Glass transition in CDW system o-TaS_3

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Abstract

We report on the experimental evidence of a glass transition in the CDW phase of orthorhombic TaS_3 at $T_g \sim 50$ K, brought by means of dielectric constant measurement. The relaxational mode exhibits in this T-range a critical slowing down instead of an expected activated behavior. New processes appear below the glass transition temperature which we attribute to the defect dynamics. There is an apparent similarity with the scenario of freezing out in supercooled liquids. However, the peculiarity of this glass transition is a very large length scale of order of μm (beyond the phase coherence length of the underlying CDW), compared to nm in supercooled liquids.

Keywords: glass transition, charge density waves, dielectric measurement, transition metal chalcogenides

1. Introduction

A charge density wave (CDW) is assumed to be in a glassy state everywhere below the Peierls transition (T_P), mainly due to the random CDW pinning. There are numerous manifestations of glassy behavior in electric, dielectric and thermal properties. In particular, low-T thermodynamical investigations reveal all characteristic features of low energy excitations in glasses [1]. The generalized viscosity of a CDW liquid is the viscosity of the "liquid of normal electrons", i.e. the electrical resistance of the motion of the CDW relative to the electron fluid. Because of the condensation of free electrons into the CDW ground state, the screening currents freeze out and the so-called Coulomb hardening is expected to be a plain activated process [2], without any critical temperature.

However, in the case of orthorhombic TaS_3 (o-TaS_3), a prototype CDW compound with T_P=210 K, the state below 100 K has been distinguished from the high T range as a "disordered state". In this cross-over regime ($T \sim T_P/3$), Cava et al. [3] found a "dramatic disappearance of a low-frequency relaxation and a strange saturation of the estimated relaxation time". A corresponding decrease of the activation energy, as well as the change of the CDW pinning accompanied by a new transport mechanism [3-7], have also been evidenced. It was suggested that at low T, soliton-like distortions of the CDW phase give rise to an extra contribution to the conductivity [4-6]. Finally, a real glass transition has been found at much lower T (T~13 K) [8], already very deep in the "disordered state".

Our aim was to find out the mechanism which causes the change of the activation energy and to study the character of the underlying processes, or more simply - to search for a proper understanding of the CDW glass.

2. Experimental

Altogether four single crystals of o-TaS_3 were studied from the same batch, but with different geometries (lengths between 2 and 20 mm and corresponding cross-sections in the range 10^{-3}-10^{-4} mm^2) for achieving better measuring conditions. The dielectric constant measurements were carried out in a two probe configuration (sample glued to the 50 μm golden wires with the silver paste), which was afterwards transformed to a four probe configuration for the electrical transport measurements on the same sample. There is no essential difference between the results for different samples [9].

The dielectric spectroscopy was performed in the span of frequencies 5MHz-1Hz and in the T-range between 20-150K. We used a frequency-response analyzer (Schlumberger SI 1260) based on the usual lock-in technique, in combination with a broad band dielectric converter as a preamplifier. This method allows impedance measurements up to 10^{14} Ω with a loss angle lower than 10^{-2} reaching even 10^{-4} at best. Here we discuss only the case of the pinned CDW, with the amplitude of the signal much lower than the threshold voltage for depinning (V_{ac}<30 mV/cm).

3. Results and Discussion

The electrical transport, measured on the sample with the smallest cross-section reported in Fig. 1., illustrates the most

pronounced changes in three T regimes, which correlate with the features in the nonlinear transport. Below 100 K, the rate of activated slowing down drops from $E_a \cong \Delta_P$ (Δ_P being the Peierls gap) to $E_a' \cong \Delta_P/3$, when the threshold filed starts to increase from its minimum value and the second threshold appears at even lower T (~70 K) [5,6,8]., as shown in the inset.

