Incommensurate superstructures in organic conductors with three-dimensional electronic spectra

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The stability of quasi-one-dimensional conductors with a half-filled band against structural transitions is investigated. It is shown that, under quite general assumptions about the form of the transverse characteristics of the electronic spectrum, the expected structural transition corresponds to the appearance of incommensurate lattice deformations. In its turn, a system that has undergone a dielectric Peierls transition can, under pressure, become unstable against spontaneous soliton-wall formation as a result of the change in the tunneling integrals. A mathematical formulation is proposed which allows a complete description of the resulting new incommensurate phase, and it is shown that the indicated mechanism leads to the appearance of a special type of free carriers in the system.

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INTRODUCTION

In the present paper we consider the Peierls structural transition in organic conductors with a half-filled band: such a transition is often referred to as the appearance of a 1:2 commensurate superstructure corresponding to the doubling of the lattice constant. Below we shall show that the weakly three-dimensional character of the electronic spectrum facilitates the development of incommensurate structures, specifically, the appearance of domain walls. We can essentially indicate two physical mechanisms for this phenomenon. Because of the congruence of the Fermi surfaces for the electrons,[1–3] the appearance of a dielectric gap makes the Peierls transition into the new phase energetically advantageous. The first mechanism consists in the fact that, if the Fermi surfaces are not entirely congruent, then the greatest advantage in energy terms is gained through the optimum choice of the nesting vector for the various sections of the Fermi surface.[4] The second mechanism is the spontaneous production of soliton walls, when the energy of production of the soliton state on one filament is canceled out by the kinetic broadening of the state in the transverse direction.[5] The two mechanisms are related to each other, owing to the fact that the pinning energy in the case of a half-filled band is comparable to the energy gained in the structural transition.

Our aim is to list the factors that facilitate the occurrence of the phenomenon, and formulate a method by which we can, in principle, study such transformations into the incommensurate structure under conditions of finite deformation. Below we show that the corresponding formulas are a natural generalization of the mathematical methods developed in the so-called soliton physics.[6,7]

Thus far, the soliton solutions on one filament of polyacetylene (see Refs. 8 and 9 for reviews) have usually been studied in connection with the unusual magnetic properties of the latter, properties which are apparently due to defects.[10] Let us emphasize again that in the present paper, in contrast to Refs. 6–10, we are interested in the thermodynamically advantageous structures in a real crystal with a three-dimensional electronic spectrum. The tunneling overlap integrals for organic materials are not too small (usually 50–150 K), and are of the order of the phonon frequencies and (or) the dielectric-transition temperature itself. The crystals of polyacetylene $(CH)_x$ are one example of a Peierls dielectric with a doubled lattice constant (i.e., with two filaments per unit cell[11]). To the same class of compounds with a half-filled band pertain, strictly speaking, materials of the type $(TMTSF)_2PF_6$ (Ref. 12) and $(TTT)_2I_3$ (Ref. 13), although the dimerization in this case is slight, and they are closer to materials with a quarter-filled band.[14]

We do not go outside the framework of a qualitative analysis, and do not study those rather complicated three-dimensional characteristics of the electronic spectrum which are manifestable in the indicated materials. In equal measure, we consider the structural transition to be a well-defined three-dimensional transition, ignoring the problem of the possible role of the fluctuations. We shall presently formulate the conditions for this.

I. THE MODEL

We shall, in accordance with the foregoing, at once consider the three-dimensional elastic properties of the lattice. In other words, the dispersion $\Delta\omega_0^2$ in the initial phonon spectrum

$$\omega_0^2(q)=\omega_0^2(2k_F,\ 0)+\Delta\omega_0^2(2k_F,\ \mathbf{k}_\perp), \tag{1}$$

is not assumed to be small:

$$\Delta\omega_0^2\sim\omega_0^2. \tag{1'}$$

Owing to this circumstance, the structural transition possesses, according to Refs. 15 and 16, a well-defined transition point T_c, and the fluctuations are weak outside the neighborhood

$$|(T-T_c)/T_c|>g_{ph}^4\omega_0^2/\Delta\omega_0^2\ll1. \tag{2}$$

The relations (1) and (2) enable us to study the characteristics of the structural transition as functions of the properties of the electronic spectrum. The latter could be entirely one-

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dimensional (plane Fermi surfaces). Strictly speaking, when the overlap of the wave functions of the electrons on neighboring chains is slight, the electron interactions should be considered within the framework of the parquet approximation,[15,17] but, let us repeat once more, below we discuss a Peierls-type structural transition whose origin is connected with the appearance of a soft mode (i.e., the onset of lattice instability). Under these conditions, it is sufficient to limit ourselves in a qualitative analysis of the phonon spectrum to the simplest diagram, shown in Fig. 1, for the polarization operator, i.e., we can generally neglect the interelectron interaction. Conceptually, with the assumptions made, our model and the so-called nesting model[1-3] do not differ in any way, except in certain characteristics stemming from the strong anisotropy of the electronic spectrum.

Among the latter is the assumption that electronic spectrum is characterized by two nearly plane Fermi surfaces near the points $p_{\parallel} = \pm k_F$. As has been assumed, the electronic spectra in the neighborhoods of these sections respectively have the form

$$\varepsilon_{1,2}=\pm v_F(p_{\parallel}\mp k_F)\pm t_{1,2}(\mathbf{p}_{\perp}). \tag{3}$$

