PHYSICAL REVIEW B VOLUME 24, NUMBER 12 15 DECEMBER 1981

Magnetoresistance and Hall effect in tetramethyl-tetraselenafulvalene-phosphorus hexafloride [$(TMTSF)_2PF_6$]

P.M. Chaikin
Department of Physics, University of California, Los Angeles, California 90024

P. Haen,* E. M. Engler, and R. L. Greene
IBM Research Labs, San Jose, California 95193
(Received 14 July 1981)

We have measured the magnetoresistance and Hall effect of tetramethyl-tetraselenafulvalene-phosphorus hexafloride as a function of temperature, magnetic field for several orientations, and electric field. For temperatures well below the metal-insulator transition we find a large positive Hall coefficient and positive magnetoresistance, indicating carrier mobilities greater than 10^5 cm^2/V sec at 4.2 K. The magnetoresistance is highly anisotropic for field orientations in the plane perpendicular to the highly conducting axis, indicating a quasi-two-dimensional band structure. The nonlinear conductivity seen with small electric fields below the metal-insulator transition has approximately the same magnetic-field behavior as does the Ohmic conductivity at the same temperature.

INTRODUCTION

The organic charge-transfer salt tetramethyl-tetraselenafulvalene-phosphorus hexafloride [$(TMTSF)_2PF_6$] has some rather extraordinary properties. At ambient pressure the material has a metal-insulator transition at $T_{MI} \sim 12$ K,[1] to a low-temperature spin-density wave (SDW) insulating phase.[2–5] In the insulating phase the application of a small electric field ~ 1 mV/cm is sufficient to produce a non-Ohmic contribution to the conductivity.[5,6] When the material is subjected to a moderate pressure, the metal-insulator transition is driven to $T=0$ and superconductivity is observed at 1.2 K and ~ 6.5 kbar.[7–9] Other members of the $(TMTSF)_2X$ family of organic salts also show quite unusual properties ranging from charge-density wave (CDW) transitions at high temperature to superconducting transitions at ambient pressure and the existence of a metallic state with no transition down to low temperatures.[1,10,11] All of these diverse ground states occur in materials with virtually the same triclinic crystal structures and lattice parameters and all are electronically $\frac{1}{4}$ filled band systems. It is remarkable to find such a vast difference in the low-temperature properties of a family with such similar molecular characteristics.

Several papers have suggested the transport and superconductivity of this series of compounds may be described as related to the highly anisotropic band structure being responsible for quasi-one-dimensional conductivity and superconducting fluctuations.[7,10] On the other hand, other workers[9,12,13] have given evidence that interchain interactions are more important in these compounds *vis a vis* previously studied organic metals, and therefore it is this increased dimensionality which is primarily responsible for the superconductivity and other properties. Magnetoresistance experiments are a conventional way of probing the band structure and its anisotropy, especially since one-dimensional conductors should show no orbital magnetoresistance whatsoever. The Hall effect provides us with information about the carrier mobility and its temperature dependence. This allows an evaluation of whether the dominant transport process both above and below the transition are of the usual single-particle character.

The nonlinear current voltage characteristic has been suggested to be of depinned spin-density wave origin.[5] Once the nature of the Ohmic carriers are known similar experiments in the non-Ohmic regime can be used to compare the carriers in that regime with the carriers which are thermally excited and responsible for the Ohmic conductivity. For example, in the well-studied case of $NbSe_3$, an additional, non-Ohmic conductivity is known to be of depinned charge-density wave origin, yet the magnetoresistance and Hall effect show no effect

from the motion of the CDW.[14] This is due to the one-dimensional motion of the CDW and the fact that it has neither transverse conductivity nor does it produce a transverse voltage which is sizable compared to that produced by the normal carriers that are present. Normal carriers experience a much larger Lorentz force due to their higher mobility.

