

Energy spectrum of Peierls semiconductors in the two-band model

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The spectrum of a Peierls semiconductor with a charge-density wave (CDW) is studied in the two-band model in the self-consistent-field approximation. It is shown that the energy gap in the single-particle excitation spectrum can have a nonmonotonic temperature dependence and can even go to zero. The temperature dependence of the CDW wave vector Q is analyzed. The relationship of the results to experiments on TaS₃ is discussed.

The kinetic properties and other characteristics of quasi-one-dimensional conductors which on cooling below a temperature T_p undergo a Peierls transition and develop a charge-density wave (CDW) have received a great deal of study in recent years. It has been found that even in weak electric fields $E \lesssim 1$ V/cm the CDW plays an important role in the kinetics of a number of inorganic compounds (TaS₃, NbSe₃, K_{0.3}MoO₃, and others). In spite of the considerable progress made toward understanding the properties of conductors with CDWs, many questions remain (see, e.g., the review by Salva *et al.*¹). For example, there is still some doubt about the activation energy of CDW conductors. The activation energy determined from the temperature dependence of the conductivity in a weak field E is generally identified with the band gap ε_g in the single-particle excitation spectrum. At the same time it is known that the conductivity can contain a contribution from excitations of the amplitude-soliton type, and the energy necessary for the formation of such excitations on a single chain is different from ε_g . Optical measurements^{2,3} in orthorhombic TaS₃ (*o*-TaS₃), which could prove the existence of amplitude solitons, give a complicated picture of the photoconductivity spectrum. The observed spectral dependence of the photoresponse, although consistent with the existing ideas about the energy spectrum of amplitude solitons, is too complex for unambiguous interpretation. In addition, the CDW wave vector Q in *o*-TaS₃ has been found to depend on the temperature. The reason for this, too, is unclear.

The majority of the theoretical papers on Peierls conductors with CDWs have, as a rule, used the extremely simple model of a one-band metal for $T > T_p$ in which the Fermi surface consists of two slightly curved planes. In the self-consistent-field approximation under the assumption that amplitude solitons can be neglected, the half-width ε_g of the band gap in this model is equal to the amplitude of the order parameter Δ and depends on the temperature in accordance with the BCS formula. At the same time, it is known that the compounds under study have a complex crystal structure with several nonequivalent chains in the unit cell.¹ It is therefore of interest to ascertain the qualitative changes that would result from allowing for the multiband nature of the energy spectrum. The necessity of this was pointed out back in Ref. 1 in connection with the interpretation of the $Q(T)$ curve in *o*-TaS₃. In addition, the influence of the multiband nature on the structure of soliton lattices arising in

systems with period doubling or approximate period doubling was studied in Ref. 4.

In the present paper we investigate theoretically the energy spectrum of a Peierls conductor in the two-band model, i.e., we assume that the Fermi surface in the metallic state consists of two pairs of curves planes. Such a spectrum might be due, for example, to the presence of two nonequivalent chains in the unit cell. Working in the self-consistent-field approximation, we find the momentum dependence of the excitation energies for $T < T_p$ and show that even this simple model gives some qualitatively new features: a fundamental restructuring of the excitation spectrum, the possibility of a gapless state of the Peierls conductor, a nonmonotonic temperature dependence of the energy gap ε_g , etc.

1. Let us consider a quasi-one-dimensional two-band metal in which both bands $E_s(p)$, where $s = 1, 2$, have *n*-type conductivity. We assume that $|P_{F_s} - Q/2| \ll Q$, i.e., the Fermi momenta p_{F_s} of both bands are close (on a scale of Q) to $Q/2$. Then the energy (measured from the Fermi energy E_F) of an electron near the right-hand ($\alpha = 1$) or left-hand ($\alpha = -1$) Fermi plane can be written in the form

$$\varepsilon_s^\alpha(k) \equiv E_s(k + \alpha Q/2) - E_F = v_s k (-1)^\alpha + \eta_s(p_\perp), \quad (1)$$

