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Charge-density-wave glass state in quasi-one-dimensional conductors

F. Nad'
Institute of Radioengineering and Electronics of the Russian Academy of Sciences, Mokhovaya 11, 103907 Moscow, Russia
and Centre de Recherches sur les Très Basses Températures, Centre National de la Recherche Scientifique,
Boîte Postale 166, 38042 Grenoble Cédex 9, France

P. Monceau
Centre de Recherches sur les Très Basses Températures, Centre National de la Recherche Scientifique,
Boîte Postale 166, 38042 Grenoble Cédex 9, France

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We have measured the real part ϵ' and the imaginary part ϵ'' of the dielectric susceptibility of the quasi-one-dimensional conductor TaS_3 in its charge-density-wave (CDW) state in the wide frequency range f (10^{-2}–10^7 Hz) in the low-temperature range (4.2–52 K). The frequency dependence of $\epsilon'(\omega,T)$ as well as $\epsilon''(\omega,T)$ show the $\ln f$ scaling and a crossover between a behavior corresponding to a Gaussian distribution of logarithms of relaxation time τ at $T \geq 30$ K and a frozen-in state with very wide τ distribution at $T \leq 24$ K. The temperature dependences of ϵ' measured at low frequencies ($f \leq 10^5$ Hz) show maxima whose positions shift to low temperatures and whose amplitudes grow with decreasing frequency. The temperature dependences of τ are characterized by two branches. With decreasing temperature the long-time branch of τ diverges (α relaxation) while the shorter-time branch shows a monotonous behavior, corresponding probably to the tunneling mechanism of CDW local motion (β relaxation). A qualitative model is suggested that describes the transition of CDW into the glass state with decreasing temperature and the main properties of this state.

I. INTRODUCTION

Since the beginning of the study of a new condensed state in solids—charge-density wave (CDW)—the description of the CDW physical nature has evolved from the hypothesis of an absolute rigid CDW to a deformable CDW with interior degrees of freedom and existing of collective excitations (CE) such as solitons and dislocations in the CDW superlattice.[1-3] At present the questions about the mechanism of CE motion and their kinetic properties especially at low temperatures when CE are the main current carriers remains very important.[4,5] Of special interest is the question about CE cooperative interaction, CE aggregation into dislocation loops and clusters and interaction of these clusters (as macroscopic objects) with impurities.

Many experiments have enabled us to obtain data on the low-temperature CDW ground state. The important deviation of temperature-dependent conductivity from activation behavior with Peierls energy gap Δ,[4,5] the considerable growth of threshold electric field E_T for the beginning of CDW motion as a whole,[1,5] the development of nonlinearity on the IV curve at threshold field $E_T' < E_T$ at low temperatures were found.[5,6] The strong frequency dependence of conductivity down to very low frequency[2,5-7] and corresponding growth of relaxation time were found.[2] The linear conductivity in weak electric field has been shown to be determined by a variable range hopping mechanism and the important role of phase-slippage and tunneling effects in this low-temperature range were underlined.[6,8-10] At very low temperatures (below ~1 K) in the course of heat-capacity studies waiting time and aging effects have been found which are typical of glassy-like states.[11] Recently, it was found that in the low-frequency range the dielectric constant shows pronounced maxima, with its amplitude and position on temperature scale being dependent on frequency.[12-14]

In spite of numerous experimental data, we consider that the clear physical understanding of CDW ground state at low temperatures is not yet obtained. As far as we know, the appropriate kinetic theory of CDW behavior at low temperatures is not yet developed in which the important role of CE and their interaction between themselves and with random strong impurities has been taken into account. Although, the theoretical studies in this direction are carried on now.[15-19]

In this experimental work, the method of dielectric spectroscopy, which we have used earlier,[14] was extended to more wide frequency range about nine octave from 10^{-2} to 10^7 Hz. We think that our data will make possible a more clear physical picture of CDW ground state at low temperatures and show the tight connection of this CDW behavior with CDW properties in the higher[20] and the lower[11] temperature ranges.

II. EXPERIMENT

We have measured the real and imaginary parts of ac conductivity of orthorhombic TaS_3 as a function of frequency in the range $10^{-2}-10^7$ Hz at fixed temperatures in the range 4.2–52 K, where we have found earlier the divergency of dielectric susceptibility.[14] In the frequency

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range 10–10^7 Hz the complex conductivity has been measured by impedance analyzer HP 4192A, under the computer control. At low temperatures, when the sample resistance was about $\sim 10^6\ \Omega$, we have used a special preamplifier which improved the resolution of the impedance analyzer in the low-frequency range ($f < 10^4$ Hz).[14] We have verified that in this frequency range the preamplifier did not introduce any noticeable phase shift.

For measurements in the frequency range 10^{-2}–10^2 Hz, we have used a homemade computer bridge.[21] The bridge is autobalanced by computer generation, with one bridge arm the sin wave with such amplitude and phase to compensate the appropriate ac signal from unknown impedance in another bridge arm. In addition, the balance of the bridge was carried out not only in respect of first harmonic of signal but in respect of 2, 3, and 4 harmonics also. The deviation from orthogonality of the signal components in phase and in quadrature was less than 10^{-3} rad.

As it is well known, the complex conductivity σ of CDW samples depends on the amplitude of the ac voltage V_{ac} and σ can vary considerably for electric field $E_{\mathrm{ac}} \geq 0.1 E_T$, especially in the low-temperature range.[20,22] We have carried out measurements of σ dependence on V_{ac} (at frequency 10 Hz) to determine the range of V_{ac} values below which σ was independent on V_{ac} (the range of linear σ). It was found that in all temperature ranges under investigation (4.2–52 K) the deviation from linearity of the real and imaginary parts of the ac conductivity of o-$\mathrm{TaS_3}$ was about 1% in the electric field about 70 mV/cm. For this reason, we have carried out our measurements with E_{ac} about 10 mV/cm. The results of the study of the nonlinear behavior of o-$\mathrm{TaS_3}$ samples in higher electric field at low temperature will be published elsewhere. Our measurements have been carried out using long o-$\mathrm{TaS_3}$ samples ($\simeq 1$ cm) to maintain the appropriate resolution of our bridges on one hand and to fulfill the conditions of linearity of the sample response on the other hand.

