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Thermodynamics in the high-field phases of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$

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We report the results of magnetocaloric-effect measurements of the field-induced spin-density-wave (FISDW) state in the Bechgaard salt $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ in fields up to 30 T at temperatures down to $T=1.6$ K. Our results confirm the phase diagram recently presented but add several insights concerning the unusual low-temperature transition between FISDW phases at 27 T. The magnetocaloric signature of this transition appears as two coupled first-order transitions. $\partial S/\partial H$ oscillates with period $H^{-1}=(255\ \mathrm{T})^{-1}$ for samples where the ClO_4 anions have ordered. Anion disorder suppresses the oscillatory behavior, but not the high-field inter-FISDW phase transition. [S0163-1829(97)00637-1]

The Bechgaard salts $(\mathrm{TMTSF})_2X$ (with anions $X=\mathrm{ClO}_4,\mathrm{PF}_6,\mathrm{NO}_3\ldots$) are organic charge-transfer salts which have served as a remarkable laboratory for the exploration of quasi-one-dimensional electron physics.[1] At room temperature they are highly anisotropic metals with typical conductivities $\sigma_a:\sigma_b:\sigma_c\simeq10^5:10^3:10^0$, and ground states ranging from metallic to superconducting to spin-density-wave (SDW) insulating to a field-induced spin-density ground state associated with the quantum Hall effect (QHE). The actually observed low-temperature behavior depends on the choice of anion, and on experimentally controllable parameters such as cooling history, pressure, and magnetic field.

The PF_6 salt and the ClO_4 salt have been studied most. At ambient pressure the $(\mathrm{TMTSF})_2\mathrm{PF}_6$ undergoes a metal-SDW transition at $T=12$ K. This transition is suppressed above a critical pressure of $p_c\simeq6$ kbar, when the material becomes a superconductor with $T_c=1.1$ K; the superconducting transition temperature decreases when the applied pressure is increased further. In moderate applied fields perpendicular to the most conducting $(a\text{-}b)$ plane a cascade of field-induced spin-density-wave (FISDW) states is observed, with quantized Hall resistances $\rho_{xy}=h/2ne^2$ per layer $(n=\ldots3,2,1)$ and a final transition to the $n=0$ insulating state.[2] This behavior is understood in terms of the "standard model," [3] in which a field-induced spin-density-wave vector is quantized along the k_x direction, with $k_x=2k_f+n\delta$, $\delta=eHb/\hbar c$ nesting the two Fermi sheets at $\pm k_f$ and giving rise to the quantized carrier pockets associated with the observed bulk QHE.

The ClO_4 salt exhibits superconductivity and a cascade of FISDW's with associated quantized Hall resistances at ambient pressure, similar to the observed behavior in $(\mathrm{TMTSF})_2\mathrm{PF}_6$ above 6 kbar. However, some experimental results for $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ cannot be explained in terms of the standard model which works so well for the PF_6 salt: (1) In the low-field cascade of FISDW's the sequence of Hall plateaus is not in the expected order, and sign changes are observed.[4] (2) Many of the phase transitions in the low-field cascade exhibit a doublet structure[5,6] instead of the single first order phase transitions of the standard model. (3) The $n=0$ insulating state is not observed in $(\mathrm{TMTSF})_2\mathrm{ClO}_4$, but one observes a very stable quantum Hall state from 7.5 to 27 T.[7,8] (4) The high-field FISDW state below $T=5.5$ K and fields above 15 T contains a first-order phase transition line,[9] which until recently had been taken as evidence for a reentrance of the metallic state. (5) H^{-1} periodic behavior reminiscent of Schubnikov–de Haas and de Haas–van Alphen oscillations is observed in transport and in thermodynamic properties in the high-field low-temperature region.[10]

A prime suspect for causing the not-quite-standard model low-temperature behavior of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ is the ClO_4 anion ordering transition along the b direction. The degree of anion order depends on the cooling rate through the transition at $T\simeq24$ K. For fully ordered $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ the unit cell is doubled in the b direction, giving rise to two open Fermi surfaces separated by an anion ordering gap.