The general relation $\varepsilon(-\mathbf{p}) = \varepsilon(\mathbf{p})$ imposes on (3) only the condition

$$t_1(-\mathbf{p}_{\perp})=-t_2(\mathbf{p}_{\perp}),$$

which introduces additional complications (see below) when there is no symmetry with respect to $p_{\parallel}\to -p_{\parallel}$. It is further assumed everywhere that the structural transition corresponds to $\mathbf{k}_{\perp} = 0$. In the tight-binding model[18] total nesting (coincidence of the Fermi surfaces) would correspond to the doubling of the lattice constant in the perpendicular direction as well. In order to make such a reconstruction disadvantageous, we shall henceforth assume that $\Delta\omega_0^2(2\kappa_F,\mathbf{k}_{\perp})>0$ in (1). Finally, let us recall that we are considering the case of strong (i.e., 1:2) commensurability, in which $2k_F = \pi/a$ (a is the initial lattice constant). We shall, allowing for this last circumstance, write the expression for the renormalized (on account of the electrons) phonon frequency in the form[19]

$$\omega^2(\mathbf{q})=\omega_0^2(\mathbf{q})-{}^1/_2[\Pi(\mathbf{q})+\Pi(\mathbf{q}-\mathbf{Q})], \tag{4}$$

where we have, for simplicity, chosen the reciprocal lattice vector $\mathbf{Q}$ as $\mathbf{Q} = (2\pi/a, 0, 0)$.

II. CHARACTERISTICS OF THE PHASE DIAGRAM1)

In this section we investigate the characteristics of the phase diagram determined by the condition

$$\omega^2(\mathbf{q})=0. \tag{4'}$$

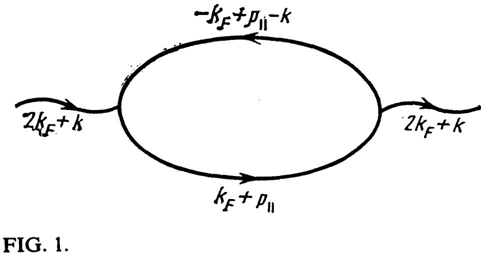

FIG. 1.

In principle, the condition (4′) determines both the structural transition temperature and, in general, the stability threshold of the normal phase as a function of the "doping" and the magnitude of the tunneling integrals, which simulates the pressure dependence. Of greatest interest here is, as it seems to us, the appearance of superstructures due to the three-dimensional character of the electronic spectrum. We shall first attempt to follow the tendency toward this phenomenon by studying the possibility of an instability in (4′) against the appearance of an incommensurate phonon vector

$$q_{\parallel}=\pi/a+k. \tag{5}$$

Let us, for simplicity, write the condition for the band to contain one electron as

$$\langle t_{1,2}(\mathbf{p}_{\perp})\rangle=0, \tag{6}$$

where the brackets denote averaging along the Fermi surface. Then $2k_F = \pi/a$. Using (6), we can take the doping into consideration by introducing a small change into the Fermi momentum:

$$k_F=\pi/2a+\delta. \tag{7}$$

Let us at once stipulate that first-order transitions are possible in the system at arbitrary $t_{1,2}(\mathbf{p}_{\perp})$. In this case Eq. (4′) is meant for the determination of the relative disposition of the boundaries of the metastable regions.

The standard computations of the polarization operator depicted in Fig. 1 will lead us to the following form of the condition (4′) (below we use a system of units in which $v_F = 1$)

$$\ln\frac{T_c}{T_{c0}}=\frac{1}{4}\left\langle\left[4\psi\left(\frac{1}{2}\right)-\psi\left(\frac{1}{2}+\frac{k+2tf+2\delta}{4\pi iT_c}\right)\right.\right.$$
$$\left.\left.-\psi\left(\frac{1}{2}+\frac{-k+2tf+2\delta}{4\pi iT_c}\right)-\text{c.c.}\right]\right\rangle, \tag{8}$$

where T_{c0} is the transition temperature when $t = \delta = k = 0$ and the function f is defined as

$$tf(\mathbf{p}_{\perp})={}^1/_2[t_1(\mathbf{p}_{\perp})-t_2(\mathbf{p}_{\perp})]. \tag{9}$$

1. The stability threshold at $T = 0$. Letting $T_c\to 0$ in (8), or recalculating (at $T = 0$) the polarization operator, we can rewrite the stability condition for the normal phase at absolute zero in the form

$$\langle\ln\{|4(tf+\delta)^2-k^2|(\gamma/\pi T_{c0})^2\}\rangle=0 \tag{8'}$$

(where γ is the Euler constant).

Let $t = 0$ (the one-dimensional problem). The residual relation

$$k^2=4\delta^2\pm(\pi T_{c0}/\gamma)^2 \tag{10}$$

describes the pinning: the instability vector does not coincide with the doubled vector $2k_F$. Qualitatively, this was first pointed out in Ref. 19. The expression (10) will figure below.

Now let there be no doping ($\delta\equiv 0$), i.e., let the unit cell contain one electron. There nevertheless remains the nontrivial dependence on k in Eq. (8′). At high $t\gg T_{c0}$ the system corresponds to a $3D$ anisotropic metal. As t (i.e., the degree of transverse overlapping) is decreased, the instability may first manifest itself as an incommensurate wave with

$k^*=k(t_{cr})\neq 0$. We shall demonstrate the fact, noted in Ref. 4, that such a situation is quite a general case by assuming that f is a step function (i.e., that $f=\pm 1$) at various parts of the cross section of the Brillouin zone [the areas of these parts should be equal in order for the fulfillment of the electrical neutrality condition (6) to be ensured]. Instead of (10), we shall derive the same equation with δ replaced by t. In the (k, t) plane this equation bounds the instability region with asymptotes that go out to infinity. A slight smoothing out of the step in the electron dispersion law will clearly lead to the situation depicted in Fig. 2.