where

$$\eta_s(p_\perp) = E_s(Q/2, p_\perp) - E_F \ll E_F, \quad v_s = |\partial E_s / \partial p_{F_s}|$$

is the modulus of the Fermi velocity in band s . The Hamiltonian of the system is of the form

$$\hat{H} = \hat{H}_e + \hat{H}_{ep} + \hat{H}_p. \quad (2)$$

Here

$$\hat{H}_e = \sum_s \varepsilon_s^\alpha(k) c_{\alpha s}^+ c_{\alpha s}, \quad \hat{H}_{ep} = \sum_s c_{\alpha s}^+ \Delta_{ss'}^{\alpha\alpha'} c_{\alpha' s'}. \quad (3)$$

The first term in (2) is the electronic part of the Hamiltonian. The electron-phonon interaction of interest here [the second term in (2)] is written in the self-consistent-field approximation. The summation in (3) is over all indices and all momenta k . The matrix elements of the order parameter are

$$\Delta_{ss'}^{\alpha\alpha'} = 0 \quad (\alpha \neq \alpha'),$$

$$\Delta_{ss'}^{\alpha\alpha'} = \Delta_{ss'}^{\alpha\alpha'} \equiv \Delta_{ss'} = g_{ss'} \langle b_q + b_{-q}^+ \rangle \quad (\alpha \neq \alpha'),$$

where $g_{ss'}$ is the matrix element for the transition of an electron from one part of the Fermi surface to the other, either

with a change in the band index ($s \neq s'$) or without a change in the band index ($s = s'$), and b_Q is the annihilation operator for a phonon having the same wave vector as the CDW. The fact the order parameter $\Delta_{ss'}$ depends only on a single pair of phonon operators b_Q, b_Q^\dagger means that we are assuming the development of a single CDW with wave vector Q . The occurrence of two vectors Q depends on the strength of the interaction between chains. For example, in the case of two types of chains, two CDWs with different wave vectors Q arise if the interaction between chains is weak. If the coupling between chains is sufficiently strong, the development of CDWs with $Q_1 \neq Q_2$ is energetically unfavorable. Such a situation occurs, for example, in NbSe₃ for $59 < T < 145$ K, in *o*-TaS₃ for $T < T_p = 215$ K, and in *m*-TaS₃ for $160 < T < 240$ K.¹ The last term in (2) describes the phonon subsystem.

We introduce Green's functions as in Ref. 5, but in the present case they are matrices not only with respect to the indices (α, α') but also with respect to the band indices (s, s') . For example, the retarded function \hat{G}^R is of the form

$$\hat{G}^R = [G_{ss'}^{\alpha\alpha'}(t, t')]^R \\ = -i\theta(t-t') \langle c_{\alpha s}(t) c_{\alpha' s'}^\dagger(t') + c_{\alpha' s'}^\dagger(t') c_{\alpha s}(t) \rangle.$$

With the aid of (2) we obtain an equation for $\hat{G}^{R(A)}$ [we will drop the superscript $R(A)$]:

$$\hat{G}^{-1}\hat{G} = [\delta_{\alpha\alpha'}\delta_{ss'}(\varepsilon - \varepsilon_s^\alpha(k)) - \Delta_{ss'}^{\alpha\alpha'}] G_{ss'}^{\alpha\alpha'} = \delta_{\alpha\alpha'}\delta_{ss'}. \quad (4)$$

Inverting the matrix \hat{G}^{-1} , we easily find the function $\hat{G}^{R(A)}$ whose poles determine the excitation spectrum. The equation for the poles is

$$\text{Det } \hat{G}^{-1} = (\varepsilon - \varepsilon_{1+})(\varepsilon - \varepsilon_{1-})(\varepsilon - \varepsilon_{2+})(\varepsilon - \varepsilon_{2-}) \\ - \Delta_1^2(\varepsilon - \varepsilon_{2+})(\varepsilon - \varepsilon_{2-}) \\ - \Delta_2^2(\varepsilon - \varepsilon_{1+})(\varepsilon - \varepsilon_{1-}) - \Delta_x^2[(\varepsilon - \varepsilon_{1+})(\varepsilon - \varepsilon_{2-}) \\ + (\varepsilon - \varepsilon_{1-})(\varepsilon - \varepsilon_{2+})] + (\Delta_1\Delta_2 - \Delta_x^2)^2 = 0. \quad (5)$$

