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Specific heat measurements of the lattice contribution and the spin-density-wave and anion-ordering transitions in the (TMTSF)₂ClO₄ salt (TMTSF ≡ tetramethyltetraselenafulvalene)

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Abstract. The specific heat of the quasi-one-dimensional organic compound (TMTSF)₂ClO₄ was measured between 1.9 and 35 K for two states corresponding to the metallic/superconducting ground state and the insulating spin-density-wave (SDW) ground state at low temperature, by varying the cooling conditions through the anion-ordering (AO) transition at 24 K. These are the first thermodynamical measurements of the SDW ground state. Like in the previously investigated compounds (TMTSF)₂X, with X = PF₆ and AsF₆, and (TMTTF)₂Br (where TMTTF ≡ tetramethyltetrathiafulvalene), the lattice specific heat shows strong deviations from a Debye behaviour, which can be explained by the quasi-one-dimensional structural character. Bumps in C/T^3 occur at $T = 3.5$ – 4 K and 5 K for the quenched SDW and relaxed metallic states respectively; these are in good agreement with the frequencies of low-lying modes detected by infrared spectroscopy for the metallic sample. In addition, analysis of the lattice contribution suggests a T^α ($\alpha = 2.7$) acoustic contribution for $T \gtrsim 2$ K, ascribed to the low dimensionality of the structure. The SDW transition was detected at $T_c = 4.5$ K, as expected from the high value of the quenching rate (of 3.3 K s^{-1}) through the AO transition (the amplitude of the anomaly represents about 3% of the total heat capacity). The AO transition was investigated either by decreasing the temperature for the slow-cooled sample or by reheating, at a similar rate, for the quenched sample; the specific heat anomalies are identical for the two procedures, due to reordering annealing effects on reheating, a phenomenon previously investigated by x-ray experiments. Surprisingly, the entropy under the AO anomaly is $R \ln(4/3)$, much lower than the $R \ln 2$ value expected for the two possible configurational orientations of the perchlorate ion in the disordered state. Similar low values of the entropy have been previously measured for the perrhenate (ReO₄) and BF₄ salts.

1. Introduction

The (TMTSF)₂X family of organic chain-like conductors has recently aroused renewed interest, as a result of its appearance in the field of superconductivity in the early 1980s [1]. Due to the strong anisotropy and subtle balance between interchain and intrachain electronic coupling, these quasi-1D conductors exhibit a variety of electronic ground states, in particular a competition between superconducting and spin-density-wave (SDW) states. Generally, the SDW ground state is suppressed by a moderate pressure, and superconductivity occurs at temperatures around 1 K. In the case of (TMTSF)₂ClO₄ (where TMTSF is tetramethyltetraselenafulvalene and ClO₄ the perchlorate ion) the role of pressure is taken by the rate of

quenching through an order–disorder anion ordering (AO) at $T_{AO} = 24$ K. Above this transition the non-centrosymmetrical anions are disordered in the triclinic $P1$ space group with two equivalent orientations. On slowly cooling through the AO transition, anions order and alternate along the b -axis only, forming a superstructure characterized by the wavevector $\mathbf{q} = (0, 1/2, 0)$ [2]. The ordering of ClO_4 anions enables the stabilization of the superconducting state at $T_c = 1.22$ K, established from thermodynamic measurements. This state has been verified by zero-field resistance, Meissner effect and specific heat studies [3, 4]. In contrast, rapid quenching (at a rate faster than 100 K min^{-1}) preserves the anion disorder and promotes a metal–insulator transition, with an electronic condensation into a SDW antiferromagnetic ground state, which is observed from NMR [5], EPR [6] and resistivity measurements [7]. In addition, the field-induced spin-density-wave state, which occurs above a few teslas in the metallic phase in relation to oscillations of the magnetoresistance, has attracted much interest as a property specific to quasi-1D conductors [8]. Recent thermal conductivity measurements on the superconducting state have been used to study the symmetry of the order parameter [9].

Specific heat measurements are a powerful tool for investigating structural, electronic and magnetic transitions, and for determining the electron and phonon contributions. They give important information about the electron density of states at the Fermi level $N(E_F)$, the electron–phonon coupling and magnetic fluctuations. In this paper, we report on new specific heat results on $(\text{TMTSF})_2\text{ClO}_4$ single-crystal samples both in relaxed (metallic) and quenched (SDW) states, measured between 1.8 and 35 K. Previously, in addition to the extensive study of field-induced SDW, two series of experiments have been reported by the same group in Orsay, using ac calorimetry, and both dealing with the metallic state, obtained with different cooling rates: one over the range of the superconducting transition (0.45–2 K [4, 10]) and the second over a larger T -interval including the AO transition at 24 K [11]. Our study continues on from our previous investigation of the specific heat of a series of organic chain-like salts: $(\text{TMTSF})_2\text{X}$, with $\text{X} = \text{PF}_6$ and AsF_6 , and $(\text{TMTTF})_2\text{Br}$ (where TMTTF is tetramethyltetrathiafulvalene) [12], with the aim of studying precisely the lattice contribution which shows generally strong deviations from a Debye 3D behaviour; in addition our goal was the investigation of the SDW transition by a thermodynamical measurement, which has not been achieved previously. Another objective was the comparative study of the AO transition measured by crossing the transition by slowly cooling, which yields the low- T metallic/superconducting ground state, or by reheating from the quenched SDW state. One can then check for a possible role of the rate of data acquisition in comparison with the slow kinetics of the transition. A preliminary description of these data was given in [12], without a detailed analysis.

2. Experimental details

Single-crystal samples (needles) of $(\text{TMTSF})_2\text{ClO}_4$ were synthesized by the standard electrochemical method [13]. The typical size of the needles is about $0.5 \times 0.5 \times 3 \text{ mm}^3$. The sample consists of about one hundred of such tiny needle crystals, amounting to 184 mg. In addition, 12.6 mg of Apiezon N grease was used to improve the thermal contact between the crystals and the silicon sample holder, in the same method as previously used for the PF_6 salt [12, 14].

The specific heat measurement was performed between 1.8 and 35 K on a ^4He cryostat with a transient-heat-pulse technique using a similar arrangement to that in our previous investigations [12, 14]. The specific heat C is calculated from the increment of the temperature $\Delta T = T - T_0$ caused by a heat pulse (duration 0.2 s at 1.7 K to several tens of seconds at 35 K, which is always 1/20 of the relaxation time τ) by using the exponential decay of the temperature increase $T(t) - T_0 = (T_p - T_0) \exp(-t/\tau)$, with the relaxation time $\tau = CR_\ell$,

where C is the total heat capacity and R_ℓ the thermal resistivity of the thermal link to the regulated cold sink. In the experiments, $\Delta T/T_0$ is always kept between 1% and 3% (1% in the vicinity of the AO transition), T_0 being the reference temperature before the heating pulse, which can be stabilized within 5×10^{-4} over several hours. The heat capacity of the sample holder has been measured in another separate experiment and its contribution to the total heat capacity was about 40–50%.

