Low-temperature thermodynamic investigation of the sulphur organic salts $(TMTTF)_2PF_6$ and $(TMTTF)_2Br$ (TMTTF≡tetramethyltetrathiafulvalene): I. General aspects

Low-temperature thermodynamic investigation of the sulphur organic salts (TMTTF)$_2$PF$_6$ and (TMTTF)$_2$Br (TMTTF $\equiv$ tetramethyltetrathiafulvalene): I. General aspects

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Abstract

A detailed thermodynamical investigation of the quasi-one-dimensional sulphur-based organic salts (TMTTF)$_2$PF$_6$ and (TMTTF)$_2$Br is presented in the temperature range from 30 mK to 7 K. In this part (part I), we consider the general aspects of the low-temperature specific heat of these materials in relationship with their ground states and we compare them with those previously measured for selenium members of the same family. All these compounds exhibit very similar thermodynamical behaviour, despite a variety of electronic ground states: spin–Peierls for (TMTTF)$_2$PF$_6$, commensurate antiferromagnetic spin modulation for (TMTTF)$_2$Br, incommensurate spin-density wave for (TMTSF)$_2$PF$_6$ (TMTSF $\equiv$ tetramethyltetraselenafulvalene). We show that the low-energy excitations which are predominant below 1 K have a similar character to that observed in glassy systems, at least on short timescales of measurements. The dynamical aspects of the non-equilibrium thermodynamics will be presented separately in the following part (part II).

1. Introduction

From abstract theoretical models of one-dimensional (1D) systems of coupled electrons and phonons, the efficient synthesis of real quasi-one-dimensional (Q1D) conductors has opened up in these two last decades a new branch in solid-state physics, i.e. 1D physics. Although the main interest today is in the sub-field of 1D nanomaterials, the knowledge accumulated from the investigation of conventional Q1D conductors is still frequently used. Among these materials, probably the more investigated are the members of the family of organic Q1D conductors

of general formula $(TMTSF)_2X$ ($X = PF_6$, AsF_6, ClO_4,...) and their sulphur analogues $(TMTTF)_2X$ ($X = PF_6$, AsF_6, SbF_6, Br, ...) [1, 2]. Their pronounced Q1D features have been for a long time considered as a realization of the prototype model for 1D electronic systems whose structure is generally unstable owing to cooperative effects and which tend to show quite a number of instabilities. First among them is the known Fröhlich–Peierls instability [3, 4], bringing about a modulated non-uniform static distribution (a density wave, DW) of either the charge or the spin density (CDW or SDW). The selenium-based compounds with PF_6 or AsF_6 anions running along zigzag TMTSF stacks exhibit a metallic behaviour down to low temperatures where, below 12 K, a transition to an incommensurate SDW state occurs. Sulphur series are especially susceptible to a dimerization, producing a gap Δ in the middle of the conduction band of the organic stacks and leading to a high-temperature $4k_F$ charge localization (k_F: Fermi momentum), around 100 K for Br compounds and 220 K for PF_6 compounds. Although there is a gap for the charge excitations, the spin degrees of freedom remain free. In this situation, the energy of the system can be described by an antiferromagnetic (AF) spin-chain Hamiltonian with an effective exchange constant, J. On a deformable lattice, the exchange integral J depends on the lattice spacing. The spin system then can gain energy by dimerizing [5]. The phase transition leading to a non-magnetic ground state (of paired spins, one per dimer) via a displacive modulation of the lattice is called the 'spin–Peierls' (SP) transition in analogy with the lattice and charge instabilities in 1D metallic compounds [4]. $(TMTTF)_2PF_6$ exhibits a SP transition [6] at $T_{SP} = 15$ K. On the other hand, the Br compound undergoes an AF ordering at $T_{AF} = 13$ K, commensurate with the crystallographic lattice [7]. These sulphur compounds exhibit spin–charge separation phenomena seen by the decoupling between the high-T charge-localization and the low-T spin-ordering transition. However, a continuous variation through a series of successive ground states from the insulating SP state to the metallic superconductor can be realized by applying pressure [2].

