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# Low-temperature thermodynamic investigation of the sulphur organic salts $(\text{TMTTF})_2\text{PF}_6$ and $(\text{TMTTF})_2\text{Br}$ (TMTTF = tetramethyltetrathiafulvalene):

## II. Dynamical aspects

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Received 21 May 2002

Published 29 August 2002

Online at [stacks.iop.org/JPhysCM/14/8583](http://stacks.iop.org/JPhysCM/14/8583)

### Abstract

This contribution is in continuation of our preceding publication (Lasjaunias J C, Brison J P, Monceau P, Starešinić D, Biljaković K, Carcel C and Fabre J M 2002 *J. Phys.: Condens. Matter* **14** 837) in which we have considered general aspects of the low-temperature thermodynamical properties of the quasi-one-dimensional organic salts based on sulphur donors with different ground states:  $(\text{TMTTF})_2\text{PF}_6$  in the spin–Peierls state and  $(\text{TMTTF})_2\text{Br}$  (TMTTF = tetramethyltetrathiafulvalene) with commensurate spin modulation. In this part, part II, we present our results on the dynamical aspects related to the non-equilibrium phenomena measured below 1 K. The metastable states excited to slightly higher temperature (by only a few per cent of the starting  $T_0$ ) relax very slowly to the heat bath environment, depending on the duration of the heat pumping. We compare the features observed in the relaxation rates in these two sulphur compounds with those measured for the incommensurate spin-density-wave compound  $(\text{TMTSF})_2\text{PF}_6$ . We discuss the possible nature of the long-living low-energy excitations lying at the origin of this complex dynamical behaviour, in relation to their ground states.

### 1. Introduction

The organic quasi-one-dimensional (Q1D) conductors of general formula  $(\text{TMTSF})_2\text{X}$  ( $\text{X} = \text{PF}_6, \text{AsF}_6, \text{ClO}_4, \dots$ ) and their sulphur analogues  $(\text{TMTTF})_2\text{X}$  ( $\text{X} = \text{PF}_6, \text{AsF}_6, \text{SbF}_6, \text{Br}, \dots$ ) (TMTTF = tetramethyltetrathiafulvalene) are considered as prototype models for 1D electronic systems [1, 2]. The  $(\text{TMTSF})_2\text{PF}_6$  and  $(\text{TMTSF})_2\text{AsF}_6$  salts are metallic down

to low temperatures, where a transition to an incommensurate spin-density wave (IC-SDW) occurs below 12 K. The sulphur-based compounds exhibit spin–charge-separation phenomena evidenced by the decoupling between a high-temperature (high- $T$ ) charge localization due to dimerization of the TMTTF molecules along the chain axis and a low-temperature (low- $T$ ) spin-ordering transition. Thus, a charge gap opens at around 220 K in  $(\text{TMTTF})_2\text{PF}_6$  and around 100 K in  $(\text{TMTTF})_2\text{Br}$  [3]. This latter compound undergoes an antiferromagnetic (AF) transition at  $T_{AF} = 13$  K, commensurate with the crystallographic lattice [4], while a non-magnetic ground state formed of paired spins via a displacive lattice modulation—a spin–Peierls (SP) commensurate transition—appears below  $T_{SP} = 15$  K in  $(\text{TMTTF})_2\text{PF}_6$  [5].

Thermodynamical investigations give information on all excitations in the system and moreover they are very sensitive to the disordered character of the systems investigated. We have compared in the preceding paper [6] the low- $T$  properties of  $(\text{TMTTF})_2\text{PF}_6$  and  $(\text{TMTTF})_2\text{Br}$ . Although exhibiting different ground states (SP and C-AF respectively), they demonstrate all the well known universal features of glasses, found systematically also in all systems with charge-density-wave (CDW) ground states [7, 8] or spin-density-wave (SDW) ground states [9]. However, in addition to the bump in the heat capacity ( $C_p/T^3$ ) and the low-energy excitations (LEE), as in conventional glasses, below 1 K very complex long-time energy relaxation with characteristic ageing effects causes peculiar non-linearity of the specific heat. If compared within the accepted phenomenology for structural glasses, these LEE show much larger density of the corresponding ‘tunnelling’ states [9]. Huge density of states, weak coupling to phonons and, consequently, very long relaxation times, which are in addition thermally activated, are the points which distinguish them most from conventional glasses.