We have measured about 10 samples of o-$\mathrm{TaS_3}$ with typical cross-sectional area $\sim 10^{-6}\ \mathrm{cm}^2$. For measurements, we have selected samples with the most regular form and with minimal external defects. The sample with two gold paint contacts has been mounted on the narrow gold strips attached by indium tubs on the sapphire substrate. The sample was cooled in zero electric field at a rate of ~ 1 K/min down to helium temperature. The majority of experiments were carried out with increasing temperature. Before measurements at a fixed temperature, the sample was held for 5 min. For all our samples under consideration the majority obtained dependences has a qualitatively similar form. Below, we will show the data for the typical detailed studied o-$\mathrm{TaS_3}$ sample, with length 9 mm, cross sectional area $\sim 2.10^{-6}\ \mathrm{cm}^2$ and room-temperature resistance $\sim 80\ \Omega$.

III. RESULTS

The real and imaginary parts of dielectric susceptibility were calculated from measured complex conductivity values $\sigma(\omega)$ by standard relations $\epsilon'(\omega) = \mathrm{Im}\sigma(\omega)/\omega$ and $\epsilon''(\omega) = [\mathrm{Re}\sigma(\omega) - \sigma_{\mathrm{dc}}]/\omega$. The value of σ_{dc} was determined, where it was possible, at low frequencies where σ_{ac} was independent on frequency.[20,22] As can be seen from Fig. 1 the $\mathrm{Re}\sigma(\omega)$ dependences at various temperatures show the peculiar "threshold" behavior as a function of frequency. In the low-frequency range at temperatures above ~ 14 K $\mathrm{Re}\sigma(\omega)$ is practically independent on frequency and it corresponds to σ_{dc} value. The growth of $\mathrm{Re}\sigma(\omega)$ begins from some "threshold" frequency which decreases with decreasing temperature. In the temperature range 14–52 K the σ_{dc} values determined from these data are thermally activated with an activation energy $\Delta_s \simeq 240$ K (inset in Fig. 1). In the temperature range below 14 K $\mathrm{Re}\sigma$ does not become constant down to the lowest frequencies of our measurements (10^{-2} Hz) and σ_{dc} value could not be evaluated with enough accuracy. In the temperature range below 14 K the $\mathrm{Re}\sigma(\omega)$ dependences proceed gradually to the power-law dependences.[7] For example, in our sample at temperature $T = 4.2$ K in the frequency range 10^{-2}–10^5 Hz the $\mathrm{Re}\sigma(\omega) \sim \omega^s$, where $s \simeq 0.8$. At the same temperature in the frequency range 10^{-2}–10^6 Hz $\mathrm{Im}\sigma(\omega) \sim \omega^{s'}$, where $s' = 0.82$. This behavior corresponds to a variable range hopping conductivity in CDW conductors.[5]

As it follows from these data and as it will be shown below, the $\epsilon(\omega, T)$ dependences differ from appropriate dependences derived from simple Debye relaxation with single relaxation time. The $\epsilon'(\omega)$ and $\epsilon''(\omega)$ dependences are in fact similar to those observed in the very wide range of various materials and systems with some disorder including glass materials.[20,22,23] In these materials, the relaxation is typically nonexponential with a very wide distribution of relaxation times. In addition, the contribution of relaxation process with very long time (i.e., at very low frequency in frequency domain representation) is very considerable. For description of these processes, phenomenological equations are often used, the most general form of which was suggested by Havriliak and Negami[22,24] to describe the dielectric relaxation in polymers:

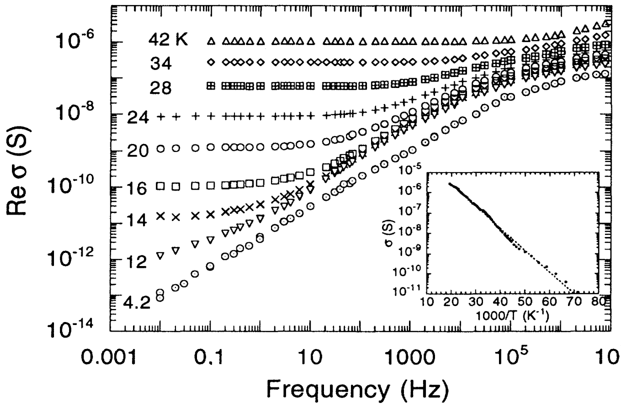

FIG. 1. The frequency dependence on the real part of ac conductivity $\mathrm{Re}\sigma$ of o-$\mathrm{TaS_3}$ at temperatures 4.2–42 K. Inset shows the temperature dependence of $\sigma = \mathrm{Re}\sigma$ at $\omega \rightarrow 0$.

$$\epsilon(\omega)=\epsilon_{\mathrm{HF}}+\frac{\epsilon_0-\epsilon_{\mathrm{HF}}}{[1+(i\omega\tau_0)^{1-\alpha}]^{\beta}}\,, \tag{1}$$

where ϵ_{HF} is the $\epsilon'(\omega)$ value for $\omega \gg \omega_0(\omega_0 \equiv \tau_0^{-1})$, ϵ_0 is $\epsilon'(\omega)$ value for $\omega \ll \omega_0$, and α and β characterize the width of the distribution of relaxation times and its nonsymmetry, respectively. In accordance with Eq. (1), which is similar to the earlier introduced Cole-Cole equation, the dependence ϵ'' and ϵ' at various frequencies should have the form of arc. The intersections of this arc with the $\epsilon''=0$ axis determine the ϵ_{HF} value for high-frequency part $\epsilon''(\epsilon')$ dependence and the ϵ_0 value for the low-frequency part. Figure 2 shows the appropriate dependences $\epsilon''(\epsilon')$ which are typical for o-TaS$_3$ samples under consideration.

