Soliton conductivity and anomalies in the temperature and field dependences of the electrical resistance of thallium capronate $CH_3—(CH_2)_4—CO_2Tl$

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(Submitted 29 April 1980)
Pis'ma Zh. Eksp. Teor. Fiz. **32**, No. 1, 14–19 (5 July 1980)

The temperature and field dependences of the electrical conductivity of a new, quasi-two-dimensional conductor—thallium capronate—were analyzed within the framework of the concepts of soliton conductivity of the charge-density wave. The parameters of ϕ solitons were obtained.

PACS numbers: 72.80.Le, 72.30. + q, 72.20.Ht

The phase of a Peierls insulator[1] in quasi-one-dimensional and quasi-two-dimensional crystals is sensitive to a strong electric field E.[2] An electric field induces a transition to the metallic state, which is manifested experimentally as an increase in conductivity with increasing field. The possibility of a transition with the formation of solitons–localized perturbations of the order parameter–was pointed out in Ref. 2. Solitons of the modulus of the order parameter, which give rise to nonlinear conductivity in a doped polyacetylene, were analyzed in Ref. 3. This case, like that examined in Ref. 2, can occur only when there is a strict doubling of the lattice constant. An electrical conductivity mechanism, which is attributable to the soliton state when the period of the charge-density wave (CDW) does not match the doubled lattice constants, was proposed in Ref. 4. In this case the solitons of the CDW phase (ϕ solitons) are the charge carriers. It is known (see, for example, Ref. 5) that the conductivity of systems with CDW at low temperatures had essentially nonlinear dependence on the electric field and temperature T. Up to now, the theories have been able to explain such dependence only in the range $T=0$[6] and in the range of high temperatures.[4] In this paper we examine a ϕ soliton model[4,6] whose dynamics are described by the sine-Gordon equation; however, the expressions for the conductivity like the E and T functions, have been obtained in a wide range of variation of these parameters.[1)] An attempt has been made to correlate the temperature and field dependences of the soliton conductivity with the experimental data for a new, quasi-two-dimensional conductor–thallium capronate.[7]

According to Ref. 6, the conductivity of ϕ solitons at low temperatures can be accounted for by the instability of the CDW ground state in the presence of an electric field, which produces in a quantum manner the soliton-antisoliton pairs. The probability of soliton-antisoliton pair production is $P \sim \exp(-S)$, where S is the action that was calculated using a Lagrangian of the CDW[6] on the extremal trajectory. To obtain the temperature dependence of P, we must calculate S for the trajectories that are periodic in imaginary time.[8] The critical dimensions of the pair is $\lambda_c = NE_\phi/2\pi e^* E = E_\phi/\epsilon$, where E_ϕ is the soliton (antisoliton) rest energy, N is the commensurability index, and e^* is the effective soliton charge. The soliton conductivity of a filament of length L has the form

$$\sigma_S = \frac{2}{N}(2\pi e^*)^2 \frac{c_0 \Lambda}{E_\phi d} \exp(-S), \tag{1}$$

where $\Lambda = \min\{L, l\}$, l is the soliton path length, $d = c_0/\omega_0$ is the soliton size, ω_0 is the Penning frequency of the CDW, and c_0 is the velocity of the "phase phonons." Using the method of Ref. 10, we can formulate an exact procedure for determining the extremal trajectories which are periodic in imaginary time and which correspond to the Lagrangian of the CDW. In this case the expression for S in the temperature region $T \ll \omega_0$ has the form

$$S = \frac{2E_\phi}{\omega_0}\left\{\gamma^{1/2} - \frac{\alpha^2}{4\gamma^{3/2}} + \frac{E_\phi}{\epsilon d}\left(\arcsin\sqrt{1-\alpha^2} + \alpha\sqrt{1-\alpha^2}\right)\right\}, \tag{2}$$

where $\gamma = 3/2$ and α is related to the temperature and field by the relation

$$\frac{\omega_0}{T} = \frac{2E_\phi}{\epsilon d}\sqrt{1-\alpha^2} + \gamma^{-1/2}\ln\alpha^{-1}. \tag{3}$$

Equation (2) allows a simplification in the limit $T \ll T_q = (2/\pi)(\epsilon c_0/E_\phi)$

$$P \sim \exp\left\{-\frac{2E_\phi}{T_q}\left[1 - \frac{T_q}{\omega_0}(4\gamma^{3/2})^{-1}\exp\left(-2\gamma^{1/2}\frac{\omega_0}{T}\right)\right]\right\}, \tag{4}$$

and for $T_q < T \ll \omega_0$

$$P \sim \exp\left\{-\frac{2E_\phi}{T}\left[1-\frac{\pi^2}{48}\left(\frac{T_q}{T}\right)^2\right]\right\}. \tag{5}$$

Equation (4) is identical to that in Ref. 6, and the exponent in Eq. (5), which is identical to that in Ref. 4, has a "classical" structure, but the pre-exponential coefficient in P [see Eq. (1)] remains a "quantum" coefficient. Note that the description of soliton conductivity, like that of a charge transfer in a gas of thermally produced soliton-antisoliton pairs,[4] is valid only for $T \sim E_\phi > \omega_0$. At lower temperatures, the quantum pair production processes are the main contribution to soliton conductivity.