Our analysis [6] of the specific heat measurements of  $(\text{TMTTF})_2\text{PF}_6$  and  $(\text{TMTTF})_2\text{Br}$ , as well as that of a selenide-based  $(\text{TMTSF})_2\text{PF}_6$  with an incommensurate SDW, was limited, in part I, to *two extreme cases*: the specific heat at ‘short time’, as determined from the response to a brief energy pulse and the specific heat at *equilibrium* obtained as the saturation value by varying the time delivery of the energy (see below for more details). We have shown that, despite different ground states, SP for  $(\text{TMTTF})_2\text{PF}_6$  (for short, S-PF<sub>6</sub>) and SDW for  $(\text{TMTSF})_2\text{PF}_6$  (for short, Se-PF<sub>6</sub>), the two systems show very similar low- $T$  thermodynamics, with LEE contributions very close in amplitude, giving rise to comparable very long relaxation times. On the other hand, in the case of the AF ground state of  $(\text{TMTTF})_2\text{Br}$  (for short, S-Br), the LEE excitations give a contribution to the short-time specific heat nearly equal to that of S-PF<sub>6</sub> and Se-PF<sub>6</sub> and show a much smaller ‘equilibrium’ long-time  $C_p$ . They have shorter relaxation times and in addition they reveal almost ‘discrete bands’ [10].

The organization of the present paper is as follows. *First*, we discuss the experimental procedure and the possible (but here rather negligible) role of the thermal link. *Second*, we present data on a single-crystalline Si sample that we consider as a reference system for this dynamics study using the same experimental arrangement. Indeed, despite the presence of LEEs, it does not show any complex heat relaxation in similar conditions. *Third*, for the three aforementioned compounds, we discuss comparatively the dynamics on the intermediate timescale, i.e. by varying the ‘waiting time’ up to the thermodynamical equilibrium time. We will show that, for both commensurate sulphur compounds, relaxation spectra show the coexistence of at least two dynamical entities.

## 2. Experimental details

### 2.1. Samples

As previously described in part I [6] and in [10], samples in the form of crystalline needles, of total amount of the order of 100 mg, were smoothly pressed between two silicon plates,

covered with a thin layer of Apiezon N grease which ensured a good thermal diffusivity. The heater was fixed on one plate, the thermometer and the thermal link to the cold sink on the opposite side. Both plates were maintained by several nylon screws in a copper frame [11]. The measurements, of either the specific heat or the temperature decay dynamics, were performed in a dilution refrigerator.

## 2.2. Thermal link

In our experimental technique [11] the sample is loosely connected through a thermal link  $R_l$  to the cold sink regulated at the reference temperature  $T_0$ . In the usual pulse technique, the heat capacity is calculated from the initial increment  $\Delta T_0$  in response to the heat pulse, the resulting temperature relaxation  $\Delta T(t)$  being an exponential decay. Some examples are shown in figure 3 of [8] and figure 5 of [12]. However, in these Q1D compounds, on lowering  $T$  below 1 K, deviations to the exponential develop progressively as a tail at long time, due to the increase of the contribution of LEEs which are not well coupled to the phonon bath. In the same time, the thermal transient  $\Delta T(t)$  depends on the duration of the heat supplied to the sample: our thermal link technique enables us to vary this duration (that we named ‘waiting time’ [13]) from a fraction of a second up to 10–15 h. The switching off of the energy supply after  $t_w$  determines the origin of time for recording the thermal transient. We briefly state that the resulting increase  $\Delta T_0$  due to the energy supply remains below 10% of the mean  $T$ , even at the lowest  $T$ . This condition enables us to define the heat capacity at long  $t_w$  by integration of the total heat release through the heat link, as discussed in part I [6].

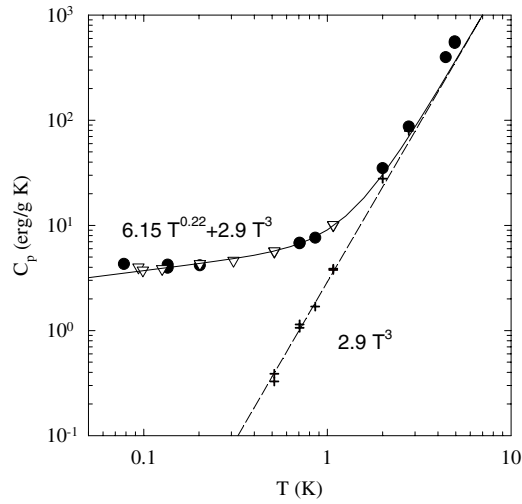
The external parameter of prime importance for the measured dynamics is the thermal link  $R_l$ . It varies from one experiment to another due to uncontrolled factors: it is not only determined by the Cu wire link, but also by a set of several nylon screws used for pressing the sample holder on the crystals. This part of  $R_l$  is very sensitive to the contact surfaces of the screws, due to the applied pressure. The latter is determined by the characteristics of the sample (compressibility, dilatation coefficient between 300 and 4 K), so the numerical value of  $R_l$  can change by a factor up to 5 among experiments on different samples [9]. However, independently of its value, the general temperature variation of  $R_l$  remains similar, close to  $T^{-2.5}$ .

