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Time-dependent specific heat below 1 K in the spin-density-wave state of $(\mathrm{TMTSF})_2\mathrm{PF}_6$

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Large time-dependence effects have been measured below 1 K in the specific heat of the spin-density-wave (SDW) compound $(\mathrm{TMTSF})_2\mathrm{PF}_6$, well below its glass transition temperature at 3.5 K. These effects indicate that most of the low-energy excitations characteristic of the disordered nature of the SDW subsystem are decoupled from the phonon bath for $t \gtrsim 1$ s. A comparison is done with the related slow heat release observed over similar long time scales (up to 10^4–10^5 s) in structurally disordered materials.

I. INTRODUCTION

Properties of broken symmetry ground states in quasi-one-dimensional (Q1D) systems, especially charge (or spin) density waves (DW's), are currently being intensively studied in condensed-matter physics. Due to the randomness and disorder resulting from interaction with randomly distributed pinning centers, DW's exist in many metastable states and consequently are characterized by a "glassy behavior" in numerous electrical or dielectric properties.[1]

These metastable states are the best revealed from low-temperature thermodynamical measurements. Thus for a broad variety of DW compounds it has been shown that additional excitations to regular phonons contribute to the specific heat C_p below 1 K.[2] On the other hand, C_p becomes strongly time dependent in this T range: initial evidence is given by the nonexponential decay of the heat relaxation after the sample has been submitted to a short heat perturbation (a pulse of 1 s or less); further evidence is the strong dependence of the kinetics of relaxation upon the duration of the heat perturbation (the effect of aging, by similarity to the spin glasses).[2,3] A typical example has already been described with the case of the charge-density-wave (CDW) compound o-TaS_3.[2–4] All these features are reminiscent of the low-T thermodynamical properties of structural glasses (SG's) or orientationally disordered crystals, i.e., orientational glasses OG's),[5–9] which are generally interpreted by the standard tunneling model.

Recently, simultaneous low-frequency dielectric measurements and calorimetric ones in the spin-density-wave (SDW) compound $(\mathrm{TMTSF})_2\mathrm{PF}_6$ (TMTSF is tetramethyltetraselenafulvalene) have presented evidence of a glass transition at $T_g \sim 3.5$ K,[10–12] well below the formation of the SDW at $T_c = 12.1$ K. Accordingly, the existence of a low-T SDW glassy phase gives stronger support to a direct comparison with thermodynamical properties of canonical SG's or OG's. In the following we will show that time-dependence effects in specific heat for DW's are much larger than in the case of canonical SG's or OG's, and that they occur under more *usual* experimental conditions. This means temperature variations which remain close to the equilibrium over the usual time spans for quasiadiabatic conditions.

II. EXPERIMENT

Here we report on a systematic investigation of the specific heat of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ in its SDW (insulating) state under various durations of the energy delivery, from about 1 s up to several tens of hours. The sample is loosely connected to the regulated cold sink at T_0 by a thermal link R_l. Depending on the mass of the sample and the value of R_l, time constants of the thermal transients in response to a heat pulse excitation vary between a few seconds at $T = 0.2$ K (for the initial regime only, see below) and $\sim$30–50 s at $T = 3$ K. Two experimental runs were performed on two samples issued from different batches. Experimental conditions and C_p data in response to *heat pulses* for the first sample are reported in Ref. 10, in the T range 0.15–7.5 K. As previously observed in CDW materials such as o-TaS_3, $(\mathrm{TaSe}_4)_2\mathrm{I}$, and NbSe_3,[2–4] a progressive deviation from an exponential decay of the transient develops on lowering T below about 0.6–0.8 K: this corresponds to a *time-dependent specific heat* which increases with time. This effect and the determination of C_p on a short-time scale (a few s) have been described in the case of TaS_3.[4] In that case, C_p is defined by the initial temperature increment determined by the initial temperature decay [method (a)] and corresponds to the minimum value of $C_p(T)$. Once subtracted, the time-

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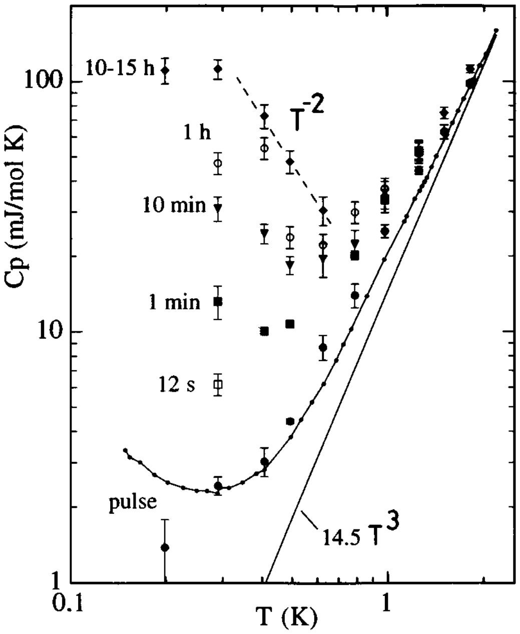