In our case, the ϵ_{HF} value and its temperature variation can be precisely determined because the appropriate ϵ'' and ϵ' values get in the high enough frequency range when the ϵ'' becomes very close to axis $\epsilon''=0$. The determination of $\epsilon_{\mathrm{HF}}(T)$ values is important because the $\epsilon'(\omega,T)$ dependences can be a combination of several contributions (for example, pristine lattice, free electrons, etc.).[23] In this case, the substitution of high-frequency contribution [ϵ_{HF} in Eq. (1)] gives us the possibility to extract more precise low-frequency contribution to $\epsilon'(\omega,T)$.

Figures 3 and 4 show the dependences $\epsilon'-\epsilon_{\mathrm{HF}}$ and ϵ'' on frequency at various temperatures calculated by the above-mentioned standard equations. Figure 3(a) shows $\epsilon'-\epsilon_{\mathrm{HF}}$ dependences (below, this quantity will be designated as ϵ') for several selected temperatures in the temperature range 4.2–24 K and Fig. 3(b) shows the appropriate $\epsilon'(\omega)$ dependences for temperature range 24–42 K. As it can be seen from Fig. 3, $\epsilon'(\omega)$ dependences in scale $\log_{10}\epsilon$ versus $\log_{10}\omega$ are qualitatively similar and with increasing temperature they move up in the temperature range 4.2–24 K and they move down in the range 24–42 K. These dependences can be presented in the form of two approximately linear sections in the logarithmic scale (i.e., power type dependences in linear scale) with temperature-dependent slope (i.e., with temperature-dependent exponent). With increasing temperature above 24 K, the crossover between these two sections shifts to a higher temperature range with a simultaneous decrease of the slope of the low-frequency part $\epsilon'(\omega)$ dependence and appropriate decrease of ϵ' variation [Fig. 3(b)].

The $\epsilon''(\omega,T)$ dependences in $\log_{10}\omega$ scale (Fig. 4) show a qualitative similarity at different temperatures. With decreasing temperature the maximum of loss function $\epsilon''(\omega)$ shifts to the high-frequency range with simultaneous decrease of its amplitude in the temperature range above 24 K.

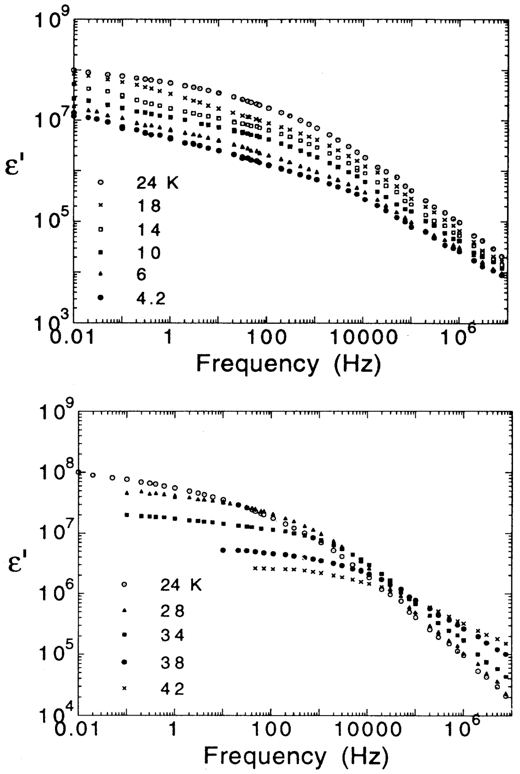

FIG. 3. (a) The frequency dependences of the real part ϵ' of dielectric susceptibility of o-TaS$_3$ in the temperature range 4.2–24 K. (b) The frequency dependences of the real part ϵ' of dielectric susceptibility in the temperature range 24–42 K.

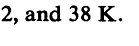

FIG. 2. Complex plane plots of the real ϵ' and imaginary ϵ'' parts of dielectric susceptibility at several temperatures 24, 28, 32, and 38 K.

Figure 5 shows the frequency dependence of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ both for three selected temperatures $T=18$, 28, and 38 K. It should be noted that the forms of $\epsilon'(\omega)$ and

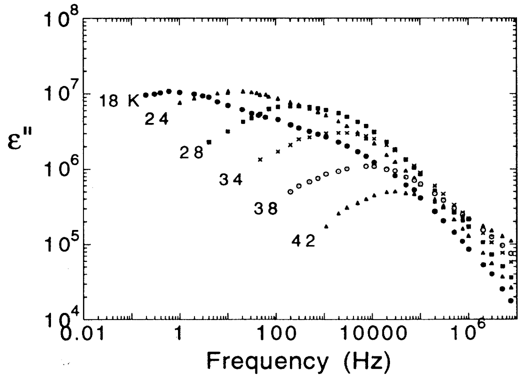

FIG. 4. The frequency dependences of the imaginary part ϵ'' of dielectric susceptibility (loss function) of o-TaS$_3$ in the temperature range 18–42 K.

$\epsilon''(\omega)$ dependences demonstrate the different behavior in the low-frequency range (below 10^3 Hz) and difference between them grows with increasing temperature. At the same time, the high-frequency branches (above $f \sim 10^4$ Hz) of these dependences are very similar to each other and they are well described by power law $\epsilon' \sim \epsilon'' \sim \omega^{-n}$.

