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CDW instability in the 2:1 organic conductor $(FA)_2PF_6$

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Abstract

We present an X-ray diffuse scattering study of the fluoranthene radical cation salt $(FA)_2PF_6$, where FA is the fluoranthene molecule, $C_{16}H_{10}$. Below room temperature this salt undergoes two successive structural phase transitions. The upper one, at $T_C \approx 200K$, breaks the face center Bravais lattice symmetry. The lower one, of the Peierls type, corresponds to the 3D ordering of quasi-1D $2k_F$ charge density waves (CDW) at $T_P \approx 180K$, temperature below which collective transport phenomena are observed. We compare this material to the Bechgaard salts $(TMTS(T)F)_2X$, of very similar stack structure but where a Peierls CDW ground state is not stabilized.

Introduction

Fluoranthene radical cation salts $(FA)_2X$, belong to a larger family of arene salts $(Ar)_2^+X^-$, where Ar is an aromatic molecule and X is a monovalent anion like PF_6^- . $(FA)_2PF_6$ is composed of slightly dimerized donor stacks of fluoranthene molecules piled in a zig-zag manner along the **a** direction [1] and whose structure strongly resembles to that of Bechgaard salts $(TMTS(T)F)_2X$. Columns of anions X separate molecular stacks in the **b** and **c** directions. Stoichiometry 2:1 and full charge transfer to the anion X lead to an average charge of 0.5 hole per FA and thus to $2k_F = 0.75a^*$ or $0.5a^*$ depending whether the average molecular periodicity $a' = (d_1 + d_2)/2$ or the true crystallographic periodicity ($a = 2a'$) is considered.

Electrical [2] and polarized reflectance [3] measurements prove that $(FA)_2PF_6$ is a very anisotropic 1D metal. Transport [2,4] and magnetic [5] measurements show the existence of a metal-insulator phase transition at $T_P \approx 180K$. Below this temperature collective transport phenomena are observed and interpreted as due to the sliding of CDW [4]. The main purpose of this paper is to present structural evidences of such a CDW transition and to clarify its relationship with the $A2/m \rightarrow P2_1/c$ structural transition previously reported by Enkelmann et al. [1].

Experimental results

We studied two crystals coming from different preparations and grown at the University of Bayreuth.

The first crystal was studied by the fixed film - fixed crystal method in order to have a general survey of the structural properties of $(FA)_2PF_6$. One observes (fig. 1) :

- quasi 1D fluctuations giving rise to $2k_F = 0.5a^*$ diffuse lines at room temperature (RT) (\blacktriangleright)

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- on the diffuse lines broad superstructure satellite reflections at the reduced wave vector $\mathbf{q}_P = (0.5, 0, 0)$ below $T_P = (179 \pm 1)K$ (\blacktriangleright)
 - new sharp reflections at $\mathbf{q}_A = (0, 1, 1)$, which break the face center symmetry of the RT structure below $T_C = (201 \pm 1)K$ (\blacktriangle).

$2k_F$ quasi-1D fluctuations are observed from 300 to 30K (the lowest temperature reached was 15K). Fig. 2 shows the temperature dependence of $T/I(2k_F)$, where $I(2k_F)$ is the $2k_F$ peak intensity. This quantity, proportional to the inverse CDW susceptibility, χ_P^{-1} , decreases linearly with T . However, in this first sample χ_P^{-1} does not vanish at T_P in agreement with the observation of only a CDW short range order below T_P . (The Scherrer formulae applied to the half width at half maximum (HWHM) of the \mathbf{q}_P reflection gives a domain length $L \approx 45\text{\AA}$).

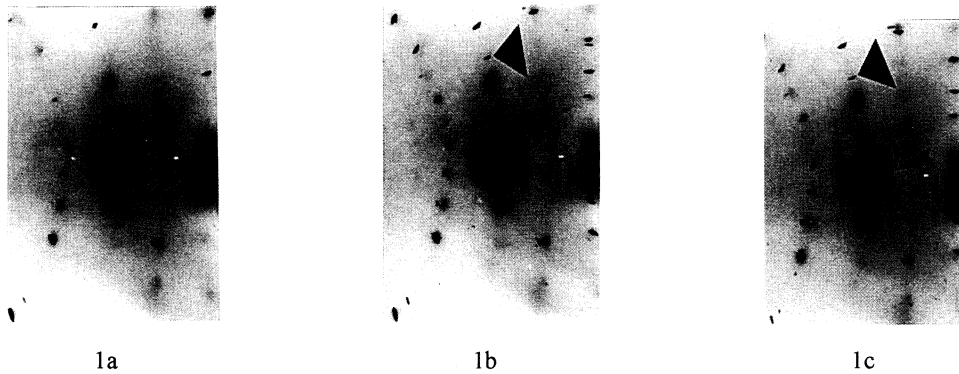


Fig. 1. X-ray patterns of $(FA)_2PF_6$ at 300K (a), 190K (b) and 175K (c). The chain axis a is horizontal.

