## Electrical conductivity of the quasi-one-dimensional compound TaS<sub>3</sub> at low temperatures

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The electrical conductivity of quasi-one-dimensional orthorhombic TaS<sub>3</sub> crystals is investigated in the 350 to 4 K temperature range and in electric fields up to 500 V/cm. It is found experimentally that at T < 100 K a considerable growth occurs of the threshold field  $E_c$  for motion of the charge density wave. Simultaneously, a new nonlinearity section appears on the current-voltage curve with a critical field  $E'_c < E_c$  whose magnitude decreases with decrease of the temperature. At temperatures below 20 K the temperature dependence of the electrical conductivity obeys a  $\sigma(T) \sim \exp[-(T_0/T)^{1/2}]$  law and the frequency dependence a  $\sigma(\omega) \sim \omega^s$  law, where  $s \approx 0.8$ . At  $T \approx 5$  K the dielectric constant reaches  $10^6$ . An analysis of the data and also of the shape of the current-voltage curve at T < 20 K shows that the most probable mechanism responsible for the dependence observed is a soliton conduction mechanism in the crystal with a certain degree of disorder and pinning of the charge-density wave.

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Tantalum trisulfate TaS<sub>3</sub> is one of the most interesting quasi-one-dimensional compounds, in which a bound structural-electronic (Peierls) transition, <sup>1-3</sup> motion of a charge density wave (CDW),<sup>4-6</sup> and narrow-band generation of high-frequency current<sup>7</sup> are observed. Its characteristic features are a high degree of one-dimensionality of the structure, commensurability of the superlattice with the initial lattice with multiplicity equal to four along the *c* axis (Refs. 2 and 3), stability to the action of the atmospheric and to thermal cycling, and also a sufficiently high phase-transition temperature ( $T_p \approx 210$  K). TaS<sub>3</sub> is a convenient material for the investigation of the physical laws that are common to all quasi-one-dimensional compounds.

Much, however, remains unclear even in the basic properties that determine the quasi-one-dimensional nature of the TaS<sub>3</sub> properties. One of the important problems is clarification of the mechanisms of the electric conductivity of TaS<sub>3</sub> at low temperatures, and in particular the contribution made to it by the nonlinear excitation of CDW solitons, the influence of the disorder of the real crystals, and the presence in them of impurities and defects. In the present paper we investigate in detail the electric conductivity of crystalline TaS<sub>3</sub> samples with orthrhombic structure in wide intervals of the temperature (350–4 K) and of the electric field (up to 500 V/cm).

## PRODUCTION OF SAMPLES AND EXPERIMENTAL TECHNIQUE

Tantalum trisulfate in the form of whisker crystals of black color with characteristic metallic luster was obtained from the elements by heating powdered tantalum in sulfur vapor. Prior to preparation of the samples, the initial components, namely tantalum (Nb content  $<5\cdot10^{-2}\%$ ,  $C < 7\cdot10^{-2}\%$ , remaining impurities  $<10^{-3}\%$ ) and sulfur ("specially pure" grade) were thoroughly outgassed by heating in vacuum and loaded in reaction ampoules made of thick-walled quartz glass. The ampoules were sealed off with continuous evacuation to  $P < 10^{-5}$  Torr. To prevent loss of sulfur in the course of the sealing, the ampoules with the reaction mixture were cooled to  $-70^{\circ}$ C. All work on the preparation of the reaction mixtures and loading the ampoules was carried out in a dry-argon box.

The ampoules with the mixture were heated for 7–15 days at 800°C and then cooled to room temperature at a rate of 10° per hour. Typical dimensions of the whisker crystals obtained in this manner were the following: thickness from several hundred angstrom to 20  $\mu$ m, length—5 to 10 mm. The chemical composition of the TaS<sub>3</sub> samples was confirmed by microprobe x-ray-emission analysis. We obtained TaS<sub>3</sub> of both monoclinic and orthorhombic modification. We report here results pertaining only to samples with orthorhombic structure. The unit-cell parameters of this structure were determined by electron-diffraction methods and were in good agreement with published data.<sup>2,3</sup>

The sample investigated was mounted on a substrate of crystalline quartz coated beforehand with gold or indium electrodes, the distance between which was  $\sim 1$  mm. The samples were connected to the electrodes either with silver paste or by cold soldering with indium. The resistance of the contacts obtained with the silver pastes at our disposal had a tendency to increase continuously after repeated thermal cycling. Contact obtained by cold soldering with indium were more stable. The contact resistance at room temperature, determined from a comparison of the measurements of the resistance of a sample by the two- and four-probe methods, did not exceed 0.1  $\Omega$ . Such contacts had good mechanical strength and reproducibility in repeated thermal cycling from room temperature to 4.2 K.