Since the physical properties of this compound are very sensitive to the cooling rate, great care was taken to control it. The sample was cooled naturally under a secondary vacuum from room temperature to 40 K, which usually takes about 24 hours. For the slow-cooled sample, data were taken with decreasing temperature from 40 K through the AO transition (at 24 K) with a constant cooling rate of 0.3 to 0.5 K h⁻¹. The procedure for the quenched state was the following: after the slow-cooling measurements, the sample was warmed up to 40 K, the liquid ⁴He pot being pumped below T_λ , and then ⁴He gas introduced at pressure of 0.2 mbar in the calorimeter to cool the sample down. The cooling procedure took a total of 40 s from 40 K to 4 K (from 30 K to 20 K in 3 s), so the average cooling rate is 3.3 K s⁻¹ through the AO transition. Thereafter, the sample was warmed up to 7.5 K for outgassing of possible He adsorption and the sample chamber pumped for 24 h in order to recover the same vacuum as was obtained in the slow-cooling experiment. The data for the quenched sample were taken with increasing the temperature at a rate of 0.5 K h⁻¹ in the region of the AO, between 18 and 28 K, with the relaxation time τ increasing from 25 to 60 s.

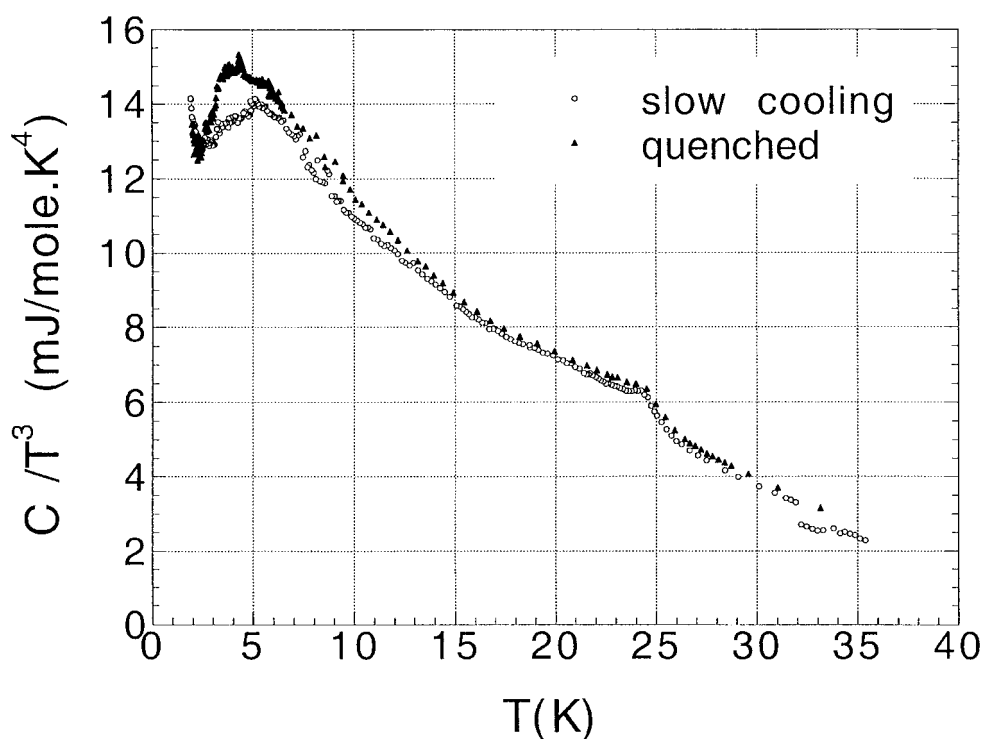
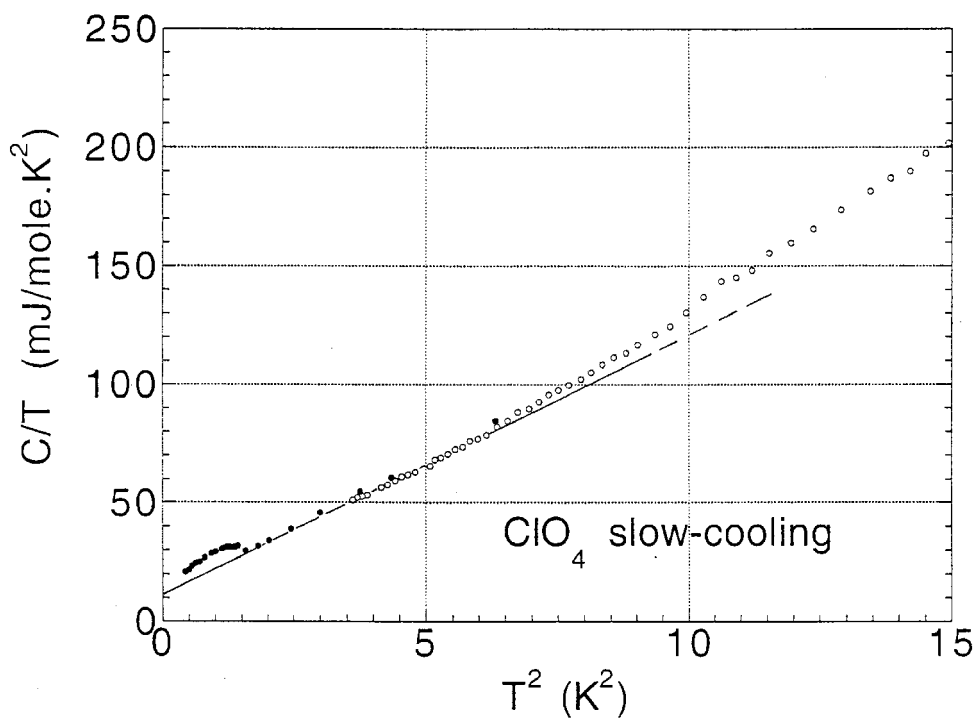


Figure 1. The specific heat, as C/T^3 versus T , of $(\text{TMTSF})_2\text{ClO}_4$ for slowly cooled (metallic state) (data: \circ) and quenched (SDW ground state) (data: \blacktriangle) samples. The anion-ordering transition appears as a local maximum at $T = 24.2$ K.



(a)

Figure 2. The low-temperature specific heat, as C/T versus T^2 , below 4 K for slowly cooled (data: \circ (a)) and quenched (data: \blacktriangle (b)) samples. Also reported ('low-temperature' data: \bullet) are results for a slowly cooled sample measured in another experimental set-up down to 0.7 K, which shows the onset of the superconducting transition at $T_c = 1.24$ K. Straight lines show the fitting with the usual $\gamma T + \beta T^3$ law.

In order to check the validity of the procedure, and especially to verify that there was no desorption of ^4He gas from the sample when reheating above 7.5 K, we have compared the values of the thermal link R_ℓ for the two experiments (quenched and slowly cooled): the difference remains generally below 10% for the whole T -range, with an agreement better than 2% for the smoothed data between 2 and 20 K. The excellent reproducibility of R_ℓ confirms the absence of possible desorption of ^4He gas.

