

Electron-hole balance and semiconductor properties of quasi-one-dimensional charge-density-wave conductors

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The position of the chemical potential μ and the temperature dependence of the charge-density-wave vector $q(T)$, which determine the type of conduction (the sign of the charge carriers) in the semiconductor state of quasi-one-dimensional conductors below the Peierls transition temperature, are calculated. The results obtained differ from the calculations previously performed. The temperature dependences of the conductivity, the thermopower, and the Hall coefficient, as well as the temperature hysteresis of the first two parameters, are discussed with consideration of the relationship between the linear electron and hole concentrations n and p per conducting chain and the magnitude of the charge-density-wave vector $\pi(p-n) = q(T) - q(0)$. It is shown that because of the dependence of q on T , the activation dependence of the conductivity $\sigma \propto \exp(-\Delta/T)$ is maintained even in the limit of unipolar conduction ($n \gg p$ or $p \gg n$), which does not have any analogy in ordinary semiconductors.
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1. INTRODUCTION

An energy gap 2Δ forms on the Fermi surface in quasi-one-dimensional conductors below the Peierls transition temperature T_P (see, for example, Ref. 1). As a result, the conductor undergoes a transition to a semimetallic state, as in the case of NbSe_3 , or to a semiconductor state, as in the case of other quasi-one-dimensional charge-density-wave conductors, which we shall examine in the present paper. In the Peierls state one-electron excitations (electrons and holes) coexist with a deformed mobile electron crystal, i.e., a charge-density wave. In an electric field below the threshold value, at which a charge-density wave cannot move in the crystal as a whole, the conductivity and other kinetic properties of the quasi-one-dimensional conductor are determined by one-electron excitations, making it similar to an ordinary semiconductor. Nevertheless, even in weak electric fields there are significant differences between the properties of quasi-one-dimensional charge-density-wave conductors and ordinary semiconductors. For example, the variation of the wave vector q of the charge-density wave is associated with the variation of its charge and, as a consequence of the number-of-particles conservation law, with the variation of the electron and hole concentrations. Therefore, the variation of the charge-density-wave vector (with the temperature or as a result of the application of an electric field) plays the same role as the doping of ordinary semiconductors, i.e., it alters the electron and hole concentrations and, consequently, the conductivity. A similar model of a quasi-one-dimensional conductor as a semiconductor with a doping level that depends on the electric or thermal history of the sample was used to qualitatively and quantitatively describe the thermopower and conductivity^{2,3} under the assumption that the deviation of the chemical potential μ from the middle of the band gap even at equilibrium is not equal to zero.³ In Sec. 2 we calculate μ and the temperature dependence of the charge-density-wave vector q . In particular, we

show that the shift of the chemical potential μ is greater in magnitude than in the calculations in Ref. 4 and depends on the form of the electron spectrum of the material not just near the Fermi energy. In Sec. 3 we analyze the relationship of the conductivity and the electron and hole concentrations to the temperature dependence of q and show that in unipolar semiconductors, such as TaS_3 and blue bronze, the temperature dependence of the conductivity is determined mainly by the temperature dependence of q .¹⁾ We discuss the results of measurements of the thermopower and the Hall effect, as well as the temperature hysteresis of the conductivity and the thermopower, in terms of the shift of the chemical potential relative to the middle of the band gap and the electron and hole contributions to the transport processes. We also show that at low temperatures the experimental data cannot be explained within the contributions of the electrons and holes alone, and it should be assumed that nonlinear charge-density-wave excitations, such as phase solitons, or charge-density-wave creep make a contribution to the conduction processes.

Below we shall use units in which $\hbar = 1$ and $k_B = 1$.