Past magnetocaloric studies of the low-field FISDW states in $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ have proven this experimental technique to be a useful tool for elucidating some subtleties in the phase diagram[5,6] and in putting to rest claims for the existence of an "arborescent" phase diagram. In this paper we report the results of a magnetocaloric investigation of the high-field FISDW phases of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$. We address the thermodynamic nature of the transitions and the role played by anion ordering.

I. EXPERIMENTAL TECHNIQUE

In our magnetocaloric experiments a small thermometer (Lakeshore Cernox CX-1010-BG) was attached to a 3.72 mg single crystal of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ with a small amount of Apiezon-N grease. Sample and thermometer were suspended in a vacuum using 13 μm diameter constantan wires. These wires provided a weak thermal link to the temperature stage of the cryostat. The sample was cooled through the anion ordering transition at a rate of 0.388 K/h, for good anion order. Data for the fast-cooled sample were obtained after cooling the sample down from 50 K at a rate of about 1 K/min. The crystal was oriented such that the applied field was along the crystallographic c^* axis, perpendicular to the most conducting planes. For the measurements the temperature of the cryostat was controlled to fixed temperatures between 1.5 and 6 K, while the field was swept up to 30 T and back down again, at constant rates of 14 and 82 mT/s. The electronic entropy of the crystal changed as the field was swept, releasing (absorbing) heat into (from) the lattice, thus raising or lowering the temperature slightly with respect to bath temperature. This temperature deviation (ΔT) was measured with the small thermometer attached to the sample and with the thermometers attached to the stage, using standard ac-resistance measurement techniques.

The temperature response ΔT is sensitive to the latent heat evolved at a first order phase transition, to continuous changes of $S(H,T_0)$ and to the sweep rate. It is determined by

$$\Delta T+\tau\frac{d(\Delta T)}{dt}=-\frac{dH}{dt}\frac{T}{K}\left(\frac{\partial S}{\partial H}\right)_{T_0}, \tag{1.1}$$

where the $\tau=C/K$ is the thermal time constant of the system, C is the heat capacity of sample and addenda, and K is the thermal conductance of the weak thermal link. The sign of the temperature excursion is opposite for up and down sweeps. Consequently the temperature deviation ΔT measured when the field is swept up can be subtracted from the deviation measured at the corresponding field during down sweeps. This eliminates any signal arising from Joule heating or other dissipative, irreversible contributions to the heating of the crystal. The background temperature of the cryostat is controlled to the same fixed temperature during up and down sweeps, using a capacitance thermometer. The temperature of the stage is measured with a separate thermometer. The difference in measured stage temperatures typically amounts to less than 2 mK between up and down sweeps, and this difference is subtracted from difference data obtained with the sample thermometer.

The amplitude of the measured temperature excursion is essentially proportional to the sweep rate, for a continuously changing $S(H)$, provided that the thermal relaxation time is sufficiently short. By contrast, the discontinuous entropy changes arising from a latent heat $L=T_0\Delta S$ give rise to a thermal response that is independent of the sweep rate but dependent on the sign of dH/dt, with $\Delta T_L(t)=(L/C)\,e^{-t/\tau}$. Thus sweeps performed at different sweep rates can be used to separate an instantaneous latent heat signal from the continuous entropy changes within a given FISDW phase.

II. RESULTS

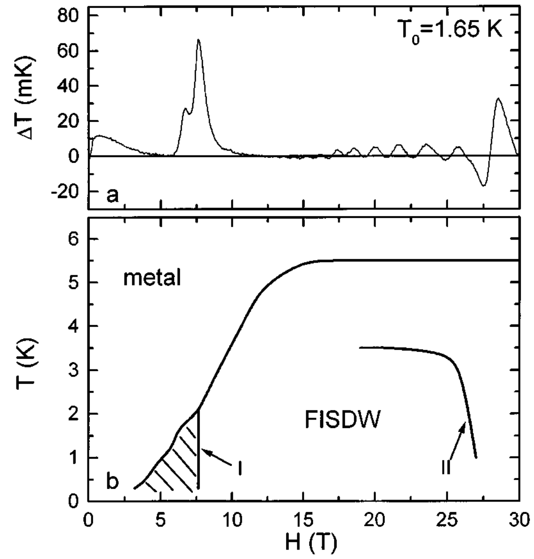

FIG. 1. (a) Magnetocaloric data at $T=1.65$ K. (b) The high-field low-temperature phase diagram of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$, from Ref. 9. Hatched area: cascade of FISDW's. I indicates the transition into the high-field state, and II the high-field inter-FISDW transition line.