Figure 6 shows the temperature dependence of exponent n which characterizes the ϵ' and ϵ'' dependences in a high-temperature range above the maximum of the loss function. These n values are in a good quantitative agreement with the range of their overlapping. As can be seen from Fig. 6, in the low-temperature range, the n value grows from 0.52 at 4.2 K with saturation on 0.68–0.7 in the temperature 20–30 K. Such an evolution of the value of the exponent n is typical for various complex systems with nonexponential relaxation.[23,25]

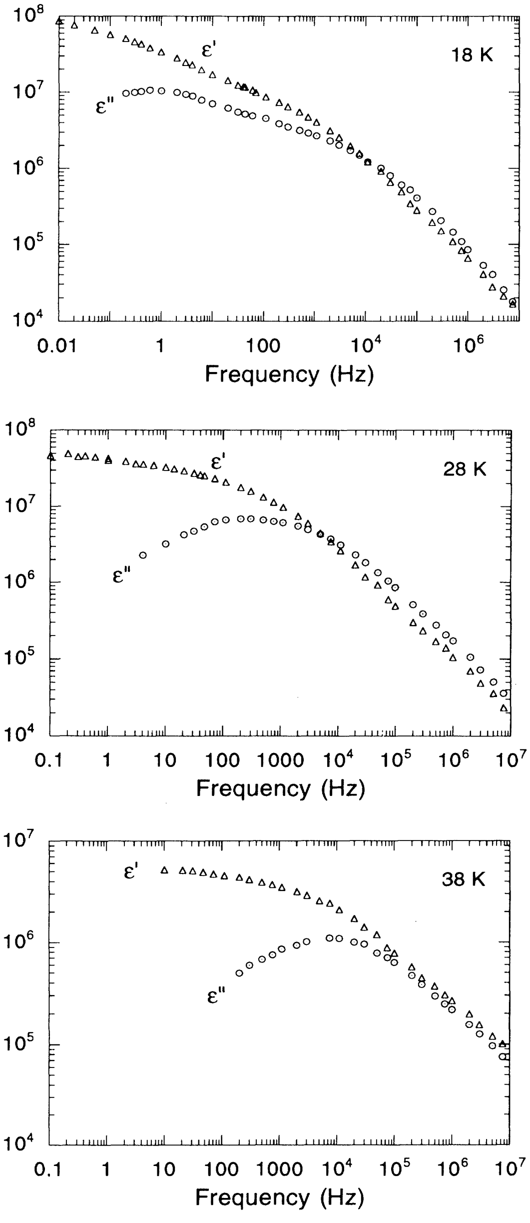

FIG. 5. Frequency dependences of the real ϵ' and imaginary ϵ'' parts of dielectric susceptibility of o-TaS$_3$. (a) Temperature $T = 18$ K; (b) $T = 28$ K; (c) $T = 38$ K.

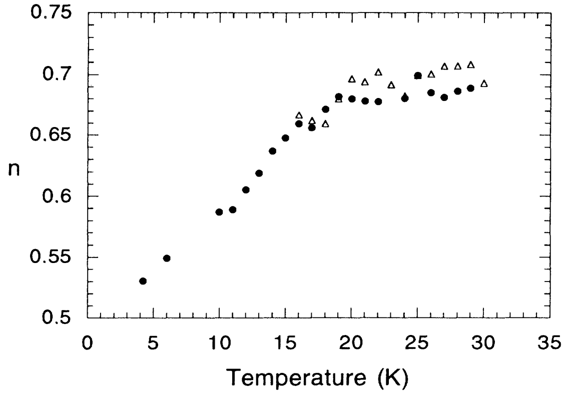

FIG. 6. Temperature dependences of exponent n in relation $\epsilon'(\omega) \sim \epsilon''(\omega) \sim \omega^{-n}$ in the high-frequency range of $\epsilon(\omega)$ dependence of o-TaS$_3$. ● denotes n values determined from $\epsilon'(\omega)$ dependences; △ denotes n values determined from $\epsilon''(\omega)$ dependences.

The temperature dependence of real part of dielectric constant $\epsilon'(T)$ shows a very interesting behavior which was briefly analyzed in (Ref. 14). Since this previous work, the frequency range for measurements has been extended by three decades in the low-frequency range, which gives us the possibility to better analyze the physical picture of $\epsilon'(\omega, T)$ divergence which was revealed earlier.[14] Figure 7 shows the $\epsilon'(T)$ dependences at several fixed frequencies in the range 10^{-2}–10^5 Hz. The temperature dependences of ϵ' measured at a frequency above $\sim 10^5$ Hz show the monotonous decrease of ϵ' with decreasing temperature. This decrease is a continuation of the decreasing ϵ' from temperature range 120–70 K, where ϵ' decreases exponentially with activation energy ~ 300 K.[14,20,26] However in the frequency range $f \le 10^5$

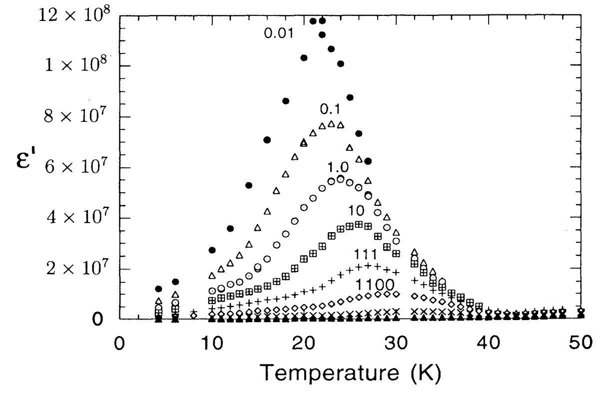

FIG. 7. Temperature dependences of the real part ϵ' of dielectric susceptibility of o-TaS$_3$ at frequencies (in Hz) indicated in the figure. Two lowest curves correspond to $f = 11$ kHz (×) and $f = 100$ kHz (▲).

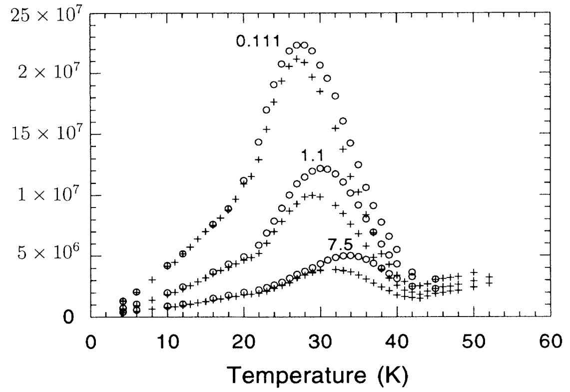

FIG. 8. Temperature dependences of the real part ϵ' of dielectric susceptibility of o-TaS$_3$ for zero field cooled case (ZFC) (+), and field (1 V/cm) cooled case (FC) (○) at indicated frequencies (in kHz).