2. POSITION OF THE CHEMICAL POTENTIAL AND MAGNITUDE OF THE CHARGE-DENSITY-WAVE VECTOR

The position of the chemical potential level and the magnitude of the charge-density-wave vector in the equilibrium state can be found from the condition for the minimum of the free energy, which consists of an electronic part and a contribution from the elastic deformation energy of the lattice

$$F = F_e + F_l. \quad (1)$$

The elastic energy is defined by the known formula¹

$$F_l = \frac{\Delta^2}{\lambda \pi v}, \quad (2)$$

where λ is the dimensionless electron–phonon coupling constant and v is the Fermi velocity. We calculate the electronic part of the free energy using the familiar expression⁶

$$F_e = \Omega + \varepsilon_F N, \quad \Omega = -T \sum_k \ln \left[1 + \exp \left(\frac{\varepsilon_F - \varepsilon_k}{T} \right) \right], \quad (3)$$

where Ω is the thermodynamic potential, N is the number of electrons, ε_F is the Fermi energy, and ε_k is the dispersion law of the quasiparticles in the charge-density-wave state, which depends on $q(T)$ and is determined by the combination of the electron energies $\varepsilon(k)$ and $\varepsilon(k \pm q)$ in the metallic state. We present the expression for ε_k for states with a momentum component along the chains $k > 0$. For states with the opposite momentum the spectrum is found with consideration of the fact that ε_k is an even function of the momentum:

$$\begin{aligned} \varepsilon_k^\pm &= \frac{\varepsilon(k) + \varepsilon(k-q)}{2} \pm \sqrt{\left[\frac{\varepsilon(k) - \varepsilon(k-q)}{2} \right]^2 + \Delta^2} \\ &+ \frac{\Delta^2}{\varepsilon(k) - \varepsilon(k+q)} + \sum_n \frac{\Delta_n^2}{\varepsilon(k) - \varepsilon_n(k+q)} \\ &+ \sum_n \frac{\Delta_n^2}{\varepsilon(k) - \varepsilon_n(k-q)}. \end{aligned} \quad (4)$$

The first two terms in (4) describe the variation of the spectrum and the formation of a gap on the Fermi surface as a result of the crossover of the states near the Fermi energy (see Ref. 1 and the references therein). The last three terms describe corrections calculated using perturbation theory to the spectrum due to states with wave numbers differing by q , whose energy differs strongly (by an amount greater than Δ) from $\varepsilon(k)$. Also, the last two terms describe corrections associated with the states $\varepsilon_n(k)$ belonging to other bands, and the symbol Δ_n in them denotes the off-diagonal components of the charge-density-wave order parameter, i.e., the matrix elements of the potential created when a charge-density wave forms, calculated for the wave functions of different bands. Terms of this type are taken into account in theories which treat the Peierls transition in multiband models.⁷ The corrections described by the last terms are usually not taken into account, since they are small compared with the first terms near the Fermi energy. We write out these corrections, since in the following we must take into account the contribution to the free energy (3) from states located far from the Fermi energy, where all the terms in (4) are small and can be of the same order. The corrections associated with other bands can be significant, if their energies differ by an amount smaller than or of the order of the Fermi energy. Such a situation is typical of most quasi-one-dimensional charge-density-wave conductors, particularly of MX_3 compounds and blue bronze.^{1,8}

Let us calculate the free energy in the case of a one-dimensional electron spectrum. We first write the expression for the concentration of particles (per chain) N . Going over from summation to integration over the momentum, we obtain

$$N = \frac{2}{\pi} \left[\int_0^{q/2} (1 - f_h) dk + \int_{q/2}^{q_m} f_e dk \right] = \frac{q(0)}{\pi}. \quad (5)$$

Here q_m is the quasimomentum on the Brillouin zone boundary, and f_e and f_h are the electron and hole equilibrium distribution functions:

$$f_e = \frac{1}{1 + \exp \left(\frac{\varepsilon_k^+ - \varepsilon_F}{T} \right)}, \quad f_h = \frac{1}{1 + \exp \left(\frac{-\varepsilon_k^- + \varepsilon_F}{T} \right)},$$

where the ε_k^\pm denote the dispersion laws of the quasiparticles above and below the energy gap that are described, respectively, by Eq. (4) with the upper and lower signs in front of the square root.

The particle density in (5) is assumed to be assigned and to be temperature-independent and, therefore, equal to its value at $T=0$, at which the states below the gap are completely filled and the states above the gap are empty, i.e., there are no electrons and holes in the crystal. Because of the quasineutrality relation, the total electron density N can be assumed constant not only in the case of a homogeneous charge-density wave, but also in the case of an inhomogeneously deformed charge-density wave with sufficiently smooth perturbations, for example, as a consequence of an interaction with impurities.

