Antiferromagnetic and structural instabilities in tetramethyltetrathiafulvalene thiocyanate [$(TMTTF)_2SCN$]

C. Coulon, A. Maaroufi, J. Amiell, E. Dupart, S. Flandrois, and P. Delhaes
Centre de Recherches Paul Pascal, Centre National de la Recherche Scientifique, Domaine Universitaire de Bordeaux I, F-33405 Talence Cedex, France

R. Moret and J. P. Pouget
Laboratoire de Physique des Solides, Bâtiment 510, Université de Paris-Sud, F-91405 Orsay Cedex, France

J. P. Morand
Ecole Nationale Supérieure de Chimie et Physique de Bordeaux, Université de Bordeaux I, 351 cours de la Libération, F-33405 Talence Cedex, France
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The low-temperature phase transitions of tetramethyltetrathiafulvalene thiocyanate are described through magnetic and structural studies. A first transition, which occurs at 160 K, drives the electron gas into a localized state and is shown to be associated with a superstructure formation. Then, the condensation of an unexpected antiferromagnetic ground state is observed around 7 K. We suggest that this striking behavior is related to the peculiar wave vector $(a^*, \frac{1}{2}b^*, \frac{1}{2}c^*)$ of the 160-K superstructure.

With the synthesis of the tetramethyltetrathiafulvalinium (TMTTF) and tetramethyltetraselenafulvalinium (TMTSF) radical cation salts[1,2] began a new exciting period for the study of organic conductors. Even if the superconductivity is the most striking low-temperature property occurring in the TMTSF series,[3–5] other distinctive instabilities have been revealed by experimental studies on these compounds. First, order-disorder transitions involving a counterion ordering sometimes occur for noncentrosymmetrical anions.[6] Moreover, a spin-density-wave (SDW) ground state was for the first time discovered as an intrinsic instability of the one-dimensional electron gas.[7,8] The condensation of this unusual ground state was recently explained by Emery, Bruinsma, and Barisic[9] as the result of the peculiar "zig-zag" structure of the conductive chains.

The TMTTF radical cation salts are isostructural to their selenium analogs[10] and the same theoretical background must also be relevant for these compounds. Experimentally, order-disorder transitions are also observed for noncentrosymmetrical anions.[6,11] Concerning the intrinsic properties of the TMTTF chains, two opposite behaviors are found. The conductivity of $(TMTTF)_2Br$ is close to that of the TMTSF salts,[11] particularly under high pressure,[12] and the recent discovery of its SDW low-temperature ground state[13,14] is also explained within the theory of Emery, Bruinsma, and Barisic.[9] On the other hand, the other TMTTF salts have a moderate longitudinal conductivity which exhibits a broad maximum around 200–250 K at ambient pressure.[11] In the frame of the Emery-Bruinsma-Barisic model this behavior is due to the growth of a charge-density wave (CDW) with the wave vector (a^*,b^*,c^*) which favors the condensation of a low-temperature spin-Peierls (SP) phase. This nonmagnetic phase has been observed below 15 K in $(TMTTF)_2PF_6$.[11,15] The qualitative difference between the SDW and the SP states is clearly established by EPR measurements: Because of the growth of an internal field, the EPR signal becomes unobservable in the SDW phase at the usual g values.[16] On the other hand, a conventional resonance line is detected in the SP phase.[11] Furthermore, the antiferromagnetic (AF) character of the SDW ground state has been characterized by the anisotropy of the static susceptibility.[7]

We describe in this Communication the low-temperature structural and magnetic properties of $(TMTTF)_2SCN$ and discuss the nature of the phase transitions observed in this compound.

