Hall Effect in the Normal Phase of the Organic Superconductor $(TMTSF)_2PF_6$

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We report accurate Hall effect measurements performed in the normal phase of the quasi-one-dimensional organic conductor $(TMTSF)_2PF_6$ at ambient pressure. The Hall coefficient is found to be strongly temperature dependent all the way from 300 K down to the spin density wave onset arising around 12 K. These new results emphasize the existence of a high temperature regime above 130 K where the Fermi liquid model is not satisfactory.

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The normal state properties of low-dimensional conductors are particularly interesting because of theoretical work which implies that electron-electron interactions in these materials lead to a complete breakdown of the usual Fermi liquid (FL) picture involving well-defined electron- or holelike quasiparticle excitations [1]. Instead, less familiar concepts such as a Luttinger liquid [2], or a marginal Fermi liquid, are expected to be more appropriate for one- and two-dimensional (1D and 2D) materials, respectively. In a Luttinger liquid the electrons combine to form separate spin and charge excitations, with different velocities, while in a marginal Fermi liquid the quasiparticle relaxation rate is comparable to its energy. In such cases the physical properties are expected to obey certain characteristic non-Fermi liquid power laws as a function of temperature and frequency. For example, the unusual normal state pseudogap [3] in quasi-2D superconducting cuprates may well be a manifestation of non-Fermi liquid behavior.

$(TMTSF)_2PF_6$ is the archetype of quasi-1D organic conductors. It belongs to a vast family of $(TM)_2X$ compounds in which optical transport [4] and NMR measurements [5] both point to a nonconventional normal phase at high temperature. The precise nature of this state is still unsettled but there is reasonably good evidence for Luttinger liquid behavior at frequencies (and temperatures) above the largest interchain transfer integral t_b. At lower frequencies there is some evidence for an additional gap (referred to as the Mott gap) of the same order as t_b arising from electron-electron interactions in a quarter filled band. dc transport along the lowest conductivity direction is also suggestive of a Luttinger liquid at high T [6] with a depletion of quasiparticle density of states near the Fermi energy [7]. However this picture must change as T is lowered because many of the properties of the $(TMTSF)_2X$ family at low T can be understood in terms of Fermi liquid theory and an open Fermi surface (FS). For example, the field-induced spin density waves (SDW) are described well by a mean-field Stoner theory involving a FS and well-defined quasiparticles [8]. Also, unusual peaks in the angular dependence of the magnetoresistance [9] can be understood in terms of quasiparticle FS orbits which are commensurate with the crystal lattice [10]. Although there is some recent evidence for non-Fermi liquid behavior at very high magnetic fields at low T this is probably because high fields restore the 1D behavior already evident at high T [9,11].

The crystallographic structure of $(TMTSF)_2PF_6$ consists of stacks parallel to the a axis, the electronic overlap integrals (t_a, t_b, t_c) are approximately 250 meV in the a direction and 20 and 1 meV in the two perpendicular directions, which are roughly along the b and c axes. Early measurements on the charge transfer conductors TTF-TCNQ [12] and HMTSF-TCNQ [13] gave a Hall constant R_H in fair agreement with simple band theory but with some uncertainty associated with the two-band nature of these quasi-1D compounds. The situation should be clearer for the single band conductor $(TMTSF)_2PF_6$. However the Hall voltage of the metallic phase has been investigated only qualitatively under a pressure of 12 kbar [14] where the low temperature data were interpreted in terms of a k-dependent scattering time on the quasi-1D Fermi surface [15].

As far as we know there are no published calculations of the Hall coefficient R_H for a Luttinger liquid. At first sight one might expect the Hall effect to be unobservably small because the collective charge excitations cannot propagate perpendicular to the 1D chains and hence σ_{xy} will be zero. However this type of argument does not work in the simple case of an extremely anisotropic FL where both σ_{xy} and σ_{yy} go to zero as t_b^2 and a finite Hall voltage, essentially arising from the Lorentz force, is both predicted and observed (see, e.g., [16]). Therefore we have measured R_H of $(TMTSF)_2PF_6$ at ambient pressure from 300 K down to the SDW transition at 12.5 K. We utilized the following geometry during the experiment; current was passed along the a axis, and the magnetic field was applied along c so that the Hall voltage developed along b. Precise measurements of R_H for quasi-1D conductors are not straightforward

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because of the difficulty in making low noise contacts and in ensuring that there is uniform current flow in the low conductivity direction at all temperatures. Although the crystals are fragile and very susceptible to microcracks or plastic deformation they must be held sufficiently firmly so that they do not move or vibrate in the applied magnetic field.

