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Effect of radiation damage on the metal-insulator transition and low-temperature transport in the tetramethyltetraselenofulvalinium PF_6 salt $[(TMTSF)_2PF_6]$

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We have measured the resistance, magnetoresistance, and nonlinear conductivity in a series of tetramethyltetraselenofulvalinium phosphorus hexafluoride $[(TMTSF)_2PF_6]$ crystals which have been damaged with 2.5-MeV protons. For radiation dosages which correspond to ~400-ppm damage we find that the effects of the damage may be simply related to an increased scattering rate in the low-temperature transport. However, even with such low values of damage the metal-insulator transition at ambient pressure is smeared and shifted to lower temperature while the superconducting transition at 11 kbar is suppressed to less than our measuring temperature of 20 mK by 100 ppm. At 1000 ppm the spin-density-wave transition is suppressed.

INTRODUCTION

The highly conducting, organic charge-transfer salts of the form tetramethyltetraselenofulvalinium$_2X$, $(TMTSF)_2X$, where X is a strong electron acceptor (e.g., PF_6, ClO_4, NO_3), are rather remarkable in the variety of low-temperature properties exhibited upon changing the anion while leaving the structure, charge transfer, and unit cell largely unchanged.[1,2] The ground states that have been reported are spin-density-wave insulator[3-6] and superconductor.[7-10] A very similar compound TMTSF-DMTCNQ (tetracyanoquinodimethane) has also shown a charge-density-wave insulator and "simple" metallic ground state at ambient and 12-kbar pressure, respectively.[11,12] Recent results suggest that some of the members of the family considered in this paper have charge-density-wave-like transitions as well, but further work has shown that this is the result of anion ordering.[13]

The most widely studied of this family of compounds is the PF_6 salt. At ambient pressure, the material is metallic down to a temperature of 12 K. At this temperature there is a sharp transition to an insulating state that has been shown rather convincingly to be a spin-density wave state,[3-6] the first quasi-one-dimensional conductor to exhibit this instability. In the insulating state it was discovered that a highly nonlinear conductivity could be induced at low applied electric field, that the metallic ESR signal could be resurrected in this small field, and that the conductivity was highly frequency-dependent at frequencies below the measured energy gap.[3,14,15] Another unusual phenomenon was the observation of a large anisotropic transverse magnetoresistance and high Hall mobility in the insulating state and a significant but smaller magnetoresistance in the metallic state above the transition.[16]

However, the reason for the great interest in the PF_6 salt, and this class of materials in general, was the discovery that application of a moderate amount of pressure could suppress the metal-insulator transition to zero temperature at which pressure (~6 kbar) the material becomes superconducting at a temperature of ~1.2 K.[7-9] This was the first organic solid to exhibit superconductivity. Subsequent investigation of other members of this family have led to additional superconductors with the ClO_4 salt exhibiting superconductivity at ambient pressure.[10]

While there is no doubt at present concerning the occurrence of superconductivity in these materials, the nature of the superconducting state and the possible existence of fluctuations due to the reduced dimensionality have yet to be exhaustively investigated. In particular, there has been the suggestion, largely based on the observation that the normal state is a spin-density wave (SDW), that the superconducting state may be triplet rather than the usual singlet. Some experiments point to a very large range for the superconducting fluctuations, possibly as high as 40 K.[17,18]

The motivation for the present work comes from the extreme sensitivity to scattering or defects which may be expected for many of the phenomena described above. SDW and charge-density-wave (CDW) transitions result from the electronic instability caused by the almost perfect nesting of different regions of the Fermi surface. When defects are added the Fermi surface is smeared out and the nesting becomes less perfect. The pinning of the density waves on different chains also inhibits the three-dimensional ordering necessary for a real phase transition.[19–23] Similarly, the pinned density waves should be considerably harder to free and therefore contribute less to any collective conductivity in the nonlinear regime. Such defect studies have shown these effects in $NbSe_3$.[24,25]

The effects of damage on the superconducting properties should prove particularly interesting. Nonmagnetic impurities have virtually no effect on the singlet superconducting state, but destroy triplet superconductivity at low levels.[26] Magnetic impurities are destructive for singlet superconductivity. If the superconducting transition temperature is lowered by the impurities, then they act as pair-breakers and should very significantly suppress any fluctuations above the transition.