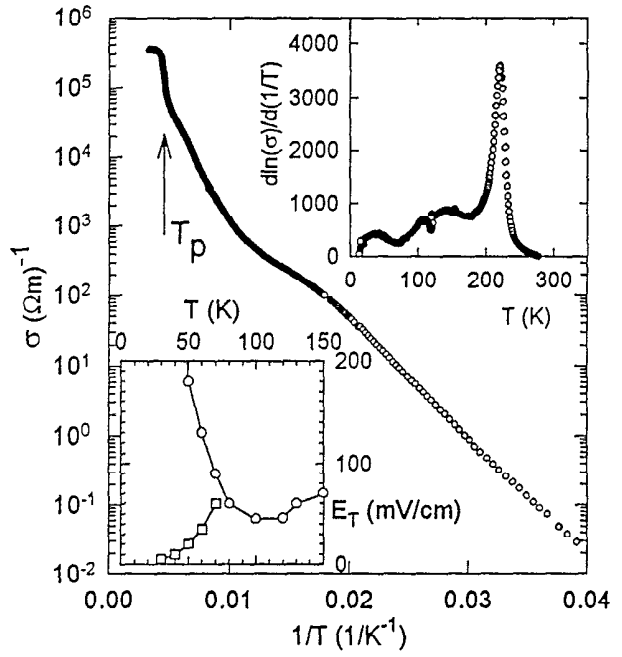

Figure 1. - Logarithm of conductivity vs. inverse temperature and its logarithmic derivative in the inset show for a o-TaS_3 the change of the character below 100 K. The lower inset shows the occurrence of the second threshold below 70 K (from ref. [10]).

The frequency dependence of the real part ε' and imaginary part ε" (in the inset) of the complex susceptibility are reported in Fig. 2. We present it for several temperatures in two characteristic temperature ranges, above and below 50 K. ε' attains extremely high values, between 10^7 and 10^9, which is one of the well known characteristics of the collective ac response of DW systems (DW superdielectrics). There is still a large high-frequency dielectric constant ε_{hf} difficult to evaluate because of our limited frequency range (ω<4-5 MHz). However, we estimated that ε_{hf} is in the range 10^6-10^7. It represents the "background" remaining from an additional oscillator strength in the frequency range of few tens of GHz [11] usually assigned to the pinned collective mode (oscillating coherently around the pinning position) [2].

Our results demonstrate the wide distribution or relaxation times. They could be fitted for temperatures above 70 K to the simplest form with variable width; Cole-Cole relaxation function:

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

where w=1/(1- α) is the halfwidth of the imaginary part of the response ε"(ω).

As it is evident from Fig. 2. that below 70 K there exist two processes, we used the sum of two Cole-Cole functions with the same parameters for the real and imaginary parts. Fig 2. shows a very good agreement between the experimental results and these simple fits.

