

# Glass transition from a slush to a real glass in charge-density-wave compound TaS<sub>3</sub>

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## Abstract

We have found by broad-band dielectric spectroscopy of charge density wave (CDW) compound TaS<sub>3</sub> that the main relaxation time representing CDW viscosity shows a critical slowing down in the range 55–50 K. At lower temperatures two additional processes appear that we assign to the defects in CDW superlattice. Based on very strong similarity with the glass transition in supercooled liquids, we propose a consistent scenario of the glass transition from a CDW slush to a real CDW glass. The length/time scales involved imply the existence of a new family of glasses in systems with the long-range order such as CDW.

*Keywords:* Glass transition; Charge-density wave; Dielectric constant

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## 1. Introduction

Last few years the peculiar low-temperature dielectric properties of charge-and spin-density waves (DW) were in the focus of interest in this field, especially because the exhibited similarities with typical glasses [1]. However, DWs have been respected in the field of glasses and supercooled liquids only as some very exotic kind of slush glasses. The most intriguing point was that the glassy behaviour and possible glass transition itself concern collective modes with a well-established long-range order. The collective sliding was one peculiarity over and above making the searching of

proper understanding of DW glass extremely complex. However, we believed that the non-linear properties related to DW pinning are intimately tied up with freezing processes.

In order to better characterise the underlying low-*T* processes and the change of their dynamics, we performed broad-band dielectric spectroscopy of CDW prototype system TaS<sub>3</sub> in the temperature range between 15 and 100 K. We found that there exists the real glass transition from the CDW slush into the CDW glass. The Coulomb hardening of CDW condensate, the main characteristics of CDW slush, does not develop gradually. In the range where previously the change of activation energy has been evidenced [2], as well as the change of CDW pinning accompanied by a new transport mechanism [3–5], we found a critical slowing down of the relaxational mode with all

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characteristics of the primary relaxation as in supercooled liquids [6].

## 2. Experimental

Four single crystals of o-TaS<sub>3</sub> have been studied with lengths between 2 and 20 mm and corresponding cross-sections in the range 10<sup>-3</sup>–10<sup>-4</sup> mm<sup>2</sup>. The measurements were carried out in two-probe configuration (samples glued to the 50 μm golden wires with the silver paste). All samples exhibited qualitatively the same behaviour in the  $T$ -range between 10 and 150 K. The complex admittance was measured in the span of frequencies 5 MHz–1 Hz by frequency response analyser (Schlumberger SI 1260) in combination with a broad-band dielectric converter (Novocontrol) as pre-amplifier. This setup allows impedance measurements up to 10<sup>7</sup> Ω with a tan δ resolution (= ratio of real-to-imaginary part of impedance, simultaneously measured) of 10<sup>-4</sup> at best. Only the case of the pinned CDW, with the amplitude of the signal much lower than the threshold voltage for depinning, is reported.

## 3. Results and discussion

The transport properties were the first to show the change of the character of CDW condensate at low- $T$ . More or less there is an agreement that for  $T < T_p/3$  ( $T_p = 210$  K being the temperature of the Peierls transition, i.e. CDW condensation  $T$  as defined in Fig. 1) the transport as well as the dielectric properties in the chain direction show the change of activated slowing down with  $E_a \cong \Delta_p$  into the range with  $E_a \leq \Delta_p/3$  ( $\Delta_p$  being the Peierls gap). Our results shown in Fig. 1 exhibit similar tendency below 70 K. In the same  $T$ -range the non-linear properties change too: The second threshold appears in the same  $T$ -range, as represented in the lower inset of Fig. 1 (borrowed from Ref. [7]).

Fig. 2 shows our results of the frequency dependence of the imaginary part  $\epsilon''$  of the complex susceptibility, evaluated from the measured sample capacitance.  $\epsilon''$  attains extremely high values, between 10<sup>7</sup> and 10<sup>8</sup>, what is one of the well-known

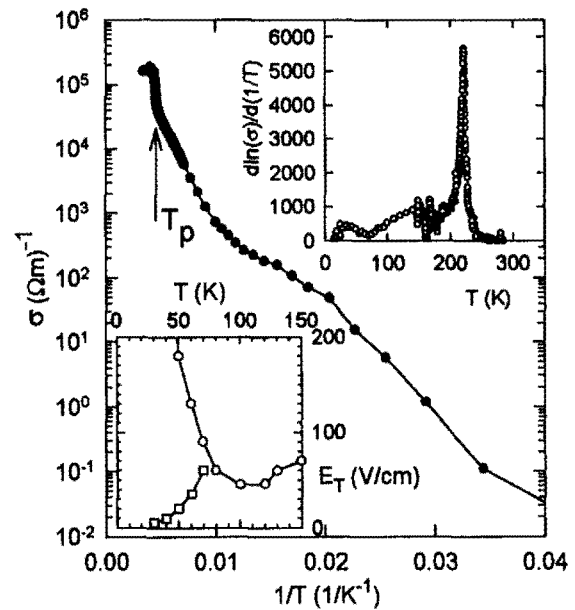


Fig. 1. Logarithm of conductivity versus inverse temperature for a o-TaS<sub>3</sub>. Corresponding logarithmic derivative in the inset is peaked at Peierls transition temperature  $T_p = 210$  K and exhibits a change of the character below 100 K. The lower inset shows the occurrence of the second threshold below 70 K (from Ref. [7]).