3. Results and analysis

3.1. Electronic and lattice contribution

The molar specific heat at constant pressure C of $(\text{TMTSF})_2\text{ClO}_4$ obtained with the two cooling rates is reported in figure 1 in the form of C/T^3 versus T between 1.8 and 35 K. The general tendency of the temperature variation is similar to those for the PF_6 , AsF_6 and Br compounds measured in the same T -range [12], except in the interval where the AO transition is observed as a maximum at $T_{\text{AO}} = 24.2$ K. On decreasing the temperature, the specific heat of the two samples ((i) quenched and (ii) slowly cooled and relaxed) shows an increasing difference, which is clearly observed between the C/T^3 bumps centred at $T = 3.5$ –4 K and 5 K, for the quenched and relaxed samples, respectively. These bumps are related to the lattice contribution,

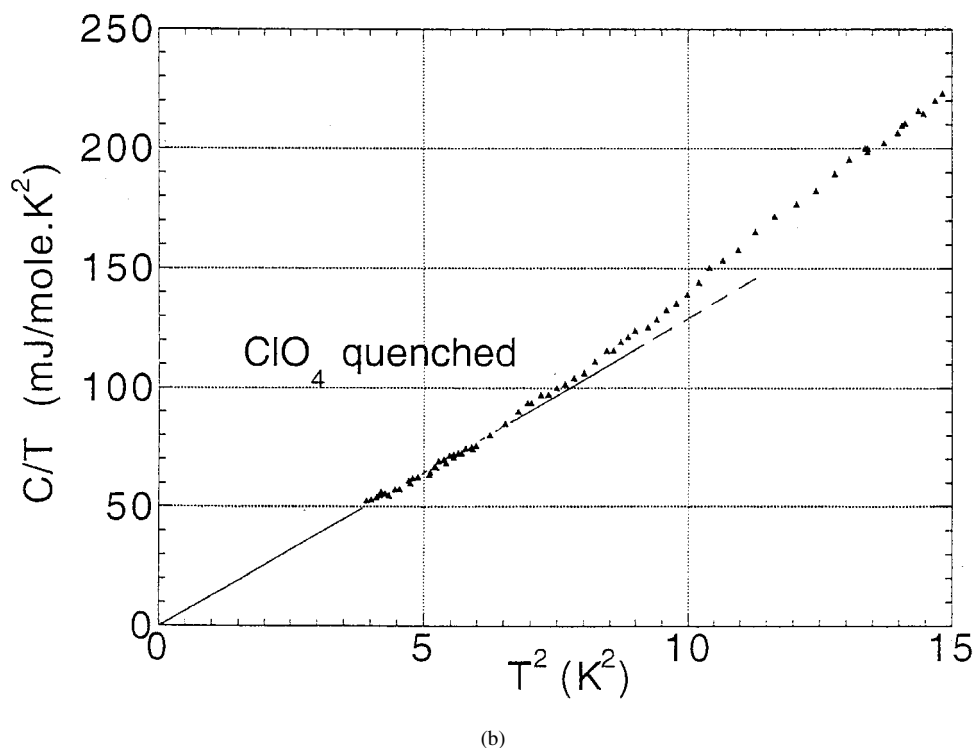


Figure 2. (Continued)

as will be discussed later in connection with the figure 3. They are also present for the PF_6 , AsF_6 and Br compounds, but at somewhat higher temperature (7 K).

In order to separate the electronic and phonon contributions in the metallic state, we have plotted the low- T specific heat as C/T versus T^2 below 4 K, in figure 2(a). In this figure we also report 'low-temperature' data for $0.7 \text{ K} \lesssim T \lesssim 2.5 \text{ K}$ (symbol \bullet), obtained for samples of the same origin, cooled through the AO transition at a similar slow rate of 0.5 K h^{-1} , and measured in a dilution refrigerator. The main difference concerns the time constants of the exponential transients in response to heat pulses, much longer (by a factor of about ~ 8 – 10) than in the present experiments, due to a larger thermal resistance R_ℓ . The superconducting transition occurs at 1.26 K (the onset of the superconducting state from high temperature) in good agreement with the data of the Orsay group [4]. These 'low- T ' data coincide well with the present data for the slowly cooled sample, between 1.8 and 2.5 K (symbol \circ , figure 2(a)), as well as with those of reference [4]. There is also some overlap with the data for the quenched sample between 1.8 and 2.5 K, but the analysis will reveal differences.

The Debye law for the lattice term (βT^3 variation) appears to be obeyed for the three series of data only up to $\sim 2.5 \text{ K}$ (figures 2(a), 2(b)). In the C/T^3 diagram of figure 3, more sensitive in showing deviations from the Debye regime, deviations clearly start above 2.3 K for the slowly cooled sample. The solid straight line in figure 2(a) represents the fitting for this sample between 1.8 and 2.5 K to the classical formula $C/T = \gamma + \beta T^2$, where $\gamma = 11.5 \pm 1.0 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $\beta = 10.9 \pm 0.3 \text{ mJ mol}^{-1} \text{ K}^{-4}$. For the quenched sample (see figure 2(b)), fitting in the same T -range confirms that there is no electronic contribution as expected for a SDW state, and a higher lattice contribution, i.e. $\gamma \equiv 0$ and $\beta = 12.8 \pm 0.3 \text{ mJ mol}^{-1} \text{ K}^{-4}$. The

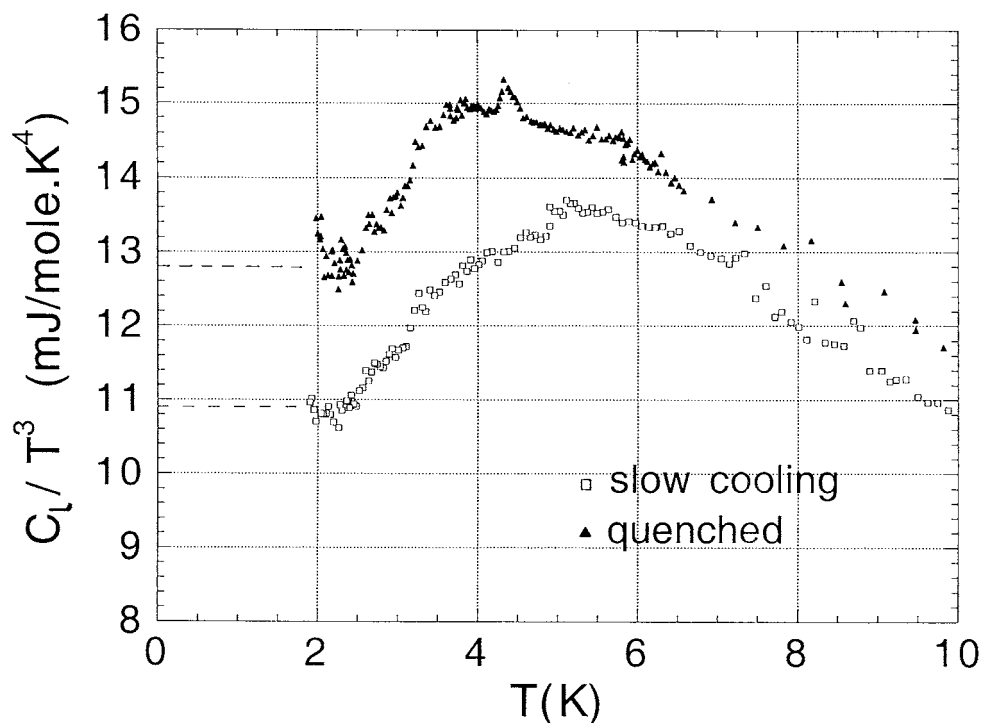


Figure 3. The lattice specific heat (C_ℓ) divided by T^3 for slowly cooled (data: \square) and quenched (data: \blacktriangle) samples. For the metallic state, C_ℓ has been obtained by subtracting the electronic γT term ($\gamma = 11.5 \text{ mJ mol K}^{-2}$) from the total C . The dashed lines on the left-hand side are the low-temperature βT^3 contributions obtained from the analysis shown in figure 2. For the quenched state, the SDW onset transition appears as the peak at 4.5 K.

Debye temperature can be calculated from the usual formula: $\theta_D^3 = \frac{12}{5}\pi^4 r R \beta^{-1}$, with R the gas constant and r the total number of atoms in the formula unit (here $r = 57$). This yields a ‘normalized’ value, which takes into account the role of optical modes at intermediate temperatures. The Debye temperatures are $205 \pm 2 \text{ K}$ for the quenched state and $216 \pm 2 \text{ K}$ for the slowly cooled state. We have used the same formula in order to compare to literature data: the Orsay group [4] gives for the slowly cooled metallic state $\gamma = 10.5 \pm 0.5 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $\beta = 11.5 \pm 0.5 \text{ mJ mol}^{-1} \text{ K}^{-4}$ (hence $\theta_D = 213 \pm 3 \text{ K}$), in excellent agreement with our results for the same state in a similar T -range[†].

