Glass transition and secondary relaxation 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.

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A charge-density wave (CDW) is the modulated electronic superstructure that appears in some quasi-one-dimensional systems at low temperatures (Ref. 1 and references therein). The low-energy dynamics of CDW systems is governed by acousticlike 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 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[2] and relaxation frequency[3,4] both scale with the ohmic conductivity. A hydrodynamic model of the CDW phase screened by uncondensed free carriers,[5,6] which includes elastic degrees of freedom, accounted well for these results. However, a qualitative change in the nonlinear conductivity occurs at lower temperatures,[7,8] where the CDW displacement is better described by creep at low or rigid sliding at high electric fields,[9,10] 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[11,12] and the intra-CDW Coulomb interaction[13] 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 paper[1] 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, which 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[14] it naturally explains the liquidlike to solidlike 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 σ_{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 $5.7\times1.2\times0.4$ mm^3 size. We measured σ_{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.

σ_{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. 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 σ_{dc}. The frequency dependence of the real (ϵ') and imaginary (ϵ'') part of the dielectric function in the units of dielectric permittivity of vacuum ϵ_0 is presented in Fig. 1. The wide steplike decrease of ϵ' with frequency and the wide maximum in ϵ'' are typical for the overdamped, or relaxational dielectric response. The relaxational processes are characterized by their amplitude $\Delta\epsilon$, mean relaxation time τ (or relaxation frequency $\nu_0=1/2\pi\tau$ which gives the position of the maximum in ϵ''), and by the width w. In order to extract these parameters, we have used the modified Debye function with variable width, also known as Cole-Cole (CC) function,

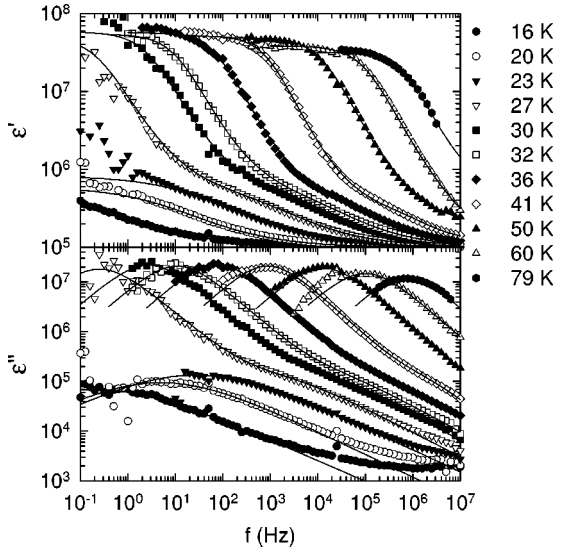

FIG. 1. Frequency dependence of the real (ϵ') and imaginary (ϵ'') part of the dielectric response at selected temperatures. Solid lines represent the fits of the data by CC function.

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

where ϵ_{HF} is the high frequency ''base line'' of ϵ'.

From Fig. 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,[3,15–17] and its features, in particular, the increase of τ 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 τ increases below 30 K without any sign of saturation. This is in agreement with data obtained from the real-time relaxation[18] and temperature scans at fixed frequency.[19] However, already at 41 K a high-frequency tail develops, evolving at low T into another well-defined relaxational process of much lower amplitude. In compliance with the results of o-TaS_3 we name the high-T process primary or α process, and the low-T one secondary or β process. This is for the first time that the second relaxational process at low temperatures has been observed in blue bronze. Our data have been fitted to two CC functions [Eq. (1)] between 41 K and 27 K, corresponding to the coexistence of α and β processes, and with a single CC function otherwise (solid lines in Fig. 1).

In Fig. 2 we present the temperature dependence of the mean relaxation times τ_α and τ_β of both processes, together with the temperature dependence of the dc resistivity. The slowing down of the α process follows an activated or Arrhenius dependence, with the activation energy of $E_a = 630$ K (slightly higher than $E_a = 530$ K obtained from dc resistivity below T_P). Such relation has been observed[19] in $K_{0.3}MoO_3$, as well as in other semiconducting CDW systems.[1,4] τ_β also follows an activated dependence with about two times lower $E_a = 325$ K, close to $E_a = 320$ K obtained from low-temperature dc resistivity. In addition, an extrapolation of $\tau_\beta(T)$ to higher temperatures indicates that α and β processes merge at about 80 K in MHz frequency range.

