PHYSICAL REVIEW B VOLUME 50, NUMBER 18 1 NOVEMBER 1994-II

Effect of impurities on the low-temperature nonlinear spin-density-wave transport

Y. M. Kim, R. Gaál,* B. Alavi, and G. Grüner
Department of Physics, University of California Los Angeles, Los Angeles, California 90024
(Received 2 May 1994)

We have measured the low-temperature nonlinear conductivity in the spin-density-wave state of $(TMTSF)_2X$ alloys. We find that an expression of $\sigma(E)=\sigma_{0E}\exp(-E_0/E)$, suggestive of a tunneling process, describes the nonlinear conduction with the characteristic field E_0 increasing with increasing disorder while σ_{0E} is independent of the impurity concentration within experimental error. We also discuss the implications of our findings.

The nonlinear and frequency-dependent transport, associated with the dynamics of the spin-density-wave (SDW) ground state has recently been explored in detail in several members of the so-called Bechgaard salts,[1] based on the molecule tetramethyltetraselenafulvalene (TMTSF). The salts $(TMTSF)_2X$ where X stands for PF_6 and similar counter ions undergo phase transitions at $T=12$ K to SDW state, as confirmed by a variety of magnetic studies.[2] At temperatures below the phase transition, yet above approximately 1 K, all the signatures of the conventional collective mode transport, which were well studied in the case of materials with a charge density wave (CDW) ground state,[3] have been also found in the case of spin-density-wave state. A pinned mode resonance has been observed at frequencies well below the single particle gap; at low frequencies a broad tail of the frequency-dependent conductivity $\sigma(\omega)$ is found due to the dynamics of the internal deformations of the collective mode.[4] When dc electric fields are applied, there is a well defined threshold field E_T beyond which nonlinear conduction starts to occur.[5,6] Current oscillations have been observed for $E>E_T$,[7] and the internal deformations also lead to long-time relaxation effects.[8] A study of alloys also indicates that the threshold field for the onset of nonlinear conduction, E_T increases as a square of the impurity concentration, suggesting that the so-called weak impurity pinning limit applies.[9] The nonlinear conduction as described above progressively freezes out with decreasing temperature,[6] again as found in the case for materials with a charge-density-wave ground state.[10]

We have found recently that at low temperatures a fundamentally different nonlinear transport occurs.[6] This nonlinear conduction is independent of the temperature and can be described over a broad range of applied electric fields by the expression,

$$\sigma(E)=\sigma_{0E}\exp(-E_0/E). \quad (1)$$

This expression, together with the temperature independence of the transport characteristics is indicative of a tunneling process. Single particle Zener tunneling,[11] for example, would have these signatures. However, the characteristic field, E_0, is orders of magnitude smaller than the estimated value which would correspond to Zener tunneling across the single particle gap,[6] ruling out simple semiconducting tunneling. Subsequent studies under pressure[12] and magnetic field[12,13] indicated that E_0 is proportional to the square of the single particle gap, while σ_{0E} is independent of the applied pressure. The external dc magnetic field, in contrast, leaves E_0 unchanged but leads to changes in σ_{0E}. The mechanism which leads to these features is unexplained at present.

In this Rapid Communication we report on our experiments conducted in $(TMTSF)_2X$ alloys where X stands for various combinations of the counterions PF_6, AsF_6, and SbF_6. We have used the high-temperature threshold field E_T as a measure of the impurity concentration and have used the findings of Traetteberg *et al.*[9] on the concentration dependence of the threshold field in order to characterize the impurity content of our specimens. With such a procedure of evaluating the concentration we find that E_0 increases with increasing impurity concentration, approximately linearly. This clearly rules out any mechanism which would depend only on intrinsic parameters of the spin-density-wave (SDW) state (such as the single particle gap).

