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Doping-induced structural phase transition in polyacetylene

Han-Yong Choi and E. J. Mele
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6396

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We consider an anisotropic planar-rotor model on a two-dimensional triangular lattice to model the dopant ordering in polyacetylene in the process of alkali-metal doping. With the combination of a Ginzburg-Landau expansion of the free energy close to the critical temperature and total-energy calculations at zero temperature, we obtain a phase diagram in the plane of temperature and alkali-metal chemical potential, which shows various modulated phases which appear in the process of alkali-metal doping of the polymer. These results are compared with experimental observations by Winokur *et al.* [Phys. Rev. Lett. **58**, 2329 (1987)].

Undoped polyacetylene is a dimerized semiconductor. The physical properties of this semiconducting material can be changed drastically through charge-transfer doping. Because of the importance of doping in modifying the electronic properties of conducting polymers, it is important to investigate the structural evolution of the polymer induced by the insertion of counter ions between polymer chains during the doping. Shacklette and Toth[1] identified structural transformations both by electrochemical measurements and by examining samples at fixed concentration with x-ray diffraction. An x-ray scattering experiment on Na-doped polyacetylene by Winokur *et al.*[2] shows new scattering peaks from $\sqrt{3}\times\sqrt{3}$ and hexagonally modulated structures of Na ions in the plane perpendicular to the chain direction.

In Ref. 3, which will be referred to as CHM in the remaining part of this paper, we have investigated an anisotropic planar-rotor model on a two-dimensional (2D) triangular lattice to model the interchain orientational ordering of polymer chains in the plane perpendicular to the chain direction. We found that this kind of a rotor model can describe a herringbone (HB) ground state with a 55° setting angle for a certain range of the interaction parameters. In this paper, we will extend this previous work to study the doping-induced phase transition. We will show that the doping-induced phase transition proceeds from the undoped HB phase to $\sqrt{3}\times\sqrt{3}$ via striped and hexagonally modulated phases. In order to study the 2D ordering phenomena we project the polymer structure along the chain direction. The mass density of each polymer chain is projected onto a rod on a 2D triangular lattice in the plane perpendicular to the chain direction. We represent each polymer chain by a rotor with a quadrupole moment[4] on a 2D triangular lattice. This approach is appropriate to Na-doped polyacetylene,[5] but presumably not for K-doped $(CH)_x$. In the K-doped sample it was observed that the undoped HB structure is transformed to the tetragonal structure.[6]

Now, we will consider a simple anisotropic planar-rotor model on a 2D triangular lattice to model transverse orientational ordering in this system. By a combination of Landau expansion of the free energy close to the critical temperature and zero-temperature energy calculations, we will construct a phase diagram of various orientationally ordered phases in the plane of temperature and chemical potential. The interaction between rotors is the same as in CHM with interaction parameters α and β as follows:

$$H_0=\alpha\sum_{\langle i,j\rangle}\cos(2\theta_i-2\theta_j)+\beta\sum_{\langle i,j\rangle}\cos(2\theta_i-2\phi_{ij})\cos(2\theta_j-2\phi_{ij})\,, \qquad (1)$$

where θ_j is the angle of the jth rotor, ϕ_{ij} is the angle of the line connecting the ith and jth rotor, with respect to the x axis of the plane perpendicular to the chain direction, as shown in Fig. 1, and the summation is over the nearest neighbors. First and second terms of Eq. (1) are the two nonvanishing invariant terms resulting from interactions between quadrupole moments. ϕ_{ij} in the second term is determined by the geometry of the underlying lattice and this term represents the anisotropic part of the interaction. Positive and negative α without the β term will favor $\sqrt{3}\times\sqrt{3}$ and ferromagnetic phase, respectively. Positive