For the purpose of investigating the more realistic dispersion law, which can arise in specific examples, it is convenient to transform (8′) (for $\delta=0$), using the following formula from Ref. 20:

$$\ln(2|\alpha|)=\int_0^\infty [J_0(x)-\cos(\alpha x)]\frac{dx}{x}. \tag{8''}$$

As a result, instead of (8′), we obtain

$$\ln\frac{t}{t_0}+2\int_0^\infty\frac{dx}{x}\langle\cos(xtf)\rangle\sin^2\frac{kx}{4}=0, \tag{11}$$

where t_0 (the stability threshold for $k=T_c=0$) is determined from the equation

$$\langle\ln(2t_0|f|\gamma/\pi T_{c0})\rangle=0. \tag{11'}$$

For the tight-binding model in the two-dimensional case, in which $f=-\cos(pa)$, the averaging over the period $(-\pi/a<p<\pi/a)$ yields the Bessel function $J_0(tx)$ under the integral sign in (11). The integration is performed in the final form. As a result, we obtain the curve shown in Fig. 3, and determined by the equations (in which $t_0=\pi T_{c0}/\gamma$)

$$t=t_0,\qquad k<2t,$$
$$k=t_0(1+t^2/t_0^2),\quad k>2t.$$

Thus, in the two-dimensional case (i.e., for a plane filled with filaments) stability arguments in the tight-binding model do not determine the symmetry (periodicity) of the dielectric phase at all.

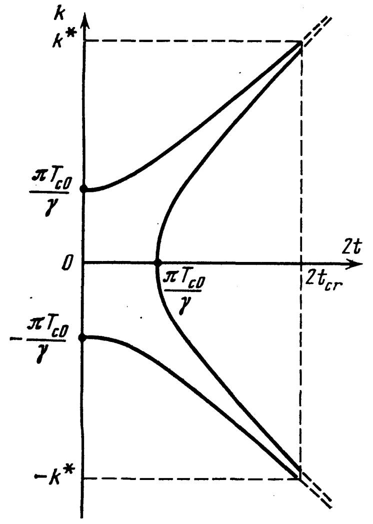

FIG. 2.

The dispersion law

$$f(p_x,\ p_y)=-\cos(p_xa)-\cos(p_ya)$$

for the three-dimensional (3D) tight-binding model of the square lattice gives us, upon being substituted into (11), the equation

$$\ln\frac{t}{t_0}+2\int_0^\infty\frac{dx}{x}J_0^2(tx)\sin^2\frac{kx}{4}=0. \tag{12}$$

The positiveness of the integral term in (12) shows that $t<t_0$ for any k, i.e., the boundary curve in the (k, t) plane has here the shape of the dashed curve in Fig. 3, thus attesting the commensurate character of the ground state for $t<t_0$. In the vicinity of $k=0$ the dashed curve behaves like

$$t-t_0=-k/4, \tag{13}$$

contrary to the quadratic behavior expected in Ref. 4. The cause of this discrepancy lies in the asymptotic expansion performed in Ref. 4, where the integration of the singular denominators [see the formula (5) from Ref. (4)] should be performed with some care.

We shall not cite any more specific examples of the dispersion law, since the foregoing is sufficient for us to understand that the following two cases are possible in real materials: the asymptotic law depicted in Fig. 2 and the above-given behavior (12) in the tight-binding 3D model. For completeness we show in Fig. 3 by the dot-dash curve the schematic behavior of the stability threshold in the case, of interest to us here, in which incommensurate structures arise. It follows from the shape of the curve that the condition $[\partial t(k)/\partial k]_{k=0}>0$ is a sufficient condition for their appearance, although not a necessary one, as demonstrated by the dotted curve, which is quite probable at any stage of the dispersion.

The sign of the derivative $[\partial t(k)/\partial k]_{k=0}$ is determined, according to (8′) or (11), by the characteristics of the vanishing of the function $f(p_x, p_y)$. If $f(p_x, p_y)=0$ on some line, and the gradient of the function in the direction perpendicular to this line is everywhere finite, then $t(k)$ is quadratic in k in the vicinity of $k=0$, although the sign of the coefficient attached to k^2 depends on the entire function as a whole (the sign is positive if the transverse gradients are large). If the function $f(p_x,p_y)$ vanishes when it possesses a saddle point, then the slope is linear in k, a fact which was demonstrated above in the tight-binding 3D model.

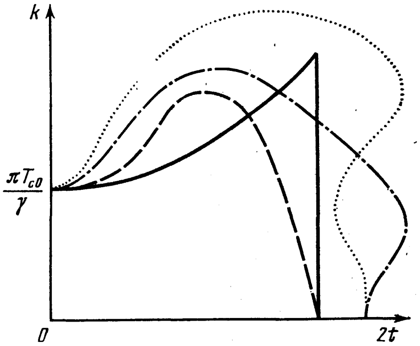

FIG. 3.

2. The transition temperature. In principle, for a fixed overlap t the system can go directly into the incommensurate phase as the temperature is lowered. But, in order to solve such a problem, we must fully investigate the shape of the instability surface $T_c(t, k)$ as determined by the conditions (4′) and (8). We limit ourselves to indicating the correspondence between the previous results and the shape of the indicated surface for $T_c \to 0$. Let us note that the expansion of the function $t(k)$ in powers of k at $T_c = 0$ was performed on the basis of Eq. (8′), which it is convenient to rewrite with the aid of (11′) in the form (when $\delta = 0$)

$$\ln\frac{t}{t_0}+\frac{1}{2}\left\langle \ln\left|\frac{f^2-k^2/4t^2}{f^2}\right|\right\rangle=0. \tag{14}$$

Using the explicit representations of $\psi(x)$, we can easily reduce the general formula (8) to a form extremely suitable for the investigation of the general character of the $T_c(k, t)$ surface at low T_c. Thus, when $k = \delta = 0$,

$$\ln\frac{t}{t_0}+\frac{1}{2}\int\limits_0^\infty\left\langle \ln\left|1-\frac{z^2}{f^2}\right|\right\rangle \operatorname{ch}^{-2}\left(\frac{tz}{2T_c}\right)\frac{t\,dz}{2T_c}=0. \tag{15}$$

If $t \gg T_c$, the dominant role in the integral in (15) is played by the small $z \sim T_c/t$. Comparing with (14), we see that, if the stability curve has the requisite bend, then T_c as a function of t also has a branch in the region $t > t_0$. This behavior is depicted in Fig. 4 in the (T_c, t) plane. It is also easy to verify that the curve in the $t = 0$ plane always has the shape shown in the same figure. The tight-binding model in the $3D$ case naturally yields a linear slope, which is shown in Fig. 3 by the dashed curve. In the $2D$ case $f = -\cos(pa)$, and we find from (15) after simple calculations that

$$T_c\approx t_0\left|\ln\frac{t_0-t}{t_0}\right|^{-1}\quad (t<t_0).$$

The two-valued $T_c(t)$ branch (for $k = 0$) indicates either a first-order phase transition from the normal into the dielectric phase, or a maximum T_c value (for a given t) corresponding to $k^* \neq 0$.