FIG. 1. Dependence of the specific heat of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ on the duration of energy delivery (t_w): from a pulse of less than 1 s up to 10–15 h. Data are reported on a log-log plot. The continuous curve represents data calculated from the initial T increment in response to heat pulses. Other data are obtained by total integration of the energy release (see Fig. 3). The straight line (T^3) is the estimated lattice contribution.

independent contributions of addenda, phonons, etc., the remaining contribution represents the low-energy excitations (LEE), defined on this short-time scale.

We have now performed a second run on another sample (0.11 g in weight), under almost similar experimental conditions, except for the value of R_l which was much smaller than in the first run, by a factor of 5 below 1 K.[13] In this experiment the dependence of C_p upon the time delivery of energy (or waiting time t_w) was studied between 0.2 and 2 K, for time spans varying from less than 1 s (pulse) up to 10–15 h ("permanent regime"). In the case of long heat delivery and time-dependent C_p, one has to regulate the power input $\dot{Q}_p$ in order to maintain constant the temperature increment $(T_i - T_0)$ above the reference T_0. When equilibrium is reached, the thermal link R_l is measured under steady-state conditions by the ratio $\dot{Q}_p/(T_i - T_0)$. Then the power is switched off and the transient $T(t)$ is recorded. The heat capacity is determined by the total heat release through the link R_l which corresponds to the overall variation of temperature from T_i to $T_0 : mC_p = Q_t/(T_i - T_0)$. Total heat release is obtained by integration over time of the instantaneous release $\dot{Q}(t) = [T(t) - T_0]/R_l$. This relation with a constant value of R_l remains valid within our linearity conditions, i.e., for a small-T excursion. This method (b) is an extension of the usual relaxation method to the case of nonexponential decay. We have also used this determination of C_p in the case of short pulses, and compared it to the usual method (a). At each temperature T_0, we have performed successive measurements corresponding to various values of t_w. During all the series, the temperature of the sample was never brought above 1.5 K.

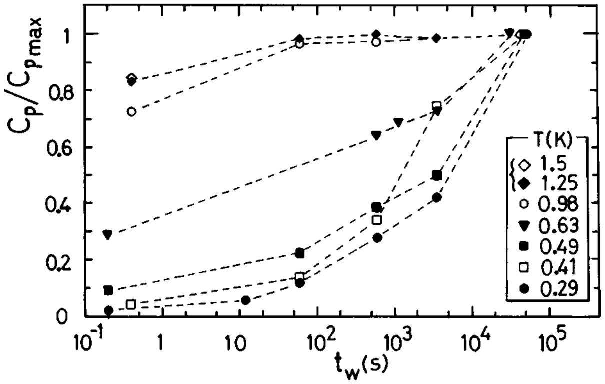

FIG. 2. Time-dependent specific heat normalized to its maximum value (for $t_w = 10\text{-}15$ h) vs t_w in a log scale at different temperatures. For pulses ($t_w < 1$ s), C_p is also obtained by integration of the heat release.

An important condition, which allows us to define C_p in this way, is that the increment $(T_i - T_0)$ remains small, as in the case of heat pulses, generally a few percent of T_0: here, up to 5–7 % maximum. We note that in the case of long heat release experiments in glasses, discussed below, the initial temperature T_i (also called the "charging" temperature) is much larger than the equilibrium one: generally $T_i \geqslant 2T_0$ or $3T_0$, and therefore any determination of C_p is forbidden in such conditions.

The main difficultly in such a long-time experiment, which determines the accuracy of data, is to achieve a good stabilization of T_0 over a *very long time scale*, up to about 24 h at the minimum temperature; indeed, the weight in the total integrated energy of the long-time relaxational process approaching T_0 is large compared to the initial part. Error bars indicated in Figs. 1 and 3 correspond to relative fluctuations of T_0 of the order of $\pm 2 \times 10^{-4}$ (which correspond to fluctuations of the heat leak $\delta\dot{Q} = \delta T_0/R_l = \pm 3$ pW at $T = 0.29$ K, in Fig. 3).