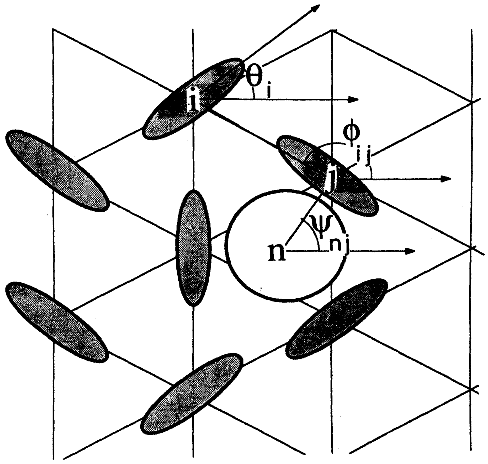

FIG. 1. Schematic diagram of the $(CH)_x$ structure with a dopant ion labeled n, projected along the chain direction. The polymer chain labeled i is represented by a rotor on a 2D triangular lattice, with a setting angle θ_i with respect to the x axis. The rotors orient themselves to open a gallery for the dopant.

and negative β without the α term will favor HB and ferromagnetic alignment of rotors, respectively. Phase diagrams of Eq. (1) as a function of temperature and interaction parameters are presented in CHM.

The interactions between a dopant and its surrounding rotors are modeled such that the rotors are rotated to open a gallery for the dopant. This effect can be represented by the following interaction:

$$H_{\mathrm{int}}=\sum_{\langle n,j\rangle}\{\gamma[\cos(2\psi_{nj}-2\theta_j)]-\mu\}x_n\,, \tag{2}$$

where x_n represents the density of dopants along the nth column, θ_{nj} is the angle of the vector connecting the jth rotor and nth dopant, and μ is the chemical potential which controls the doping density. For positive values of γ, this term will orient the rotor to be perpendicular to the vector between the rotor and the dopant. We take interaction parameters $\alpha=-1$ and $\beta=2$ to ensure that the HB phase is realized as the ground state for the undoped problem.[3] Then, the Hamiltonian is given by $H=H_0+H_{\mathrm{int}}$. We solve the Hamiltonian with a Landau expansion of the free energy close to the critical temperature and by energy calculation at zero temperature, and interpolate between these to obtain a phase diagram in the plane of the temperature and chemical potential.

We want to calculate the free energy F, which can be expressed in terms of the density matrix as $F=E-TS=\mathrm{Tr}\{\rho H+T\rho\ln\rho\}$. The mean-field approximation consists of taking ρ as the product of single-site density matrices as $\rho=\prod_i\rho_i$. Close to the critical temperature, the order parameters become very small, so that we can expand the free energy in powers of the order parameters. Here, we generalize CHM and carry out the analysis for the interaction between a dopant and surrounding rotors given by Eq. (2). We take

$$\rho_i=\frac{1}{2\pi}\left[1+\sum_{m=1}^{\infty}[C_i(m)\cos(2m\theta_i)+S_i(m)\sin(2m\theta_i)]\right], \tag{3}$$

with order parameters $C_i(m)$ and $S_i(m)$, which are allowed to depend on the site index i. The dominant order parameters are $C_i(1)$ and $S_i(1)$ which correspond to quadrupole interactions, other ones can only be induced by either $C_i(1)$ or $S_i(1)$. Then, the thermal averages are given by

$$\langle\cos(2m\theta_i)\rangle=\mathrm{Tr}[\rho\cos(2m\theta_i)]=\tfrac{1}{2}C_i(m)\,,$$

$$\langle\sin(2m\theta_i)\rangle=\mathrm{Tr}[\rho\sin(2m\theta_i)]=\tfrac{1}{2}S_i(m)\,.$$

In the mean-field approximation,[7] we can write the free energy as

$$F_{\mathrm{int}}=\sum_n(A_n-\mu)x_n+T[x_n\ln x_n+(1-x_n)\ln(1-x_n)] \tag{4}$$

with

$$A_n=\sum_j\gamma[\langle\cos2\theta_j\rangle\cos2\psi_{nj}+\langle\sin2\theta_j\rangle\sin2\psi_{nj}]\,.$$

