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Defect-concentration dependence of the spin-density-wave transport in the organic conductor $(TMTSF)_2PF_6$ (TMTSF=tetramethyltetraselenafulvalene)

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We have studied the effects of chemical impurities and x-ray irradiation-induced defects on the electric-field-dependent conductivity in the spin-density-wave (SDW) state of the organic conductor $(TMTSF)_2PF_6$. For a large number of nominally pure samples the temperature dependence of the threshold field agrees with theoretical predictions that assume weak coupling between the SDW and chemical impurities. For irradiated samples the threshold field increases linearly with the defect concentration and its temperature dependence corresponds to that expected in the strong-coupling limit.

Fröhlich conduction arising from the sliding of the charge-density-wave (CDW) condensate under an applied electric field is a well established phenomenon in a number of anisotropic conductors, both organic and inorganic.[1] Recently, the non-Ohmic dc conductivity,[2–4] the frequency-dependent conductivity,[5] and preliminary evidence for narrow-band noise[4] were reported in the spin-density-wave (SDW) ground state of some Bechgaard salts $(TMTSF)_2X$ (where TMTSF is tetramethyltetraselenafulvalene), indicating Fröhlich conduction. Theoretically, the translational symmetry of the SDW state is broken, as for a CDW state, by impurities, crystalline defects, and/or by commensurability with the underlying lattice.[6] Consequently, a finite threshold field is expected for SDW conduction. Indeed, sharp threshold fields in the range of 4–40 mV/cm have been found in three different materials measured until now [$X = NO_3$,[2] PF_6,[3] and quenched(Q-) ClO_4 (Ref. 4)].

In a recent paper we have reported experiments on the electric-field-dependent conductivity in the SDW state of the model compound $(TMTSF)_2PF_6$.[3] Well below the transition temperature (T_c), there was clear evidence for an increased dc conductivity above a finite threshold field of about 4 mV/cm, in comparison to 25 and 40 mV/cm found for the Q-ClO_4 and NO_3 compounds, respectively. While the threshold field (E_T) was temperature independent below $T_c/2$ as for the materials measured previously, it was found to decrease on approaching T_c, and then increase sharply at T_c.[2] We have suggested that such a behavior shows that the dominant pinning mechanism in pristine samples could be the commensurability pinning. Indeed, fourth order longitudinal commensurability between the SDW and the underlying lattice[7] is not unexpected for the PF_6 compound since proton NMR studies estimate the magnetic-distortion wave vector to be close to the $(0.5a^*, 0.25b^*)$ value, ignoring the third c^* direction.[8,9] Here, one has to keep in mind that if the dimerization is negligibly small, i.e., $a^* = a'^*/2$, it follows that $\mathbf{Q}_{SDW} = (0.25a'^*, 0.25b^*)$.[1] However, for some other samples, the SDW transition was smeared out and E_T showed a steady increase towards T_c, as expected if impurity pinning is dominant.[3] As the latter behavior was obtained for samples with painted contacts which displayed some resistance jumps associated with microcracks on cooling, we concluded that the commensurability pinning in pristine samples might be easily overcome by the impurity pinning in strained samples. This result raised a more general question about the nature and the concentration of defects needed to make the impurity pinning dominant.

Therefore, we have undertaken a systematic study of the influence of pinning centers on E_T in pristine samples from different chemical batches and in samples with a controlled amount of x-ray irradiation-induced defects. All samples studied in the present work were mounted in the strain-free fashion described previously in Ref. 3. By monitoring the electrical resistivity continuously while cooling we could verify that externally induced defects like microcracks did not occur. Nevertheless, we find that even in the absence of microcracks the SDW transition and, in particular, its sharpness and the low-field resistivity behavior close to T_c, are quite sensitive to the quality of a particular batch of samples, and so is the non-Ohmic conductivity. Therefore we believe that even impurities created during standard electrochemical crystal growing might cause the impurity pinning to be strong enough to overcome the originally dominant commensurability pinning. Therefore, the subtle balance between commensurability and impurity pinning is not primarily a consequence of the technique used to make contacts, instead it is determined by the chemical purity of the original samples.

In this paper we report a study of the effect of irradiation-induced defects on the non-Ohmic transport in the SDW state of $(TMTSF)_2PF_6$. All measurements have been done on samples from the same batch. We

studied six pristine samples and they all show a sharp phase transition at 11.1 ± 0.1 K and non-Ohmic conductivity above E_T of 7 ± 0.5 mV/cm at 4.2 K. E_T is temperature independent below $T_c/2$ and increases at high temperatures, reaching a value of about 18.5 mV/cm at $0.9T_c$. Irradiation-induced defects lead to a smearing of the originally sharp transition and also modify the electric-field-dependent transport. In particular, at low temperatures E_T increases linearly with defect concentration and, its rise approaching T_c, as well as the magnitude of the excess conductivity, becomes appreciably smaller. We will show that such behavior might well be explained in the framework of a recent theory by Maki and Virosztek[7] in which the phason dynamics is determined by commensurability and/or impurity pinning.