The measurement in the temperature interval 350-4 K were carried out in the cryostat in which the sample was in a hermetically sealed chamber filled with helium gas at low pressure. To maintain the temperature constant we used an automatic electronic system with a semiconductor diode as the heat sensor. The accuracy with which the temperature

was maintained was  $\pm 5 \cdot 10^{-2}$  K over 30 minutes. The temperature was measured with a germanium thermometer.

Measurements of the electric conductivity in direct current were made with the aid of an electrometer with input reesistance higher than  $10^{14} \Omega$ , with precautions made to protect against vibration and leakage in the electric system and the cryostat. The total leakage resistance was not less than  $10^{13} \Omega$ ). In strong electric fields (E > 100 V/cm) and at high temperature (T > 40 K) the self-heating of the samples was prevented by performing the measurements by a pulse method with a two-channel pulsed synchronous storage unit. The pulse duration was 1  $\mu$ sec and the pulse repetition frequency  $\sim 10^2$  Hz. The use of this method makes it possible to reach fields 300 V/cm and 500 V/cm at nitrogen and helium temperature, respectively.

## **EXPERIMENTAL RESULTS**

We measured the thermal conductivity and currentvoltage characteristics (CVC) of 20 TaS<sub>3</sub> samples with orthorhombic structure in a wide temperature interval (350–4 K) and of electric fields  $(10^{-2}-5\cdot10^2 \text{ V/cm})$ . In addition, at low temperatures (4 < T < 40 K) we investigated the dependence of the electric conductivity on the frequency in the range 3–  $10^5 \text{ Hz}$ . Some of the results of these investigations were presented in our earlier papers.<sup>6,8</sup>

Figures 1 and 2 show the temperature dependence of the electric conductivity  $\sigma$ , normalized to its room-temperature value  $\sigma_r$ , in a weak electric field [on the linear sections of the CVC) for several typical TaS<sub>3</sub> samples. For comparison, Fig. 1 shows also the results<sup>4</sup> of measurement of  $\sigma(T)$  of orthorhombic samples up to 80 K. The good agreement of these plots, and also the results of electron-diffraction investigations (see above), show that samples obtained by us had an orthorhombic structure. In particular, the dependence of the derivative  $d (\log \sigma)/d (1/T)$  (Fig. 1) has in the range 300–

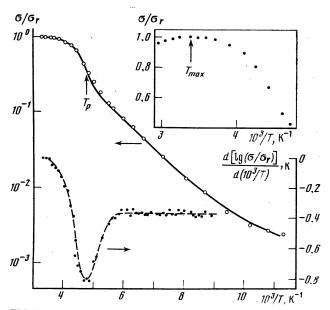


FIG. 1. Temperature dependence of the electric conductivity  $\sigma$  normalized to its value  $\sigma$ , at room temperature to TaS<sub>3</sub> (O—sample No. 19). Solid line —plot of  $\sigma(T)/\sigma$ , from Ref. 1. Inset— $\sigma(T)/\sigma$ , dependence at  $T > T_P$  (O—sample No. 18).

100 K only one minimum at 210 K. This temperature,  $T_P = 210$  K, will be taken by us to be the temperature of the Peierls transition.

The temperature dependence of  $\sigma(T)$  in the range 350-4 K (Figs. 1 and 2) can be divided into four characteristic regions:  $1-T > T_p$ ;  $2-T_p > T > 100$  K; 3-100 > T > 20 K; 4-20 > T > 4 K (the values of the end-point temperature are approximate). When the temperature is lowered from 350 to 230 K,  $\sigma$  first increases slowly and nonlinearly with T (inset of Fig. 1), reaches a maximum at  $T \approx 290$  K, and then decreases smoothly down to  $T \approx 230$  K. The CVC of samples in this temperature region are linear within the limits of the errors of our experiment. With further lowering of the temperature one observes a rather abrupt decrease of  $\sigma$  with a maximum negative derivative at  $T_p = 210$  K.

In the 200–100 K region one observes on the log  $(\sigma/\sigma_{\rm cr}) = f(1/T)$  a section close to linear, corresponding to activated conductivity with energy  $\Delta \approx 800$  K = 70 meV. The value of  $\Delta$  varies somewhat from sample to sample, from 775 to 850 K. Its smaller values are close to the results of Ref. 5. In some samples we measured also the transverse electric conductivity  $\sigma_1$ . The ratio  $\sigma_{\parallel}/\sigma_1$  exceeded 100 and changed little in the region 200–100 K.<sup>4</sup> It must be noted, however, that at  $T \gtrsim T_P$  a distinct maximum was observed on the temperature dependence of  $\sigma_{\parallel}/\sigma_1$ , just as in Ref. 9.

