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SOME PROPERTIES OF THE $(TMTSF)_2X$ SUPERCONDUCTORS*

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Measurements of the anisotropy of the critical field in $(TMTSF)_2X$ superconductors are presented. The results show that the a axis H_{c2} is Pauli limited based on a T_c near 1K. The large energy gap obtained from tunneling data is therefore thermodynamically untenable in terms of the present critical field studies and the superconductivity is singlet rather than triplet. Moreover, we find that low levels of irradiation induced defects eliminate the superconductivity in the ClO_4 and PF_6 salts and leave the thermopower of the ClO_4 salt below 100K unchanged. These results are incompatible with the proposal for 1D superconducting fluctuations below 40K. A discussion of the arguments for and against the occurance of superconducting fluctuations in the $(TMTSF)_2X$ salts is given with emphasis on the role of interchain interactions and other possible interpretations of the tunneling data.

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INTRODUCTION

The observation of superconductivity with transition temperatures (T_c) less than 1.5K is now well established in the $(TMTSF)_2X$ class of organic solids.[1-4] Less well established is the exciting suggestion[5] that one-dimensional (1D) superconducting (SC) fluctuation effects can exist up to temperatures as high as 40K. The strongest experimental evidence for the presence of superconducting fluctuations is the tunneling data of More et al.[6] discussed by Jerome[7] at this conference. They report observation of a large superconducting gap in both the PF_6 salt at 11 kbar (2Δ=3.6 meV=41.8K) and in the ClO_4 salt at ambient pressure (2Δ=5.5 meV=63.8K). In this paper, we will present results which show that such large superconducting gaps are inconsistent with the more reproducible and reliable critical field data from which the gap is also available. Specifically, we find that the magnetic critical field, H_{c2}, in both salts appears to be paramagnetically (Pauli or Spin) limited on the basis of a transition temperature of about 1K, i.e., 2Δ~3.5K and is not determined (as it should be) by the large gap found in the tunneling experiment. Furthermore, other experiments suggest that a substantial interchain interaction is present in the $(TMTSF)_2X$ materials along the b^* direction. It is difficult to reconcile this 2D interaction with the large range of 1D SC fluctuations reported by Jerome and coworkers. Our critical field data also suggests that the superconductivity in the $(TMTSF)_2X$ materials is singlet and not triplet.

CRITICAL FIELD EXPERIMENTS

There have been several studies of the magnetic critical field, H_{c2}, in the superconducting $(TMTSF)_2X$ salts. The critical field in the direction parallel to the high conductivity a axis is reported[5,8] as being more than an order of magnitude larger than the perpendicular H_{c2}. The previously reported H_{c2} anisotropy has been cited for evidence of superconducting fluctuations and quasi-one-dimensional superconductivity[5] in the PF_6 salt. The high value for the a axis critical field has been used as evidence for triplet superconductivity[9] again in the PF_6 salt under pressure.

Our measurements show a large anisotropy of H_{c2} within the perpendicular (b^*c^*) plane. This is shown in Fig. 1 for the ClO_4 salt. Therefore, prior estimates of the parallel (a axis) to perpendicular H_{c2} anisotropy are too large since H_{c2a} is only slightly larger than H_{c2b^*}, as shown in Fig. 2. The error in the previous measurements comes from an inaccurate alignment of the perpendicular field with respect to the b^* axis. The details of our measurements are reported elsewhere,

however, it is important to note that we get accurate (<0.2 degrees) alignment of the magnetic field along b^* and c^* directions (i.e., in the entire basal plane). The a axis alignment was more difficult and we estimate our alignment was good to better than two degrees so that our H_{c2a} measurement may have been low by as much as 30%.

