Low-frequency dielectric response of the charge-density wave in (TaSe₄)₂I

R. J. Cava, P. Littlewood, R. M. Fleming, R. G. Dunn, and E. A. Rietman

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 16 July 1985)

We have found the charge-density wave (CDW) in (TaSe₄)₂I to display a low-frequency dielectric relaxation characterized by a distribution of relaxation times. The mean relaxation times vary between approximately 10^{-4} and 10^{-8} sec in the temperature range of 90 to 180 K, and display an Arrhenius temperature dependence with the same activation energy (1436 K) as the normal resistivity. This is the only material thus far studied where such a straightforward connection between CDW relaxation and the band gap has been observed.

INTRODUCTION

(TaSe₄)₂I undergoes a metal-semiconductor phase transition at 263 K due to the development of a charge-density wave (CDW).[1-3] It is a member of a small class of anisotropic materials with CDW's that can be depinned from the underlying lattice with the application of small electric fields.[4] These compounds display enhanced conductivities at frequencies on the order of megahertz. We have recently shown that this enhanced conductivity is best described as being due to the dielectric relaxation of the CDW in response to the small ac driving field.[5] The relaxation is described to an excellent approximation by an empirical modification of the expression for a Debye relaxation that allows for the existence of an asymmetric distribution of relaxation times associated with a single type of relaxation process. The complex dielectric constant $[\epsilon(\omega) = i\sigma(\omega)/\omega]$ is given by[6]

$$\epsilon(\omega) = \epsilon_{HF} + (\epsilon_0 - \epsilon_{HF})/[1 + (i\omega\tau_0)^{1-\alpha}]^\beta ,\qquad (1)$$

where τ_0 is the mean relaxation time, ϵ_0 and ϵ_{HF} are frequency-independent dielectric constants for $\omega \ll 1/\tau_0$ and $\omega \gg 1/\tau_0$, respectively (static and high-frequency dielectric constants), and α and β describe the width and skewness of the distribution of times. For a nondistributed Debye process, $\alpha = 0$ and $\beta = 1$.

With use of expression (1) the dielectric response at low frequencies has been analyzed in the CDW bearing materials pure[5] and doped[7] $K_{0.3}MoO_3$, NbSe₃,[5] and TaS₃.[8,9] Although Eq. (1) fits the data well for all compounds, the detailed temperature dependences of the static dielectric constants, mean relaxation times, and shapes of the distribution are considerably different for the different materials. In pure $K_{0.3}MoO_3$ both ϵ_0 and τ_0 increase in a thermally activated manner with decreasing temperature, each with a different activation energy. These energies are on the order of but not equal to the activation energy for the resistivity. At a fixed temperature, ϵ_0 decreases dramatically and τ_0 increases dramatically for the addition of both weakly and strongly pinning impurities to $K_{0.3}MoO_3$. The width of the distribution of relaxation times also increases. The temperature dependences for the doped bronzes are more complex than in the pure case, with increasing and/or temperature-independent ϵ_0's and

thermally activated increasing τ_0's with decreasing temperature. Again, neither parameter shows the same temperature dependence as the resistivity. The behavior for orthorhombic TaS₃ is significantly different, showing first an exponential increase with decreasing temperature in ϵ_0 at high temperature and then a dramatic decrease beginning at approximately 100 K, finally indicating the complete disappearance of the low-frequency relaxation at approximately 65 K.[8,9] The disappearance of the low-frequency relaxation at low temperatures in TaS₃ coincides with the disappearance of thermal hysteresis effects in such properties as resistivity and Seebeck coefficient.[8] In this paper we report the low-frequency dielectric response of the CDW in (TaSe₄)₂I between 90 and 180 K, and find it to display still another type of behavior, with the mean relaxation time of the CDW scaling with temperature exactly as does the normal resistivity. Both the dielectric constant ϵ_0 and the threshold field E_T show a much weaker temperature dependence.

