Glass transition in the charge density wave system $K_{0.3}MoO_3$

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Low frequency dielectric spectroscopy and thermally stimulated discharge measurements of charge density wave (CDW) system $K_{0.3}MoO_3$ are presented. Below 80 K two distinct relaxational processes are observed, which freeze at finite temperatures bearing close resemblance to the phenomenology of the dielectric response of glasses. We compare our results to the case of o-TaS$_3$ in which the glass transition on the level of CDW superstructure has been recently reported and discuss the possibility that it is a universal feature of CDW systems.

PACS numbers: 71.45.Lr, 77.22.-d, 64.70.Pf

A charge density wave (CDW) is the modulated electronic superstructure that appears in some quasi one-dimensional systems at low temperatures (for an extensive list of references see 1). The low energy dynamics of CDW systems is governed by acoustic-like excitations of the phase of the complex order parameter. Apart from the metal-semiconductor transition at a finite temperature $T_P$ that is inherent to the CDW formation, the most striking features of CDW systems are an extremely high dielectric constant and nonlinear conductivity at already low electric fields. At the origin of these phenomena is pinning of the CDW by impurities that locks the CDW at the preferred position, which in turn shifts the onset of CDW sliding to a finite electric field, the so-called threshold field $E_T$. In addition, impurity pinning destroys long range phase coherence and breaks the CDW into domains.

The CDW dynamics turns out to be strongly temperature dependent, as CDW current and relaxation frequency both scale with the ohmic conductivity. A hydrodynamic model of the CDW phase screened by uncondensed free carriers, which includes elastic degrees of freedom, accounted well for these results. However, a qualitative change in the nonlinear conductivity occurs at lower temperatures, where the CDW displacement is better described by creep at low or rigid sliding at high electric fields, which both neglect elastic degrees of freedom. It is consistent with the response of CDW in the descreened limit, where the free carrier concentration is too low to screen elastic phase deformations and the intra-CDW Coulomb interaction makes them energetically unfavorable.

Despite numerous evidences that the transition from screened to unscreened response really occurs at finite temperatures, not enough attention has been given to the transition itself. Our recent papers on wide frequency and temperature range dielectric spectroscopy of the CDW system o-TaS$_3$ was devoted to this particular problem. We have shown that the low frequency relaxational process, that is related to the dynamics of elastic phase deformations, freezes at finite temperature, and that a secondary process appears at lower temperatures. As the temperature evolution of both processes bears close resemblance to the dielectric response of glasses, it naturally explains the liquid-like to solid-like transition as the glass transition on the level of the CDW superstructure. In this communication we show that a similar scenario exists in the most widely investigated CDW system $K_{0.3}MoO_3$ (blue bronze), which might point to the universality of the glass transition in CDW systems.

DC conductivity $\sigma_{DC}$, I/V characteristics (nonlinear conductivity), AC conductivity $\sigma(\omega)$ and thermally stimulated depolarization (TSD) have been measured in the direction of the highly conducting axis. Results on two samples did not show any significant difference and we present them for one of 5.7x1.2x0.4 mm$^3$ size. We measured $\sigma_{DC}$ and I/V characteristics in four contact configuration and $\sigma(\omega)$ and TSD in two contact configuration. The contacts were made by clamping 25 µm gold wires with silver paste to gold pads evaporated on the crystals.

$\sigma_{DC}$ has been measured between 300 K and 10 K and the I/V curves between 70 K and 10 K. The $\sigma(\omega)$ has been measured in the frequency range $10^{-1} Hz$ - $10^7 Hz$ at fixed temperatures between 80 K and 10 K. We used the frequency-response analyzer Schlumberger (SI 1260) in combination with a broad band dielectric converter (Novocontrol) as a preamplifier. We have verified that the signal amplitude of $V_{ac}$=20 mV kept the response in linear regime. For TSD measurements we used Keithley 617 electrometer as both voltage source and current meter. The sample was cooled in electric fields ranging from 0.4 V/cm to 40 V/cm. After removal of the electric field at low -T the sample was connected in a short circuit and the discharge current was recorded during the constant rate heating.