Figure 1(a) shows typical magnetocaloric data obtained at $T=1.65$ K, where we have subtracted the down sweep from the up sweep. (The observed temperature excursions for fields below 6 T may be due to magnetic impurities in the thermometer.) Figure 1(b) shows the phase diagram previously obtained for this material from a number of transport and magnetization measurements. We can clearly identify the entropic signatures associated with the transition from the metallic to an FISDW state at $H=6$ T, followed by the transition to the very stable high-field phase at 7.5 T. This transition [labeled I in Figs. 1(b), 2, 3(b), and 4] is associated with the most pronounced heat release. In the high-field phase we observe the gradual emergence of oscillatory behavior of the electronic entropy up to the field of 27 T. These magnetocaloric temperature oscillations are not centered on the mean temperature $\Delta T=0$; they arise from a decrease of the electronic entropy in a stepwise manner between $H=15$ T and $H=25$ T. At $H=27$ T the next phase transition to the very high-field FISDW state occurs [This transition is labeled II in Fig. 1 and subsequent Figs. 1(b), 2, 3(b) and 4]. In this last phase the amplitude of the magnetocaloric oscillations is greatly enhanced.

Figure 2 shows a set of magnetocaloric sweeps obtained at different base temperatures, providing an overview of the data spanning the entire phase diagram established in Ref. 9 and shown in Fig. 1(b). For all temperatures at 5 K or below we observe magnetocaloric oscillations in the high-field FISDW states, and no such oscillations at $T=6$ K, consistent with a metal-FISDW phase boundary at $T=5.5$ K, between $H=15$ T and $H=30$ T. We can trace the evolution of the magnetocaloric peaks and dips, from the lowest temperature of 1.64 K to the highest temperature of $T=6$ K: The prominent peak at $H=28.5$ T decreases in amplitude as the temperature is raised, vanishing between $T=5$ K and $T=6$ K, where the metal-FISDW transition occurs. The other oscillation features, however, evolve differently as temperature is raised. Relative maxima (minima) of the magnetocaloric signal at $T=1.64$ K turn into relative minima (maxima) at $T=5.0$ K, a behavior reminiscent of magnetization results

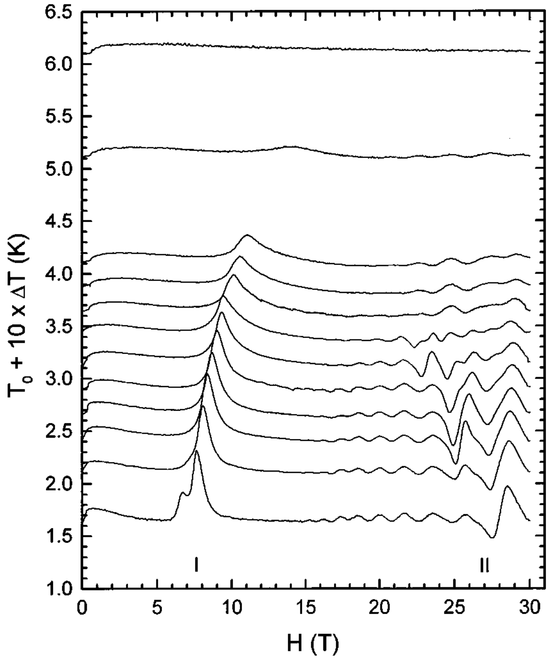

FIG. 2. Magnetocaloric data covering the high-field phase diagram, (anions are well ordered), obtained at base temperatures T_0 of 1.65, 2.1, 2.4, 2.65, 2.9, 3.15, 3.4, 3.63, 3.85, 4.1, 5.1, and 6.1 K. The field sweep rate was ±82 mT/s. For clarity the data is plotted as $10\times\Delta T+T_0$.

where maxima (minima) turn into minima (maxima) in a similar fashion.[9] This is not surprising, as $(\partial S/\partial H)_T=(\partial M/\partial T)_H$ by the Maxwell relation linking the partial derivatives of S and M, both of which oscillate in field.