EXPERIMENTAL

Single crystals of (TaSe₄)₂I were grown from stoichiometric mixtures of the elements in sealed, evacuated quartz tubes by vapor transport for two weeks in a 600–550 °C thermal gradient. Crystals for dielectric studies were mounted on sapphire substrates. Current flow was along the crystallographic c axis in a two-probe measurement configuration. Ultrasonic indium contacts were applied to the samples. Analysis of the data in the complex impedance plane[5] showed these contacts to have negligible contact resistance and capacitance at all temperatures studied. Real and imaginary parts of the conductivity were measured between 5 Hz and 7 MHz at 20 points per frequency decade by a Hewlett-Packard HP4192A impedance analyzer. We surveyed the dielectric response for several samples at temperatures near 100 K and found them all to have the same general behavior. We selected for more detailed study the crystal with the lowest threshold field (E_T) for nonlinear conductivity, and the lowest characteristic relaxation frequencies. That sample was basically tabular in shape, of dimension $0.51 \times 0.51 \times 2.66$ mm. The dielectric response was studied between 90 and 180 K at 5-K intervals by mounting

the sapphire substrate on the cold finger of a closed-cycle helium refrigerator. Measurements were made on heating. The rms signal amplitude employed was less than 6% of E_T at all temperatures. We tested the response for ac signals up to twice that level and found it to be independent of signal amplitude in that range.

RESULTS

The dielectric response of the CDW in $(TaSe_4)_2I$ between 90 and 180 K is fit very well by expression (1), indicating as in other materials that the relaxation of the CDW can be described as a single process with a distribution of characteristic times. The data were fit from a minimum frequency where $\epsilon'(\omega)$ and $\epsilon''(\omega)$ were both significant, to a frequency of 7 MHz, where the stray admittances from the measurement circuit were less than 3% of the measured admittances; this involved between 120 and 150 observed $\epsilon(\omega)$ values, dependent on the temperature. Fits were obtained by minimization of the average agreement index, defined in Table I, by variation of ϵ_0, ϵ_{HF}, α, β, and τ_0. At high temperatures, ϵ_{HF} was excluded from the fits as it was not significant. Estimates in the errors of the parameters are ±0.02 for α and β, $\pm3\%$ for ϵ_0 and τ_0, and $\pm5\%$ for ϵ_{HF}. Values for the parameters are presented in Table I. The agreements, which are between 1% and 2%, except at low temperatures where there is scatter in the low-frequency data, indicate the high quality of the fits. The data for three temperatures are presented in Fig. 1, along with the calculated values from Eq. (1) and Table I.

There are both similarities and differences in the characteristics of CDW relaxation in $(TaSe_4)_2I$ and the
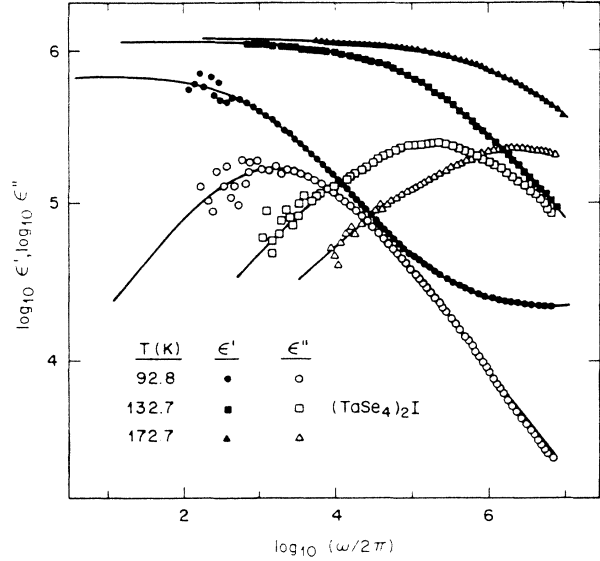

FIG. 1. Frequency dependence of the real (solid symbols) and imaginary (open symbols) parts of the dielectric constant for $(TaSe_4)_2I$ at three representative temperatures. Solid lines from fits of Eq. (1) to the data and parameters in Table I.

materials previously studied. Most striking is the relatively low value of the static dielectric constant ϵ_0, which is on the order of 10^6 in the temperature range studied. this is significantly lower than that observed for $NbSe_3$, TaS_3, and pure $K_{0.3}MoO_3$, but is in the order of those we have observed in the doped $K_{0.3}MoO_3$ bronzes. Further similarity to the CDW relaxation in the doped bronzes can be found in the relatively low value of ϵ_{HF}, and the broad,

TABLE I. Parameters describing the low-frequency dielectric response of the charge-density wave in $(TaSe_4)_2I$, where $\epsilon(\omega)=\epsilon_{HF} + (\epsilon_0-\epsilon_{HF})/[1 + (i\omega\tau_0)^{1-\alpha}]^\beta$.

