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Resistivity of the organic superconductor ditetramethyltetraselenafulvalenium perchlorate, $(TMTSF)_2ClO_4$, in its relaxed, quenched, and intermediate state

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The intermediate state of $(TMTSF)_2ClO_4$ is characterized by resistance and magnetoresistance measurements to consist of an inhomogeneous mixture of superconducting and spin-density-wave regions, whereas the quenched state is purely insulating with a phase-transition temperature $T_{SDW} = 6.05$ K and a zero-temperature gap $2\Delta(0) = 22\ K = 3.52 T_{SDW}$, close to the mean-field value.

In the family of the Bechgaard salts $(TMTSF)_2X$ (TMTSF denotes the organic molecule tetramethyltetraselenafulvalenium and X stands for a variety of inorganic anions) the perchlorate compound ($X = ClO_4$) is the only member up to now that exhibits superconductivity at ambient pressure. This ground state is in close competition with an insulating one. Experimentally either state may be realized by modification of the cooling procedure below about 40 K. After Takahashi, Jérome, and Bechgaard,[1] the slowly cooled ground state (0.1 K/min)—the "relaxed state"—is completely superconducting below 1.2 K, whereas the rapidly cooled state (>50 K/min)—the "quenched state"—is insulating. The latter one was identified by resistivity, NMR, EPR, and antiferromagnetic resonance measurements as a magnetic, namely, a spin-density-wave (SDW) state.[1-3] The origin of this "ground-state degeneracy" is a structural phase transition at 24 K due to an ordering of the noncentrosymmetric perchlorate anions characterized by a wave vector $q = (0, \frac{1}{2}, 0)$.[4] In the relaxed state, the anions are ordered. Fast cooling through the phase-transition region freezes the high-temperature disorder, thus creating the quenched state. It is possible to switch reversibly between these two states by simply warming up the sample above 40 K and using either cooling procedure. Intermediate states with a SDW precursor to the superconducting state may be obtained in two different ways, either by using intermediate cooling speeds or by quenching from different temperatures T_Q in the critical region around 24 K with a rapid cooling rate.

In this Rapid Communication we report on low-temperature magnetoresistance measurements of $(TMTSF)_2ClO_4$ in states with various degrees of anion disorder characterized by the different quenching temperatures T_Q (thus ranging from the relaxed states via several intermediate states to the quenched state).

The preparation of the $(TMTSF)_2ClO_4$ crystal is discussed in detail in Ref. 5. The resistance measurements were carried out with a standard low-frequency (30 Hz) ac method. The electrical leads (copper wire of 0.017-mm diam) were attached to the single-crystal sample with silver paint. The sample was thermally anchored to the mixing chamber of a dilution refrigerator and its crystal a axis was roughly oriented parallel (to within 15°) to the magnetic field of a small superconducting solenoid (maximum field 9 kG). The intention was to compare the properties of the crystal as a function of magnetic field in its various intermediate states rather than to study the magnetic-field dependence on a distinct orientation.

Initially the sample was measured in its relaxed state (cooling speed less than 0.1 K/min). The procedure to produce an intermediate state whose degree of anion disorder was characterized by the quenching temperature T_Q was as follows. The sample was warmed up to 40 K to assure that the high-temperature disorder was fully developed, then slowly cooled down to T_Q (less than 0.2 K/min) and then quenched from T_Q to liquid-helium temperature by simultaneously switching off the sample heater and introducing He gas into the vacuum chamber of the dilution refrigerator. The cooling rates thus obtained were always greater than 60 K/min. Resistance data were always taken upon slowly warming (~ 0.2 K/min) up from the lowest temperature. They are displayed in Figs. 1(a) to 1(c) for the variously disordered states. The order-disorder phase transition occurs at 25 K and is indicated by the change of the slope of the resistivity in the relaxed state (this feature was originally pointed out by Gubser *et al.*).[6] A remarkable fact is that all states, even those that have been quenched from above the phase-transition temperature, approach the resistivity of the relaxed state already below 25 K and show the same change of the slope, when slowly warmed up. This annealing behavior of disordered states below the anion ordering temperature will be discussed in detail below.