The influence of this ‘extrinsic’ parameter on the heat transient dynamics was studied by numerical simulations using equivalent  $RC$  circuits [14]. The role of  $R_l$  is important, as it is the first element in the series of the  $RC$  circuit. In that work we have simulated the transients  $\Delta T(t)$  in two experiments on  $(\text{TMTSF})_2\text{PF}_6$  compound, with the same sample but a five times smaller  $R_l$  in the second case. Our simulation at 0.2 K demonstrated that just a corresponding change in  $R_l$  with unchanged ‘intrinsic part’ of the system yields the experimentally obtained modification of the transient; for the waiting time of 10 h the distribution shifts from  $2 \times 10^3$  to  $10^2$  s. However, the main characteristics remain unaffected—such as the asymmetry (here it is Gaussian-like in shape) and the width (here the FWHM remains equal to two decades in time).

In the present study, we mainly compare the dynamics of the SP state of S- $\text{PF}_6$  and of the AF one of S-Br (partly reported in [10]). The ratio of the values of  $R_l$  in the two experimental conditions was only 2–2.7 between 0.1 and 1 K. This small variation enables a reliable comparative study and allows us to conclude that the role of  $R_l$  cannot destroy the close similarity of the dynamics of these two commensurate compounds.

## 3. Results and discussion

At the beginning of our study of heat relaxation in CDW systems, as the reference system we used another Q1D crystalline compound which is insulating at low  $T$ , and which behaves like



**Figure 1.** The specific heat of a single-crystalline sample of Si (undoped) measured with two different heat links: triangles and filled black circles. The fit below 2 K (full curve) gives  $C_p = AT^{0.22} + BT^3$  and the phonon term  $BT^3$ : crosses and dashed curve.

a purely Debye phononic system, without a LEE contribution and time dependence effects [15]. This was proof of the origin of these effects being related to the CDW superstructure.

To provide more convincing evidence of the irrelevance of the role of the absolute value of  $R_l$  to the shape of the distribution  $g(\log \tau)$  and, more fundamentally, to show the absence of any long-time temperature tail in similar experimental conditions for a ‘normal’ crystal, we have performed experiments on a single crystal of Si of good quality. Despite the presence of extra-phononic excitations with amplitude and temperature dependence somewhat similar to those in the case of Q1D materials, single-crystalline Si sample can be considered as a reference system for the absence of time-dependent effects.

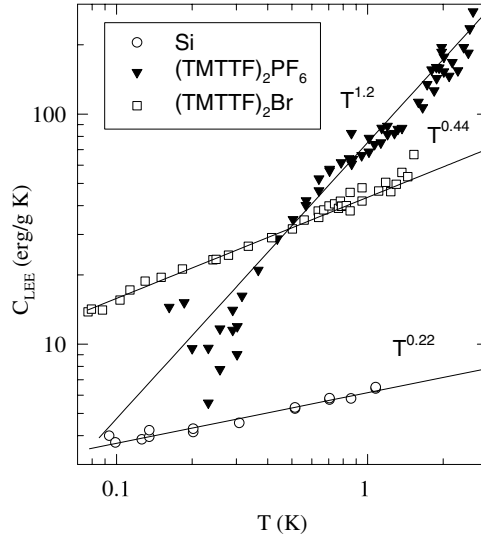
### 3.1. The Si sample as a reference system

In the nominally undoped form [16] and when implanted with ions to low doses [17], crystalline Si exhibits low- $T$  mechanical or thermal transport properties due to structural defects which can be treated as two-level systems (TLS) in glasses, in particular with a wide spectral density of states and a strong coupling to phonons demonstrated by the resonant scattering of phonons in the low- $T$  thermal conductivity measurements [17]. In our experiment, we have made measurements on a large single crystal of 2 g mass, using exactly the same experimental conditions as for the organic materials. We performed two different runs, using two different thermal links, reproducing rather well the extreme values of  $R_l$  measured in our series of Q1D materials. The first  $R_l$  corresponded to the case of the experiment on  $(\text{TMTSF})_2\text{AsF}_6$  [12] or the present S-PF<sub>6</sub>; above 0.4 K, the second  $R_l$  was about 3–5 times larger than the first one. We verified that the two series of data gave the same heat capacity, as reported in figure 1.