Single crystals of $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ as well as $(TMTSF)_2(0.5)PF_6(0.5)AsF_6$ were grown at UCLA by the electrochemical process with corresponding ratio of starting materials. The alloys of $(TMTSF)_2(0.85)AsF_6(0.15)SbF_6$ and $(TMTSF)_2(0.75)AsF_6(0.25)SbF_6$ were grown at Orsay by Dr. C. Lenoir. The four electrical contacts were prepared by evaporating Ag or Au on the surface including both ends to ensure the homogeneous current injection. The electrical leads were glued with silver paint or mechanically pressed on the metallic pads by gold wires. To prevent any possible extrinsic damages in the samples a slow cooling rate of 0.2 K/min was employed. At 4.2 K the differential resistance was measured with dc biased ac current at low fields, and the current-voltage characteristics were also recorded by dc fields. At high electric fields a pulse technique was employed. The pulse duration was kept shorter than the time required to heat the lattice beyond which a monotonic current increase and voltage decrease could be observed. The results of three measurement methods agree in their overlapping electric field ranges. At pumped ^{3}He temperatures, the large resistivity prevents the differential resistance measurement due to the large capacitance arising mainly from the probe lines, and we used a low pass filtered four-probe dc method to improve the signal-to-noise ratio. The intermediate field range was covered by the four-probe pulse method until the rising time of differential voltage amplifiers set a

0163-1829/94/50(18)/13867(4)/$06.00 © 1994 The American Physical Society

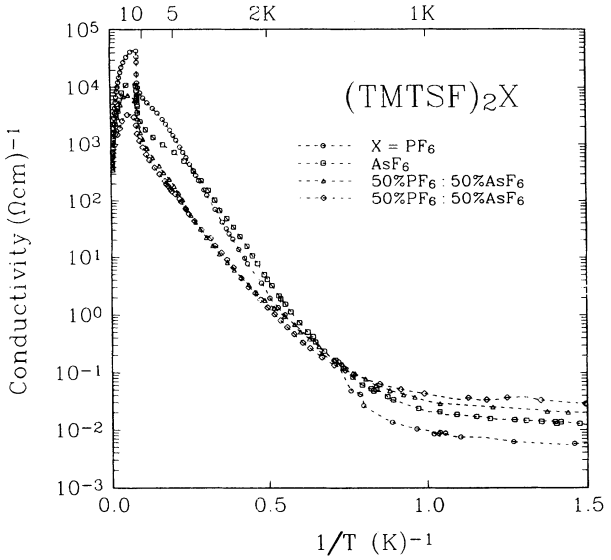

FIG. 1. The temperature dependence of the conductivity for pure $(TMTSF)_2PF_6$, $(TMTSF)_2AsF_6$, and alloys of $(TMTSF)_2(0.5)PF_6(0.5)AsF_6$. For all results, the conductivity is normalized to the conductivity of pure PF_6 measured at room temperature.

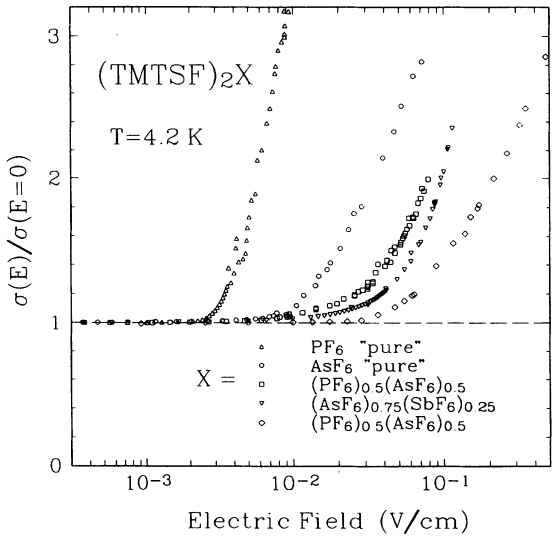

FIG. 2. The electric field dependence of cordial conductivity at 4.2 K. Each curve is normalized to the Ohmic conductivity at the $E \rightarrow 0$ limit.

lower limit for the pulse width. To achieve a faster resolution at higher fields, we eliminated the voltage amplifier by employing the two-probe pulse method with a fast Tektronix AM 503 current amplifier. Again, we obtained the same results utilizing the different techniques.

In Fig. 1 we display the low field, Ohmic conductivity of the materials we have investigated. Although we have found slight differences in the room temperature conductivity values of the various specimens, we believe that these are due to uncertainties in the evaluation of the sample dimensions, and at these high temperatures the resistivity is dominated by phonon scattering with impurity, thus, scattering plays a minor role. Assuming that Matthiessen's rule holds and the relaxation rate $\Gamma = \Gamma_{ph}(T) + \Gamma_{imp}$ with Γ_{imp} independent of the temperature, the temperature dependence of the resistivity shown in Fig. 1 clearly demonstrates that $\Gamma_{imp} \ll \Gamma_{ph}$ at room temperature in the alloys. Therefore we normalized all conductivity values to the common room temperature value of 350 $(\Omega\ \mathrm{cm})^{-1}$. While the nominally pure specimens have a larger residual resistivity ratio, RRR (defined as the ratio of the resistivity at 300 K and at 20 K, above the transition) this ratio decreases with increased alloying.