Although all these DW compounds exhibit very different ground states, they have a similar low-temperature heat capacity and dielectric response behaviour resembling that observed in glasses and disordered systems [8]. In the case of CDWs, specifically for TaS_3, distinctive relaxation processes were shown to freeze when screening of CDW deformations becomes ineffective [9]. In the SDW state of $(TMTSF)_2PF_6$ a calorimetric glass transition was demonstrated at 3.5 K [10]. Apart from these additional specific heat contributions above 1 K in all $(TMTSF)_2X$ and $(TMTTF)_2X$ salts investigated, there are similar low-energy excitations (LEEs) contributions dominant below 1 K. As in the case of CDW ground states, these excitations exhibit very peculiar dynamical properties which can be understood only if they are very weakly coupled to the phonon bath; this makes a specific distinguishing point regarding the overall similarity with conventional glasses [12]. From this point of view, it is very important to better identify the common microscopic origin of LEEs and more specifically the basic characteristics of the topological disorder, which is naturally expected to be related to the DW superstructure.

With this motivation, we have measured the low-T thermodynamical properties of $(TMTTF)_2PF_6$ in its SP ground state. Additional new measurements on $(TMTTF)_2Br$ obtained under different dynamical conditions from those published previously [13] and extended to a lower T-range—down to 30 mK—are also reported. The data are analysed in comparison with those measured for $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ in their SDW ground states. In this first part (part I), we present the results on the low-T specific heat, while the second part (part II) will be devoted to dynamical (time dependence) aspects.
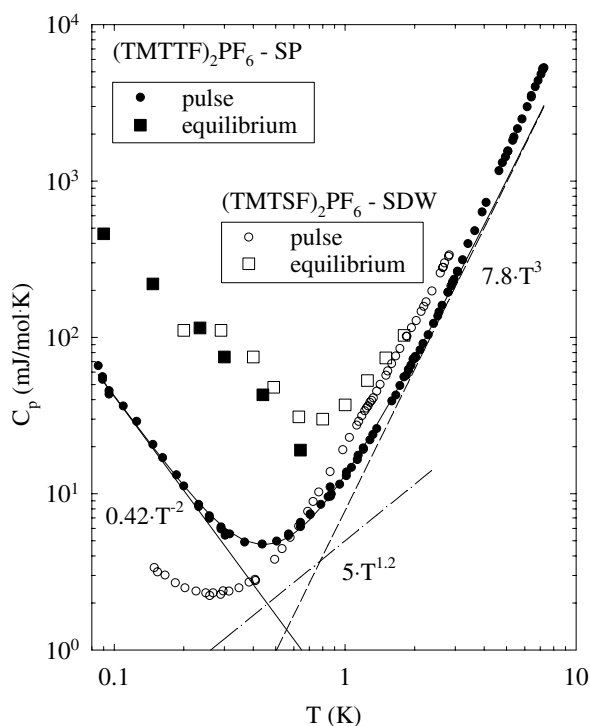
Figure 1. The specific heat of (TMTTF)$_2$PF$_6$ measured in two extreme dynamical conditions; short-pulse C_p and the total (integrated) specific heat C_{eq} in thermodynamical equilibrium, compared to that of (TMTSF)$_2$PF$_6$ under similar dynamical conditions [11].