In order to describe the large magnetoresistance and Hall mobility in terms of a conventional single-particle model it is necessary to envision extremely large mean free paths.[16] By introducing a controlled amount of disorder we can directly test these ideas and thus determine what part of the observed phenomena must be attributed to collective effects and fluctuations.

EXPERIMENT

The radiation damage was performed at the California State University, Los Angeles, using their Van der Graaf accelerator with a proton beam of 2.5 MeV. The samples were mounted with silver paste at their ends to a quartz slide that was thermally anchored with Crycon grease to a water cooled substrate holder. Ion current levels were kept sufficiently low that sample heating during irradiation was not a problem. A typical ion current density was 15 nA/cm^2. The dosage was calculated from the ion current density and the exposure time. While the actual damage fraction can only be estimated in the computations below, the relative damage should be directly proportional to the dosage and this is consistent with all of our measurements.

One of the major problems in radiation damage studies of conducting organic crystals is the calculation of the proportionality constant between the dosage and the fractional damage. The easiest calculation, and the one which is appropriate for metals, is to assume that the displacements occur via Rutherford scattering of the protons by the nuclei of the molecules being irradiated. For this model[27] the fractional damage is given by

$$c \sim 5\times 10^{-20}\phi \ , \tag{1}$$

where c is the damage fraction and ϕ is the flux in $protons/cm^2$. For example, using this computation we find that the three least damaged samples in our study have 0.03-, 0.1-, and 0.3-ppm defects.

These estimates are low, however, because the main energy-loss mechanism for the protons in traversing the crystal is through electronic excitations.[23] In inorganic metals, the high density of mobile electrons serves to dissipate this energy without the production of additional ion displacements. However, in the conducting charge transfer salts of organic molecules, the electronic excitations do contribute to radiation damage. This point has been under extensive investigation by Mihaly and Zuppiroli. In a series of papers involving careful studies of different conducting organics under x-ray irradiation, they have shown that the total energy dissipated into the electrons is the relevant quantity for calculating the amount of damage. Their conclusion is that the number of damaged molecules is the total energy absorbed by the electrons during the radiation divided by an energy per molecule that ranges from 7 keV for TMTSF-DMTCNQ to 100 keV for TTT_2I_3 [(tetracyanotetracene)$_2$(iodide)$_3$].

From the energy loss profile of the elements in $(TMTSF)_2PF_6$ we compute the electronic energy loss[28] as

$$E \sim 21\ \text{keV}/\mu\text{m} \ , \tag{2}$$

in units of keV/μm, so that a 10-μm sample absorbs 210 keV from the incident proton. Assuming that the energy needed to damage a molecule is 7–8 keV, approximated from the results of Ref. 23, we can compute the fractional damage. Using this method we arrive at

$$c \sim 1.4\times 10^{-17}\phi \ , \tag{3}$$

which corresponds to a defected molecule concentration for our three least-damaged samples of 10, 30, and 100 ppm. This is a factor of 300 times larger than what is expected from Rutherford scattering and therefore constitutes the major damage mechanism. Note, however, that the value of 7 − 8 keV per damage molecule is only an estimate and that the real value may be from slightly higher to an order of magnitude lower damage, if $(TMTSF)_2PF_6$ lies within the range found in Ref. 23 for similar materials.

Aside from computations, the amount of damage may be estimated from the change in the conductivity.[21,23] Ideally, this measurement is performed by measuring the resistivity ratio or the resistivity at low temperatures. Unfortunately for the present samples there are many resistance jumps during the cool-down from room temperature to liquid-nitrogen temperature at ambient pressure. These jumps are related to changes in the current paths caused by sample cracking or changes at the electrical contacts so that the geometry for evaluating the resistivity from the resistance is not known well enough to obtain numbers for the damage fraction. On the other hand, we are able to measure the resistivity ratio under pressure and the low-temperature magnetoresistance at ambient pressure. (These measurements will be discussed at length below.) From these measurements we are able to say that radiation damage of 100 ppm is equivalent to a transport scattering rate which is double the value obtained for the pure samples. Using our previous estimates[16] of the mean free path in pure samples at 4.2 K (5000 Å) we obtain a mean free path of 2500 Å for the 100-ppm sample.