Single crystals of $(TMTSF)_2PF_6$ with typical dimensions of $3 \times 0.07 \times 0.05$ mm^3 were selected from the same batch and exposed to unfiltered radiation from a Cu x-ray tube (35 kV, 24 and 20 mA). The concentration of irradiation-induced defects were determined using a TMTSF-DMTCNQ (DMTCNQ=dimethyletetracyanoquinodimethane) crystal as a reference sample. The correspondence between damage rates and resulting resistance changes of TMTSF-DMTCNQ was established in previous studies.[10] The field-dependent conductivity was measured by a pulse method as described previously.[11] Furthermore, under favorable circumstances checked by standard tests for sample heating we were able to determine E_T by using the much more sensitive dynamic resistance measurement technique. At very low temperatures and for high low-field resistances a standard dc technique was also used.

Figure 1 shows the temperature dependence of the low-field resistance for a nominally pure sample and for samples irradiated up to a molar defect concentration (c) of 0.04% . All samples had the same room-temperature conductivity $\sigma_{RT} = 500 \pm 100\ (\Omega\,\mathrm{cm})^{-1}$. However, the resistivity ratio (RR) between the room-temperature value and the minimum reached just above the SDW phase transition decreases strongly with the defect concentration. For pristine samples the transition temperature is $T_c = 11.1 \pm 0.1$ K. The width of the transition is defined as the full width at half maximum of $d\log_{10} R/d(1/T)$. The transition remains sharp for small defect concentrations (for $c \leq 0.004\%$, $\delta T_c \approx 0.2$ K), but T_c shifts toward higher temperature by about 1 K. However, at higher doses ($c \geq 0.008\%$) the transition broadens substantially and T_c decreases again (see inset of Fig. 1). The broadening is reflected by the increase of the transition width δT_c and the decrease of the peak height of $d\log_{10} R/d(1/T)$ versus T. The activation energy Δ already becomes smaller at low defect concentrations, while for large concentrations Δ cannot be determined accurately because of the curvature of the $\log_{10} R$ versus $1/T$ plot (Table I).

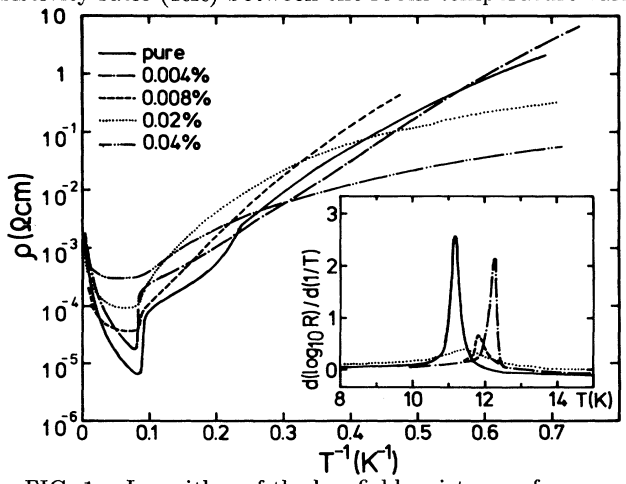

FIG. 1. Logarithm of the low-field resistance of pure and irradiated samples from the same batch. The inset shows the logarithmic derivative (R in Ω, T in K) vs temperature for the same samples.

Figure 2 shows the field-dependent conductivity for pristine and irradiated samples at 4.2 K versus the logarithm of the electric field. For the former, the sharpness of the threshold field was checked by dynamic resistance measurements (Fig. 3). This result definitely proves the existence of a finite threshold field for the SDW transport. The value of E_T increases with the defect concentration and the magnitude of the extra conductivity becomes smaller. The temperature dependence of E_T for different defect concentrations is given in Fig. 4. In the low-temperature range 1.2–4.2 K, E_T is temperature independent for both pure and irradiated samples. For the pure sample E_T displays a steady and rather large increase above 4.2 K towards T_c: $E_T(0.9T_c)/E_T(T_{\min}) \approx 2.6$. However, already a very small defect concentration of 0.002% is sufficient to diminish this rise significantly: E_T stays constant until $\sim 0.8T_c$ and then increases only slightly: $E_T(T_c)/E_T(T_{\min}) = 1.35 \pm 0.15$. It is also important to note that E_T does not diverge. However, as Joule heating prevented us from checking this feature for other samples and irradiation doses, we cannot rule out this possibility completely. Finally, checks for nonlinearity performed at temperatures above T_c did not show any extra contribution to the conductivity in the metallic region. The inset of Fig. 4 displays the low-temperature threshold field as a function of defect

