Cascade of Field-Induced Phase Transitions in the Organic Metal Tetramethyltetraselenafulvalenium Perchlorate [$(TMTSF)_2ClO_4$]

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We present specific-heat measurements as a function of field (3–6 T) and temperature (0.35–1.7 K) of a single crystal of the organic conductor tetramethyltetraselenafulvalenium perchlorate [$(TMTSF)_2ClO_4$]. The small electronic contribution, 40 nJ/K, shows clearly above a temperature-dependent threshold field, a series of jumps and peaks. The phase diagram deduced from this magnetocalorimetric investigation exhibits in the threshold region indications of a partial reentrance of the normal metal in between semimetallic regions.

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The organic superconductors tetramethyltetraselenafulvalenium fluorophosphate [$(TMTSF)_2PF_6$] and tetramethyltetraselenafulvalenium perchlorate [$(TMTSF)_2ClO_4$] display a very unusual phase transition at low temperature if a magnetic field is applied along the least-conducting axis c^*. The normal metal observed above the superconducting critical field $H_{c2}(c^*)$ transforms into a field-induced spin-density-wave state above a temperature-dependent threshold field $H_0(T)$. An indication of this transition was first reported in the pressure-stabilizing metallic phase of the PF_6 salt.[1] The magnetoresistance displays above the transition Shubnikov–de Haas–type oscillations.[2] The angular variation of their frequency implies closed orbits in the (a,b) plane and open orbits in the c^* direction.[3] Therefore, the Fermi surface is supposed to be essentially two dimensional at high field. The same oscillations have been observed in the magnetotransport of the ClO_4 salt.[3,4] Specific-heat measurement indicates that a phase transition separates the low-field quasi one-dimensional metallic phase from the high-field semimetallic state.[5,6] In this phase the observation of steplike Hall voltage at low temperature pointed out similarities to the quantum Hall effect observed in two-dimensional semiconductors. However, the temperature dependence of the transport properties suggests that these steps are related to a series of phase transitions.[7–9] Various models have been proposed in order to explain the anomalous properties of the high-field phase.[10–14] In this Letter we report the first investigation of the field-induced spin-density-wave state by direct measurement of the specific heat at constant temperature as a function of a magnetic field $H \| c^*$, and we wish to demonstrate that real phase transitions, induced by quantum effects, separate different semimetallic states. Moreover, we focus our attention on the threshold-field region and propose a complex phase diagram with a partial reentrance of the normal metal in between the semimetallic state.

The applied magnetic field was oriented along the c^* axis, i.e., perpendicular to the higher-conducting plane (a,b). A microlithography process and a thin-film technique on sapphire were used as a means to produce a sample holder with a very low heat capacity [$c(1\ K,6\ T) = 2$ nJ/K, dashed line in the insert of Fig. 1]; its contribution was subtracted from the total heat capacity. It represents between 7% and 20% of the sample electronic heat capacity. Two sets of experiments were performed on the same relaxed crystal[15] by use of an ac calorimetric technique. In the first one we measure the heat capacity at constant field as a function of the temperature; in the second one we measure directly the heat capacity at constant temperature as a function of the field.

The sample assembly heater-thermometer-sample is connected to a thermal bath at a temperature T_0. A small ac voltage, $\nu = 2$ Hz, is applied to the heater in order to produce a small thermal oscillation $\delta T = 4$ mK and a mean temperature T_1. The magnetic field is then swept slowly at a rate of 1 Oe/sec and the specific heat at constant temperature T_1, averaged over a 2-

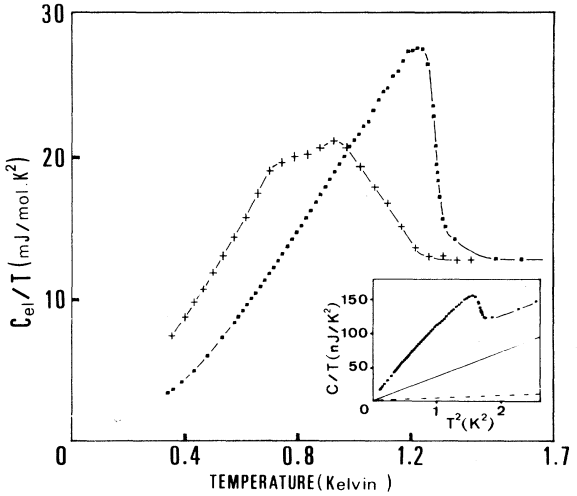

FIG. 1. Electronic specific heat C_{el}/T of 1 mole of $(TMTSF)_2ClO_4$ vs temperature. Plus and square symbols represent respectively the 5.3- and 6.1-T data.

min period, is recorded directly as a function of the field. The absolute electronic specific-heat accuracy, in the whole field and temperature ranges, has been estimated to be better than 7%, 2% from the measuring procedure and 5% caused by a magnetic-impurity contribution. But the relative accuracy is clearly better than 0.5%. It must be noted that a conventional calorimetric experiment includes both thermal excitations and latent-heat contributions. This is clearly not the case in the present experiment where the latent heat is evacuated through the thermal link with a characteristic time constant $\tau = 0.5$ s, which must be compared with the 2-min period of the averaging of the thermal oscillations.