Here $\varepsilon_{s\pm} = \varepsilon_s^\alpha(k)$ for $\alpha = \pm 1, s = 1, 2$, and $\Delta_{1(2)} = \Delta_{11(22)}, \Delta_x = \Delta_{12} = \Delta_{21}$. From Eq. (5) one can in principle find the spectrum $\varepsilon(k)$ for various relationships among the parameters of the system. For general relationships among the parameters, however, the analysis is too complicated. Therefore, to obtain a qualitative understanding of the behavior of the system, let us first consider the simplest, symmetric case. We assume that $\Delta_1 = \Delta_2 = \Delta$ and $kv_1 = kv_2 \equiv \xi$. We then obtain from (5) a biquadratic equation¹⁾ for the energy $\varepsilon \equiv \varepsilon - \eta$, where $\eta = (\eta_1 + \eta_2)/2$. By solving this equation we find two branches of excitations:

$$\varepsilon_{1,2}^2 = a^2 + \xi^2 + \Delta^2(1 + \gamma^2) \pm 2[a^2(\xi^2 + \Delta^2) + \Delta^4\gamma^2]^{1/2}. \quad (6)$$

Here $\gamma = \Delta_x/\Delta$, and $2a = (\eta_1 - \eta_2) = E_1(Q/2, p_1) - E_2(Q/2, p_1)$ is the distance between the bands in the metallic state at $p = Q/2$. The excitation energy $\tilde{\varepsilon}$ is measured from the midpoint between the bands. Figure 1 shows the dependence of the excitation energy $\tilde{\varepsilon}$ on the "momentum" $\xi = kv$ in the case $a < \Delta$ (Fig. 1a) and $a > \Delta$ (Fig. 1b). One can obtain $\tilde{\varepsilon}(\xi)$ in the other quadrants by a mirror reflection with respect to the $\tilde{\varepsilon} = 0$ and $\xi = 0$ axes. The values of $\tilde{\varepsilon}$ at the extrema are given by

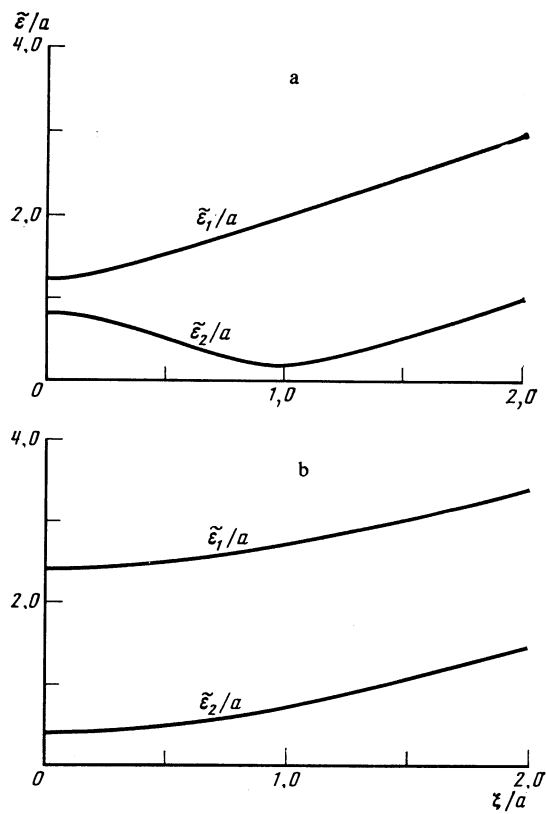


FIG. 1. Excitation energy $\tilde{\varepsilon}$ as a function of "momentum" $\xi = kv$ for a) $\Delta = 0.2a$ and b) $\Delta = 1.5a$. In both cases $\gamma = 1$. All quantities are normalized to a .