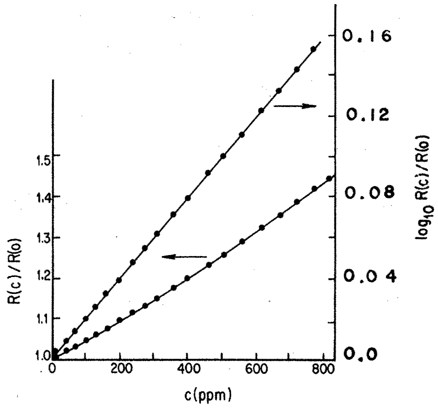

FIG. 1. Room-temperature resistance change as a function of fractional damage [calculated from Eq. (3)] measured *in situ* during the irradiation.

In Fig. 1 we show the resistance of a crystal of $(TMTSF)_2PF_6$ as a function of dosage measured *in situ* at room temperature during the proton irradiation. As can be seen, the resistance rises by 30% for a dosage of 600 ppm calculated from Eq. (3). In TMTSF-DMTCNQ and TTF-TCNQ,[20,23] the fractional damage which causes a 30% increase in the resistivity at room temperature is ∼2000 ppm. The increase in resistivity from the damage is proportional to the conductivity anisotropy[21] and room-temperature measurements indicate an anisotropy in the plane containing the two highest conducting axis of 120 for TTF-TCNQ, 160 for TMTSF-DMTCNQ, and 360 for $(TMTSF)_2(PF)_6$. If we use the anisotropy from Ref. 1 to calculate the fractional damage from the equations in Ref. 21, we obtain a value of 800 ppm rather than 600 ppm for a 30% increase in resistivity at 300 K. This gives us confidence in our assignment of the damage as the values calculated from the flux and observed in the resistivity change agree quite well.

In Fig. 2 we show the resistance as a function of magnetic field at ∼4.2 K for the pure and radiation-damaged samples. The field is aligned along the *c* axis by mounting the crystals so that the platelet faces are perpendicular to the magnetic field. Detailed measurements of the temperature and orientation dependence of the magnetoresis-

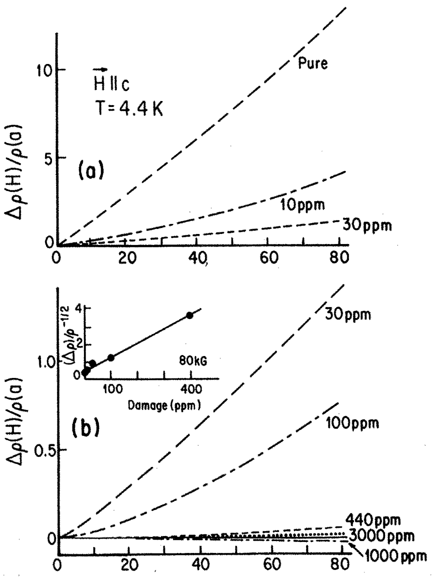

FIG. 2. Magnetoresistance as a function of magnetic field for samples which have been damaged to various degrees. Note the change of scales for (a) and (b). The inset shows the reciprocal square root of the magnetoresistance which should be proportional to the scattering rate [see Eq. (5)].

tance have been previously published.[16] The c axis corresponds to the direction of highest magnetoresistance indicating the presence of a quasi-two-dimensional band structure which allows electron orbits in the ab plane. We have previously shown that the extremely large values of magnetoresistance found for the pure material arise from a high mobility and long mean free path along the a direction. Within the usual picture of band transport, the magnetoresistance is related to the scattering time by

$$\frac{\Delta\rho}{\rho} \approx (\omega_c \tau)^2 , \tag{4}$$

where ω_c is the cyclotron frequency. As the crystals are damaged, the scattering time is decreased and the magnetoresistance is greatly reduced.

