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HIGH ELECTRIC FIELD TRANSPORT IN $(TMTSF)_2PF_6$ [BIS-TETRAMETHYLTETRASELENAFULVALENE HEXAFLUOROPHOSPHATE] AT LOW TEMPERATURES

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We obtain electron and hole mobilities from the measured Hall mobility of $(TMTSF)_2PF_6$. At 4K these are greater than $10^6 cm^2/Vsec$ and agree with the mobility calculated for acoustic phonon scattering. The initial increase of conductivity in dc fields found at low temperatures in this material can be accounted for by single particle effects, specifically heating of the carriers by the field. To explain further increases we suggest that the gap is spatially nonuniform. This could be accounted for by dislocations.

INTRODUCTION

$(TMTSF)_2PF_6$ is a quasi-one-dimensional organic salt whose dc conductivity σ increases on cooling from 10^3 $ohm^{-1}cm^{-1}$ at 300K to over 10^5 $ohm^{-1}cm^{-1}$ at 20K, levels off somewhat with further cooling and then decreases rapidly.[1] Although the details of the decrease were

reported differently by different experimental groups,[1,2,3] it is now generally agreed that at ambient pressure there is a metal-to-semiconductor transition taking place at a temperature $T_{MS} \simeq 12K$.[3] It has also been established that the transition is to a spin density wave (SDW) state[4] rather than the charge density wave (CDW) state that is the usual ground state in this family of quasi-one-dimensional organic conductors. It was first reported by Walsh et al[2] that the dc conductivity is nonlinear, starting to increase with field at a few mV/cm at T=4K, for example. This feature, plus the reappearance of the ESR line at 4K under a small microwave field ("spin resurrection") led Walsh et al to conjecture that the nonlinear increase in σ is due to SDW's depinned by the electric field, reminiscent of CDW's so depinned in $NbSe_3$.[5] Detailed measurements of the frequency,[3] electric[3] and magnetic[7] field dependences by Chaikin et al showed, however, that the behavior of σ is quite different from that of $NbSe_3$, casting doubt on the conjecture of depinned SDW's. Chaikin et al suggested that the nonlinearity could be due to single carrier effects, notably heating of the carriers by the field and resultant effects such as impact ionization.[3] The suggestion of hot electrons was bolstered by Hall effect measurements which gave a Hall mobility $\mu_H \simeq 10^5 cm^2/V$ sec at 4K.[7]

In this paper we begin by discussing the theory of single particle transport at temperatures below that for which the gap appears. Since the conductivity mobility μ is what determines the onset of hot carrier effects, we use the theory to derive a value for μ from the measured μ_H, concluding that $\mu > 10^6 cm^2/V$ sec. This

value is found to agree well with μ calculated for acoustic phonon scattering, indicating that that is the dominant scattering process at these temperatures in $(TMTSF)_2PF_6$. We have studied the variation of σ with E for carriers scattered by acoustic phonons[8] and find that with the value of μ obtained from μ_H we can account for the initial increase in σ (warm electron range) at the low dc fields for which it is observed. Further, the theoretical prediction that $\sigma \propto E^2$ for the warm electron range is in fair agreement with what is found experimentally.[3] To account for the variation in σ beyond the warm electron range, and for various unusual features of the conductivity, Hall effect and magnetoresistance of $(TMTSF)_2PF_6$, we suggest that the gap is nonuniform in actual samples. One source of such nonuniformity is dislocations, whose effects we will explore. We suggest that dislocations and other defects may play an important role in the spin resurrection in microwave fields.

LOW-FIELD MOBILITY BELOW T_{MS}

What gives rise to a CDW or SDW distortion in a quasi-one-dimensional crystal is the mixing of an occupied state with wave vector k with the state $k\pm 2k_F$, k_F being the Fermi wave vector, the states having opposite spin in the SDW case. The wave function in the distorted state may be written as the superposition

$$\psi_i = u_i \psi_k + v_i \psi_{k-2k_F}, \quad i=1,2 \qquad (1)$$

where 1 refers to states above the gap, 2 to states below. The coefficients u_i and v_i may be determined by

perturbation theory,[9] which also yields the expression for the energy in the distorted state[10]

$$E_k=(\varepsilon_{k-2k_F}+\varepsilon_k)/2\pm\{(\varepsilon_{k-2k_F}-\varepsilon_k)^2+4\Delta^2\}^{1/2}/2, \quad (2)$$

where ε_k is the one-electron energy measured from the Fermi energy ε_F and 2Δ the gap. This expression is valid for either the CDW or SDW case. For the half-filled band case eq. (2) can be simplified because $\varepsilon_k=-\varepsilon_{k-2k_F}$. In the temperature range where $k_BT<<\Delta$ we may expand eq. (2) keeping terms no higher than $(k-k_F)^2$, k_F now being the band edge. The result may be written