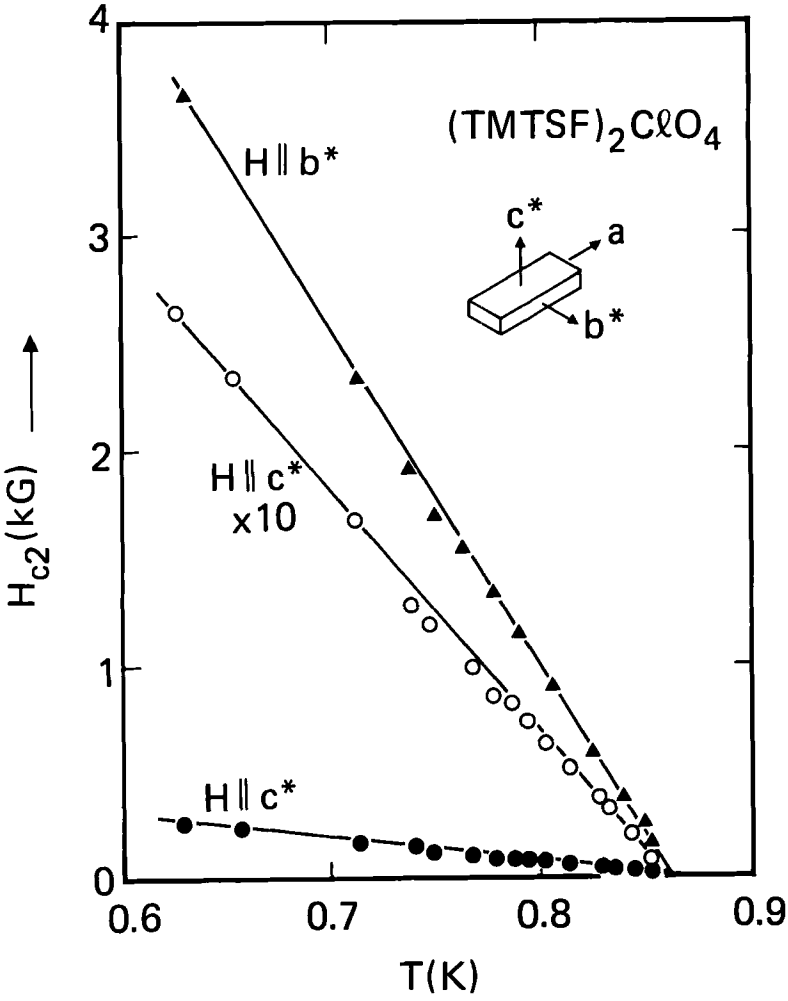

FIGURE 1 Temperature dependence of the critical field of $(TMTSF)_2ClO_4$ along the b^* and c^* directions.

At 0.55K we find H_{c2a} ~11 kGauss in good agreement with previous measurements[8] for the value of dH_{c2a}/dT. For the PF_6 salt the measurements must be done under pressure so that accurate alignment is difficult for all directions. Our results are shown in Fig. 3 and they exhibit the same anisotropic behavior found in the ClO_4 salt at ambient pressure. The anomalous curvature for H_{c2a} has been reported previously[5] and its origin is not presently understood.