Below the transition temperatures the pure specimens have a well defined single particle gap and $\sigma(T)$ has an exponential temperature dependence,

$$\sigma(T) = \sigma_{0T} \exp(-\Delta/k_B T). \quad (2)$$

Alloying leads to smearing of the gap and to an increased low-temperature conductivity, due to impurity conduction processes. The transition also progressively broadens with increasing disorder; this has been found also earlier by others.[9]

The I-V characteristics were studied at 4.2 K, and the cordial conductivity, $\sigma = j/E$, where j and E are current density and electric field on samples, normalized to the low field Ohmic value is displayed in Fig. 2. In all samples we observe clear nonlinear conduction, and we have defined the threshold electric field, E_T, as the field where the conductivity exceeds by 5% the Ohmic value. For alloys with larger E_T, the nonlinear current rises less sharply than in the pure compounds indicating possible existence of the slight distribution of pinning forces within the samples. We note that the E_T value of the nominally pure AsF_6 salt is approximately 6 mV/cm, somewhat larger then E_T found in our nominally pure salts of $(TMTSF)_2PF_6$ and the threshold field reported in the AsF_6 salt.[9] This is consistent with the temperature dependence of conductivity, which shows a smaller residual resistivity ratio in the metallic state and larger impurity conductivity at low temperature in our $(TMTSF)_2AsF_6$ specimen.

The low-temperature nonlinear behavior found in the alloys and in the nominally pure specimens are displayed in Fig. 3. The full lines are fits to Eq. (1), and these give the parameters σ_{0E} and E_0. It is evident from the figure that, except at low electric fields, a tunneling expression adequately describes the nonlinear conduction process. We argued elsewhere[13] that the behavior at low fields is due to electric field induced transitions between impurity states. This fact agrees qualitatively with our recent observation on conduction anisotropy.[14] At the high electric field region, where the conductivity behavior is given by Eq. (1), we observe two important tendencies. First the high-field limit of the conductivity (σ_{0E}), is, within our accuracy, independent of the impurity concentration and comparable to the normal state conductivity. This has been confirmed on a limited number of specimens where cooling did not result in cracking and consequently to sudden artificial jumps in resistivity. Second the characteristic field (E_0) increases with increasing

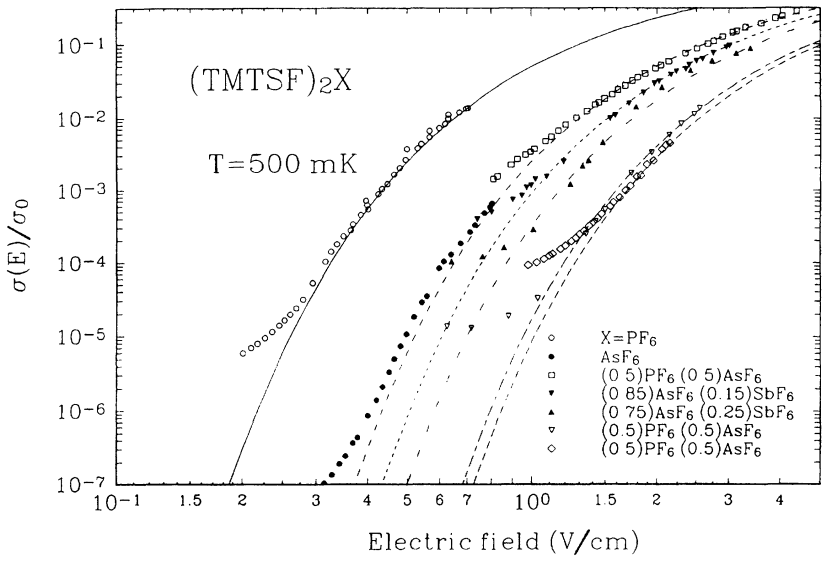

FIG. 3. The cordial conductivity at 500 mK measured on nominally pure specimens and on alloys. The conductivity is normalized to the $E\rightarrow\infty$ limit, σ_{0E}. The lines are fits to Eq. (1). The E_0 values obtained from the fit are displayed in Fig. 4.

disorder. The variation, however, is weaker than the increase of the threshold field (E_T) observed at high temperatures.