We shall attempt to use the concepts to explain the anomalies of the temperature and field dependences of the electrical conductivity of thallium capronate: $CH_3-(CH_2)_4-CO_2Tl$, whose structure apparently corresponds to parallel conducting filaments that are embedded in layers separated by an organic layer. The synthesis and identification of this compound using a method analogous to that of Ref. 11 enabled us to obtain purer samples than those examined earlier by us. The fine crystalline powder was remelted in an evacuated ($p \sim 10^{-3}$ mm Hg) and sealed-off quartz ampule at a temperature $T = 230 \pm 2$ °C and slowly cooled (10 deg/hour); as a result, we obtained polycrystals with grain sizes of 2–6 mm. The large grains made it possible to measure the anisotropy of the electrical conductivity $\sigma_{\|}/\sigma_{\perp}$ by using the two-probe method in the compensating mode. At room temperature this value was $\sigma_{\|}/\sigma_{\perp} \sim 10^6$, $\sigma_{\|}^{293K} \approx 20$–$100$ (ohm·cm)$^{-1}$; the longitudinal conductivity was metallic type and the transverse conductivity was semiconductor type. The slit width determined in the graph in Fig. 1 is 5 eV in the region 0–150 °C and ~ 3 eV in the region 150–240 °C. The melting points of thallium capronate $T_1 = 150 \pm 1$ °C, corresponding to the transition to liquid-crystal state, and $T_2 = 223 \pm 1$ °C, corresponding to the transition to an isotropic liquid, which were determined by us by using the standard method, are in good agreement with the data.[11,12] The conductivity anisotropy almost disappears in the transition from the solid phase to the liquid crystal, and the $\sigma(T)$ dependence

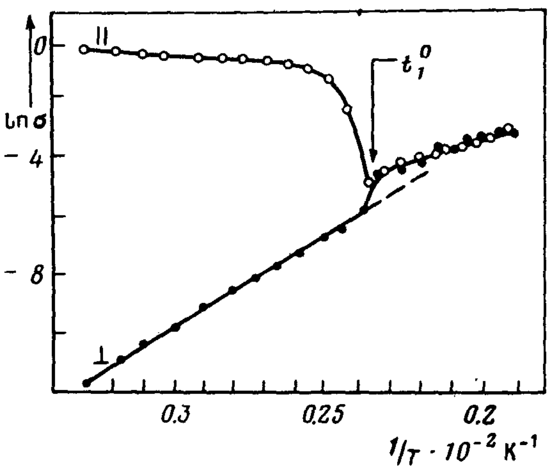

FIG. 1. Longitudinal σ and transverse $\sigma_{\perp}$ conductivity of thallium capronate in the temperature range 300–500 K.

becomes semiconducting type. The characteristic features of the temperature dependence of the electrical conductivity at 4.2 K $\leqslant T \leqslant$ 300 K are (see Fig. 2): 1) a step with a change in the curve slope at $T = 190$ K, which resembles the anomaly corresponding to formation of a CDW in the transition-metal dichalcogenides $NbSe_3$ and in certain other small size conductors; 2) a characteristic non-ohmic resistance analogous to the observed low-temperature[5] anomaly in $NbSe_3$ that can be suppressed with an electric field ($T \sim 40$ K); 3) an absence of temperature dependence of the conductivity below 40 K.

To isolate the soliton contribution to the conductivity and compare it with the experiment, we write the soliton component of the conductivity in the form [see Eq. (4)]:

$$\sigma_S = \sigma_* \exp\left\{-\frac{2E_\phi}{T_q}\right\} = \sigma_0 \exp\left\{-\frac{E_0}{E}\right\}, \qquad T < T_q . \tag{6}$$

We determine $E_0 = 0.2$ V/cm from the plot of the dependence of $(\ln\sigma_0 - \ln\sigma_s)$ on $1/E$ (Fig. 3). The E_0 is related to E_ϕ by the relation $E_\phi = (2e^* E_0 c_0/N)^{1/2}$. Assuming that $e^* \sim e$, $N \sim 1$, $c_0 \sim 10^7$ cm/sec (Ref. 6), and the effective mass of the CDW $m^* \sim$ 10–100 m, we obtain $E_\phi \sim$ 10–100 K. The temperature T_q can be determined from the equation $T_q = 4e^* E c_0/N E_\phi$, where $E \sim$ 10 V/cm is the field intensity at which the nonlinear resistance disappears at $T \sim 40$ K ($T_q \sim$ 10 K). The value of E_ϕ, which was estimated from the temperature dependence in the region $T_q < T$ by using Eq. (5), agrees in order of magnitude with that determined from the field dependence. The contribution of thermally excited solitons for $T_q < T$ cannot be isolated exactly, be-