At this step, it is interesting to note that, in contrast to our previous results for PF_6 , AsF_6 and Br salts [12], which all undergo metal–insulator transition at $T_c \simeq 12 \text{ K}$ with a SDW insulating ground state, the specific heat of the relaxed metallic sample is completely independent of the timescale of the experiments, as proved by the overall excellent agreement between the results from the two transient-heat-pulse methods (which differ by a factor of ~ 10 in the values of τ) and the ac ($f = 8 \text{ Hz}$) method of the Orsay group. We have previously pointed out the occurrence of large time-dependent effects in the SDW ground state [12]. In the case of the

[†] The alternative definition of the Debye temperature is the true acoustic definition, taking into account only the three acoustic branches. This definition, only valid in the T -range of the T^3 -variation, enables a direct comparison to be made to the sound velocities if they are available, which is not the case for this compound. In that case $(\theta_D^{\text{ac}})^3 = \frac{12}{5}\pi^4 R \beta^{-1}$, which yields $\theta_D^{\text{ac}} = 56.1 \pm 0.5 \text{ K}$ for the slowly cooled sample and $53.2 \pm 0.5 \text{ K}$ for the quenched state.

quenched sample, with a SDW state below 4.5 K (see later), we have no available comparison to another experimental method.

In figure 3 we have reported the temperature dependence of the lattice contribution divided by T^3 from 1.8 to 10 K, after removing the electronic contribution γT for the metallic sample. The dashed lines on the left-hand side represent the low-temperature βT^3 limit obtained from the previous C/T versus T^2 analysis, that we consider as the Debye limit regime. The lattice specific heat is characterized by bumps centred at about 3.5–4 K for the quenched state and 5 K for the slowly cooled state. Similar bumps were observed for PF_6 , AsF_6 and Br salts, at higher temperature (about 7.0 K for all three samples). We consider these low-temperature bumps to be related to low-frequency phonon modes, common to this quasi-1D structural family. Similar low-frequency modes have been measured in the specific heat of other quasi-1D compounds, as a maximum in C/T^3 at 12 K in the blue bronze $\text{K}_{0.3}\text{MoO}_3$ [15, 16], 7 K in the Pt-chain compounds ‘KCP’ [17] and down to 1.7 K in $(\text{TaSe}_4)_2\text{I}$ [18]. Their origins are low-lying transverse acoustic or optical modes, related to the 1D structural property [16].

In a natural way, we simulate such optic-like modes by discrete Einstein oscillators, as we have done for the PF_6 salt, in close connection with the frequencies measured by means of far-IR reflectivity which are available for both PF_6 [19] and metallic ClO_4 [20]. In the case of PF_6 , for the electric field parallel to the a -axis, two sharp peaks were measured at 18 cm^{-1} and $45 \pm 5\text{ cm}^{-1}$ (equivalent to 26 K and 64 ± 7 K). Two similar modes, but shifted towards lower frequency, were measured for metallic ClO_4 at 7 and 25 or 29 cm^{-1} (equivalent to 10 and 36–41 K [20]). At first sight, the shift of the C/T^3 maximum from 7 K for PF_6 to 4 or 5 K for ClO_4 seems well correlated with that of the two first IR modes for each compound. Also in a first approximation, we can account for the C/T^3 maximum below 8 K for metallic ClO_4 by an Einstein contribution of energy $E_1 = 26$ K (almost the mean value of the two first IR modes) in addition to the low- T Debye limit, but obviously such an analysis fails at higher temperature due to the very rapid decrease in C/T^3 †.

A small peak at $T = 4.5$ K for the quenched sample appears as the signature of the SDW transition. We will discuss this in more detail later in the text.

Independently of the contribution of the Einstein modes, the rapid decrease of C/T^3 in the higher-temperature range cannot be explained by the usual assumption of deviation of the acoustic contribution from the T^3 -law starting at least around $\theta_D/20$: it is the same argument that we have already used for PF_6 , with a similar value of θ_D (198 K). For instance, for the quenched state with $\theta_D = 205$ K the generalized Debye function starts to deviate from the cubic low- T regime only at $T \sim 16$ K, and at $T = 26$ K the calculated deviation reaches 10% while the measured deviation is larger than by a factor of two. We have previously analysed the acoustic phonon contribution in this T -range using a T^α ($\alpha < 3$) power law. Such a sub-cubic regime for the lattice contribution can be interpreted within the model of Genensky and Newell [21] as originating in the strong anisotropy of the force constants along or between adjacent chains. In an intermediate-temperature range, the abnormal contribution varying as $T^{2.5}$ for the transverse vibrations and the usual T^3 -contribution from longitudinal vibrations result in a total specific heat varying as T^α , with the power-law coefficient α lying between 2.5 and 3. At low temperatures, the crossover temperature T^* between the low- T Debye regime and the T^α -regime is determined by the ratio $\Gamma/\sqrt{4\kappa}$, i.e. $T^* \simeq \theta_D(\Gamma/\sqrt{4\kappa})$, Γ being the force constant of adjacent chains and κ the bending force constant along one chain. This model has been applied in the case of chain-like compounds such as polymers, e.g. crystalline metallic polysulphur nitride $(\text{SN})_x$ [22], hexagonal selenium [23] and crystalline polyethylene [23, 24],

† It is not clear whether the shift from 5 K to 3.5–4 K between relaxed and quenched samples can be explained in relation with the IR reflectivity experiments. The reader might wish to refer to reference [19] and particularly the discussion of figure 9 in this reference.

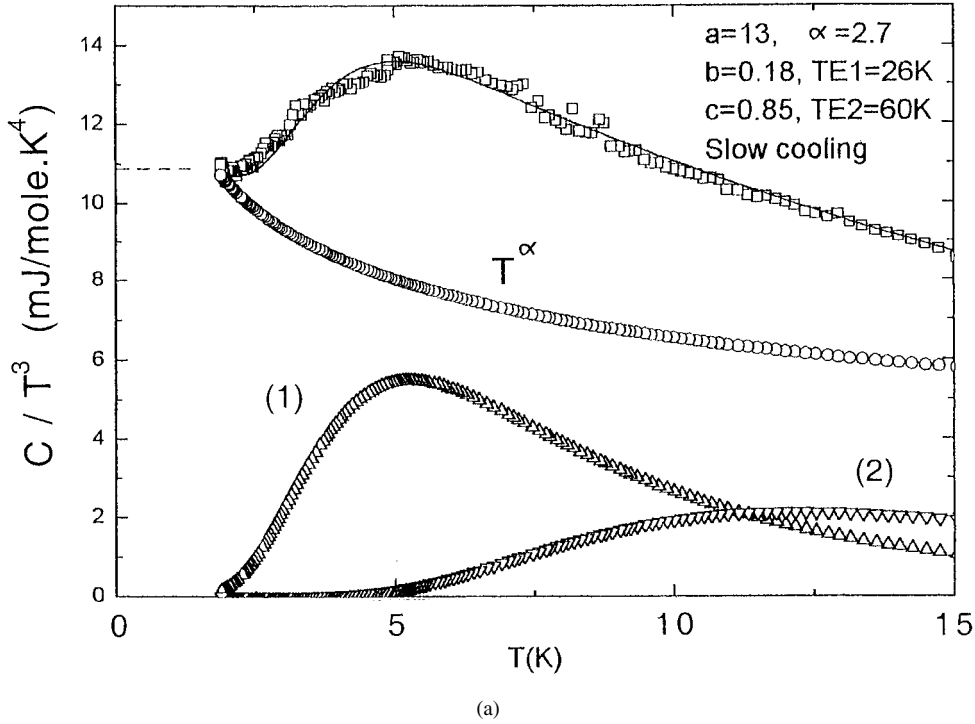


Figure 4. The process of fitting of the lattice contribution for data below 15 K, for both samples. Above 2 K, C_ℓ is analysed as the sum of an acoustic T^α -contribution and two Einstein contributions. The frequencies of the first Einstein mode θ_1 are in good agreement with those of the low-lying optical modes measured by IR reflectivity for the metallic sample. Values of the parameters are reported in table 1.

