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Specific-Heat Study of the Anomalous Quantum Limit of (TMTSF)$_2$ClO$_4$

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We report calorimetric measurements of the organic conductor (TMTSF)$_2$ClO$_4$ in the quantum limit. In addition to the field-induced spin-density-wave (FISDW) phases, we have measured the magnetic-field-dependent specific heat associated with the recently discovered reentrant phase. In terms of a semiempirical model, we find that the reentrant transition is second order, but that the electronic density of states is greatly reduced in the reentrant phase. We also observe a specific-heat signal corresponding to the anomalous "fast oscillations" which are known to coexist with the FISDW phases.

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The independent prediction[1] and experimental discovery[2] of the reentrant phase line in the Bechgaard salt (TMTSF)$_2$ClO$_4$ near 30 T has shown that this material continues to be of fundamental interest in experimental studies of low-dimensional electronic materials.[3] (TMTSF)$_2$ClO$_4$ is an electronically anisotropic organic conductor (TMTSF denotes tetramethyltetraselenafulvalene). It is superconducting below 1.3 K. Since the ClO$_4$ anions are not centrosymmetric, they can order at low temperature. This anion ordering behavior occurs at 24 K. In an applied magnetic field, it becomes an open-orbit quasi-one-dimensional metal, and at a threshold field it undergoes a second-order field-induced phase transition to a state with closed orbits. For increasing magnetic field, a series of field-induced spin-density-wave (FISDW) phases appear. Above 8 T, the final FISDW is reached. Anomalous "fast oscillations," which are periodic in inverse field, appear both below and above the threshold field.[4] A comprehensive phase diagram of (TMTSF)$_2$ClO$_4$ is presented in Fig. 1.

The *reentrant* behavior involves a transition from this final FISDW state back to the lower-dimensional metallic state. This new phenomenon takes place in the quantum limit ($\hbar\omega_c \gtrsim k_B T$) of the material, and its existence falls outside the scope of the so-called "standard model"[5] (a weak-coupling nesting model), which has successfully described the threshold field and FISDW transitions at lower magnetic fields. A critical comparison of the theory and experiment has been given recently.[6,7] Although the theory does not predict reentrance or fast oscillations, it does allow model-independent thermodynamic relationships between the magnetization[8] and specific heat[9] and the second-order phase line $T_c(H)$ which separates the metallic and ordered states. Theoretical attention has recently focused on the origin of the anomalous quantum-limit behavior, and two distinct theoretical descriptions of the reentrant behavior have been proposed: Yakovenko[1] was first to predict the reentrant phase, and gave a field dependence of $T_c(H) = 1/H^{\nu}$ arising from 1D fluctuations. These fluctuations have also been invoked by Heritier, Pesty, and Garoche.[10] The exponent ν depends on the strength (and sign) of the intrachain interactions. However, the value of ν needed to describe the observed fast decrease in $T_c(H)$ at reentrance appears to be unphysical. Lebed and Bak[11] have treated both the reentrance and the anomalous fast oscillations in terms of an anion gap in the electron spectrum. They predict a reentrant field