In a conventional material, the effects of a small amount of radiation damage can be incorporated into an increased scattering rate. The total scattering is the sum of the scattering present in the undamaged material plus a term proportional to the number of defects. Taking the scattering rate per damaged molecule as $1/\tau_d$ we would have

$$\frac{1}{\tau} = \frac{1}{\tau_p} + \frac{c}{\tau_d} , \tag{5}$$

where τ_p is the scattering time in the pure material. According to Eq. (4) we can test this hypothesis by plotting the reciprocal square root of the measured magnetoresistance as a function of the calculated damage. Such a plot is shown in the inset in Fig. 2. Up to a concentration of defects of 1000 ppm, the fit is quite good confirming our view that single particle scattering can explain the low-T transport in $(\mathrm{TMTSF})_2\mathrm{PF}_6$. For higher concentrations the analysis is not meaningful, since the magnetoresistance is too small for an accurate determination, with the 3000-ppm sample showing a small negative magnetoresistance. Note that the 100-ppm damaged sample has a scattering rate which is twice that of the undamaged crystal. This shows that these electrochemically grown crystals are extremely pure in comparison with other organic solids and is consistent with the high mobility and long mean free path found in the previous magnetoresistance work[16].

In Fig. 3 we show the resistance of one pure and two damaged samples under a pressure of 11 kbar, as a function of temperature from 300 to 0.1 K. No superconductivity was found in the damaged samples down to 20 mK (our experimental limit). As has previously been noted by several authors, when samples are cooled in a liquid pressure medium the tendency to show resistive jumps is greatly reduced. It is therefore possible to compare the resistivity ratios of our samples under these conditions. Since under this pressure there is no metal-insulator transition at any temperature studied, the difference in the low temperature resistance is entirely due to increased scattering. Plotting the resistivity ratio at 1 K in the inset in Fig. 3 we can easily see that the scattering rate is again linear with the defect concentration (at least for three points) and that a concentration of 100 ppm produces an additional scattering approximately equivalent to that present in the pure sample. The resistivity ratio for the most highly damaged sample in this figure is greater than 10 so that the error caused by directly normalizing at room temperature is less than 10%.

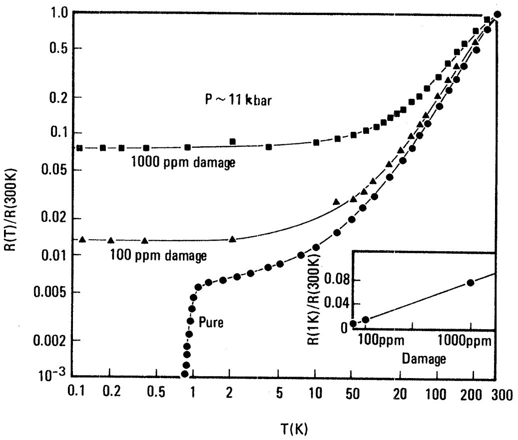

FIG. 3. Temperature dependence of the resistivity under pressure for several values of damage. The pressure was set at ~14 kbar at room temperature and was measured to be ~11 kbar at 4.2 K. The inset shows the damage dependence of the 1-K resistance on a linear plot. No superconductivity was observed in the damaged samples down to 20 mK.

The fact that the defect scattering obtained from two different measurements agree quite well and are consistent with the defect concentration that we calculate from the electronic energy loss and the resistivity changes seen by other groups, gives us confidence in the assignment of the amount of damage per dose that appears in Eq. (3).

The resistance as a function of temperature is shown in an Arrhenius plot in Fig. 4 for the pure and irradiated samples at ambient pressure in the region of the SDW transition and below. As mentioned above, we do not have accurate measurements of the absolute (or even relative) values of the resistance. The data shown are therefore nor-

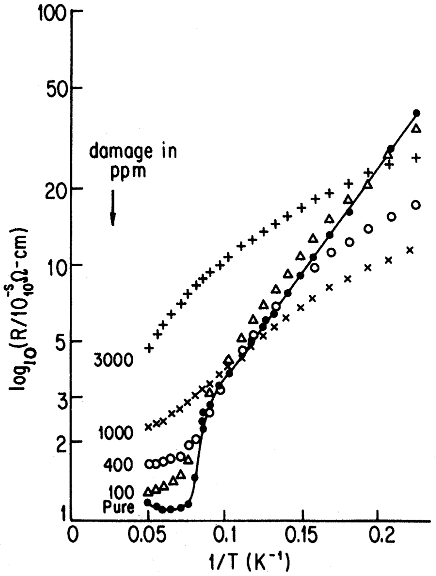

FIG. 4. Temperature dependence of the resistance of samples with various amounts of damage in the region of the metal-insulator transition. The values are scaled at 20 K assuming Eq. (5), thus only the temperature dependence is known experimentally, not the absolute value.