The dependence of the electric conductivity on the electric field in the temperature range 160-4 K is shown in Fig. 3. In the temperature region 160–60 K the  $\sigma(E)$  dependences have a qualitatively similar form:  $\sigma$  is independent of E up to a certain critical (threshold) field  $E_c$ , to which corresponds a linear (ohmic) section of the CVC. The nonlinearity of the CVC appears only at  $E > E_c$ , and it corresponds to an increase of the electric conductivity of the sample. The transition to nonlinear conductivity takes place quite smoothly, and on our curves there is no abrupt break at  $E \approx E_c$ . In the region T > 70 K, the critical field  $E_c$  was defined by us as the field at which the deviation of the CVC from linearity is double the experimental error. It must be noted that the value of  $E_c$  and the abruptness of the transition vary from sample to sample: in samples with smaller values of  $E_c$  the change to an increase of  $\sigma$  was more abrupt. On the curves obtained for  $TaS_3$  in Ref. 5, the kink on  $\sigma(E)$  was abrupt, and the value of  $E_c$  there was also smaller (2.2 V/cm). In the case of NbSe<sub>3</sub> there is also observed a connection between  $E_c$  and the abruptness of the transition, on the one hand, and the number of impurities and defects and the homogeneity of the distribution, on the other.<sup>10</sup> With decreasing temperature of our samples, the regions of the transition to the nonlinear conductivity became smeared out on the  $\sigma(E)$  plot, just as in Ref. 7.

From our data (Fig. 3) it follows that the critical field  $E_c$ changes substantially with temperature. Figure 4 shows the  $E_c(T)$  dependence obtained by us for three samples of TaS<sub>3</sub>. With decreasing temperature, the value of  $E_c$  first decreases slowly. Starting with  $T \approx 130$  K, a faster decrease of  $E_c$  is observed, down to a minimum at  $T \approx 100$  K.

The next temperature region is 100–20 K (Fig. 2). Its characteristic features are the following: a rather abrupt kink on the  $\sigma(T)$  plot, taking place in a narrow temperature

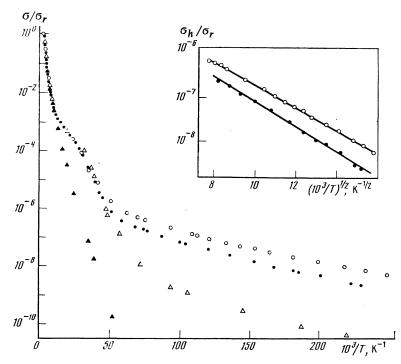


FIG. 2. Temperature dependence of the electric conductivity  $\sigma/\sigma_r$  in the interval 350-4 K. Inset—value of  $\sigma_h/\sigma_r$  at temperatures below 20 K. The solid line corresponds to  $\sigma \propto \exp[-(T_0/T)^{1/2}]$  (Ref. 15). Samples: No. 14-O, No. 15- $\triangle$ , No. 19- $\bullet$ .  $\blacktriangle$ -relative transverse electric conductivity.

interval; the absence of linearity on the plot of  $\log(\sigma/\sigma_r) = f(1/T)$ , namely, an inflection is observed for our samples in the range 40–50 K. If we compare the  $\sigma(T)$  dependence obtained for our samples with the data of Ref. 4, they

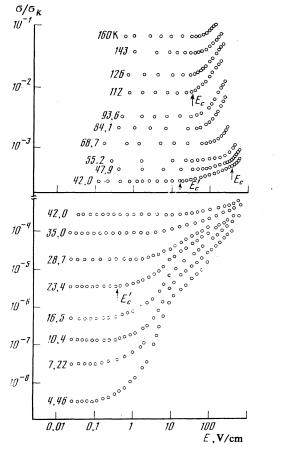


FIG. 3. Electric conductivity of  $TaS_3$  vs the electric field at various temperatures marked next to the curves.  $E_c$  and  $E'_c$  are the critical fields (sample No. 19).

are in good agreement in the region up to 100 K (Fig. 1) and differ in the region 100–20 K (20 K is the lowest temperature measured in Ref. 4). No inflection is observed in Ref. 4 at  $T \approx 40-50$  K. Following the inflection and down to 20 K,  $\sigma$ decreases by two orders of magnitude with an activation energy  $\approx 230$  K approximately 3.5 times smaller than in the region 200–100 K. The transverse conductivity  $\sigma_1(T)$  continues to decrease at T < 100 K, with an activation energy close to its value in the 200–100 K region, where it is the same for  $\sigma_{\parallel}$  and  $\sigma_{\perp}$ .<sup>4</sup> The difference between the activation energies of  $\sigma_{\parallel}$  and  $\sigma_{\perp}$ , which appears at T < 100 K, leads to an increase in the anisotropy of the crystal: compared with the 200–100 K region, the ratio  $\sigma_{\parallel}/\sigma_{\perp}$  increases by 100 times at T = 40 K, i.e., the crystal becomes much more one-dimensional.