$C_p$  below 2 K can be analysed as the sum of  $C_{LEE}$ , with a sub-linear power-law variation, and a cubic contribution  $BT^3$ :

$$C_p = AT^{0.22} + BT^3 \quad (1)$$

with  $A = 6.1 \text{ erg g}^{-1.22} \text{ K}^{-1.22}$  and  $B = (2.85 \pm 0.05) \text{ erg g}^{-1} \text{ K}^{-4}$ . From the numerical value of the phononic term, we obtained the Debye temperature  $\theta_D$ , between 620 and 630 K, which agrees very well with the literature data [18].  $\theta_D = 630 \text{ K}$  is the average of tabulated values,



**Figure 2.** Comparison of the power-law contribution of the LEE  $C_{LEE}$  in crystalline Si and in organic salts  $(\text{TMTTF})_2\text{Br}$  and  $(\text{TMTTF})_2\text{PF}_6$ .

indicating a quite large sensitivity of  $\theta_D$  to different conditions of preparation. We note that the  $C_{LEE}$ -value for this Si sample lies close to that of the Q1D compound  $\text{NbSe}_3$  between 0.2 and 1 K [8]. In figure 2 we present the LEE contribution,  $C_{LEE} = AT^{0.22}$ , of crystalline Si and the short-time power-law ( $AT^\nu$ ) contribution (see part I) of both S-Br and S- $\text{PF}_6$ . This comparison stresses the similarity of these contributions, despite large differences in the exponent  $\nu$ .

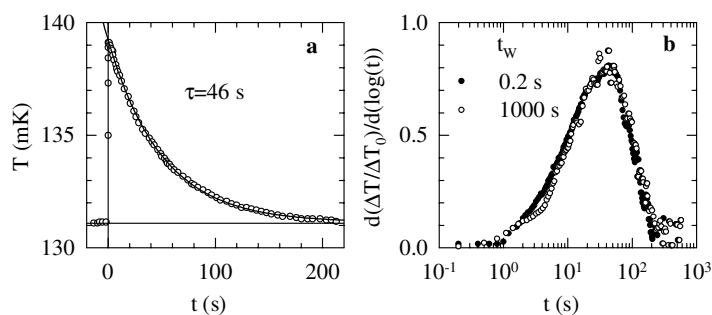
### 3.2. Dynamics of energy relaxation

In the conditions where the contribution of LEEs to the specific heat dominates over the other terms (phonons and addenda), we have observed a highly non-exponential relaxation in almost all DW systems; this relaxation can be satisfactorily fitted, at least in the initial decay period ( $\leq 10^2$  s), with a phenomenological stretched-exponential function [7]:

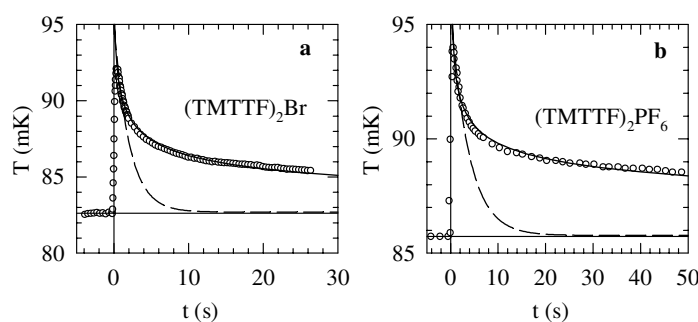
$$\Delta T/\Delta T_0 \approx \exp[-(t/\tau)^\beta] \quad (2)$$

with  $\beta$  the stretching parameter. In the high- $T$  limit the relaxation recovers an exponential decay, so  $\beta(T > 1 \text{ K}) = 1$ ; however,  $\beta(T)$  decreases when  $T$  is decreased, leading to a very slow relaxation. Some structures in the relaxation, particularly at long times, can be more naturally detected in the variation of  $\Delta T/\Delta T_0$  versus  $\ln t$ . They become even more visible if one looks at the relaxation rate itself, i.e. if one differentiates the signal:  $S = d(\Delta T/\Delta T_0)/d \ln t$  (note here that we usually use ‘ $\log_{10} t$ ’ in our analysis and in our figures). Thus, we can get direct information on the distribution of the relaxation times  $g(\ln \tau)$ , as the relaxation  $\Delta T(t)/\Delta T_0$  can be expressed as  $\Delta T(t)/\Delta T_0 = \int_{t_0}^{\infty} g(\ln \tau) \exp(-t/\tau) d \ln \tau$ , with  $t_0$  being a short-time cut-off [13].

In figures 3 and 4 we demonstrate the striking difference in dynamics of energy relaxation between the Si sample (figure 3) and organic DW materials (figure 4), all exhibiting dominant LEEs in the same  $T$ -range. At  $T = 0.13 \text{ K}$ , the specific heat of Si is essentially due to the LEEs contribution (the lattice contribution is  $< 0.2\%$ ). However, as seen in figure 3(a), the thermal transient follows a pure exponential decay. Moreover, it does not show any



**Figure 3.** (a) Exponential decay ( $\tau = 46$  s) of the transient response  $\Delta T(t)$  after a heat pulse of 0.2 s in Si. (b) The logarithmic derivative  $d(\Delta T/\Delta T_0)/d \log t$  for Si at  $T = 130$  mK either after a heat pulse of 0.2 s or after a ‘waiting time’ of 1000 s: both responses correspond to the pure exponential decay, with the Debye width of 1.14 decades.