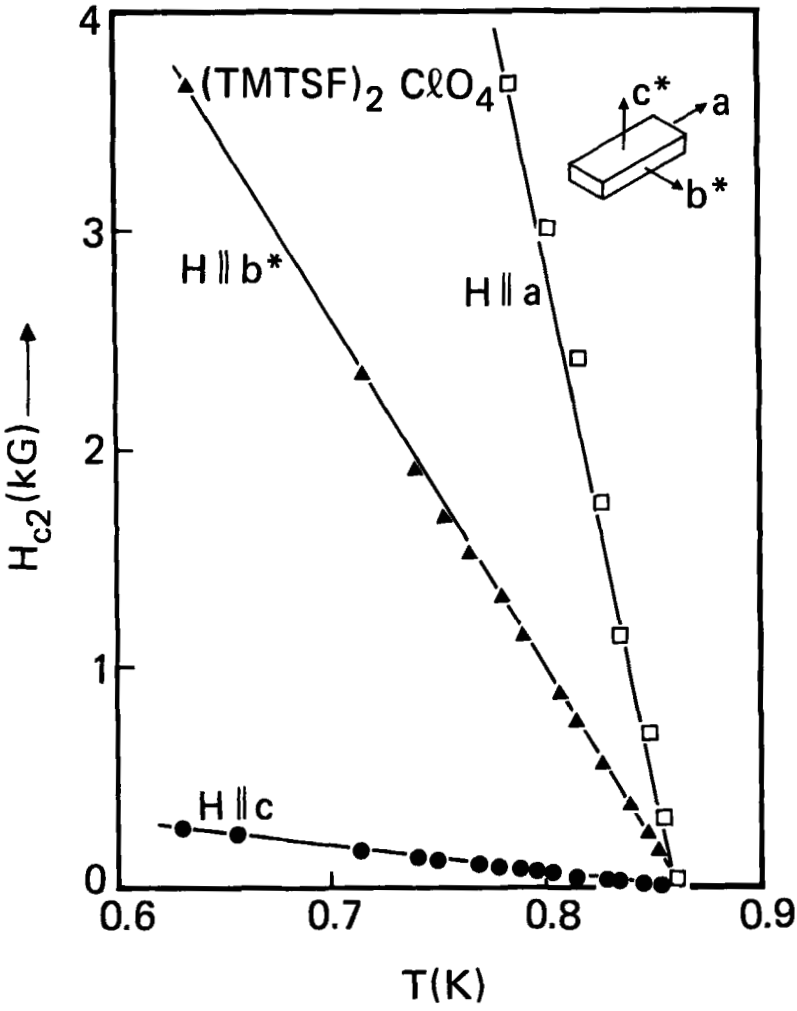

FIGURE 2 Temperature dependence of the critical field of $(TMTSF)_2ClO_4$ along the a, b^* and c^* directions.

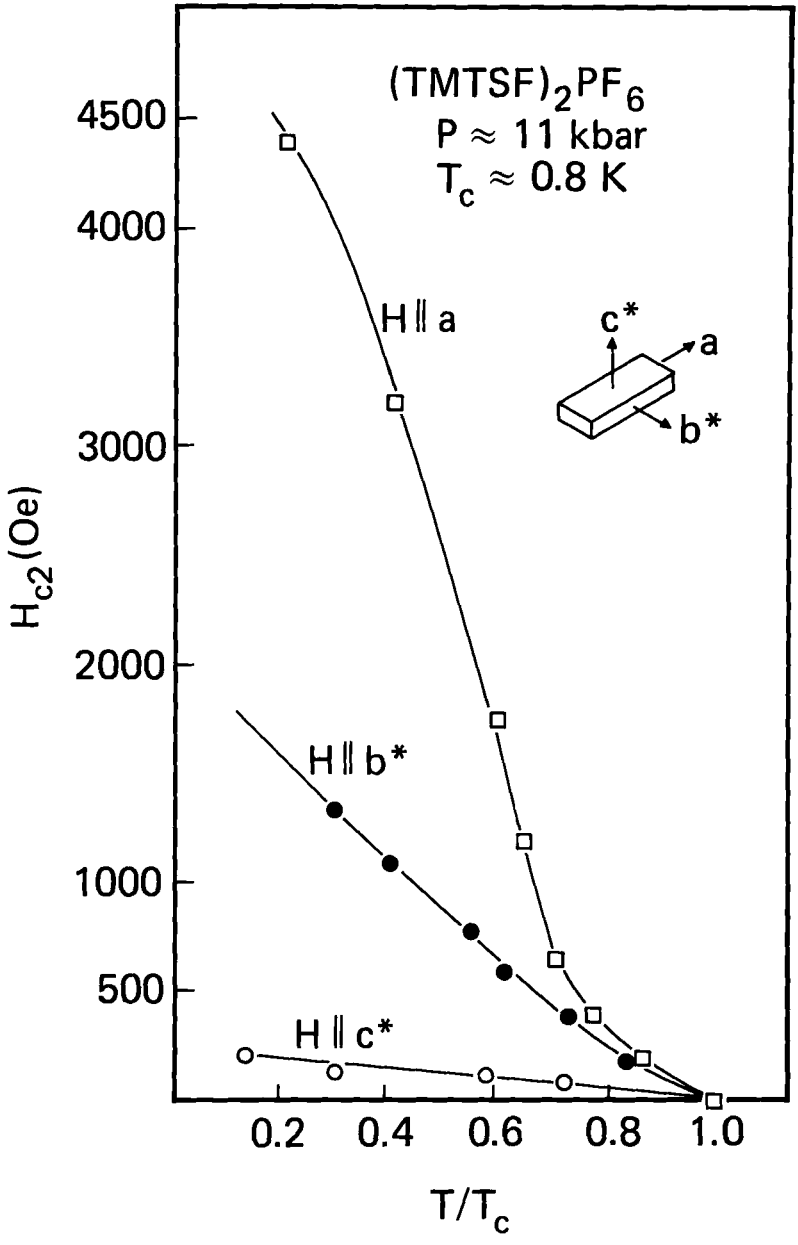

FIGURE 3 Temperature dependence of the critical field of $(TMTSF)_2PF_6$ along the a, b^* and c^* directions.