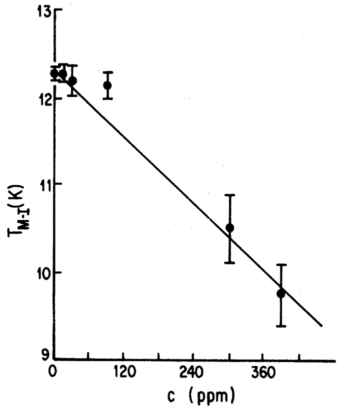

FIG. 5. Damage dependence of the metal-insulator transition temperature.

malized so that there 20-K values obey Matthiessen's rule (additivity of scattering mechanisms) with the scattering rates from the magnetoresistance study. It is debatable whether Matthiessen's rule should be applicable in these materials,[19–23] but from the insets in Figs. 2 and 3 it seems appropriate. We do not wish to make any particular point about the actual values of the resistance in Fig. 4, only the temperature dependencies.

The general features of the transition region and the insulating state are quite similar to what has been seen in CDW systems. At temperatures above the metal-insulator transition temperature there is a resistivity minimum which is pushed to increasingly high temperatures as damage or disorder is introduced. The transition itself is rather sharp in the pure sample but is smeared with additional disorder and shifted to lower temperature. If the transition temperature is defined by the maximum of the logarithmic derivative of the resistance versus temperature, we find $dT_{M\text{-}I}/dc$ of 60 K/% damage as shown in the inset in Fig. 5. The low-temperature resistance for the damaged samples shows a strong deviation from simple activated behavior and is characteristic of disordered semiconductors. For a concentration of 1000 ppm the damage has completely destroyed the transition. The disorder is sufficiently strong that the material can no longer be reasonably described as metallic, but rather is a disorder-localized insulator. The resistance for this sample is increasing as temperature is decreased from room temperature.

Our primary findings on the effects of damage on the superconducting transition are shown in Fig. 3. The 11-kbar data for the pure sample show a superconducting transition which begins at above 1 K and reaches its midpoint at ~0.8 K. Typically, samples of the PF_6 salt at this pressure show superconducting transition temperatures between 0.7 and 1.0 K.[7–10] For the damaged samples there is no evidence of a superconducting transition down to 20 mK for either 100 or 1000 ppm. Thus damage on the scale of 100 ppm is sufficient to destroy the superconducting state.

In Fig. 6 we show some conductivity versus electric field characteristics, illustrating the nonlinear behavior seen in the SDW state below the transition. The data shown were taken for all samples at 4.4 K with samples sitting in a copper can under an atmosphere of helium gas. While the conductivity of the pure sample does not show as strong a nonlinearity at low electric fields as we and other groups have reported, these results are typical of what we observe for the samples from the batch with which the damage studies have been performed. The effects of the damage are to further suppress the nonlinear conductivity. However, there still does not appear to be a well defined threshold field as was found in the depinning of the CDW state in $NbSe_3$ both with and without damage.

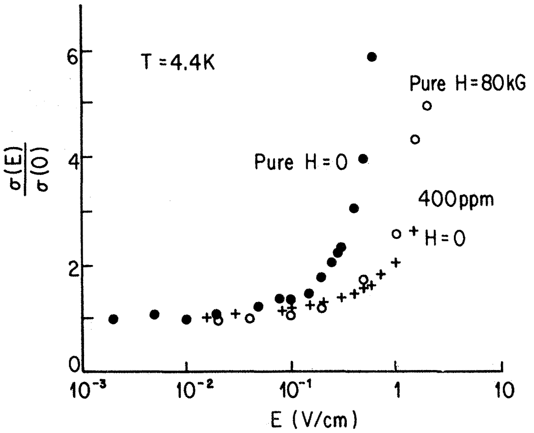

FIG. 6. Electric field dependence of the conductivity in the insulating state. Data are shown for a pure sample, the same sample in a magnetic field, and a sample which has been radiation damaged.