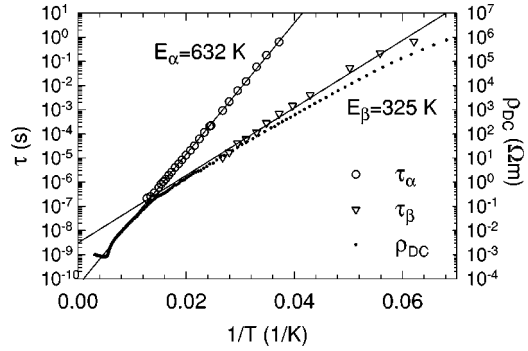

FIG. 2. Temperature dependence of the characteristic relaxation time of α and β processes presented in Arrhenius type plot together with the scaled dc resistivity. Solid lines are fits to the activated behavior.

The temperature evolution of the dielectric response presented in Fig. 2 we find typical for glasses.[14] In this respect we are able to estimate the glass transition temperature T_g by adopting the convention that at T_g $\tau \sim 100$ s. Extrapolating our data we obtain $T_{g\alpha} \approx 23$ K for the α process, and $T_{g\beta} \approx 13$ K for the β process. Such definition of T_g is to some extent arbitrary, particularly for activated temperature dependence[20] of τ, however it comes from the necessity to mark the onset of the glass phase on experimental, i.e., accessible time scales.

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.[21] One TSD spectrum obtained on the same sample as used for dielectric spectroscopy is presented in Fig. 3. Two peaks observed reveal the freezing of two relaxation processes. The higher one (α) is situated at 30 K, and

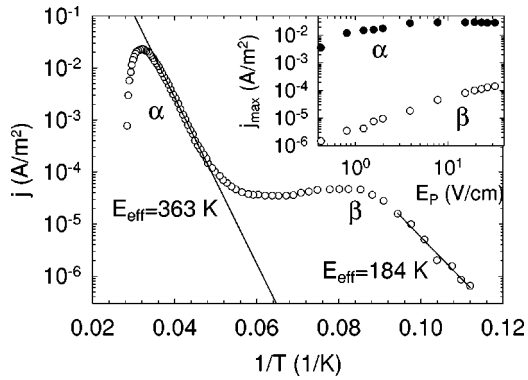

FIG. 3. TSD current spectrum recorded at constant heating rate of 10.5 K/min after cooling from 50 K in electric field of $E_P = 4.4$ V/cm. Two maxima correspond to the freezing of α and β processes. Solid lines are fits to the activated current increase. The inset shows the dependence of the current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

TABLE I. Effective dielectric data obtained from the TSD spectrum in Fig. 3 and corresponding dielectric spectroscopy data.

peak/process	T_{max} (K)	ω_{eff} (1/s)	$\Delta\epsilon_{eff}$	ϵ''_{eff}	T_g (K)	$\Delta\epsilon(\sim T_g)$	$\epsilon''(\sim T_g)$
α	31	0.076	2.6×10^8	7.2×10^7	23	6×10^7	3×10^7
β	12.5	0.16	5.1×10^5	9.1×10^4	13	4×10^5	8×10^4

the lower one (β) at about 12.5 K, in rough agreement with the dielectric spectroscopy data. The α peak with very similar features has already been observed before[22] by the TSD method.

From TSD spectra one can obtain several parameters, such as the effective activation energy of the current increase E_{eff}, the position of the maximum T_{max}, the maximum current density j_{max}, and the relaxed polarization P. In combination with the known heating rate h and the polarizing electric field E_P, it enables the estimation of related dielectric parameters[21] such as the effective relaxation rate $\omega_{eff}=(E_{eff}\cdot h)/(k_B\cdot T^2_{max})$, the maximum value of ϵ'' at T_{max} $\epsilon''_{eff}\approx j_{max}/(\omega_{eff}\cdot E_P)$ and the static dielectric constant $\Delta\epsilon_{eff}=P/E_P$, as given in Table I.

The parameters estimated for the β peak in TSD very nicely coincide with the parameters of the β process obtained from dielectric spectroscopy, which is not the case for the α peak. In order to explain this, we present in the inset of Fig. 3 the dependence of the TSD current maxima on the E_P for both peaks. While the β peak is in the linear regime in the entire range, the α peak approaches saturation already for the lowest applied fields. It has been shown that both dc bias[3] and increased signal amplitude[15] in dielectric spectroscopy lead to the increase of $\Delta\epsilon$ and τ, therefore it is reasonable that the α 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 o-TaS_3. The dynamics of the α process has been thoroughly considered theoretically, and it has been successfully modeled by the dynamics of the local elastic deformations of the CDW phase.[6] Therefore the freezing of these excitations reduces the phase space and represents essentially the change in the ground state in the same way as in structural glasses. This claim can be supported by a number of other experimental results that point to the changed properties of $K_{0.3}MoO_3$ in the range below 40 K down to 20 K such as closing of the thermal hysteresis in the dc conductivity, the appearance of a second E^*_T, an anomaly in proton channeling, the disappearance of metastabilities in ESR spectra.[23] Also, the changes in the lattice parameters[24] of $K_{0.3}MoO_3$ observed below 50 K indicate that the glass transition on the level of the CDW superstructure might affect the host lattice as found[25] for TaS_3.