There are two pairbreaking effects of the magnetic field, orbital and spin, which must be considered in evaluating the critical field. We concentrate first on the orbital part. The anisotropy in H_{c2} may be due to either an anisotropic effective mass or to geometrical size effects (when a characteristic sample dimension becomes small compared to the penetration depth).[10] The angular dependence of H_{c2} is given by:

$$\left(\frac{H \sin\theta}{H_{cc}}\right)^2 + \left(\frac{H \cos\theta}{H_{cb}}\right)^2 = 1 \tag{1}$$

for the effective mass case and by:

$$\left|\frac{H \sin\theta}{H_{cc}}\right| + \left(\frac{H \cos\theta}{H_{cb}}\right)^2 = 1 \tag{2}$$

for the size effect case. In Fig. 4 we have plotted the fits to these two functional forms along with the experimental data. As can be seen it is very difficult to decide the mechanism from the angular dependence.

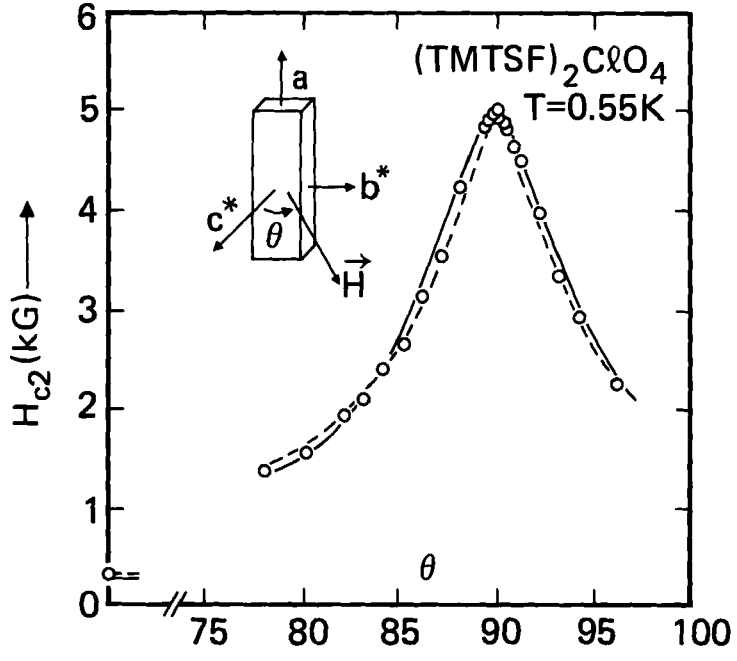

FIGURE 4 Angular dependence of the critical field of $(TMTSF)_2ClO_4$ in the b^*-c^* plane.

Conventionally, it has been found that the real signature of the size effect is an anisotropy which is temperature dependent in the region just below the transition temperature.[11] As can be seen in Fig. 1, by comparing H_{cb} with the enlarged H_{cc} data, the anisotropy is quite temperature independent. This rules strongly for the effective mass model. The critical field may then be related to the coherence lengths by:

$$H_{c2i}(T) = \frac{\varphi_o}{2\pi\ \xi_j(T)\xi_k(T)} \quad \text{or} \quad \frac{dH_{c2i}}{dT}\Big|_{T_c} = \frac{\varphi_o}{2\pi\xi_j(0)\xi_k(0)T_c} \qquad (3)$$

where φ_o is the flux quantum, ξ_i is the coherence length along the i direction and i, j, k are any cyclic permutation of the directions a, b*, c*. The coherence lengths may then be related to the conductivity (or transfer integrals) by

$$\frac{\xi_i}{\xi_j} = \left(\frac{\sigma_i}{\sigma_j}\right)^{1/2} \qquad (4)$$

where $\sigma_i/\sigma_j=(t_i/t_j)^2$ when the conductivity is diffusive (i.e., quasi 1D case) in the perpendicular direction and $\sigma_i/\sigma_j=t_i/t_j$ when the conductivity is coherent (i.e., 3D case) in the perpendicular direction.

From the data shown in Fig. 1 we can evaluate the ratio of coherence lengths between the b* and c* directions by taking the ratio of H_{cb} to H_{cc} and dividing out ξ_a. We find $\xi_b/\xi_c=20$, which would imply a ratio of conductivities $\sigma_b/\sigma_c=400$ at room temperature where the transverse conductivity is diffusive. Although detailed anisotropic conductivity measurements have not been made in the ClO_4 salt in the b*, c* directions, the anisotropy observed[12] in the similar material $(TMTSF)_2PF_6$ is ~400. Thus we may conclude that the anisotropy we observe in the b*-c* plane is consistent with an orbital pairbreaking mechanism coupled with bandstructure anisotropy.