**Figure 4.** Transient response  $\Delta T(t)$  after (a) a heat pulse of 0.3 s at  $T \approx 85$  mK in  $(\text{TMTTF})_2\text{Br}$  (see [10]) and (b) a heat pulse of 0.5 s at  $T \approx 90$  mK in  $(\text{TMTTF})_2\text{PF}_6$ . Strong deviations from the possible initial exponential decay (shown by the dashed curve) occur after a few seconds. The decay is fitted by a stretched exponential (full curve).

waiting time dependence up to  $10^3$  s. In figure 3(b) we have shown the variation with time of  $S = d(\Delta T/\Delta T_0)/d \log t$  for two extreme waiting times (short pulses of 0.2 s and  $t_w = 10^3$  s). The data are totally superimposed. This result (no waiting time dependence effect at very low  $T$ , no deviation from an exact exponential) can be considered as the reference for the study of organic crystals with various ground states measured in similar experimental conditions to Si. The specific heats of both Si and organic 1D materials have rather large LEE contributions, but their couplings to the phonon heat bath are totally different: the LEEs of Si—as the reference system—are tightly coupled to the phonon bath, as demonstrated in the low- $T$  thermal conductivity [17] or by the absence of a deviation from an exponential for the transient  $\Delta T(t)$  (figure 3). The latter proves that the corresponding relaxation times are much shorter than the experimental time constant, which means that, with comparable amplitudes of  $C_{LEE}$ -contributions, the effective coupling to the phonon bath should be much better for the Si sample. This is not the case for S- $\text{PF}_6$  and S-Br sulphur compounds. In the same  $T$ -range ( $T \sim 0.1$  K) as for Si, the relaxation after a short heat pulse in figure 4 shows after a few seconds a strong deviation from an exponential decay, whereas the relaxation dynamics of crystalline Si obeys perfectly an exponential variation up to 200 s.

The evolution of the relaxation rates at two different temperatures as a function of  $t_w$  (from a fraction of a second up to 10–15 h) is presented in figure 5 for S- $\text{PF}_6$  and in figure 6 for

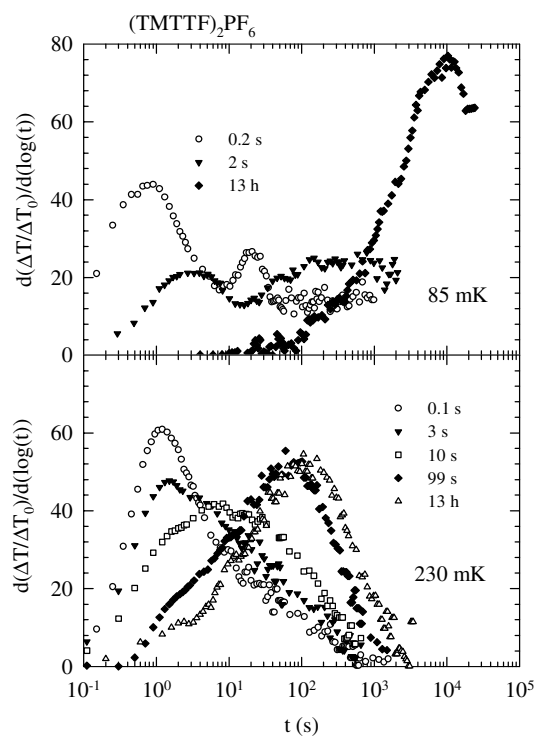
S-Br and Se-PF<sub>6</sub>. The thermodynamical equilibrium is generally reached for the maximum  $t_w$ -value (with the exception of the case of Se-PF<sub>6</sub> for which, at  $T = 123$  mK, the equilibrium needs a  $t_w$  much longer than 10–15 h).