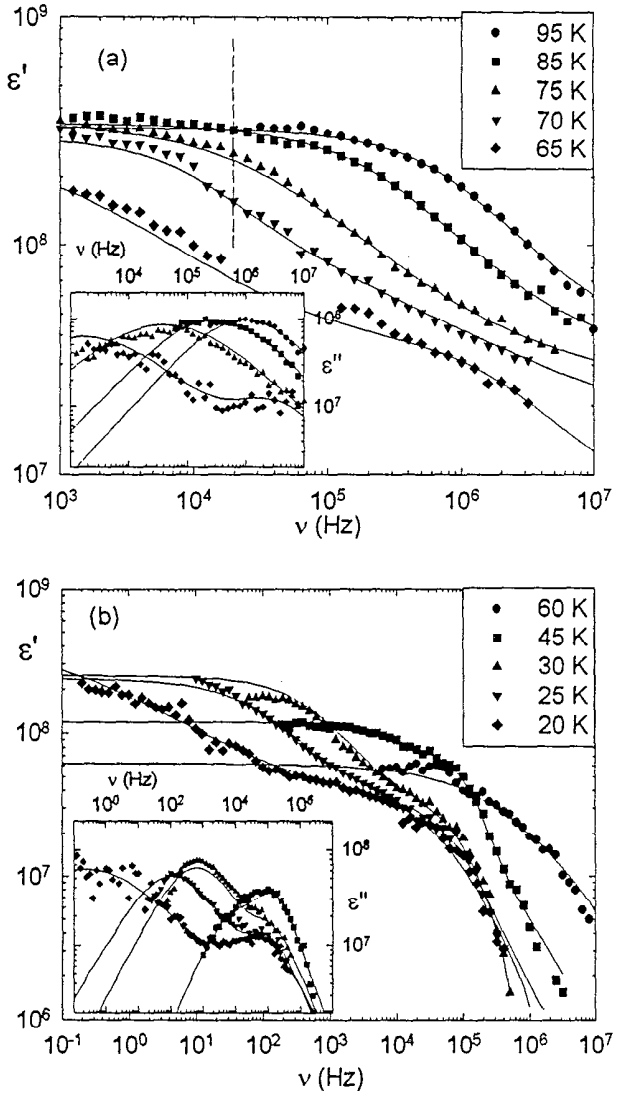

Figure 2. - Frequency dependence of the real part of the dielectric constant of pinned o-TaS_3: a) for temperatures 60 K < T < 100 K, b) for temperatures 20 K < T < 60 K. Corresponding imaginary parts are in insets. The part above the vertical line in (a) represents the experimental window used in [3].

Indeed, our results show that the strength of the relaxational mode does not change drastically with T, as explained by Cava et al. [3]. We were able to spread the experimental window used by Cava et al. for almost two decades towards lower frequencies. Because of the fast disappearance from this frequency window, only the high frequency tail remains in the range used by Cava, bearing as the consequence the apparent change of the amplitude. Underneath the remaining tail develops a new feature. Its evolution at lower T is shown in Fig. 2b. Two

new modes evolve with very different dynamics and strength. We call them β and β_0 processes.

The characteristic relaxation rates for three processes are presented in Fig. 3. along with the high-frequency mode due to the pinning of the CDW [11]. For comparison, we also show the results obtained by Cava et al.

Our results give for the first time direct evidence that the activated slowing down of the relaxational mode (Coulomb hardening) turns into critical slowing down.Instead of the simple activated behaviour with the activation energy of the order of the Peierls gap, below 100K the characteristic frequency of the α process rather follows much steeper law. It can be nicely fit to the Vogel-Fulcher phenomenological formula $\nu=\nu_0\exp(E_\alpha/T-T_0)$, with $\nu_0=2.4\ 10^7\ s^{-1}$, $E_\alpha=145K$ and $T_0=51K$. Below this freezing temperature, two new processes appear. Fig. 3. associates strongly with the temperature dependence of the viscosity near the glass transition in a supercooled liquid (shown in the inset). In this context we propose the following scenario for the DW glass, which can be followed along the temperature dependence of relaxation rates of all processes detected by our dielectric spectroscopy.

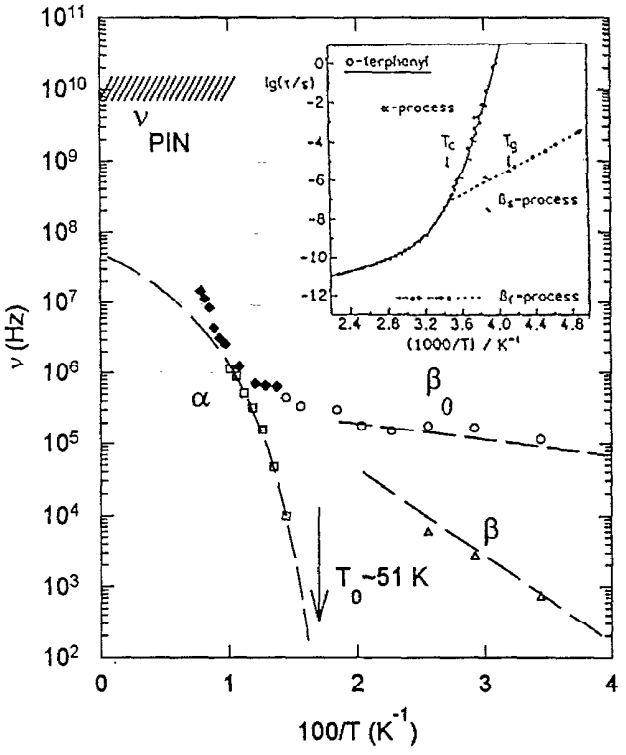

Figure 3. - Arrhenius plot of relaxation rates for α, β, and β_0 processes. The pinning frequency is added (after ref. [11]), as well as the results of Cava et al. [3] - full symbols. Note the strong similarity with supercooled liquids, shown for o-terphenyl in the inset (after ref. [12]).