The dielectric function $\epsilon(\omega)$ has been calculated from $\sigma(\omega)$ after subtraction of $\sigma_{DC}$. The frequency dependence of the real ($\epsilon'$) and imaginary ($\epsilon''$) part of the dielectric function in the units of dielectric permittivity of vacuum $\epsilon_0$ is presented in figure [1]. The wide step-like decrease of $\epsilon'$ with frequency and the wide maximum in $\epsilon''$ are typical for the overdamped, or relaxational dielectric response. The relaxational processes are characterized by their amplitude $\Delta \epsilon$, mean relaxation time $\tau$ (or relaxation frequency $\nu_0 = 1/2\pi \tau$ which gives the position of the maximum in $\epsilon''$) and by the width $\omega$. In order to ex-
extract these parameters, we have used the modified Debye function with variable width, also known as Cole-Cole (CC) function:

$$\epsilon(\omega) = \epsilon_{HF} + \frac{\Delta\epsilon}{1 + (i \cdot \omega \cdot \tau)^{1/w}}$$

(1)

where $\epsilon_{HF}$ is the high frequency “base line” of $\epsilon'$.

From figure [1] it is evident that the low frequency dielectric response of $K_{0.3}MoO_3$ cannot be attributed to a single relaxation process. The process that dominates at higher temperatures has already been reported in several papers, and its features, in particular the increase of $\tau$ at low temperatures, correspond well to the published data. Due to the extended low frequency window we have been able to follow the temperature evolution to much lower temperatures and we can see that $\tau$ increases below 30 K without any sign of saturation. This is in agreement with data obtained from the real time relaxation and temperature scans at fixed frequency. However, already at 41 K a high frequency tail develops, which evolves at low temperatures into another well defined relaxation process of much lower amplitude. In compliance with the results of $\alpha$-TaS$_3$ we name the high temperature process primary or $\alpha$ process, and the low temperature one secondary or $\beta$ process. This is for the first time that the second relaxation process at low temperatures has been considered and characterized in blue bronze, although signs of the high frequency tail of the primary process can also be seen in Ref. 19. The data have been fitted to two CC functions (Eq. (1)) between 41 K and 27 K, corresponding to the coexistence of $\alpha$ and $\beta$ processes, and with a single CC function otherwise. The fits are represented with solid lines in figure [1].

In figure [2] we present the temperature dependence of the mean relaxation times $\tau_\alpha$ and $\tau_\beta$ of both processes, together with the temperature dependence of the DC resistivity. The slowing down of the $\alpha$ process follows an activated or Arrhenius dependence, with the activation energy of $E_\alpha=630$ K (slightly higher than $E_\alpha=530$ K obtained from DC resistivity below $T_P$). Such relation has been observed in $K_{0.3}MoO_3$, as well as in other semiconducting CDW systems. $\tau_\beta$ also follows an activated dependence with about two times lower $E_\beta=325$ K, close to $E_\beta=320$ K obtained from low temperature DC resistivity. In addition, an extrapolation of $\tau_\beta(T)$ to higher temperatures indicates that at about 80 K the $\alpha$ and $\beta$ processes merge. This kind of temperature evolution is very similar to the one observed in the CDW system $\alpha$-TaS$_3$, but also in glasses in the vicinity of the glass transition temperature. For structural glasses there is a convention that the glass transition temperature $T_g$ is the one at which the relaxation time exceeds $10^3$ seconds, signifying that the corresponding process becomes so slow that it cannot contribute to the dynamics of the system in the experimental time window. Based on the extrapolation of the activated fits we obtain $T_{\alpha g} \approx 23$ K for the $\alpha$ process, and $T_{\beta g} \approx 13$ K for the $\beta$ process.