Hz the $\epsilon'(T)$ dependences show pronounced peaks the amplitude of which grows with decreasing frequency and their maxima shift to the low-temperature range (Fig. 7). In the temperature range below these maxima $\epsilon'(\omega,T)$ dependences have a qualitatively similar form but with considerable frequency dispersion. These curves have been measured with increasing temperature after cooling the sample in zero electric field [zero field cooled (ZFC)]. We have carried out also the measurements of $\epsilon'(T)$ dependences after cooling of the sample from room temperature in the constant electric field 1 V/cm (FC). Figure 8 shows the appropriate $\epsilon'(T)$ dependences for frequencies of 111 Hz, 1.1 kHz, and 7.5 kHz. In the temperature range from 4.2 K up to $\simeq 22$ K the ZFC and FC dependences are very similar. However, with increasing temperature after the FC procedure the amplitudes of $\epsilon'(T,\omega)$ peaks increase and positions of maxima and $\epsilon'(T,\omega)$ branches descending above maxima temperatures shift to higher-temperature range. The shift is smaller for lower frequencies. Probably, such behavior at $T > 20$ K corresponds qualitatively to a frozen CDW state with a small ϵ' value determined by the contribution of small enough CDW regions. This contribution is practically independent on the ZFC or FC sample prehistory. With increasing temperature above $\epsilon'(T)$ maximum, the contribution of large CDW regions becomes important. This contribution seems to increase in the case of cooling in a nonzero electric field because of the polarization of these large CDW regions. Generally speaking this behavior is similar to behavior of glassylike materials, for example, orientational glasses,[27] near phase transition. In the same temperature range where we observed the $\epsilon'(T)$ divergence, we have observed the divergence of 2, 3, and 4 harmonics of the main signal,[28] which is also typical for temperature range near phase transition critical temperature.[29]

IV. DISCUSSION

As can be seen from above-mentioned data the properties of quasi-one-dimensional conductors with CDW at low temperatures are very similar to typical properties of the wide range of glass materials with nonexponential relaxation.[23] Below we will discuss the peculiarities of the CDW ground state at low temperature which confirm this approach.

According to Fig. 4, the frequency dependences of ϵ'' at various temperatures are very similar in log-log scale. It can be easily verified by a simple shift of these curves along two $\log_{10}$ axis bringing into coincidence the $\epsilon''(\omega,T)$ maxima especially for high-temperature range above 30 K. It means that for CDW conductors as well as for many other disorder materials scaling is observed in the scale $\log_{10}\omega$ but not ω. However, with decreasing temperature the low-frequency branch (below a loss peak frequency) becomes more flat which corresponds to the extension of $\epsilon''(\omega,T)$ curves into the low-frequency range. The loss function form changes from practically symmetrical in the temperature range $T \geq 30$ K to more and more nonsymmetrical at lower temperatures (see Fig. 5). The temperature variation of frequency dependence of the real part of the dielectric constant $\epsilon'(\omega,T)$ corresponds also to this behavior (Fig. 3). In the low-frequency range ($f \leq 10^3$ Hz) $\epsilon'(\omega,T)$ dependences are close to linear in log-log scale, i.e., they correspond to equation $\epsilon'(\omega) \sim \omega^{-m}$, where m grows gradually from $\simeq 0.1$ to 0.25 with decreasing temperature.

The high-frequency branches of the loss functions are more similar with the temperature variation. In the whole temperature range where $\epsilon''(\omega)$ was determined (16–52 K), we found that $\epsilon'' \sim \omega^{-n}$ with exponent n dependent on temperature. As it has been shown above (Fig. 5) in the high-frequency range $\epsilon'(\omega)$ dependence has the similar form $\epsilon' \sim \epsilon'' \sim \omega^{-n}$ with approximately the same exponent $n(T)$ (Fig. 6). The similarity of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ dependences in the high-frequency range and the decrease of exponent n with decreasing temperature are typical features of the behavior of glassy materials approaching to some critical temperature.[23,25,31] The decrease of n is associated with the growth of correlation in the transition between energy states in two-level system.[23] In the case of CDW systems it may correspond to the growth of correlation of transitions of solitons and dislocations between metastable states in the potential relief created by random strong impurities centers.[14] It means that the behavior of these collective excitations becomes more and more cooperative. They demonstrate a tendency to agglomeration and to formation of dislocation loops and clusters.[16]

The description of the behavior of many glass materials, especially near their phase transition, very often uses the hypothesis about dynamic scaling.[25,31,32] This hypothesis is based on the suggestion that the scaling methods of space renormalization of static systems can be transferred to the study of dynamic of such systems as a function of time.[30–32] On this base, the dynamic effects in disordered glass materials have been considered.[30–32] In particular, it was shown[31] that in enough correlated systems with some disorder, the distribution of logarithms of the relaxation times is a Gaussian:

$$P(\ln\tau) = \frac{1}{\sqrt{2\pi}\lambda}\exp - \frac{[\ln^2(\tau/\tau^*)]}{2\lambda^2}\ , \tag{2}$$

where τ^* is the most probable value of relaxation time and λ corresponds to the width of the distribution. Taking into account this suggestion it was shown that in the frequency domain $\epsilon'(\log_{10}\omega)$ dependence corresponds to an error function. In this case, the relation between ϵ' and ϵ'', which in the general case is determined by Kramers-Kronig relations, is reduced to the so-called "$\pi/2$ rule":[33]

$$\epsilon''(\log_{10}\omega) = -\frac{\pi}{2}\frac{d\epsilon'(\omega)}{d\log_{10}\omega} . \qquad (3)$$