DISCUSSION

In some of the more recent treatments of the problem of radiation damage in conducting organic crystals, it has been suggested that the main effect of the defects is to damage molecules on the conducting chain so that electrons must hop to another chain in order to contribute to the conductivity.[21–23] The resistivity is then described as being the sum of the longitudinal resistivity plus the transverse resistivity times the concentration of damaged molecules. The consequence of this picture is that the longitudinal conductivity acquires more and more of the diffusive character and temperature dependence of the transverse conductivity. This appears to be in direct contradiction to our findings at low temperature. We find that the magnetoresistance is well described within a band model in which the effect of the damage is to increase the scattering rate. If we assume that the electron motion involves diffusive transverse jumps at the damage sites, our treatment in terms of coherent orbital motion would certainly break down and the magnetoresistance would be considerably smaller. Moreover, both the magnetoresistance and the resistivity ratio of the samples measured under pressure (Figs. 2 and 3) indicate that Matthiessen's rule is applicable at low temperature.

We suggest that the difference between our results and those previously reported lies both in the amount of damage and in the anisotropy and mean free path of the materials used. In order for the previous treatments to be correct, the material must be quasi-one-dimensional in the sense that the transverse motion is not coherent. This implies that an electron cannot coherently transfer from one chain to another in a time that is shorter than its scattering time on the original chain. If the transfer rate is faster than the scattering rate, the motion is more accurately described as anisotropic two or three dimensional. In the previous models, the compounds under consideration were assumed to have large anisotropies and short mean free paths, either intrinsically or caused by the damage. In the present case, the magnetotransport as well as the radiation studies indicate that the mean free path is long for the pure material.

Qualitatively, we would expect a cross over to one-dimensional behavior when the mean free path becomes smaller than the unit-cell dimension times the anisotropy in the transfer integrals, i.e., $t_{\perp} < \hbar/\tau_{\parallel}$ or $l < at_{\parallel}/t_{\perp}$. From room-temperature conductivity measurements and from the plasma frequency anisotropy[29] the *ab* axis effective mass anisotropy is ~ 20. Since the low temperature mean free path is dominated by the induced defects we would require a defect concentration of $\sim 5\%$ in order to observe the one-dimensional behavior seen in other samples. Similarly, in order to observe the one-dimensional size quantization effects which lead to an activated longitudinal conductivity, we would require a defect concentration of $\sim 5\%$. Since all of our samples have been subjected to considerably less damage than these values, we believe that a two-dimensional band treatment is more appropriate at low temperature. At room temperature, we expect the previous treatments to be correct as the mean free path is small.

We now return to the effects of the damage on the metal-insulator transition and the low-temperature conductivity. From Fig. 4 we see that there are four phenomena which accompany the introduction of disorder. $T_{M\text{-}I}$ is reduced, the transition is smeared, the temperature at which the metallic state has its maximum conductivity is increased, and the low-temperature conductivity is less activated and probably has a larger absolute value. (Note that we do not have absolute values for the conductivities shown in Fig. 4.) All of these features have been noted previously in charge-density-wave systems after irradiation, but this is the first such study of a spin-density-wave system, and we must therefore discuss what similarities and differences are expected.

For the case of the CDW the defect or impurity acts as a scattering site and thus broadens the crystal momentum states. This smearing of the Fermi surface can decrease the condensation energy into the CDW state which opens a gap at the Fermi surface. Since the SDW is also the result of a Fermi surface instability from nested regions in k space, it should show a similar effect: a reduction of its transition temperature. The pairbreaking effects of different impurities (forward and backward scattering, spin and nonspin flip) on the different one-dimensional ground-state order parameters have been discussed in Ref. 26. They treat the depression of the mean-field transition temperature. However, since the material is highly anisotropic, a larger effect on the three-dimensional ordering which sets the observed metal-insulator transition temperature is the ability of the density wave on the chains to attain a transverse phase locking. Impurities in a CDW produce a potential which simultaneously pins the phase of the charge-density wave locally, and locally enhances the amplitude (in forming a large quasi-one-dimensional Freidel oscillation). The phase locking in the impurities or defects inhibits the transverse phase locking to neighboring chains and reduces the ordering temperature. The local enhancement of the order parameter (the amplitude of the CDW) in response to its conjugate field (the impurity potential) also decreases the number of carriers available for transport above the transition and limits the mobility of the remaining carriers.