$$E_k=\pm(\Delta+\hbar^2(k-k_F)^2/2m) \quad (3)$$

where m is the effective mass of an electron or hole, given by, respectively

$$m_{n\atop p}=\langle m\rangle\ (1\mp\alpha),\ \alpha<<1 \quad (4)$$

$\langle m\rangle$ being the average of m_n and m_p. For the tight-binding case

$$\varepsilon_k=(\varepsilon_o/2)(\cos k_Fb-\cos kb), \quad (5)$$

where ε_o is the bandwidth and b the lattice constant. With (5), eq (2) yields for states close to k_F

$$\langle m\rangle=\left(\frac{2\hbar^2}{\varepsilon_o b^2}\right)\frac{2\Delta}{\varepsilon_o\sin^2k_Fb} \quad (6)$$

and

$$\alpha = 2\ \Delta \cos k_F b / \varepsilon_o \sin^2 k_F b. \qquad (7)$$

Note that the expression in parentheses in eq. (6) is the mass at the bottom of the undistorted band. Thus, as noted earlier,[11] the average mass is reduced by a factor of the order of Δ / ε_o, while the difference in masses, according to (4) and (7), is of the order of $(\Delta / \varepsilon_o)^2$.

For $(TMTSF)_2PF_6$ ε_o=1eV,[1] b=3.65 Å and sin $k_F b$=0.707, leading to a value for the mass at the bottom of the undistorted band close to the free electron mass m_o. Combining this with Δ =24K, obtained from the slope of ln σ vs 1/T between 10 and 4K,[7] we find $< m > = 0.0095 m_o$ and $\alpha = -0.006$. If we had taken ε_k in the form for free electrons $< m >$ and α would both be smaller, although of the same order of magnitude.

Given the fact that the slope of ln σ vs 1/T, from which we obtained Δ, is constant down to 4K, conduction down to 4K at least is by both electrons and holes. Neglecting a factor of order unity, which is determined by the shape of the constant energy surfaces and the energy-dependence of the scattering relaxation time τ, we may write $\mu_H = \mu_p - \mu_n$. One possible source of difference between μ_p and μ_n is the difference in wave functions of electrons and holes in the SDW state, which could result in a difference in the matrix element for scattering. As noted earlier, the large μ_H suggests that acoustic phonon scattering is dominant. In addition, the electrochemical process by which $(TMTSF)_2PF_6$ is made is expected to be self-purifying.[12] Consistent with this this material shows little if any sign of

residual resistance, under sufficient pressure to make it metallic, down to the superconducting transition at 1K.[13] We have evaluated the matrix elements for scattering by long wavelength acoustic phonons (required to conserve energy and momentum in the scattering process)[9] in terms of u_i and v_i of eq. (1) and find that for k close to k_F there is negligible difference between those for electrons and holes. In fact there is negligible difference between these matrix elements for the distorted state and the matrix element for the metallic state, unlike the case for superconductivity.[14] The other source of difference between μ_n and μ_p is the difference in effective masses. If $\mu \propto m^r$,

$$\mu_H = | 2 r \alpha < \mu > | \qquad (8)$$

where α is given by eq. (7) and $< \mu >$ is the average of electron and hole mobilities. The value of r depends on the scattering mechanism but, whatever the mechanism, its magnitude should certainly lie in the range 0.5 to 3. With $\alpha = -0.006$ for $(TMTSF)_2PF_6$ and $\mu_H = 10^5 cm^2/Vsec$ we deduce from eq. (8) that $< \mu > \; > \; 3 \times 10^6 cm^2/Vsec$ at 4K.

To calculate the mobility due to acoustic mode scattering, μ_{ac}, we use the usual first order perturbation theory. The reciprocal of the scattering time is given by

$$\frac{1}{\tau(k)} = \frac{2\pi}{\hbar} \sum_{k'} | M(k,k') |^2 \rho(E_{k'}) \qquad (9)$$

where M(k,k') is the matrix element and $\rho(E_{k'})$ the density of states. For thermal electrons, i.e., elec-

trons with small $(k-k_F)$, where, as noted above, the matrix element below T_{MS} has the same form as for the metallic state,[15]

$$|M(k,k')|^2 \propto \frac{(k-k_F)^2}{\omega} \begin{cases} n_q & \text{absorption} \\ n_q+1 & \text{emission} \end{cases} \qquad (10)$$

Since equipartition holds for the phonons that interact with thermal electrons we may write

$$|M(k,k')|^2 \propto (k-k_F)^2/\omega^2 \qquad (11)$$

Making use of $\omega \propto (k-k_F)\, v_s$ and $\rho(E_k) \propto (k-k_F)^{-1}$ we find for k close to k_F

$$\tau_{ac}(k) \propto (k-k_F) \propto \left(E_k \mp \Delta\right)^{1/2}, \qquad (12)$$

where the upper sign holds for electrons, the lower for holes. Thus within the range of k for which our approximations hold more energetic electrons are scattered less.