We note that the expression for the number of particles (5) can be rewritten in the form of an equation relating the charge-density-wave vector $q(T)$ to the electron and hole concentrations n and p :

$$n = \frac{2}{\pi} \int_{q/2}^{q_m} f_e dk, \quad p = \frac{2}{\pi} \int_0^{q/2} f_h dk, \quad (6)$$

$$q - q(0) = \pi(p - n). \quad (7)$$

It follows from (7) that the deviation of the charge-density-wave vector from its value at zero temperature is exponentially small at low temperatures $T < \Delta$, since $n, p \propto \exp(-\Delta/T)$.

Combining (3) and (5), we obtain a simple expression for the electronic part of the free energy:

$$\begin{aligned} F_e &= \frac{2}{\pi} \int_0^{q/2} \varepsilon_k^- dk - \frac{\varepsilon_F}{\pi} [q - q(0)] + \frac{2T}{\pi} \\ &\times \left[\int_0^{q/2} \ln(1 - f_h) dk + \int_{q/2}^{q_m} \ln(1 - f_e) dk \right]. \end{aligned} \quad (8)$$

We now find a relation that specifies the equilibrium value of the charge-density-wave vector from the condition $\partial F / \partial q = 0$. Performing some relatively simple transformations and using the condition that the number of particles be constant, we obtain

$$\begin{aligned} \mu = & \frac{\partial}{\partial q} \left[\frac{\Delta^2}{\lambda v} + 2 \int_0^{q/2} [\varepsilon_k^- - \varepsilon(k)] dk \right] - \frac{[q - q(0)]v}{2} \\ & + T \ln \frac{1 + \exp[-(\Delta - \mu)/T]}{1 + \exp[-(\Delta + \mu)/T]} \\ & + 2 \int \left(f_h \frac{\partial \varepsilon_h}{\partial q} + f_e \frac{\partial \varepsilon_e}{\partial q} \right) dk, \end{aligned} \quad (9)$$

where ε_e and ε_h are the energies of the electrons and holes, respectively, measured from the middle of the band gap, $\mu = \varepsilon_F - \varepsilon(q/2)$ is the deviation of the chemical potential level from the middle of the band gap, and v is the Fermi velocity.

Let us now analyze the expression obtained under the condition $\Delta > T$. It holds in charge-density-wave semiconductors at practically all temperatures. It is easy to see that the last three terms on the right-hand side of (9) are exponentially small when $\Delta > T$ [the first of them is small because of Eq. (7)]. Thus, when the exponentially small corrections are neglected, the position of the chemical potential level is determined by the first term in (9), which includes lattice and electronic parts. The lattice part can be represented in the form

$$\Delta^2 \frac{\partial}{\partial q} \left(\frac{1}{\lambda v} \right) = \Delta^2 \frac{\partial}{\partial q} \left(\frac{\pi \omega_q}{2g^2} \right),$$

where ω_q is the phonon frequency and g is the electron-phonon coupling constant. If the dependence of g on q is neglected, as in Ref. 4, it turns out that the lattice contribution to the chemical potential shift is proportional to the velocity of the phonons with the momentum q . However, generally speaking, g depends on the wave vector, and significant variations of g in response to variation of the wave vector by an amount of the order of the reciprocal lattice vector should be expected. Since in quasi-one-dimensional conductors q is of the order of the reciprocal lattice vector, the function $g(q)$ can lead to a contribution to μ that is comparable to the contribution due to the dependence of ω_q on the wave vector. The order of magnitude of the lattice contribution to the chemical potential shift can be estimated as

$$\mu_l = O \left(\frac{\Delta^2}{\lambda \varepsilon_F} \right), \quad (10)$$

and the sign of μ_l is determined by the specific form of the dependences of λ and the Fermi velocity on the wave vector.

The electronic contribution (the second term under the differentiation sign) is determined by the integral of the difference between the electron energies in the presence of a charge-density wave and in the metallic state. This integral diverges logarithmically at large distances from the Fermi energy and therefore depends on the dispersion law of the electrons far from ε_F . In Ref. 4 the analogous contributions from large energies were disregarded as being dependent on the cutoff energy and therefore not having any physical meaning. We do not see any basis for discarding this contribution, which is similar to the familiar logarithmically di-

verging integral under the gap self-consistency condition that is obtained when the free energy (1) varies with respect to Δ .