3. Commensurate dielectric phase at $T = 0$. For completeness of the picture, let us discuss how the system might behave if it started from the dielectric phase ($T = 0$). For $t = 0$ the energy spectrum of the electrons in the commensurate phase has the gap

$$\Delta_0=\pi T_{c0}/\gamma. \tag{16}$$

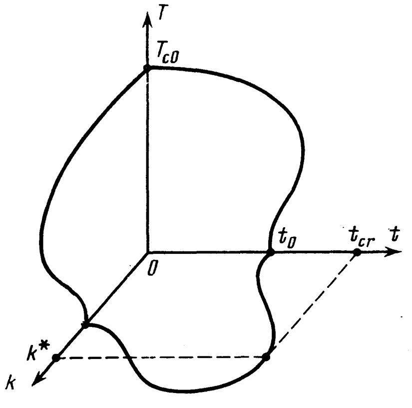

FIG. 4.

For a finite t the energy spectrum consists of two branches:

$$\varepsilon_{1,2}=\delta\mu+tf\pm(\Delta^2+u^2)^{1/2}, \tag{17}$$

where

$$u=p_\parallel+{}^1/_2[t_1(\mathbf{p}_\perp)+t_2(\mathbf{p}_\perp)]. \tag{17′}$$

The chemical-potential shift $\delta\mu$ occurs on account of the indirect gap if the bottom of the "conduction band" and the top of the "valence band" asymmetrically shift, as a result of the transition to (17), relative to the old reference point. This circumstance introduces significant complications into any specific computation; therefore, below we assume, for simplicity, a spectrum such that $\delta\mu \equiv 0$. The analytic form of the difference

$$\Delta E=E_{\text{csw}}-E_{\text{met}}$$

between the electron energies in the metallic phase and the state with a commensurate structural wave depends on the relation between the quantity $tf_{\max}$ and Δ, i.e., on whether the system is a dielectric or it contains electron-hole "pockets", causing it to behave like a semimetal. In the first case

$$\Delta E=-\frac{1}{\pi}\left[\frac{\Delta^2}{2}+\Delta^2\ln\frac{2E^*}{\Delta}-\langle t^2(\mathbf{p}_\perp)\rangle\right]. \tag{18}$$

When $tf_{\max} > \Delta$, we have

$$\Delta E=-\frac{1}{\pi}\left[\frac{\Delta^2}{2}+\Delta^2\ln\frac{2E^*}{\Delta}\right]+\frac{1}{\pi}\langle t^2(\mathbf{p}_\perp)\rangle+\frac{1}{\pi}\int\limits_{|t(\mathbf{p}_\perp)|>\Delta}\frac{d\mathbf{p}_\perp}{S}\times\left[-|t(\mathbf{p}_\perp)|[t^2(\mathbf{p}_\perp)-\Delta^2]^{1/2}+\Delta^2\ln\frac{|t(\mathbf{p}_\perp)|+[t^2(\mathbf{p}_\perp)-\Delta^2]^{1/2}}{\Delta}\right], \tag{18′}$$

where E^* is the cutoff parameter and S is the cross-sectional area of the unit cell.

Adding to (18) and (18′) an elastic term, E_{el}, proportional to Δ^2/g_{ph}^2, and varying the resulting expressions with respect to Δ, we see that, for $tf_{\max} < \Delta$, the quantity $\Delta = \Delta_0$. The energy difference (18) depends, of course, on t, and, as t increases, the system eventually goes over into the metallic state. How this transition occurs depends on the characteristics of the electronic spectrum. Let us assume that $tf_{\max} > \Delta_0$, and that the system contains electron-hole pockets. Varying (18′) with respect to Δ, we obtain a condition for the determination of the the gap in the form

$$\ln\frac{\Delta}{\Delta_0}+\int\limits_{|t(\mathbf{p}_\perp)|>\Delta}\frac{d\mathbf{p}_\perp}{S}\operatorname{arch}\left[\frac{|t(\mathbf{p}_\perp)|}{\Delta}\right]=0. \tag{19}$$

For the purpose of carrying out specific calculations, it is again convenient to transform (19), using the representation (see Ref. 20)

$$\int\limits_0^\infty[1-\cos(\alpha x)]J_0(\beta x)\frac{dx}{x}=\begin{cases}\operatorname{arch}(|\alpha|/|\beta|), & |\beta|<|\alpha|,\\ 0 & |\beta|>|\alpha|.\end{cases}$$

We obtain

$$\ln\frac{\Delta}{\Delta_0}+\int\frac{dx}{x}[1-\langle\cos(xtf)\rangle]J_0(\Delta x)=0. \tag{20}$$

Let us set $t^*f_{\max} = \Delta_0$. Let the pockets for $t > t^*$ have the form of ellipsoids in the neighborhoods of the corresponding

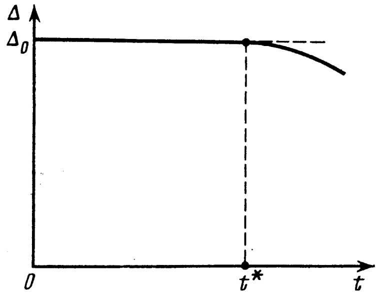

FIG. 5.