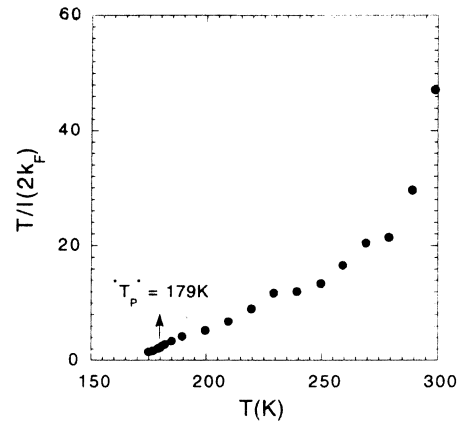


Fig. 2. Temperature dependence $\chi_P^{-1} \sim T/I(2k_F)$.

An accurate study of the two structural transitions was performed by a counter method on the second crystal. Figs. 3 and 4 show respectively the temperature dependence of the intensity of the \mathbf{q}_P and \mathbf{q}_A superlattice reflections, $I(\mathbf{q}_P)$ and $I(\mathbf{q}_A)$ respectively, as well as their HWHM ; at $T = 30K$: $I(\mathbf{q}_A) \approx I(\text{Bragg}) \approx 100 I(\mathbf{q}_P)$. Note that the width of the \mathbf{q}_P reflection amounts to that of the main Bragg reflections (i.e. the experimental resolution) which means that the sample has achieved a CDW long range

order. Surprisingly, the q_A reflections seem to have a width slightly larger than the experimental resolution. $I(q_P)$ increases sharply below T_P without a detectable hysteresis. $I(q_A)$ increases linearly below T_C but does not saturate at low temperature. The second crystal has slightly lower critical temperatures [$T_C = (194 \pm 1)K$, $T_P = (176.7 \pm 0.3)K$] than the first one.

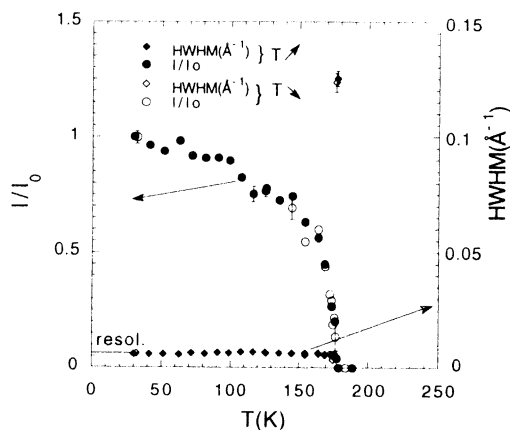


Fig. 3. Temperature dependence of the normalized integrated intensity and HWHM of the q_P reflection upon cooling and heating.

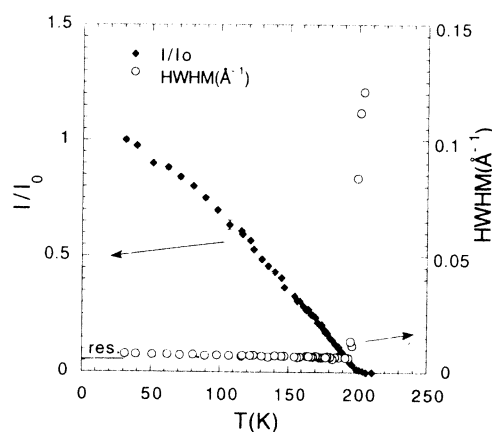


Fig. 4. Temperature dependence of the normalized integrated intensity and HWHM of the q_A reflection.

Discussion

$(FA)_2PF_6$ undergoes two structural transitions which are apparently decoupled because the linear dependences of χ_{ρ}^{-1} (fig. 2) and of $I(q_A)$ (fig. 4) are not modified at T_C and T_P respectively. The upper transition corresponds to the $A2/m \rightarrow P2_1/c$ structural change previously ascribed to an interstack staggered rotation of the FA molecules (fig. 5b) [1]. The lower one is a Peierls transition. It is announced by an important regime of $2k_F$ quasi-1D fluctuations causing the opening of a pseudogap in the density of state which affects the thermal dependence of the conductivity [2] and magnetic susceptibility [5] above T_P . The linear decrease of $\chi_{\rho}^{-1}(2k_F) \approx T - T_P$ recalls that measured in the blue bronze [6] where the Peierls instability is driven by an important electron-phonon coupling. The interchain zero wave vector components of q_P imply that the CDWs are in-phase along the 2nd neighbouring stacks in b and c directions. In principle a structural refinement is necessary in order to determine the phase shift ϕ between the 1st neighbouring CDWs (fig. 5c) (a phase $\phi = \pi$ is expected for equal Coulomb interactions between them). Finally, our investigation shows that the spatial extent of the CDW order in $(FA)_2PF_6$ is very sensitive to the crystal quality (i.e. to chemical damage of the FA molecule).

