NOTE

Structure and Conductivity of Bilinear Organic Compounds

J. C. PHILLIPS

Bell Laboratories, Murray Hill, New Jersey 07974

The relationship between crystal structures and metallic conductivities of linear organic materials such as TTF-TCNQ is explained in terms of strong lateral elastic interactions between chains. A microdomain model is presented in which at high temperatures there are, in general, two coexisting phases on each stacked molecular chain.

Many anomalies in the structural and transport properties of bilinear organic conductors (such as TTF (*1*)– or HMTSF (*2*)–TCNQ) have become evident in recent work. The present model relates these anomalies to the general theory of two-phase behavior in soft lattices which undergo Martensitic transformations (*3–5*). Similar anomalies have also been observed (*6, 7*) in high-T_c superconductors such as V_3Si, Nb_3Sn, and Nb_3Ge. At high temperatures, T_p Peierls charge density waves (CDW) form superlattice embryos (*4*) of a second phase embedded (*5*) in the very high temperature phase ($T > T_p$). At a much lower temperature, $T_c \sim (0.05–0.25)T_p$, the embryos order to form a super-superlattice (single phase). Because of their peculiar geometrical configuration, the bilinear compounds exhibit a series of low-temperature ordering transitions T_{c1}, T_{c2}, ...

The most striking structural anomalies are connected with the absolute instability of the reported crystal structures (*8*). From the observed periodicities of the CDW, one infers that each molecular chain contains a charge of order $\pm 0.5 \ e$ per molecule, which implies strong Coulomb attractions between the chains. However, at their point of closest approach oppositely charged molecules are separated by $\gtrsim 3 \ \text{Å}$, i.e., more than two bond lengths. At such large distances there are no repulsive forces to balance the Coulomb

attraction. Thus the reported crystal structures must be incomplete. The most natural way to stabilize the structures appear to be to introduce bridge molecules (such as HCN) during growth of the crystal which are not observed by X-ray scattering. A concentration of 0.1 % of these could suffice to stabilize the structure. As an alternative, one could allow the chains to buckle every hundred molecules or so. (When $(KBr)_{0.25}$ is removed from $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$, the $Pt(CN)_4$ chains buckle at every fourth molecule (*9*).) One hesitates to regard these molecules as impurities, because (like the Br ions in KCP) they may play an essential rôle in stabilizing the structure; thus one expects their arrangement to be periodic, corresponding (if the chains strongly resist bending) to a long period $L \sim 100b$, where b is the axial lattice constant.

The most difficult transport anomaly arises if one assumes that the dominant paths for axial currents are confined to isolated chains (independent chain model). The Peierls CDW indicate (*10, 11*) the formation, e.g., in TTF–TCNQ, of insulating phases with growing intensity as T is decreased from $T_p \gtrsim 200°K$ to $T_c \lesssim 60°K$ (the various T_{ci} are discussed later). Yet as T decreases and the chains become more insulating, the axial conductivity increases (*1, 2*) ($d\log\sigma_b/d\log T \sim -2.3$). My model resolves this paradox by assuming that all current paths are percolative, alternately

traversing metallic segments along adjacent chains, and avoiding insulating CDW embryos, as shown in Fig. 1. This hopscotch process is made possible by the interchain bridge molecules, which, as we have seen above, are similar to the (widely spaced) rungs of a ladder. Most of the resistance along these paths is associated with interchain hopping; because the bridge molecules are weakly bound, the scattering is strongly anharmonic.

Below T_{c1} (=53°K in TTF–TCNQ and 110°K in HMTSF–TCNQ) lateral ordering of metallic and insulating segments occurs. In TTF–TCNQ the ordered geometry consists of lateral stripes of metallic and insulating microdomains, which causes the conductivity to freeze-out below 53°K. In HMTSF–TCNQ a checkerboard geometery prevails, so that below 110°K the conductivity may still increase with decreasing temperature.

