

LOW ENERGY EXCITATIONS AND RELATED PHENOMENA IN CDW COMPOUNDS AT VERY LOW TEMPERATURES

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ABSTRACT

We have measured the specific heat and the energy relaxation dynamics on several charge density wave compounds (NbSe_3 , TaS_3 , $(\text{TaSe}_4)_2\text{I}$, $\text{K}_{0.3}\text{MoO}_3$) at very low temperatures ($T \leq 1$ K). All these quasi one-dimensional compounds exhibit an excess heat capacity contribution C_p following a T^ν law with $\nu < 1$. In the same temperature range the energy relaxation is not exponential and aging effects are present.

INTRODUCTION

It has been shown that due to the randomness in the impurity distribution the charge density wave (CDW) ground state in the pinned state comprises many metastable states which can be defined as local deformations of the CDW phase with respect to the ion lattice [1]. The existence of a large number of metastable states is a common feature of disordered materials. This in general leads to anomalous behaviour of relaxation at long times. Relaxation studies are very useful in order to extract the barrier distribution and for better understanding of dynamics. As in other disordered materials (glasses, spin-glasses or polymers) the CDW metastable states are expected to contribute to the thermodynamical properties at very low temperature. We have performed measurements of specific heat and of dynamics in energy relaxation on several CDW compounds (NbSe_3 , TaS_3 , $(\text{TaSe}_4)_2\text{I}$, $\text{K}_{0.3}\text{MoO}_3$) at very low temperatures ($T \leq 1$ K). The technique we used is a transient heat pulse technique in which the specific heat is calculated from the decay of the temperature increment after a heat pulse, as $\Delta T(t) = \Delta T_0 \exp(-t/\tau)$ with $\tau = C_p R_t$ (R_t being the thermal resistivity of the thermal link to the cold sink). In the following we present our main results in three parts concerning the extra contribution to the specific heat below 1 K, the non-exponential relaxation of energy and aging phenomena in the energy relaxation.

(received December 26, 1989)

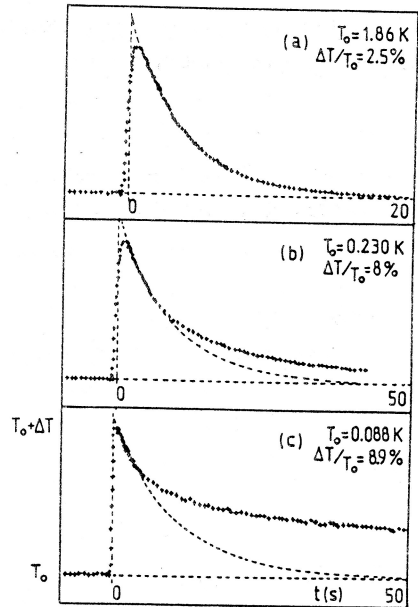
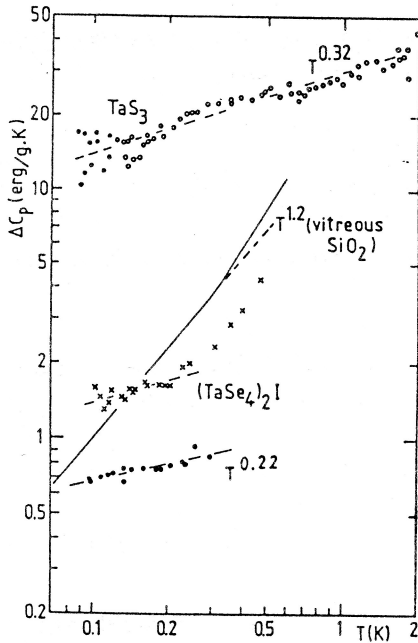


Fig. 1 - Residual specific heat versus T after subtraction of the phonon contribution and of the nuclear hyperfine contribution for three different compounds : TaS_3 [6], $(\text{TaSe}_4)_2\text{I}$ (two samples [4,9]) and vitreous silica [8] showing T^ν power law behaviour.

Fig. 2 - The decay of the temperature increment ΔT in TaS_3 after a heat pulse (of 0.2 to 0.5 s and $\Delta T/T_0 = 9\%$) shows a deviation from an exponential law (dashed lines) when the temperature is lowered. The "short time" specific heat is deduced from the initial part of decay.