Figure 1 displays in a C/T vs T diagram the electronic contribution to the molar specific heat obtained after subtraction of the phonon contribution. Black squares show the 6.1-T data. At 1.3 K a specific-heat anomaly separates the high-temperature normal metal from the field-induced state. The jump of the electronic specific heat, $\Delta C/\gamma T_c = 1.4$, is followed by a rapid decrease associated with the opening of the field-induced spin-density-wave gap at the Fermi level. The occurrence of this second-order phase transition with a BCS-type jump, $\Delta C/\gamma T_c = 1.43$, is a clear indication that we are in the weak-coupling limit. The corresponding gap is found to be $2\Delta = 0.3$ meV. The integration of the electronic specific heat below T_c indicates that 90% $\pm$ 10% of the normal-metal electrons are affected by the transition at 6.1 T. The field-induced character is clearly exemplified by the two curves in Fig. 1. As the field is reduced T_c decreases from 1.3 to 1 K. The specific-heat anomaly at 5.3 T, plusses in Fig. 1, displays a very peculiar shape; this unusual shape can result from a series of unresolved phase transitions. The critical temperatures have been extracted from the numerical calculation of the corresponding T_c distribution by the assumption of a weak-coupling limit. The distribution exhibits two peaks around the two T_c values of 1.05 and 0.80 K. This interesting result cannot be considered as a final proof for a series of phase transitions. For a temperature just below T_c the order parameter of a second-order phase transition is close to zero, and if the two T_c are close enough, there is no clear jump on going from one phase to the other. This difficulty can be overcome by performance of a direct specific-heat measurement at constant temperature as a function of the magnetic field. In a previous work,[6] the field dependence of the specific heat was deduced from a set of measurements performed at constant field; for each field, an electronic contribution γT was estimated and the resulting γ values plotted against the magnetic field. This procedure has led to a misevaluation of the field dependence of γ at low field. In the present experiment, the direct field measurement, the single-crystal sample, the design of a new sample holder with a very low heat capacity (inset in Fig. 1), and the absence of a Schottky anomaly associated with magnetic impurities[16] ($\Delta c/c < 5\%$ below 5 T in the normal state) allow an accurate determination of the electronic specific heat.

The result for the electronic molar specific heat is presented in the peculiar plot of C/T vs H for various fixed temperatures. Above T_c the density of states at the Fermi level is not affected by the magnetic field in the 3–5-T range, and consequently the present results do not support the suggestion of large one-dimensional superconducting fluctuations. The four curves in Fig. 2 display the electronic specific heat in the reduced range of 3–6 T. Two kinds of anomalies can be considered: specific-heat peaks and jumps. Jumps are observed at 3.5, 4.1, 4.3, and 4.9 T for a fixed temperature T_1 equal, respectively, to 0.38, 0.49, 0.73, and 0.89 K; they separate the low-field normal metal from the high-field phases. The transitions are very abrupt; a 60% increase in the electronic specific heat is observed for a 3% field variation. The threshold fields $H_c(T)$ are accurately determined by the midheight values of the jumps. At variance with transport properties that relate to the first-order derivate of the free energy, the larger singularities of the electronic specific heat are observed around the threshold field. This property allows a precise description of the phase diagram in this region. The specific jumps lie below the BCS value observed in the variable-temperature experiments at 6.1 T, first because the $\{C,H\}$ plane does not cut the curves around their maxima, and second because at lower field the specific-heat jumps observed in