For fields between 20 and 25 T this change in behavior occurs near $T=3.5$ K, in agreement with earlier findings of an inter-FISDW transition line there. Measurements of the temperature dependence at $H=24.5$ T had shown the magnetization to jump as this phase boundary was crossed.[9] The magnetocaloric signal, at the same field, exhibits a similar effect. In Fig. 2 we see that there is a ΔT maximum at 24.5 T for traces at 5.1, 4.1, 3.9, and 3.6 K. However, at 3.4 K the curve shows a distinct minimum at 24.5 T. This negative value of ΔT persists in the lower temperature traces down to 1.5 K. This is consistent with a discontinuous entropy change associated with a first-order phase transition at $T=3.5$ K. The magnetocaloric minimum at $H=27.5$ T also vanishes as we follow it up in temperature, to be replaced by a gradually emerging peak at higher temperatures. This evolution is unexpected because the sample is already in the very high-field phase, but there appears no discontinuous behavior which would suggest a phase transition.

Using the data of Fig. 3 we can distinguish latent-heat signatures from the smooth variation of the entropic background signal. Figure 3 shows two traces obtained at the same base temperature of 2.1 K, where we have again subtracted up sweep data from down sweep data. The two traces differ because they were obtained at sweep rates of 82 mT/s and 14 mT/s for Figs. 3(a) and 3(b), respectively. We have set the ΔT axis ranges in plots (a) and (b) to have the same ratio as the ratio of the sweep rates for the respective traces. This permits easy comparison of the two data sets. If the magnetocaloric signal scaled exactly with the sweep rate, then the two graphs would have to look exactly alike in the entire field region. Indeed for the most part Fig. 3(b) looks like a noisy version of Fig. 3(a), showing that the magnetocaloric signal scales with the sweep rate rather well for most of the field range. The metal-FISDW transition near $H=7$ T, the H^{-1} periodic oscillations up to 25 T, and the final peak at $H=28$ T scale with the ratio of the sweep rates. As was discussed earlier the part of the signal scaling with the sweep rate can be attributed to continuous changes in $S(H)$ occurring over a finite field range. The situation is quite different in the vicinity of $H=26$ T, where the scaling with field sweep rate breaks down. Figure 3(b) shows a pronounced transition signature associated with the high-field inter-FISDW transition. This signature is not diminished proportionally to the sweep rate, which is evidence for a significant latent heat contribution to the signal. Furthermore the transition appears to be doubled, in that there is a latent heat dip (entropy uptake) followed subsequently by a latent heat peak (entropy loss), as we follow the signal from lower to higher fields, suggesting the presence of a pair of coupled first-order transitions. This is surprising. We would have expected a single sharp dip at this temperature if there was a first-order transition from an ordered to a disordered phase on increasing field. Similarly a single dip would result in going from a fully gapped phase (insulator) to a phase where there is finite density of states at the Fermi surface. The doubled magnetocaloric structure is somewhat reminiscent of the doubled transition lines observed in the lower field cascade of inter-FISDW transitions in $(TMTSF)_2ClO_4$.[5]

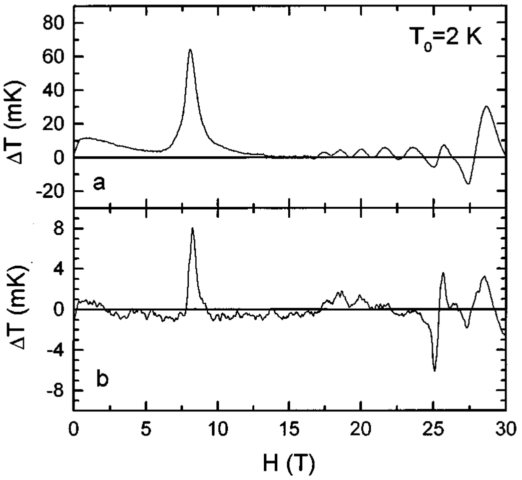

FIG. 3. Magnetocaloric data obtained at two different sweep rates permitting the identification of a doubled latent heat signature at $H\simeq 26$ T.