EXTRA CONTRIBUTION TO C_p BELOW 1 K

Beyond the regular phonon contribution in T^3 , an excess specific heat is measured below 1 K which can be analyzed as a power T^ν law, with the exponent ν included between 0.2 and 0.8 depending upon the compound. Such an extra-phononic specific heat contribution has been found for the first time in $\text{K}_{0.3}\text{MoO}_3$ and $(\text{TaSe}_4)_2\text{I}$. Dahlhauser *et al.* [2] found $\nu = 1$ in blue bronze, while our recent measurements [3] yield a value closer to $\nu = 0.6$ between 0.1 K and 0.5 K. In $(\text{TaSe}_4)_2\text{I}$ we have reported [4] $\nu = 0.2$ between 0.1 and 0.25 K. However, when measurements are not performed at low enough temperatures as by Brown *et al.* [5], a pseudo-linear term can be found which in fact results only from a cross-over between two different temperature-dependent regimes (Fig. 1), the higher temperature regime originating in the phason excitations [4]. In TaS_3 a well-defined $T^{0.32}$ law extends up to 2 K [6] (Fig. 1) and in NbSe_3 recent results give $C_p \sim T^{0.8}$ up to 1 K [7].

There is a large spread for the amplitude of this extra-contribution, with a factor of about 20 times larger in TaS_3 when compared to $(\text{TaSe}_4)_2\text{I}$ (see Fig. 1). However the values remain in the same range of order as for glassy materials, for instance the vitreous silica SiO_2 [8] (shown also on

Fig. 1), for which this contribution is ascribed to two-level system (TLS) tunneling excitations. Moreover the amplitude of the low-energy excitations (LEE) is sample dependent without clear connection with the purity of the crystal [9].

For all the CDW conductors that we have measured, in the region where the excess specific heat due to LEE is dominant, there is a deviation from an exponential decay for the thermal transients without any possibility of fit by an exact exponential in the whole time range. We have to point out that the "short time" heat capacity was determined from the initial exponential decay (Fig. 2).

NON-EXPONENTIAL RELAXATION OF ENERGY

For more detailed investigation of the phenomenon of long time relaxation we chose TaS₃ [10] because the temperature range in which the excess specific heat is observed is the largest. It is clearly shown in Fig. 2 that this phenomenon is increasingly pronounced when decreasing temperature even in the region where the hyperfine nuclear contribution is dominant [6] suggesting that nuclei are necessarily coupled to the excitations which are responsible for the non-linear transients.

Relaxation in glassy materials is often analyzed by the product of a power law and a stretched exponential :

$$\Delta T \sim (t/\tau_p)^{-\alpha} \exp[-(t/\tau_p)^\beta] \quad (1)$$

The coefficient β measured in conditions of short temperature perturbation (pulses with $\Delta T/T_0 =$ a few %) is temperature dependent, increasing from the value $\beta = 0.3$ at the lowest temperature up to 1 at $T = 0.5-0.6$ K (Fig. 3). Above this temperature the relaxation is a simple exponential. The second

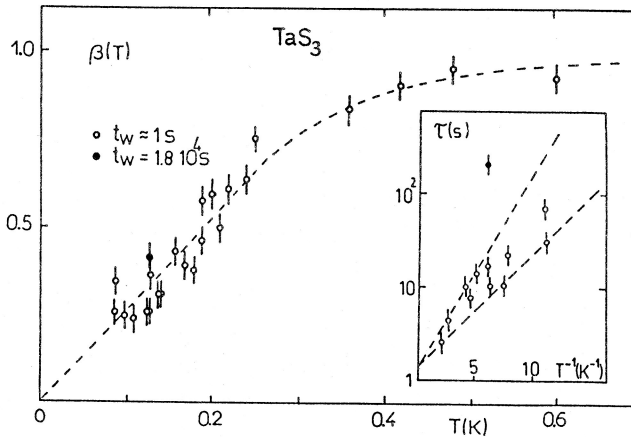


Fig. 3 - Temperature dependence of the parameters β and τ_p (Equat. 1) in the case of short heat pulse conditions. Also indicated at $T = 0.165$ K (black dots) the values for a long temperature perturbation (see Fig. 4 and 5).