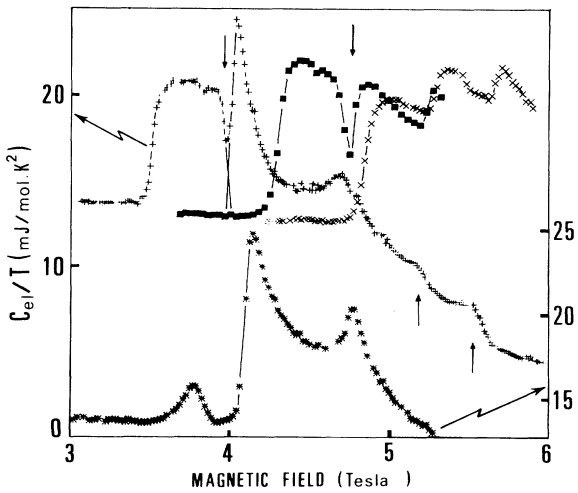

FIG. 2. Electronic specific heat C_{el}/T of 1 mole of $(TMTSF)_2ClO_4$ vs magnetic field. Plus, star, square, and cross symbols represent respectively the 0.38-, 0.49-, 0.73-, and 0.89-K data.

the fixed-field experiments are smaller than the BCS prediction. The threshold deduced from the first specific-heat jump exhibits a peculiar temperature dependence. A weak increase is observed as long as the first anomaly is present. As the temperature increases, the first anomaly disappears, and the threshold field is rapidly shifted to the next anomaly. For the 0.38- and 0.73-K curves, a very peculiar variation of the specific heat is observed 0.5 T above the first positive jump; it is indicated by the upper arrows in Fig. 2. A 20% decrease of the electronic specific heat is observed for a 2% field variation; this abrupt reduction of the second derivative of the free energy must be a phase transition. It is immediately followed by a third jump corresponding to a 50% increase of the specific heat for a 2% field variation. This third jump in the opposite direction must correspond to a distinct phase transition. The peculiar variation results from the finite width of the transitions. This has been illustrated by the solid line drawn by extrapolation of the jumps on the 0.38-K curve. The two lines cross at the midheight between the normal-metal and the observed values; consequently we are confident that this negative jump corresponds to a local restoration of the normal metal. This is also clearly exemplified by the 0.49-K curve where the specific heat returns to the normal-metal value after the first anomaly. This reentrance of the normal metal is not a general feature of the field dependence of the specific-heat curve; in the 0.89-K curve a single jump separates the normal metal from the high-field state. A series of specific-heat peaks are clearly observed at high field; these are a clear indication of phase transitions between different semimetallic states. They appear in the field region where the first jumps are observed between the plateaus of the Hall voltage. At low temperature the size of the peaks and the electronic contribution decrease as the field increases. This evolution at constant temperature is assumed to be caused by a corresponding increase of the gap.

For each temperature the critical fields H_c were evaluated from the specific-heat peaks and jumps. A complete phase diagram was built from these data and is presented in Fig. 3 in a T vs H diagram. Two symbols, plus and cross, are used, respectively, to display the jumps and the peaks observed at constant temperature; the squares represent the T_c observed in the experiment performed at constant field. The solid lines plotted by extrapolation between experimental points separate the high-field state into a series of five distinct semimetallic phases. A partial reentrance of the normal between phases I, II, and III is associated with the nonmonotonic variation of $T_c(H)$ with increasing field. This can be explained by the competition between the condensation energy of the spin-density-wave phases and the quantization of closed orbit in magnetic field.

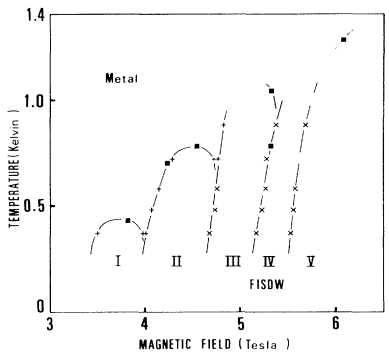

FIG. 3. Phase diagram of the $(TMTSF)_2ClO_4$. Plus and cross symbols are used to represent respectively jumps and peaks in the specific heat measured at constant temperature. Square symbols are used to represent the critical temperatures observed at fixed field.

A final remark concerns recent magnetization measurements performed on the same salt.[17] The comparison is not straightforward because in the threshold region it is difficult to detect the singularity of the magnetization corresponding to the large specific-heat jump. This is well exemplified by the 0.6-K data where the threshold fields are 4.2 and 5.2 T, respectiviely, for the specific heat and the magnetization. In the high-field region the situation is reversed, and large magnetization jumps are observed in a region where thermal excitations display a series of small peaks.

The present calorimetric investigation clearly shows a series of field-induced phase transitions between different electronic states in the high-field phase of the organic conductor $(TMTSF)_2ClO_4$. We observe, respectively, jumps and peaks at normal-metal–spin-density-wave and at the spin-density-wave–spin-density-wave phase transitions. It is proposed that the competition between the quantization of closed orbits and spin-density-wave energy is responsible for the partial reentrance observed in the threshold region.

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