- (i) A first difference between the three compounds is the much shorter time span for reaching equilibrium for the S-Br compound (figure 6). This is observed either for the overall time span of  $g(\log \tau)$  which is about one decade shorter than for the other two compounds at the same temperature, or for the time needed for reaching the thermodynamical equilibrium, namely  $t_w = 40$  min at  $T = 79$  mK. This value has to be compared to several hours for S-PF<sub>6</sub> and more than 10–15 h for Se-PF<sub>6</sub>.
- (ii) A large difference occurs in  $g(\log \tau)$  between the S-Br and S-PF<sub>6</sub> compounds, on one hand, and the Se-PF<sub>6</sub> compound, on the other hand. Instead of a broad, almost symmetric (Gaussian-like; see below) distribution which moves along the timescale on increasing  $t_w$ , similarly to ageing effects observed in spin glasses (as seen in Se-PF<sub>6</sub>), the two sulphur compounds show a common behaviour at variance to the previous one, revealing almost ‘discrete bands’ of the relaxation time. These ‘bands’ occur at short and at long time and their width becomes narrower depending on  $t_w$ . This is especially clear at short  $t_w$  (up to  $\sim 10$  s) where the distribution, in both sulphur compounds, is very broad compared to that in Se-PF<sub>6</sub>. For  $t_w = 10$  s at  $T \approx 80$ –85 mK, the relaxation rate is almost constant over three decades, corresponding to a very peculiar behaviour of the transient dynamics:  $\Delta T(t) = \Delta T_0 \log t$ , typical of random materials. This persists in S-Br up to 130 mK. Particularly striking also is the close similarity of dynamics at the minimum  $T$  (79–85 mK) for S-Br and S-PF<sub>6</sub>. Most illustrative is the evolution of the dynamics with increasing  $t_w$  in the spectrum of S-PF<sub>6</sub> at  $T = 230$  mK: one can analyse the full spectrum with three features separated from each other by one decade (at 1, 10 and  $10^2$  s). On increasing the waiting times, most of the weight is progressively moved to the distribution centred at longer time: the short-time peak at 1–2 s decreases to the advantage of the one at 100 s. Similarly, the same behaviour occurs also in S-Br at 130 mK.
- (iii) Finally, the spectra at *equilibrium* (presented separately for S-PF<sub>6</sub> at different temperatures in figure 7) are rather asymmetric, with a rapid decrease at long time. This is to some extent reminiscent of an exponential decay (cf figure 3 for crystalline Si), for  $T \leq 250$  mK in the case of S-PF<sub>6</sub>. However, the width remains broader than for a pure Debye relaxation. This asymmetry is also a characteristic of S-Br, and is at variance to the almost symmetric distribution (on the  $\log_{10} t$  scale) for Se-PF<sub>6</sub>, as was previously also observed for TaS<sub>3</sub> [13], this latter CDW compound being very similar in many respects to the SDW Se-PF<sub>6</sub> [19].

$S = d(\Delta T/\Delta T_0)/d \ln t$  has the general shape of a Gaussian function of  $\ln t$ , whose maximum is at  $\tau_m$  and whose width  $\lambda$  (at half-height) is related to  $1/\beta$ . In fact, the logarithmic derivative of a stretched-exponential function  $d(\exp[-(t/\tau)^\beta])/d \ln t$  and a Gaussian function in  $\ln t$  of width  $\lambda$ :  $\exp[-(\ln(t/\tau_m)/\lambda)^2]$  can be made tangent to each other [20] and to the experimental  $S(\ln t)$  data around their maximum at  $\tau_m$ , with the width  $\lambda = 1/\beta$ . We will discuss these matters related to our systems in more detail in the forthcoming publication [21].

We show in figure 7 how the discrete ‘bands’ in the relaxation rate at the thermodynamic equilibrium of S-PF<sub>6</sub> can be well deconvoluted into two Gaussian functions representing the slow and the fast LEE responses. Unlike the broad homogeneous distribution of relaxation times in the incommensurate SDW state of Se-PF<sub>6</sub> (indicating however a strong disorder), in the commensurate spin–Peierls state of S-PF<sub>6</sub> two dynamically distinct entities appear below 1 K. At higher  $T$ , the fast contribution plays the dominant role in the dynamics. However, at





**Figure 5.** Dynamics of the energy relaxation defined as  $d(\Delta T/\Delta T_0)/d \log t$  (reported in semi-log plots) at different waiting times  $t_w$  for  $(\text{TMTTF})_2\text{PF}_6$  at  $T = 85$  and  $230$  mK.

the lowest  $T$ , the slow entity dominates both the dynamics and the thermodynamics. Without the fast entity, there would be almost no response within  $10^3$  s!

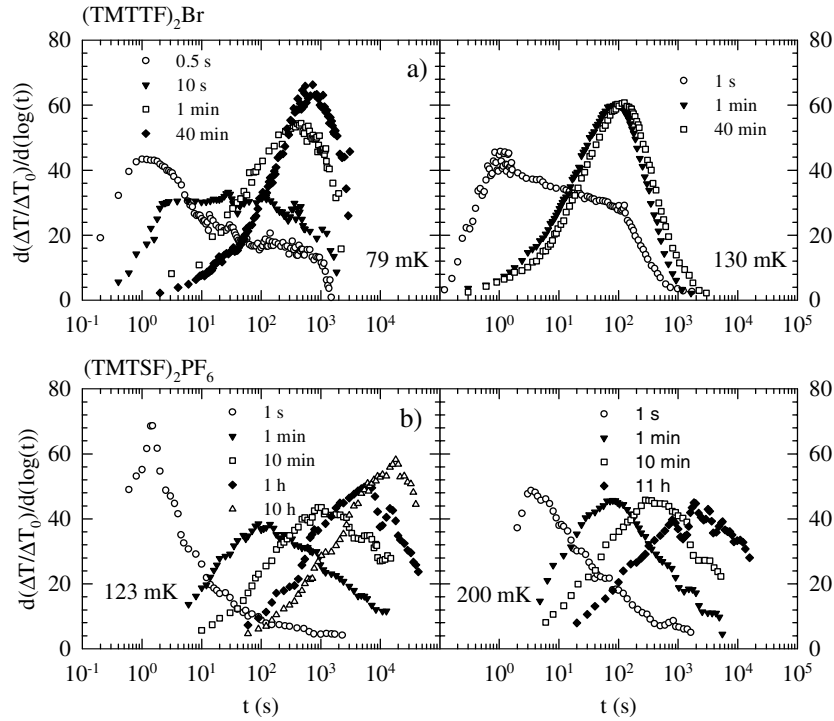
Similarly, but on a much shorter timescale, such a deconvolution can be carried out for the commensurate AF S-Br. Although there are some specific differences from the case of S-PF<sub>6</sub> [22], the common characteristic of the two systems is the heterogeneity of their relaxation rates, dominated by a bimodal dynamics, similar  $T$ -dependences of the relaxation times, separated by one decade in time.