maximum and minimum points:

$$|f-f_{max}|=(\alpha p_x^2+\beta p_y^2)/S.$$

In this case the appearance of pockets represents the so-called Lifshitz 2.5-order transition, and the behavior of Δ, given by

$$\frac{\Delta-\Delta_0}{\Delta_0}=-\frac{4\pi}{3(\alpha\beta)^{1/2}}\left(\frac{2t^*}{\Delta_0}\right)^{1/2}\left(\frac{t-t^*}{t^*}\right)^{3/2}, \tag{21}$$

is depicted in Fig. 5. Two simple examples show that the situation can be complicated. Choosing, as was done above, a step Fermi surface, we obtain two solutions directly from (19):

$$\Delta=\Delta_0,\quad t<\Delta,\qquad \Delta=\Delta_0(2t/\Delta_0-1)^{1/2},\quad t>\Delta,$$

which clearly indicates a first-order phase transition. Indeed, it follows from the expression (18) for $E=E_{\rm el}+\Delta E$ that it is more advantageous for the system to be in the metallic state (with $k=0$) when $t>\Delta_0/\sqrt{2}$. At the same time, according to Eq. (10) (with δ replaced by t), the metallic state is unstable! We conclude from this that the transition into the incommensurate state is possible in the case of a more realistic Fermi surface that nevertheless bears the features of this steplike curve (large gradients of f).

The second example is the tight-binding $2D$ model: $f=-\cos(pa)$. The integral with two Bessel functions in (20) yields the step:

$$\Delta=\Delta_0=\pi T_{c0}/\gamma,\quad t<\Delta,$$
$$t=\Delta_0,\quad t>\Delta.$$

[In this case $\beta\equiv0$ in (21).]

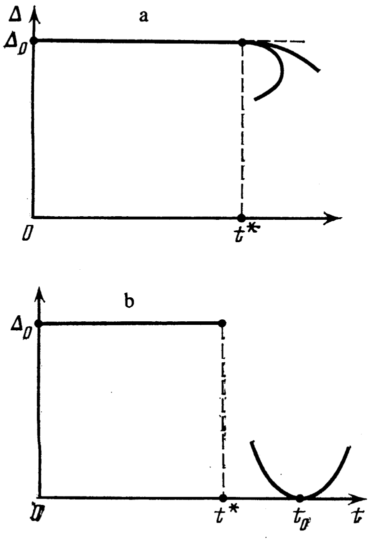

FIG. 6.

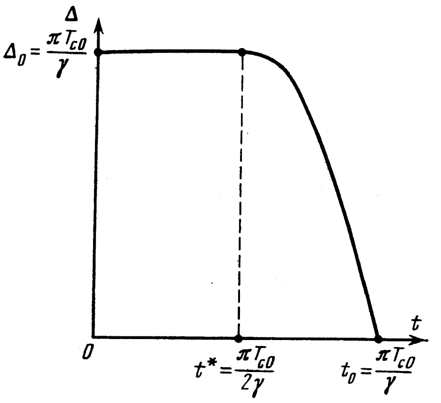

FIG. 7.

Figure 6(a) depicts the possible behavior of Δ beyond the point t^* after the appearance of the pockets; Fig. 6(b), the behavior near the point t_0. Let us point out that the appearance of the $\Delta(t)$ branch in the region $t>t_0$ is uniquely connected with the corresponding knee of the instability curve for $T=0$ [Eq. (11)] by the relation

$$\ln\frac{t}{t_0}+\frac{4}{\pi}\int_0\frac{dy}{(1-y^2)^{1/2}}\int_0^\infty\frac{dx}{x}\langle\cos(tfx)\rangle\sin^2\left(\frac{\Delta xy}{2}\right)=0,$$

which is obtained by combining (11), (11′), and (8′) with Eq. (20) ($\Delta_0=\pi T_{c0}/\gamma$). Let us emphasize that the relative disposition of t_0 and t^* depends on the model.

According to (11′), in the case of the tight-binding $3D$ model we have

$$t^*=\pi T_{c0}/2\gamma=t_0/2.$$

The form of the solution for $\Delta(t)$ is shown in Fig. 7 in accordance with (13), which indicates a second-order phase transition region. Because of the complexity of the integration in (18) and (18′), we did not seek the transition points. Summarizing the results obtained in this section, we note the following. We have shown that a comparison of our results regarding the stability of a $3D$ anisotropic metal with the properties of the dielectric phase reveals such behavior of $T_c(t)$ and $\Delta(t)$ which allows us to believe that the pressure-induced structural phase transitions often have in realistic models the character of second-order transitions, and (or) are associated with the appearance of an incommensurate phase.[2)] The mechanism underlying the formation of incommensurate structures in a system initially in the dielectric phase, i.e., the spontaneous formation of soliton walls, is found in Ref. 5.

III. THE INCOMMENSURATE SUPERSTRUCTURE

The question arises whether it is possible, at least in principle, to compare the energies of the various phases, and determine the character of the transition, for which purpose we need first and foremost a mathematical method that allows us to find the free energy of the incommensurate phase in the case of a finite value of the distortion. The key point is the fact that the distortion (or the "gap") is incommensurate only in respect of the longitudinal component of the wave vector, i.e., the superstructure depends on one coordinate. Because of this, it is possible to generalize for the study of the properties of organic conductors with a 3*D* electronic spectrum the mathematical tools developed for the construction of soliton solutions in one-dimensional physics.[6,7]

