $T < 38$ °K.

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