As a result of the detailed investigation of the  $\sigma(E)$  dependence in the temperature region 100-40 K, we observed singularities which are typical of all the investigated samples (Figs. 3 and 4). Starting approximately with 100 K, the critical field  $E_c$  increases (Fig. 4). At the same time, a new section with increasing electric conductivity appears on the  $\sigma(E)$ plot, and precedes the section of the strong nonlinearity at  $E \gtrsim E_c$  (Fig. 3, curves T = 55.2, 47.9, and 42 K). This second nonlinearity begins at  $E \gtrsim E'_c \ll E_c$ ; it is characterized by a slower growth of  $\sigma$  than at  $E > E_c$ . The value of the second critical field  $E'_{c}$  that exists in the region 60 > T > 4 K was determined by us from the deviation from linearity on the CVC (see above). In the temperature interval 60-40 K, where two nonlinearity sections are observed simultaneously, the field  $E_c$  increases abruptly and reaches the maximum accessible in our measurements, namely 380 V/cm. In this narrow temperature interval the value of  $E_c$  was determined from the point of transition from a weak to a strong nonlinearity on the field dependence of the nonlinear form of the conductivity, plotted in a doubly logarithmic scale. With decreasing temperature, the field  $E_c$ , in contrast to  $E_c$ , de-

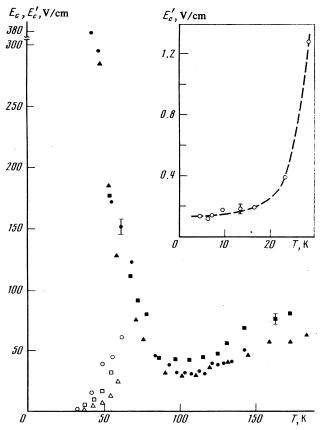


FIG. 4. Temperature dependence of the critical fields  $E_c$  and  $E'_c$  for TaS<sub>3</sub>. Inset- $E'_c(T)$  dependence at low temperatures.  $E_c$  for the samples:  $\blacksquare$ -No. 16,  $\blacktriangle$ -No. 17,  $\bigcirc$ -No. 19,  $E'_c - \Box$ ,  $\triangle$ ,  $\bigcirc$  for the same samples, respectively.

creases rapidly.

As can be seen from Figs. 1 and 2, the temperature dependence of the relative conductivity  $\sigma(T)\sigma_r$  for different samples are qualitatively similar in the entire investigated temperature range 350-4 K. In the interval 350-100 K they differ very little also quantitatively. With decreasing temperature, the plots of  $\sigma(T)/\sigma_r$  begin to diverge, becoming considerably different at T < 20 K. But we emphasize once more that their qualitative form is the same also at 4 < T < 20K. At the start of the fourth temperature region (20-4 K) the slope of the  $\sigma(T)$  plot decreases smoothly (Fig. 2). In the transition region  $T \leq 20$  K the electric conductivity  $\sigma(T)$  can be represented as a sum of two components: activated  $\sigma_a(T)$ with activation energy  $\approx 230$  K, which continues from the region T > 20 K, and a component  $\sigma_{k}(T)$  with a different temperature dependence. Subtracting from the total  $\sigma(T)$  the value of  $\sigma_a(T)$ , we obtain the  $\delta_h(T)$  dependence. We note that the contribution  $\sigma_a(T)$  to the total conductivity  $\sigma(T)$  decreases rapidly with decreasing temperature, and already at  $T \approx 17$  K it does not exceed 10% of  $\sigma(T)$  (Fig. 2). We have observed that the  $\sigma_h(T)$  dependence turns out to be close to the low log  $[\sigma_h(T)/\sigma_r] \propto [-(T_0/T)^{1/2}]$  (inset on Fig. 2; the exponents 1/4 and 1 give larger deviations from linearity), i.e., close to a law of the Mott type for hopping conduction  $\sigma_h$  with variable length of the hop for the case of a quasi-onedimensional conductor.<sup>11,12</sup> In the region 20-4 K this law is valid for all the samples measured by us. With decreasing relative  $\sigma$ , the value of  $T_0$  increases from 370 to 470 K.