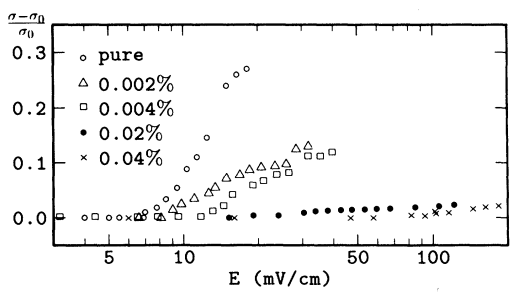

FIG. 2. Non-Ohmic conductivity vs logarithm of electric field (E) for pure and irradiated samples at 4.2 K.

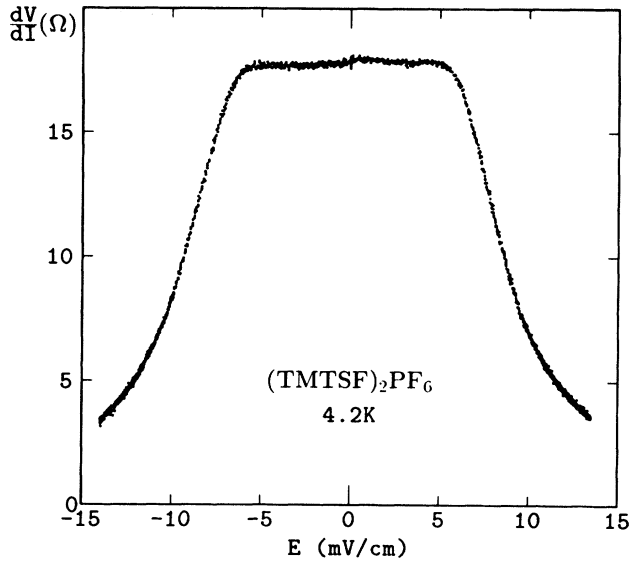

FIG. 3. Dynamic resistance (dV/dI) vs electric field (E) for a pure sample at 4.2 K.

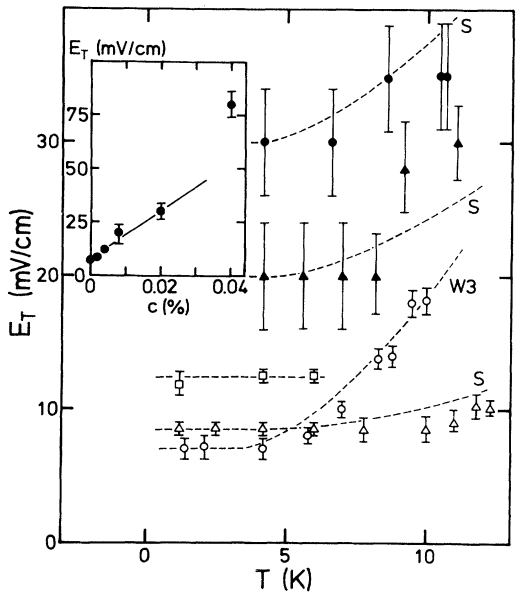

FIG. 4. Threshold field (E_T) vs temperature (T) for pure sample (open circle), 0.002% (open triangle), 0.004% (square), 0.008% (solid triangle), 0.02% (solid circle) of molar concentration of defects. Dashed lines are fits after Ref. 7 either in the strong-pinning limit (S) or in the three-dimensional weak-pinning limit ($W3$). The inset shows the low-temperature value of the threshold field vs defect concentration (c). Error bars are smaller than symbol size unless explicitly shown.

concentrations showing a linear relationship up to about 0.02%. A defect concentration of 0.04% is already high enough to smear the SDW transition almost completely, and the development of the SDW order parameter at low temperatures becomes much more gradual (see Fig. 1 and inset).

Nonmagnetic impurities and commensurability are expected to pin the sliding of charge- and spin-density lattices.[6] As we have already pointed out the SDW wave vector in $(TMTSF)_2PF_6$ seems to be close to commensurability (N=4). Hence, it is not surprising that the commensurability potential can play some role. Indeed, for samples from one particular batch E_T falls with increasing temperature in qualitative agreement[3] with the theoretical prediction of the phenomenological model by Maki and Virosztek for commensurability pinning[7], namely:

