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Low-temperature divergence of the polarizability in charge density wave compounds

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We have found that the dielectric constant of the quasi one-dimensional conductors with a charge-density wave (CDW) shows a peak in the low temperature range. This peak can only be detected at frequencies below 100 kHz and its position is shifted at lower temperatures with decreasing frequencies. In the same temperature range the relaxation time grows drastically. These features are usually characteristic of a transition to a glassy-like state in systems with some disorder. We suggest a qualitative model which describes the behavior of CDW near this transition. These results provide a direct experimental evidence that with decreasing temperature the CDW turns into a glassy-like state which consists of large enough domains frozen in the CDW electron crystal. This state is characterized by many metastable realizations, hopping conductivity, non-exponential relaxation of perturbations, very large relaxation time and aging effects, features which are indeed observed in experiments.

1. Introduction

The dielectric response of the pinned charge density wave (CDW) in quasi one-dimensional (Q1D) compounds has been extensively explored in the last years [1]. Developing a linear theory of deformable CDW pinned by weak disorder, it has been shown [2] that the dielectric function is divided in two parts: a high frequency peak due to absorption close to the pinning frequency and a low frequency loss peak due to localized pinned collective excitations with a wide distribution of corresponding modes. These local deformations are screened by normal electrons. The dynamical screening being proportional to the single particle resistivity, consequently the main relaxation time τ of this distribution is expected to increase in a thermally activated manner, when T is reduced, with an activation energy in the range of the Peierls gap [2]. Such a behavior has been qualitatively found in dielectric measurements of $K_{0.3}MoO_3$ and orthorhombic TaS_3 (o- TaS_3) above $T \sim 60$ K.

For $K_{0.3}MoO_3$, τ follows a thermally activated law [3] with activation energy of 829 K (to be compared to the CDW band gap of 1020 K) in the temperature range between 60 K and 100 K. In the case of o- TaS_3 [4] the activation of τ was only found between 130 and 100 K with an activation energy of 400 K (the CDW band gap is 800 K). Moreover, surprisingly the low frequency CDW relaxation was shown to disappear between 115 and 65 K [4].

If the models considering only the elastic deformation of the CDW can give the explanation for the gradual freezing of CDW below the Peierls transition, they cannot account for the very slow relaxation dynamics with very low activation energies (1-2 K) in the temperature range $T < 1$ K where ergodicity breaking with evolving "aging" effects have been recently established [5]. This very low temperature state has revealed many features similar to glassy-like state. In fact it was missing the link in relaxation studies between these two different temperature-frequency windows. We have extended the dielectric constant, ϵ , measurements of $K_{0.3}MoO_3$ and o- TaS_3 down to helium temperature.

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In this communication we show that the temperature dependence of ϵ measured at low frequencies, f , below 100 kHz exhibits a large peak which magnitude and position on the temperature scale are dependent on frequency. The observed divergence of $\epsilon(T, f)$ is a characteristic feature of a transition of the CDW into a new glassy-like state, as it takes place in many other disordered materials such as orientational and dipolar glasses [6], spin glasses [7]...

2. Experimental results

We have measured the real and imaginary parts of conductivity of quasi 1D conductors in the frequency range from 11 Hz up to 10 MHz between 4.5 K and T_p . The most part of experiments was carried out on ten samples of orthorhombic TaS_3 (o- TaS_3). Additionally two samples of monoclinic TaS_3 and three samples of blue bronze $\text{K}_{0.3}\text{MoO}_3$ have been studied. Typically, the TaS_3 samples were ≈ 10 mm long with a cross-sectional area $S \sim 10^{-6} \text{ cm}^2$; the length of $\text{K}_{0.3}\text{MoO}_3$ samples was 5-6 mm and $S \sim 10^{-3}-10^{-4} \text{ cm}^2$.

The measurements were carried out using a Hewlett Packard HP 4192A impedance analyzer in the frequency range between 11 Hz up to 10 MHz. For measurements of high impedance samples at low temperature we improved the resolution of the impedance analyzer with the use of an additional preamplifier. We have verified that in low frequency range below 10 kHz the preamplifier did not introduce any noticeable phase shift. Owing to these improvements we were able to carry out measurements at lower temperatures in comparison with previous experiments [3,4].

Fig. 1 shows the temperature dependence of the real part of the dielectric constant $\epsilon'(1/T)$ of an o- TaS_3 sample (sample 1) for $4.5 < T < 200$ K at a frequency of 100 kHz and in the temperature range $4.5 < T < 50$ K at frequencies 10 kHz, 1.1 kHz, 111 Hz and 11 Hz.

Figure 1 : Variation of the real part ϵ' of the complex dielectric constant of orthorhombic TaS_3 as a function of the inverse temperature at given frequencies (1 : 11 Hz, 2 : 111 Hz, 3 : 1.1 kHz, 4 : 10^4 Hz, 5 : 10^5 Hz).