In order to verify that the two processes really freeze at finite temperatures, we have employed TSD measurements, a general method of investigating low frequency dielectric properties of high resistivity solids via the study of thermal relaxation effects. One TSD spectrum obtained on the same sample as used for dielectric spectroscopy is presented in figure [2]. Two peaks observed reveal the freezing of two relaxation processes. The higher one ($\alpha$) is situated at 30 K, and the lower one ($\beta$) at about 12.5 K, in rough agreement with the dielectric spectroscopy data. The $\alpha$ peak with very similar features has already been observed before by the TSD method.

From TSD spectra one can obtain several parameters,
such as the effective activation energy of the current increase \( E_{\text{eff}} \), the position of the maximum \( T_{\text{max}} \), the maximum current density \( j_{\text{max}} \) and the relaxed polarisation \( P \). In combination with the known heating rate \( h \) and the polarizing electric field \( E_P \), it enables the estimation of related dielectric parameters\(^3\) such as the effective relaxation rate \( \omega_{\text{eff}} = (E_{\text{eff}}/h)/(k_B T_{\text{max}}^2) \), the maximum value of \( \epsilon' \) at \( T_{\text{max}} \) \( \epsilon'_{\text{max}} \approx j_{\text{max}}/(\omega_{\text{eff}} E_P) \) and the static dielectric constant \( \Delta \epsilon_{\text{eff}} = P/E_P \), as given in table II.

The parameters estimated for the \( \beta \) peak in TSD very nicely coincide with the parameters of the \( \beta \) process obtained from dielectric spectroscopy, which is not the case for the \( \alpha \) peak. In order to explain this, we present in the inset of figure the dependence of the TSD current maxima on the \( E_P \) for both peaks. While the \( \beta \) peak is in the linear regime in the entire range, the \( \alpha \) peak approaches saturation already for the lowest applied fields. It has been shown that both DC bias\(^6\) and increased signal amplitude\(^\text{13}\) in dielectric spectroscopy lead to the increase of \( \Delta \epsilon \) and \( \tau \), therefore it is reasonable that the \( \alpha \) process freezes at higher temperatures and has higher polarizability in the saturated regime.

Our results unambiguously show the existence of two relaxation processes in the low frequency dielectric response of the CDW system K\(_{0.3}\)MoO\(_3\), which is a completely novel feature. Moreover, we have shown that the temperature evolution follows the same scenario as for the glass transition in \( \alpha\)-TaS\(_3\). The dynamics of the \( \alpha \) process has been thoroughly considered theoretically, and it has been successfully modeled by the dynamics of the local elastic deformations of the CDW phase\(^\text{28}\). Therefore the freezing of these excitations reduces the phase space relaxation rate \( \epsilon \)

...and \( \Delta \epsilon \) for the \( \beta \) process is smaller than for the \( \alpha \) process, its value is still too high to represent the single particle response. We present in figure the T-dependence of \( \Delta \epsilon \) for both processes and compare it with the inverse value of two threshold fields measured in the same sample. Both processes obey approximately the relation \( \Delta \epsilon \cdot E_T = \text{const} \). This has already been established for the \( \alpha \) process in several CDW systems\(^29\), in corresponding T-ranges, as well as for the \( \beta \) process in \( \alpha\)-TaS\(_3\). This close relation to the second threshold field, as well as the activated increase of \( \tau \) following \( \sigma_{\text{DC}} \) support its CDW origin. Therefore, the \( \beta \) process should represent the dynamics of the remaining degrees of freedom of the CDW after the elastic ones are frozen, i.e. topological or plastic deformations, such as solitons, domain walls or dislocation loops. These can contribute to the low frequency dielectric response\(^30\), as well as to linear and non-linear conductivity\(^31\). Localized midgap states have indeed been observed in femtosecond spectroscopy\(^32\). The approach based on coexistence of