The nature of the two-dimensional percolation process introduces a second critical
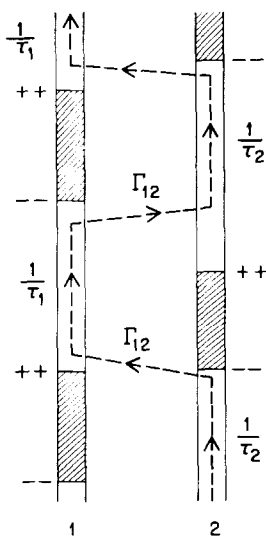
temperature T_{c2}. This is the temperature at which $l_c = l_{c1} + l_{c2} = l_{i1} + l_{i2} = l_i$, where l_{c1} means the length of a conducting microdomain on chain 1, etc., and i means insulating CDW. Quite generally $dl_c/dT > 0 > dl_i/dT$, so that (barring impurity pinning) as T is decreased from high T ($l_i = 0$), one will reach T_{c2}. At this point σ_b will decrease rapidly; the order of the phase transition involved depends on whether $T_{c1} \lessgtr T_{c2}$, and the importance of interchain domain wall interactions (12). In TTF–TCNQ, it appears (12) that $T_{c2} = 60°K$ and in HMTSF–TCNQ $T_{c2} = 32°K$.

Because of the embryonic character of lateral structural ordering, striational structure (short-range order of bundles of chains over distances d) occurs between T_{c1} and T_p. The striational structure means that there is, in general, no relation between conductivity along the a-axis (chain $1 \to 2 \to 1 \to 2$, etc.) and along the b-axis, except that $\sigma_a \ll \sigma_b$ because of interchain hopping resistance. On the other hand, for $T-T_{c1} \to 0+$ a phenomenon similar to critical opalescence is expected, namely, the characteristic length λ for current fluctuations should be proportional to $(T-T_c)^{-1/2}$. When $\lambda \gg d$ the striational structure can be neglected and the system appears to be homogeneous. In this limit $d\log\sigma_a/d\log T = d\log\sigma_b/d\log T$, and this condition can serve as a decisive test to distinguish one-phase independent chain models from the present two-phase percolative chain model. Preliminary results indicate (13) that this condition is indeed satisfied in TTF–TCNQ.

Because embryonic behavior is a characteristic property of soft lattices (3–7), from a phenomenological viewpoint we believe there is already adequate precedent for our model. However, the simple bilinear structure itself makes it possible to identify the configuration coordinates and constraints responsible for the coexistence of phases. Suppose we could actually isolate the two chains; each would have its own axial lattice constant, b_1 or b_2, and in general $b_1 \neq b_2$. Now the chains are brought together, charge transfer occurs, and the new axial lattice constants $\tilde{b}_1$ and $\tilde{b}_2$ are still not equal in general. This can be resolved, if $\tilde{b}_2 > \tilde{b}_1$, by introducing vacancies on the second chain (e.g., in $(TTF)_{12}-(SCN)_7$).

FIG. 1. Current paths in the hopscotch model of bilinear conductivity. The intrachain conductivities $\sigma_{1,2}^m$ are proportional to $1/\tau_1$ and $1/\tau_2$, respectively. The interchain conductivity is proportional to Γ_{12}. Because of lateral microdomains, there is a distribution of Γ_{12} values. Under the influence of an external field space charge accumulates at the metal (unshaded)–semiconductor (shaded) interfaces, so that there are voltage drops laterally even when the external field is parallel to the chains.

Another possibility, if $\tilde{b}_2$ and $\tilde{b}_1$ are close enough, but not too close, is to have $\tilde{b}_1 = 1.01\tilde{b}_2$, as occurs (14) in (TTF) $_5I_7$. Still another possibility arises if we recognize that $b_{1i} \neq b_{1c}$, i.e., the axial lattice constants depend on whether one is in the insulating or conducting phase, and $|b_{1,2i} - b_{1,2c}|/b_{1,2} \lesssim 0.01$. Then if the microdomain conductive length on the first chain is $f_1 L$, etc., the condition $f_1 b_{1i} + (1 - f_1)b_{1c} = f_2 b_{2i} + (1 - f_2)b_{2c}$ is a constraint which reduces interchain elastic misfit energy. The values of $f_1(T)$ and $f_2(T)$ will depend on intrachain electronic energies and residual interchain strain energies.

Comparison with other systems (3–7) suggests that it should be possible to observe coexisting microdomain phases in bilinear organic conductors. However, we believe that the present model is very attractive even without such direct confirmation, because it explains (for example) the very large qualitative difference (1, 2) in $\sigma_b(T)$ between TTF– and HMTSF–TCNQ. The present model differs fundamentally from single-phase models which invoke sliding Fröhlich condensates (15, 16) to resolve transport anomalies, or which make use of Landau–Ginsberg descriptions of structural phase transitions (17). The general drawback of the former is that pinning by impurities is expected to quench the conductivity. The latter, on the other hand, encounter difficulties in explaining hysteresis effects. Finally, neither model encompasses both the structural and transport anomalies, which in our model are resolved simultaneously.

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