From the anisotropy in the magnetoresistance we find that the band structure of $(TMTSF)_2PF_6$ is best described as two dimensional rather than one dimensional at temperature below the metal-insulator transition temperature. From the Hall-effect measurement we find an extremely large a axis mobility which is at least 10^5 cm^2/V sec at 4.2 K. The non-Ohmic conductivity is very magnetic field dependent showing virtually the same behavior as the carriers which are thermally excited. This is in direct contrast to what is seen in $NbSe_3$ and together with the high mobility leads us to suspect that single-particle effects may play at least some role in the non-Ohmic conductivity which is observed.

EXPERIMENTAL RESULTS

The single-crystal samples used in this study were prepared by an electrocrystallization technique similar to that described in Ref. 1. We have found that the solid-state properties of the TMTSF salts are not a sensitive function of the conditions of electrocrystallization. The metal-insulator transition observed in our $(TMTSF)_2PF_6$ by a number of different experiments is 12 K. The superconducting transition observed under pressure is 1.3 K at 6.5 kbar. Hence these samples are analogous to those prepared and studied by other groups.

In Fig. 1 we show the four-probe resistivity as a function of temperature for zero applied magnetic field and for 80 kG applied approximately along the c axis, perpendicular to the platelet and to the current which was supplied along the highly conducting a axis. This magnetic field orientation produces the highest magnetoresistance. The data taken in zero magnetic field shows the metal-insulator transition at 12 K and the presence below the transition of an activation energy of ~ 24 K which would correspond to half of the energy gap ($\Delta \sim 2$ meV). The resistance in a magnetic field is considerably higher at low temperature reaching a factor of ~ 20 times the $H=0$ value at 4.2 K. As temperature is increased toward the metal-insulator transition the magnetoresistance decreases, but

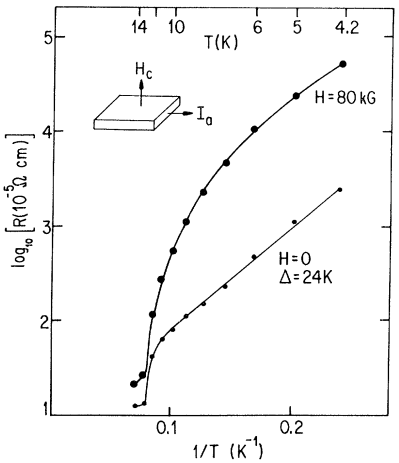

FIG. 1. Temperature dependence of the a-axis resistance of $(TMTSF)_2PF_6$ for zero magnetic field and an 80-kG field applied along the c axis.

remains sizable in the metallic state, giving a ratio of about 50% higher at 80 kG than at $H=0$ for temperature just above the transition. The magnetoresistance then decreases rapidly and is virtually unobservable above 30 K.

This anomalously large transverse magnetoresistance has previously been observed by Jacobsen *et al.*[13] However, they reported that the magnetoresistance was isotropic within a factor of 2 in the c-b plane perpendicular to the highly conducting a axis. In contrast we find a huge anisotropy in the transverse magnetoresistance which is very important for understanding the band structure of $(TMTSF)_2PF_6$. In experiments performed on platelike crystals in a superconducting magnet to a field of ~ 80 kG, we have roughly ($\pm$ 5°) oriented the crystals with the field either parallel or perpendicular to platelets and perpendicular to the needle axis along which the current was supplied. In general we find a high magnetoresistance for the field perpendicular to the platelets and, as shown in Fig. 2, a much smaller magnetoresistance for samples with the field aligned along the platelets. X-ray crystallography of some of the crystals indicates that the direction perpendicular to the platelet is approximately the c axis and the platelet plane is approximately the b-a plane. We have assumed throughout this work that the morphology of all the crystals is the same as described above. We have found no exceptions to this assumption in terms of higher magnetoresistance values along the platelet as compared to perpendicular to the platelet.