Let us discuss the electronic contribution μ_e to the chemical potential shift (9) calculated for different forms of the electron spectrum. We note at once that the order of magnitude of this contribution is the same as that of the lattice contribution, i.e.,

$$\mu_e = O \left(\frac{\Delta^2}{\lambda \varepsilon_F} \right), \quad (11)$$

and the sign of μ depends on the form of the electron spectrum and on the degree of filling of the electron band.

We first consider the electronic contribution to μ_e with neglect of the influence of the other bands. For a parabolic dispersion law at small values of Δ/ε_F we obtain

$$\mu_e = \pm \frac{\Delta^2}{4\varepsilon_F} \left(\ln \frac{8\varepsilon_F}{\Delta} - \frac{3}{2} \right), \quad (12)$$

where the plus and minus signs refer to the cases of electron and hole conduction, respectively. We note that the value of μ obtained and the corresponding value of $q(T) - q(0)$ are large compared to the results in Ref. 4. In fact, from (6) and (7) it follows that

$$\begin{aligned} q(T) - q(0) = & - \frac{2}{\pi v} \sqrt{\frac{2}{\pi}} \Delta T \\ & \times \exp \left(- \frac{\Delta}{T} \right) \sinh \left(\frac{\mu_e + \mu_0}{T} \right), \end{aligned} \quad (13)$$

where

$$\mu_0 = \mp \frac{1}{4} T \frac{\Delta}{\varepsilon_F}$$

takes into account the difference in the density of states between the electron and hole bands. As we see, μ_0 is Δ/T times smaller in order of magnitude than μ_e and has the opposite sign. We note that the dependence of q on T obtained in Ref. 4 was associated specifically with μ_0 in a first approximation. Thus, under the quadratic dispersion law the sign of the majority charge carriers in the charge-density-wave state is the same as in the metallic state.

It follows from (13) that the deviation of the charge-density-wave vector from its value at zero temperature decreases exponentially as the temperature is lowered, the activation energy being close to Δ ($\mu \ll \Delta$).

For the case in which the electron energy above the Peierls transition temperature is described in the model of strongly coupled electrons $\varepsilon(k) = \varepsilon_0 - (W/2)\cos(ak)$, μ_e is given by

$$\mu = \frac{W}{2} \left[\cos Q - \cos 2Q - \sqrt{\delta^2 + \sin^4 Q} + \frac{\delta^2}{2\sin^2 Q} \left(\cos Q \ln \frac{\tan Q}{\tan(Q/2)} + 1 - \frac{1}{\cos Q} \right) - \int_0^Q \frac{\sin Q \sin^2 x}{2\sqrt{\delta^2 + \sin^2 Q \sin^2 x}} dx \right], \quad (14)$$

where $Q = q(0)a/2 = \pi a/\lambda_{CDW}$, λ_{CDW} is the period of the charge-density wave, and $\delta = 2\Delta/W$.

According to (14), the sign of μ depends on the degree of filling of the band. If the Fermi energy is close to the band extremum, the majority carriers in the charge-density-wave state have the same sign as in the metallic state, but when the degree of filling of the band approaches half, the sign of the majority carriers changes. In addition, the sign of μ depends on δ and Δ/ε_F . For example, if quadrupling of the period occurs when a charge-density wave forms, as in orthorhombic TaS₃ ($Q = \pi/4$) or K_{0.3}MoO₃ ($Q = 3\pi/4$), the sign of μ_e corresponds to the same type of conduction in the states with and without a charge-density wave when $\delta < 0.26$ ($\Delta/\varepsilon_F < 0.9$), but its sign changes at larger values of Δ/ε_F . If the band is almost half filled, as in (NbSe₄)_{10/3}I, the appearance of a charge-density wave results in a change in the sign of the majority charge carriers under the dispersion law under consideration for all values of $\Delta/\varepsilon_F < 1$.