The dependences of the electric conductivity on the electric field obtained by us in the temperature region (42-4 K) are shown in the lower part of Fig. 3. Characteristic features of these dependences are the following: constancy of  $\sigma$ in the weak-field region  $E < E'_c$  (linear sections on the CVC); rapid growth of the electric conductivity (by several decades) at  $E > E'_c$  (strong nonlinearity of the CVC); the mutual approach of the  $\sigma(E)$  dependences in the region of strong electric fields (E > 100 V/cm), i.e., the weak dependence on the temperature in these fields; the growth of the amplitude of the nonlinearity and the decrease of the value of  $E'_c$  with decreasing temperature. These  $\sigma(E)$  dependences are qualitatively similar to the corresponding dependences of hopping conductivity with variable hop length, calculated in Refs. 13 and 14. It should be noted that for samples with a larger relative conductivity, at T < 20 K, the relation log ( $\sigma$ /  $\sigma_r \propto f(\log E)$  at  $E > E'_c$  was closer to linear, the growth of  $\sigma(E)$  in the field interval up to  $\approx 500$  V/cm was smaller by a decade, and  $E'_{c}$  was larger.

We have measured the electric conductivity of TaS<sub>3</sub> samples with small values of  $\sigma(T)/\sigma_r$ , with alternating current in the low-frequency region from 3 to  $10^5$  Hz (Fig. 5). At T = 4.28 K,  $\sigma(\omega)$  follows the  $\sigma \sim \omega^5$  law, similar to the law for the frequency dependence of the hopping conductivity with variable length of the hop in disordered structures.<sup>15</sup> The value of s in our case is 0.83, i.e., it agrees well with the theoretically calculated value 0.8 for hopping conductivity.<sup>15</sup> With increasing temperature, the dispersion of  $\sigma(\omega)$ decreases, this being due apparently to the decrease of the contribution of this type of conductivity (of the hopping type) to the total conductivity of the crystal. From measurements of the phase shift of the signal we determined also the dielectric constant in the investigated temperature and frequency regions. It turned out to be unusually large:  $\varepsilon = 10^6$ at T = 4.38 K and  $\omega/2\pi = 10^2$  Hz. We note that the large value of  $\varepsilon$  is typical of many quasi-one-dimensional conductors.<sup>16</sup> These measurements were made in a field  $E < E'_c$ , but special experiments have shown that at  $E > E'_{c}$  the value of  $\varepsilon$ on the nonlinear part of the CVC does not change within the limits of our experimental error.

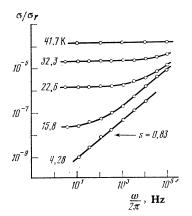


FIG. 5. Electric conductivity of  $TaS_3$  in alternating currents vs its frequency at various temperatures marked next to the curves.

## **DISCUSSION OF RESULTS**

On the basis of the foregoing, as well as of the data published earlier, 1-8 one can picture, with different degrees of certainty, the basic stages of the changes that occur in the quasi-one-dimensional conductor TaS<sub>3</sub> with decreasing temperature. At temperatures higher than the one at which the maximum of  $\sigma$  is reached ( $T_{\text{max}} = 290$  K) the electric conductivity increases nonlinearly with decreasing T (inset of Fig. 1). Here  $TaS_3$  behaves as a metal with a short mean free path and accordingly low mobility  $\sim 1 \text{ cm}^2/\text{V}\cdot\text{sec.}^{17}$  This character of the  $\sigma(T)$  dependence is apparently connected with the phenomenon of partial localization, due to strong scattering, the main contribution to which is made by the large number of disordered impurities and defects. In the region  $T_{\text{max}} > T > T_P$ , the increase of  $\sigma$  gives way to a decrease, the main cause of which are apparently the fluctuations of the order parameter, which set in already at  $T \approx 300$  $K > T_P$  (Ref. 3). The appearance of these fluctuations can lead both to an increase of the carrier scattering and to a decrease in their number because of the onset of a Peierls gap as a result of fluctuations.

