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Phason and Metal-Insulator Domain Walls in TTF-TCNQ

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Recent data on the temperature dependence of Young's modulus, E_B, of unclamped, equilibrated samples of TTF-TCNQ are analyzed in terms of a combined microdomain-phason model. The appearance of miniature mean-field anomalies in $E_B\,(T)$ near 38 and 52°K is explained in terms of phason quartet and pair condensation, respectively, while a subminiature anomaly at 34°K is attributed to the disappearance of TCNQ metal–insulator microdomain interfaces.

Ishiguro, Kagoshima, and Anzai (IKA) (*1*) have measured Young's modulus in TTF-TCNQ for $15°\mathrm{K} < T < 300°\mathrm{K}$ in a geometry which corresponds to an unclamped sample. This bilinear (two-strand) organic conductor has received much attention because of its large, highly anisotropic and anomalously temperature-dependent electrical conductivity, and because it passes through many low-temperature phase transitions. Diffraction studied on unclamped samples have shown thermal hysteresis near the 38°K low-temperature phase transition (*2*), presumably produced by shape-dependent strain fields, so that the structural character of the transition has been obscured by its sluggish nature, reminiscent of Martensitic transitions (*3*). The geometry of IKAs experiment apparently generates equilibrated domain structures which have not been achieved in previous studies of this material, presumably because IKAs applied vibrational forces unpin domain walls to bring them to equilibrium positions at each temperature.

In this paper the very important equilibrated data of IKA are combined with X-ray and neutron diffraction data to construct a theoretical model of the microscopic structure of TTF-TCNQ as a function of temperature. Two theoretical discussions, one of distorted (MAD) (*4*) charge density waves (CDW), (*5*) the other of coexisting elastic microdomain metallic and insulating phases in bilinear structures (the "hopscotch" model) (*3*), are used to introduce two kinds of domain walls (phasons (*5*) and ordinary metal–insulator interfaces (*3*)). The diffraction data, and most directly the IKA data, are interpreted as providing evidence for the ordering and creation and/or extinction of these domain walls at different temperatures.

The most important property of both kinds of domain walls that is associated with each is a characteristic length. For the phasons this length is determined essentially by the wave vector $\tilde{q}_p$ of the Peierls CDW. (In a system which is metallic at high temperatures, one usually has $\tilde{q} = 2\hat{k}_F$, where $\hat{k}_F$ is a characteristic Fermi wave vector, but one can equally well have phasons and incommensurate CDWs generated by internal strain fields in *fully insulating ferroelastic* crystals such as (*6*) K_2SeO_4.) The spacing l of the phasons is given by

$$l_p = 2b(G/(\tilde{q}_p - mG/n)) \qquad (1)$$

where b is the axial lattice constant, $G = 2\pi/b$, the reciprocal lattice vector, and $\tilde{q}_p - mG/n = \delta$ is the incommensurability wave vector;

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mG/n is the wave vector of the most favorable commensurate *b*-axis superlattice (*5*). Note that l_p (which is probably of order 5–10 b) is a characteristic property of the *insulating* phase.

In TTF-TCNQ we have a bilinear structure. in which a metal–insulator transition is taking place. Thermodynamically this introduces extra degrees of freedom, corresponding to a structure of coexisting phases (amplitude-modulated CDW) along each of the two chains (*3*). These chains are expected, all other things being equal, to have axial lattice constants b_1 and b_2 which differ by an amount of order 1 %; such a difference has actually been observed (*7*) in $(TTF)_5I_7$. Thanks to the metal–insulator transition, however, there are actually two axial lattice constants $b_j^{i,m}$ (corresponding to the insulating and metallic phases for $j = 1, 2$) for each chain; these are also expected to differ by about 1 %. Because of the gross mismatch between b_1 and b_2, there is a characteristic repeat length of a metal–insulator microdomain pair given by (*3*)

$$L_A \sim b^2/(b_2 - b_1). \qquad (2)$$

Also to reduce interchain elastic strain energy the metallic and insulating fractions $f_j^{i,m}$ of chains $j = 1$, 2 will satisfy the condition $(f_j^i + f_j^m = 1)$

$$f_1^i b_1^i + f_1^m b_1^m = f_2^i b_2^i + f_2^m b_2^m. \qquad (3)$$

with $f_j^{i,m} = f_j^{i,m}(T)$ and $df_j^m/dT > 0$.