To better determine the degree of anisotropy, we have mounted several crystals in a probe which fits

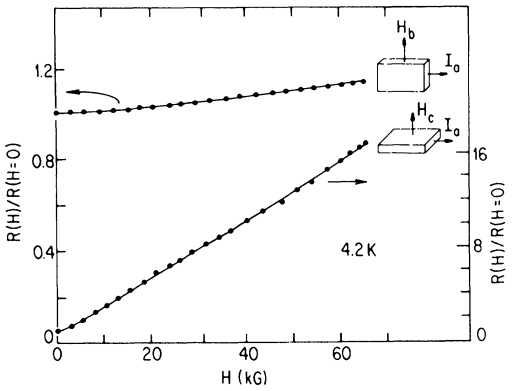

FIG. 2. Magnetic field dependence of the resistance at 4.2 K for fields aligned along the c and b axis.

in a Dewar with a rotatable NMR magnet. For measurements made at 5 kG and 4.2 K if we adjust the orientation of the magnet such that we obtain a minimum in the magnetoresistance ($\Delta\rho/\rho$), the value we observe is more than 3 orders of magnitude less than what we find when the magnet is rotated by 90°. Thus the transverse $\Delta\rho/\rho$ anisotropy is at least 10^3 at 4.2 K.

In Fig. 3 we show the Hall coefficient measured as a function of reciprocal temperature. One inset in Fig. 3 illustrates our experimental geometry.

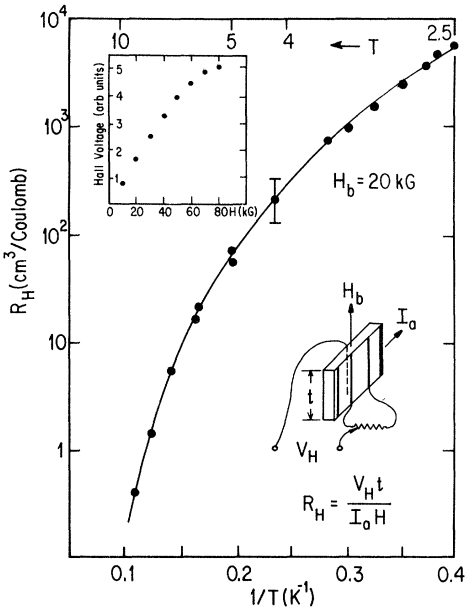

FIG. 3. Hall coefficient as a function of temperature. Top inset shows the magnetic field dependence of the Hall voltage at 4.2 K.

The Hall-effect measurement was done in the conventional five-probe configuration with the magnetic field aligned roughly parallel to the crystal b axis. This orientation was chosen to minimize the effects of the magnetoresistance which are large for $\vec{H}||c$. The Hall coefficient is large, positive, and approximately exponential in reciprocal temperature as expected for the semiconducting phase. If we assume a single carrier picture the Hall effect gives a carrier concentration of 9×10^{15} carriers/cm^3 at 4.2 K. The other inset in Fig. 3 shows the magnetic field dependence of the Hall voltage. Up to $\sim$50 kG the relationship is linear.

The Hall mobility which is the product of the Hall coefficient times the conductivity ($\mu_H = R_H\sigma_a$) is plotted in Fig. 4. In evaluating the Hall mobility we have used the published values for the electrical conductivity as a function of temperature down to 20 K (as found in Ref. 1) to normalize our data. The temperature dependence from 20 K down is from our own measurements with the above normalization. During cooldown to liquid nitrogen temperatures, virtually all of our samples showed the commonly observed resistance jumps (probably caused by microcracks) so that the conductivity ratio from room temperature to the resistivity minimum at $\sim$18 K was typically a factor of 10 rather than the factor of $\sim$100, found when samples are cooled without resistance jumps. The measured Hall coefficient is determined from the strength of the magnetic field and the actual current that flows through the sample:

$$R_h = \frac{V_H t}{I_a H}\ , \tag{1}$$

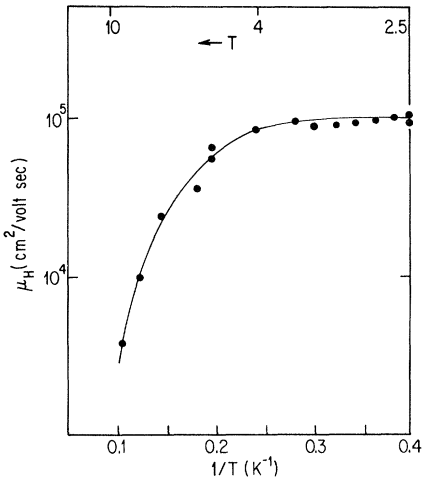

FIG. 4. Hall mobility as a function of temperature.

where V_H is the Hall voltage, t is the thickness, and I_a the current along the a axis (see inset on Fig. 3). From sample to sample the measured R_H is independent of the measured conductivity, being an intrinsic property of the material and not related to possible sample cracks. The conductivity, on the other hand, may be severly limited by the resistance jumps and it is for this reason that we have normalized our results at 20 K. Typically, all of the resistive jumps or cracks that we see occur above 60 K.

It is interesting to note in passing that the resistance jumps do *not* seem to effect the magnetoresistance. We see the same $\Delta\rho/\rho$ at 80 kG in samples with vastly different resistivity ratios and indeed obtain the same value as Ref. 15 in which no resistive jumps were present. This indicates that the increased resistance after the jumps should not be regarded as being in series with the sample. A more appropriate model is that the cracks reduce the effective cross section and that the conducting paths which remain are still intrinsic to the material.

We now turn our attention to the nonlinear contribution to the conductivity which is observed for electric fields of ~ 1 mV/cm but becomes comparable to the normal conductivity at ~ 10 mV/cm. In Fig. 5 we have plotted the longitudinal electrical conductivity as a function of electric field strength for a sample at 2 K. Measurements were done with voltage pulses on the time scale of 10 μsec and a duty cycle of $\sim 10^{-3}$. Care was taken to avoid sample heating by varying pulse width and repetition rate where needed. With an applied field of ~ 500 mV/cm the conductivity has increased by a factor of more than 5.

We have also made pulsed measurements on the same sample in the presence of a 50-kG magnetic field roughly aligned along the c axis (direction of largest magnetoresistance). The Ohmic part of the conductivity is reduced by a factor of 7. If the nonlinear conductivity were associated with a massive one-dimensional depinned collective mode we would expect virtually no effect from the applied magnetic field. The result would be two parallel curves displaced along the σ axis. What is actually observed is that the nonlinear conductivity is greatly suppressed by the applied magnetic field.

When the electric field-dependent conductivity is normalized by its $E=0$ value the curves for $H=0$ and $H=50$ kG fall on top of one another to a good approximation, Fig. 6. Thus the magnetic field has the same effect on the carriers responsible for the non-Ohmic conductivity as it has on the normal carriers. This would lead one to the conclusion that both sets of carriers have the same mobilities and anisotropies and are most probably the same carriers.

DISCUSSION

If we assume that the conductivity is intrinsic in the semiconducting regime, the number of electrons and holes is equal and the material is compensated. In the high-field regime the magnetoresistance will then follow[16,17]:

$$\frac{\Delta\rho}{\rho} = \frac{\mu_e \mu_h H^2}{c^2} \,. \tag{2}$$

In this limit the large value of the magnetoresistance that is seen perpendicular to the platelet can be understood in terms of a high mobility. Taking the electron and hole mobilities as approximately equal we find that the mobility must be greater

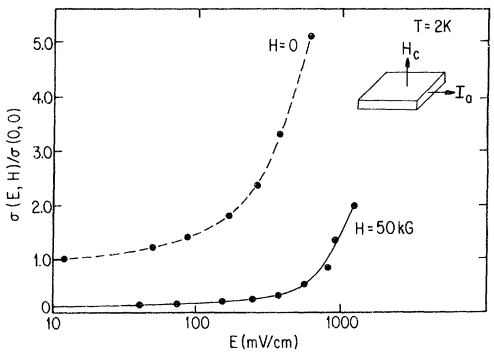

FIG. 5. Electric field dependence of the conductivity with and without application of a strong transverse magnetic field.