and also for low-dimensional charge-density-wave (CDW) compounds such as NbSe₃ [25] or the Pt-chain compound KCP [17]. In the case of the latter CDW compounds, T^* was estimated to be of the order of 1 K or less.

Due to the presence of the order-disorder transition at 24 K, we have limited the upper fitting range to 15 K, instead of 35 or 40 K as in our previous study [12]. We have introduced two Einstein modes of frequencies θ_1 and θ_2 , the first one being directly related to the far-IR data, the second as a free parameter, so the fitting expressions are

$$C = \begin{cases} \beta T^3 + bC_{\theta_1} \simeq \beta T^3 & (T < T^*) \\ aT^\alpha + bC_{\theta_1} + cC_{\theta_2} & (T > T^*). \end{cases}$$

In the formula, C_θ is the Einstein specific heat[†]. Note that β is not a free parameter: it is determined from the C/T -versus- T^2 analysis of figure 2. Results of the fitting procedure are shown in figures 4(a) and 4(b) for slowly cooled and quenched samples, respectively, and the fitting coefficients are reported in table 1. We note that for both states, the θ_1 -value is in good agreement with the average of the two first IR modes.

Let us now discuss some points regarding the acoustic contribution. First, the low- T cubic limit is somewhat larger in the quenched state than in the relaxed one: this can be naturally

[†] The Einstein specific heat $C_\theta = 3R(\theta/T)^2 \exp(\theta/T)/[\exp(\theta/T) - 1]^2$, where R is the gas constant and θ the Einstein temperature.

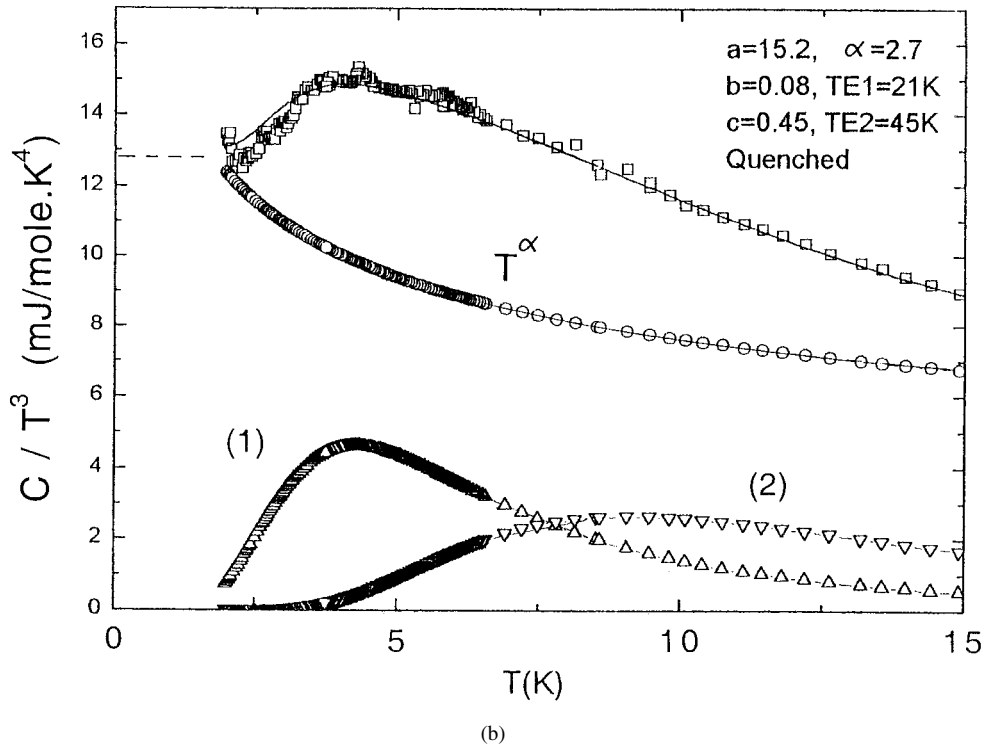


Figure 4. (Continued)

Table 1. Parameters used in fitting the lattice contribution for the two states of $(\text{TMTSF})_2\text{ClO}_4$, with the formula $C = \beta T^3 + bC_{\theta_1}$ ($T < 2 \text{ K} = T^*$) and $C = aT^\alpha + bC_{\theta_1} + cC_{\theta_2}$ ($T > 2 \text{ K} = T^*$). All parameters are in units of $\text{mJ mol}^{-1} \text{K}^{-1}$ for C . θ_D is the Debye temperature extracted from the lattice β -coefficient as defined in the text. Values of β and θ_D for the metallic state from reference [4] are reported for comparison.

State	α	a	θ_1 (K)	b	θ_2 (K)	c	β ($\text{mJ mol}^{-1} \text{K}^{-4}$)	θ_D (K)
Slowly cooled (metallic)	2.7	13	26	0.18	60	0.85	10.9 ± 0.3	216 ± 2
Quenched (SDW below 4.5 K)	2.7	15.2	21	0.08	45	0.45	12.8 ± 0.3	205 ± 2
Metallic state (from reference [4])							11.5 ± 0.5	213 ± 3

explained by the more disordered structural state of the anions in the quenched state. Second, a significant difference between the ClO_4 and PF_6 , AsF_6 and Br salts is that the α -coefficient of the T^α power law is closer to 3 (with the same value of 2.7 for both states) for ClO_4 than 2.4 ± 0.1 as for the three other salts: this means that the anisotropy of the lattice force constants is less for ClO_4 than for the other salts. Third, there is probably some uncertainty in the determination of the crossover value T^* : from the raw C/T^3 data, deviation from the cubic regime occurs between 2 and 2.5 K. We estimate that $T^* = 2 \text{ K}$ is the lower limit, so it remains in agreement with the value of 2.5 K obtained for the other three salts PF_6 , AsF_6 and Br .

3.2. SDW transition

In figure 5 we report C/T^3 for the T -range where the anomaly ascribed to the SDW transition in the quenched sample occurs. Indeed, this transition is expected to occur around 4 K for a quenching rate of 3.3 K s^{-1} through the anion-ordering (AO) transition [26,27]. This is the first thermodynamical observation of the SDW transition in the ClO_4 salt. Similarly to the case for the PF_6 , AsF_6 and Br compounds, its shape is rather symmetric and is not the λ -shape characteristic of a mean-field (MF) second-order transition. Nevertheless, we have attempted a MF-like analysis, as shown in figure 5: we can estimate a possible ΔC jump at $T_c = 4.45 \text{ K}$, with $\Delta C/T^3 \simeq 0.7 \text{ mJ mol}^{-1} \text{ K}^{-4}$; using the usual BCS expression $\Delta C = 1.4\gamma T_c$ for the electronic condensation [28], this yields a γ -value of $\simeq 10 \text{ mJ mol}^{-1} \text{ K}^{-2}$, which is similar to the values for metallic slowly cooled ClO_4 obtained by the Orsay group and in this work.