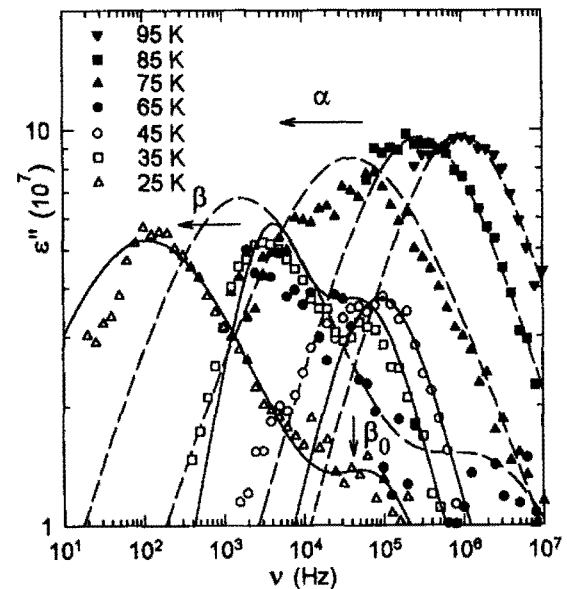


Fig. 2. Frequency dependence of the imaginary part  $\epsilon''$  of the dielectric susceptibility of pinned o-TaS<sub>3</sub> with Cole-Cole fits. The fit for 65 K is uncertain and should be considered as the guide for the eye. The relaxational mode ( $\alpha$  process) disappears from the experimental window on approaching  $T_g \sim 50$  K and two new processes appear below,  $\beta$  and  $\beta_0$ .

characteristics of CDW systems (DW superdielectrics). Below  $\sim 120$  K we were able to observe the low-frequency relaxational process (full symbols in the Fig. 2) that we named  $\alpha$  process. The position of the peak, roughly corresponding to the characteristic frequency of the process, shifts towards lower frequencies until it disappears completely from our experimental window at 65 K. Below that temperature there remains a high-frequency process (shown at 55 K) that further splits into two processes:  $\beta$  process that moves to lower frequency and  $\beta_0$ , the process that is positioned at approximately  $10^4$ – $10^5$  Hz and only slightly depends on  $T$ .

We have used a Cole–Cole relaxation function to fit our results as it can account for the wide distribution of relaxation times, the consequence of the random CDW pinning, which seems to change with  $T$ , especially for  $\alpha$  and  $\beta$  processes

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}. \quad (1)$$

Because of our limited frequency range ( $\omega < 4\text{--}5 \times 10^6$  Hz) a large high-frequency dielectric constant cannot be very precisely defined. However, we estimated that  $\varepsilon_\infty$  is in the range  $10^6$ – $10^7$ . Its origin is an additional oscillator strength in the frequency range of few tens of GHz [8, 9] usually assigned to the pinned collective mode (which oscillates around the pinning position).

The characteristic relaxation rates for three processes are presented in Fig. 3, along with the high-frequency mode due to the pinning of CDW. Our results give for the first time the direct evidence that the activated slowing down of CDW slush turns into the critical slowing down, i.e. the transition from CDW slush to the real CDW glass below 50 K. It contradicts the previous interpretation of Cava et al. [10] who noticed that in the range 115–65 K there is a “dramatic disappearance of a low-frequency relaxation and a strange saturation of the estimated relaxation time below 80 K”. As we have gained almost two decades towards lower frequencies, it enables us to show that the strength of the relaxational mode does not change drastically with  $T$ , but its fast disappearance from this frequency window has for the consequence the

apparent change of the amplitude, as only the high-frequency tail remains in this range.