We believe that from 300 to 130 K the present results may be typical of weakly coupled Luttinger chains. At lower temperatures there appears to be a dimensional crossover towards a 2D FL while below 50 K R_H drops and eventually changes sign because of the gradual growth of SDW correlations.

Measurements were performed in a 13/15 T magnet using a low noise sample probe equipped with a 360° rotatable cold stage. The dimensions of the two crystals for which data are reported here were $(a \times b \times c) = (3000 \times 250 \times 225)\ \mu\text{m}^3$ for the UCLA crystal and $(3000 \times 150 \times 75)\ \mu\text{m}^3$ for the Risø crystal. At 300 K the conductivity anisotropies are $\sigma_a/\sigma_b = 80$ and $\sigma_a/\sigma_c = 3 \times 10^4$ [17]. The well-known eight terminal configuration was used and contacts were made to the (ac) sides of the crystal by evaporating gold pads and attaching 12.5 μm diameter gold wire with *Dupont 4929* silver paint. The two pairs of contacts near the ends of the crystal were used to supply a constant amplitude, 72 Hz current of 30 to 100 μA. The magnetic field was applied along the c axis and the contacts were sufficiently uniform in the c direction to ensure that the current flowed in the (ab) plane. This was checked by verifying that the room temperature conductivity corresponded to the value expected for the a axis, namely, $500-800\ (\Omega \cdot \text{cm})^{-1}$ and that the conductivities obtained from the two pairs of voltage contacts had the same magnitude and T dependence to within 10%–20%. The length of the crystals ensured that the current flow was mainly along the a axis and the Hall voltage developed perpendicular to this direction. (Note that because of the symmetry of the Hall tensor this should not affect the value of R_H, as shown, for example, by the paper of van der Pauw [18]). The resistive offset of opposite pairs of Hall contacts could often be reduced by a factor of 10 by injecting a larger fraction of the measuring current into one of the current contacts. This made the Hall measurements less sensitive to small temperature drifts during reversals of the magnetic field. Because of the large electrical anisotropy the equivalent isotropic samples [19] have dimensions of $(a \times b \times c) = (260 \times 200 \times 3300)\ \mu\text{m}^3$ and $(200 \times 120 \times 1100)\ \mu\text{m}^3$, respectively, at room temperature. Thus they are by no means of the ideal thin-ribbon or "matchstick" shape [20] and it is therefore important to note that the same values of $R_H(T)$ and $\rho_{xx}(T)$ were obtained for both crystals as shown later in Figs. 1 and 2.

The data had to be taken at temperatures stabilized to within 0.05 K, the sample being turned slowly by 180° several times in a fixed field, typically 8 T. Special software was written to process the data, eliminating any points for which the measured voltages were not drifting uniformly with time. Checks for linearity of the Hall signal were made at various temperatures for fields of 4, 8, and 12 T. The full angular dependence of the in- and out-of-phase Hall and magnetoresistance voltages was also checked at several fields and temperatures. These showed that possible systematic errors in the Hall voltage at 8 T from unwanted common mode signals are less than 5% of the typical Hall voltage of 30 nV. In order to establish the magnitude of $R_H(T)$ precisely it was important to avoid any irreversible jumps in the longitudinal resistance $R_{xx}(T)$, which are often a problem when cooling such crystals. $R_{xx}(T)$ was monitored throughout and we found no evidence for such jumps. Although very slow cooling rates (2–5 K/h) were normally used, we believe that the key precaution, which prevented such jumps, was drying the silver paint for 1 h at 300 K in a dynamic vacuum of 10^{-4} mbar.

Figure 1 shows the $R_H(T)$ results for two crystals from different batches out of a total of seven investigated. The data for the other crystals were rejected because of irreversible jumps mentioned above or unsatisfactory angular dependences or noise levels. The sign of $R_H(T)$ was found to be positive (holelike) by comparison with a standard thin film copper sample mounted in exactly the same way. This implies that in the low temperature SDW phase $R_H(T)$ is negative which agrees with an investigation which mainly focused on the field-induced SDW phases in the very same