(i) In the high frequency range (20 GHz) there is a well characterized **pinned phase mode** (this frequency acts as a gap in the phason spectrum). It has all the characteristics of the β **fast process**, however at lower frequency than in "regular" glasses due to larger length scales involved because of the collective effect.

(ii) The pinned configurations and the local modes of oscillations of the CDW are disordered on a typical length scale ξ_{LR} ≈μm called Lee-Rice length. 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. **The relaxational mode** which emerges from the pinned mode we recognize as **the primary, α process**. An applied field induces internal fields in the domain of the local mode and screening currents by free carriers, which dissipate energy resistively. Hence, the generalized CDW viscosity scales with the normal resistivity, $\eta\sim\rho_n$. We accept it as an excellent "microscopic" model for decoupling of two modes (α and β-fast) which also gives almost all necessary elements for the understanding of the CDW viscosity. However, this model provides a mechanism of noncritical slowing down. As our α process exhibits critical slowing down, existing theories of elastic CDW cannot produce the right description. They should take into account cooperativity effects between various domains of coherent phase volume.

(iii) **Cooperativity effects** start to be involved **below 70 K** when the slope of the α relaxation gives the apparent activation energy larger than the Peierls gap. This happens in the frequency range below MHz in comparison to regular glasses where it happens in GHz range. The facts that the "microscopic" peak appears in GHz range and that dynamics of α relaxation changes in MHz range indicates that the length scales are 2-3 order of magnitude larger than in supercooled liquids (few nm).

(iv) Two new processes appear below T_g: We assign the one with the larger strength and the activation energy E_a^1 ≈300 K to the **secondary, β process**. The third one, **$\beta_\bullet$ process,** remains at higher frequency $\omega\sim10^5$Hz and moves slowly in temperature with an activation energy of E_a^2 ≈10-20 K (Fig. 3.). We believe that both processes below T_g represent the defect structure in the DW glass. In the frame of the previous scenario for the glass transition in CDWs, worked out in detail above, the natural continuation could be that below T_g ~ 50 K remains a "liquid of DW defects" trying to form a periodic lattice of phase kinks. Pinning of the new structure (defect pinning) could cause similar absorption in MHz range as the CDW pinning in GHz range and give rise to the **$\beta_\bullet$ process.** The main reason of rigidification of these plastic deformations is the screening of nonuniform distortions.

Finally, we compare our results (Fig. 4a.) with the detailed study of low-T dielectric properties of o-TaS_3 performed by Nad' and Monceau [8] (Fig. 4b.). The minimum between α and β process is at lower temperature in Ref. [8], but as the authors noticed, it depends essentially on the purity of the sample. The maximum in ε'(ω) at T~120 K was unfortunately not investigated in the whole frequency range (only for 500 kHz, Fig. 1. in Ref. [8a]. Our results below 50 K demonstrate almost equal characteristics. Moreover, it seems that the two processes we refer as β and β_0 which are well distinguished in our measurements, exist also in Fig. 5. of Ref. [8a] but their relative strengths are different. Although at first glance our interpretations seem to be entangled (our β process is called α process in Ref. [8]), they comply with one clear observation that there exists a cascade of glass transitions. There is evidence of

critical slowing down of our β process at T ~ 15 K. It seems that the β process of the glass transition we find at 50 K can turn into the primary process of the next successive glass transition at 15 K!