In addition, as was noted above, according to (4) and (9) the chemical potential shift can vary in the presence of other bands that make a contribution to μ_e comparable to the contribution of the principal band, if their energy differs by an amount smaller than or of the order of the Fermi energy.

Thus, the chemical potential shift from the middle of the Peierls gap is determined by the form of the dispersion law of the material and Δ and can be determined only from the magnitude of the curvature of the electron dispersion law near the Fermi energy. This does not contradict the experimental data, since there are materials in which the sign of the majority charge carriers below T_p is the same as in the metallic state [for example, TaS₃ and (NbSe₄)_{10/3}I], as well as materials in which the sign of the charge carriers changes when a charge-density wave forms (blue bronzes).

According to (11) and (12), in a first approximation the shift of μ_e does not depend on the temperature and is larger than the value obtained in Ref. 4. However, in real charge-density-wave semiconductors the inequalities $T < \Delta < \varepsilon_F < W$ (W is the width of the band in the metallic state) hold without a large margin, and the corrections in the second approximation can be important. Three-dimensional effects can also play a significant role. Nevertheless, as the calculation shows, in all cases

$$q(T) - q(0) \propto \exp(-\Delta^*/T),$$

where $\Delta^* \approx \Delta$.

3. CHARGE-DENSITY-WAVE VECTOR AND CONDUCTIVITY. ANALYSIS OF EXPERIMENTAL DATA

The conductivity σ of quasi-one-dimensional conductors below the Peierls transition temperature is known to decrease according to a thermal activation law with an activation energy close to Δ . This result is usually interpreted on the basis of the theory that the properties of a Peierls conductor are similar to the properties of an intrinsic semiconductor. The shift of μ and the presence of a temperature dependence of the charge-density-wave vector indicate, however, that a Peierls conductor should be regarded as a doped semiconductor with a variable doping level, and the question of interpreting the temperature dependence of σ requires a more careful analysis.

The conductivity was calculated on the basis of the microscopic theory in Refs. 9 and 10 for the case of elastic scattering characterized by forward and backward electron scattering (i.e., with and without variation of the momentum component along the chain by an amount close to twice the Fermi momentum) in the absence of a charge-density wave. Since at temperatures below the Peierls transition temperature the quasiparticles are superpositions of electron states with opposite momenta along the chains, the quasiparticle momentum scattering time is expressed in terms of the scattering probability using energy-dependent coherence factors. As a result, the free transit time acquires a different temperature dependence than in the metallic state. The results of the conductivity calculation in Ref. 9 can be represented in a descriptive form:

$$\sigma = \frac{e^2 n \tau_n}{m_n} + \frac{e^2 p \tau_p}{m_p}, \quad (15)$$

where the electron and hole effective masses are much smaller than the band electron mass $m_b = d^2 \varepsilon(k)/dk^2|_{k=q/2}$:

$$\frac{1}{m_{n,p}} \approx \frac{v^2}{\Delta} + \frac{1}{m_b} = O\left(\frac{\varepsilon_F}{\Delta} \frac{1}{m_b}\right), \quad (16)$$

and the quasiparticle momentum scattering time at $T < \Delta$ has the form

$$\tau_{n,p} = \sqrt{\frac{2T}{\pi\Delta}} \frac{1}{v_f + v_b/2} \quad (17)$$

and is expressed in terms of v_f and v_b , i.e., the reciprocal forward and backward scattering times for electrons in the metallic states. In Eqs. (15) and (17) we neglected the small differences between the electron and hole scattering times. The electron and hole densities calculated under the same conditions using Eq. (6) are described by the formulas

$$n = \sqrt{\frac{2}{\pi}} \frac{m_n T}{\pi} \exp\left(-\frac{\Delta - \mu}{T}\right),$$

$$p = \sqrt{\frac{2}{\pi}} \frac{m_p T}{\pi} \exp\left(-\frac{\Delta + \mu}{T}\right). \quad (18)$$

In some charge-density-wave conductors one type of carrier predominates. For example, measurements of the thermopower and the Hall coefficient show that in fields be-