There is a strong similarity with the corresponding plot for supercooled liquids around their glass transition, as demonstrates the inset of Fig. 3 for *o*-terphenyl [11]. An enormous increase of the viscosity upon cooling causes the relaxation time  $\tau$  of the main, so-called  $\alpha$ , or primary relaxation to increase faster than activated (or Arrhenius). So, below glass transition temperature  $T_g$  ( $T$  at which  $\tau \sim 10^3$  s) it goes out from the experimental window.  $\beta$  (or Johari–Goldstein) relaxation takes place at lower temperatures [12, 13] and is a genuine feature of glass formers below  $T_g$ . It has activated behaviour with the activation energy much lower than any apparent activation energy obtained from the slope of  $\alpha$  relaxation. The third process observed by neutron and light scattering techniques in

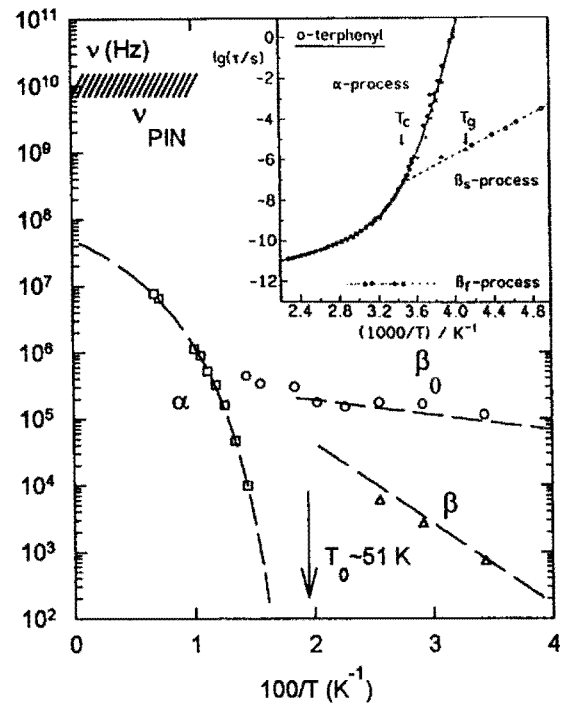


Fig. 3. Arrhenius plot of relaxation rates for  $\alpha$ ,  $\beta$ , and  $\beta_0$  processes. The dashed lines represent Vogel–Fulcher fit  $\nu = \nu_0 \exp(E/(T - T_0))$  for  $\alpha$  process with parameters  $\nu_{0\alpha} = 2.4 \times 10^7$ ,  $E_\alpha = 145$  K and  $T_0 = 51$  K, and the activated behaviour for  $\beta$  with  $\nu_\beta = 1.2 \times 10^7$ ,  $E_\beta = 280$  K and  $\beta_0$  with  $\nu_{\beta_0} = 5.4 \times 10^5$  and  $E_{\beta_0} = 52$  K. The pinning frequency  $\nu_0 = 20$  GHz is added (after Refs. [8, 9]). Note the strong similarity with supercooled liquids, shown for *o*-terphenyl in the inset (after Ref. [11]).

THz range and referred as  $\beta_{\text{fast}}$  is closely connected to the  $\alpha$  process. According to the very popular mode coupling theory (MCT) the  $\alpha$  process is responsible for diffusive motion and the  $\beta_{\text{fast}}$  is attributed to strongly anharmonic motions of a limited number of molecules trapped in cages formed by their neighbours [14]. It is not clear whether the “slow  $\beta$ ” process is also in some way related to the “fast  $\beta$ ”, as these processes are widely separated in frequencies and have to be probed by different experimental techniques (neutron and dielectric experiments probe usually different correlation functions).

Based on glass concepts, we propose the scenario for freezing of CDW which can account for the temperature dependence of relaxation rates of all processes detected by our dielectric spectroscopy and given in Fig. 3. Well-characterised pinned phase mode [8,9] is situated at frequency of the order of 10 GHz that corresponds to the gap in the phason spectrum. It has all characteristics of the  $\beta_{\text{fast}}$  process, however at lower frequency than in “regular” glasses due to larger scales involved because of the very large coherence length of this collective mode. The relaxational mode emerging from the pinned mode we recognise as the primary,  $\alpha$  process. The pinned configurations and the local modes of oscillations of the CDW are disordered on a typical length scale  $\zeta_{\text{LR}} \sim 1 \mu\text{m}$  called Lee–Rice length. Applied field induces internal fields in the domain of the local mode which induce screening currents of free carriers which dissipate energy resistively. These fluctuations strongly modify the dielectric response of the system at lower frequencies and the dielectric function develops a low-frequency loss peak in addition to the absorption close to the pinning frequency [15]. We accept it as an excellent “microscopic” model for decoupling of two modes ( $\alpha$ - and  $\beta$ -fast). That model, unfortunately, gives only a mechanism of non-critical slowing down, and the  $\alpha$  process shows a real critical slowing down in the range  $\sim 50$  K. The theories of elastic CDW should also take into account cooperativity effects between various domains of coherent phase volume, which in our case start to be involved below 70 K in MHz frequency range, when the slope of the  $\alpha$  relaxation gives the apparent activation energy larger than the Peierls

gap. Similar change of dynamics in supercooled liquids occurs in GHz range and it was interpreted as the precursor of cooperativity effect on the length scales of few nm [16,17]. The so-called microscopic peak appears in THz range, as noticed before. Corresponding frequency ranges for the CDW glass are 2–3 order of magnitudes smaller indicating the characteristic length scales more than 100 times larger than in supercooled liquids. What is consistent with our interpretation is that the characteristic length of CDW glass is Lee–Rice phase-correlation length of the order of few  $\mu\text{m}$ . We are preparing the investigation of the evolution of separation between pinned mode and relaxational mode at higher frequencies (up to few GHz) in order to see if the change of the dynamics follows the scenario predicted by MCT.