III. RESULTS AND DISCUSSION

C_p data obtained with both methods between 0.2 and 2 K are reported in Figs. 1 and 2 and the corresponding thermal transients at $T = 0.29$ K in Fig. 3. We first discuss data obtained in response to *heat pulses*. As in our previous experiment,[10] almost no deviation to an exponential regime, and therefore no time dependence of C_p over a time span between 1 and several tens s, could be detected above $T \sim 1$ K. Results above 2 K were discussed elsewhere.[11,12] In this T range C_p is dominated by the lattice contribution, and exhibits a jump between 3 and 4 K, that we have ascribed to a glassylike transition occurring in the electronic SDW subsystem. Below 2 K, and down to 0.4 K, C_p defined by method (a) is reproducible to within 20% with data of the first sample[10] despite the large variation of R_l and consequently of the time constant of the transients (by a factor of 4). As shown in Fig. 1, and previously discussed in Ref. 10, C_p deviates progressively from a T^3 law on decreasing T, due to the presence of additional contribution of LEE's. This deviation is accentuated below 0.5 K, simultaneously with the occurrence of nonexponential kinetics. Finally, below 0.3 K, an upturn appears, but of smaller amplitude than in the

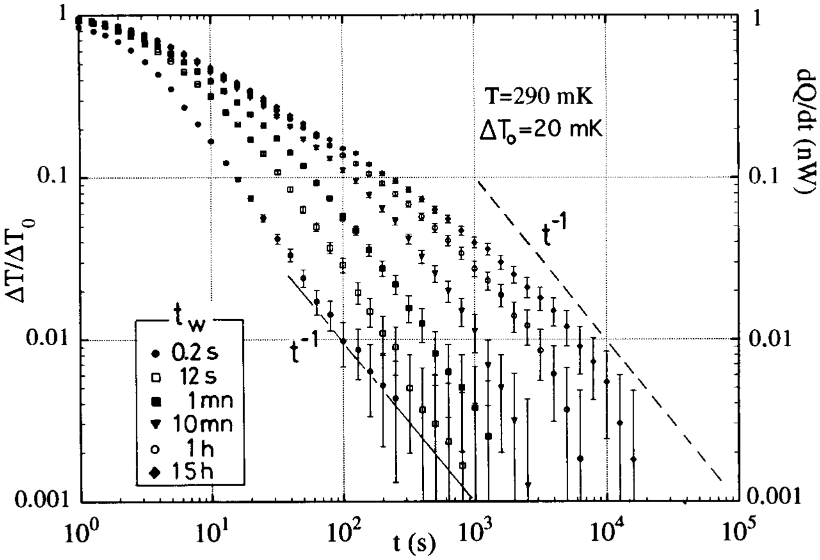

FIG. 3. Temperature decay $\Delta T(t)/\Delta T_0$ (left scale) and corresponding heat release (right scale) vs time, for different values of t_w, at $T=0.290$ K. The origin of time starts when energy delivery is switched off. Initial increment ΔT_0 represents 7% of T_0. Error bars represent relative fluctuations of $\pm 2\times 10^{-4}$ in the reference temperature T_0. The t^{-1} lines are shown for comparison.

previous experiment. The excellent reproducibility ($\leqslant 5\%$) between the two experiments in the T range 1.5–3 K where the lattice term βT^3 is dominant, confirms the β value of (14.5 ± 0.5) mJ/mol K^4.

Now we compare results obtained by method (b), i.e., by integration of the total-energy release for increasing durations t_w of the energy delivery. When compared with method (a) for pulse conditions there is a generally good agreement (except at $T=0.2$ K), although data are systematically larger below 1.5 K. However, as soon as t_w increases, C_p shows a strong nonlinear effect: it becomes very sensitive to t_w on lowering T below 0.8 K, as shown in Fig. 1. At a fixed temperature C_p increases with t_w, but it reaches a saturation: there is no more evolution of $C_p(t)$ at $T=0.2$ K when one increases t_w from 12 to 24 h. We have already observed this saturation effect for large values of t_w in the *dynamics* of the relaxation process $\Delta T(t)$, either in TaS$_3$,[3] or in the previous experiment in (TMTSF)$_2$PF$_6$ where a preliminary study of the kinetics was done.[2] We interpret this saturation by the fact that the DW subsystem reaches its own thermodynamic equilibrium over time scale of $\sim 10^4$ s at $T\simeq 0.2$ K. In Fig. 2 we have reported the variation of C_p normalized to its maximum value as a function of t_w. The time dependence effect on C_p is tremendously large. At $T=0.3$ K it can be seen that C_p for $t_w\sim 10$ h is *50 times larger* than the value defined on a short-time scale.