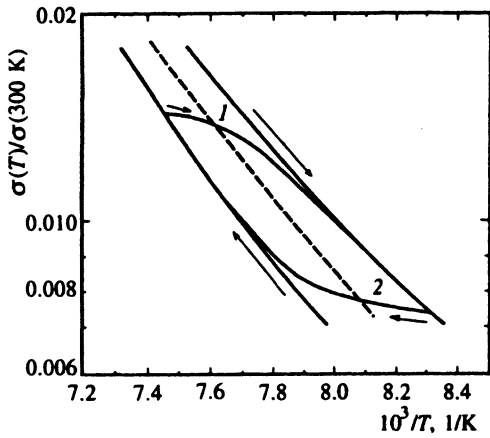


FIG. 1. Typical hysteresis loop in the temperature dependence of the conductivity of orthorhombic TaS_3 . A similar dependence is observed in $\text{K}_{0.3}\text{MoO}_3$.

low the threshold value blue bronze is an n -type semiconductor,^{11,12} and TaS_3 is a p -type^{13,14} and even a unipolar semiconductor.¹⁴ According to (7) and (15), in such materials

$$\sigma \approx \frac{e^2 \tau_{n,p} |q(T) - q(0)|}{\pi m_{n,p}}, \quad (19)$$

and, therefore, the temperature dependence of the conductivity is determined by the temperature dependence of q with accuracy to the relaxation time $\tau_{n,p}$ (17), which is less strongly dependent on the temperature. This apparently paradoxical conclusion, however, does not contradict the dependence $\sigma(T) \propto \exp(-\Delta/T)$, since $q(T) - q(0)$ also obeys a thermal activation dependence with an activation energy close to Δ (Refs. 11, 15, and 16).

Let us now analyze the experimental data on the temperature hysteresis of the conductivity, which is attributed³ to the presence of a barrier to the formation of defects in the electron crystal that provide for a 2π phase change i.e., to variation of the charge-density-wave vector. Figure 1 presents a typical hysteresis loop of the temperature dependence of the conductivity for orthorhombic TaS_3 . The upper and lower curves were obtained during continuous cooling and heating, respectively, and correspond to the greatest deviation from the equilibrium state, which is described by the curve that is located in the middle of the loop and depicted by a dashed line. The slope of this curve specifies the activation energy and is related to the Peierls gap Δ . When the direction of variation of the temperature is reversed (curve 1 or 2), q does not vary in the initial moment (the deviation of q from the equilibrium value is equal to the phase gradient). Thus, at a given temperature q can have different values, depending on the temperature history of the crystal. It is seen from Fig. 1 that the initial slope of curves 1 and 2, which corresponds to a fixed value of q , is much smaller than the slope of the equilibrium curve and the curves corresponding to saturation, and they characterize a state with an altered charge-density-wave vector. It can be concluded that the conductivity is, in fact, determined by the magnitude of the vector q , in agreement with Eq. (19) for the conductivity. It

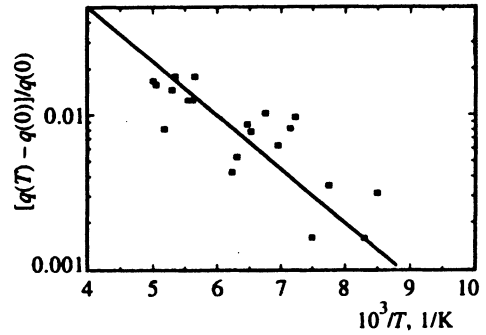


FIG. 2. Temperature dependence of the relative deviation of $q(T)$ from $q(0) \equiv 0.2505c^*$ in TaS_3 (■—data from Ref. 15; the solid line corresponds to an activation energy of 800 K).

can be stated that a kind of self-doping of the charge-density-wave semiconductor takes place: the change in the charge-density-wave vector (expansion or contraction of the electron crystal) regulates the electron or hole concentration, so that the conductivity and the change in the charge-density-wave vector $q(T) - q(0)$ obey the same thermal-activation law with accuracy to a weaker (nonexponential) temperature dependence of the quasiparticle momentum scattering time τ_q . Our arguments are consistent with the results of the direct measurement of the temperature dependence of q (Fig. 2) taken from Ref. 15. Although the spread of the experimental points is very large, they still fit the activation dependence with an activation energy of 800 K, which is close to the value of Δ in TaS_3 .