By minimizing Eq. (4) with respect to x_n, we eliminate x_n from the free energy in favor of A_n. We obtain

$$F_{\mathrm{int}}=\sum_n T\ln(1-x_n)=-\sum_n T\ln(1+e^{(\mu-A_n)/T})\,. \tag{5}$$

Close to the transition temperature A_n, which is expressed in terms of $\langle\cos2\theta_n\rangle$ and $\langle\sin2\theta_n\rangle$, and thus in terms of C_n and S_n, becomes very small. Hence, we expand the free energy of Eq. (5) in powers of C_n and S_n. Then, we make a Fourier transform to momentum space as

$$C_i(m)=\frac{1}{N}\sum_{\mathbf{r}_i}C_m e^{i\mathbf{q}\cdot\mathbf{r}_i}\,,$$

along with the similar expression for $S_i(m)$. The second-order term of F ($=F_0+F_{\mathrm{int}}$), within the space spanned by $C_1(\mathbf{q})$ and $S_1(\mathbf{q})$ which are the dominant variables in this problem, is

$$F^{(2)}=(C_1(\mathbf{q}),S_1(\mathbf{q}))\chi^{-1}(\mathbf{q})\begin{pmatrix}C_1(\mathbf{q})\\ S_1(\mathbf{q})\end{pmatrix}. \tag{6}$$

The inverse susceptibility tensor $\chi^{-1}(\mathbf{q})$ is not diagonal in general. However, for an appropriately chosen wave vector $\mathbf{q}$, it can be diagonalized to yield eigenvalues

$$\Gamma_{cc}(\mathbf{q})=2\gamma_2^2\left[\beta+\alpha-\frac{\Gamma^2}{T}\right]+\gamma_2\left[2\alpha+\frac{3}{2}\beta+4\frac{\Gamma^2}{T}\right]+T-\alpha-\beta-2\frac{\Gamma^2}{T}\,, \tag{7a}$$

$$\Gamma_{ss}(\mathbf{q})=2\gamma_2^2\left[\alpha+3\frac{\Gamma^2}{T}\right]+\gamma_2(2\alpha+\tfrac{3}{2}\beta)+T-\alpha-6\frac{\Gamma^2}{T}\,, \tag{7b}$$

with

$$\gamma_2=-\cos(q_y a)\quad\text{and}\quad\Gamma=\frac{\gamma}{2\cosh(\mu/2T)}\,.$$

The transition temperature at a given chemical potential μ corresponds to the maximum temperature with respect to $\mathbf{q}$, which satisfies either $\Gamma_{cc}(\mathbf{q})=0$ or $\Gamma_{ss}(\mathbf{q})=0$. The transition temperatures from orientationally disordered to ordered phases obtained this way are plotted in Fig. 2. At the tetracritical point where the disordered and $\sqrt{3}\times\sqrt{3}$ phase meet (point C in Fig. 2), the transition temperatures corresponding to $C_1(\mathbf{q})$ and $S_1(\mathbf{q})$ are the same. The parameter γ is chosen to be three, such that the doping density at point C is about 10%, assuming that there is one dopant ion per four carbons along the chain in the $\sqrt{3}\times\sqrt{3}$ phase. The overall structure of the phase diagram is not sensitive to the small variation of the parameter, and in fact the $\sqrt{3}\times\sqrt{3}$ phase is stabilized for any positive γ. The transition line to the left-hand side of point C corresponds to the ordering of $S_1(\mathbf{q})$ and the transition line on the right-hand side to that of $C_1(\mathbf{q})$. Note that the transition temperature from disordered to HB,s corresponds to the criticality of $S_1(\mathbf{q})$ at temperature $T_c=\alpha+\frac{3}{2}\beta$, in agreement with the result of CHM.