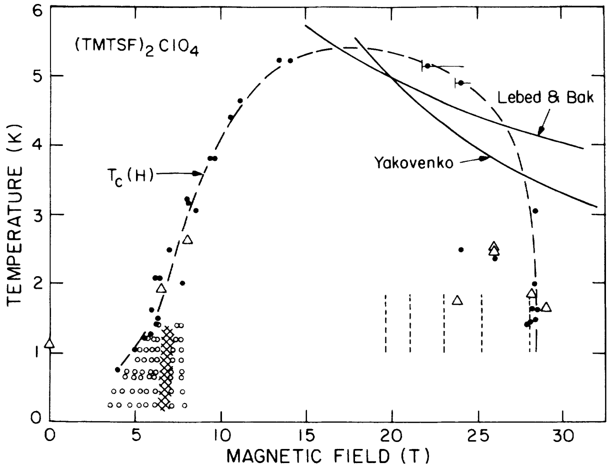

FIG. 1. B-T phase diagram of (TMTSF)$_2$ClO$_4$ based on our heat-capacity measurements. Solid circles: specific-heat jumps observed in magnetic-field sweeps (up to 30 T). Dashed guideline: $T_c(H)$. Open circles: FISDW phases. Triangles: phase transitions observed in temperature sweeps at constant field. Shaded region: negative Hall phase. Solid lines: theoretical reentrant phase lines (Yakovenko theory, $\nu = 1$; Lebed and Bak theory, oscillatory behavior not shown). Dotted vertical lines: position of fast oscillations.

dependence of $T_c = 1/H^{1/2}$. The curvature of this variation is at variance with the existing data.[2] Moreover, they show, as a result of their model, that the fast oscillations are a series of phase transitions (in the quantum limit) between competing SDW phases with a periodicity of $1/H$ which are superimposed on the $1/H^{1/2}$ phase line. This oscillatory behavior of the $T_c(H)$ line is not observed experimentally.[2]

In this paper we present the first specific-heat measurements on $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ in the quantum limit above 11 T. We have employed the small-sample ac calorimetric method[12] on individual 1-2-mg single crystals of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ oriented with the field along the c^* axis. In each run, one crystal was affixed with silver paint to a 0.5-mg 50-μm-thick sapphire platform supported by four 93%-Au-7%-Cu 1.85-mil wires (with an effective thermal conductivity of 750 nW/K at 1 K) to a temperature controlled heater block. A 0.17-mg thin-film thermometer[13] with negligible magnetoresistance at high fields on a separate sapphire substrate was either affixed to the platform with silver paint or directly to the sample with a thin film of Apiezon grease. The calorimeter apparatus was sealed in a small vacuum can and placed in a ^{3}He one-shot or dilution refrigerator. The cooling rate varied between 40 and 4 mK/min through the anion ordering transition at 24 K, with no observable systematic differences. Experiments were carried out in a variety of high-field and superconducting magnets at the Francis Bitter National Magnet Laboratory (FBNML) in Cambridge, Massachusetts, and at the High-Field Magnet Laboratory at the University of Nijmegen in Nijmegen, The Netherlands.

The magnetic-field-dependent variation of the specific heat ($\Delta C/T$) at constant temperature versus field of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ from a FBNML hybrid magnet run is shown in Fig. 2. A smoothly varying addenda of order 10% (due to paramagnetic impurity effects) has been separately measured up to 24 T at the same series of fixed temperatures, extrapolated to 30 T, and subtracted from the data presented here. We note that the magnetic-field dependence of the addenda above 5 T (to 24 T) is flat to within a few percent over our accessible range of temperature. Evident in Fig. 2 are details of the behavior of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ in the quantum limit. For the temperatures shown, we observe not only specific-heat peaks associated with the low-field threshold and FISDW phases, but additional structure at high magnetic fields: a peak which corresponds to the reentrant phase line, and a series of oscillations periodic in $1/H$ with a temperature-independent frequency of 257 T (most pronounced in our 1.52-K data). We further note that there is a local minimum in the specific heat near 15 T which is higher than the low-field value at 3.08 K, but which drops significantly with respect to the low-field value at low temperatures. Finally, we see that the size of the reentrant jump becomes substantially less than the threshold and FISDW jumps at low temperatures. Similarly, the value of the specific heat in the reentrant phase falls below the low-field value at lower temperatures. Note that since these measurements were in the *isothermal* as opposed to the adiabatic limit with respect to changes in the magnetic field, no magnetocaloric contributions to the specific heat were measured. [Simultaneous measurements of the sample temperature showed no features corresponding to the specific-heat jumps associated with $T_c(H)$ or the FISDW transitions.]