Let us explain these ideas by demonstrating again how they are connected with the three-dimensional character of the phonon spectra. Indeed, in the inhomogeneous phase, the lattice distortion has, generally speaking, the form

$$V(\mathbf{r})\sim\sin\left(\frac{\pi x}{a}\right)\sum_{\mathbf{k}_\perp}\Delta_{\mathbf{k}_\perp}(x)\exp(i\mathbf{k}_\perp\mathbf{r}_\perp), \qquad (22)$$

where the $\Delta\,\mathbf{k}_\perp(x)$ are slowly-varying functions of the coordinate x. Then the energy functional of the system (at zero temperature) can be written in the form

$$W=\int\limits_{E(\mathbf{p}_\perp)<\mu}\frac{d\mathbf{p}_\perp}{S}\sum E(\mathbf{p}_\perp)+\sum_{\mathbf{k}_\perp}\int dx\,\frac{|\Delta_{\mathbf{k}_\perp}(x)|^2}{g^2}$$
$$+\sum_{\mathbf{k}_\perp}\int dx\,|\Delta_{\mathbf{k}_\perp}(x)|^2\left(-\frac{1}{g^2}+\frac{1}{g^2_{\mathbf{k}_\perp}}\right), \qquad (23)$$

where the $E(\mathbf{p}_\perp)$ are the transverse-momentum ($\mathbf{p}_\perp$) dependent energy levels in the field $V(\mathbf{r})$;$g_{\mathbf{k}_\perp}$ is the electron-phonon interaction constant, g being the maximum value of the function $g_{\mathbf{k}_\perp}$. We can assume without loss of generality that $g=g|_{\mathbf{k}_\perp=0}$ and $\delta g^2_{\mathbf{k}_\perp}\sim g^2\ll 1$.

As usual, in consequence of the cancellation of the logarithmic contributions, the first two terms in (23) together are of the same order of magnitude as Δ^2, whereas the last term is of the order of

$$\Delta^4\delta g_{\mathbf{k}_\perp}^4/g^4\gg\Delta^2.$$

(The dispersion $\delta g^2_{\mathbf{k}_\perp}$ of the dimensionless interaction amplitude includes, generally speaking, the dispersions of both the phonon frequency and the interactions themselves.)

Let us write the electron wave functions in the deformation field (1) in the form ($\mathbf{k}_\perp=0$)

$$\psi_{\mathbf{p}_\perp}(x)=\psi_{\mathbf{p}_\perp+}(x)\exp(i\pi x/2a)+\psi_{\mathbf{p}_\perp-}(x)\exp(-i\pi x/2a),$$

where the $\psi_{\mathbf{p}\perp\pm}(x)$ are slowly-varying—in comparison with the atomic scale—functions of x that satisfy the equations

$$[-id/dx+t_1(\mathbf{p}_\perp)-E(\mathbf{p}_\perp)]\psi_{\mathbf{p}_\perp+}(x)+i\Delta(x)\psi_{\mathbf{p}_\perp-}(x)=0, \qquad (24)$$
$$[id/dx-t_2(\mathbf{p}_\perp)-E(\mathbf{p}_\perp)]\psi_{\mathbf{p}_\perp-}(x)-i\Delta(x)\psi_{\mathbf{p}_\perp+}(x)=0.$$

Let us make the following change of variables in (24):

$$\psi_{\mathbf{p}\perp\pm}(x)=\psi_\pm(x)\exp[-it^-(\mathbf{p}_\perp)x], \qquad E(\mathbf{p}_\perp)=E+t(\mathbf{p}_\perp),$$
$$t^-(\mathbf{p}_\perp)={}^1/_2[t_1(\mathbf{p}_\perp)+t_2(\mathbf{p}_\perp)], \qquad t(\mathbf{p}_\perp)=[t_1(\mathbf{p}_\perp)-t_2(\mathbf{p}_\perp)]/2.$$

Then the functional (23) has the form

$$\frac{W}{L}=\frac{\langle\Delta^2\rangle}{g^2}+\frac{1}{L}\int\limits_{E<\alpha(\mathbf{p}_\perp)}\frac{d\mathbf{p}_\perp}{S}\int\frac{dN}{dE}[E+t(\mathbf{p}_\perp)]dE, \qquad (25)$$
$$\alpha(\mathbf{p}_\perp)=\mu-t(\mathbf{p}_\perp).$$

Here L is the length of the system, dN/dE is the density of states, and E is the eigenvalue of the Hamiltonian

$$\hat{H}=i\begin{pmatrix}-\dfrac{d}{dx} & \Delta(x)\\ -\Delta(x) & \dfrac{d}{dx}\end{pmatrix},\quad \hat{H}\psi=E\psi,\quad \psi=(\psi_+,\psi_-). \qquad (26)$$

The functional (25), (26) is similar to the earlier investigated[6,7] functional of the one-dimensional Peierls model. It is well known that functionals of this type have extrema in the class of the so-called finite-band potentials $\Delta(x)$ (see Ref. 7). Let us consider the simplest case of potentials with two forbidden bands. To it corresponds a lattice deformation of the form of a single-phase superstructure:

$$\Delta(x)=\Delta_k\,\mathrm{sn}(x\Delta_k/k,\ k),$$

where sn is the elliptic sine and Δ_k and k are parameters to be determined. In this case the electronic spectrum (26) has two forbidden $E^2_-<E^2<E^2_+$ and three allowed $E^2>E^2_+$, $E^2<E^2_-$ bands (Fig. 8).

The parameters Δ_k, k and E_+, E_- are connected by the following relations[6]:

$$k=(E_+-E_-)/(E_++E_-), \qquad \Delta_k=E_+-E_-.$$

The number of states in the central band is equal to $2n$, where

$$n=E_+/K(r), \qquad r=(E_+^2-E_-^2)^{1/2}/E_+.$$

According to Ref. 7, the density of states is equal to

$$\frac{1}{L}\frac{dN}{dE}=\frac{2|E(E^2-C)|}{\pi R^{1/2}(E^2)}, \qquad C=\frac{E(r)}{K(r)}E_+^2,$$

$$R(E^2)=E^2(E^2-E_-^2)(E^2-E_+^2),$$

and $E(r)$ and $K(r)$ are complete elliptic integrals.