The nature of the phase transition can be determined from higher-order terms of the free energy. As explained in Appendix A of CHM, we introduce normal modes x_A, x_B, x_C, y_A, y_B, and y_C to diagonalize the second-order

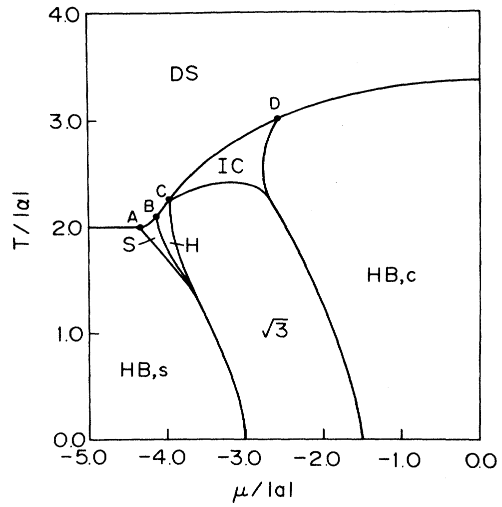

FIG. 2. Phase diagram in the plane of temperature and alkali chemical potential, showing various phases occurring in the process of the alkali doping. Interaction parameters are chosen for $\alpha=-1$, $\beta=2$, and $\gamma=3$. DS, $\sqrt{3}$, HB, S, H, and IC represent orientationally disordered, $\sqrt{3}\times\sqrt{3}$, striped, hexagonally modulated, and incommensurate phases, respectively. The HB,c phase and the HB,s phase imply that $\cos(2\theta)$ and $\sin(2\theta)$ become critical first as the temperature is reduced, respectively. See the text for further details.

terms of the free energy.[3,7] We then minimized F with respect to the y's, which is less critical than the x's in the incommensurate (IC) phase between HB,s and $\sqrt{3}\times\sqrt{3}$, and obtain F in powers of the x's up to the fourth order. After some straightforward algebra, we obtain

$$\begin{aligned} F=F_0+F_{\text{int}}=&\tfrac{1}{2}[T-T_s(\mu)](x_A^2+x_B^2+x_C^2)\\ &+u(x_A^2+x_B^2+x_C^2)^2\\ &+w(x_A^2x_B^2+x_B^2x_C^2+x_C^2x_A^2)\,, \end{aligned} \tag{8}$$

where

$$u=\frac{T}{16}+6R^4b^4\,, \tag{9a}$$

$$w=\frac{b^4R^4n(1-n)\gamma^4}{T^4}\times\left[(1-6n+6n^2)-\frac{6TR^2a^2(1-2n)}{\Gamma_{cc}}\right], \tag{9b}$$

with

$$n=\frac{1}{1+e^{-\mu/T}},\quad R=\frac{\gamma}{2}\frac{n(1-n)}{T}\,,$$

$$a=\left[1+\cos\left(\frac{\pi}{3}t\right)\right]^2 \text{ and } b=3\sin^2\left(\frac{\pi}{3}t\right). \tag{10}$$

In Eq. (10), t varies within 0 to 1, $t=0$ and 1 correspond to HB and $\sqrt{3}\times\sqrt{3}$ phases, respectively. Both of $3u+w>0$ and $u>0$ are satisfied at all μ, which implies that the transition from disordered to ordered phases is continuous. The first term of Eq. (8) is the second-order term of the free energy investigated so far. $T_s(\mu)$ is determined from Eq. (7b). The second and third terms of Eq. (8) are the isotropic and anisotropic part of fourth-order terms with coefficients u and w as given in Eq. (9). Note that the expansion is valid near the transition temperature, except very near the tetracritical point C. Positive w corresponds to a single condensation with one of x_A, x_B, and x_C nonvanishing, while negative w implies a simultaneous condensation of the three. Then $w<0$ $(w>0)$ corresponds to a striped (hexagonal) modulated phase. We find that w is positive at point A and changes sign between points A and C of Fig. 2. Therefore, we have a first-order transition from striped to hexagonally modulated phases within the IC phase between HB,s and $\sqrt{3}\times\sqrt{3}$.