The result is a temperature-dependent resistivity increase as the transition is approached from above. Coupled with the pinning of any fluctuating collective contribution to the conductivity,[30] these effects account for the increase in the temperature of the conductivity maximum as damage is increased. The random impurity potential, possibly enhanced by the Freidel oscillation cloud which surrounds it, also acts below the transition, in the insulating state, as a disorder potential which smears the density of states at the gap edge and introduces lower energy localized states which are responsible for the decrease in the activation energy and increased low-temperature conductivity.[19–23]

For the SDW the conjugate field is a staggered magnetic field. Although a single spin can couple to the order parameter via the exchange interaction we expect that this should be a considerably weaker coupling than the direct electrostatic coupling of the disorder potential to the CDW. The fact that the SDW does not have charge density implies that it will not couple to lowest order with the direct electrostatic potential from the defect. Assuming that about half of the defects introduced are spin defects while all are potential defects and that the potential scattering by the defect is stronger than the exchange scattering, we would expect the equivalent amount of damage to have a greater effect on the transition temperature of a CDW than on an SDW. We note that the value of $dT_{M\text{-}I}/dc$ we have obtained is within error the same as that obtained for TTF-TCNQ.[31] All of the other effects associated with the pinning of a density wave should then be applicable to our results with the exception that the pinning per impurity is weaker in the SDW case and that there is no enhancement of the Friedel oscillations. One of the points that remains to be experimentally explored is the number of spins introduced per defect and the exchange interaction with the conduction electrons.

While the number of spins produced by low radiation damage (less than 1000 ppm) was too small to measure without difficulty we were able to measure the ESR spin susceptibility on more highly damaged samples. For a sample with 0.9% calculated defects the susceptibility shows a Curie-type tail in the region from 10 to 40 K. Assuming that the high-temperature susceptibility of this sample is the same as that of undamaged samples we can use the ratio of the susceptibility at high and low temperature as an absolute calibration for the Curie term. We find that the susceptibility at 10 K is approximately 3 times the value at 40 K, which implies a spin concentration of $(8\pm2.5)\times10^{-3}$ spins/molecule. Thus each defect produces $0.6-1.2$ free spins.

We now turn to the question of the effects of the defects on the superconducting transition which is observed under a pressure of 11 kbar in pure samples at a temperature of ~ 1 K. As was seen in Fig. 3, the superconducting transition was suppressed in a sample which had been irradiated to a defect concentration of 100 ppm. If the primary effect of the defects was to increase the potential scattering, this would have a negligible effect on the superconducting transition temperature for usual singlet superconductivity. The effect of nonmagnetic impurities is to change the density of states at the Fermi energy.[26] Such a change in the density of states would, of course, effect the SDW transition at ambient pressure as well. For 100 ppm there is only a small change in the SDW transition so that the density of states is not significantly affected.

The triplet state is easily destroyed by potential scattering[26] and the present results may be used as evidence that a small amount of defects destroys the triplet state. However, recent critical field experiments that we have performed on the compound $(TMTSF)_2$ ClO_4 prove that the superconductivity in that material is singlet.[32] We therefore believe that the superconductivity in the PF_6 salt is most likely singlet as well. Moreover, we must have some form of magnetic interaction in order to suppress the SDW state with defects, and these magnetic interactions act as pairbreakers for the singlet superconductivity.

The ESR indicates the presence of free spins. The remaining question is their exchange coupling. Since the pinning and disorder which destroyed the SDW state at ambient pressure was also related to the impurity exchange coupling, we can use a very crude argument to see whether there is sufficient pairbreaking to destroy singlet superconductivity. In the 1000-ppm sample measured at ambient pressure the effects of the disorder exchange potential on the SDW were enough to completely smear out the metal-insulator transition. The exchange scattering rate must therefore have been the same order of magnitude as the transition temperature (~ 12 K) or the semiconducting energy gap. The 100-ppm sample should then have a spin exchange scattering rate which corresponds to one tenth of this or ~ 1.2 K. The superconducting transition temperature is reduced to zero when the pairbreaking rate is approximately equal to the superconducting T_c. The suppression of superconductivity under pressure for 100 ppm of damage is thus well within the range that may be explained in terms of singlet superconductivity. We note the crudeness of this argument in that we have claimed that the main effect of the spins on the SDW state is in pinning the SDW on different chains and preventing three-dimensional ordering while the effect on the superconductivity is taken as a mean-field depression of T_c. Nonetheless, both are related to the exchange coupling of the conduction electrons with the spins. We note, however, that this amount of damage seems too small to explain the elimination of superconductivity with a mean field $T_c \approx 10$ K. This would then argue against the proposal[17] that superconducting fluctuations are important at temperatures up to 40 K in $(TMTSF)_2PF_6$.