As in the one-dimensional case,[6,7] the following self-consistency condition obtains here:

$$\frac{1}{g^2}+\frac{1}{\pi}\int\limits_{E<\alpha(\mathbf{p}_\perp)}\int dE\,\frac{d\mathbf{p}_\perp}{S}\,\frac{E\,\mathrm{sign}(E^2-E_-^2)}{[(E^2-E_-^2)(E^2-E_+^2)]^{1/2}}=0. \qquad (27)$$

Under the condition (27) the system's energy (25) is equal to

$$W=\frac{1}{2\pi}\left[-E_+^2-E_-^2+4E_+^2\frac{E(r)}{K(r)}\right]+2n\int\limits_{t(\mathbf{p}_\perp)<\mu}\frac{d\mathbf{p}_\perp}{S}t(\mathbf{p}_\perp)$$
$$-\frac{1}{\pi}\int\limits_{|\alpha(\mathbf{p}_\perp)|<E_-}\frac{d\mathbf{p}_\perp}{S}[(E_-^2-\alpha^2)(E_+^2--\alpha^2)]^{1/2}$$
$$+\left(\int\limits_{-E_-<\alpha(\mathbf{p}_\perp)<0}-\int\limits_{E_->\alpha(\mathbf{p}_\perp)>0}\right)\frac{d\mathbf{p}_\perp}{S}t(\mathbf{p}_\perp)\Phi(\mathbf{p}_\perp), \qquad (28)$$

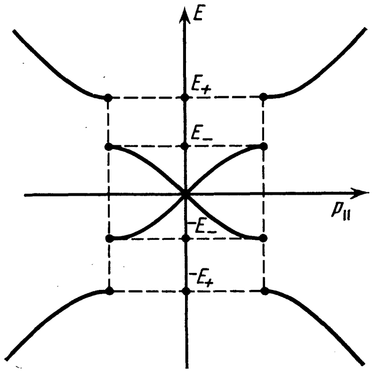

FIG. 8.

where

$$\Phi(\mathbf{p}_\perp)=\frac{1}{L}\int\limits_{|\alpha(\mathbf{p}_\perp)|}^{E_-}\frac{dN}{dE}dE=\frac{2}{\pi}\left\{E_+\frac{E(r)-K(r)}{K(r)}F\left(\varphi,\frac{E_-}{E_+}\right)\right.$$
$$\left.+E_+E\left(\varphi,\frac{F_-}{E_+}\right)-|\alpha|\left(\frac{E_-^2-\alpha^2}{E_+^2-\alpha^2}\right)^{1/2}\right\},$$
$$\varphi=\arcsin\left[\frac{E_+}{E_-}\left(\frac{E_-^2-\alpha^2}{E_+^2-\alpha^2}\right)^{1/2}\right] \qquad (29)$$

and $F(\varphi, E_-/E_+)$ and $E(\varphi, E_-/E_+)$ are elliptic integrals.

In the one-dimensional problems considered earlier,[6,7] the inhomogeneous state arose as a result of a change in the electron concentration. In this case the chemical potential μ always lay in the forbidden band. The two free parameters E_+ and E_- were determined in terms of the given electron concentration n and from the self-consistency condition.

In the problem being solved by us, the magnitude of the chemical potential is not *a priori* known, and, thus, the free parameters are the three parameters μ, E_+, and E_-. We can obtain two relations connecting them from the self-consistency condition (27) and the condition for the conservation of the total number of particles. The last free parameter is determined by minimizing the energy (28), (29).

The condition for the particle-number conservation can clearly be written in the form

$$\int\frac{d\mathbf{p}_\perp}{S}\int\limits_{E<\alpha(\mathbf{p}_\perp)}\frac{dN}{dE}dE=\text{const.}$$

Taking account of the fact that two states in the middle band are combinations of one state from the conduction band and one state from the "valence" band of the dielectric phase,[21] we have

$$n\left(1-2\int\limits_{\alpha(\mathbf{p}_\perp)>0}\frac{d\mathbf{p}_\perp}{S}\right)=\left(\int\limits_{-E_-<\alpha(\mathbf{p}_\perp)<0}-\int\limits_{E_->\alpha(\mathbf{p}_\perp)>0}\right)\frac{d\mathbf{p}_\perp}{S}\Phi(\mathbf{p}_\perp). \qquad (30)$$

Equation (30) has a simple meaning: the central band should on the average be half-filled.

Let us use the above-obtained general relations to study the behavior of the system near the instability point of a homogeneous Peierls state, where the lattice deformation has the character of widely spaced domain walls occurring in the background of the Peierls structure. To do this, we must investigate Eqs. (27)–(30) for small E_-, i.e., for $E_-\to 0$. Let us first consider the condition (30) for particle-number conservation. For a given $t(\mathbf{p}_\perp)$ function, the chemical potential μ_0 (for $E_-=0$) is determined from the requirement that the contour l on which $t(\mathbf{p}_\perp)=\mu_0$ divide the cross section of the Brillouin zone into two equal—in area—parts.

It follows from (30) that, for $E_-\neq 0$,

$$\mu=\mu_0+O(E_-^2/E_+^2).$$

Let us note that, when $t(\mathbf{p}_\perp)$ has a sufficiently symmetric shape, we have $\mu\equiv\mu_0$, whereas in the case of arbitrary $t(\mathbf{p}_\perp)$ we can assume that $\mu=\mu_0=\text{const}$ only with specified accuracy.

Let us now consider the self-consistency condition (27). It can be written in the form

$$\ln\frac{\Delta_0^2}{E_+^2-E_-^2}=2\int\limits_{|\alpha(\mathbf{p}_\perp)|<E_-}\frac{d\mathbf{p}_\perp}{S}\ln\frac{(E_+^2-\alpha^2)^{1/2}+(E_-^2-\alpha^2)^{1/2}}{(E_+^2-E_-^2)^{1/2}}, \qquad (31)$$

where $\Delta_0\sim E^*\exp(-\pi/g^2)$ is the gap in the homogeneous Peierls dielectric.

