Influence of the Cooling Rate on the Superconducting Properties of the Organic Solid Di-Tetramethyltetraselenafulvalenium-Perchlorate, $(TMTSF)_2ClO_4$

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Specific-heat measurements on the organic solid di-tetramethyltetraselenafulvalenium-perchlorate $(TMTSF)_2ClO_4$ demonstrate that T_c decreases as much as 22%, when the cooling rate below 40 K is changed from 0.1 K/min (relaxed state) to 10 K/min (quenched state). The phenomenon is fully reversible as indicated by annealing experiments. The parameters of the superconducting state, the specific-heat jump, the entropy, and the upper critical fields ($\|c^*$) are strongly affected by the quenching process. A possible explanation is that quenching freezes out lattice disorder.

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The observation of superconductivity with transition temperature (T_c) about 1 K is well established in the $(TMTSF)_2X$ family of organic solids.[1] $(TMTSF)_2ClO_4$ is at present the only material which exhibits the transition at ambient pressure, established by zero resistance[2] and Meissner effect.[3] Recently specific-heat measurements on single crystals also detected the superconducting (SC) state.[4] The bulk nature of the superconductivity is indicated by the sharpness ($\Delta T/T = 4\%$) and the amplitude ($\Delta c/\gamma T_c = 1.67$) of the specific-heat anomaly. Less well established is the exact value of T_c and critical field H_{c2}. We report experimental data which show that these latter parameters are strongly affected by the thermal history of the sample. We find that superconductivity is suppressed by a thermal quenching process and optimized by slow cooling. The phenomenon is reversible and the quenched sample can be annealed at about 40 K.

The solids of the $(TMTSF)_2X$ family crystallize in the triclinic cell $P\bar{1}$ and exhibit highly anisotropic properties.[1] In the present experiment eight aligned single crystals weighing altogether 3.2 mg were glued on a thin sapphire slab placed in thermal contact with a heat sink. The ac calorimetry technique used has proved to yield accurate results on minute heat capacities as described elsewhere.[5] A flat response was obtained between 2 and 16 Hz and 8 Hz was chosen as the working frequency. The amplitude of the temperature oscillation was below 5 mK to avoid rounding effects in the critical region. The amplitudes were numerically averaged and the whole process was monitored by a minicomputer. The absolute value of the specific heat was obtained by subtracting the sample-holder heat capacity, determined in a separate run, from the rough data. Data were obtained in zero field ($H \leq 0.2$ Oe) and with the field aligned along c^* ($\pm 5°$). c^* is the lowest H_{c2} axis[6] and is perpendicular to the high-conductivity a axis.

In Fig. 1 is shown the molar electronic specific heat of $(TMTSF)_2ClO_4$ obtained after subtraction of the phonon contribution. This was deduced from measurements at higher temperature and corresponds to $\theta_D = 213$ K. The three curves are obtained with the same sample after different thermal treatments which leave θ_D unchanged.

Curve a displays data for the so-called *relaxed state* obtained by cooling the sample slowly from 40 to 0.4 K at a rate of 0.1 K/min. Curve b represents data for the *quenched state* recorded after cooling the sample from 40 to 0.4 K at a rate of ~ 10 K/min. Curve c shows data after the sample was quenched from 70 K instead of 40 K (at the same rate). The striking difference is the strong decrease of the specific-heat anomaly as-

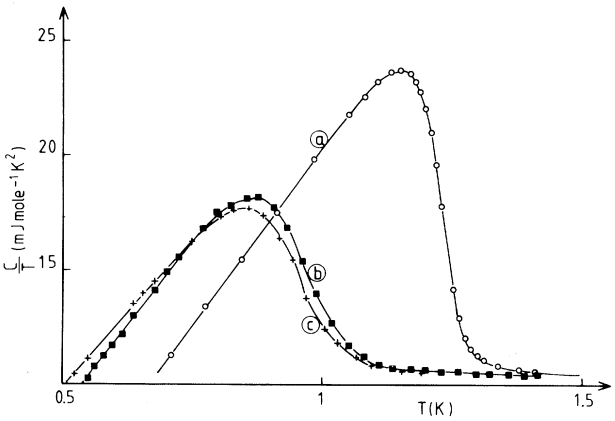

FIG. 1. Molar electronic specific heat of $(TMTSF)_2ClO_4$: curve a, after slow cooling (relaxed state); curve b, after fast cooling from 70 K (quenched state); and curve c, after fast cooling from 40 K.

sociated with the superconducting transition when the sample has been quenched. By use of entropy considerations, T_c and the specific-heat jump $\Delta C/\gamma T_c$ can be obtained from the plots.