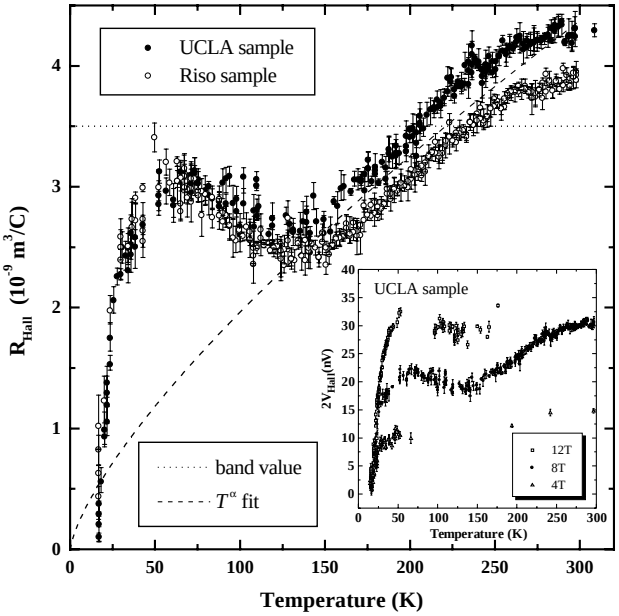

FIG. 1. Hall constant of UCLA (full circles) and Risø (open circles) samples vs temperature. The dotted line indicates the Hall constant derived in a band model, and the dashed line is a T^α power law fit with $\alpha = 0.73$. Inset: Data collected on the UCLA sample at 4, 8, and 12 T.

geometry [21]. The dotted line in Fig. 1 shows the value expected from band theory with a scattering time which is constant over an open Fermi surface [12,22]. Namely,

$$R_H = \frac{1}{n|e|}\,\frac{k_{\mathrm{F}}a}{\tan k_{\mathrm{F}}a}\,. \tag{1}$$

In (1) $k_{\mathrm{F}}a = \pi/4$ (one-quarter filling) and the density of carriers amounts to one hole per unit cell of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ so $n = 1.4 \times 10^{21}$ cm^{-3}. As mentioned already, in band theory a finite Hall voltage is expected even for arbitrarily small interchain coupling (provided the band is not half full). Mathematically this is because both the Hall conductivity σ_{xy} and the transverse conductivity σ_{yy} are proportional to t_b^2 where t_b is the transverse tight-binding transfer integral. Physically it is because there is always a Lorentz force acting on the carriers, which for a single band will always give a measurable Hall voltage. The Hall signal saturates around room temperature at a value which is very close to the band value. Because of sample stability no data could be collected above 320 K. A 45% drop in $R_H(T)$ is achieved on cooling down to 125–130 K where a shallow minimum is observed. Upon further cooling the Hall constant increases again and passes through a local maximum around 60 K. Below this temperature the Hall signal falls off sharply then goes through zero at 17 K and becomes negative as the SDW state is approached.

An interesting feature of the Hall constant shown in Fig. 1 is the temperature dependence displayed between 300 K and the temperature of the local minimum around 120–130 K. The very sharp falloff below 50 K must be linked with the proximity of the SDW state at 12 K. There is a large magnetoresistance in this region (as shown in the lower inset of Fig. 2) but R_H remains linear down to 25 K (inset of Fig. 1). Focusing on the data above 50 K we can say that $R_H(T)$ starts from the band value at elevated temperatures and tends to reach that value again at lower T after passing through a minimum around 130 K. As shown by the dashed line in Fig. 1, a T^{α} power law fit above 130 K gives $\alpha = 0.73 \pm 0.02$.

Yakovenko and Zheleznyak [23] have discussed our preliminary Hall data within a FL picture. In their model, umklapp scattering gives rise to two "hot spots" on each sheet of the Fermi surface and the corresponding variation of the scattering time over the Fermi surface causes R_H to be very T dependent. In their picture the phase angle φ in the transverse tight-binding dispersion of the transverse energy [10], namely, $\varepsilon_y(k_y) \sim \cos(k_y - \varphi)$ is a crucial parameter. This phase factor also enters into the determination of the modulation vector of the spin density wave state. Analyses of the NMR line shapes in $(\mathrm{TMTSF})_2\mathrm{PF}_6$ [24,25] give $\mathbf{Q} = [2k_{\mathrm{F}}, (0.20\text{–}0.25)2\pi/b]$ for the (ab) plane components and consequently $\varphi \sim (0.25\text{–}0.30)\pi$. It is not at all clear whether this value of φ can account for the behavior of R_H reported here. Moreover the R_H data in Fig. 1 do fit a power law above 140 K and do