The temperature dependence of $(C_p)_{\max}$ (Fig. 1) indicates the tail of a Schottky anomaly ($\propto T^{-2}$) below 0.6 K, saturating in a plateau at $T=0.3$ K.[14] This T^{-2} dependence was already observed in TaS$_3$, for which a similar analysis was also done.[15]

Clearly this nonlinear behavior is related to the kinetics of the LEE's, as in the case of structural glasses. The progressive deviation of C_p from the background T^3 law for increasing t_w is the manifestation of the decoupling of the LEE's from phonons at least over time scale $\geqslant 1$ s. We note that this time scale is very large in comparison to structural glasses: here almost *all* (98%) of the specific heat at $T=0.2$ K is decoupled from phonons at $t=1$ s, whereas a similar decoupling occurs in a-SiO$_2$ at $T=0.1$ K, at only 15 μs.[5]

IV. COMPARISON WITH STRUCTURAL GLASSES

As we are not aware of other examples of similar time-dependence effects below 1 K except for SG's (or OG's), we intend to compare our results in DW systems to some model glasses. In these systems, the time dependence of C_p occurs below 1 K for the time scale $\sim 10^{-5}$–10^{-1} s with a logarithmic time variation. No time dependence is observed in the t range $\sim 10^{-1}$–10^2 s, which is the usual time span for quasiadiabatic conditions, either in SG's (SiO$_2$, Refs. 5, 6, and 9) or OG's [KBr:KCN (Ref. 8)], whereas we have here large effects in this range. In addition, long-time heat release is observed in the t range 10^2–10^5 s, well obeying a law $\dot{Q}(t)\propto t^{-1}$ in various disordered systems.[5,7,17–19] This dependence is a direct consequence of the logarithmic time dependence of the specific heat, a prediction of the tunneling model (TM) of two-level systems,[7,20]

Obviously, much larger effects are measured in DW's than in glassy materials: (a) A $C_p(t)$ effect already exists in the t range 1–10^2 s. (b) The amplitude of the LEE contribution decoupled from phonons is much larger. The long-time equilibrium value *increases* as T^{-2} at low T. (c) Long-time heat release exists under experimental conditions which remain within the linearity conditions: $T_i\simeq T_0$.

Now a qualitative comparison of our data to the predictions of the TM can be done. It is clear from Fig. 2 that in the T range $T\lesssim 0.5$ K, where C_p is the most sensitive to t_w, variations are not logarithmic functions of the time. In this range, variations of C_p represent essentially those of C_{LEE}, due to the vanishing lattice contribution (see also Fig. 4). It is interesting to note that the deviation (an upward curvature) looks very similar to that in vitreous silica,[5,6] although the time scales are very different.

The second way to compare our data to the case of glasses is to analyze the slow heat release $\dot{Q}(t)$ which is directly given by $\Delta T(t)/R_l$, t being the time elapsed after switching off the heat input (or letting cool down the sample from some initial temperature $T_i\gg T_0$ in the case of glasses). In Fig. 3 we have reported the thermal transients at $T=0.290$ K corresponding to increasing waiting times. Concerning a

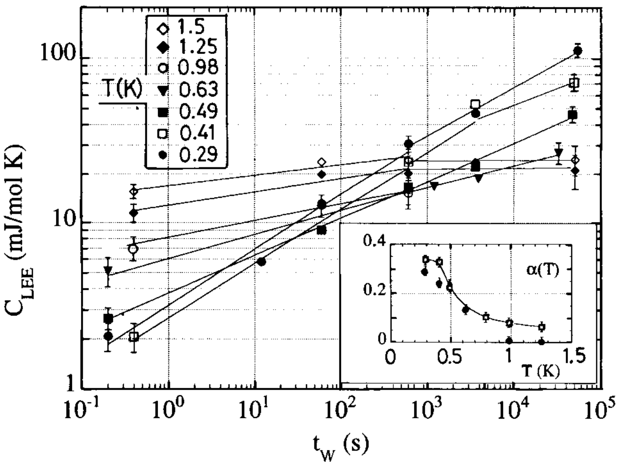

FIG. 4. Log-log plot of the low-energy excitation contribution to the specific heat of $(TMTSF)_2PF_6$, $C_{LEF} \propto t_w^{\alpha}$, as a function of the duration of the heat perturbation, t_w, at given temperatures (same symbols as in Fig. 2). Inset: temperature dependence of coefficient α: (○) for short times $t_w < 600$ s; (●) for large $t_w > 600$ s.

possible t^{-1} variation, this can be obeyed for $t_w \lesssim 1$ min and for time $\gtrsim 10$ s. However, for longer waiting times, deviations increase. We do not have to take into account the initial decay regime within a few seconds. Indeed, we have verified that this initial time constant is essentially determined by the time-independent contributions (addenda plus phonons), which confirms that most of LEE contribution is decoupled from phonons on this time scale. We conclude at this stage that it is difficult to reconcile our data with the predictions of the TM.