The superconducting state of the relaxed sample exhibited a small resistive contribution in series, as has often been observed by other authors as well.[7] This is probably due to microcracks in the chains that occur during the cooling process and which also show up in subsequent resistance jumps during cooling. Superconductivity was confirmed by the magnetic field dependence of the resistivity at constant temperature: The zero field resistance value increased as the field was increased and reached saturation in large enough fields (due to the fact that our field was limited to 9 kOe, we could observe saturation behavior only at temperatures not too much below T_c).

Very similar magnetoresistance behavior was found in the various disordered states at low temperatures, even for

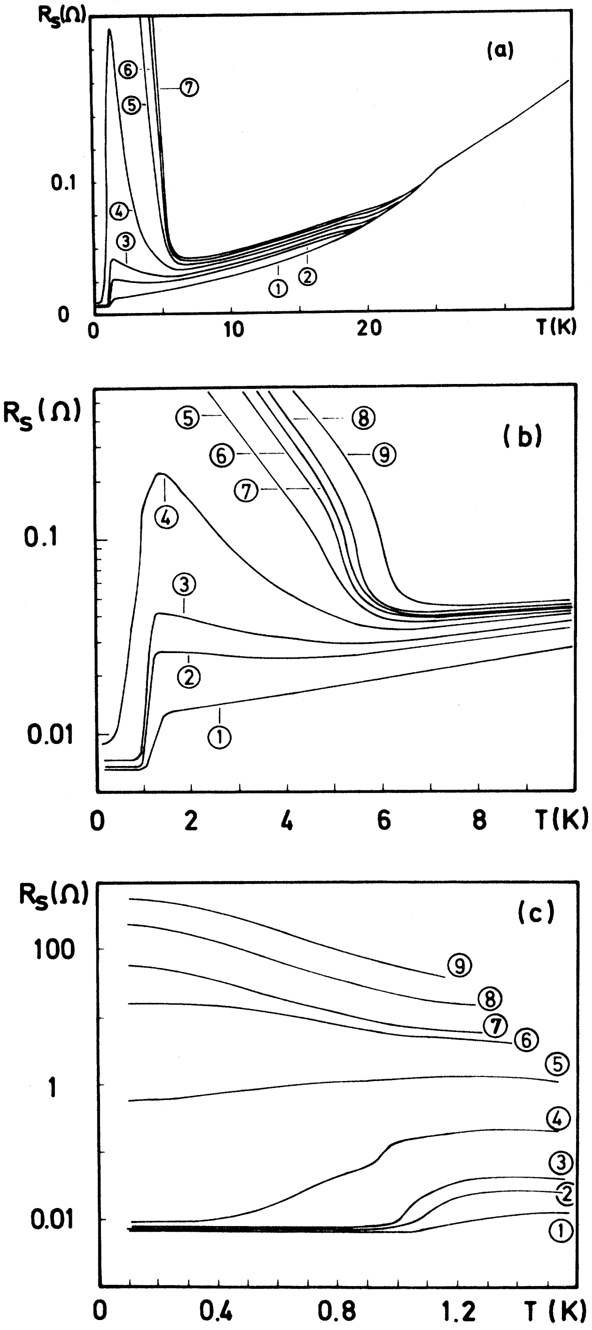

FIG. 1. Resistance vs temperature (taken upon slow warming) of (TMTSF)$_2$ClO$_4$ in states with various degrees of anion disorder, characterized by T_Q. ① to ⑨: $T_Q=0$ (relaxed state); $T_Q=22$ K; $T_Q=23$ K; $T_Q=24$ K; $T_Q=24.5$ K; $T_Q=25$ K; $T_Q=26$ K; $T_Q=28.5$ K; $T_Q=35$ K.