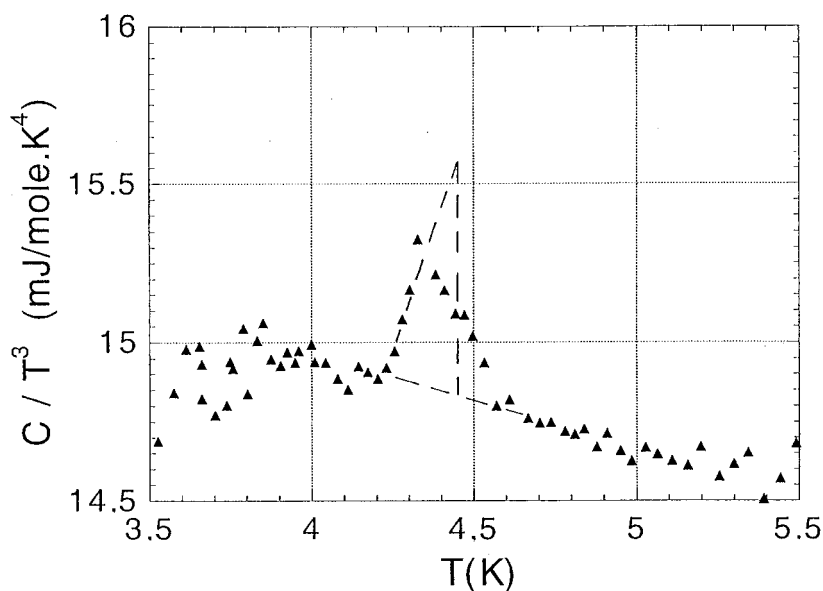


Figure 5. C/T^3 versus T for the quenched sample in the vicinity of the onset of the SDW transition. The attempt at a mean-field jump analysis is shown by the dashed lines.

To estimate the precision of γ , we notice that the transition contribution is only 3% of the total C and the data scattering is 1%–1.5% of the total C between 4 and 5.5 K, so the uncertainty in γ is about 30–50%. The relatively good agreement with a MF analysis indicates that free electrons are completely condensed due to the opening of the SDW gap, and that the SDW originates from the contribution of itinerant electrons.

The present value of γ is considerably smaller than that estimated for PF_6 and AsF_6 salts (and to a lesser extent than that estimated for the Br salt) [12], for which large discrepancies with the MF analysis were pointed out. For the ClO_4 salt, we obtain a phonon dimensionality parameter $\alpha = 2.7$ for both states at $T \gtrsim 2 \text{ K}$. This suggests that the lattice specific heat deviates less from the Debye law for ClO_4 than for PF_6 , AsF_6 and Br (α is close to 2.5 for the latter three compounds). Then the effective electronic dimensionality is higher for ClO_4 , in agreement with the description of the general phase diagram of $(\text{TMTTF})_2\text{X}$ and $(\text{TMTSF})_2\text{X}$, which could explain why the MF analysis is much more nearly correct for ClO_4 , for both quenched and relaxed states, than for PF_6 , AsF_6 and Br. We note that the Orsay group obtained a ratio

$\Delta C/\gamma T_c = 1.67$, instead of 1.43 for exact MF-BCS theory, at the superconducting transition for the metallic state [4].

We have checked for first-order effects with great care by analysing the data in the transition region. We did not find any step in the perfect exponential decay of the sample temperature after the heat pulse, which means that no latent heat is involved during the transition within the experimental resolution. The peak position is highly reproducible in experiments with increasing or decreasing temperature (the cooling and heating rates are both around 0.3 K h^{-1}). This means that no hysteresis was observed. Therefore, from our accurate measurements, we confirm that the SDW transition is second-order type without any detectable character of first-order-like hysteresis and latent heat. We reached the same conclusion for the PF_6 , AsF_6 and Br salts that we previously made measurements on [12].

3.3. Anion order–disorder transition

Data are reported for the whole T -range as C/T versus T^2 in figure 6 for both samples; they show the progressive evolution from the regime of the low- T ($\gamma T + \beta T^3$) limit to the anion-ordering transition at $T^2 = 585 \text{ K}^2$ ($T_{\text{AO}} = 24.2 \text{ K}$). On increasing T , data firstly go beyond the low- T regime (the straight line represents the slowly cooled metallic state with $\gamma = 11.5 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $\beta = 10.9 \text{ mJ mol}^{-1} \text{ K}^{-4}$), which corresponds to the excess C/T^3 phonon contribution (see figure 3 for C_ℓ/T^3) with a maximum at $T = 5 \text{ K}$ for the metallic state, and thereafter cross this limit regime again at $T^2 = 100 \text{ K}^2$. At higher T , C/T progressively

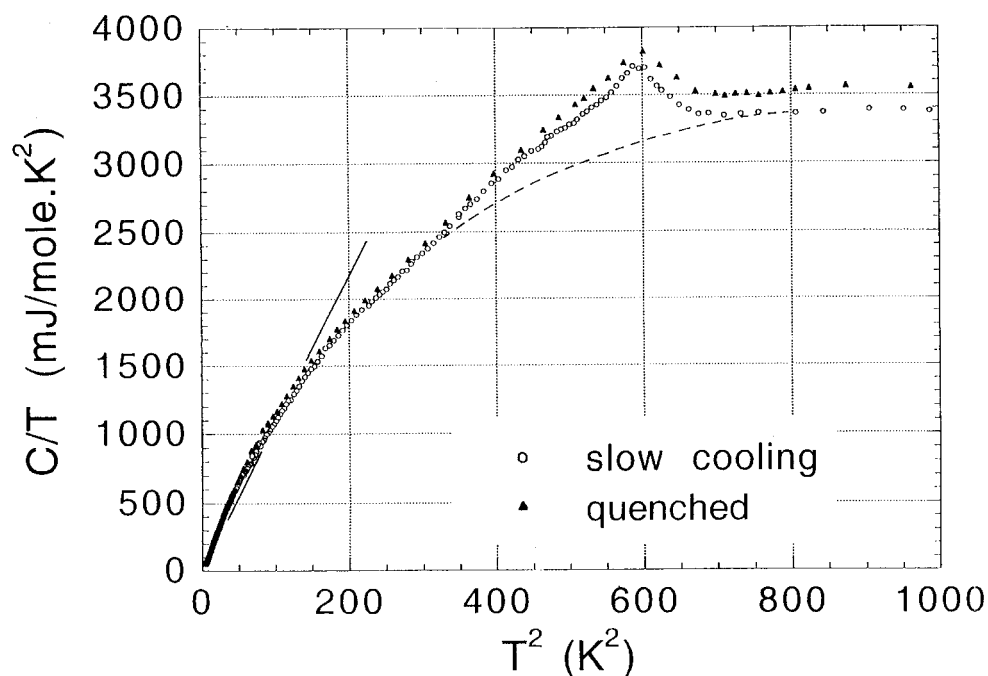


Figure 6. The specific heat as C/T versus T^2 over the whole temperature range investigated for slowly cooled (data: \circ) and quenched (data: \blacktriangle) samples. The straight line on the low- T side shows the $\gamma T + \beta T^3$ regime defined as shown in figure 2 for the slowly cooled sample. Also shown is the background used to estimate the anomaly of the anion-ordering transition at $T_{\text{AO}} = 24.2 \text{ K}$, for the slowly cooled sample.

saturates and clearly shows the AO transition as the local maximum at $T = 24.2$ K. In this T -range, the electronic contribution is totally negligible for the metallic sample.