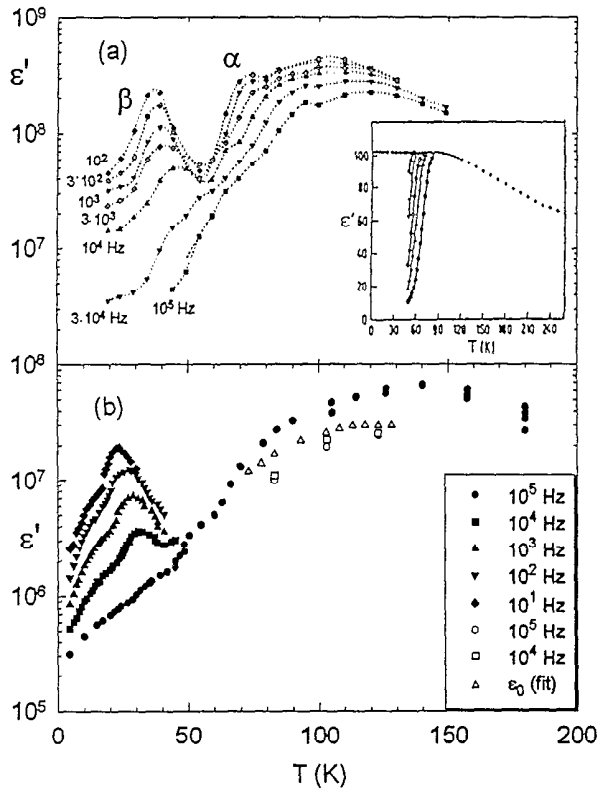

Figure 4. a) Temperature dependence of the real part ε' of the dielectric susceptibility of o-TaS_3. In the measured frequency range exists above 60 K only α process from which, on the branches for frequencies $\omega<10^5$ Hz, the secondary, β process emerges with the weak traces of β_0 process bellow 30 K. Inset shows corresponding plot for deuteron glass DRADP (from ref. [11].).b) Results obtained by other authors (Cava et al. [3] - empty symbols and Nad and Monceau [8] - full symbols) show very good agreement with ours.

The direct evidence of a real glass transition now sheds more light on numerous unusual phenomena observed in o-TaS_3 in the same temperature range. The most recent one is an anomalous gradual stiffening below 50 K [14]. Although the shear compliance does not show any frequency dependence, it does not disprove the existence of the glass transition. As it is found experimentally, especially for the case of the pinned CDW, the corresponding time scales of shear relaxation are much longer than seconds. Usually the time scales for different properties in glasses do not correspond without certain scaling.

Nevertheless, we still have to answer some questions. The first is the interplay between the glass transition and incommensurate-commensurate CDW transition [15]. The rigidification of the CDW which is very close to commensurate could deform the host lattice and alter the degree of commensurability. The second is that the main characteristics of the nonlinear properties are affected by this transition. That seems to be natural, as the pinning mechanism is at the basis of the CDW glassy properties. We already have some evidence that the applied electric field changes the scenario of the glass transition. Further investigation of β and β_0 processes might provide a new insight into the nature of the LEEs giving rise to the well known specific heat anomalies in glasses.

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4. References

[1] K. Biljaković in Physics and Chemistry of Low Dimensional Inorganic Conductor, Plenum, NATO-ASI Series B: Physics, Vol. **354** (1996) 357
[2] B. Littlewood, Phys. Rev. B **36** (1987) 3108
[3] J. Cava et al., Phys. Rev. B **31** (1985) 8325
[4] T. Takoshima et al., Solid State Commun. **35**, (1980) 911
[5] S. K. Zhilinski et al., Sov. Phys. JETP **58** (1) (1983) 211
[6] F. Ya Nad', Pis'ma Zh. Eksp. Teor. Fiz. **58** (1993) 107
[7] S. V. Zaitsev - Zotov, Phys. Rev. Lett. **71** (1993) 605
[8] F. Nad and P. Monceau, Solid State Commun. **87**, 13 (1993) and Phys. Rev. B **51**, 2052 (1995)
[9] K. Biljaković et al., Physica B **244** (1998) 167 and D. Starešinić et al., aps1998feb20_001 e-print article
[10] M. E. Itkis at al, J. Phys.: Condens. Matter **2** (1990) 8327
[11] D.Reagor and G.Grüner, Phys. Rev. Lett. **56** (1986) 659, S.Sridhar et al., Phys. Rev. B **34** (1986)2223
[12] E.Rössler, Phys. Rev. Lett. **69** (1992) 1620
[13] Z.Kutnjak et al., Phys. Rev. Lett. **70** (1993) 4015
[14] X. Zhan and J. W. Brill, this conference
[15] H. Salva et al. Phys. Mag. B **49** (1984) 385