those with quench temperatures higher than $T_Q=25$ K. At 0.1 K the magnetoresistance $(\rho_H-\rho_0)/\rho_H$ in 8.6 kOe was 56% for $T_Q=26$ K, 21% for $T_Q=28.5$ K, and still 5% for $T_Q=35$ K. We interpret this as evidence for varying small amounts of disconnected superconducting regions in these states, in agreement with the model of an inhomogeneous mixture of superconducting and SDW regions deduced previously from Meissner effect measurements.[8] The percolation threshold for a complete superconducting path through the sample is reached for a quench temperature T_Q between 24 and 24.5 K. From the field sweeps at constant temperature we inferred the upper critical field H_{c2} (defined as midpoint of the transition) in the states with various degrees of anion disorder. When plotting H_{c2} against temperature, we always observe a linear decrease of H_{c2} towards T_c. With increasing anion disorder, the magnitude of H_{c2} first decreases to about 40% for a quench temperature of $T_Q=24$ K and then increases again for states with greater disorder, ending up (at $T_Q=28.5$ K) with a value approximately 15% higher than the relaxed one. The onset near T_c was broadened with growing disorder in the sample, indicating a spread in T_c of the different superconducting regions.

The previously observed decrease of H_{c1} (the field of first flux penetration into the sample in the Meissner measurements) with increasing anion disorder was explained with an increasing type-II character of the superconducting regions.[8] This observation is not consistent with the above mentioned H_{c2} measurements (except for the slight increase of H_{c2} above the relaxed value for highly disordered states), since the observed drop in H_{c1} amounts to more than one order of magnitude.

However, the data in Ref. 8, may not have been a measure of the true value of H_{c1}, for the following reason: If the superconducting state is spatially inhomogeneous, then, with increasing anion disorder, the superconducting domains can be less and less connected by Josephson tunneling currents, which can break down in fields lower than H_{c1}. This could mimic field penetration at much lower fields than the H_{c1} field of individual domains. On the other hand, the observed upper critical field H_{c2} should not depend on spatial inhomogeneity. Additional observations are the shifts of different characteristic temperatures for the variously ordered states, defined as follows:

(i) T_c, defined as linear extrapolation to "zero" resistance, decreases from T_c (relax) $=1.10$ K to T_c (for $T_Q=24$ K) $=0.86$ K.

(ii) $T_{\max}$, the temperature of the resistivity maximum, decreases with increasing T_Q from $T_{\max}$ (for $T_Q=22$ K) $=1.47$ K to $T_{\max}$ (for $T_Q=24.5$ K) $=1.26$ K.

(iii) $T_{\min}$, the temperature of the resistivity minimum increases with increasing T_Q from $T_{\min}$ (for $T_Q=23$ K) $=5.5$ K to $T_{\min}=7.72$ K for the quenched state (for $T_Q=35$ K).

(iv) T_{SDW}, the temperature of the phase transition as defined by the maximum of $d\ln R/dT$ increases with increasing T_Q from T_{SDW} (for $T_Q=24.5$ K) $=4.8$ K to $T_{\mathrm{SDW}}=6.05$ K for the quenched state.

Below T_{SDW}, an energy gap can be calculated from $\Delta(T)=k_BT\ln(R/R_0)$, where R_0 is the value of the resistance minimum. Below 2 K the resistivity deviates somewhat from the activated behavior, but a $\Delta(0)=11$ K may be extrapolated from the temperature dependence above. $2\Delta(0)/k_BT_{\mathrm{SDW}}=3.64$ is in excellent agreement with the mean-field value of 3.52.

It has been indicated already that the annealing of the disorder sets in at temperatures below the ordering transition. We have investigated this annealing behavior closer by slowly warming up the sample in the quenched state to various annealing temperatures T_A (0.2 K/min) and subsequently cooling back at the same speed. The results together with the quenching properties are shown in Fig. 2. The