One specific difference to the ordinary glasses more is the relatively high intensity of the  $\beta$  relaxation, as nicely demonstrates Fig. 4. This pronounced feature below  $T_g$  cannot be observed in supercooled liquids, spin glasses or some other types of glasses, as  $\beta$  relaxation is few orders weaker

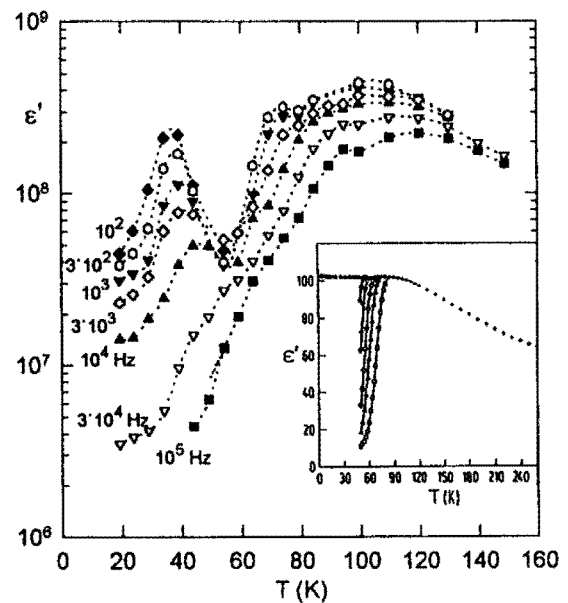


Fig. 4. Temperature dependence of the real part  $\epsilon'$  of the dielectric susceptibility of pinned o-TaS<sub>3</sub>. For the most of the supercooled liquids or other glasses it is impossible to detect the  $\beta$  process remaining below  $T_g$  because of its very small intensity. Inset shows corresponding plot for deuteron glass DRADP (from Ref. [25]).

in intensity than the main,  $\alpha$  relaxation. We believe that in the case of CDW the  $\beta$  relaxation represents the dynamics of CDW defects. Below  $T_g$  there remains a “liquid of DW defects” trying to form a periodic lattice of phase kinks.  $\beta_0$  process might represent the pinning of the new structure (defect pinning) that could cause similar absorption in MHz range as the CDW pinning in GHz range. The  $\beta$  process, and its slowing down (more elaborated in Ref. [6]) manifests the rigidification of these plastic deformations due to the screening of non-uniform distortions, as it has been explained by Volkov in his low- $T$  soliton lattice model [18]. Our explanation of the  $\beta$  process in terms of DW defects can be related to the recently appeared theoretical model for the general, material-independent description of glass formation [19, 20]. It is based on the concept of the “non-lattice” defects which diffuse both locally and through the structure of a solid, maintaining a spatially and temporally random distribution.

The direct evidence of a real glass transition gives natural explanation for numerous unusual phenomena observed in o-TaS<sub>3</sub> in the same temperature range (Ref. [21] and references therein). Especially interesting is the interplay between the glass transition and the incommensurate–commensurate transition in CDW [22]. The rigidification of CDW which is very close to be commensurate could deform the host lattice and alter the degree of commensurability. It might be mediated by the impurity interaction as there are similar effects in SDW where there is no electron–phonon interaction.

There is still an open question which we hope to answer in the near future; the characterisation of the LEEs giving rise to the well-known specific heat anomalies in glasses [1]. As there is an indication that the  $\beta$  process might freeze too [6, 23], we hope to show that  $\beta_0$  or/and some new branch of the  $\beta$  process could give contributions to low- $T$   $C_p$  and the very slow dynamics characterised by the activation energy of 1–2 K [1, 24].

We are aware that our explanation is somehow provocative from the traditional point of view of CDW as well as glass community, because we are

dealing with the systems with established long-range order where the disorder manifests on length scales of the order of  $\mu\text{m}$ . Nevertheless, we believe that the new results and our explanation will bring DW systems into the focus of new conceptual investigation in the field of glasses. Further investigation in the frequency range up to few GHz, with the aim to verify the MCT approach on the pinning and relaxational modes, might bring additional arguments for our interpretation.

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