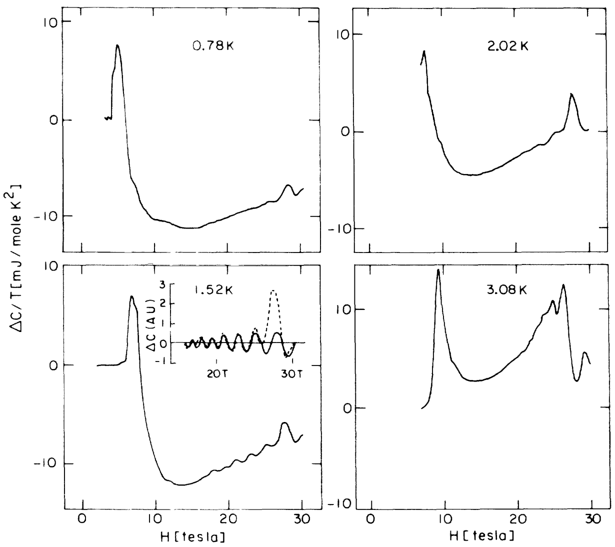

FIG. 2. Magnetic-field-dependent variation of the specific heat ($\Delta C/T$) of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ at four temperatures from an FBNML hybrid run. Inset: Simple model of fast oscillations (solid line) compared to heat-capacity data at 1.52 K (dotted line) to show relative contributions of the reentrant jump and the coexisting oscillations.

The phase diagram shown in Fig. 1 is based entirely on our results, and its general form is in excellent agreement with previous transport,[14] magnetization,[2] and specific-heat[9] work. For completeness, we have measured the threshold field and FISDW phases below 10 T in a superconducting magnet at low temperatures. The shaded area corresponds to the region of the anomalous negative Hall effect.[15] The larger phase boundary indicated as $T_c(H)$ shows the reentrant character at high fields. Phase transitions identified from temperature-sweep data taken at constant field (including the superconducting transition for zero field) are also shown.

We now discuss our results in light of recent theoretical work. Montambaux *et al.*[7] have provided a model-independent thermodynamic relationship between $T_c(H)$ and the magnetic-field-dependent specific heat. The calculation is obtained by assuming a BCS-like form for the second-order metal-to-SDW transition, and by taking the $T_c(H)$ curve from the phase diagram as input, computing $C_p(T/T_c(H))$ for constant T. In this calcula-

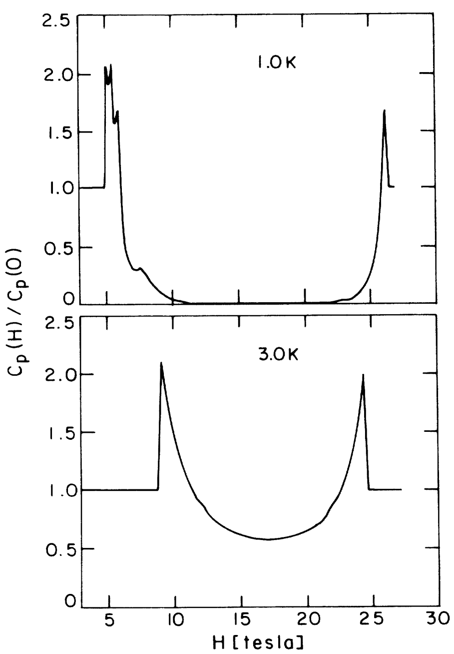

FIG. 3. Theoretical predictions for the magnetic-field-dependent heat capacity from Ref. 7.

tion, the density of states below the threshold field and above the reentrant phase line are assumed to be the same. We show the results of this calculation in Fig. 3 for temperatures close to those reported in Fig. 2. We see that the agreement between theory and experiment is qualitatively satisfactory. This is strong evidence that the reentrant phase is second order, but it is clear by comparison with the data that the density of states in the reentrant metallic phase has been reduced at low temperatures.