The combined phason and coexisting structural phase model is shown in Fig. 1, which also indicates the "hopscotch" mechanism (*3*) for achieving large values of $\sigma_b(T)$ for 54°K < T < 300°K. Note that phason domain walls are about 10 times as numerous as metal–insulator domain walls; however, the *number* of phason domain walls (as distinct from their spacing) is proportional to $f_1^i(T) + f_2^i(T)$. (We do not distinguish between l_1 and l_2.)

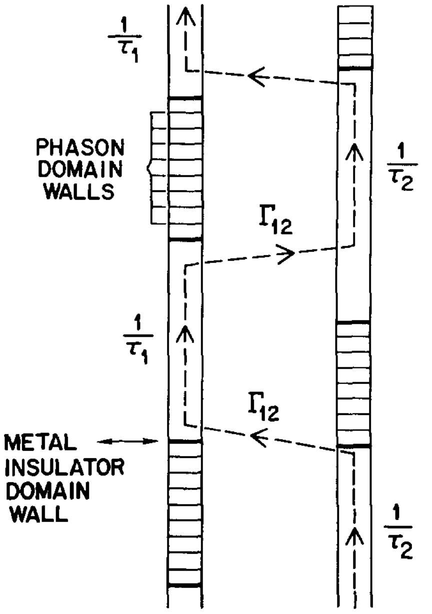

Fig. 1. Amplitude- and phase-modulation of charge density waves in a bilinear organic conductor such as TTF-TCNQ. Each chain is divided into alternating metallic and insulating segments with $l_m + l_i = L_A$ (amplitude-modulated CDW). Each insulating segment contains phason domain walls with an average spacing l_p. The current carrying paths have the form indicated by the dotted lines; the resistivity at high temperatures is dominated by the interchain scattering rate Γ_{12} and not by the intrachain relaxation times $\tau_{1,2}$. At high temperatures $E_B(T)$ is dominated by $l_i(T)$, while the mean-field behavior 0°K < T < 53°K is produced by a lateral order–disorder (Bragg–Williams) transition of the insulating regions. Finally, the miniature and subminiature mean-field transitions near 34, 40, 47, and 53°K are related to phason and metal–insulator domain walls as described in the text.

With this lengthy introduction we are now in a position to describe specifically all the features contained in the dramatic data of IKA, which are reproduced in a smoothed and labeled form (for the reader's convenience) in Fig. 2. The linear structure resists shear weakly, corresponding to a small elastic modulus in the metallic state at high temperatures. With decreasing temperatures a highly complex series of metal–insulator transitions takes place. Because of the one-dimensional character of the structure, the effects of these transitions on the Young's modulus are approximately superposable. Thus the transitions can be interpreted not

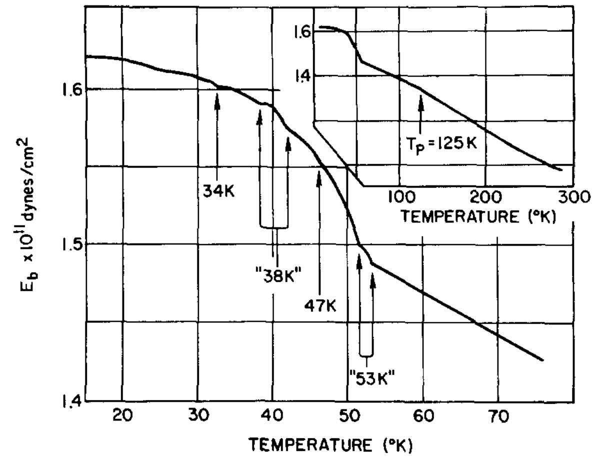

FIG. 2. For the reader's convenience the very important data of Ishiguro, Kagoshima and Anzai (Ref. (*1*)) are reproduced schematically and labeled. The original experimental points are shown in Ref. (*1*).

only qualitatively but even semiquantitatively with the aid of diffraction data which exhibit (only) spatially averaged effects of the complex internal domain pattern which develops with decreasing temperature T.

With T decreasing from 300 to 150°K (inset to Fig. 2) E_b increases and $|dE_b/dT|$ is larger between 150 and 250°K than it is between 250 and 300°K. I interpret this as a consequence of the stiffening of the lattice along the c-axis, because the dispersion curves for transverse acoustic b-axis phonons with c-axis polarization are very flat (*2*) from the zone boundary almost to $k = 0$ at an effective temperature near 250°K. Diffraction data (*8*) have shown that CDW form at T_p, which appears to be about 125°K in this sample. (Values of $T_p = 150$°K have been reported for other samples in diffraction studies (*8*).) The formation of incommensurate CDW reduces $|dE_B/dT|$ because of a weaker electron-ion interaction. This is shown in Fig. 2 by a change in slope at T_p, but more data points between 70 and 125°K might show mean-field type curvature in this range.