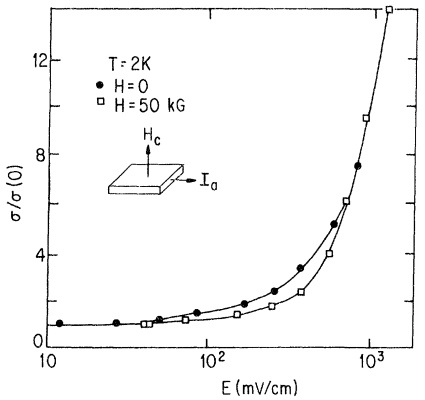

FIG. 6. Electric- and magnetic-field-dependent conductivity normalized at the low electric field value.

than 10^4 cm^2/V sec to explain the magnitude of the magnetoresistance (at 4.2 K). This is then a lower limit on the high mobility carrier if the mobilities are not equal. Under these assumptions the anisotropy in the magnetoresistance is explained by an anisotropic effective mass which is much heavier in the c direction than in the b direction.

In a two-carrier system the Hall mobility is actually a lower limit for the mobility of either the electrons or the holes, whichever is the dominant carrier. To illustrate this in Eq. (3) we have written the Hall coefficient in the high-field limit for the case of an equal number of electrons and holes,

$$R_H=\frac{1}{n\,|e|\,c}\,\frac{\mu_h-\mu_e}{\mu_h+\mu_e}\ . \tag{3}$$

In the case where one of the carriers has sufficiently higher mobility than the other, the measured Hall coefficient provides the number of carriers correctly. For cases where neither mobility is negligible the Hall coefficient overestimates the number of carriers. The Hall mobility in the analogous regime is

$$R_H\sigma=\mu_h-\mu_e\ . \tag{4}$$

Again if one carrier dominates, the mobility is correctly obtained, whereas in the general case the measured mobility is less than the larger of the two mobilities and is therefore a lower limit. Taking Eqs. (2) and (4) literally, we obtain $\mu_h=1.2\times10^5$ cm^2/V sec and $\mu_e=0.24\times10^5$ cm^2/V sec at 4.2 K.

A value of the Hall mobility of 10^5 cm^2/V sec is an extremely large number for any material (although not unheard of in pure inorganic semiconductors).[16] This is the largest value reported for an organic compound, but is comparable to what has been measured in hexamethylenetetraselenafulvalene-tetracyanoquinodimethane (HMTSF-TCNQ) at low temperature under pressure.[17]

Such large mobilities seem to violate our intuition as to the purity and perfection of these quasi-one-dimensional conductors which are supposedly very sensitive to disorder. Similar magnitudes are to be found only in the most carefully prepared low band-gap semiconductors such as InSb.[16]

One might expect that the low effective mass resulting from the small SDW gap is partially responsible for the high mobility. For a $\frac{1}{4}$ filled tight-binding band the effective mass which results from the opening of a gap at the Fermi surface is

$$\frac{1}{m_a^x}=\frac{Wa^2}{\sqrt{8}\hbar^2}\left[1\pm\frac{W}{\sqrt{2}E_g}\right] \tag{5}$$

where W is the bandwidth, E_g the energy gap, and a the lattice parameter. For $(TMTSF)_2PF_6$, $W/E_g\simeq200$ so that the mass of the electrons and holes after formation of a gap is $\frac{1}{200}$ of the band mass in the metallic state, calculated to be approximately a free-electron mass. A similar effective mass results in the nearly-free-electron model where the electron and hole masses are enhanced by $4E_F/E_g$ when a gap is opened.