The nonlinear characteristic is also strongly effected by the radiation damage, with a general shift to a higher field before the conductivity increases above its low-field value. In the much more well-studied system $NbSe_3$ the effect of damage was to increase the threshold field at which the nonlinear behavior set in.[24,25] In the present case, neither the pure nor the damaged samples indicate a threshold field. We have seen in the discussion of the effects of the impurities on the metal-insulator transition that the spin-density waves are pinned by defects. It is therefore reasonable to expect that if the additional conductivity is due to the collective depinning of the SDW, the presence of the defects will raise the characteristic field. If the SDW state is composed of small domains or the pinning potential is strong, the defects will add to the spread in any threshold field. On the other hand, if the pinning is weak (as one might expect for a spin-density wave and spin defects) and the correlation length large, the SDW will adjust itself to the average defect exchange potential and we would expect a threshold behavior to become visible as the spread in threshold fields sharpened.[33]

We emphasize again that the nonlinear effects that we have observed in the present study are smaller and at higher field than those previously reported. While we do not believe that the effects at present are due to the cracking of the samples, which is a continual problem that was also found in the samples used in previous studies, we cannot rule this out. If large inhomogeneities in the distribution of electric currents and fields are responsible for the nonlinear effects, then anything which increased the resistivity of the samples would tend to shift the characteristic field to higher values. Although we do not believe this is the effect we are observing, we point out that it is consistent with the reduction of the nonlinearity by the defects. If the nonlinear effects were related to "hot electrons," the relevant parameter is the electron mean free path.[34] The damage reduces the mobility and the mean free path in the way that we have seen in the analysis of the magnetoresistance data. The mobility of the electrons in the 300-ppm damaged sample is about a factor of 4 smaller than that of the pure sample (see Fig. 2). This may correspond to the factor of 4 difference in the electric field dependence seen in the pure and damaged sample.

From the present study it is therefore not possible to distinguish between the different possible mechanisms which may be responsible for the nonlinear conductivity, since all of the models predict qualitatively the same effects upon damaging the samples. It is evident from these measurements that a high degree of purity and a long mean free path are necessary to observe the nonlinearities in organic conductors.

CONCLUSIONS

For a low level of radiation damage we have found that the defects created can best be regarded as increasing the scattering rate rather than fundamentally changing the dimensionality or mechanism of electron transport at low temperature. This is consistent with our understanding of $(TMTSF)_2PF_6$ as a two- or three-dimensional, highly anisotropic, high mobility material at low temperatures. With damaged molecules up to 1000 ppm the interchain transfer at 4 K is still coherent, as evidenced by the magnetoresistance.

The defects have then been used to find the effect of disorder on the spin-density-wave transition, the superconducting transition, and the nonlinear conductivity. In order to explain the reduction of both the SDW and the superconducting transitions, it was necessary to assume that the fraction of the defects (approximately $\frac{1}{2}$) corresponding to free spins have an exchange interaction with the conduction electrons. The damage effects on the SDW transition are quite similar to the CDW transition, but are larger per molecular defect than the CDW case. The damage smears and lowers the SDW transition, raises the temperature of the conductivity maximum, and increases the low-temperature insulating state conductivity.

The reduction of the superconducting transition temperature under pressure to below 20 mK can be understood within the singlet state theory by assuming that the defect spins are acting as pair-breakers. We estimate the amount of exchange scattering from the effect of the defects on the SDW transition and we find that it is sufficient to lower T_c to zero.

The damage serves to suppress the nonlinear conductivity so that higher electric fields are required, but fails to produce a sharp threshold field. More detailed theory and experiments are necessary to distinguish the mechanism for the nonlinearity, since all models predict qualitatively the same behavior with damage.

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