Previous measurements in a similar T -range ($25 \leq T^2 \leq 1250$ K²) were reported by the Orsay group [11] for a quenched sample (with a rate of 10 K min⁻¹, which is not sufficient to obtain the SDW ground state [10, 26, 27]) and a relaxed one (at a rate of 0.1 K min⁻¹); they only differ, at maximum by $\sim 5\%$, in the vicinity of the transition. Unlike our data, which slightly deviate from the $\gamma T + \beta T^3$ limit regime up to $T \simeq 10$ – 15 K, those of reference [11] go substantially beyond this limit regime (defined with similar values of γ and β —see section 3.1) even at low temperature. At $T = 10$ K, the deviation for the data of [11] is by a factor of two, whereas in our case there is near coincidence with the low- T regime. This large departure, which occurs very rapidly between 2 and 5 K, was not discussed in reference [11].

Continuing this deviation, the data of reference [11] for the quenched state exceed our present data by about 50% in the range from 20 to 30 K. This could perhaps explain the large difference between the entropies below the AO transition obtained by the two groups, as will be discussed later.

In order to estimate the excess specific heat related to the transition, we have subtracted from the total C a background (the dashed curve in figure 6 for the slow-cooled sample; an identical procedure was used in the case of the quenched sample) defined by a polynomial fit of the data outside the transition region, i.e., below 15 K and above 27.5 K, in a similar way to in reference [11], but at a somewhat smaller value of the upper limit (30 K in [11]). The resulting excess is reported in figure 7 for both states: it exhibits a well-defined asymmetric

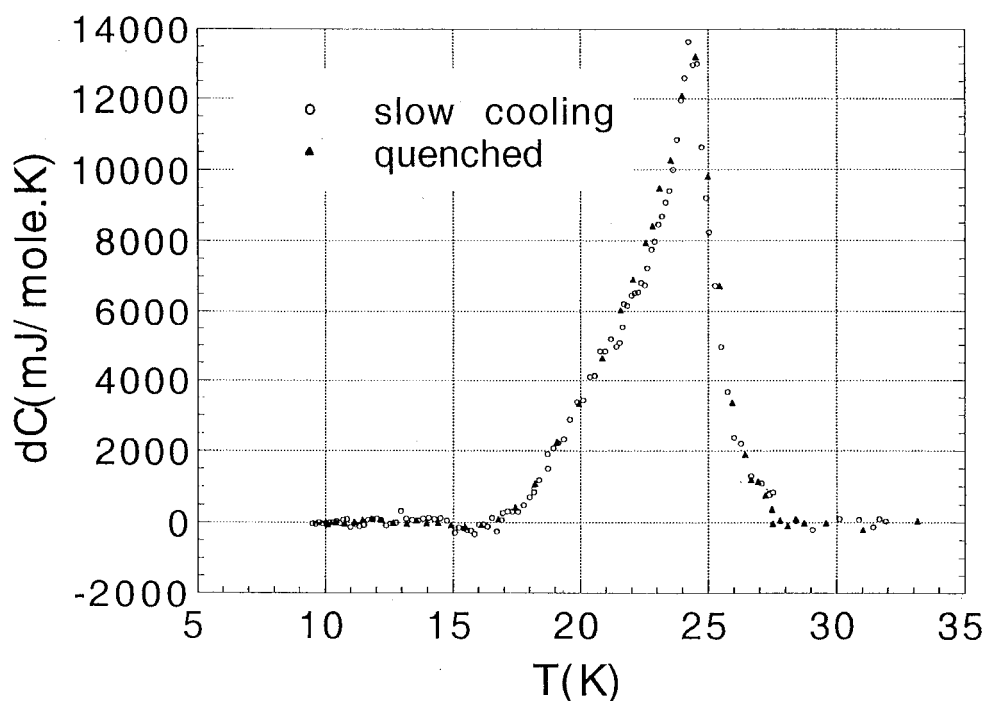


Figure 7. The specific heat dC of the anion-ordering transition, for both samples, estimated as the difference from the background, as shown in figure 6 for the slowly cooled sample.

shape characteristic of a second-order transition, with the maximum at $T_c = 24.2$ K, as reported in initial x-ray investigations [29]. We recover the same amplitude of the anomaly for both samples despite the small ($\sim 5\%$) difference in absolute value of C above the AO transition.

At first sight, it seems surprising that one recovers exactly the same anomaly since, if one could preserve the anion disorder of the quenched sample, one would recover a much lower entropy than for the relaxed ordered sample. This can be explained by the experimental data-acquisition procedure. For the slow-cooled sample, measurements are done on cooling at a rate of 0.3 K h^{-1} between two successive data points. This is a sufficiently low rate for obtaining a fully ordered sample[†]. However, for the quenched sample, data are taken on reheating, at a similar rate of $0.3\text{--}0.5 \text{ K h}^{-1}$. We interpret the similarity of the AO anomaly for the reheated quenched sample as being due to disorder annealing effects which start to occur at temperatures 5 K below the AO transition, i.e. at $17\text{--}18$ K [29–31]. The kinetics of anion reordering has been carefully studied by means of x-ray measurements [31] and we can conclude that our low reheating rate allows a spontaneous reordering of the anions on approaching T_{AO} .

The integration of the excess dC , as defined in figure 7, yields the entropy under the transition:

$$\Delta S = \int_{16 \text{ K}}^{28 \text{ K}} \frac{dC}{T} dT = 0.287R = R \ln(4/3)$$

with $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, the gas constant, in comparison with a value $R \ln(2)$ expected for an order–disorder transition with two possible configurations for the ClO₄ tetrahedron in the high-temperature disordered state [29]. This ideal value for fully ordered anions seems to have been measured for the relaxed state, obtained at a cooling rate of 6 K h^{-1} , by the Orsay group [11]. For the quenched state, they measured an entropy reduced to 80% of that for the relaxed state, which means that the annealing effects were smaller than in our case, but the experimental data-acquisition procedure is not detailed in reference [11].

Similar values of the entropy lower than the ideal $R \ln(2)$ value have been measured for the AO transition in (TMTSF)₂ReO₄ (perrhenate) and (TMTSF)₂BF₄ salts [32]. For the perrhenate salt, a great sensitivity of the value to the crystal used has been reported; it varies between $R \ln(1.25)$ and $R \ln(1.6)$ for two samples characterized by a well-shaped peaked anomaly. More strikingly, the smallest entropy is obtained for the sharpest transition, which probably corresponds to the fewest defects. A similar low value, $R \ln(1.2)$, was measured for the BF₄ salt. In the framework of a two-configuration state in the disordered phase, these results imply that ordering is generally incomplete at the transition, from the thermodynamic measurements.

We can consider two possible origins for the large differences in specific heat above 5 K compared to the findings of reference [11], particularly as regards the entropy of the transition: one due to the dynamics of the measurements and the other due to the difference in amount/‘quality’ of sample.

- (i) In contrast with the ac method ($f = 8$ Hz) of reference [11], a semi-adiabatic method is used by us, with a relaxation time constant $\tau = R_\ell C$ of several tens of seconds between 20 and 30 K. After the heat pulse (with a T -excursion of about 1% of the mean temperature), the immediate cooling rate provided by the thermal relaxation is much larger than the ‘mean’ cooling rate. We can estimate a maximum value of this instantaneous rate of 9 K h^{-1} at 30 K and 16 K h^{-1} at 20 K, to be compared with the ‘mean’ value of 0.3 K h^{-1} . However, such a value remains in a range which ensures that at least 95% of the ClO₄ ions become ordered (see figure 3 in reference [31]).