Under the assumption of such a reduced mass the mean free path necessary to obtain a mobility of 10^5 cm^2/V sec at 4.2 is 300 Å. With a free-electron mass the mean free path would be 5000 Å. An effective mass of $m_e/200$ would put us in the extreme quantum limit at 4 K with a magnetic field of 250 g for isotropic bands. However, the band structure is highly anisotropic for $(TMTSF)_2PF_6$. The mobilities and cyclotron frequencies as relevant for magnetoresistance and Hall effect are then obtained from the effective cyclotron masses given by

$$m_{Hb}=\sqrt{m_a^x m_c^x}\ ,\quad m_{Hc}=\sqrt{m_a^x m_b^x}\ , \tag{6}$$

where m_{Hi} is the cyclotron mass when the magnetic field is aligned along the ith axis for either valence or conduction band. When anisotropy is to be included there is also a replacement of the scattering time by the average $\langle\tau^2\rangle/\langle\tau\rangle$.

The anisotropy observed in the conductivity by Jacobsen *et al.*[15] suggests that $m_b\approx300m_e$ so that $m_{Hc}\approx m_e$ and this value takes us out of the quantum limit at 4.2 K until we reach ~60 kG. Thus the large magnetoresistance may be explained in terms of conventional magnetotransport and an unusual band structure resulting from the opening of a small gap in a highly anisotropic system.

The small effective mass ($m_a^x\approx m_e/200$) is only appropriate at low temperatures where the thermally occupied states are at the bottom of the band and thus feel the strong curvature caused by the opening of the gap. This may explain the large temperature dependence of the mobility seen both in Hall mobility measurements and in the temperature dependence of the magnetoresistance.

We can understand the anisotropy of the magnetoresistance from Eqs. (2) and (6) which lead to

$$\frac{\Delta\rho_c}{\Delta\rho_b}\approx\frac{m_b^x}{m_c^x}\ . \tag{7}$$

From our measurements the ratio of the magne-

toresistance is 100 to 1000, which leads to values of m_b^x/m_c^x which are comparable to those observed in the conductivity anisotropy.[15] We expect that the band picture is appropriate in the $\vec{a}$-$\vec{b}$ plane, whereas the transfer integral is too small along $\vec{c}$ for coherent motion. We therefore conclude that the band structure is best described as two dimensional.

What is more perplexing is that similar magnitudes for the magnetoresistance have been reported for $(TMTSF)_2PF_6$ under pressure where the metallic state is stabilized and the mass is not decreased by a gap.[12] In the metallic state at ambient pressure ($T > T_{MI}$) Jacobsen *et al.* have attributed the sizable magnetoresistance to anisotropic scattering on an almost planar Fermi surface. A similar explanation may pertain to the metallic state under pressure.

The effect of the magnetic field on the nonlinear conductivity implies either that the additional current is deflected by the Lorentz force or that the additional current is suppressed. The former explanation is most easily understood if the additional carriers are the same as those thermally generated and hence having the same mobility. Such an effect might arise from hot electrons exciting additional carriers across the gap. A moving spin-density wave would only show a similar magnetoresistance if the mobility were the same as the free carriers.

A suppression of SDW motion might arise if the pinning force or mobility of the spin-density wave were affected by the magnetic field. Without a magnetic field the spin-density wave has a uniform charge density. Application of magnetic field increases one spin component and thus results in a small charge-density wave which may pin its further motion. We would then expect a shift in the electric field necessary to move the SDW but with a similar amplitude to the additional conductivity. Although this cannot be ruled out, the agreement between the normalized nonlinear effects with and without a magnetic field tend to disagree with this picture. Attempts to measure the Hall effect in high electric fields have not yet been successful.