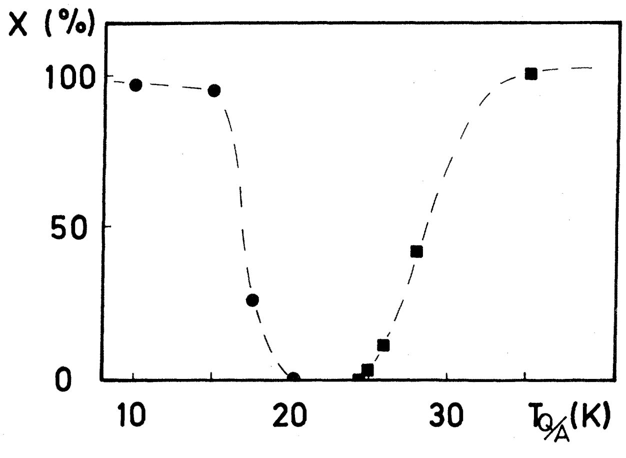

FIG. 2. Changes in the resistivity of the disordered state at 0.1 K upon quenching (■) from different temperatures T_Q as well as upon annealing (●) the quenched state at T_A. X is the resistivity at 0.1 K measured in units of the one for the completely disordered state ($T_Q = 35$ K).

main feature is that annealing the disordered state at $T_A = 20$ K almost leads back to the relaxed state (the resistivity lies in between the relaxed and $T_Q = 22$ K state, closer to the relaxed one). This behavior is in agreement with EPR data[2] and x-ray intensity measurements of the satellite reflections.[9]

The magnetoresistance $\Delta\rho/\rho_0$ in the relaxed state in a field of 8.6 kG at temperatures below 10 K (but above T_c) is positive, and decreasing in magnitude with increasing anion disorder. It always remains positive above T_{SDW}. For quench temperatures larger than 25 K it becomes negative, the change in sign occurring approximately at T_{SDW}. This negative magnetoresistance has so far only been observed in irradiated Bechgaard salts such as $(\mathrm{TMTSF})_2\mathrm{PF}_6$ (Ref. 10) and has there been attributed to decreased exchange scattering between the conduction electrons and the field oriented magnetic moments of spin defects. In the state with frozen anion disorder, no unpaired spins are present. We think that the negative magnetoresistance rather resembles the one in $(SN)_x$ where doping with bromine leads to an increased disorder and a negative magnetoresistance as well.[11] A decreasing cyclotron radius enhances the probability of the carriers not to hit the interfaces between superconducting and SDW regions in the perchlorate, thus reducing the scattering rate. We thus believe that the negative magnetoresistance is further support of the model of coexistence of superconductivity and SDW in different regions of the sample.

We want to point out another analogy between the perchlorate and the hexafluorophosphate $(\mathrm{TMTSF})_2\mathrm{PF}_6$. In the critical pressure region (~ 6.5 kbar) superconductivity and a precursing SDW were observed as an upturn in the resistivity before the superconducting drop.[12] NMR measurements of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ under pressure support the view that this state consists of a mixture of superconducting and SDW regions.[13] However, the experimental conditions leading to the intermediate state are different in the two cases. In the ClO_4 it is due to partially frozen anion disorder, whereas the centrosymmetric PF_6 is driven into this state by the application of pressure. The interplay between the SDW and superconducting ground state of the Bechgaard salts has been treated theoretically in an anisotropic two-dimensional Hubbard model with an added BCS-type attractive interaction between electrons and with the intercolumnar transfer energy t' as critical parameter.[14] These calculations rule out the possibility of a microscopical coexistence of the two ground states, which is in agreement with our experimental finding. The disorder in the ClO_4 anion leads to a small change in the lattice parameters[9] and thus to a change of the transfer integral, as does pressure in the case of the PF_6. As the transition between superconductivity and SDW is very sensitive to small variations of t',[14] sample inhomogeneities may play an important role in the nucleation of one phase out of the other, so that the resultant structure in the critical region is a mixture of superconducting and SDW islands in the sample.

In conclusion, then, we have characterized states with various degrees of frozen anion disorder (via the quenching technique) by resistance and magnetoresistance measurements of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$. The low-temperature resistivity changes over several orders of magnitude from the relaxed to the quenched state. In the intermediate state, our data are consistent with the coexistence of superconducting the SDW domains in the sample.

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