It is straightforward to calculate energies of various periodic structures at zero temperature. We find a first-order transition from HB,s to $\sqrt{3}\times\sqrt{3}$ phases at $\mu_c^{(1)}=3(\frac{1}{2}+\frac{3}{4}\beta-\gamma)$, which is equal to -3 for $\beta=2$ and $\gamma=3$. There is another first-order transition from $\sqrt{3}\times\sqrt{3}$ to HB,c phases at $\mu_c^{(2)}=\frac{3}{2}(-\frac{1}{2}+\frac{5}{4}\beta-\gamma)$, which is equal to $-\frac{3}{2}$ for $\beta=2$ and $\gamma=3$. Combining these energy calculations at zero temperature and the Landau expansion close to the critical temperature, we obtain the phase diagram in the plane of temperature and chemical potential, as shown in Fig. 2. DS, HB,s, $\sqrt{3}$, and HB,c respectively, represent orientationally disordered, herringbone "sine" [in the sense that $S_1(\mathbf{q})$ becomes critical first], $\sqrt{3}\times\sqrt{3}$, and herringbone "cosine" phases. There are IC phases between HB,s and $\sqrt{3}\times\sqrt{3}$, and between $\sqrt{3}\times\sqrt{3}$ and HB,c. Within the IC phase between HB,s and $\sqrt{3}\times\sqrt{3}$, S and H represent striped and hexagonally modulated phases, respectively. The striped phase configuration is schematically shown in Fig. 3(a). A small amplitude of the rotors in the diagram represents the region where the rotors are thermally orientationally disordered, it consists of undoped HB,s phases separated by orientationally disordered regions. A hexagonally modulated phase is shown in Fig. 3(b), a hexagonal network of domain walls separates three states of the $\sqrt{3}\times\sqrt{3}$ phase. The dopants go into the open galleries formed by the rotors. The period of modulations of both of these incommensurate phases varies continuously as the temperature and chemical potential are varied.

In our mean-field calculation, the doping-induced structural phase transition proceeds from the undoped herringbone to the $\sqrt{3}\times\sqrt{3}$ phase via striped and hexagonally modulated phases. Both of the striped and hexagonally modulated phases are incommensurate ones, and their periods vary continuously as the temperature and chemical potential are varied. Because their symmetry groups are not related to each other, the transition from one to the other phase is first order. It is interesting to note that the transition from striped to hexagonally modulated phases is first order and occurs at about 6% doping level, where the first-order-like "insulator-metal" transition[8] was observed. It will be very interesting to investigate the possible interplay between these transitions. In the x-ray scattering experiment of Na-doped *trans*-$(\mathrm{CH})_x$, however, Winokur *et al.* observed that the doping induces a structural transition from the HB,s to the $\sqrt{3}\times\sqrt{3}$ phase via disordered and hexagonally modulated phases.[2] We should point out that an important parame-