$$\varepsilon_{1,2}(0) = |(a^2 + \Delta^2\gamma^2)^{1/2} \pm \Delta|, \quad \tilde{\varepsilon}_m = \gamma\Delta(a^2 - \Delta^2)^{1/2}/a. \quad (7)$$

The $\tilde{\varepsilon}_2$ minimum given by $\tilde{\varepsilon}_m$ exists and is different from $\tilde{\varepsilon}_2(0)$ if

$$\Delta^2 < \Delta_c^2 \equiv 2a^2/[1 + (1 + 4\gamma^2)^{1/2}]. \quad (8)$$

Consequently, the energy gap ε_g is equal to $\tilde{\varepsilon}_m$ for $\Delta < \Delta_c$ and to $\tilde{\varepsilon}_2(0)$ for $\Delta \geq \Delta_c$.

It is interesting to track the change in ε_g as a function of the quantity Δ/a . Figure 2 shows $\tilde{\varepsilon}_{1,2}(0), \tilde{\varepsilon}_m$, and ε_g as functions of Δ/a for two values of γ [see Eq. (7)]. It is seen that ε_g has a nonmonotonic dependence on Δ/a . This circumstance can lead to a nonmonotonic temperature dependence of the gap. If $\Delta(0) > a\sqrt{2}$, where $\Delta(0)$ is the value of the order parameter at $T = 0$, then ε_g will first increase with increasing temperature and then will decrease to zero. In addition, if $\gamma \neq 1$ there can be a gapless state in which $\varepsilon_g = 0$ but $\Delta \neq 0$. It follows from (7) that the gap in the spectrum goes to zero at $\Delta = 0$ and $\Delta^2 = a^2(1 - \gamma)^{-1}$.

2. Let us now calculate the density of states $N(\varepsilon)$. Using (4) to determine the functions $\hat{G}^{R(A)}$ and neglecting the curvature of the Fermi surface, we find

$$N(\varepsilon) = \text{Sp} \int d\xi (\hat{G}^R - \hat{G}^A) \\ = \frac{1}{4} \int d\xi [\delta(\varepsilon - \tilde{\varepsilon}_1) + \delta(\varepsilon + \tilde{\varepsilon}_1) + \delta(\varepsilon - \tilde{\varepsilon}_2) + \delta(\varepsilon + \tilde{\varepsilon}_2)]. \quad (9)$$

Thus, if the smearing of the spectrum is ignored $N(\varepsilon)$ has a square-root singularity at the extrema

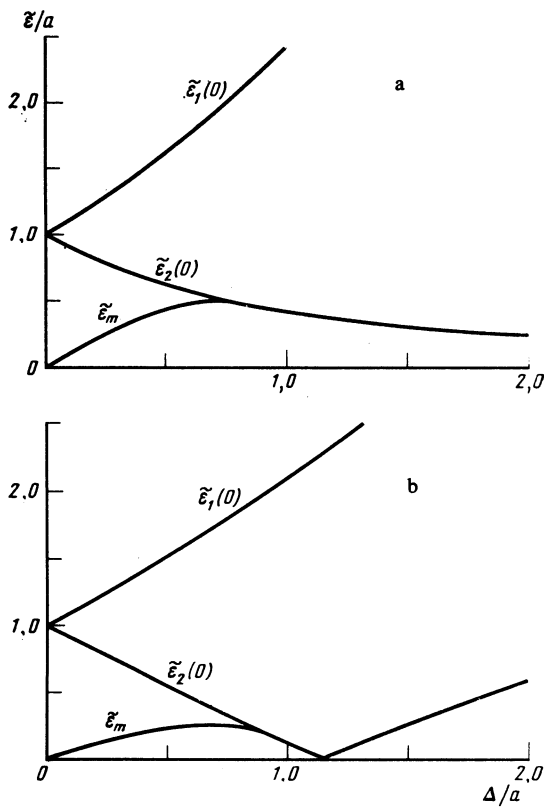


FIG. 2. Minima of the function $\tilde{\epsilon}(\xi)$ versus Δ for a) $\gamma = 1$ and b) $\gamma = 0.5$.