Inasmuch as our CDW system at low temperatures is very similar to the above-mentioned disordered systems, we have enough physical bases to compare our experimental results with some results of dynamic scaling theory. Figure 9 shows the experimental data $\epsilon''(\log_{10}\omega)$ and data calculated by relation (3). In the temperature range $T \geq 30$ K the agreement between these data is satisfactory (within $\sim 10\%$). With decreasing temperature, the forms of the experimental and calculated curves remain qualitatively similar but a quantitative difference grows (at $T = 24$ K it is about 30%). Additionally, in the frame of this approach the effective width λ of the loss peak $\epsilon''(\omega)$ should be proportional to $(\log_{10}\omega_p)^{0.5}$, where frequency ω_p corresponds to the maximum of the loss peak. Figure 10 shows the temperature variation of the loss function $\epsilon''(\omega,T)$ in semilogarithmic scale to make the form of the function more clear. The corresponding dependence λ^2 from $\log_{10}\omega_p$ is shown on Fig. 11. As it can be seen from Fig. 11 the relation $\lambda^2 \sim \log_{10}\omega_p$ is indeed observed in the temperature range above ~ 30 K. Thus, in this temperature range, the form of the loss function is very similar to Gaussian. However, with decreasing temperature, it deviates from Gaussian (Fig. 11). Here, it should be noted the qualitative difference in behavior $\epsilon''(\omega)$ dependences in the low-temperature and the high-temperature ($T > 24$ K) ranges (Fig. 5). In the temperature range below 16 K the loss peak has not enough frequency extension (range) to be detected in the frequency domain under consideration ($f_{\min} - 10^{-2}$ Hz). In the temperature range $16 < T < 24$ K ϵ'' peaks shift to the high-frequency range and surpass the shoulder of $\epsilon''(\omega)$ dependences at frequencies below 10^3 Hz. Variation of their amplitude ϵ''_p is very small. However, at $T > 24$ K the amplitudes ϵ''_p begins to decrease $\epsilon''_p \sim \omega_p^{-\alpha}$ with $\alpha \simeq 0.7$ in parallel to the high-frequency branch of the loss function $\epsilon''(\omega)$ (Fig. 4). In other words, near $T = 24$ K, we observe a crossover from practically independent ϵ''_p to dependence $\epsilon''_p \sim \omega^{-\alpha}$. As it was shown in Ref. 23 such a variation of $\epsilon''(\omega,T)$ dependences is typical for materials undergoing dipole alignment transition with finite critical temperature.

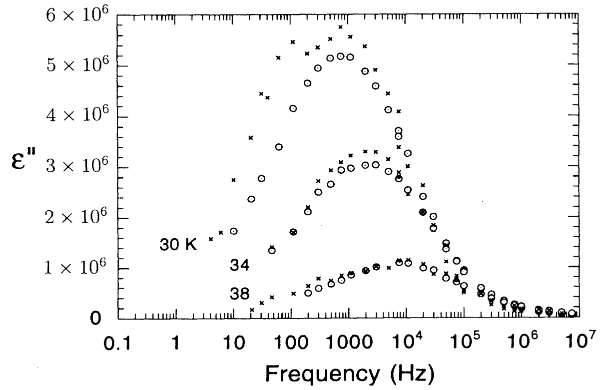

FIG. 9. Frequency dependences of imaginary part of dielectric susceptibility ϵ'' of o-TaS$_3$ at 30, 34, and 38 K. ●, experiment data; ×, data calculated by the equation $\epsilon'' = -\pi/2(d\epsilon'/d\log_{10}\omega)$.

As it is known the temperature variation of the shape of the loss spectrum represents a criterium for the detection of order change in material under investigation.[23] As follows from the above-mentioned data and their analysis, the dielectric properties of CDW change drastically across the temperature range near ~ 24 K, which can be due to CDW transition into a glassylike state.

We have given earlier[14] a qualitative explanation of the growth of ϵ' with decreasing temperature (Fig. 7) on the base of the appropriate growth of the CDW coherence length approaching to the low temperature range with the simultaneous growth of the relaxation time τ. Consequently, the ϵ' value measured on low but finite frequencies begins to decrease. When the growing τ value becomes comparable with the ac field period $(2\pi f)^{-1}$ as a result of dynamic retarding effect, the dynamic slowing down behavior is observed.[34] In Ref. 14, the temperature dependence of relaxation time has been evaluated by plotting of $\tau \equiv (2\pi f)^{-1}$ as a function of temperature T_m of the $\epsilon'(T)$ maximum measured at fixed frequencies f (Fig. 7). Presently, we think that the more accurate estimation of the relaxation time can be done by determination of the deflection point on $\epsilon'(T)$ curve which corresponds to the transition (with decreasing temperature) from the fast growth ϵ' to approaching to the maximum with a following slowing down. This point corresponds to the negative minimum of temperature derivative of $d\epsilon'(T)/dT$.

Figure 12 shows the temperature dependence of "average" relaxation time τ^*, which has been calculated by such a method. The $\tau^*(1/T)$ experimental dependence is noticeably different from linear in this scale. In our opinion, this dependence can be fitted most accurately by a slowing down equation $\tau^* \simeq \tau_0(1 - T_c/T)^{-z\nu}$ with $\tau_0 \simeq 10^{-11}$ s, $T_c \simeq 15$ K, and $z\nu \simeq 24$. The τ_0 and T_c magnitudes are close to the appropriate value determined by us earlier.[14]

On the same Fig. 12, we show the dependence of $\tau_p \equiv (\omega_p)^{-1}$ extracted from the temperature dependence of the frequency ω_p corresponding to the maximum of the loss function ϵ''_p (see Figs. 9 and 10). In the high-temperature range above ~ 32 K, the dependences $\tau^*(1/T)$ and $\tau_p(1/T)$ are very close. However, with decreasing temperature, they become more and more different. The experimental $\tau_p(1/T)$ dependence shows a noticeable convex curvature. It means that for this branch $\tau_p(1/T)$ dependence the effective height of barriers decreases with decreasing temperature. In the physical sense such a type of $\tau_p(1/T)$ dependence corresponds more probably to dominant contribution of tunneling mechanism in conductivity[6,9,10] and polarization.[36] In