### 3.3. Discussion of the microscopic origin

Finally, we discuss the relation of the observed dynamics to the corresponding ground states. The relaxation rate distributions shown in figures 5 and 6 show very clearly the difference in behaviour of the energy relaxation at low  $T$  between S-PF<sub>6</sub>, S-Br and Se-PF<sub>6</sub>. Recall that the ground state of Se-PF<sub>6</sub> is IC-SDW, that of S-Br is C-AF and that of S-PF<sub>6</sub> a spin-Peierls state.

First, the energy relaxation rate distribution of the IC-SDW of  $(\text{TMTSF})_2\text{PF}_6$  is very similar to that measured in IC-CDW. In fact, it was shown from structural studies [4, 23] that there is a survival of an electronic CDW below  $T_N$  in Se-PF<sub>6</sub>. The ground state of this compound below  $T_{SDW}$  is now believed to be a mixture of a SDW and a CDW.

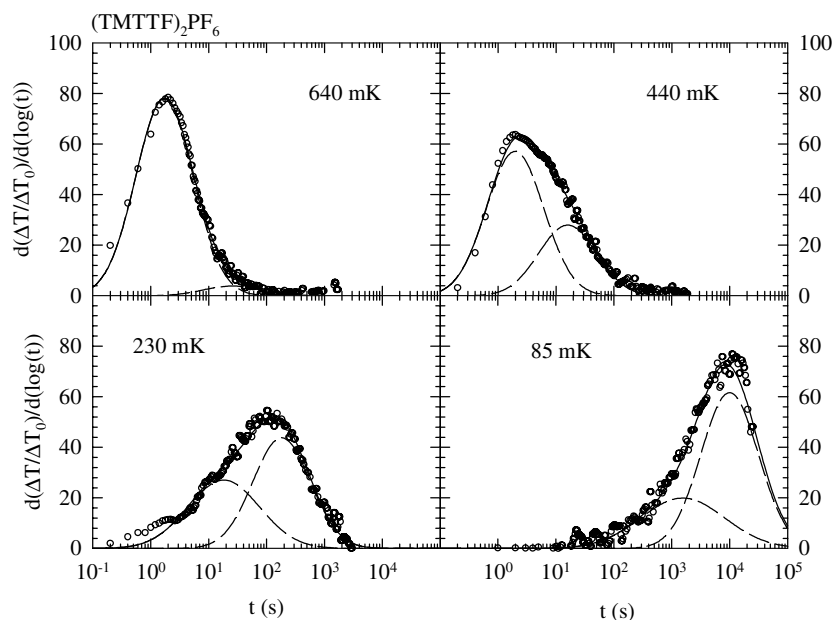
On the other hand, the existence of a new intermediate charge-ordered (CO) phase was recently found in all the  $(\text{TMTTF})_2\text{X}$  with centrosymmetric X anions [24]. This transition occurs in the temperature range (around 100 K) between the high-temperature transition where electronic localization sets in and the low-temperature transitions of AF or SP type. The absence



**Figure 6.** The dynamics of the energy relaxation defined as  $d(\Delta T/\Delta T_0)/d \log t$  (reported in semi-log plots) at different waiting times  $t_w$  for (a)  $(\text{TMTTF})_2\text{Br}$  at  $T = 79$  mK and 130 mK, (b)  $(\text{TMTSF})_2\text{PF}_6$  at  $T = 123$  and 200 mK.

of a magnetic anomaly at the CO transition indicates that only charge degrees of freedom are involved. Charge disproportionation was evidenced below  $T_{CO}$  [25], the temperature at which the real part of the dielectric susceptibility is divergent [24]. In a recent model, the transition near  $T_{CO}$  was ascribed to the combined effects of the reordering of the charge density on TMTTF chains and the shift of anion chains—a transition of ferroelectric type at  $q = 0$  [26]. Deviation from the Curie and Landau theory near  $T_{CO}$  is an indication that the role of defects in the CO state is due to impurities, dislocations and polydomains with different polarizations. Due to the strong anisotropy of the Q1D materials, the strongly favoured defects are charge-soliton-like discommensurations.