Since $\tau_{ac}(k)$ is independent of k', solution of the Boltzmann equation is straightforward and yields

$$\langle \mu_{ac} \rangle \propto \frac{M v_s^2 (k_B T)^{-1/2}}{b^3 \langle m \rangle^{3/2} (\partial t/\partial u)^2} \qquad (13)$$

Here M is the mass of a lattice ion, which was taken arbitrarily as 408 a.m.u. (in between the values for TMTSF and PF_6) and $v_s = 3\times10^5$ cm/sec at 4K.[16] The quantity $(\partial t/\partial u)$, the rate of change in the transfer integral with nearest neighbor displacement, was taken as 0.3eV/A from comparison of theory with experimental ρ vs T for this compound at $T > T_{MS}$.[17] With these parameters we

find from the theory leading to eq. (13) that $<\mu_{ac}>$ =1x10^{6}cm^2/Vsec at 4K. From eq. (13) we also deduce r=3/2 which, inserted in eq. (8), gives $<\mu>$ =6x10^{6}cm^2/Vsec. The fact that the calculated μ_{ac} is smaller than $<\mu>$ determined from μ_H is probably due to the value taken for $\partial t/\partial u$ being too large. As suggested in reference 17, half or more of the scattering attributed to acoustic phonons may be due to anion rotation. We conclude that for the highly conducting a direction the mobility in the range 10 to 4K at least is determined by acoustic phonon scattering.

HIGH-FIELD EFFECTS

Knowing the scattering mechanism we can calculate the effect of a high electric field on the electron and hole distributions and on the conductivity. We simplify the calculation by assuming that the carrier distributions are Maxwellian with a temperature T_e that is a function of electric field. Conservation of energy requires that the rate of energy gain from the electric field $e\mu(T_e)E^2$, equals the rate of energy loss to phonons. From eq. (12) we deduce that $\mu(T_e)=\mu_o(T_e/T)^{1/2}$, where μ_o is the low-field mobility at the lattice temperature T. For T_e not much greater than T, or the warm electron region, we find that the change in μ, $\Delta\mu$, at a field E is given by

$$\frac{\Delta\mu}{\mu_o}=\frac{\pi}{16}\left(\frac{\mu_o E}{v_s}\right)^2 \qquad (14)$$

With μ_o=6x10^{6}cm^2/Vsec, the value deduced from the mea-

sured μ_H, eq. (14) leads to $\Delta\mu/\mu_o \simeq 3\%$ at a field of 20 mV/cm, within a factor 2 of the observed percent change in σ, $\Delta\sigma$, at 4K.[3] It has been found also that $\Delta\sigma/\sigma_o$ varies at low E's as a power of E between 1.0 and 2.0,[3] in approximate agreement with eq. (14).[18] A possible origin for these small discrepancies will be discussed below.

For carrier energies much beyond k_BT a couple of the approximations made in deriving (12) no longer hold, with the result that τ no longer increases with increasing E_k. The integration for μ must be carried out numerically and we find that μ only increases $\sim$ 10% for Δ =24K before decreasing with further increase in field. Thus the observed decrease in resistance by a factor $\sim$ 5 in 500mV/cm at 4K cannot be explained by this mechanism. It cannot be explained by impact ionization of impurities because the constant slope (corresponding to Δ) of ln σ vs 1/T means there is no contribution of impurities to σ above 4K. Nor can it be explained by impact ionization creating electron-hole pairs because the electron temperatures we calculate for 4K making the most favorable assumption, i.e., that there is only acoustic scattering, are not high enough. We suggest that at least part of the increase comes from spatial variation of the gap. This gives rise to barriers that are more easily surmounted by hot electrons. These barriers should be at most a few K in height, corresponding to gap variations of no more than 10 to 15% over most of the sample. Further, the distance between barriers should be many mean free paths to be consistent with the high μ observed at 4K. We believe that these barriers originate from defects in the material, dislocations

being a prime source as will be shown in the next section. We will also show that a spatially varying gap can explain many other unusual effects that have been observed in this material.