Figure 3 presents the analogous data for blue bronze ($\text{K}_{0.3}\text{MoO}_3$, an n -type semiconductor below T_p with a transition to hole conduction in the metallic state) from Ref. 16. The points lie on a straight line corresponding to an activation energy ≈ 750 K. A similar analysis of the results in Ref. 11 gives an activation energy of 630 K. The figure also pre-

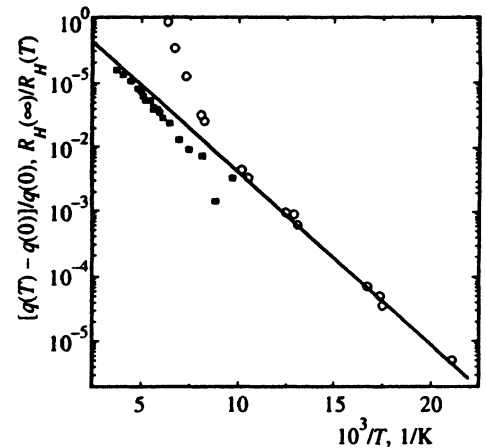


FIG. 3. Temperature dependence of the relative deviation of $q(T)$ from $q(0) \equiv 0.2502b^*$ in $\text{K}_{0.3}\text{MoO}_3$ (■—data from Ref. 16) and of the reciprocal Hall coefficient normalized to $1/R_H(\infty)$ [○—data from 12, where the value of $R_H(\infty)$ was obtained by extrapolating $\log R_H$ from $1/T$ to $1/T=0$]. Within unipolar conduction both parameters are equal to the ratio of the quasiparticle concentration to the total concentration of conduction band electrons. The slope of the solid line corresponds to an activation energy of 616 K.

sents the data from the measurements of the Hall effect in Ref. 12: $R_H(\infty)/R_H(T)$. In the unipolar limit both quantities should have the ratio of the concentration of quasiparticles to the total concentration of electrons condensed in the charge-density wave. In fact, the results in Refs. 12 and 16 not only give similar activation energies, but lie practically on a single straight line, although totally different quantities were measured. The observed deviation of the "Hall concentration" of carriers from the activation law at high temperatures is clearly attributable to the increasing concentration of minority carriers near T_p , where the transition from hole conductivity to electron conductivity occurs in blue bronze. Thus, as in orthorhombic TaS₃, the deviation of q from its value at $T=0$ is proportional to the concentration of the majority charge carriers [see (7)].

The relationship between the magnitude of the vector q and the type and value of the conductivity can also be illustrated in the case of measurements of the thermopower S and its hysteresis in different substances. In analogy to Eq. (15) we can write a descriptive expression for S :

$$S \approx \frac{p(\Delta + \mu)/T - n(\Delta - \mu)/T}{e(p+n)} \approx \frac{\mu}{T} - \frac{\Delta}{T} \tanh \frac{\mu}{T}, \quad (20)$$

where we have again neglected the difference between the scattering times, and in the second equality we also neglected the difference between the electron and hole effective masses. For a unipolar p -type semiconductor, such as orthorhombic TaS₃, Eq. (20) gives $S \approx \Delta/T$, which agrees well with the experimental value of about 600 $\mu\text{V/K}$ at 120 K (Ref. 13). The plots of $S(T)$ exhibit hysteresis,¹³ which, according to the semiconductor model under consideration, is attributable to the shift $\delta\mu$ of the chemical potential from its equilibrium position, as in the case of the conductivity. The magnitude of the hysteresis $\delta S/S$ in orthorhombic TaS₃ amounts to about 5% at 120 K. According to (20), $dS/d\mu = 1/T$, from which it follows that $\delta\mu \approx 3 \text{ meV}$.²⁾ In the case of unipolar conduction the hysteresis $\delta\sigma/\sigma = \delta\mu/T$. This relation gives $\delta\sigma/\sigma \approx 30\%$, in good agreement with typical experimental values.¹⁸