Two remarkable features are noticeable :

- The peak in ϵ' at $T \approx 120$ K where ϵ' reaches $\approx 7 \times 10^7$. Between 100 K and 50 K, ϵ' decreases exponentially with an activation energy of ~ 300 K. For frequencies higher than 100 kHz, ϵ' decreases monotonously down to $\epsilon' = 3 \times 10^5$ at $T = 4.5$ K ($f = 100$ kHz).
- The second peak in ϵ' below $T = 50$ K at low frequencies ($f < 100$ kHz). With decreasing frequency the magnitude of peaks increases considerably and the maximum of $\epsilon'(T)$ shifts to lower temperatures. The detailed dependence of ϵ' with f and T is drawn in Fig. 2. Below 200 Hz the initial parts of $\epsilon'(T, \omega)$ curves are very close to each other and the deviation from this envelope occurs at lower T as frequency is decreased.

Figure 2 : Variation of the real part ϵ' of the complex dielectric constant of orthorhombic TaS_3 as a function of temperature at given frequencies (Hz) 1-11, 2-31, 3-47, 4-111, 5-200, 6-500, 7- 1.1×10^3 , 8- 2×10^3 , 9- 5×10^3 , 10- 10^4 , 11- 2×10^4 , 12- 10^5 .

We have obtained similar results on $\text{K}_{0.3}\text{MoO}_3$ as shown in Fig. 3a. Measurements at lower temperature as those reported in ref. 3 have previously been reported [8,9] and the peaks observed have been explained as resulting from glassy dynamics of the pinned condensate. In the following we will propose another explanation such as the glass-like state in CDW is established through a phase transition. For comparison with other systems we have drawn in Fig. 3b the variation of the real part of the dielectric constant as a function of frequency and T for the dipolar glass $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ [10]. Interestingly the dielectric relaxation of this compound exhibits two modes : a monodispersive at high frequency ($\sim 10^8$ Hz) and a polydispersive at temperature-dependent frequencies between 10^1 and 10^8 Hz. This low frequency dispersion peak extrapolates to ∞ at T_c .

3. Discussion and conclusions

The dynamics of the dielectric relaxation reflects the decay of the induced polarization of the CDW resulting from local deformations. For a single degree of freedom the decay of the polarization follows an exponential law $P(t) = P_0 \exp(-t/\tau)$ which leads to the dielectric Debye response $\epsilon(\omega) = \epsilon_{\text{HF}} + [(\epsilon_0 - \epsilon_{\text{HF}})/(1 + i\omega\tau)]$ where ϵ_0 is the static dielectric constant and ϵ_{HF} the high frequency limit. When many metastable states are involved the well accepted common idea [1] is still to consider an unique relaxation process but with a distribution of times (or distribution of pinning energies) through a distribution function $g(\tau)$ such as : $P(t) = P_0 \int g(\tau) e^{-t/\tau} d\tau$ and consequently $\epsilon(\omega) = \epsilon_{\text{HF}} + (\epsilon_0 - \epsilon_{\text{HF}}) \int (g(\tau) d\tau) / (1 + i\omega\tau)$. The real difficulty is the characterization of $g(\tau)$, a problem which is also faced in similar cases as in spin glasses for instance. Then it was found more successful to fit the data with an empirical form of $\epsilon(\omega)$. Good fits were obtained from expression used to describe dielectric relaxation in polymers [1,3] :

$$\epsilon(\omega) = \epsilon_{\text{HF}} + \frac{\epsilon_0 - \epsilon_{\text{HF}}}{[1 + (i\omega\tau)^{1-\alpha}]^\beta}$$

Figure 3: a) Variation of the real part ϵ' of the complex dielectric constant of $K_{0.3}MoO_3$ as a function of temperature at given frequencies: 1: 100 kHz, 2: 10 kHz, 3: 5 kHz, 4: 2 kHz, 5: 1.1 kHz, 6: 500 Hz, 7: 200 Hz, 8: 111 Hz, 9: 31 Hz. b) Variation of the real part ϵ' of the complex dielectric constant of $K_{0.974}Li_{0.026}TaO_3$ as a function of temperature at given frequencies (from ref. 10).

where α and β characterize the width and the skewness of the distribution of relaxation times. Following this procedure it was shown that the main relaxation time is thermally activated with an activation energy of the order of the CDW gap. This result has been explained as resulting from the enhanced damping of the CDW by normal electrons [2]. Then it is largely believed that this screening effect is the unique feature which dominates the dielectric response down to the lowest temperatures. We do not agree with this point of view. First as it has been recalled above, the activated regime of τ in $K_{0.3}MoO_3$ [3] and especially in $o-TaS_3$ [4] has been measured in a restricted temperature range. Second the theory in ref. 2 predicts a shoulder in ϵ' (and a peak in ϵ'') the magnitude of which is temperature independent (see Fig. 4 in ref. 2). On the contrary our data in Fig. 2 and 3a show a monotonic increase of ϵ' at the peak, suggesting a divergence of the polarizability when T is reduced.