The next abrupt decrease of the electric conductivity at  $T \leq 210$  K followed by assumption of  $\sigma(T)$  of an activation character with  $\Delta \approx 800$  K is due to a bound electron-structure transition (Peierls transition), corresponding to the appearance of a superstructure in the initial TaS<sub>3</sub> lattice with formation of a charge-density wave<sup>1-3</sup> and gap  $2\Delta$  in the energy spectrum of the electrons.<sup>4,5</sup> It must be noted that in the transition region the ratio  $\sigma_{\parallel}/\sigma_{\perp}$  has a rather abrupt maximum (see also Ref. 9). This feature is apparently connected with the softening of the phonon mode which takes place in the transition region.<sup>18</sup>

In the temperature region 200–100 K the longitudinal dependence in a weak field is ensured principally by free electrons (the thermal-activation energy is  $\approx 800$  K) and has an ohmic character (Fig. 3). The free electrons determine also the transverse conductivity  $\sigma_{\perp}$ . Therefore, the ratio  $\sigma_{\parallel}/$  $\sigma_1$  in this temperature interval changes little. The CDW in weak fields is immobile because of pinning by the impurities or by the initial lattice.<sup>4,5</sup> When a certain critical value of the field  $E_c$  is exceeded, the CDW begins to move and contribute to the current,<sup>4,5,19</sup> and a strong nonlinearity appears on the CVC, corresponding to a growth of  $\sigma$  (Fig. 3). There exists a definite correlation in the change of the described properties from sample to sample. For samples which can be regarded as "pure" compared with the others, the following attributes are typical: a) a larger abruptness of the phase transition on  $\sigma(T)$  at  $T \approx T_P$ ; b) a lower activation energy in the region 200-100 K; c) a more abrupt transition on the  $\sigma(E)$  dependence at  $E \gtrsim E_c$ ; d) a lower value of the critical field  $E_c$ ; e) a larger value of the relative electric conductivity in the temperature region below 20 K (Fig. 2). Analysis of these data allows us to conclude that our samples contain an appreciable amount of impurities and defects, which influence substantially the sample properties. A similar situation apparently takes place also in another quasi-one-dimensional material, Qn(TCNQ), where the smearing of the phase transition is also attributed to an increase in the impurity density.<sup>20</sup> These data show that in our samples the pinning of the CDW is determined to a considerable degree by impurities and defects. The long-range order of the CDW is then upset,<sup>21</sup> the value and the scatter of the pinning fields of the different segments of the CDW increases, and it is this which yields the observed experimental picture.

As seen from Fig. 4, the value of  $E_c$  changes substantially with temperature. At  $T \leq 130$  K there is observed a decrease of the critical field, a minimum of  $E_c$  is reached at  $T \approx 100$ , followed by a steep increase of  $E_c$  up to value 380 V/cm determined by the capabilities of our measurements. This behavior is most likely due to the incommensurability-commensurability transition observed with the aid of electron-diffraction investigations at  $T \approx 130$  K (Ref. 22).

In the region  $T \approx 100$  K, when a rapid increase of  $E_c$  sets in, the function  $\sigma(T)$  becomes more gently sloping (Fig. 2). In the temperature interval 40–50 K it acquires a small bend and next, down to 20 K, a nearly activated region with energy  $\approx 230$  K. The transverse conductivity  $\sigma_{\perp}$  at T < 100 K decrease with a considerably larger activation energy (Fig. 2). Correlating with these changes of  $\sigma(T)$  are also the new peculiarities that appear on the  $\sigma(E)$  plot (Fig. 3). With continuing increase of  $E_c$ , the  $\sigma(E)$  plot reveals gradually a nonlinear contribution from some process with a critical field  $E'_c \ll E_c$  (Fig. 3, curves at T = 55.2, 47.9, and 42 K).

Several explanations can be offered for these results and those following. First, at  $T \approx 100$  K there can occur a new structural transition with restructuring of the electron spectrum and with appearance of a new activation energy (200 K and a new CDW system). The previously published x-ray structural analysis data<sup>2</sup> do not provide direct proof of the presence of such a transition. On the other hand, the already mentioned recent results of a careful electron-diffractin investigation<sup>22</sup> offer evidence of a certain change that takes place at  $T \approx 130$  K in the structure of orthorhombic TaS<sub>3</sub>, of the incommensurability-commensurability type, although apprently not radical enough to explain the observed change in the activation energy by a factor 3-4, which occurs at  $T \approx 100$  K (Fig. 2). Nonetheless, one cannot exclude fully a connection between the transition of Ref. 22 and the changes in the  $\sigma(T)$  and  $\sigma(E)$  dependences observed by us at lower temperatures.

Second, one could assume that the  $\sigma(T)$  plot at T < 100K begins to be influenced by the contribution of some impurity states of semiconducting type with activation energy lower than 800 K, i.e., with energy levels in the forbidden band. In this case, however, such an activation energy should be possessed also by the transverse conductivity  $\sigma_1$ , i.e., these impurities should supply electrons also for this conductivity. In experiment, as already mensioned, one observes a decrease of  $\sigma_1$  with an activation energy close to the earlier one (to T > 100 K) and a stronger increase of the anisotropy, i.e., the contribution of the free electrons becomes very small.