Single crystals of $(TMTTF)_2SCN$ were grown using the electrochemical technique.[2] Their electrical behavior is similar to the previously reported one[11]: A broad maximum of conductivity is observed around 240 K. Then a sharp phase transition occurs at 160 K and the compound becomes an insulator at lower temperature. The high-pressure phase diagram has been established by Parkin, Coulon, and Jerome[17] and is similar to that of $(TMTSF)_2ReO_4$.[18] For this reason it has been suggested that this transition might be induced by an ordering of the SCN anions. To clarify this point an x-ray study combining the "monochromatic Laue" and Weissenberg

techniques was undertaken. Monochromatic Laue patterns from $(TMTTF)_2SCN$ clearly reveal the formation of superlattice reflections below 160 K. But at the difference of those already observed in $(TMTSF)_2ReO_4$ they belong to layers of main Bragg reflections perpendicular to the a stacking direction. No superstructure reflections or diffuse scattering at the $a^*/2(2k_F)$ wave vector could be detected down to 18 K. In addition, a Weissenberg reciprocal-lattice plane of one of these layers, presented in Fig. 1, shows more clearly that these superstructure reflections are characterized by the wave vector $(a^*,\frac{1}{2}b^*,\frac{1}{2}c^*)$ [instead of $(\frac{1}{2}a^*,\frac{1}{2}b^*,\frac{1}{2}c^*)$ for $(TMTSF)_2ReO_4$ (Ref. 6)]. By analogy with the structural analysis performed in the latter compound,[6] an anion ordering (and possible change in the dimerization of the TMTTF stacks) is probably involved in the 160-K phase transition of $(TMTTF)_2SCN$. Structural refinements are necessary to deepen this aspect.

The paramagnetic susceptibility does not show any anomaly at 160 K. It is a smoothly decreasing function of temperature down to 7 K, where another phase transition is revealed by a sharp minimum of the paramagnetism. Figure 2 gives the three principal components of the g factor and linewidth (ΔH) EPR resonance line. An unexpected maximum of ΔH occurs around 30 K. Then a divergence of the linewidth is observed and the resonance signal becomes broad and undetectable below 10 K. In the same temperature range, the g-factor components become strongly temperature dependent. The anisotropy of susceptibility ($\Delta\chi$) has been measured, as a function of the temperature and magnetic field strength, using Krishnan's method.[19] This method gives the difference between the two principal susceptibilities in the plane of rotation of the crystal. The principal axes were found to be approximately along crystallographic directions[10] a,b^*,c^*; their accurate determination will be given elsewhere.[20] The results are presented in Fig. 3. They indicate a strong decrease of the paramagnetic susceptibility along the b^* axis at low field for $T < 7$ K. The anisotropy is removed above this temperature or for a critical value ($H_c \cong 9000$ G) of the applied magnetic field.

The EPR and $\Delta\chi$ results suggest an antiferromagnetic ordering below 7 K. The divergences of both linewidths and g components of the EPR signal above the transition temperature are typical of the behavior of a quasi-one-dimensional insulating antiferromagnet[21]; they give account for the growth of the short-range order of the spins. The magnetic properties below the phase transition are consistent with an easy