From the data of Fig. 3, the magnitude of energy release at large time ($t \sim 10^3$–10^4 s) corresponding to long waiting time ($t_w = 15$ h), is $\dot{Q} = 4 \times 10^{-2}$ nW (or 4×10^{-1} nW per gram of material) at $t = 10^3$ s, and $\dot{Q} \simeq 5 \times 10^{-3}$ nW (or 5×10^{-2} nW/g at $t = 10^4$ s. A direct comparison to glassy materials is not possible, since the experimental procedure is very different. We mention that in vitreous silica for $T_0 = 0.2$ K and for a "charging" $T_1 = 1.0$ K, a heat release of less than 10^{-2} nW/g is measured at $t = 10^3$ s, which is an order of magnitude smaller than here. In polymers, heat release per unit mass of ~ 0.1 and 2 nW/g were measured in polystyrene (PS) and polymethylmethacrylate (PMMA), respectively, for $T_0 = 90$ mK and $t = 10^4$ s, but after cooling from 80 K.[19]

Finally, the dynamics of the relaxation process due to LEE can be estimated more precisely. After subtraction of the phonon contribution, the contribution from LEE to the specific heat, C_{LEE}, is drawn in a log-log plot in Fig. 4 as a function of t_w at given temperatures. C_{LEE} can be analyzed by a power-law dependence: $C_{\mathrm{LEE}} \sim t_w^{\alpha}$. α can be estimated for short $t_w \lesssim 600$ s or long $t_w \gtrsim 600$ s. The temperature dependence of the power-law exponent α for both short times (empty symbols) and long times (full symbols) reported in the inset of Fig. 4 demonstrates the very pronounced increase of the LEE contribution below ~ 0.6 K.

The unusually long LEE relaxation times measured in DW systems are especially interesting with respect to the universal features of glasses. Whereas for glasses the specific heat, measured in similar experimental conditions as here, reaches its equilibrium value within a few seconds, here C_p continues to evolve up to 10^4–10^5 s. In the framework of the TM, this would imply a much larger value of τ_{min}, the shortest relaxation time of the tunneling systems via the phonons,[20] and consequently a different scattering strength of phonons by LEE's than in glasses. A value of τ_{min} of the order of ~ 0.1–1 s, as estimated from Fig. 2, would imply a very weak coupling of the LEE's to the high-frequency phonons responsible for thermal transport: this is confirmed by the absence of specific additional scattering in the phonon thermal conductivity ($K \sim T^3$, as for crystals) of CDW compounds below 1 K,[21] contrary to the glasses. This situation is quite similar to the case of the deutered mixed crystals $Rb_{1-x}(ND_4)_xD_2PO_4$ (Ref. 22) among the family of OG's.

Also at variance with the TM model, the relaxation process of the LEE's at the thermal equilibrium is thermally activated with an activation energy of ~ 1 K.[3,16] Internal degrees of freedom in the DW state responsible for these long-time relaxation processes have only recently been studied. Collective excitations are described as dislocation loops or solitons (dislocation loop of a small radius). Kinetics of these excitations at low temperature include aggregation into dislocation loops and clusters, and interaction of these clusters with impurities.[23] Recently, nucleation of local CDW deformation have been described from the DW interaction with strong pinning centers[24] which also cause metastable states to form. Time-dependent specific heat has been ascribed to the relaxation of these metastable states when the DW is close to commensurability.[25] The specific heat at saturation is shown to follow the law of a distribution of Schottky anomalies, in qualitative agreement with the result shown in Fig. 1.

V. CONCLUSION

In conclusion, the progressive increase of C_p with the duration of the heat perturbation indicates how heat is poured out into more and more low-energy modes of the DW system. These modes are strongly decoupled from the phonon bath. DW exhibit long-time relaxation in the quasiadiabatic conditions where glasses show no time dependence.

ACKNOWLEDGMENTS

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