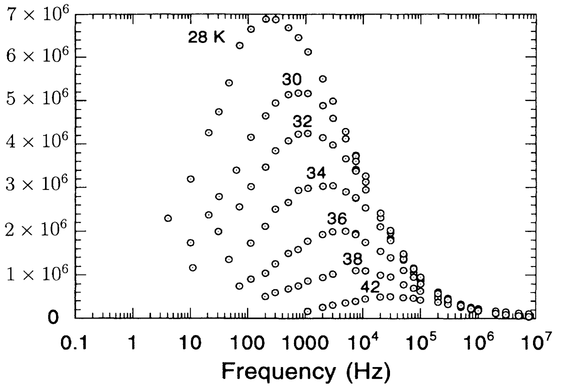

FIG. 10. Frequency dependences of imaginary part of dielectric susceptibility ϵ'' of o-TaS$_3$at several temperatures.

the case of existence of interaction between single tunneling transitions the experimental $\tau_p(1/T)$ dependence can correspond to a similar type of a slowing down relation, but with negative T_c value, i.e., $\tau_p \sim \tau_p^0(1-T_c/T)^{z\nu}$.[34,36] Indeed our experimental dependence can be satisfactory fitted by this relation with $\tau_p^0 \simeq 10^{-11}$ s, $T_c \simeq -30$ K, and $z\nu \simeq 24$ (Fig. 12). Perhaps it points out the possibility of some cooperative mechanism also on this branch of $\tau(1/T)$ dependence.

As it was noted above, in the high-temperature range both relaxation processes merge and they are characterized by activation behavior with common relaxation time $\tau \sim \tau_0 \exp(\Delta/T)$, where $\tau_0 \sim 10^{-11}$ s, $\Delta \simeq 780$ K, which value is closed to Peierls energy gap in o-TaS$_3$. The comparison of our data with those of Cava *et al.*,[20] who have measured relaxation in o-TaS$_3$ at more higher temperatures, shows a good agreement between them, not only in magnitude of Δ but also in the magnitude of τ^*.

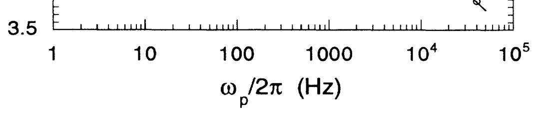

FIG. 11. Dependence of square effective width λ^2 of $\epsilon''(\log_{10}\omega)$ loss functions of o-TaS$_3$ on frequency $\omega_p/2\pi$ corresponding to the maximum of the function. Dashed line corresponds to dependence of $\lambda^2 \sim \log_{10}\omega_p$.

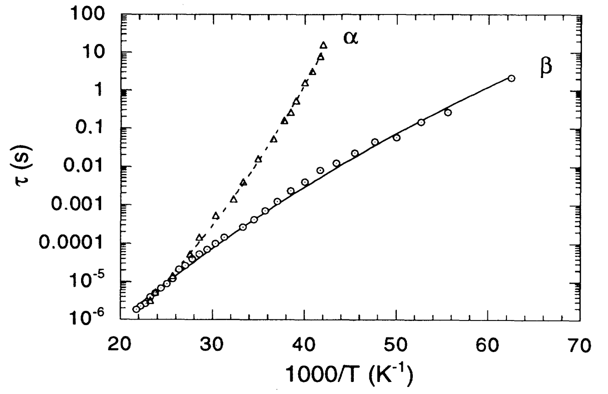

FIG. 12. Temperature dependence of relaxation times τ of o-TaS$_3$. $\triangle,\tau$ value determined from deflection points of $\epsilon'(T,\omega)$ dependences; $\bigcirc,\tau$ value determined from position of maximum of $\epsilon''(\log_{10}\omega)$ dependences.

V. THE QUALITATIVE PHYSICAL MODEL OF THE CDW GLASSYLIKE STATE

As it can be seen from above-mentioned data the CDW ground state changes considerably with decreasing temperature in the range 52–4.2 K. The $\epsilon'(T)$ divergence, sharp growth of relaxation time, ϵ' and ϵ'' scaling in $\log_{10}\omega$ scale, etc., have been observed. These results cannot be explained in the frame of Debye relaxation with one relaxation time. The simple fit of the experimental data with phenomenological relations of Havriliak-Negami-type gives us the possibility to determine a set of parameters characterized by the distribution of the relaxation time but it does not allow us to understand the physical mechanism of CDW behavior in these conditions. Below we shall briefly describe a qualitative picture of the evolution of CDW ground state at its transition into a glassylike state with decreasing temperature.

After the CDW formation at the Peierls transition temperature T_p (in o-TaS$_3$ $T_p \simeq 220$ K) the conductivity in the temperature range $T_p/2 < T < T_p$ in a weak electric field E below the threshold field E_T is determined by electrons and holes thermoactivated across the Peierls gap Δ. The CDW interaction with impurities has a character of weak collective pinning,[37,38] which determines the large ϵ' magnitude in this temperature range.[1–3] With decreasing the temperature below $\simeq T_p/2$, the number of free electrons and holes becomes very small. The main contribution to the conductivity and susceptibility begins to occur from the local CDW deformations both thermoactivated and nucleated from the CDW interaction with strong pinning centers.[5,14,26,36] These CDW deformations, which we will call below solitons, are the defects and dislocations nucleated in the CDW superlattice. These solitons correspond to CDW phase variation on $\pm 2\pi$ along one (or a small number) of CDW chains on short distance.[5,14,26,39] The characteristic energy of the soliton nucleation corresponds to the energy of an interchain interaction, which in turn is equal to the energy of three-dimensional ordering of CDW $\sim kT_p$.[6,40,41] The change of slope of $\sigma(1/T)$ from the value equal to Δ below the Peierls transition to the energy $\sim kT_p$ at T below 100 K (inset on Fig. 1, see also Refs. 4–7) and activated decrease of ϵ' with energy $\sim$300 K are in favor of the above-mentioned model.

With decreasing temperature down to $\sim$40 K, these 2π solitons turn out to predominantly interact with single strong pinning centers distributed randomly in the CDW superlattice. In the weak electric field, the dielectric susceptibility will be determined by summary effects of polarization and dipole interaction between these random distributed solitons. In this temperature range, the CDW as a whole is unmovable. Its main kinetic properties are determined by the motion of these soliton excitations in the potential relief created by random impurities. In the CDW case as well as in a lot of other disordered systems, the two-level model can be used for description of transitions between potential minima of this potential relief.