2. Experimental procedure

The specific heat measurements on 100 mg of (TMTTF)$_2$PF$_6$ crystals were performed in a dilution cryostat spanning the temperature range between 80 mK and 7 K, using a transient-heat-pulse method with a similar sample arrangement to that in our previous investigations [11, 13–15]. In this method the sample is loosely connected to the thermal bath by a thermal link. In normal conditions, C_p is determined by the initial (exponential) T-decay in response to a heat pulse. However, in Q1D systems, we have observed a progressive deviation from an exponential decay of the transient on lowering T below ∼0.5 K, indicating a time-dependent, or non-equilibrium, specific heat. In that case, we used the convention to define, by continuity from higher temperatures, C_p from the initial T-increment following the heat pulse [15]; this yields the 'short-time' value. On the other hand, the use of a thermal link enables us to calculate the specific heat from the total integration of the heat relaxed through it, since the sample ΔT increment remains small (<10% of the mean T) [11]. By varying the time delivery of the energy, we have observed a saturation value where we consider that the thermodynamical equilibrium is reached; this can need durations up to 12–13 h for (TMTSF)$_2$PF$_6$ and (TMTTF)$_2$PF$_6$. The sample of (TMTTF)$_2$Br (60 mg) on which we previously made measurements [13] was rearranged and mounted in another more powerful dilution cryostat for measuring its C_p down to 30 mK. In order to improve the thermal diffusivity below 100 mK, one Au foil (with a Au wire directly soldered to it) was inserted between two layers of crystals. Thus the effective thermal link became 4–5 times smaller than in the measurements reported in [13], allowing us to reach the lowest temperature of 30 mK.
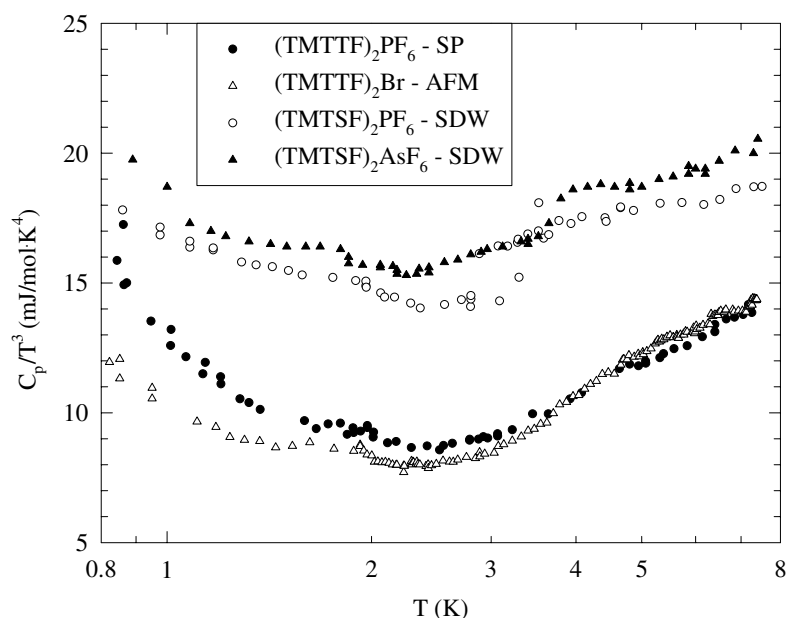
Figure 2. The variation of the specific heat of $(TMTTF)_2PF_6$ defined on the short timescale divided by T^3 between 0.8 and 8 K compared to that for $(TMTSF)_2AsF_6$ [14], $(TMTSF)_2PF_6$ (see e.g. [11] and references therein) and $(TMTTF)_2Br$ [13].

3. Results

In figure 1 we present a comparison between the temperature dependences of C_p for $(TMTTF)_2PF_6$ and of $(TMTSF)_2PF_6$ [11] determined in two extreme cases: one corresponding to a 'short timescale' with duration of the heat pulses of less than 1 s; the other in thermodynamic equilibrium, when the time dependence of C_p is exhausted (intermediate-timescale cases will be discussed in part II). A strong similarity is found between the results for the two compounds. Above 1.5 K, C_p closely follows the T^3-dependence; the difference in amplitude displayed in figure 2 is related to the different organic backbones. Below 1 K, C_p gradually deviates from T^3 to finally reach a T^{-2}-variation. We have ascribed this 'hyperfine' contribution observed in all these Q1D compounds to the high-temperature tail of a Schottky anomaly resulting from metastable LEE states of the DW ground state closely speparated in energy [16] and not from a nuclear origin [13, 14]. This is why we retain this terminology (hyperfine) further in the text.

One can also note the similarity in amplitude of the equilibrium long-time specific heat for the two compounds despite their different ground states. In the following, we will discuss each contribution to C_p and compare their amplitudes in several members of this Q1D organic family in order to better understand their similarities and specific differences.

3.1. Lattice contribution

The lattice contribution is the best represented in a C_p/T^3 plot versus T. In figure 2, we compare four compounds: two selenides: $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$, for short Se–PF$_6$ and Se–AsF$_6$; and two sulphides: $(TMTTF)_2PF_6$ and $(TMTTF)_2Br$, for short S–PF$_6$ and S–Br. The lattice contribution follows a T^3-law only in a small temperature range below 3 K.