It has been shown in previous calorimetric studies[16] to 10 T that the magnitude of the specific-heat jump at the metal-to-SDW boundary is not a constant ratio of the normal-state electronic specific heat (as would be given by a BCS model of a second-order phase transition with a single gap, where $\Delta C/1.43\gamma T_c = 1$), but varies with field. This is due to the complex gap structure of the FISDW spectrum.[17] Our determination of this effect is in agreement with Ref. 16: We find that for fields greater than 8 T, the ratio is nearly 4 times larger than the lower-field values (which are ≤ 1 times BCS). In the quantum limit, near 15 T, the ratio is about 2.5 times BCS. Such large values are not explained by the standard model. In the reentrant regime, the appropriate comparison is between the reentrant jump and the specific heat C_{re} in the high-field reentrant phase. To address this last point, and to better quantify the trends apparent in Fig. 2, we concentrated the efforts of one hybrid run on a single temperature where we could measure both the threshold and reentrant behavior, and where the superconducting transition was also measured. In this run, taken at 1.45 K, the jump at the threshold field yielded a value of 1.3 times BCS. At the reentrant transition, we compare the reentrant jump with the estimated electronic specific heat *above* the transition. At reentrance, the value is about 0.9 times BCS. We note that the reduction in the electronic specific heat in the reentrant metallic phase is about 50% at 1.45 K. Hence both the value of the high-field metallic specific heat and the size of the jump at the phase boundary are consistent within a simple BCS model, but with a decreasing electronic density of states. We note that at reentrance, transport measurements[18] show a rapid increase in resistance and corresponding vanishing Hall signal. This behavior has been interpreted recently in terms of localization.[19]

Our data, and the data of previous workers,[2] indicate that the field dependence of the reentrant phase boundary is very large. The magnetic Clausius-Clapeyron relation for a second-order phase transition is

$$(\Delta C)_{H=H_c} = -T[\partial(M_n - M_s)/\partial H]_{H_c}(\partial H_c/\partial T)^2 .$$

For a finite change in the susceptibility at reentrance, a divergence in the slope of $T_c(H)$ leads to a vanishing specific-heat jump. This is the general trend of our data. By comparison, the theoretical field dependences $T_c(H) = 1/H^{\nu}$ from Ref. 1 or $T_c(H) = 1/H^{1/2}$ from Ref. 11 (see Fig. 1) do not follow the experimental $T_c(H)$. By inspection, an exponent $\nu \gtrsim 1$, which is unphysical, would be needed to explain the slope of the reentrant phase line. We do not see the huge oscillations of $T_c(H)$ predicted by Ref. 11. We believe further theoretical work is needed to provide a satisfactory description of field dependence of $T_c(H)$ along the reentrant phase boundary.

Finally, we turn to the observed fast oscillations. They are not only evident in the specific-heat signal, but their contribution is comparable to the size of the reentrant jump at some temperatures. It is also apparent from our results that the oscillations may persist *above* the reentrant phase line. Assuming conventional Shubnikov-de Haas oscillations with an effective electron mass of unity (m_0) allows us to differentiate the oscillatory behavior from the reentrant transition, and a standard magnetic quantum oscillation treatment with $1.0m_0$ and $T_{\mathrm{Dingle}} = 2.4$ K yields the fit in the inset in Fig. 2 for 1.52 K. By using the results from magnetization data,[20] the quantized edge state model[21,22] places an upper limit of $0.2m_0$ on the effective mass. This corresponds to a specific-heat signal nearly 200 times *less* than that observed.[23] In the recently proposed anion-gap model[11] it is predicted that the oscillations (in the quantum limit) arise from a series of phase transitions between two competing SDW phases. A periodic $1/H$ variation of T_c, when applied to the BCS model, would give a corresponding variation in the magnetic-field-dependent specific heat. Careful experimental work is necessary, however, to verify the existence of a phase line associated with an oscillating transition temperature. Additionally, if the oscillations in the specific heat do indeed remain in the reentrant metallic phase (as the 1.52-K data suggest) then they cannot be explained by the present anion-gap model, since it predicts a termination of these oscillations at reentrance.[24]

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