Let us now consider an example of another charge-density-wave conductor $(\text{NbSe}_4)_{10/3}\text{I}$, in which measurements of the hysteresis of the thermopower were recently performed.¹⁹ The hysteresis of S in this substance is enormous. For example, in the region of the thermopower maximum at 180 K, S varies in the range from 80 to 250 $\mu\text{V/K}$ upon the transition from heating to cooling. Also, the value of S is significantly smaller than $\Delta/T \approx 1800 \mu\text{V/K}$, i.e., the value which would be observed for unipolar conduction [according to the activation energy for conduction $\Delta = 3720 \text{ K}$ (Ref. 19)]. It therefore follows that the conduction is far from unipolar and that the shift of μ from the middle of the gap is smaller than T (an evaluation gives $\mu \approx 10 \text{ K}$). In this case $dS/dT \approx -\Delta/T^2$. Then the observed value $\delta S = 170 \mu\text{V/K}$ corresponds to $\delta\mu \approx 17\text{K} \approx 1.5 \text{ meV}$. This value is approximately the same as in orthorhombic TaS₃, but the hysteresis of the conductivity in $(\text{NbSe}_4)_{10/3}\text{I}$ does not exceed 2%. This is also consistent with the semiconductor model: taking into account that for $\mu < T$ we have $\delta\sigma/\sigma = (\delta\mu/T)(2\mu/T)$, we

obtain $\delta\sigma/\sigma \approx 1\%$, in agreement with the experimental data.¹⁹

Thus, the relationship between the dependence of q on T and the temperature hysteresis of the conductivity and of the thermopower of charge-density-wave semiconductors having either unipolar conduction or conduction with electron and hole contributions of similar magnitude becomes clear within the model under consideration. It is interesting that $\sigma(T) \propto \exp(-\Delta/T)$ even in the unipolar limit. In this case a fundamental difference is exhibited between charge-density-wave semiconductors and ordinary semiconductors, in which the conductivity depends weakly on the temperature in this case.

One of the significant consequences of the analysis performed is the lack of any indications of the incommensurate-commensurate transition postulated in several papers.¹⁵

At low temperatures charge-density-wave semiconductors display considerable deviations from the temperature dependences of the conductivity and the thermopower discussed here. For example, in orthorhombic TaS₃ the activation energy for conduction along chains decreases at liquid-nitrogen and lower temperatures.^{20,21} These variations are accompanied by an abrupt decrease and even a change in the sign of the thermopower.^{13,19} At the same time, the activation energies for the Hall coefficient and the conductivity perpendicular to the chains vary only slightly,^{14,22} ruling out an explanation within the chemical potential shift.³⁾ We cannot explain such low-temperature behavior within our semiconductor model. This behavior is most likely due to the appearance of a new mechanism of conduction along the chains involving nonlinear charge-density-wave excitations, for example, solitons, or to charge-density-wave creep. In both cases we are dealing with the spatially inhomogeneous motion of a charge-density wave. The hypothesis of a soliton contribution was advanced back in the early papers.²⁰ This theory is supported by recent theoretical results,^{23,24} which suggest that the motion of inhomogeneous perturbations of the phase of a charge-density wave (particularly, solitons) should make a contribution to the thermopower that opposes the contribution of the majority carriers. The hypothesis of charge-density-wave creep was utilized in Ref. 25 to account for the features of the low-temperature conductivity of TaS₃.

4. CONCLUSIONS

In the present work we have analyzed the semiconductor model of a Peierls conductor. It has been shown that the correspondence between the temperature dependences of the charge-density-wave vector and the conductivity can be understood within this model. It has also been shown that the sign of the majority current carriers is determined by the details of the band structure of quasi-one-dimensional conductors. The region of applicability of the semiconductor model has been established. It has been shown, in particular, that at comparatively low temperatures the predictions of the semiconductor model deviate from the observed temperature dependences of the conductivity and the thermopower, attesting to the appearance of a new contribution to the conductivity.

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- ¹This question was also addressed in Ref. 5.
²This value can be regarded as a measure of the limiting stress of the charge-density wave needed to alter q (Ref. 17).
³Recent, as yet unpublished calculations performed by one of us (S.N.A.) show that pinning centers lead to a different chemical potential shift in different chains, causing a large increase in the local value of the conductivity along chains without a considerable increase in conductivity in the perpendicular direction.
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