Quantitatively and qualitatively there is a strong similarity between both selenide compounds on one hand and both sulphide ones on the other. Thus two conclusions can be drawn:

(a) First, since in the $T > 1$ K range, C_p is dominated by the lattice contribution (and eventually by some configurational additional contributions for glassy phases above $T_g \approx 3$ K in the case of selenide salts), one concludes that this lattice term is mainly determined by the TMTTF or TMTSF molecules forming the stacks, the role of anions being negligible. Our previous analysis of Se–PF$_6$ [17] and Se–AsF$_6$ [14] yielded a common $\beta = C_p/T^3 = 14.5 \pm 0.5$ mJ mol^{-1} K^{-4}, corresponding to a Debye temperature (normalized by the number of atoms per molecule) of 200 K. In the case of the S–Br, we found $\beta = 7.8$ mJ mol^{-1} K^{-4} (or $\Theta_D = 236$ K) [13]. For S–PF$_6$ the present analysis of both C_{LEE} and the lattice contribution (see, below, the short-timescale analysis for $T < 1$ K) yields the same value as that for S–Br, namely $\beta = 7.8$ mJ mol^{-1} K^{-4}.

(b) Second, there is no anomaly in C_p/T^3 at $T \sim 3$–3.5 K for the two sulphide compounds, at variance with the case for both selenide compounds, where a dynamical time-dependent anomaly occurs [10, 14]. In particular, we reached the conclusion that the jump in C_p around 3.5 K in (TMTSF)$_2$PF$_6$ had the characteristics of freezing in supercooled liquids [10]. This kind of anomaly does not appear either in the commensurate ground state of the S–Br salt or in the SP state of the S–PF$_6$ salt. However, an additional discontinuity is observed at $T = 1.9$ K in the S–PF$_6$ salt similar to that previously reported in Se–PF$_6$, Se–AsF$_6$ and S–Br salts as seen in figure 2. This discontinuity, which in the present case is just at the limit of our experimental accuracy, was interpreted for (TMTSF)$_2$PF$_6$ as a sub-phase transition in the SDW ground state. This result leads to the hypothesis that this discontinuity is not related to any superstructure induced in these salts, but probably results from the stacks along the chains.

Above $T = 2.5$ K, C/T^3 for (TMTTF)$_2$PF$_6$ increases sharply up to 7.3 K. Similarly to the case for Se–PF$_6$, Se–AsF$_6$ and S–Br, this behaviour can be interpreted as a phonon dimensionality crossover from a low-T 3D behaviour towards a lower-dimensionality T^α-behaviour with $\alpha = 2.3$–2.5 [18].

3.2. Low-energy excitations (LEEs)

The most prominent property of C_p at low temperatures in DW systems is the large contribution of long-living metastable states which becomes dominant below 1 K. We compare in figure 3 the C_p-data for S–PF$_6$ (already shown in figure 1) with those for S–Br for two extreme dynamical conditions: C_p corresponding to the initial response to a short pulse and to 'pulses' sufficiently long to achieve the thermodynamical equilibrium. Data for S–Br were obtained down to 30 mK using two different experimental conditions (sample mounting and dilution cryostats) as described in the experimental part. In addition, we also report C_p-data for the short-time-pulse technique determined by the integration method for the whole response.