The data are listed in Table I together with data from two other experiments: *d*, quenching a relaxed sample from 15 K (no effect), and *e*, annealing the quenched sample (full restoration). The data demonstrate that T_c is decreased by 22% and 24% by quenching from 40 and 70 K, respectively (*b* and *c*). These values are in good agreement with the spread of previously published data for T_c.[2,3,6,7] The specific-heat jump is also strongly reduced by the quenching process to a value below the BCS prediction for the weak-coupling case.

In the relaxed state, well below the transition, the specific heat follows an exponential relationship. By extrapolation to $T=0$ and subsequent integration we obtain a thermodynamical critical field $H_c(0)$ of 44 ± 2 Oe. We also observe that the entropy difference vanishes at T_c in accordance with a second-order phase transition.

In the quenched state it clearly appears that much less entropy is involved in the superconducting transition. By comparison with the relaxed state we find that only $(50\pm 10)\%$ of the electronic specific heat is involved in the superconducting pairing. Another salient feature of our data is that the superconducting transition width is increased from $\Delta T_c/T_c = \pm 4\%$ to $\Delta T_c/T_c \sim \pm 10\%$ by quenching. One possible explanation could be that the quenched state is less homogeneous than the relaxed one at the scale of the smallest coherence length. On the contrary if inhomogeneity is not involved in the transition width we must call upon departures from the mean-field behavior. As is shown in Fig. 2 this departure follows quite well a $[(T-T_c)/T_c]^{-3/2}$ dependence for temperatures far enough above T_c. Within a classical picture of the thermodynamical fluctuations[8] this would denote a one-dimensional regime restricted to a very narrow temperature range. This is very unlikely because our measurements in high magnetic field[4,9] have shown that fluctuations greatly reduce the electronic contribution to the specific heat by a pseudogap effect at least up to 3 K. Therefore the sharpness of the superconducting transition should indicate more likely that fluctuations are fully developed thermodynamically just above T_c and that their three-dimensional condensation only involves the locking of their phase. A theoretical treatment of this situation has been worked out very recently and gives a satisfactory agreement with our observations.[10]

TABLE I. Critical temperature and specific-heat jump for $(TMTSF)_2ClO_4$ subjected to various heat treatments as described in text.

	T_c (K)	$\Delta C/\gamma T_c$
a	1.221	1.67
b	0.950	1.14
c	0.93	1.10
d, *e*	1.22	1.67

Specific-heat results obtained under small magnetic fields are plotted in Figs. 3(a) and 3(b) for the relaxed and quenched states, respectively. As is generally observed for type-II superconductors, the amplitude of the specific-heat anomaly decreases and the width of the transition increases with increasing fields. For each curve the applied field equals the upper critical field $H_{c2}(T)$ at the temperature $T_c(H)$ of the jump. Thus we obtain the temperature dependence of $H_{c2}^{c^*}$ shown in Fig. 4. We observe that the slopes $(dH_{c2}^{c^*}/dt_c)_0$ amount to 1090 and 780 Oe in the relaxed and quenched states, respectively [$t_c = T_c(H)/T_c(0)$ is the reduced critical temperature]. Note also that the critical field displays an upward curvature below $t \sim 0.73$ in the quenched sample. A Ginzburg-Landau theory of coupled superducting filaments[11] explains this type of curvature by the decoupling of the filaments when the transverse coherence length becomes smaller than their separation. Such an explanation would

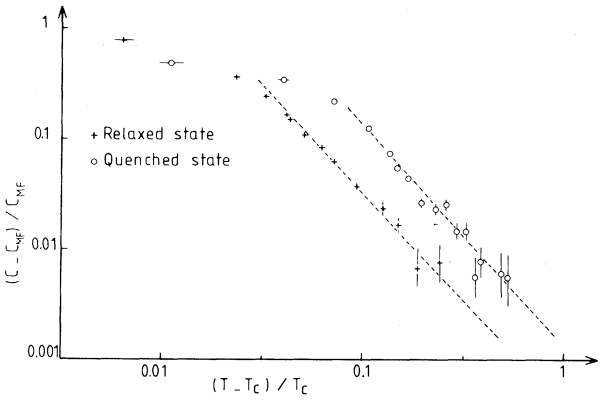

FIG. 2. Deviation from the mean-field behavior in the vicinity of the superconducting transition. C_{MF} and T_c are the mean-field values derived from the entropy argument.