We believe that the relations observed by us can most probably be explained on the basis of the assumption of gradual appearance, at T < 100 K, of a new soliton conduction mechanism.<sup>4,23-26</sup> In electric field  $E < E_c$ , the CDW is pinned and makes no contribution to the electric conductivity. There can exist in it, however, two types of excitationsamplitude and phase solitons. The amplitude solitons in the case of TaS<sub>3</sub> (n = 4) should be neutral,<sup>23</sup> and they apparently cannot ensure its electric conductivity. The most probable are topological solitons with charge 2e, corresponding to a local change of the phase of the CDW by  $2\pi$  (Refs. 24, 25), which does not lead to a substantial increase of excitation energy, despite the presence of interaction between the filaments. The activation energy  $\Delta_s$ , of such solitons, is lower than the activation energy of the amplitude solitons and is of the order to  $T_P$  under the conditions  $T_P < \Delta$ . In our case  $T_P = 210$  K and  $\Delta_s \approx 230$  K, i.e., the agreement is good enough. In a weak electric field, the solitons make an ohmic contribution to the electric conductivity,<sup>26</sup> and in a stronger field the contribution becomes nonlinear. Topological solitons are pinned by impurities and defects. However, the pinning field for them is weaker than for CDW, and this also agrees with experiment. The reason for this is that the CDW moves in correlated manner simultaneously on several filaments of the crystal, and a defect on even one filament does not interfere with the motion of the soliton on the other. At the same time, the solitons cannot go over from filament to filament, and this explains the increase of the anisotropy at T < 100 K. The inflection of  $\sigma(T)$  at  $T \approx 40$  K can be connected with the dependence of the soliton mobility on the temperature.

With decreasing temperature, the number of solitons decreases and the degree of their localization increases. This leads to a considerable decrease of the conductivity due to their activated motion. As a result, at  $T \approx 20$  one observes a transition to a new region with a more gently sloping nonlinear dependence of  $\sigma(T)$ . Features of this region are the following: 1) the temperature dependence of  $\sigma(T)$  follows the law  $\sigma \propto \exp[-(T_0/T)^{1/2}]$ , i.e., a law of the hopping-conduction type with variable length of the hop for the quasi-onedimensional case<sup>11,12</sup>; 2) strong nonlinearily of the CVC sets in at small critical values of the fields  $E'_{c}$ , whose strength decreases with decreasing temperature; 3) the frequency dependence (Fig. 5) follows the law  $\sigma \sim \omega^5$ , where  $s \approx 0.8$ . The value of  $\varepsilon$  reaches large values,  $10^5 - 10^7$ , and does not change at  $E > E'_{c}$ . We note that if the nonlinear part of the CVC were connected with the CDW motion, then  $\varepsilon$  should decrease in the case of a moving charge-density wave.<sup>27</sup> The value of  $\sigma(T)$  in this temperature region depends substantially on the impurity density in the samples (Fig. 2). In our opinion, the higher the relative  $\sigma$ , the fewer impurities in the samples. In our case the impurities do not supply electrons as in semiconductors, and serve only for pinning and scattering, just as in metals. This result correlates with the abruptness of the transition of  $\sigma(T)$  at  $T \approx T_P$  and of  $\sigma(E)$  at  $E \approx E_c$ , and also with the relatively lower value of  $E_c$  in "pure" samples. All these dependences observable by us are attributes of the presence, in a system with a certain degree of disorder, of hopping-type conduction with a variable length of the hops.<sup>15,8</sup>

From our results one cannot draw at present any final unambiguous conclusions concerning the electric conduc-

tion mechanism in the quasi-one-dimensional conductor TaS<sub>3</sub> in the entire temperature range 350-4 K. The least understandable is apparently the temperature region 100-40 K. Nonetheless it is clear even now that at  $T < T_P$  the electric conductivity of TaS<sub>3</sub> cannot be explained on the basis of only single-electron mechanisms and is determined to a considerable degree by the motion of collectivized electrons: the charge density wave and its nonlinear excitations-solitons. In the crystals obtained by us, a very important role is played by the impurities and defects: they serve as centers for pinning both the CDW and the solitons, and determine the value of the electric conductivity at temperature lower than 20 K. It can be assumed that at these temperatures the electric conduction is by the solitons, which move jumpwise from one pinning center to another with the CDW immobile, and is qualitatively similar to the hopping conduction between disordered centers.<sup>15</sup> The presence of an immobile but polarizable CDW manifests itself in the tremendous value of the dielectric constant.