Above 1 K, C_p is mainly determined by the lattice contribution (close to T^3), with similar values for the two compounds, as previously discussed. Below 1 K, there is a large separation (splitting) of the data, depending on the compound. In this temperature range, C_p is determined by low-energy, slowly relaxing, extra-phononic excitations (LEE). Similarly to that of S–PF$_6$, the specific heat of S–Br salt is strongly dependent on the timescale. C_p increases on increasing the duration of energy delivery, but in the limit low-T regime always goes like T^{-2}. We also note that C_p for S–PF$_6$ is much larger than for S–Br for similar dynamical conditions: the characteristic 'hyperfine' T^{-2}-contribution observed on short timescales is
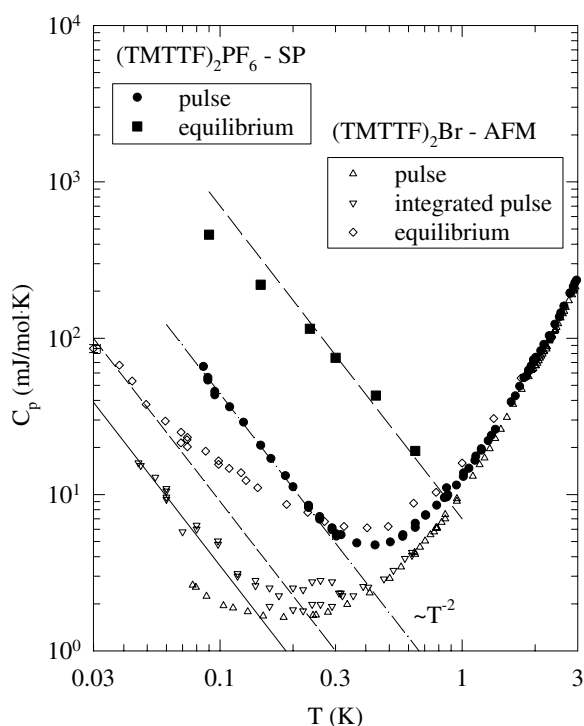
Figure 3. The temperature variation of the specific heat of $(TMTTF)_2PF_6$ (as in figure 1) and of $(TMTTF)_2Br$ measured down to 30 mK. Dark squares and empty diamonds ($\Diamond$) correspond to the thermodynamical equilibrium value C_{eq} of $(TMTTF)_2PF_6$ and of $(TMTTF)_2Br$ derived from integration of the energy release. Data obtained from pulses for $(TMTTF)_2Br$ are split into two branches: (downward-pointing triangles) from integrated pulse relaxation and (upward-pointing triangles) from the exponential fit of the initial part of the response. The two determinations converge at $T \geqslant 0.5$ K. The lines (continuous or dashed) represent the hyperfine T^{-2}-contribution of C_{LEE}.

very large ($C_h T^{-2} = 42$–$45 \times 10^{-2} T^{-2}$ mJ mol^{-1} K^{-1}) in comparison to those for the other three organic salts.

Now, we examine in more detail the important question of the possible observation of the maximum of the Schottky anomaly at sufficiently low T. This problem was raised in studies on Se–PF$_6$ [11] and S–Br [13]. For Se–PF$_6$ it remains unclear whether the reported saturation of C_p in 'equilibrium' conditions around 250 mK was really the maximum of the Schottky anomaly or just an artefact due to the very long time necessary for establishing the thermodynamical equilibrium (the equilibrium time constants approach a day). On the other hand, the maximum in C_p at around 110–120 mK for S–Br was obtained from the analysis of transient-heat-pulse regimes over an intermediate timescale (see figure 3(b) and 4 in [13]), whereas data determined in the integration method for the thermal equilibrium do not show any evidence of a maximum [13].

This is why we have extended measurements on S–Br at lower temperatures down to 30 mK. The use of a much smaller thermal link to the cold sink has given us the advantage of reaching thermodynamical equilibrium within waiting times of only 30 or 40 min. The overlap of the two experiments around 90–120 mK (symbols: empty diamonds) is excellent. Results shown in figure 3 indicate that there is no trend towards a saturation for the T^{-2}-regime
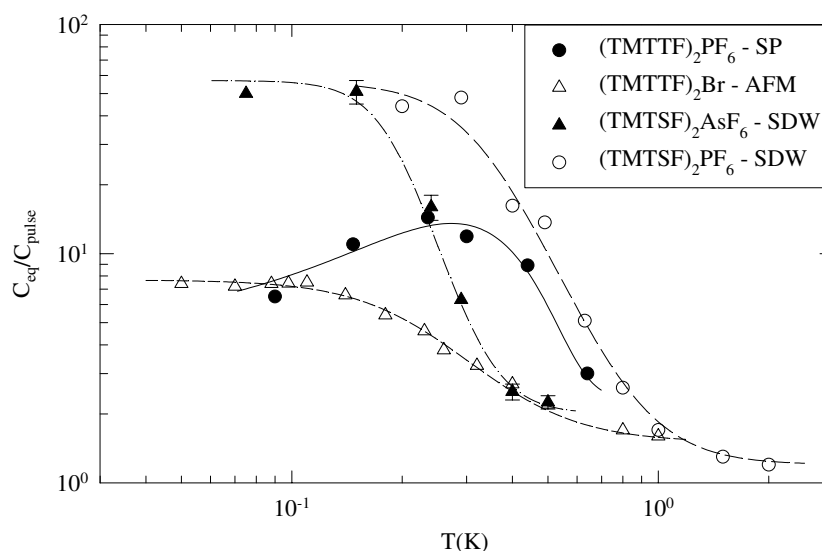
Figure 4. Comparison of the amplitude of the time dependence of the specific heat in (TMTSF)$_2$PF$_6$, (TMTSF)$_2$AsF$_6$, (TMTTF)$_2$PF$_6$ and (TMTTF)$_2$Br measured as the ratio between the specific heat obtained under equilibrium conditions, C_{eq}, and the short-timescale specific heat, C_p.