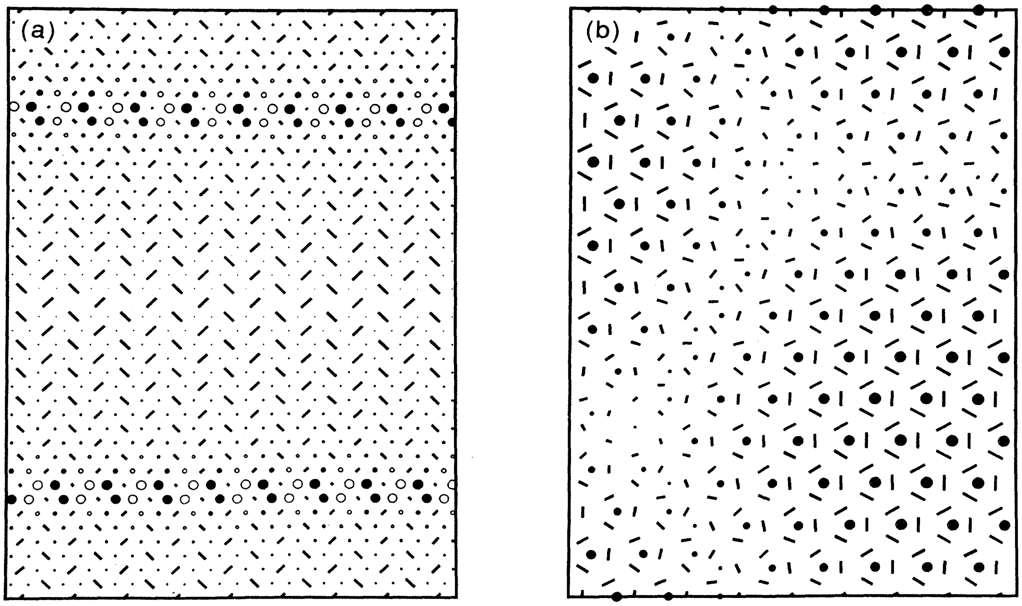

FIG. 3. Schematic diagram of S and H phases of the phase diagram shown in Fig. 2. The periods of modulation of these phases vary continuously as the temperature and the chemical potential are varied. A small amplitude of a rotor represents the orientationally disordered region, and the size of a circle is approximately proportional to the excessive density of dopants. (a) is for the striped phase, where a solid circle represents excessive doping density and an open circle depleted density. (b) is for a hexagonally modulated phase, where a hexagonal network of domain walls separates three states of the $\sqrt{3}\times\sqrt{3}$ phase.

ter in comparing our mean-field calculation with experimental observations is the correlation length ξ along the chain direction for the orientation of the $(CH)_x$ chain. If ξ is much larger compared with a lattice constant, then the mean-field analysis presented in this paper is appropriate. On the other hand, if ξ is comparable with the lattice constant, then the fluctuation effects neglected in this treatment should be important. We expect that in this case there may be a disordered region between the HB,s and $\sqrt{3}\times\sqrt{3}$ phases extending down to the low-temperature region, as was first pointed out by Coppersmith *et al.*[9] Further research including both of these ordering phenomena will be quite interesting.

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[4] We should also include a dipole moment in addition to the quadrupole moment to represent the chain, because a polymer chain is not perfectly symmetric under a rotation by π with respect to the chain axis. However, because of the dominance of quadrupole over dipole moments, it does not make any difference close to the critical temperature if we do not include the dipolar interaction.

[5] In the x-ray diffraction experiment on Na-doped $(CH)_x$, (020) and (110) peaks are always very close to each other (Ref. 2), which implies that the underlying triangular lattice is preserved. Therefore, translational displacements are not important in the process of structural modulations of Na-doped *trans*-$(CH)_x$.

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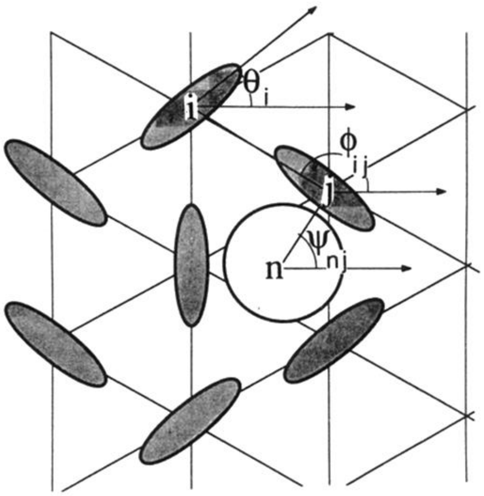

FIG. 1. Schematic diagram of the $(CH)_x$ structure with a dopant ion labeled *n*, projected along the chain direction. The polymer chain labeled *i* is represented by a rotor on a 2D triangular lattice, with a setting angle θ_i with respect to the *x* axis. The rotors orient themselves to open a gallery for the dopant.