In Ref. 1 we state that the freezing of the α process in o-TaS_3 occurs when there are not enough free carriers to screen efficiently the local phase deformations. We have set a criterion for the critical density to be about one free carrier per domain of phase coherence. From extrapolation of the high-temperature activated decrease of conductivity we estimate the critical density at T_g for $K_{0.3}MoO_3$ to be about 3×10^{13} e/cm^3. The corresponding volume is 3.3×10^{-14} cm^3, which is only by a factor of 2 smaller than the phase-coherence volume obtained from x-ray diffraction.[26] Therefore the same criterion is applicable for $K_{0.3}MoO_3$ as well.

Although $\Delta\epsilon$ for the β process is smaller than for the α process, its value is still too high to represent the single-particle response. We present in Fig. 4 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 $\Delta\epsilon\cdot E_T=const.$ This has already been established for the α process in several CDW systems,[27] in corresponding T ranges, as well as for the β process[1] in o-TaS_3. This close relation to the second threshold field, as well as the activated increase of τ_β following σ_{dc} support its CDW origin. Therefore, the β 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[28,29] as well as to linear and nonlinear conductivities.[30,31] Localized midgap states have indeed been observed in femtosecond spectroscopy.[32] The approach based on coexistence of local (''strong'') and collective (''weak'') pinning,[29,31,33] or plastic and elastic deformations of the phase could also naturally account for the coexistence of α and β process, particularly, as it has been established that the pinning is locally always strong.[34]

Temperature evolution of α and β processes observed in the two CDW systems o-TaS_3 and $K_{0.3}MoO_3$ share some

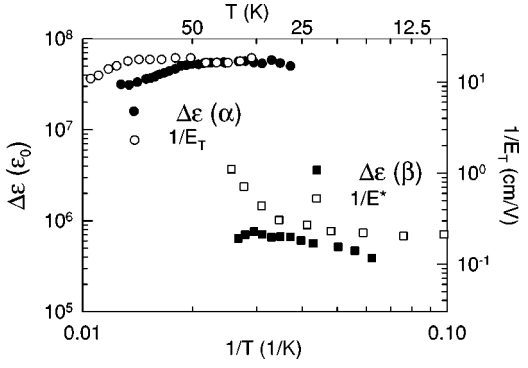

FIG. 4. Temperature dependence of $\Delta\epsilon$ for α and β processes plotted together with the inverse values of two threshold fields observed in high (E_T) and low (E^*_T) temperature range.

common properties. In both systems the β process splits from the α process in MHz frequency range and the activation energy $E_{a\beta}$ is about two times smaller than $E_{a\alpha}$. Also, $\Delta\epsilon_\alpha$ is comparable in both systems. However, unlike in $K_{0.3}MoO_3$, τ_α in o-TaS_3 deviates from an activated behavior[1] on approaching T_g. Such increase of the effective activation energy close to T_g as in o-TaS_3 is characteristic of fragile glasses,[35] while strong glasses obey an Arrhenius behavior as in blue bronze. The differences between strong and fragile behavior result from the different topography of the phase space.[20] 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 CDW's.

The difference between o-TaS_3 and $K_{0.3}MoO_3$ exists also in the amplitudes of the relaxation processes. While $\Delta\epsilon_\alpha$ in blue bronze is almost preserved in the entire T range, in o-TaS_3 it decreases strongly on approaching T_g. On the other hand, $\Delta\epsilon_\beta$ is comparable to $\Delta\epsilon_\alpha$ in o-TaS_3, while in $K_{0.3}MoO_3$ it is almost two orders of magnitude smaller. The smaller $\Delta\epsilon_\beta$ in $K_{0.3}MoO_3$ 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[36] and in the low-temperature up turn in magnetic susceptibility,[37] 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-TaS_3, whereas in strong glasses like $K_{0.3}MoO_3$ prevails the ''background loss'' contribution[38] below T_g.

In conclusion, we have shown that the glass transition scenario previously seen in o-TaS_3 exists also in $K_{0.3}MoO_3$. 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[20] might help in understanding the pinning properties of CDW systems and shed light on the differences between o-TaS_3 and $K_{0.3}MoO_3$.

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