down to 30 mK and that $C_{h-eq}T^{-2} = 0.09\ T^{-2}$ mJ mol^{-1} K^{-1}. Experiments have also been performed from $T = 0.6$ K down to 45 mK with short-time-heat-pulse conditions and analysed using the energy-integration method. C_p-data for these conditions are shown as empty triangles ($\triangledown$) in figure 3. There is also an excellent agreement down to 0.2 K with the previous data obtained with a larger thermal link and determined from the initial T-decay of the heat pulse [13]. At lower T, C_p obtained from energy integration increases more rapidly to finally reach the T^{-2}-variation below 0.1 K. This difference between the C_p-values obtained from the two analyses is the result of the large deviation of the transient from the exponential decay. As soon as an upwards deviation from a pure exponential variation occurs due to a slow heat release (consequently indicating a time dependence of the specific heat), the integration method yields a larger C_p-value. The one obtained from the initial transient analysis really yields the minimum possible value of C_p ($\triangle$).

The relative contribution of the metastable states to the specific heat can be evaluated from the ratio $R = C_{eq}/C_p$ between the value of the specific heat obtained in equilibrium conditions, C_{eq}, and in short-timescale conditions, C_p. The temperature variation of this ratio is plotted in figure 4 for both S and Se salts. Although C_p depends on the duration of the pulse and can be smaller for shorter pulses, the comparison between these systems is made for similar experimental conditions.

Metastable states start to contribute when R increases above 1, which occurs for all compounds below 1 K. Typically the ratio R increases rapidly upon decreasing temperature and saturates at low temperatures. One can see that R reaches a value of about 50 at $T = 0.2$ K for Se–PF$_6$ and Se–AsF$_6$, for which the ground state is an incommensurate SDW. However, this value of 50 is a minimum value because it is not certain that below 0.2 K the thermodynamical equilibrium was reached within our experimental window. For the commensurate AF S–Br, the saturation of R is around 7 and only reached below 100 mK. Below 1 K, the temperature variation of R for SP S–PF$_6$ is very similar to that of Se–PF$_6$, but it saturates at a value of 15 at $T \sim 0.3$ K and finally decreases at lower temperatures.
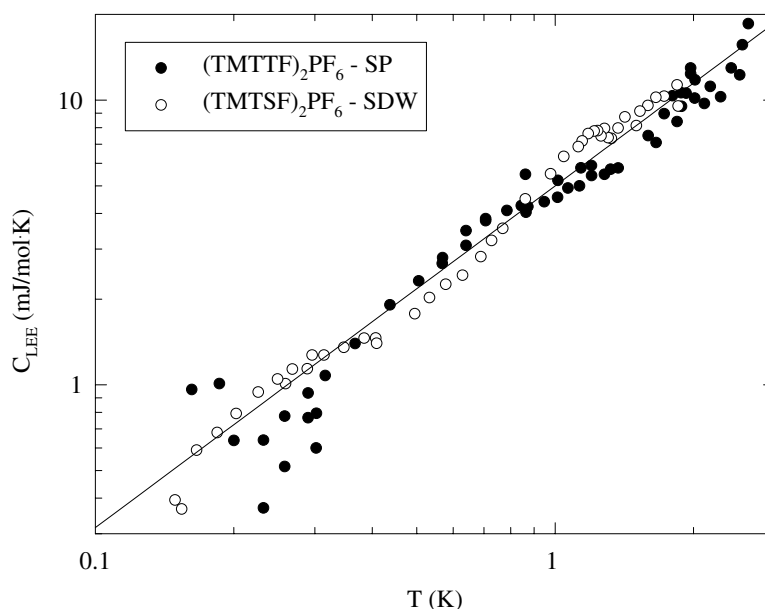
Figure 5. The contribution of low-energy excitations to the short-timescale specific heat of $(TMTTF)_2PF_6$ compared to that of $(TMTSF)_2PF_6$ [11].