For $E_-\to 0$ we find from (31) that

$$\Delta_0^2=E_+^2-E_-^2+2\Delta_0\int\limits_{|\alpha(\mathbf{p}_\perp)|<E_-}\frac{d\mathbf{p}_\perp}{S}[E_-^2-\alpha^2(\mathbf{p}_\perp)]^{1/2}, \qquad (32)$$

the integral term being of the order of E^2_-. For small E_-, we can, using (32), write the expression (28) for the energy in the form

$$W=-\Delta_0^2/2\pi+nA+nE_-^2B, \qquad (33)$$

$$A=\frac{2\Delta_0}{\pi}+2\int\limits_{t(\mathbf{p}_\perp)<\mu_0}t(\mathbf{p}_\perp)\frac{d\mathbf{p}_\perp}{S}, \qquad (34)$$

$$B=\frac{1}{2\pi\Delta_0}-\frac{1}{2S}\oint\limits_{l}\frac{dl}{\beta(l)},\quad \beta(l)=\left|\frac{dt(\mathbf{p}_\perp)}{d\mathbf{p}_\perp}\right|_{t(\mathbf{p}_\perp)=\mu_0}, \qquad (35)$$

where $\beta(l)$ is the transverse component of the electron velocity on the contour l.

The quantity A is the energy required to produce one domain wall. When $t(\mathbf{p}_\perp)\equiv 0$, it goes over into the soliton energy $E_s=2\Delta_0/\pi$ for the one-dimensional Peierls model.[6,21] The formula (34) shows that interchain electron jumps decrease the quantity A, and, as was first noted in Ref. 5, the quantity A can change its sign when the function $t(\mathbf{p}_\perp)$ has the proper form. The condition $A=0$ is the threshold for absolute instability of the homogeneous Peierls state.

The quantity B characterizes the interaction energy of the domain walls. As in the one-dimensional model, this energy decreases exponentially as the wall spacing increases. But, if in the one-dimensional case we always have $B>0$ (Ref. 8), now, as can be seen from (35), we can, in principle, choose the function $t(\mathbf{p}_\perp)$ such that $B<0$. When $B>0$ the instability of the homogeneous state will develop as a (pressure-induced) second-order phase transition, while when $B<0$ the phase transition will occur discontinuously at some $A>0$. No unique relation exists between A and B. The periodic state considered by us is the alternative to the flow of particles from the valence into the conduction band of the Peierls dielectric, a flow which leads to the formation of electron-hole pockets (i.e., to the occurrence of the 2.5-order Lifshitz transition).

The latter clearly begins when

$$\max_{\mathbf{p}_\perp}t(\mathbf{p}_\perp)-\min_{\mathbf{p}_\perp}t(\mathbf{p}_\perp)=2\Delta_0. \qquad (36)$$

This condition, in its turn, does not depend on the inequalities for A and B. Consequently, the dielectric Peierls state can, for different $t(\mathbf{p}_\perp)$ functions, go over into the three-dimensional (anisotropic) metallic state in any one of three different ways. Specifically, this can occur through a homogeneous 2.5-order Lifshitz, a first-order, or a second-order, transition into the state with a periodic superstructure.

As in the preceding section, let us consider as an example the two-dimensional tight-binding model $t(\mathbf{p}_\perp)=-t\cos(ap)$. This model is highly degenerate. Indeed, the electron-hole pockets are formed at $t = \Delta_0$. According to (34) and (35), A and B vanish simultaneously at this same point. Thus, the critical points of all the phase transitions coincide. Let us recall that this model exhibited a similar degeneracy in its phase diagram in the region of instability of the metallic state.

The above-obtained results show that the formation of the metallic sections of the Fermi surface as the overlap integral between the chains increases is possible on account of two mechanisms. In the first case small electron-hole pockets are formed in the cross section of the Brillouin zone when the condition (36) is fulfilled. The states corresponding to them adjoin in terms of energy the valence and conduction bands. In the second case one isolated cylindrical Fermi surface with a finite cross section is formed in the Brillouin zone.

The possibility that more complicated deformations of the lattice will lead to the appearance on these Fermi surfaces of new small forbidden bands cannot be ruled out. In the first case this can be regarded as an effect of the three-dimensional electron-hole pairing; in the second case, this would correspond to a deformation $\Delta(x)$ that produces an additional forbidden band near $E = 0$. The corresponding $\Delta(x)$ deformations can be investigated through a simple generalization of the methods used above. However, without carrying out these calculations, we can, using the results obtained in Ref. 7, indicate a form of the electronic spectrum (a step Fermi surface) for which an additional forbidden band is certainly not produced.

In the present paper we have not investigated the physical manifestations of the specific free carriers that appear as a result of the appearance of the domain walls. Let us, by way of a simple illustration, note that the two mechanisms underlying the formation of metallic Fermi surfaces can be distinguished by measuring the conductivity anisotropy near the transition. The conductivity in the transverse direction should increase sharply when the metallization involves the formation of domain walls, whereas in the case of pocket formation the anisotropy essentially does not change.

In conclusion, let us note that the results obtained in Sec. III can mainly be applied to materials with incommensurate superstructures, materials such as TTF-TCNQ and $\mathrm{NbSe_3}$. There also exist solitons with a half-filled central level in the case, corresponding to these systems, of the Peierls model with a complex order parameter $\Delta(x)$ (Ref. 22).

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1) Some of the results of this section were obtained in collaboration with J. Sah.

2) It is appropriate to emphasize that the character of the transition is not necessarily symmetry-related, but is a consequence of the microscopic (i.e., electronic) nature of the mechanism underlying the transition.

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