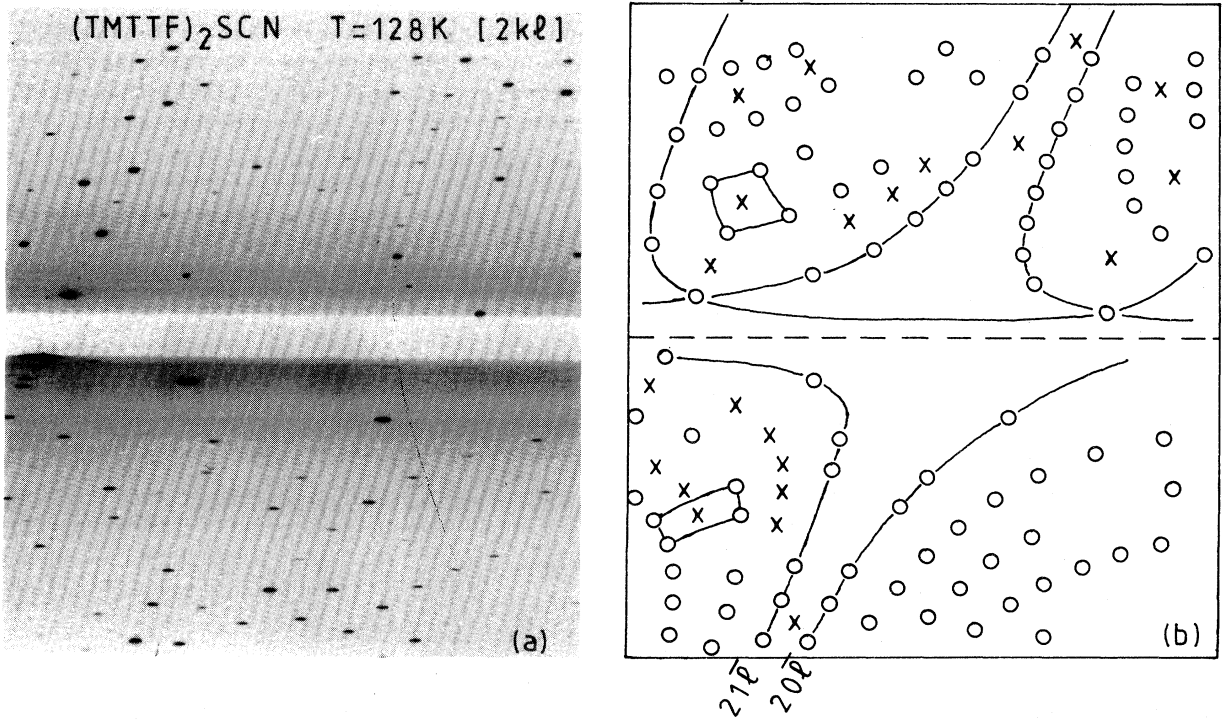

FIG. 1 (a) $[2,k,l]$ Weissenberg photograph of $(TMTTF)_2SCN$ at 128 K. (b) Schematic pattern illustrating (a): Superstructure reflections (crosses) are located on the center of reciprocal cells of the main lattice (circles) thus giving a reduced wave vector of $(0,\frac{1}{2},\frac{1}{2})$. Two of these cells are drawn for clarity.

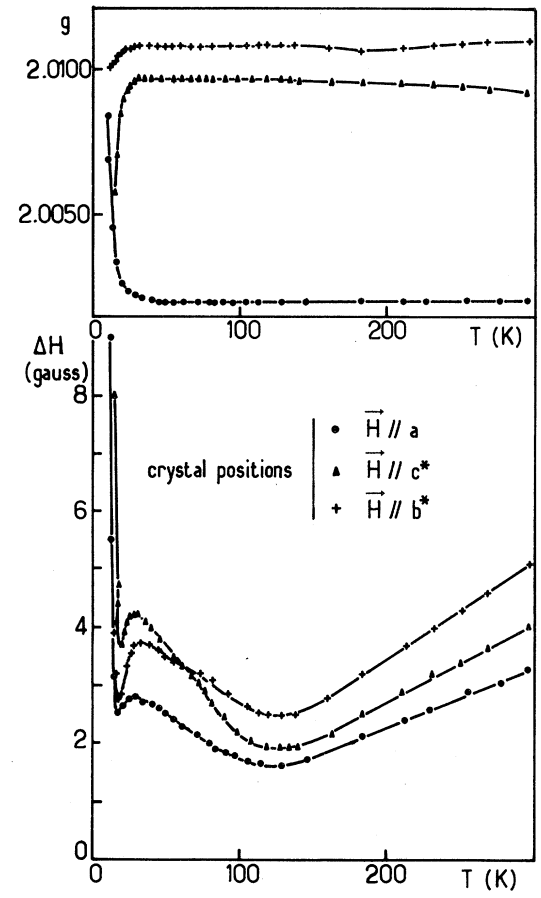

FIG. 2. EPR (X band) g-factor and linewidth (ΔH) principal components.

axis close to b^* and a spin-flop field of nearly 9000 G.[22]