More information about LEEs can be obtained by comparing their contributions to C_p on the short timescale. Like in our previous analysis [11, 13, 17], short-time C_p-data are well described between 7 K and the lowest T by

$$C_p = C_h T^{-2} + A T^\nu + \beta T^3.$$

The two first terms are the 'hyperfine' and the power-law contributions of the LEE and the third one is the usual phonon contribution. The best fit to the data for $(TMTTF)_2PF_6$ below 2 K is

$$C_p = 0.42 T^{-2} + 5 T^{1.2} + 7.8 T^3 \ (\text{mJ mol}^{-1} \text{ K}^{-1})$$

to be compared to

$$C_p = 0.065 T^{-2} + 5 T^{1.2} + 14.5 T^3 \ (\text{mJ mol}^{-1} \text{ K}^{-1})$$

for $(TMTSF)_2PF_6$ (from data in figure 1 in [11]).

In figure 5 we have drawn the temperature dependence of the power-law T^ν-contribution of C_{LEE} in both S–PF$_6$ and Se–PF$_6$. It appears that the contributions of the LEE are nearly identical in the commensurate SP and in the incommensurate SDW ground states. This magnitude is also comparable to that for the S–Br compound [13].

4. Discussion

Our present results show that the short time scale low-temperature specific heat of S–PF$_6$ is characterized by a very large hyperfine coefficient C_h of 0.42–0.45 mJ K mol^{-1}, but the power-law LEE contribution is of the same order of magnitude as in compounds of the same family, either with a SDW or AF ground state.

Indeed, the magnitude of the hyperfine coefficient is much larger compared to those for the three other salts. We do not have a definitive explanation for so large an effect. One possibility

might be that, in the case of S–PF$_6$, C_p would depend on time on a much shorter scale than the other salts and that with a pulse duration of 1 s, the transient-heat-pulse regime is already on an intermediate timescale. We have recently [13, 14] reached the conclusion that the hyperfine $C_h T^{-2}$ contribution, even on the short timescale, has its origin in metastable LEEs and not a nuclear contribution. Although there exists some general correlation between the amplitudes of C_h and of the LEE (power-law) contribution, it is far from an exact proportionality. That means that first, the distribution energy of the LEEs, $g(E) \sim E^{1-\nu}$, is continuous down to very small energies (at least down to $E \approx 0.3$–0.4 K, corresponding to 70 mK, the minimum temperature reached), and, second, that the splitting between the two well defined levels at the origin of the characteristic T^{-2}-tail of the Schottky anomaly is of the order of or less than $\Delta E = 50$–100 mK. In the case of the long-time equilibrium data for S–Br, the absence of a deviation from T^{-2} down to 30 mK yields $\Delta E_{max} \approx 50$ mK.

It is interesting to note that, unlike the power-law T^{ν}-contribution, the hyperfine T^{-2}-contribution is very sensitive to the experimental timescale, even in the short-time-pulse conditions. In addition, it is this term which drastically increases between pulse and long-time equilibrium conditions (figure 1), to finally overcome the power-law contribution.

The LEE contributions in S–PF$_6$ (SP) Se–PF$_6$ (SDW) being high and comparable hints that one should consider a common origin. As in S–PF$_6$ there are no SDW excitations, we are led to the conclusion that the residual LEE contributions, at the origin of the large dynamical effects, are due to the charge degrees of freedom. Indeed, for a SDW, at first order in the electron–impurity interaction there is no pinning by non-magnetic impurities because the total electron density is constant. However, the interaction between impurities and conduction electrons may generate a small distortion of the charge density near impurity sites in the form of Friedel oscillations with a periodicity half the SDW wavelength [19]. This charge distortion couples to the electric field and is responsible for non-linear transport properties as in the CDW case. In this respect, the LEEs in incommensurate CDWs and SDWs have common features and the fact that we find that their contributions to the specific heat are similar confirms this.

The (TMTTF)$_2$X salts are already dimerized at room temperature. They undergo a Mott–Hubbard localization (a $4k_F$ superstructure) below T_ρ with the opening of a charge gap, the spin susceptibility being Pauli-like down to low temperatures. Below T_{SP}, around 15 K, due to elastic distortions of the lattice, the dimer lattice dimerizes and forms a tetramerized lattice (a $2k_F$ transition similar to the canonic Peierls distortion) of a non-magnetic phase.