We now turn our attention to the anisotropy in the a-c* or a-b* planes where most of the previous attention has been focused. Following the same line of reasoning which led to the explanation of the data in the b*-c* plane, we would expect the ratio of the critical fields along a and b* to be proportional to the square root of the conductivity anisotropy. We find $\sigma_a/\sigma_b\approx25$ at 300K as shown in Fig. 5. Optical plasma frequency measurements[13] at 25K give an even higher value, $\sigma_a/\sigma_b\approx100$. From Eq. 3 and 4 and Fig. 4 the calculated H_{c2a} at T=0.55K is then $\gtrsim25$ kGauss. This value is above the value that we or any other group have found and is outside the possible error due to misalignment. We must therefore conclude that the critical field along the a axis is not to be associated with an orbital effect but is limited to a much smaller value by some other mechanism.

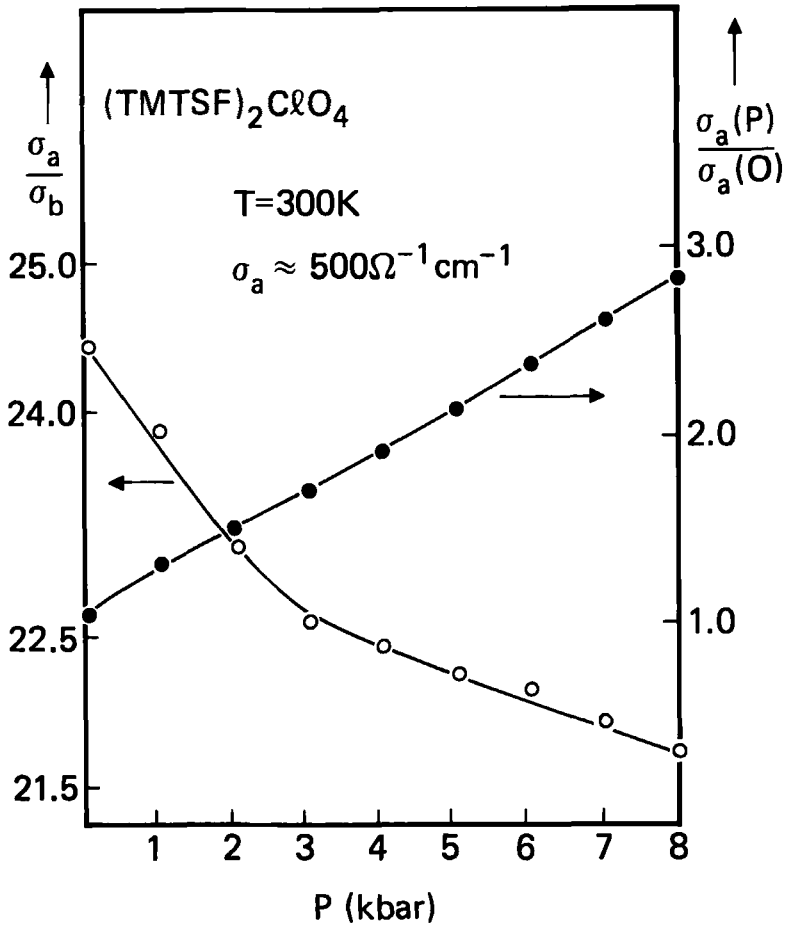

FIGURE 5 Montgomery method determination of conductivity anisotropy σ_a/σ_b, as a function of pressure at room temperature for $(TMTSF)_2ClO_4$. Pressure variation of σ_a is also shown.

The spin pairbreaking is the logical alternative. The Pauli limit for the critical field of a superconductor is related directly to its transition temperature by $H_p(0)=18.4T_c$ kG in the case of small spin orbit scattering. For our samples this value is 15.91 kG at T=0 for a T_c of 0.86K. Using pairbreaking theory[14] we can calculate H_p at 0.55 K as 11.8 kG. This value is in agreement with the experimental finding both in this work and by other groups.[8]