While chemical analysis would give the concentration of the constituents for the alloys, this procedure cannot be used to evaluate the residual impurity concentration in the specimens. Consequently, the concentration, c, has to be evaluated using other methods. With various signatures of impurity effects various parameters could, in principle, be used to evaluate the impurity concentration. Attempting to define c through the broadening of the transition was not successful due to scattering of the data. The low-temperature low field conduction, which increases with increasing disorder (see Fig. 1)—as expected for conduction involving localized impurity states—could also be analyzed in order to extract the overall strength of disorder in the specimens. In order to do so, the detailed form of the temperature dependence would be needed, as this temperature dependence (and also the impurity concentration dependence) depends on the dimension of the hopping conduction process. Our experiments conducted over a limited temperature domain do not allow such analysis.

We have therefore used the threshold field E_T as the measure of the impurity concentration. Earlier studies of the Orsay group[9] gave evidence that E_T is proportional to a square of the impurity concentration, as expected for weak impurity pinning. Because of some gradual onset of the nonlinearity, as shown in Fig. 2, definition of E_T is somewhat arbitrary. We have therefore used two measures of E_T, one where the conductivity exceeds the low field conductivity by 5% called E_{T1}, and one where the nonlinear conductivity is equal to the Ohmic part (i.e., the conductivity exceeds by 100% of the Ohmic conductivity) called E_{T2}. This latter electric field is significantly larger than E_{T1} as evident from Fig. 2.

In Fig. 4 we have plotted E_0 versus E_T where both parameters are evaluated as discussed before. The full line is the relation of

$$E_0=\gamma E_{T1}^{1/2}, \tag{3}$$

with a constant $\gamma\approx 60$ (V/cm)$^{1/2}$. In the figure the relation between E_0 and E_{T2} is also shown, and this relation can approximately be described by $E_0 \propto E_{T2}^{1/3}$ (dashed line). As mentioned before the threshold field, E_T was found to be proportional to the square of the impurity concentration.[9] If this observation is correct, then the characteristic field E_0 either increases linearly with the impurity concentration, $E_0 \propto c$, or has a somewhat weaker than linear concentration dependence.

Next we discuss the implications of our findings. The magnitude of the high field conductivity σ_{0E} and the observed magnetoresistance[13] are similar to what is observed for the conductivity created by carriers thermally excited over the single particle gap. These carriers lead to a conductivity given by Eq. (2) and we find that $\sigma_{0E}\approx\sigma_{0T}$ within our experimental accuracy. Also, σ_{0T} and σ_{0E} have the same

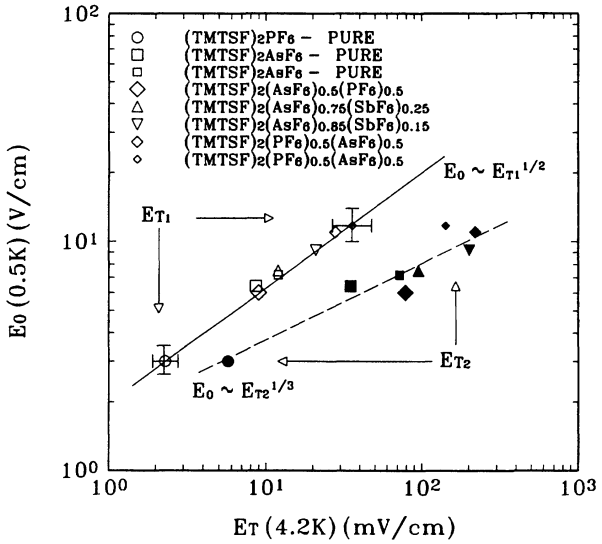

FIG. 4. E_0 versus E_{T1} and E_{T2} for various nominally pure compounds and for alloys. The open symbols refer to E_{T1} and the solid symbols to E_{T2}. The values for E_{T1} and E_{T2} are determined from Fig. 2 as described in the text, and the E_0 values are obtained using the fits to Eq. (1) in Fig. 3. The full line is a fit to Eq. (3), and the dashed line is corresponding to a power law of 1/3.