The simplest and most natural explanation for the heterogeneous bimodal dynamics observed in the commensurate ground state for both sulphur compounds is that there are separate manifestations of domains and domain walls—as discommensurations or localized soliton dynamics. For nominally IC systems, but close to commensurability, there is a large distribution of sizes of domains, but also of domain walls, resulting in the homogeneous distribution of the corresponding relaxation times. For nominally commensurate systems, domain walls have energetically preferable sizes and consequently better defined energy splitting of the corresponding metastable states. We can give a more precise estimate of the size of the domain walls (i.e. the soliton width  $\xi_S$ ) for both compounds, where  $\xi_S = (\epsilon_0/\Delta_0)a$  in units of the interatomic distance  $a$ ,  $\epsilon_0$  is the bandwidth and  $\Delta_0$  is the relevant gap of the excitations. In the case of IC-SDW- $\text{PF}_6$ , the spin/charge gap is  $\sim 40$  K, whereas for C-SP- $\text{PF}_6$ , the charge gap (relevant for LEEs) is  $\sim 900$  K. Supposing similar bandwidths in the



**Figure 7.** Possible deconvolution of the relaxation time spectra at thermodynamical equilibrium for  $(\text{TMTTF})_2\text{PF}_6$  as the sum of two Gaussian distributions corresponding to fast and slow processes. The width of the slow process corresponds to the Debye one.

two systems,  $\epsilon_0 \sim 1$  eV, one obtains  $\xi_S \sim 500\text{--}600a$  [27] and  $\xi_S \sim 10\text{--}15a$  for IC and C compounds respectively. This numerical estimate confirms the better definition in energy for domain walls in commensurate compounds.

The bimodal dynamics differentiates between the dynamics within the domains (fast) and the domain walls (slow), the latter being determined by the long equilibrium time related to pinning defects [28]. Within the  $T$ -range investigated, we see from figure 7 that the relative weight of slow domains in the dynamics grows at the expense of the fast ones when the temperature is decreased. However, when one estimates the contribution to the heat capacity of both kinds of entity, it appears that the fast process contributes by a constant factor (about 20%) to the total  $C_p$  in the  $T$ -range below 0.5 K [22], which is in good agreement with the ratio of relaxation times (figure 7).

A similar evolution in temperature of the bimodal dynamics, i.e. both fast and slow processes also being separated by one decade in time, and hence following the same  $T$ -dependence, has been observed in the supercooled state of a fragile glass former [29] at the approach to the glass transition. The bimodal dynamics was there related to the same atomic species:  $\text{NO}_3^-$  ions. In such a framework, one could expect the slowing down of the slow entities to be the precursor behaviour for a new freezing transition in the  $T$ -range of 0.1 K or less. This was proposed in a recent phenomenological random energy (trap) model compatible with our experimental results [30].

#### 4. Conclusions

Our investigation of the low- $T$  thermodynamical properties of the organic salts based on the sulphur donor TMTTF reveals some specific dynamical features related to the ground

states exhibited by these compounds: spin–Peierls in (TMTTF)<sub>2</sub>PF<sub>6</sub> and AF in (TMTTF)<sub>2</sub>Br. Common general properties—the extremely long dynamics of energy relaxation and related non-equilibrium phenomena caused by specific LEE—are similar to those previously found for (TMTSF)<sub>2</sub>PF<sub>6</sub> in an IC-SDW ground state [9] and in some IC-CDW systems [7].

In a separate measurement done under similar experimental conditions on a reference system for this dynamics study—single-crystalline Si—we have demonstrated that, regardless of the existence of comparable additional TLS contributions, the dynamics exhibited was Debye-like, as expected if the TLSs are tightly coupled to the lattice (i.e. exact exponential decay and no time-dependent effects). This is a direct proof that DW-TLSs are strongly decoupled from phonons and have a very specific origin compared to that in conventional disordered systems.

We claim that the DW-TLSs are caused by the charge organization and the pinning effects [28]. They have a wide distribution of relaxation times revealed in the energy relaxation. The heterogeneous dynamics was observed for nominally commensurate sulphur systems (with SP and AF ground states, compared to more homogeneous dynamics found in previously investigated IC-CDW systems). The bimodal dynamics obtained in thermodynamical equilibrium for  $T < 0.5$  K naturally imposes the role of discommensuration defects, with two timescales resulting from intra-domain and domain wall dynamics.

We hope that our investigation will help in resolving some controversies [31] concerning the real ground states of these systems. Finally, it gives some parameters for the quantification of theoretical models which could explain the essential features of the defects of the underlying superstructure causing such an amazing dynamics.

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