The range of nonlinearities we have investigated is not as extensive as in the published literature. For values of the non-Ohmic conductivity which approach or exceed those found in the metallic state, an explanation in terms of hot-electron effects seems unreasonable in that the number of excited carriers would be enough to destroy the gap and therefore the high mobility. Clearly, more experiments and theory are needed to understand both the nonlinear magnetotransport and the effect of a transverse field on a moving SDW.

CONCLUSION

We have shown that $(TMTSF)_2PF_6$ has a large Hall effect and large anisotropic transverse magnetoresistance in its low-temperature semiconducting state. The band structure is best described as quasi-two-dimensional and the mobility of the carriers is extremely high ($\sim 10^5$ cm^2/V sec at 4.2 K). The absence of a shift in transition temperature in a field of 80 kG is in agreement with the low-temperature state being a spin-density wave. Finally, the nonlinear conductivity is strongly suppressed by the magnetic field in contrast to the behavior of depinned CDW's in $NbSe_3$.

We would like to acknowledge very useful discussions with G. Grüner and T. Holstein. Research at UCLA was supported by Grant No. NSF DMR-79-08560, and an A. P. Sloan Foundation Fellowship. Research at IBM was partially supported by the ONR.

---

*Permanent address: CRTBT, CNRS, Grenoble, France.

[1]K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen, and N. Thorup, Solid State Commun. 33, 1119 (1980).

[2]J. C. Scott, H. J. Pedersen, and K. Bechgaard, Phys. Rev. Lett. 45, 2125 (1980).

[3]A. Andrieux, D. Jérome, and K. Bechgaard, J. Phys. Lett. 42, L87 (1981).

[4]K. Mortensen, Y. Tomkiewicz, T. D. Schultz, and K. Bechgaard, Phys. Rev. Lett. 46, 1234 (1981).

[5]M. W. Walsh, Jr., F. Wudl, G. A. Thomas, D. Nalwajek, T. J. Hauser, P. A. Lee, and T. Poehler, Phys. Rev. Lett. 45, 829 (1980).

[6]P. M. Chaikin, G. Grüner, E. M. Engler, and R. L. Greene, Phys. Rev. Lett. 45, 1874 (1980).

[7]D. Jérome, A. Mazaud, M. Ribault, and K. Bechgaard, J. Phys. (Paris) Lett. 41, L95 (1980).

[8]K. Andres, F. Wudl, D. B. McWhan, G. A. Thomas, D. Nalewajek, and A. L. Stevens, Phys. Rev. Lett. 45, 1449 (1980).

[9]R. L. Greene and E. M. Engler, Phys. Rev. Lett. 45,

1587 (1980).
[10]A. Andrieux, C. Duroure, D. Jérome, and K. Bechgaard, J. Phys. Lett. 40, L381 (1979); A. Andrieux, P. M. Chaikin, C. Duroure, D. Jérome, C. Weyl, K. Bechgaard, and J. R. Andersen, J. Phys. (Paris) 40, 1199 (1979).
[11]S. S. P. Parkin, M. Ribault, D. Jérome, and K. Bechgaard, unpublished.
[12]J. F. Kwak, J. E. Schirber, R. L. Greene, and E. M. Engler, Phys. Rev. Lett. 46, 1296 (1981).
[13]C. S. Jacobsen, D. B. Tanner, and K. Bechgaard, Phys. Rev. Lett. 46, 1142 (1981).
[14]G. X. Tessema and N. P. Ong, Bull. Am. Phys. Soc. 26, 449 (1981) and unpublished; K. Kawabata, M. Ido, T. Sambongi, unpublished.
[15]C. S. Jacobsen, K. Mortensen, M. Weger, and K. Bechgaard, unpublished.
[16]A. C. Beer, *Galvanomagnetic Effects in Semiconductors* (Academic, New York, 1963).
[17]J. R. Cooper, M. Weger, G. Delplanque, D. Jérome, and K. Bechgaard, J. Phys. Lett. 37, L349 (1976).