The implications of these results are twofold. First, the measured Pauli limiting field is determined by a T_c of approximately 1K. The large gap observed in the tunneling experiment on the ClO_4 salt implies a T_c near 18K. If this were correct, then the Pauli limit should be $H_p \approx 330$ kOe. This is far above our estimated orbital critical field of $H \geq 25$ kOe and means that we should have measured a larger H_{c2a}. Thus the proposal for a high 1D transition temperature and a large range of 1D superconducting fluctuations in the ClO_4 salt is inconsistent with the critical field results. The same conclusion is found for the PF_6 salt based on the H_{c2} data of Fig. 3, although the results are more uncertain because of the poorer alignment. We note that critical field results obtained in granular aluminum superconductors support our conclusions. In granular Al a Pauli limiting field is observed and is always determined by the meanfield T_c even when T_c^{3D} is greatly suppressed by reducing the coupling between Al grains.[15] Secondly, the observation of a Pauli limiting field in agreement with the usual theory implies that the superconductivity is singlet and not triplet in nature. A triplet superconductor would be expected to have a very large spin pairbreaking field.

1D FLUCTUATIONS: FACT OR SPECULATION?

Over the past two years Jerome and coworkers[5,7] have presented an impressive array of experimental data which supports the view that superconducting fluctuations play an important role in the transport properties of the PF_6 and ClO_4 salts of TMTSF below about 40K. This data suggests that the (TMTSF)$_2$X salts are highly one-dimensional such that the mean field superconducting T_c on the 1D stacks of TMTSF is above 10K whereas the 3D T_c (resulting from interchain Josephsen coupling) is near 1K. Schulz[5] has developed a theory which can explain the experimental results in terms of 1D superconducting fluctuations within a Ginzburg-Landau formalism.

Our view is that the interchain interactions are too large in the (TMTSF)$_2$X salts for the theory of Schulz to be applicable. The major interchain interaction is between Se atoms on neighboring TMTSF molecules approximately along the b^* direction. Band structure calculations[16,17] show that the transfer integral along b^* is about 1/10 of that along the stacking (a) axis. This is large enough to cause considerable warpage of a 1D Fermi surface, although not strong enough to cause a closing of the Fermi surface. Experimental evidence for significant interchain interaction has come from the observation of Schubnikov de Haas oscillations,[18] a plasma edge[13] in the b^* direction at 25K and measurements of the anisotropy of the transverse

magnetoresistance[19] at low T and the conductivity under pressure[3] at low T.

The early experiments[5] which led to the suggestion of 1D fluctuations below ~40K in the PF_6 salt were the large transverse magnetoresistance, the high conductivity at 4K and its continued temperature variation down to T~1K and the anisotropy of the critical field. More recent experiments[18] have shown that an equally plausible interpretation of the magnetoresistance and low T conductivity is a high a axis mobility for the carriers and a moderate b^* interchain interaction. The results presented above show that prior attempts to obtain information about the band structure anisotropy from the critical field anisotropy in the directions parallel and perpendicular to the a axis are not reliable since in previous measurements no care was taken to determine which of the perpendicular directions was observed and the basal plane H_{c2} is very anisotropic.

The latest experiments supporting the fluctuation picture are the tunneling results on the PF_6 and ClO_4 salts. The large gaps observed imply a high mean field T_c ($\geq$10K) and a wide range of SC fluctuations. However, as discussed above, our critical field results show that the mean field T_c cannot be much greater than 1K. An independent argument is the following. The thermodynamic critical field, H_c, is given by

$$H_c^2/8\pi = \frac{N(0)\Delta^2}{2} . \qquad (5)$$

If 2Δ=40K then $H_c \approx$2kG from Eq. 5. But both Jerome[5] and we agree that in the c^* direction H_{c2} is 200-400G. Thermodynamically H_c must be less than the smallest orbital critical field so we cannot have the large gap claimed by the tunneling experiments. In addition, we see no evidence for SC fluctuations in the thermopower of the ClO_4 salt. As shown in Fig. 6 the temperature dependence of the thermopower is very similar to that of the other $(TMTSF)_2X$ salts in their nonsuperconducting state.[20] More significantly, we find alloying the ClO_4 salt with IO_4 or introducing ~100 ppm defects by X-ray irradiation both destroy the 3D superconductivity at low T (and also any 1D fluctuations which are present[21]) and yet the temperature dependence of the thermopower is unchanged. If SC fluctuations were present in the pure ClO_4 salt we would have seen an increase in the thermopower below ~50K upon irradiation.