The physical properties of the $(TMTTF)_2X$ salts can be discussed within the theory of Emery, Bruinsma, and Barisic.[9] According to this work, the growth of a CDW with the wave vector (a^*,b^*,c^*) drives continuously the TMTTF chains into an insulating state (i.e., without any phase transition) and favors the condensation of a low-temperature SP phase. Only the a^* (i.e., $4k_F$) component is important to describe the one-dimensional electronic localization. On the other hand the three components of the wave vector are essential to understand the competition between the AF and SP ground states. In $(TMTTF)_2PF_6$ the periodicity of the 15-K structural distortion has been recently determined.[23] The obtained wave vector is $(\frac{1}{2}a^*,\frac{1}{2}b^*,\frac{1}{2}c^*)$, i.e., half of the CDW wave vector, and the nonmagnetic phase is favored by the coupling between the CDW and the SP order parameters.[24,25]

In $(TMTTF)_2SCN$ the insulating state does not appear gradually in temperature, as considered by the theory of Emery, Bruinsma, and Barisic,[9] but abruptly after a structural phase transition occurring at 160 K where a maximum of the logarithmic derivative of the conductivity is observed.[11] This phase transition is not detected on the magnetic susceptibility. In this respect the change below 160 K of the $4k_F$ potential in the chains direction coming from the SCN ordering (and from a possible increase of the TMTTF dimerization) may favor the Mott-Hubbard localization of one electron per diad. Another important consequence of the structural phase transition which promotes the $(a^*,\frac{1}{2}b^*,\frac{1}{2}c^*)$ periodicity is that a further growth of the (a^*,b^*,c^*) CDW is excluded. No

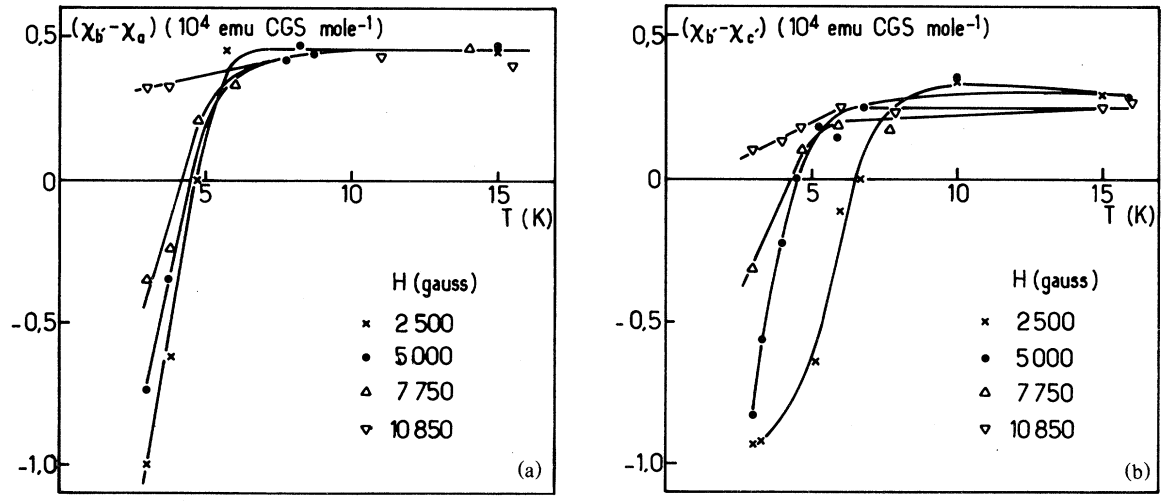

FIG. 3. (a),(b) Anisotropy of the magnetic susceptibility for different values of the magnetic field (b' and c' are close to b^* and c^* axes, respectively).

relevant coupling between the $(a^*,\frac{1}{2}b^*,\frac{1}{2}c^*)$ CDW and the $(\frac{1}{2}a^*,\frac{1}{2}b^*,\frac{1}{2}c^*)$ SP order parameter can be established and the nonmagnetic ground state observed in $(TMTTF)_2PF_6$ cannot develop at low temperature. More physically the transverse components of the 160-K distortion correspond to an antiphase ordering between charged chains which minimizes their Coulomb repulsion.[26] With this configuration a spin-Peierls displacement of charges along a may be energetically less favorable than the observed antiferromagnetic ordering of the spins. In addition, the anion ordering could give some distinctive characters to the AF phase. For example, the anisotropy field could be enhanced and be at the origin of the g-factor temperature dependence below 40 K (see Fig. 2).