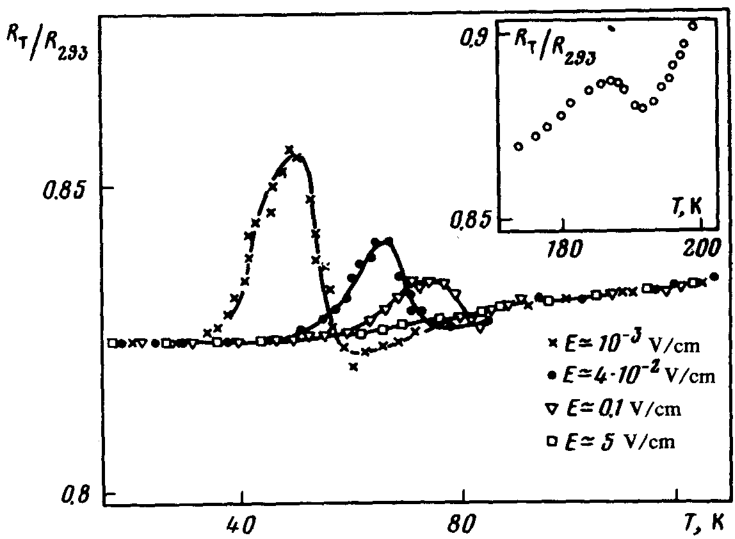

FIG. 2. Anomalies of the relative electrical resistance $R_T/R_{293\,K}$ of thallium capronate at different electric-field intensities E.

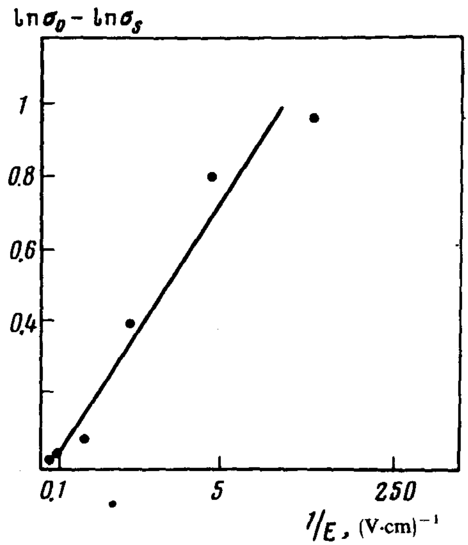

FIG. 3. Variation of the nonlinear conductivity of thallium capronate in the region of electric-field intensities E corresponding to the condition $T < T_q$, as a function of $1/E$.

cause of the narrow temperature interval $\Delta T \sim 20$–30 K in which the anomaly is observed. The value of T_q increases with increasing E, consistent with the trend determined from Eq. (4).

Thus, an analysis of the field and temperature dependences of the electrical conductivity of thallium capronate makes it possible to use the soliton conductivity of the CDW in small-size systems with a Peierls transition to qualitatively explain the experimental data.

[1)]A detailed discussion of the theoretical results will be published in the journal "Fizika Nizkikh Temperatur" ("Soviet Journal of Low-Temperature Physics").

[1]H. Frölich, Proc. R. Soc. London Ser. A **223** (1954).

[2]I. O. Kulik, Pis'ma Zh. Eksp. Teor. **22**, 73 (1975) [JETP Lett **22**, 32 (1975)].

[3]W. P. Su, J. R. Schrieffer and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979); M. J. Rice, Phys. Lett. A **71**, 152 (1979).

[4]M. J. Rice, A. R. Bishop, J. A. Krumhansl, and S. E. Trullinger, Phys. Rev. Lett. **36**, 432 (1976).

[5]M. J. Cohen, B. R. Newmann, and A. J. Heeger, Phys. Rev. Lett. **37**, 1500 (1976); R. Fleming and C. C. Grimes, Phys. Rev. Lett. **42**, No. 21 (1979); P. Monceau, N. P. Ong, A. M. Portis, A. Meerschaut, and J. Rouxel, Phys. Rev. Lett. **37** 602 (1976).

[6]K. Maki, Phys. Rev. Lett. **39**, 46 (1977).

[7]A. E. Gvozdev and A. A. Mamalui, In: Material 20-go Vsesoyuznogo soveshchaniya po fizike nizkikh temperatur NT-20 (Proceedings of 20th All-Union Conference on Low-Temperature Physics NT-20), Pt. 1, 1979, p. 160; A. E. Gvozdev and A. A. Mamalui, Fiz. Nizk. Temp. **5**, 79 (1979) [Sov. J. Low Temp. Phys. **5**, 38 (1979)].

[8]R. Feynman and A. Hibbs, Kvantovaya mekhanika i integraly po traektoriyam (Quantum Mechanics and Trajectory Integrals), Mir, Moscow, 1968.

[9]S. Coleman, Phys. Rev. D **15**, 2929 (1977).

[10]H. J. Katz, Phys. Rev. D **17**, 1056 (1978).

[11]A. Mc Killop, D. Bromley, and E. C. Taylor, J. Org. Chem. **34**, 1172 (1969).

[12]R. Walter, Ber. B **59**, 962 (1926).