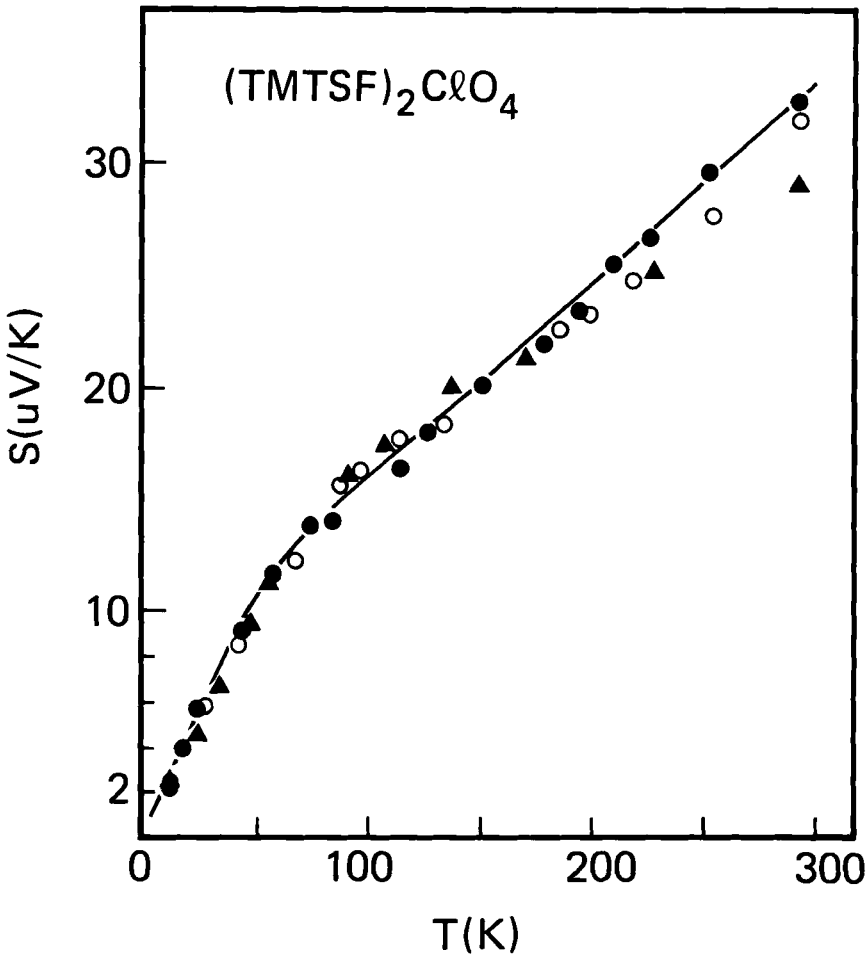

FIGURE 6 Temperature dependence of the thermopower of pristine $(TMTSF)_2ClO_4$ (closed circles), $(TMTSF)_2(ClO_4)_{0.95}$ $(IO_4)_{0.05}$ [▲], X-ray irradiated $(TMTSF)_2ClO_4$ [open circles].

The effect of low levels of 2 Mev proton irradiation on the PF_6 salt under pressure is shown in Fig. 7. A defect concentration of 100 ppm is sufficient to destroy the superconductivity and change the low T resistivity. We find that the resistivity at 4K obeys Mathiessens' rule for the irradiated samples which implies that no SC fluctuations are present in samples with more than 100 ppm defects. This rapid elimination of SC fluctuations appears to be inconsistent with a high mean field T_c. In most superconducting materials T_c is depressed only about 1K per 1% spin defect.[22]