Identifying the maximum of ϵ' in Fig. 3a such as $\tau = 1/2\pi f$ we have plotted the temperature dependence of the main relaxation time of $o-TaS_3$ in Fig. 4. The $\tau(1/T)$ can be fitted by a Fulcher-Vogel law: $\tau = \tau_0 \exp[B/k(T_m - T_0)]$ with the parameters $\tau_0 \approx 10^{-9}$ s, $B = 200$ K and $T_c = 13$ K. A critical slowing down equation: $\tau = \tau_0(1 - T/T_c)^{-zv}$ can also be used indicating a real transition at T_c where τ diverges with $\tau_0 = 10^{-9}$ s, $T_c = 17$ K and $zv = 13$ as shown by the solid line in Fig. 4.

The temperature dependence of the dielectric constant in the whole temperature range below the Peierls transition of CDW systems has been little investigated. In ref. 11 we have proposed a qualitative description of the variation of ϵ with T and ω which will be now shortly summarized. Several lengths are under consideration: the phase coherence length L , the average distance between impurities L_i , and the screening length ℓ . While in the temperature range of the Peierls transition L is large and the pinning weak, at lower temperature the pinning exhibits the features of strong pinning. Then the CDW phase is fixed at strong pinning centres and the main phase variation proportional to $m \times 2\pi$ will occur near these centres on a length of 5-10 lattice constants. One can imagine the CDW ground state as randomly frozen strong centres, near which the CDW phase abruptly changes by $\pm 2\pi m$ i.e. solitons and antisolitons are nucleated. We believe that such a CDW ground state is realized at $T \approx 40$ K near the minimum of $\epsilon'(T)$ (Fig. 3a). When T is reduced below 40 K, the screening does not play any important role ($\ell > L_i$) but because the CDW stiffness still increases, local CDW homogeneity is favoured. In such structures with random interaction

or random field a phase transition to a glassy-like state is possible for dimensionality more than 2 [12].

The approach of the critical temperature is characterized by the growth of coherence length, the growth of clusters with local ordering, the divergence of the dielectric constant and the growth of relaxation time τ . Fig. 2, 3a and 4 have shown these features for o-TaS₃. Our results are at variance with those of ref. 4 where the dielectric relaxation disappeared below 65 K.

Then the main problem brought by these experiments is, beyond a fitting to empirical laws, the mechanism of relaxation. If a non Debye dielectric response can be expressed in terms of a distribution of relaxation τ however it is not obvious that an interacting many-body system can be reduced to a simple superposition of one-body behaviour. So one should consider that the relaxation takes place through a hierarchy of metastable states as proposed by Palmer *et al.* [13] for which the response function to an electric field step is a stretched exponential $[\exp(-t/\tau)^n]$. This function has been shown to describe many experimental findings in spin glasses for example. Above T_g the relaxation time is given by an Arrhenius function but near T_g τ varies faster than with Arrhenius.

Figure 4 : Temperature dependence of the average relaxation time τ (maximum of ϵ' in Fig. 2) of orthorhombic TaS₃ as a function of temperature. Solid curve corresponds to slowing down equation : $\tau = \tau_0(1-T_c/T)^{-zv}$ with $\tau_0 \approx 10^{-9}$ s, $T_c = 17$ K and $zv \approx 13$.

However from Fig. 4 it is clearly needed to extend the dielectric response at lower frequencies for a more accurate determination of the critical indexes. We have also performed similar measurements [14] in the spin density wave (SDW) organic compound : (TMTSF)₂PF₆ which exhibits a SDW transition below 12 K. We have found that below 4 K ϵ' increases for all frequencies and exhibits a pronounced maximum, the magnitude and the position of which depend on frequency. The temperature dependence of the ϵ' maximum can be plotted with the Vogel-Fulcher law with $10^{-9} \leq \tau_0 \leq 10^{-8}$ s, $8 < B < 10$ K and $1.2 < T_0 < 2$ K or with the slowing down expression with $10^{-10} \leq \tau_0 \leq 10^{-9}$ s, $6 < zv < 8$ and $2.2 < T_c < 2.3$ K. The occurrence of a glass transition in this compound has become more evident from the calorimetric study reported in these proceedings [15] which shows that the specific heat anomaly depends on the kinetic conditions and previous thermal history such as isothermal annealing.

In conclusion we have shown that the dielectric constant of charge density wave (also spin density wave) of quasi one-dimensional conductors shows a peak at low temperature and a slowing down of the mean relaxation time. These features are usually characteristics of a transition to a glassy-like state in systems with some disorder

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