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- <sup>1</sup>T. Sambongi, K. Tsutsumi, Y. Shiozaki, *et al.*, Sol. St. Commun. **22**, 729 (1977).
- <sup>2</sup>K. Tsutsumi, T. Sambongi, S. Kagoshima, and T. Ishiguro, J. Phys. Soc. Japan 44, 1735 (1978).
- <sup>3</sup>C. Roucau, R. Ayroles, P. Monceau, *et al.*, Phys. Stat. Sol. (a) **62**, 483 (1980).
- <sup>4</sup>T. Takoshima, M. Ido, K. Tsutsumi, *et al.*, Sol. State Commun. **35**, 911 (1980).
- <sup>5</sup>A. H. Thompson, A. Zettl, and G. Grüner, Phys. Rev. Lett. **47**, 64 (1981).
- <sup>6</sup>S. K. Zhilinskii, M. E. Itkis, F. Ya. Nad', I. Yu. Kal'nova, and V. B.
- Preobrazhenskiĭ, Inst. Rad. Electron. Preprint No. 21, 1981. <sup>7</sup>G. Grüner, A. Zettl, W. G. Clark, and A. H. Thompson, Phys. Rev. **B23**,
- 6813 (1981).
- <sup>8</sup>S. K. Zhilinskii, M. E. Itkis, F. Ya. Nad', I. Yu. Kal'nova, and V. V.
- Preobrazhenskiĭ, Abstracts, 22nd All-Union Conf. on Low-Temp. Physics, Kishinev, 1982, part 2, p. 88.
- <sup>9</sup>M. Ido, K. Kawabata, and T. Sambongi, Mol. Cryst. Liq. Cryst. 81, 91 (1982).
- <sup>10</sup>P. Monceau, J. Richard, and M. Renard, Phys. Rev. **B25**, 931 (1982).
- <sup>11</sup>V. K. S. Shante, C. M. Varma, and A. N. Bloch, Phys. Rev. **B8**, 4885 (1973).
- <sup>12</sup>S. A. Brazovskiĭ, Zh. Eksp. Teor. Fiz. 76, 1000 (1979) [Sov. Phys. JETP 49, 504 (1979)].
- <sup>13</sup>N. Aspley and H. P. Hughes, Phil. Mag. 31, 1327 (1975).
- <sup>14</sup>B. I. Shklovskiĭ, Fiz. Tekh. Poluprov. 6, 2335 (1972); 13, 93 (1979) [Sov. Phys. Semicond. 6, 1964 (1973); 13, 53 (1979)].
- <sup>15</sup>N. Mott and E. Davis, Electronic Processes in Non-Crystalline Materials, Oxford, 1971.
- <sup>16</sup>L. I. Buravov, M. L. Khidekel', I. F. Shchegolev, and E. B. Yagubskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **12**, 142 (1970) [JETP Lett. **12**, 99 (1970)].
- <sup>17</sup>N. P. Ong. G. X. Tessema, V. Verma, *et al.*, Mol. Cryst. Liq. Cryst. **81**, 41 (1982).
- <sup>18</sup>L. P. Gor'kov, E. N. Dolgov, and A. G. Lebed', Zh. Eksp. Teor. Fiz. 82, 613 (1982) [Sov. Phys. JETP 55, 342 (1982)].
- <sup>19</sup>S. N. Artemenko and A. F. Volkov, Zh. Eksp. Teor. Fiz. 81, 1872 (1981) [Sov. Phys. JETP 54, 992 (1981)].
- <sup>20</sup>G. Mihaly, A. Jánossy, J. Kürti, et al., Phys. Stat. Sol. (b) 94, 287 (1979).
- <sup>21</sup>K. B. Efetov and A. I. Larkin, Zh. Eksp. Teor. Fiz. 72, 2350 (1977) [Sov. Phys. JETP 45, 1236 (1977)].
- <sup>22</sup>P. Monceau, Int. Conf. on the Phys. and Chem of Conducting Polymes,

Abstracts, France, 1982. <sup>23</sup>S. A. Brazovskiĭ, Zh. Eksp. Teor. Fiz. 78, 677 (1980) [Sov. Phys. JETP 51, 342 (1980)].
<sup>24</sup>B. Horovitz and J. A. Krumshansl. Sol. St. Commun. 26, 81 (1978).

<sup>26</sup>S. E. Trullinger, M. D. Miller, R. A. Guyer, et al., Phys. Rev. Lett. 40,

206 (1978). <sup>27</sup>G. Grüner, Mol. Cryst. Liq. Cryst. 81, 17 (1982).

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