ORIGINS AND EFFECTS OF SPATIALLY VARYING GAP

Since the gap in $(TMTSF)_2PF_6$ has been shown to be highly pressure-sensitive,[13] any defect that produces a dilatation should have an effect on the gap locally. Consider the stress due to a single edge dislocation. In the plane perpendicular to the dislocation axis the average of the diagonal components of the stress tensor, or the "hydrostatic pressure" due to the dislocation, is given by[19]

$$\langle \text{stress} \rangle = - \frac{1-2\nu}{1-\nu} \frac{B \beta \sin\theta}{2 \pi r}, \qquad (15)$$

where r and θ are the polar coordinates in this plane, β is the Burgers vector (a multiple of the lattice constant), B the bulk modulus and ν Poisson's ratio. We can estimate this for TTF-TCNQ for which B at low temperatures has been measured,[20] its value being 2×10^{11} dynes/cm.^{2} The value of ν must lie between 0 and 0.5 and we have taken it as 0.25. For $\theta = \pm \pi/2$, we find from eq. (15) that $\langle \text{stress} \rangle = \mp 21 (\beta/r)$ kbar. The gap has been found to vanish at 9 kbar.[13] Thus the rate of decrease of the gap with pressure is on the average 11%/kbar or $\sim$ 5K/kbar. We assume that an equal rate of increase holds for negative pressure. For β of 1 lattice constant, which is typical, a change of as much

as 5K in the gap will be found at a distance of 21 lattice constants. Due to the 1/r dependence of the stress, the change falls off slowly with distance. This could easily be the origin of the gap variation we have postulated to explain the increase in σ with E. Such gap variations could account for the increase in σ with frequency above 1GHZ[21] and the decrease in slope of ln σ vs 1/T found below 4K. Although there should be as many regions with increased gap as with decreased gap, the latter will dominate σ at low temperatures. Strains could also account for the different values of T_{MS} found by different experimenters.[1,2,3]

Closer to the dislocation lines the strains are larger. According to (15), for $r \lesssim 3\ \beta$ the average stress would be sufficient to wipe out the gap. Of course, this equation is based on continuum elastic theory and may not be valid for such small distances. On the other hand, eq. (15) describes the stress for a single edge dislocation and it could well be much larger for dislocations bunched together. The poor mechanical properties of $(TMTSF)_2PF_6$ make it not unlikely that there are bunched dislocations in this material. This could result in the existence of metallic regions for temperatures below the apparent T_{MS} and regions with fully developed gap ($\Delta > 24K$) above the apparent T_{MS}. The existence of such regions could explain a number of effects that are otherwise difficult to account for. For example, the observation[3] of an increase in σ with E at 20K, of comparable magnitude and at comparable E to what is observed below 12K, can be attributed to the hot electron effects we have been discussing in semiconduct-

ing regions existing in series with the metallic regions. It would not be possible to obtain any heating of the carriers in the metallic regions at these fields since μ in these regions, deduced from the measured σ and the known charge transfer, is less than 1000 $cm^2/Vsec$. By similar arguments the large magnetoresistance observed[7,1] for several degrees above the apparent T_{MS} can be attributed to such semiconducting regions. It should also be noted that the existence of such inhomogeneities in high μ material would have considerable effects on magnetoresistance and Hall measurements.[22]

The existence of metallic and small gap regions below the transition may also be connected with the observation of the reappearance of the electron spin resonance line in microwave fields estimated as $\sim$ 100 mV/cm at 4K.[2] It is expected that the microwave power be concentrated in metallic and small gap regions, rather than spread uniformly through the sample. This could result in local heating, destroying the gap in some regions and restoring some of the ESR signal. This might account for the step-like nature of the spin resurrection observed in thick samples,[2] where there could be a number of separate metallic and small gap regions with different extent and degree of disturbance.

CONCLUSIONS

From the measured μ_H, using the fact that only the mass difference contributes to the difference in mobilities, we deduce that $\mu_n \simeq \mu_p = 6 \times 10^6 cm^2/Vsec$ at 4K. In comparing this with μ's deduced from magnetoresistance and Hall measurements,[7] one should remember that there is

considerable evidence that the samples are inhomogeneous, which can cause considerable error in magnetoresistance and μ_H.[22] The mobility we calculate for acoustic phonon scattering is in reasonable agreement with μ deduced from μ_H. With this high value of μ heating of the carriers by the field can account for the initial increase of σ with E. A model with spatially varying gap can account for a good part or all of the remainder of the nonlinearity in σ and for a number of other phenomena observed in this material as well. The spatially varying gap may be due to dislocations, small angle grain boundaries, etc., which can lead to metallic regions below T_{MS}, high gap regions above T_{MS}. Such inhomogeneities would contribute to the spin resurrection observed in microwave fields.

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