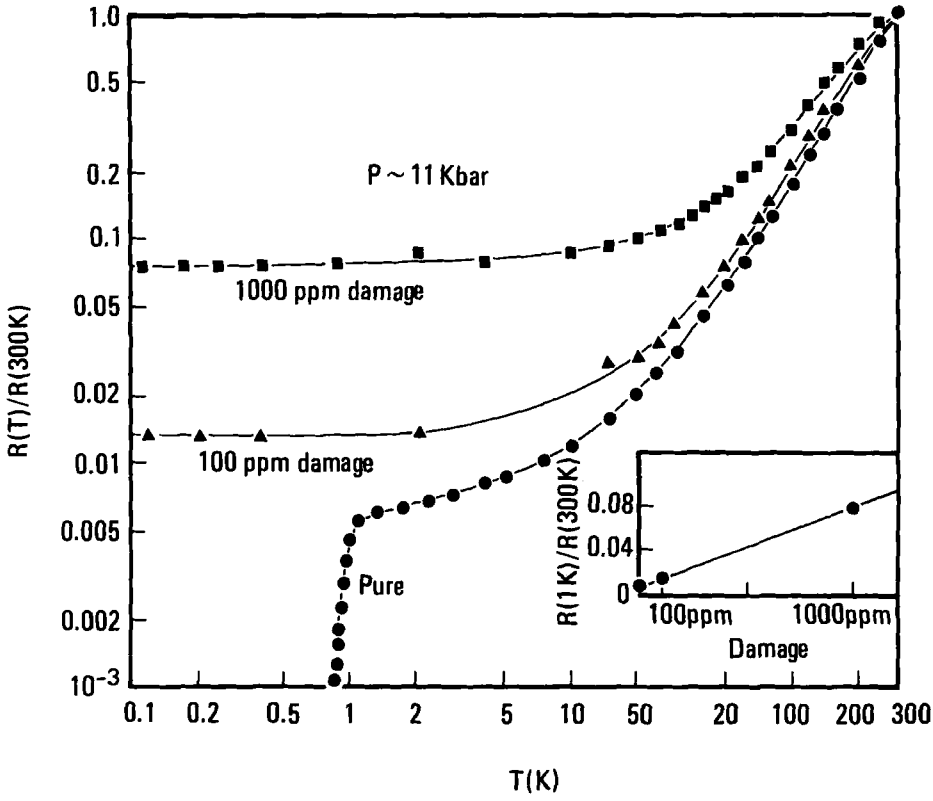

FIGURE 7 Temperature dependence of resistivity of $(TMTSF)_2 PF_6$ at 11 kbar pressure for various amounts of radiation induced damage. Insert shows damage dependence of resistivity at T=1K.

Since the tunneling data is incompatible with our critical field data we must consider other interpretations for the tunneling results. The tunneling barrier used by More et al.[6] is a Schottly barrier formed by an evaporated film of tellurium doped GaSb. It is well known[23] that off stoichiometric films of GaSb are superconducting with T_c as high as 8K. Moreover, Ga or Sb films prepared in the presence of small amounts of oxygen can be superconducting[24] with T_c near 8K. It is certainly possible that such superconducting Ga or Sb phases could be formed on the (TMTSF)$_2$X surface during the tunnel junction preparation. We note that the gap calculated from the tunneling resistance in the PF_6 salt is too large. If one does a proper gap construction[25] of the data one obtains $2\Delta \approx 2.8$ meV which is the same gap as found in Pb with $T_c = 7.2$K. This value of T_c is close to that observed in some GaSb films. The data reported for the ClO_4 salt is not of sufficient quality to do a reliable gap construction.

Another possible explanation for the tunneling data is the presence of a SDW gap in the superconducting state. Previous magnetoresistance experiments have suggested[18] that the SDW state may coexist with the superconducting state in the PF_6 salt. The observation[26] of antiferromagnetic resonance and superconductivity in the ClO_4 salt at ambient pressure implies a coexistence in this salt also. Theoretical work[27] has also shown that such a coexistence is possible if the SDW gap is opened on part of the Fermi surface. If a SDW gap exists in the superconducting state then it can explain a number of puzzling features of the tunneling data. More et al.[6] report that the tunneling gap in the PF_6 salt does not decrease in magnitude until near 15K or for perpendicular magnetic fields as high as 20 kOe (at 50 mK). Moreover, they observe at 50 mK (at low bias) a small gap, characteristic of a low T_c superconductor. These observations would suggest that two gaps are present, a large nonsuperconducting gap (possibly of SDW origin) and a small superconducting gap (characteristic of $T_c \approx 1$K). Finally, the ClO_4 tunneling data is very anomalous.[7] Although of much poorer quality than the PF_6 data, it suggests that the ClO_4 salt is more one-dimensional than the PF_6 salt (since the reported 1D pseudo gap is much larger and T_c^{3D} is the same as PF_6). However, the plasma energy measurements of Jacobsen et al.[13] and our conductivity anisotropy data shown in Fig. 5 show that the ClO_4 salt is less one-dimensional than the PF_6 salt.

CONCLUSION

We have discussed critical field experiments on the ClO_4 and PF_6 salts of TMTSF which show that the H_{c2} along the a axis is Pauli limited with a $T_c \approx 1K$. The tunneling data which suggests a large 1D superconducting pseudogap and a wide range of 1D superconducting fluctuations is incompatible with this result. We presented some alternative explanations for the tunneling data. In addition, we reported transport results on irradiated samples which show no evidence for superconducting fluctuations above $T_c \approx 1K$.

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