Besides fluoranthene salts, a $2k_F$ CDW instability is also observed in 2:1 substituted perylene radical cation salts [7], but not in the Bechgaard salts. Table 1 compares more quantitatively $(FA)_2PF_6$ with the Bechgaard salts $(TMTSF)_2PF_6$ and $(TMTTF)_2PF_6$ which have the same charge transfer and stack structure. The electron-electron interactions (leading to a spin susceptibility enhancement proportional to $t_{\parallel}\chi_{spin}$) increase from FA to TMTSF then to TMTTF salts while the ground state evolves from $2k_F$ CDW to spin density wave (SDW) then to spin-Peierls (SP), respectively. Only in $(TMTTF)_2PF_6$ a true $4k_F$ charge localization is observed. Table 1 shows that the degree of dimerization δ of the stacks does not follow the strength of Coulomb interactions, probably because δ is mainly determined by the interactions between σ electrons on the donors and anions and not by the $4k_F$ response

of the π electron clouds. The efficient screening of Coulomb interactions in the FA salts can be simply understood by the strong polarizability of the Ar molecules composed of a large number of rings.

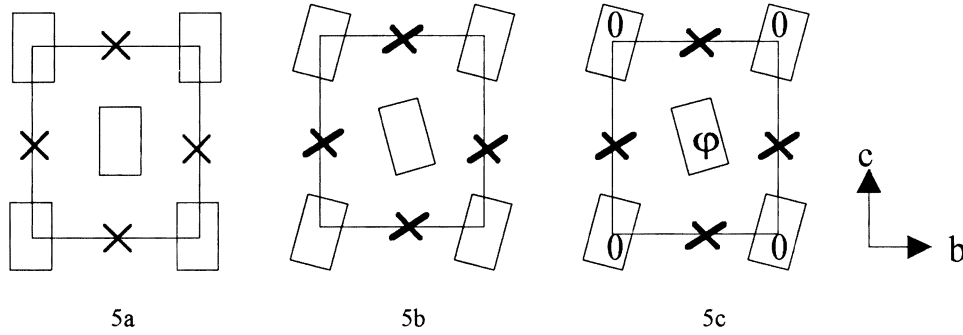


Fig. 5. Schematic representation of the projection along a direction of the structure of the $(FA)_2PF_6$ at RT (a), between T_c and T_p (b) and below T_p (c). ϕ is the phase shift between 1st neighbouring CDWs. The FA stacks are represented by open rectangles and the PF_6^- anions by crosses.

Table 1. Comparison between some physical properties of $(FA)_2PF_6$ and of the Bechgaard salts $(TMTSF)_2PF_6$ and $(TMTTF)_2PF_6$.

	donor molecule	RT structure	$\delta^{RT} = \frac{d_2 - d_1}{d_2 + d_1}$	$\sigma_{ }^{RT} (\Omega cm)^{-1}$	$\frac{\sigma_{ }}{\sigma_{\perp}}$	$t_{ }^{opt} (eV)$	$\chi_{spin}^{RT} (emu/mol)$	4k _F charge localisation	ground state
FA_2PF_6		A2/m	7.6×10^{-3}	$10^2 - 10^3$	$\sim 10^4$	0.35	1×10^{-4}	NO	CDW (180K)
$TMTSF_2PF_6$		$P\bar{1}$	4×10^{-3}	540	$\frac{\sigma_a/\sigma_b' \sim 10^2}{\sigma_a/\sigma_c' \sim 10^4}$	0.25	2.5×10^{-4}	NO	SDW (12K)
$TMTTF_2PF_6$		$P\bar{1}$	14×10^{-3}	40	?	0.20	6×10^{-4}	YES $T_p \approx 230K$	SP (15K)

Conclusion

Below room temperature $(FA)_2PF_6$ undergoes two close but independent structural transitions. The upper one corresponds to that previously reported in ref. [1]. The lower one is a commensurate CDW Peierls transition which provides the structural proof of the collective transport phenomena observed below 180K [4]. However, it is interesting to remark that the threshold field measured in $(FA)_2PF_6$ (0.1-1V/cm [4]) is not so different from that observed in $\sim 3/4$ and $\sim 1/4$ filled band metals such as the blue bronzes (~ 50 mV/cm) [8] and TaS_3 (200-300mV/cm) [6] whose CDW are incommensurate. This means either that $(FA)_2PF_6$ could be considered as a $3/4$ filled band metal (i.e. $2k_F = 0.75a^*$) where the pinning effects due to commensurability are weak, or that the observed nonlinear conductivity is due to slight deviations from the ideal 2:1-stoichiometry, as pointed out elsewhere [9].

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