In Ref. 23 for a description of such systems a hierarchy of transitions has been considered including the thermoactivated transition over the barriers and tunneling transition between correlated states, the contribution of which increases with decreasing temperature. Additionally, the importance of interaction between the "units" taking part in relaxation in comparison with models with wide distribution of relaxation times of noninteracting "units" was underlined. In the frame of this general model a lot of effects, observed in disordered materials with nonexponential relaxation, can be explained. The observed facts in this CDW work such as the similarity in $\epsilon'(\omega)\sim\epsilon''(\omega)\sim\omega^{-n}$ in the high-frequency range of the loss f function, the possibility of their scaling in $\log_{10}\omega$ scale, and peculiarities of temperature variation of $\epsilon''(\omega)$ dependences follow from this model.

However, for the description of random systems the hypothesis about energy distribution of barrier height and about the effect of this distribution on relaxation time, which is exponentially dependent on barrier height, is more often used.[33] In the range of not very low temperatures (in our case 30–40 K), when the main role is due to the activation transition over barriers, the relaxation time can be defined by relation $\tau=\tau_0\exp(\Delta/T)$ taking into account the barrier distribution $P(\Delta)$. Then, considering also the restriction of time window in experimental conditions, groups of barriers can be selected which may or may not be overcome during this time and as a result the equation for susceptibility turns out to be a function of combination of $T\log_{10}\tau$ (in time domain) and $T\log_{10}(\omega^{-1})$ (in frequency domain).[30–33] From this it follows, for example, the $\pi/2$ rule for $\epsilon'(\omega)$ and $\epsilon''(\omega)$, and the relation $\lambda^2\sim(\log_{10}\omega_p)^{-1}$ in the case of Gaussian log-normal distribution. As it was shown above, these results are in agreement with our experimental results in the temperature range 42–30 K, which points out the possibility of using this approach for our CDW system. As it was noted in Ref. 33, these suggestions can be applied to many disordered systems including systems which do not undergo any phase transition with decreasing temperature.

In the case of CDW systems, however, as was shown above, the ϵ' divergence as well as the divergence of higher harmonics, the violation of $\pi/2$ rule are observed which probably indicates the approach to some transition temperature. For example, Ma[32] pointed out that the Gaussian approximation becomes invalid near a phase transition due to the increase of correlated state contributions and a very large growth of fluctuations. Our observation of a divergence of high harmonics in the same temperature range, where we have observed appropriate divergence of first harmonics, points out also the increasing role of cooperative interactions, because these interactions determined by higher-order terms in a system response corresponded to higher harmonics. Such a behavior is typical in the temperature range near a phase transition including the transition into glassylike state.

In this spirit we think that the main cause of $\epsilon'(T)$ growth is the increase of the CDW rigidity with decreasing screening of its defects (solitons) by free carriers.[14,15,18,19,38] The more rigid CDW tries to be more homogeneous, which can promote the depinning of some CDW local regions from strong pinning centers after the overcoming local critical CDW tension.[14,38,35] As a result the CDW coherence length and dielectric constant will increase. Moreover, the growth of the soliton size can also develop which will also promote the ϵ' growth. The similar effect was theoretically considered in Ref. 18 but without taking into account the random distribution of impurities and barrier heights and the existence of a nonexponential relaxation.

As it can be seen from our experimental data the $\epsilon''(\omega)$ dependence, which reflects the energy distribution of relaxation times, is spread out considerably to low-frequency range. The dependence of average relaxation time determined from $\epsilon'(T)$ divergent dependence, is well fitted by slowing down relation with finite $T_c\simeq 15$ K and $z\nu=24$. We think that this relaxation time corresponds to relaxation of large CDW regions (α relaxation) and it grows with increasing of size of these regions.[42] With further decreasing temperature these CDW regions could not follow the ac field due to large growth of the relaxation time and ϵ' begins to decrease, i.e., a slowing down behavior takes place.

The second (faster) branch of $\tau(1/T)$ dependence, which is shown in Fig. 12, seems to correspond to relaxation on considerably smaller scale (β relaxation) regions in the order of value, where solitons are developed or dissipated. Probably they correspond to phase-slip regions with typical size in the range of one unit cell of CDW superlattice.[6,8] In the context of a transition hierarchy model[23] in this temperature range, the interaction between metastable states and tunneling phenomena become very important.

The dynamic scaling hypothesis is also very productive for the explanation of these phenomena. In this case, the interaction is indirectly taken into account because the following steps of renormalization process are dependent from previous ones which leads to the hierarchical successive relaxation. Depending on the barrier behavior when temperature is reduced, three cases seem to be possible: with increasing of barrier height the real phase transition with finite $T_c>0$ will be realized, with constant barrier height we can observe the activation behavior with $T_c = 0$ and, finally, with decreasing of effective barrier height, we can observe a so-called negative critical temperature.[31,34]

At $T < T_c$ or at $T \rightarrow 0$, the relaxation time becomes so long that the system has not enough time to approach equilibrium in real experimental conditions. The system is frozen in some metastable state with a giant relaxation time, i.e., it approaches to true glass state. In the case of CDW systems, as it was shown above, its ground state has a lot of common features with other glasses. In this temperature range, the CDW is in a frozen state. The CDW collective excitations—solitons—are pinned on impurities. The conductivity is carried out by rarely jumps of these solitons by means of tunneling transitions[6,9,10,36] and it corresponds to variable range hopping conductivity. The motion of large CDW regions as a whole is frozen and it gives a small contribution ϵ'. However, on a microscopic scale, the relaxation is yet possible and the ϵ' value is determined by β relaxation with temperature-dependent relaxation time. Perhaps, the "activation energy" in this case corresponds to the system temperature. The distribution of relaxation time is very wide but it is restricted by β relaxation from high and α relaxation from low-frequency ranges. The effect of waiting time and the aging effect begins to play an important role and the CDW system turns into the state which has been studied in details in the set of publications.[11,43]

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