In conclusion, we have shown that $(TMTTF)_2SCN$ is a unique compound among the TMTTF series. A $4k_F$ structural transition drives the electronic gas into a localized state without opening a gap in the magnetic excitations. Because of the periodicity of the corresponding superstructure, the low-temperature SP phase is not favored and an unexpected AF ground state occurs whose origin is completely different from that of the SDW phase of $(TMTTF)_2Br$.

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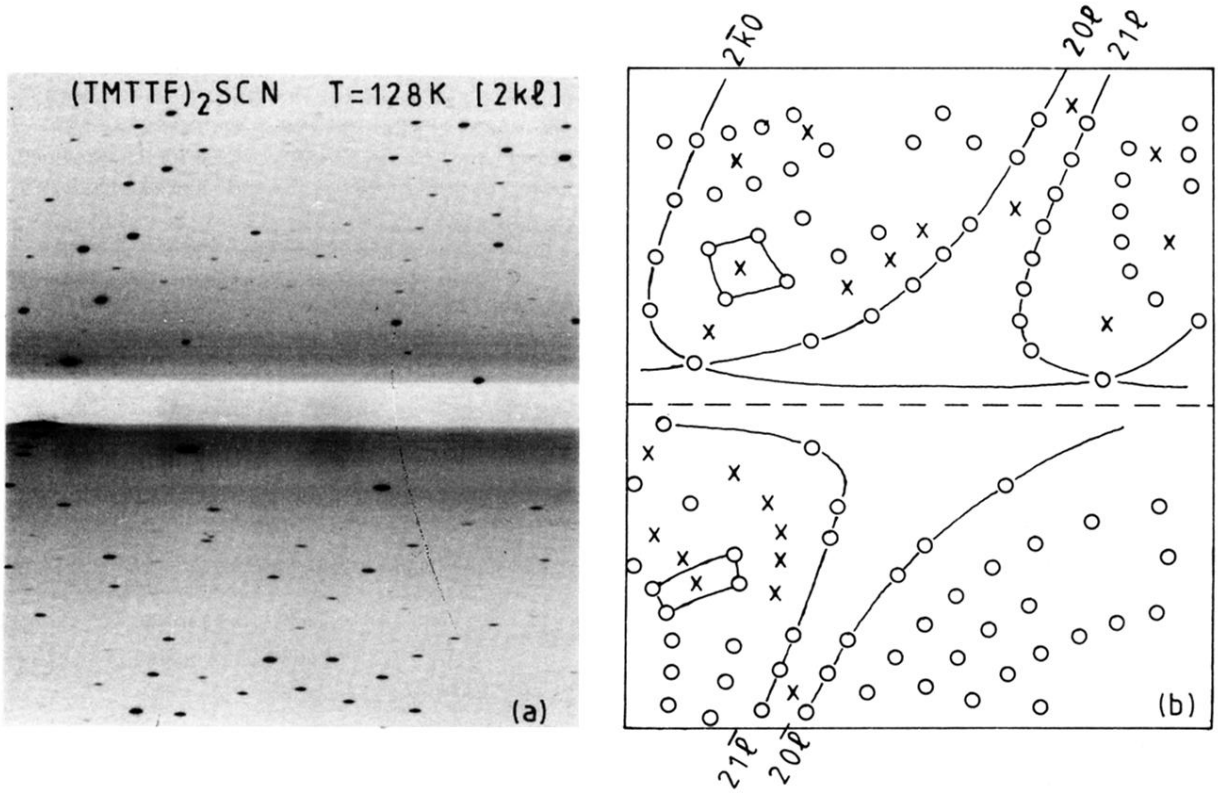

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