$$E_T^c(T)/E_T^c(0) = [\Delta(T)/\Delta(0)]^4[\rho/\rho_S(T)], \quad (1)$$

where $\Delta(T)$, ρ, and $\rho_S(T)$ are the SDW gap, the total electron density, and the density of electrons condensed in the SDW, respectively. However, for samples from other batches, the impurity potential appears to be the dominant pinning mechanism. This subtle interplay between impurity and commensurability pinning seems to be difficult to control chemically and we conclude that the latter behavior is more general. Following Fukuyama, Lee, and Rice, for an incommensurate density wave it is important to discriminate between the strong- and weak-pinning limits.[12] Maki and Virosztek have derived expressions for the SDW threshold field at zero temperature and for its temperature behavior in these two limits.[7] For pristine $(TMTSF)_2PF_6$ samples studied here we find E_T constant up to 4.2 K and increasing until T_c is reached: $E_T(T \to 0) = 7\pm0.5$ mV/cm and $E_T(T \to T_c)/E_T(T \to 0) \approx 3$. This behavior is in good agreement with what is expected for weak pinning between the SDW and impurities:

$$E_T^W(T)/E_T^W(0)$$

$$= \{[\Delta(T)/\Delta(0)] \tanh[\Delta(T)/2T][\rho/\rho_S(T)]\}^4. \quad (2)$$

Upon irradiation the low-temperature value of the

TABLE I. Some parameters for pure and irradiated samples. The amplitudes of $d\log_{10} R/d(1/T)$ are normalized by the value for a pure sample.

c (%)	σ_{RT} $(\Omega\,\mathrm{cm})^{-1}$	RR	T_c (K)	δT_c (K)	2Δ (K)	$d\log_{10} R/d(1/T)$
Pure	500±100	260	11.1	0.2	39	1
0.002	500±100	122	12.1	0.2	34	1
0.004	500±100	98	12.3	0.2	34	1
0.008	500±100	28	11.8	0.4	34	0.25
0.02	500±100	17	11.2	2	23	0.13
0.04	500±100	10	9.2	5	23	0.013

threshold field increases linearly with the defect concentration and E_T displays only a slight increase close to T_c: $E_T(T \to T_c)/ E_T(T \to 0) = 1.35 \pm 0.15$. Both results indicate that x-ray irradiation-induced defects act as strong-pinning centers being more strongly coupled to the SDW than chemical impurities in pristine samples. In the strong-pinning limit the low-temperature value of E_T is given by

$$E_T^S(0) = Q/e(n_i/n_e)(\pi N_0 V)^2 \Delta_0, \quad (3)$$

where $Q = 2k_F$ is the SDW wave vector, e is the electronic charge, n_e is the electronic concentration, and N_0 is the electronic density of states. V, n_i, and Δ_0 are the impurity potential, the impurity concentration, and the SDW gap, respectively. Taking the known defect concentrations $(n_i)_1 = 0.002\%$ and $(n_i)_2 = 0.02\%$ and the measured values of the gaps $\Delta_1(0) = 34$ K and $\Delta_2(0) = 23$ K, we get $[E_T^S(0)]_2/ [E_T^S(0)]_1 \approx 7$ which is reasonably close to the observed ratio $E_T(0.02\%)/E_T(0.002\%) = 3.5$. Furthermore, in the strong-pinning limit the temperature dependence is given by

$$E_T^S(T)/E_T^S(0) = [\Delta(T)/\Delta(0)] \tanh[\Delta(T)/2T][\rho/\rho_S(T)]. \quad (4)$$

$E_T(T)$ is constant at low temperature and gradually increases up to $E_T^S(T_c)/E_T^S(0) \approx 1.33$. Again, our result is very close to the theoretically expected one.

Finally, the increase of the SDW transition temperature for low-irradiation doses deserves some attention. Such an effect, although surprising, is not unknown. A similar increase but accompanied by the broader transitions was observed by Mortensen *et al.* for $(TMTSF)_2PF_6$ samples doped with TMTTF.[13] The authors proposed several possible explanations. One is an increase in the density of states near the Fermi energy and another an increase in electronic one-dimensionality. It is unclear to us at the moment why small irradiation doses would give either of these two effects.

In conclusion, we have observed for the first time a defect-concentration dependence of the spin-density-wave transport in an organic conductor. For most pristine $(TMTSF)_2PF_6$ samples (except one of the batches studied in Ref. 3) the commensurability pinning is overcome by weak impurity pinning. In this case the threshold field is independent of temperature below $T_c/2$ and increases substantially at higher temperature. Its value was also determined for the first time by the more sensitive dynamic resistance measurement methods, and a minimum value of 6.3 mV/cm is in a good agreement with the one obtained from the standard pulsed method (7 ± 0.5 mV/cm). Irradiation-induced defects increase the value of the threshold field linearly with defect concentrations and diminish its rise close to T_c. In addition, the magnitude of the field-dependent conductivity strongly decreases. This behavior is fairly well explained in the framework of recent theories for the sliding SDW mode pinned by impurities and irradiation-induced defects in the weak- and strong-coupling limits, respectively.

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