$$N(\epsilon) \propto [\tilde{\epsilon} - \tilde{\epsilon}_{1,2}(0)]^{-1/2}, \quad N(\epsilon) \propto [\tilde{\epsilon} - \tilde{\epsilon}_m]^{-1/2}.$$

Let us now turn to the self-consistency condition, which determines the temperature dependence of the order parameter Δ . The equation of motion for the phonon operators easily yields

$$\Delta = i(\lambda/2\pi) \int d\xi \int d\epsilon [G_{11}^{+-} + G_{22}^{+-} + G_{12}^{+-} + G_{21}^{+-}]. \quad (10)$$

Here $G_{ss'}^{\pm} = (G^R - G^A)_{ss'}^{\pm} \tanh(\epsilon/2T)$, and $\lambda = g^2/\omega_Q v$. For simplicity we have ignored the dependence of η on p_1 and considered the special case $\Delta_1 = \Delta_2 = \Delta$, $v_1 = v_2 = v$, and $\nu = 1$. Substituting into (10) the expressions for $\hat{G}^{R(A)}$ from (4) and performing the integration over ϵ , we get

$$1 = \lambda \int_0^{\epsilon_0} \frac{d\xi}{\epsilon_1^2 - \epsilon_2^2} \left[\frac{\epsilon_1^2 - \xi^2}{\epsilon_1} \tanh \frac{\epsilon_1}{2T} - \frac{\epsilon_2^2 - \xi^2}{\epsilon_2} \tanh \frac{\epsilon_2}{2T} \right], \quad (11)$$

where ϵ_1 and ϵ_2 are given by (6) for $\eta = 0$ and $\gamma = 1$. Let us consider (11) at low temperatures, where the difference between Δ and $\Delta(0)$ is small. The correction giving the difference between Δ and its value at $T = 0$ for $a \ll \Delta$ is

$$\Delta - \Delta(0) = \Delta(0) \left[\left(\frac{\pi T a^6}{64 \Delta^7} \right)^{1/2} e^{-a^2/2\Delta T} - \left(\frac{\pi T}{\Delta} \right)^{1/2} e^{-2\Delta/T} \right]. \quad (12)$$

Thus, it follows from (12) that at low temperatures the first term is greater than the second term and that Δ increases with increasing T . However, since the coefficient of the exponential are small the increase in Δ is extremely small and is practically unnoticeable. The function $\Delta(T)$ obtained by numerical integration of (12) is shown in Fig. 3, along with the temperature dependence of the gap ϵ_g .

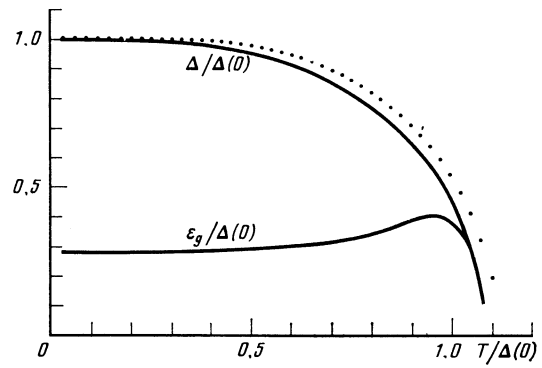


FIG. 3. Temperature dependence of the order parameter Δ and of the half-width ϵ_g of the band gap for $a = 0.8\Delta(0)$. The points show the BCS curve for $2\Delta(T)$.