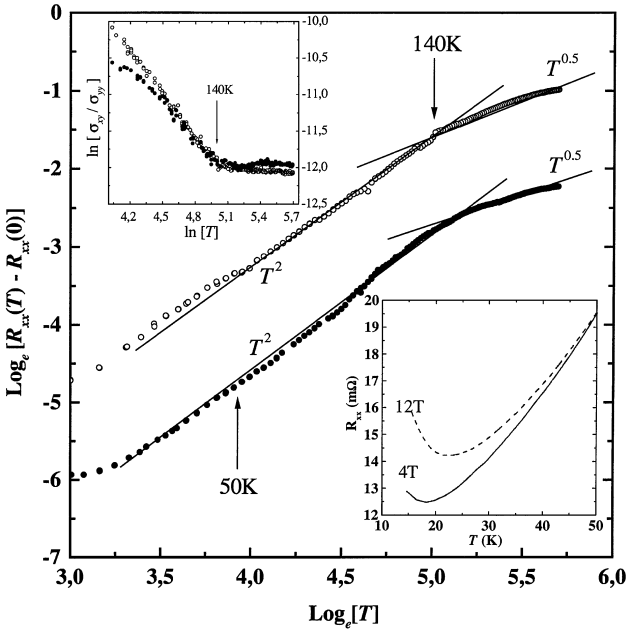

FIG. 2. Longitudinal resistivity vs T corrected for thermal expansion. Full, open circles: UCLA, Risø samples. Bottom inset: Magnetoresistance onset below 55 K. Top inset: $\ln[\sigma_{xy}/\sigma_{yy} = R_H H/\rho_{xx}]$ vs $\ln T$.

appear to extrapolate to zero. The latter behavior would be purely coincidental in the FL picture of Ref. [23]. Resistivity measurements provide further evidence against a conventional FL picture since the a, c [6] and b [17] directions all show different T dependences. (We should note that the behavior in the b direction is controversial at present because there is disagreement between two recent measurements [6,26].) In the absence of any theory of R_H for weakly coupled Luttinger chains only qualitative arguments are hereafter proposed. At high enough temperatures one might expect the collective charge excitations to break up into conventional quasiparticles, thus restoring the band value. It is also probable that σ_{xy} would fall to zero as $T \to 0$ because the collective charge excitations cannot propagate perpendicular to the chains. However, as in the band case, in order for R_H to be zero, σ_{xy} must go to zero faster than σ_{yy}. The reason for this is less obvious unless, for example, there is exact symmetry for positively and negatively charged excitations. The ratio σ_{xy}/σ_{yy} is equal to $R_H H/\rho_{xx}$ and can therefore be derived from the data in Figs. 1 and 2. In order to obtain meaningful fits to power laws and extrapolations to low T, the data have to be corrected to constant volume, i.e., for the effects of thermal expansion [27]. These corrections have a strong effect on ρ_{xx} because of the strong pressure dependence of ρ_{xx} (25% per kilobar at all T) and the relatively large thermal expansion. The pressure dependence of R_H is not known but it is likely to be small above 140 K because the carrier density is fixed by chemical considerations and does not change significantly with pressure. After correction, ρ_{xx} follows a reasonably good T^2 law between 30 and

130 K and probably another power law, with the exponent α close to 0.5, between 170 and 300 K as shown in Fig. 2. The ratio σ_{xy}/σ_{xx} or equivalently $R_H H/\rho_{xx}$ fits a $T^{-2.3}$ power law between 130 and 60 K (upper inset of Fig. 2) but is constant or even increases slightly with T above 140 K (the latter behavior would support the suggestion that R_H extrapolates to zero at low T). In other words the behavior of the longitudinal resistivity becomes compatible with electron-electron scattering processes in a FL below 130 K, the same temperature at which the Hall resistivity starts to increase. Overall, several types of experiments support a picture in which the coupling along the b axis becomes significant below 130 K giving rise to an anisotropic quasi-2D electronic system at lower temperatures.

It is instructive to compare on the energy scale basis our present crossover region with the Mott gap observed by Vescoli *et al.* [4] in the far-infrared conductivity of the title compound. The related structure is centered around 200 cm^{-1}. This value is also reminiscent of the *bare* coupling along the b axis t_b^0 derived from extended Hückel calculations. Our observation strongly suggests that the changeover from a 1D to 2D regime in the normal phase of $(TMTSF)_2PF_6$ is triggered by an energy scale close to the bare interchain coupling t_b^0 which in turn coincides with the Mott gap value (Δ_M). However, considering the optical data [4] showing a very small spectral weight in a zero frequency mode it would not be meaningful to compare the small density of carriers at 20 K derived from the low frequency mode with the value of the Hall constant in the high temperature regime in the absence of any theory for the Hall voltage in a non-Fermi liquid 1D conductor.

In conclusion our Hall effect measurements are strongly suggestive of different regimes in the normal state of $(TMTSF)_2PF_6$. We believe that the high temperature phase is a correlated state compatible with a Luttinger liquid or narrow gap Mott insulator ($T > \Delta_M$). Below 130 K or so b coupling starts being a relevant process and coherence might be expected for transport along the b direction. Therefore in this region and at lower temperatures the electronic properties would evolve towards those of an anisotropic Fermi liquid.