![FIG. 3: TSD current spectrum recorded at constant heating rate of 10.5 K/min after cooling from 50 K in electric field of \( E_P=4.4 \) V/cm. Two maxima correspond to the freezing of \( \alpha \) and \( \beta \) processes. Solid lines are fits to the activated current increase. The inset shows the dependence of the current peak values on the polarizing electric field for two processes.](image)

![FIG. 4: Temperature dependence of amplitude \( \Delta \epsilon \) of \( \alpha \) and \( \beta \) processes plotted together with the inverse values of two threshold fields observed in high (\( E_T \)) and low (\( E_T' \)) temperature range.](image)
local ("strong") and collective ("weak") pinning, or plastic and elastic deformations of the phase could also naturally account for the coexistence of α and β processes, particularly as it has been established that the pinning is locally always strong.

The temperature evolution of α and β processes observed in the two CDW systems o-TaS₃ and K₀₃MoO₃ share some common properties. In both systems the β process splits from the α process at frequencies around 1 MHz and the activation energy $E_{act}$ is about two times smaller than $E_{αα}$. Also, $ΔT_{α}$ is comparable in both systems. However, unlike in K₀₃MoO₃, $τ_{β}$ in o-TaS₃ deviates from an activated behaviour on approaching $T_g$. Such increase of the effective activation energy close to $T_g$ as in o-TaS₃ is characteristic of fragile glasses, while strong glasses obey an Arrhenius behaviour as in blue bronze. The differences between strong and fragile behaviour result from the different topography of the phase space. In CDW systems the phase space is essentially created through pinning, so the modification of the potential energy landscape reflects the changes in pinning properties. This might finally bring a completely new light to the problem of pinning in the field of CDWs.

The difference between o-TaS₃ and K₀₃MoO₃ exists also in the amplitudes of the relaxation processes. While $ΔT_{α}$ in blue bronze is almost preserved in the entire T-range, in o-TaS₃ it decreases strongly on approaching $T_g$. On the other hand $ΔT_{β}$ is comparable to $ΔT_{α}$ in o-TaS₃, while in K₀₃MoO₃ it is almost two orders of magnitude smaller. The smaller $ΔT_{β}$ in K₀₃MoO₃ would be consistent with the smaller number of topological defects and therefore larger phase coherence volume. The same difference in amplitude is also observed in the low temperature power-law contribution to the heat capacity and in the low temperature up-turn in magnetic susceptibility, where both phenomena are again attributed to topological defects of the phase. Again, fragile glasses typically exhibit a pronounced β process just as in o-TaS₃, whereas in strong glasses like K₀₃MoO₃, there persists only the "background loss" contribution to the low frequency dielectric response below $T_g$.

In conclusion, we have shown that the glass transition scenario previously seen in o-TaS₃ exists also in K₀₃MoO₃. This could represent a universal feature of CDW systems as it explains the transition to the low temperature CDW state and accounts quantitatively for its properties. New approaches to the glass transition based on the phase space landscape might help in understanding the pinning properties of CDW systems and shed light on the differences between o-TaS₃ and K₀₃MoO₃.

### Table I: Effective dielectric data obtained from the TSD spectrum in figure [3] and corresponding dielectric spectroscopy data

| peak/process | $T_{max}$ (K) | $ω_{eff}$ (1/s) | $Δε_{eff}$ | $ε''_{eff}$ | $T_g$ (K) | $Δε(∼T_g)$ | $ε''(∼T_g)$ |
|--------------|---------------|----------------|------------|-------------|-----------|------------|-------------|
| α            | 31            | 0.076          | 2.6·$10^3$ | 7.2·$10^7$  | 23        | 6·$10^7$   | 3·$10^7$    |
| β            | 12.5          | 0.16           | 5.1·$10^3$ | 9.1·$10^4$  | 13        | 4·$10^5$   | 8·$10^4$    |

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