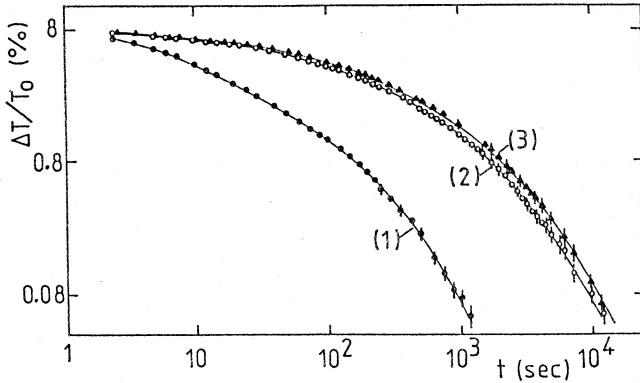


Fig. 4 - Variation of $\Delta T/T_0$ in TaS₃ as function of time at $T = 0.165$ K. The fits are Equat. 1 with appropriate parameters. The different conditions of temperature perturbation (1), (2) and (3) are schematically shown in the inset of Fig. 5.

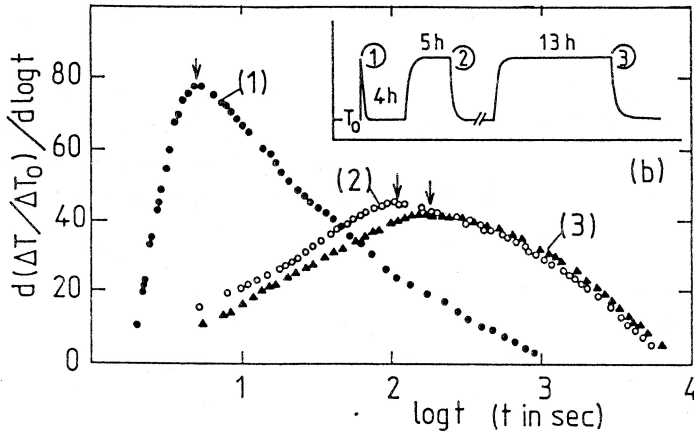


Fig. 5 - Time dependence of the relaxation rate $\partial(\Delta T/\Delta T_0)/\partial \log t$ in TaS₃, at $T = 0.165$ K for the three conditions of applied heat flow as shown in the inset.

parameter -the average relaxation time τ_p - shows an Arrhenius variation with an activation energy of 0.3-0.4 K in the same temperature region (Fig. 3). From our results we can conclude that thermally activated processes dominate and not tunneling states as in structural glasses for very low temperatures. A very small perturbation in energy (as small as 10^{-6} eV) enables the CDW system to explore many neighbouring metastable states, showing up a very broad distribution for relaxation processes. At the same time the influence of duration of the applied perturbation is significant, as it can be seen from Fig. 4 and Fig. 5.

AGING EFFECTS

A characteristic feature of glassy materials is aging property, as demonstrated in spin-glasses [11] when the response of the system after the perturbation has been switched off depends on the time this perturbation has been applied. Borrowing a similar terminology, we have shown that in CDW systems aging effects are also clearly demonstrated, with energy relaxation occurring at longer time when the perturbation ΔT has been applied longer. Similarly to spin-glass experiments, this time plays the role of "waiting time". The fact that the curves for the shorter waiting time (heat pulse) (1) and for longer waiting times (2) and (3) can be superposed by a horizontal shift in the log-log plot (Fig. 4) means that all the characteristic times in the energy relaxation should be multiplied by some factor (~ 10) when the waiting time is longer. The wide relaxation time distribution $g(\tau)$ for the energy of metastable states can be obtained from the partial derivative $\partial\Delta T(t)/\partial\log t$ as shown in Fig. 5 for three different waiting times. For a given waiting time t_0 , $g(\tau)$ shows a peak at t_m of the order of t_0 which shifts towards longer time for longer t_0 . The linear correlation between t_m and t_0 , as it is the case in spin-glasses occurs only at lowest temperatures ≈ 0.1 K [7]. We observed similar effects for all CDW compounds.

CONCLUSION

All the CDW compounds with non-linear transport properties show the existence of an extra contribution to the specific heat at very low temperature with a T^v law ($v < 1$). The energy relaxation extends to very long times, exhibiting aging effects. As for spin-glasses, thermodynamical measurements reveal thermal hopping over a large distribution of barriers between CDW metastable states with an arbitrarily low height.

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