After the experimental work reported here was completed we received a preprint reporting independent Hall measurements on $(TMTSF)_2PF_6$, in a different geometry, performed by Mihály *et al.* [26].

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[1] H. J. Schulz, Int. J. Mod. Phys. B **5**, 57 (1991); in *Mesoscopic Quantum Physics*, edited by E. Akkermans, G. Montambaux, J.-L. Pichard, and J. Zinn-Justin (Elsevier, New York, 1995), p. 533; P. B. Littlewood, in *Mesoscopic Quantum Physics*, p. 69; J. Voit, Phys. Rev. B **47**, 6740 (1992).
[2] F. D. M. Haldane, J. Phys. C **14**, 2585 (1981).
[3] For a review, see J. R. Cooper and J. W. Loram, J. Phys. I (France) **6**, 2237 (1996).
[4] A. Schwartz, M. Dressel, G. Gruner, V. Vescoli, L. Degiorgi, and T. Giamarchi, Phys. Rev. B **58**, 1261 (1998); V. Vescoli, L. Degiorgi, W. Henderson, G. Gruner, K. P. Starkay, and L. K. Montgomery, Science **281**, 1181 (1998).
[5] C. Bourbonnais *et al.*, Phys. Rev. Lett. **62**, 1532 (1989); P. Wzietek, F. Creuzet, C. Bourbonnais, D. Jérome, K. Bechgaard, and P. Batail, J. Phys. I (France) **3**, 171 (1993).
[6] J. Moser, M. Gabay, P. Auban-Senzier, D. Jérome, K. Bechgaard, and J.-M. Fabre, Eur. Phys. J. B **1**, 39 (1998).
[7] C. Bourbonnais and D. Jérome, Science **281**, 1155 (1998).
[8] M. Héritier, G. Montambaux, and P. Lederer, J. Phys. (Paris) Lett. **45**, L-943 (1984); G. Montambaux, M. Héritier, and P. Lederer, Phys. Rev. Lett. **55**, 2078 (1985).
[9] G. M. Danner and P. M. Chaikin, Phys. Rev. Lett. **75**, 4690 (1995).
[10] K. Yamaji, J. Phys. Soc. Jpn. **51**, 2787 (1982).
[11] K. Behnia *et al.*, Phys. Rev. Lett. **74**, 5272 (1995).
[12] J. R. Cooper, M. Miljak, G. Delplanque, D. Jérome, M. Weger, J.-M. Fabre, and L. Giral, J. Phys. (Paris) **38**, 1097 (1977).
[13] J. R. Cooper, M. Weger, G. Delplanque, D. Jérome, and K. Bechgaard, J. Phys. (Paris) **37**, L-349 (1976).
[14] K. Murata, Physica (Amsterdam) **185C–189C**, 2685 (1991).
[15] N. A. Fortune, P. J. Fons, and K. Murata, Synth. Met. **70**, 1001 (1995).
[16] M. Petravić, L. Forró, J. R. Cooper, and F. Levy, Phys. Rev. B **40**, 2885 (1989).
[17] J. Moser, Ph.D. thesis, University of Paris XI, 1999 (unpublished).
[18] L. J. van der Pauw, Philips Res. Rep. **13**, 1 (1958); **16**, 187 (1961).
[19] H. C. Montgomery, J. Appl. Phys. **42**, 2971 (1971).
[20] A. B. Pippard, *Magnetoresistance in Metals* (Cambridge University Press, Cambridge, England,1989).
[21] J. R. Cooper, W. Kang, P. Auban, G. Montambaux, D. Jérome, and K. Bechgaard, Phys. Rev. Lett. **63**, 1984 (1989).
[22] K. Maki and A. Virosztek, Phys. Rev. B **41**, 557 (1990).
[23] V. M. Yakovenko and A. T. Zheleznyak, Synth. Met. **103**, 2202 (1999).
[24] J. M. Delrieu, J. Phys. (Paris) **47**, 839 (1986).
[25] T. Takahashi, J. Phys. Soc. Jpn. **55**, 1364 (1986).
[26] G. Mihály, I. Kézsmárki, F. Zámborszky and L. Forró, preceding Letter, Phys. Rev. Lett. **84**, 2670 (2000).
[27] P. Auban-Senzier, D. Jérome, and J. Moser, in Proceedings of the High Magnetic Field Conference at Tallahassee, 1998 (to be published).