3. In the symmetric model (with $v_1 = v_2$ and $\Delta_1 = \Delta_2$) studied in paragraph 2 above, the CDW wave vector is given by $Q = (p_{F1} + p_{F2})$, and the Fermi level passes midway between the bands. If the bands are asymmetric, the Fermi level is shifted, and the CDW wave vector depends on the temperature.²⁾ Analysis of the form of $Q(T)$ for an arbitrary shape of the spectrum $E_{1,2}(p)$ leads to awkward expressions. Let us therefore consider a simplified model with a linear dispersion relation $E_1 = kv_1 + a$ and $E_2 = kv_2 - a$ with only slightly different velocities $v_{1,2} = v(1 \pm \delta v/v)$, where $\delta v/v \ll 1$. Let us also suppose that the electron-phonon interaction constants g_{11} and g_{22} differ only slightly: $g_{11(22)} = (1 \pm \delta g/g)$, where $\delta g/g \ll 1$. Then the excitation energies $\pm \tilde{\epsilon}_s^{(0)}$ (here the $\tilde{\epsilon}_s^{(0)}$ are the arithmetic values of the roots in (6), $s = 1, 2$) are changed in comparison with (6) by an amount

$$\delta \tilde{\epsilon}_s = (-1)^s [(\xi^2 \delta v/v) + (\Delta^2 \delta g/g)] [a^2 (\xi^2 + \Delta^2) + \Delta^4 \gamma^2]^{-1}. \quad (13)$$

To find the equilibrium value of Q and $E_f \equiv \mu$ we must minimize the free energy $F = \mu N - \Omega$ for a specified number of particles. The minimization leads to the condition $\partial \Omega / \partial Q = 0$, where Ω is given by the familiar expression

$$\Omega = T \sum_n \int_0^{\epsilon_Q} d\xi \ln \frac{1}{2} \left[1 + \tanh \frac{\tilde{\epsilon}_n + E_Q - \mu}{2T} \right]. \quad (14)$$

Here

$$\tilde{\epsilon}_n = \tilde{\epsilon}_n^{(0)} + \delta \tilde{\epsilon}_n = (-1)^s \tilde{\epsilon}_s^{(0)} + \delta \tilde{\epsilon}_s, \quad n = \{s, s'\}, \\ s, s' = 1, 2, \quad E_Q = vQ/2.$$

The condition that $\Omega(Q)$ be an extremum leads to the equation

$$2(E_Q - \mu) - \frac{1}{2} \sum_{n=1}^4 \int_0^{\epsilon_Q} d\xi \tanh \frac{\tilde{\epsilon}_n + E_Q - \mu}{2T} \\ + \frac{\delta v}{v} \sum_{n=1}^4 \int_0^{\epsilon_Q} d\xi \left[1 - \tanh \frac{\tilde{\epsilon}_n + E_Q - \mu}{2T} \right] \frac{d\tilde{\epsilon}_n}{da} = 0. \quad (15)$$

If $\delta v = 0$, Eq. (15) is solved by $Q_0 = 2\mu/v = 2k_F$. For $T > T_p$, when $\Delta = 0$, Eq. (15) becomes an identity, i.e., the vector Q is indeterminate, as it should be in this case. Let us suppose $\Delta \neq 0$ (i.e., $T < T_p$) and substitute into (15) expressions (6) and (13) for the branches of the spectrum of exci-

tations $\bar{\varepsilon}_n$. Then Eq. (15) and conservation of particles yield

$$v\delta Q \equiv v(Q - Q_0) = (2B - AC)/(2 - C), \quad (16)$$

where

$$A = \frac{\delta v}{v} \sum_{n=1}^4 \int_0^{\varepsilon_Q} d\xi \frac{d\bar{\varepsilon}_n^{(0)}}{da} \tanh \frac{\bar{\varepsilon}_n^{(0)}}{2T},$$

$$B = \sum_{n=1}^4 \int_0^{\infty} d\xi \frac{\delta \varepsilon_n}{2T} \cosh^{-2} \frac{\bar{\varepsilon}_n^{(0)}}{2T}, \quad C = \sum_{n=1}^4 \int_0^{\infty} d\xi \frac{d\bar{\varepsilon}_n^{(0)}}{2T} \cosh^{-2} \frac{\bar{\varepsilon}_n^{(0)}}{2T}.$$