Finally, Fig. 4 shows data from the same sample obtained with the same field sweep rate of 82 mT/s, when it has been cooled through the anion ordering transition temperature at a about 1 K/min, which is too fast a rate for attaining (good) anion order. This has dramatic effects. Figure 4 shows that ΔT and thus $\partial S/\partial H$ no longer oscillates. On the other hand, both the metal-FISDW transition at $H=8$ T and the inter-FISDW transition at the high field still exist, although they occur at transition fields slightly different from those of the ordered sample; the phase diagram is robust, with respect to anion disorder.

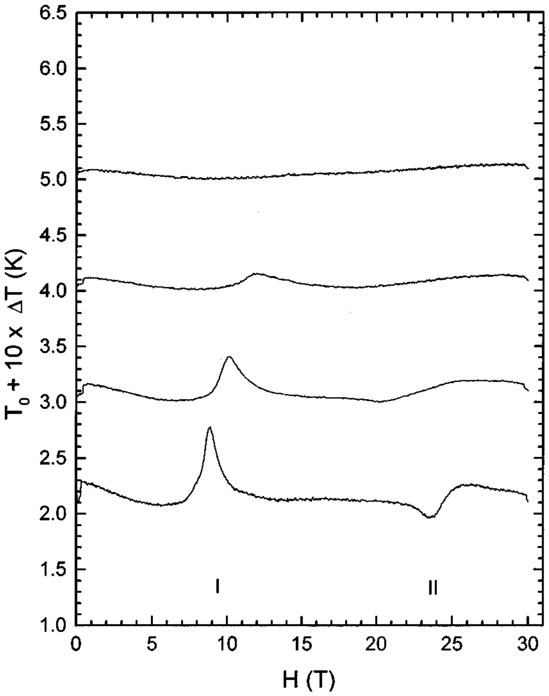

FIG. 4. Magnetocaloric data obtained on the same sample, with disordered anions, obtained at base temperatures T_0 of 2, 3, 4, and 5 K. The field sweep rate was ± 82 mT/s. For clarity the data is plotted as $10 \times \Delta T + T_0$.

It is generally accepted that the thermodynamic ''rapid oscillations'' seen in the FISDW phase at the period $H^{-1} = (255\ \mathrm{T})^{-1}$ are the result of the doubling of the Fermi surface from the anion ordering (which doubles the unit cell and gives a slightly different potential to alternating chains of TMTSF ions). Although the FISDW transition at ''27 T'' [II in Fig. 1(b)] and the nature of the high-field phase are not understood, it has often been suggested that they too are related to the anion ordering. The fast-cooled data in Fig. 4 strongly support the idea that the rapid oscillations are the result of anion ordering—they disappear when the anions are disordered. However, it suggests that the 27 T transition is still present when the anions are disordered.

CONCLUSION

Magnetocaloric studies provide a sensitive probe of the thermodynamics of a system. The present work demonstrates that the phase diagram compiled from a variety of other measurements and shown in Fig. 1(b) is largely correct and corresponds to thermodynamically distinct phases. In particular, for both fast- and slow-cooled samples we find no evidence of a phase transition above 5.5 K in fields to 30 T. Sweeping field 0–30 T there is a single transition for the temperature range 5.5–3.5 K. Below 3.5 K a stable high-field phase is entered on increasing field above 8 T and there is a further transition to another phase at $H \simeq 27$ T. The latter transition seems to be more complex than originally envisioned with a double structure in entropy vs field. Directly integrating dS/dH as a function a field to find the total entropy loss is straightforward, but suffers from the fact that slight shifts in the measurement of a constant term in dS/dH may lead to large errors in the integral. Nonetheless it is worth remarking that the entropy loss integrated to 30 T at a base temperature of 2 K is 3 times larger than the total electronic entropy expected from a metal with an electronic specific heat $C_{\mathrm{el}} = \gamma T$, where $\gamma \simeq 11$ mJ/mole K^2.[11] Furthermore, the integrated entropy for the quenched samples appears to be yet another factor of 2 higher. Finally we note that the comparison of the slow and rapidly cooled samples proves that in the FISDW state there are thermodynamic ''rapid oscillations'' due to the anion ordering, but the degree of anion disorder sufficient to destroy the thermodynamic oscillations has little effect on the overall nature of the phase diagram including the unusual high-field transition.

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