[†] From figure 3 in reference [31], more than 90% of ClO₄ ions are ordered if the cooling rate is $\lesssim 0.7 \text{ K min}^{-1}$ (or 40 K h^{-1}).

- (ii) The second point is as regards the total amount of individual crystals. We use a much larger amount than the Orsay group (they indicate eight single crystals of total weight 3.2 mg in reference [4]). In view of a possible large degree of sensitivity of the AO entropy in different crystals, as revealed for the ReO_4 and BF_4 salts, one can suppose that in the present experiment, where we have not selected just a few samples, our data may reflect a larger distribution of entropy values.

We can conclude at this step that, despite the non-ideal character of the transition (i.e. $S < R \ln 2$), the ordering conditions remain ones which stabilize a low-temperature metallic state with the same characteristics (electronic density of states at E_F and superconducting transition) as previously defined [4].

We have checked for possible first-order effects in the AO transition. From these thermodynamic data, as in the case of the SDW transition, we conclude that the AO transition is second order, or the first-order character is very weak. We have also analysed the data in order to check for possible Gaussian critical fluctuations in the dC excess, since the x-ray diffraction studies indicate quasi-isotropic pretransitional fluctuations extending up to 30–40 K [33]: in that case, the mean-field treatment and usual (3D) Gaussian fluctuations could be observed. But there is no possibility of fitting the dC tails by power laws as functions of the reduced temperature $t = |1 - T/T_c|$. Instead, a semilogarithmic plot of $\ln(dC)$ versus t (see figure 8) allows a good fitting for either $T < T_c$ or $T > T_c$ in the range 19 to 27.5 K with

$$dC = dC_0 \exp(-mt) \quad \text{with } dC_0 = 13840 \pm 50 \text{ mJ mol}^{-1} \text{ K}^{-1}$$

and $T_c = 24.23$ K; $m^-(T < T_c) = 7.6 \pm 0.1$ and 6.2 ± 0.1 for the slow-cooled and quenched samples respectively; $m^+(T > T_c) = 22 \pm 2$ for both samples, which are indistinguishable within the data dispersion. Downward deviations from this law occur either at $T > 27.5$ K or $T < 18.5$ K; these are probably the effects of the imprecision of the background determination.

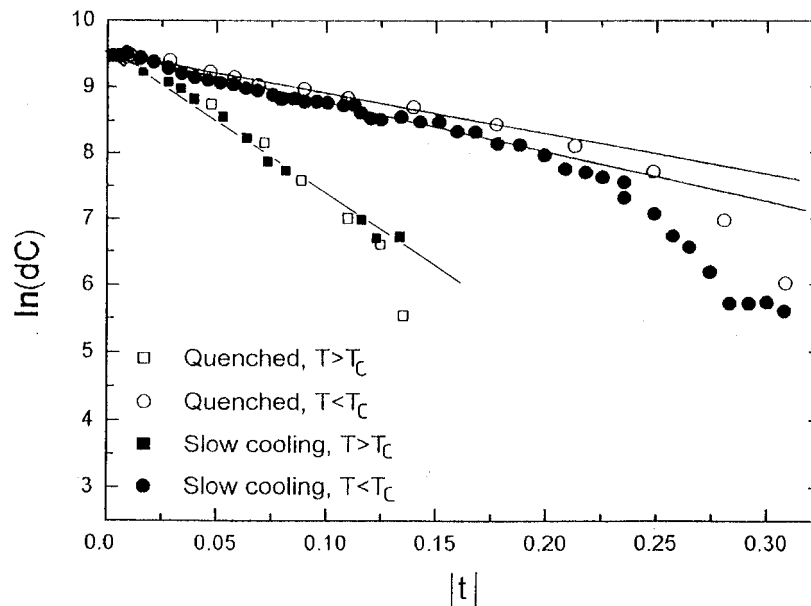


Figure 8. A semilogarithmic plot of the data of figure 7, versus the reduced temperature $t = |1 - T/T_c|$ with $T_c = 24.23$ K.

The discontinuity of the slope of $\ln(dC)$ at $T = T_c$ confirms the generally admitted second-order character of this structural phase transition, in contrast to the (weak) first-order character in the case of ReO_4 and BF_4 anions [32]. Failure of the mean-field and ordinary fluctuations treatment in the vicinity of the transition can be tentatively explained by the predominant quasi-1D character of the anion–anion interactions. Ordering of the anions results in alternation along the b -axis only, corresponding to a superstructure of wavevector $(0, 1/2, 0)$. In addition, there is a weak interaction of the anions with the (TMTSF) organic stacks, which show only very weak distortion at the transition, in contrast to the case of ReO_4 salt with a distortion of the organic stacks [33, 34], and a weak first-order character of the transition [32].

4. Conclusions

Continuing on from our previous work on the thermodynamical properties of the quasi-one-dimensional organic compounds $(\text{TMTSF})_2\text{X}$, $\text{X} = \text{PF}_6$ and AsF_6 , and $(\text{TMTTF})_2\text{Br}$, we have now investigated the $(\text{TMTSF})_2\text{ClO}_4$ salt obtained either by slow cooling or quenching through the anion-ordering transition, which corresponds to metallic/superconducting and SDW ground states, respectively. We have now a general overview of the behaviour of the Bechgaard salts in this T -range (2–40 K). The specific heat is for all of the series characterized by a C/T^3 bump below 10 K, due to the non-Debye behaviour of the lattice contribution, which is centred at $T = 5$ K for the relaxed state and 4 K for the quenched state, to be compared to $T = 7$ K for the three compounds PF_6 , AsF_6 and Br. We were able to obtain a good numerical simulation of the C/T^3 variation, by means of additive contributions of single-frequency optic-like modes, in good agreement with optical reflectivity measurements, and of a T^α ($\alpha = 2.7$ for both slowly cooled and quenched samples) acoustic contribution. The α -value being lower than 3 reflects the strong anisotropy of the lattice force constants along and between chains, for these quasi-1D structures. However, this anisotropy appears to be smaller in the case of ClO_4 salts in comparison with the PF_6 , AsF_6 and Br salts, with $\alpha = 2.3$ – 2.5 .

We have carefully studied the AO transition ($T_{\text{AO}} = 24.2$ K), with the two experimental procedures of cooling, for the slowly cooled sample, and reheating, for the quenched sample. Within these kinetic conditions, there are no differences between the specific heat anomalies of the structural transition, which means that the reordering of the anions could progressively occur within our experimental timescale on approaching the transition from low temperatures. This is also in agreement with the structural x-ray studies. However, despite our supposing a full ordering of the anions with these kinetic conditions, the estimated entropy under the anomaly is lower than the ideal $R \ln(2)$ value, expected for the two possible configurations of the ClO_4 tetrahedron in the disordered state.

The SDW transition, measured for the first time by the calorimetric technique, was detected at $T_c = 4.5$ K, as expected for the high quenching rate of 3.3 K s^{-1} through the AO transition. It can be roughly analysed within a mean-field analysis of the electronic condensation, contrary to the previous results on the other three salts. We also mention the absence of time-dependent effects of the specific heat, at least in the case of the metallic state—also in contrast with our previous investigations of the insulating SDW ground state. This is a strong indication that a time effect is inherent to the pinned SDW ground state.

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