At this point, it may be useful to make a comparison of the low-T specific heat in the SP state of S–PF$_6$ and that of inorganic CuGeO$_3$ ($T_{SP} = 14.2$ K) [20]. This latter compound, despite the 1D character of its spin chains, has a 3D lattice and in addition is an insulator over the whole temperature range. In CuGeO$_3$, below 1 K, i.e. for values of T/T_{SP} similar to those for S–PF$_6$, there is no time dependence effect in C_p, although there are extra-phononic residual excitations (the collective magnetic excitations have exponentially vanished due to the opening of the gap at T_{SP}) [21]. This additional contribution shows a slow increase like $\sim T^{-0.5}$ below 0.3 K (not a hyperfine T^{-2}-term) which seems to saturate down to 40 mK, with a shape resulting from a broad distribution of Schottky anomalies (or a Schottky anomaly with multiplet upper levels), without dynamical effects. A possible explanation for this contribution would come from residual free spins $s = 1/2$ due to impurities or magnetic chain-breaking defects which generate unpaired free spins, both being present even in nominally pure samples [22].

In the present S–PF$_6$ organic material, we consider that the LEEs are related to disorder in the tetramerized SP ground state. These lattice degrees of freedom ($2k_F$ fluctuations) may induce charge fluctuations, similarly to those observed in other compounds. Indeed, a persistence of a charge modulation has been observed in the commensurate AF phase of S–Br as small $2k_F$ CDW fluctuations of SP type which persist below the AF phase transition

temperature, T_N [23]. Simultaneously $4k_F$ satellites have been observed at $T < T_N$ due to the magnetoelastic coupling of the lattice with the AF modulation. This $4k_F$ lattice displacement leads to a charge modulation which gives the large contribution to the dielectric response [24]. But, as will be described in paper II, the dynamical properties of LEEs in such commensurate systems as S–PF$_6$ and S–Br show significant differences in the spectrum of relaxation times compared to incommensurate SDW systems. The defects in the electronic charge subsystem are better described as discommensurations (or localized solitons) or slight distortions in the commensurate superstructures.

5. Conclusions

In conclusion, the thermodynamical properties of (TMTTF)$_2$PF$_6$ in its SP ground state show strong similarities with other organic conductors of the TMTSF and TMTTF families, despite the very different electronic ground states: SP, SDW or AF order. Firstly, the lattice specific heat of (TMTTF)$_2$PF$_6$ is a very close to that of (TMTTF)$_2$Br, with a rapid deviation from a T^3-variation above 3 K, and without any anomaly at 3.5 K as observed for the Se compounds ((TMTSF)$_2$PF$_6$ and (TMTSF)$_2$AsF$_6$) and ascribed to a dynamical glassy-like transition.

Secondly and more surprising, below $T = 1$ K, the metastable LEE contribution to C_p related to the disordered character of the electronic subsystem is very similar either to that for (TMTSF)$_2$PF$_6$ in its SDW ground state or to that for (TMTTF)$_2$Br in its AF ordered ground state. This contribution can be analysed using a T^ν-power law remarkably similar in amplitude to that for (TMTSF)$_2$PF$_6$, and a hyperfine T^{-2}-contribution, again very dependent on the time span of the experiment. These results are at variance with the low-temperature behaviour of C_p for the model SP compound CuGeO$_3$ (which is an insulator at all temperatures) with a 3D lattice. In this latter, low-energy LEEs which are the origin of a very different $C_p(T)$ dependence, with the absence of any time effect, are identified with free-electronic spins $S = 1/2$ related to impurities or specific defects like breaking of the magnetic chains.

The LEE properties presented here are much more similar to those of other Q1D DW compounds. In comparison to the previously studied SDW cases, the absence of electronic spins (apart from residual impurities) hints at a purely electronic charge origin—as there could be in the SDW state of (TMTSF)$_2$PF$_6$ if one considers the mixed CDW/SDW character of this ground state. In the case of this nominally commensurate electronic ground state, defects at the origin of LEEs are plausibly ascribed to discommensurations (domain wall dynamics) as slight deviations from exact commensurability.

The data discussed here correspond to the two extreme cases for the experimental time span: C_p obtained either under short-time-heat-pulse conditions or in the long-time equilibrium conditions. The intermediate timescale will be discussed in paper II (on dynamical aspects), together with the influence of the commensurability on the homogeneity/discreteness of the measured relaxation spectra.

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