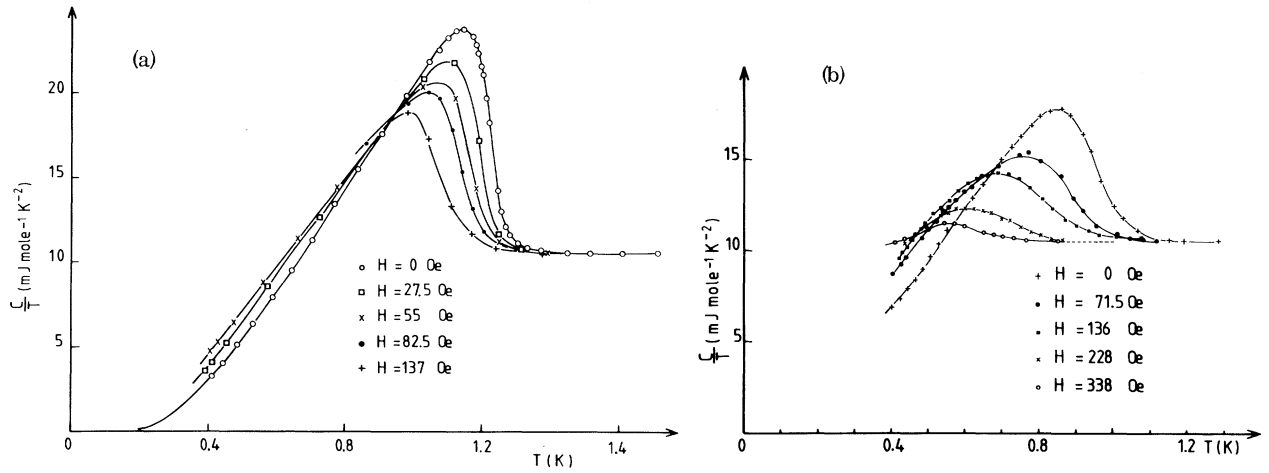

FIG. 3. Molar electronic specific heat of $(TMTSF)_2ClO_4$ in small magnetic fields ($\| c^*$) (a) in the relaxed state and (b) in the quenched state.

indicate therefore a smaller transverse coherence length in the quenched state. Within the framework of the same theory the slope of the critical field H_{c2} near $t_c = 0$ is given by

$$(dH_{c2}{}^{c^*}/dt_c)_0 \approx \varphi_0/2\pi\xi_a(0)\xi_b(0),$$

where ξ_a and ξ_b are the characteristic coherence lengths perpendicular to the applied field. If we apply this model we find that quenching enhances the coherence lengths. This is rather unlikely and we propose another explanation. Our measurements under high magnetic field[4,9] and the NMR measurements of Takahashi, Jérome, and Bechgaard[12] have shown that a magnetic [spin-density wave (SDW)] state could be restored below 1.4 K in annealed samples whereas it appears already at 4 K in quenched samples. We shall assume that the quenched samples might contain some proportion of this SDW phase even in zero field. This is to be connected with the observation, sometimes, of a resistivity upturn preceding the superconducting transition[13]; this behavior is very similar to what is observed in $(TMTSF)_2AsF_6$ in the pressure range where the superconducting phase reenters within the SDW phase.[14] Probably the upturn in $(TMTSF)_2ClO_4$ appears only in the samples which have been cooled rather rapidly below 40 K. Then if they contain some proportion of the SDW phase this could explain first the reduction of the entropy involved in the SC transition and its broadening due to the mixture of the two phases and secondly the decrease of the transition temperature and of the critical field $H_{c2}{}^{c^*}$ if we assume that the SDW regions destabilize the SC region roughly as magnetic impurities do.[15]

The cooling-rate effect is certainly related to a structural phase transition occurring between 20 and 40 K. It could involve an ordering of the counterions (ClO_4) or of the methyl groups and affect the relative stability of the SC and SDW states via a slight modification of the dimerization.[16,17]

Further experiments are necessary in order to know if a similar effect occurs when the counterions are octahedral.

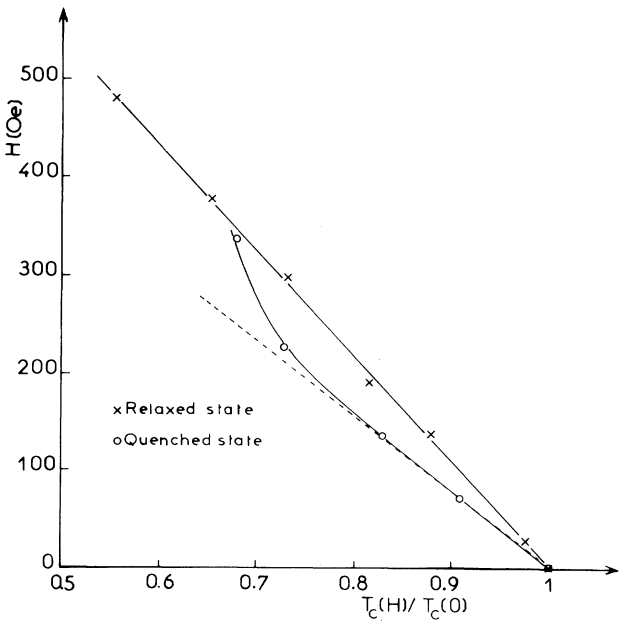

FIG. 4. Upper critical fields $H_{c2}{}^{c^*}$ of $(TMTSF)_2ClO_4$ in the quenched and relaxed states.