It follows that at low temperatures $T \ll \Delta$, the difference between Q and $Q_0 = (p_{F1} + p_{F2})/2$ is exponentially small (the coefficients B and C are exponentially small). The difference δQ changes with increasing temperature. It follows from (16) that the relative change in δQ at $T \sim \Delta$ is equal to $\max\{\delta v/v, \delta g/g\}$. It can be found by numerical evaluation of the integrals in (16). Let us confine ourselves here to a calculation of δQ in the limit $T \gg \Delta$, i.e., for temperatures near T_p . In this case we have

$$v\delta Q = \begin{cases} -\frac{a}{2} \left[\frac{\delta v}{2v} + \frac{\delta g}{g} \right], & a \ll T \\ \frac{2\pi^2}{7\zeta(3)} \frac{T^2}{a} \left[\frac{\delta v}{2v} - \frac{\delta g}{g} \right], & a \gg T \end{cases} \quad (17)$$

Thus as the temperature decreases, the difference between the CDW wave vector Q and Q_0 changes from the value given by (17) to a value of zero.

4. Our analysis above has shown that allowance for the multiband nature of the conductor even in the simplest model leads to an unusual energy spectrum for the Peierls semiconductor.

First of all, the minima of the restructured conduction bands can be found both for a single value of the wave vector and for different values. Since the distance $2a$ between the bands depends on p_1 , the energy gap ε_g also depends on p_1 . Consequently, the band structure in a real substance with a CDW can be extremely complicated.

Second, the band minima have an unusual dependence on the order parameter Δ . While $\bar{\varepsilon}_1(0)$ for the upper band increases with increasing Δ , $\bar{\varepsilon}_2(0)$ for the lower band decreases with increasing Δ ; this can lead to a nonmonotonic temperature dependence of the gap ε_g (see Fig. 3). For such a dependence to be realized, it is necessary that Δ at low temperatures be greater by a factor of $1/\sqrt{2}$ than the distance between bands in the metallic state. We note that in real substances the transverse dispersion of the electron spectrum and the fluctuations not taken into account here should lower the temperature of the Peierls transition in comparison with the curves of Fig. 3.

We also note that the self-trapping of the excitations, which is accompanied by a deformation of the lattice (the formation of solitons), gives rise to a change in the spectrum obtained here (see, e.g., the review by Heeger *et al.*⁶ and the literature cited therein). However, if the interaction between chains is sufficiently strong, i.e., if the dependence on p_1 is substantial, then the formation of self-trapped excitations on just one chain becomes unfavorable. In this case either the spatially homogeneous state studied here is realized or else domain walls can arise if $\eta(p_1)$ has a suitable form.⁷

It is difficult to compare our results directly with experimental data, since the parameters of the band structure of many substances are unknown. One suitable object for comparison might be TaS₃, in which the quasi-one-dimensionality assumed here is more pronounced than in NbSe₃, for example. Unfortunately, there is little information in the literature about the band structure of TaS₃. Nevertheless, we should mention the experimental data¹ on *o*-TaS₃, which are in qualitative agreement with our conclusions here. For example, a nonmonotonic temperature dependence was found for the activation energy determined from the temperature dependence of the resistivity of *o*-TaS₃ in weak fields. A change in the vector Q with temperature was also observed. In addition, a nonmonotonic temperature dependence was found for the ratio of the CDW current to the oscillation frequency of the current. This ratio is proportional to the number of condensed electrons and depends on the gap width $2\varepsilon_g$, which, as we have said, has a nonmonotonic dependence on T .

We are grateful to Yu. I. Latyshev, who stimulated our interest in this problem in a discussion of experimental results.

¹In the present case of a symmetric spectrum, the Fermi level passes midway between bands E_1 and E_2 for $p = Q/2$. The function η is therefore nonzero only insofar as it depends on the transverse momentum p_1 .

²The presence of transverse dispersion $\eta(p_1)$ can be an additional cause of temperature dependence of the wave vector Q .

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