The broad mean-field behavior between 15 and 52°K in Fig. 2 is explained in the elastic microdomain model as the result of two factors: the ordering of the insulating domains (see Fig. 1) so that they are aligned in a stripe geometry at low temperatures, and the growth of the length l_i of the insulating segments

$$l_i = (f_1{}^i + f_2{}^i)L, \tag{4}$$

with decreasing T. This latter effect is also present in the disordered state ($T > 54$°K) when the former effect is largely absent.

The most remarkable features of the IKA data in Fig. 1, which we believe have not been observed previously because the samples were clamped and/or not equilibrated, are the miniature mean-field curves between 38 and 42°K as well as between 52 and 54°K. Hysteresis in unclamped but nonequilibrated samples had been observed (*1*) previously near 38, but not 53°K. In some theoretical models it is supposed that the CDW form at $T_p = 53$°K, in which case no miniature mean-field curve, similar to that observed at 38°K, could be obtained.

Our explanation for the miniature mean-field curves near 40 and 53°K is based on the observation (*2*) that A, the modulation period (in a units) changes from 1 (54°K) to 2 (52°K) and from 3 (42°K) to 4 (38°K). We assume that all the insulating microdomains contain MAD phasons, and that these lock together in pairs between 54 and 52°K in an ordering transition; this would naturally stiffen the lattice against shear. Between 52 and 47°K A is constant at 2, but it becomes nonintegral and increases smoothly (9) between 47 and 42°K from 2 to 3. Thus there is a rapid linear increase in E_b from 52 to 47°K, representing presumably a linear increase in $l_l(T)$. The value of $|dE_b/dT|$ is much greater between 52 and 47°K than it was between 60 and 54°K because paired phasons ($A = 2$) are much stiffer than single phasons ($A = 1$).

Discommensuration of A between 47°K ($A = 2$) and 42°K ($A = 3$) reduces $|dE_b/dT|$, as one would expect. Quartet locking of phasons occurs as ordering takes place between 42 and 38°K, where $A = 4$.

A weak mean-field anomaly in X-ray intensities was reported (*10*) near 34°K. Very close inspection of Fig. 2 reveals a subminiature mean-field anomaly just above the noise level at 34°K. The strength of this anomaly is about 0.1 that of the miniature mean-field anomaly at 40°K. It is thus an ideal candidate for the disorder–order transition which would occur when one chain (presumably TCNQ) goes entirely insulating, i.e., all its metal–insulator domain walls disappear. Clearly this must happen (*3*) to at least one type of chain as $T \rightarrow 0$, and the magnitude of the effect on E_b is compatible with the estimated relative density of the metal–insulator domain walls to the phasons. This interpretation is consistent with spin resonance and magnetic susceptibility studies (*11*) which show the TCNQ susceptibility going to zero very near 34°K. Previously I had assumed (*3*) that the TCNQ chains became insulating at 38°K; the new interpretation presented here resolves the discrepancy in the earlier model between phase transitions at 34 and 38°K.

The structural model presented in Fig. 1 reconciles phason (phase-modulated) and microdomain (amplitude-modulated) fine structures; it explains how ferroelectric domain behavior (*6*) (characteristic of uniaxial structures) (*12*) can occur with high metallic conductivity (*3*).

Postscript. After this manuscript was completed a phason instability model was proposed by P. Bak (*Phys. Rev. Lett.* **37**, 1071 (1976)). His model differs from mine in several fundamental respects: (1) He asserts that Peierls distortions form at 54°K, while in my model the distortions form at 125–150°K. (2) He asserts that the 47–49°K transition arises from the initiation of phason motion along the *b*-axis. In my model the 47–49°K transition is initiated by the temperature dependence $l_l(T)$ of the length of Peierls phases along the *b*-axis. The motion of the (amplitude-modulated) metal–semiconductor interface drives the lateral alignment of the (phase-modulated) phason domain walls. (3) Bak's model is translationally invariant, while mine contains two characteristic domain lengths, l_p and L_A. (4) It is a crucial feature of Bak's model that the 54 and 38°K transitions are second- and first-order, respectively. In my model both transitions are "first-order" with respect to $l_l(T)$ (the longitudinal variable) and become second-order (miniature mean-field curves) through lateral alignment of phason domain walls.

Acknowledgments

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