In summary, we have clearly established that superconductivity in $(TMTSF)_2ClO_4$ is strongly affected by quenching from rather low temperatures (20–40 K). This phenomenon is reproducible and the relaxed state is fully restored by an annealing at 40 K followed by slow cooling. In the quenched state the critical temperature is reduced by 22% and only one-half of the electronic entropy is still involved in the superconducting condensation. The upper critical field is also reduced and the transition is broadened; we suggest that these modifications are related to a reappearance (induced by quenching) of the SDW state which mixes with the normal SC state.

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[1]For recent reviews, see Proceedings of the International Conference on Low Dimensional Solids, Mol. Cryst. Liq. Cryst. 79, 357–707 (1982).

[2]K. Bechgaard, K. Carneiro, M. Olsen, F. B. Rasmussen, and C. S. Jacobsen, Phys. Rev. Lett. 46, 852 (1981).

[3]H. Schwenk, K. Neumaier, K. Andres, F. Wudl, and E. Aharon-Shalom, Mol. Cryst. Liq. Cryst. 79, 277 (1982).

[4]P. Garoche, R. Brusetti, D. Jérome, and K. Bechgaard, J. Phys. (Paris), Lett. 43, L147 (1982).

[5]P. Garoche, P. Manuel, J. J. Veyssié, and P. Molinié, J. Low Temp. Phys. 30, 323 (1978).

[6]R. L. Greene, P. Haen, S. Z. Huang, E. M. Engler, M. Y. Choi, and P. M. Chaikin, Mol. Cryst. Liq. Cryst. 79, 539 (1982).

[7]D. U. Gubsen, W. W. Fuller, T. O. Poehler, D. O. Cowan, M. Lee, R. S. Potember, L. Y. Chiang, and A. N. Bloch, Physica (Utrecht) 108B, 1185 (1981).

[8]W. J. Skocpol and M. Tinkham, Rep. Prog. Phys. 38, 1049 (1975).

[9]R. Brusetti, P. Garoche, and K. Bechgaard, to be published.

[10]C. Bourbonnais and H. J. Schulz, to be published.

[11]L. A. Turkevich and R. A. Klemm, Phys. Rev. B 19, 2520 (1979).

[12]T. Takahashi, D. Jérome, and K. Bechgaard, to be published.

[13]S. S. P. Parkin, M. Ribault, D. Jérome, and K. Bechgaard, J. Phys. C 14, 5305 (1981).

[14]R. Brusetti, M. Ribault, D. Jérome, and K. Bechgaard, J. Phys. (Paris) 43, 801 (1982).

[15]A similar effect is found in the ternary rare-earth compounds where antiferromagnetism and superconductivity can coexist; see, for example, H. C. Hamaker and M. P. Maple, Physica (Utrecht) 108B, 757 (1981); for the effect of magnetic impurities on H_{c2} see J. Sosnowski, M. Drys, and T. Mydlarz, Phys. Status Solidi (a) 57, 337 (1980), and references therein.

[16]B. Horovitz, H. Gutfreund, and M. Weger, Mol. Cryst. Liq. Cryst. 79, 598 (1982).

[17]V. J. Emery, R. Bruinsma, and S. Barisic, Phys. Rev. Lett. 48, 1039 (1982).

Reconstruction Mechanism and Surface-State Dispersion for Si(111)-(2 × 1)

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Pseudopotential total-energy calculations show that the π-bonded chain reconstruction of the Si(111)-(2×1) surface can be reached from the ideally bonded surface without increasing the total energy by more than 0.03 eV/(surface atom). Hence, the chain surface can be formed easily in the cleavage process. The minimum-energy chain geometry is determined, and the corresponding surface-state dispersion is in remarkable agreement with recent angle-resolved photoemission experiments.

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The π-bonded chain model for the Si(111)-(2×1) surface was proposed by Pandey[1] mainly because of its ability to explain spectroscopic data. In this paper we show that the chain surface is an easily accessible final state of the cleavage process, and suggest a path in atom coordinate space by which the reconstructed surface may be reached.

The chain model requires that the bonding topology of the surface be changed from that of the ideal surface. It has been argued that this geometry, although lower in energy than the minimum-