magnetoresistance within the experimental uncertainty, and this indicates that single particle carriers are created by the tunneling process. As mentioned before, this would happen for Zener tunneling. However, for a single particle gap $\Delta = 22$ K the Zener expression,[11]

$$E_0 = (\pi^2/4)\ \Delta^2/e\varepsilon_F a\ , \qquad (4)$$

would lead to $E_0 = 600$ V/cm with $\varepsilon_F = 0.5$ eV and $a = 3$ Å, significantly larger than the values displayed on Fig. 3. Our experimental result on the impurity dependence of E_0 also rules out conventional Zener tunneling directly. It has been suggested that a tunneling involving solitons, which are created by commensurability effects, might be responsible for the nonlinearity.[15] However, such effect should also not depend on the amount of disorder. Tunneling from impurity states within the single particle gap to extended states is also a possibility.[13] However, if tunneling occurs from independent impurity states, then increasing disorder would lead, to first order, to the increased number of impurity states without modifying the position of the impurity levels. As E_0 is related to the energy of the relevant states, this would lead to an increased tunneling current and unchanged E_0, in contrary to what has been observed. It has been suggested recently that tunneling through the modification of the amplitude of spin density wave may occur.[16] The application of electric field would lead to the collapse of the SDW amplitude within a region, the dimensions of which may be determined by parameters such as the overall impurity potential. The process would also lead to single particle states within the collapsed region in tentative agreement with the experimental findings.

We thank C. Lenoir for preparing the specimens used in this study. Useful discussions with D. Jérome, G. Mihály, and O. Traetteberg are gratefully acknowledged. This research was supported by the National Science Foundation Grant No. DMR 92-18745 and US–Hungary International Grant No. 90-2946.

---

*Permanent address: Central Research Institute for Physics, Budapest, Hungary.

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

[2] D. Jérome and H. Schulz, Adv. Phys. **31**, 299 (1982), and references therein.

[3] G. Grüner and A. Zettl, Phys. Rep. **119**, 117 (1985).

[4] S. Donovan, Y. Kim, L. DeGiorgi, and G. Grüner, J. Phys. I (France) **3**, 1493 (1993).

[5] S. Tomić, J. R. Cooper, D. Jérome, and K. Bechgaard, Phys. Rev. Lett. **62**, 462 (1989); T. Sambogi, K. Nomura, T. Shimizu, K. Ichimura, N. Kinoshita, M. Tokomoto, and H. Anzai, Solid State Commun. **72**, 817 (1989); W. Kang, S. Tomic, J. R. Cooper, and D. Jérome, Phys. Rev. B **41**, 4862 (1990).

[6] G. Mihály, Y. Kim, and G. Grüner, Phys. Rev. Lett. **67**, 2713 (1991).

[7] K. Nomura, T. Shimizu, K. Ichimura, T. Sambongi, M. Tokumoto, H. Anzai, and N. Kinoshita, Solid State Commun. **72**, 1123 (1989); G. Kriza, G. Quirion, O. Traetteberg, W. Kang, and D. Jérome, Phys. Rev. Lett. **66**, 1922 (1991).

[8] G. Mihály, Y. Kim, and G. Grüner, Phys. Rev. Lett. **66**, 2806 (1991).

[9] O. Traetteberg, C. Lenoir, Y.-S. Huang, G. Kriza, G. Quirion, P. Auban-Senzier, W. Kang, P. Batail, and D. Jérome, Synth. Met. **56**, 2785 (1993); O. Traetteberg, G. Kriza, C. Lenoir, Y.-S. Haung, P. Batail, and D. Jérome, Phys. Rev. B **49**, 409 (1994).

[10] R. M. Fleming, Phys. Rev. B **22**, 5606 (1980); G. Kriza and G. Mihály, Phys. Rev. Lett. **23**, 2529 (1986).

[11] J. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, Cambridge, England, 1972).

[12] O. Traetteberg, G. Kriza, and G. Mihály, Phys. Rev. B **45**, 8795 (1992).

[13] Y. M. Kim, H. Jiang, G. Mihály, and G. Grüner (unpublished).

[14] At $T = 0.5$ K, the field dependent conductivity between surface (voltage) contacts and between cross section (current) contacts as well as four-probe conductivity shows that conduction anisotropy at low fields is more than one order of magnitude weaker than at the high-field nonlinear range. The four-probe measurement in all its field range coincides with the measurement between current contacts. At low fields all measurements produce the identical result. At the high-field nonlinear range, however, the high-field limit conductivity (σ_{0E}) between surface contacts is scaled down by more than one order of magnitude compared to those of two others while the characteristic field (E_0) does not vary among three different contact methods.

[15] W. Wonneberger, Solid State Commun. **80**, 953 (1991).

[16] B. Ivlov (private communication).