Temperature (K)	ϵ_0	ϵ_{HF}	α	β	τ_0 (sec)	$\omega_0/2\pi$ (Hz)	Agreement R (%)[a]
177.7	1.13×10^6		0.54	1.09	3.60×10^{-8}	4.42×10^6	1.3
172.7	1.15×10^6		0.54	1.09	5.10×10^{-8}	3.12×10^6	1.4
167.6	1.16×10^6		0.54	1.09	7.00×10^{-8}	2.27×10^6	1.3
162.6	1.18×10^6		0.54	1.09	9.50×10^{-8}	1.68×10^6	1.7
157.7	1.17×10^6		0.53	1.09	1.25×10^{-7}	1.27×10^6	1.7
152.7	1.17×10^6		0.53	1.09	1.79×10^{-7}	8.89×10^5	1.9
147.7	1.16×10^6		0.51	1.09	2.65×10^{-7}	6.01×10^5	2.0
142.8	1.15×10^6		0.51	1.09	3.70×10^{-7}	4.30×10^5	2.0
137.8	1.13×10^6		0.49	1.09	5.10×10^{-7}	3.12×10^5	1.8
132.7	1.10×10^6		0.47	1.09	7.70×10^{-7}	2.07×10^5	1.4
127.6	1.05×10^6	1.6×10^4	0.45	1.09	1.16×10^{-6}	1.37×10^5	1.7
122.6	1.01×10^6	1.6×10^4	0.43	1.09	1.80×10^{-6}	8.84×10^4	1.6
117.7	9.68×10^5	1.6×10^4	0.43	1.09	2.82×10^{-6}	5.64×10^4	2.0
112.7	9.34×10^5	1.6×10^4	0.43	1.09	5.10×10^{-6}	3.12×10^4	1.8
107.8	8.90×10^5	1.9×10^4	0.41	1.09	9.70×10^{-6}	1.64×10^4	1.8
102.8	7.90×10^5	1.9×10^4	0.39	1.06	1.74×10^{-4}	9.15×10^3	1.8
97.7	7.26×10^5	2.0×10^4	0.39	1.06	3.65×10^{-5}	4.36×10^3	2.0
92.8	6.40×10^5	2.0×10^4	0.39	1.06	8.20×10^{-5}	1.94×10^3	2.8
87.8	5.56×10^5	2.0×10^4	0.39	1.06	1.60×10^{-4}	9.95×10^2	4.2

[a]$R = \sum_\omega [|\epsilon'_{obs}(\omega)-\epsilon'_{calc}(\omega)| + |\epsilon''_{obs}(\omega)-\epsilon''_{calc}(\omega)|]/\sum_\omega[\epsilon'_{obs}(\omega) + \epsilon''_{obs}(\omega)]$.

only weakly-temperature-dependent distribution of relaxation times (α), which is also seen in TaS_3. In $(TaSe_4)_2I$ the distribution seems to get slightly sharper with decreasing temperature, with the skewness (β) being relatively temperature independent. Surprising are the very long mean relaxation times of the CDW. At 93 K, for instance, the relaxation time for the CDW in this sample, 8.2×10^{-5} sec, is almost 2 orders of magnitude longer than that we have observed in the pure bronze at 91 K $(4.5 \times 10^{-7}$ sec). $(TaSe_4)_2I$ is unusual among the compounds so far studied, as it has a low static dielectric constant and long CDW relaxation times: For the doped bronzes with low ϵ_0's the relaxation times are many orders of magnitude shorter than those found here for $(TaSe_4)_2I$.

The temperature dependencies of the CDW relaxation parameters in $(TaSe_4)_2I$, as found in Table I, are presented in Figs. 2 and 3. The static constant ϵ_0 changes by approximately a factor of 2 between 90 and 180 K, increasing with increasing temperature, and reaching a broad maximum at about 150 K. This is in general agreement with the 1-MHz ϵ' data reported for $(TaSe_4)_2I$ (Ref. 10) although our observed ϵ_0 are smaller. The value of ϵ' at 1 MHz would be at first above ω_0 and then below ω_0 for our sample in the temperature range of the measurement in Ref. 10. The temperature dependence of ϵ_0 in $(TaSe_4)_2I$ is significantly different from that in $K_{0.3}MoO_3$, which decreases with increasing temperature, and although it is similar to that in orthorhombic TaS_3, it does not show

such a dramatic disappearance of the relaxation at low temperatures. The low-frequency relaxation in $(TaSe_4)_2I$ may, of course, disappear at temperatures lower than those of this measurement. We have also measured the temperature dependence of the threshold field of this sample[11] and found it to decrease with increasing temperature, by a factor of about 30—40 % over the temperature range of this experiment. The threshold fields, which are between approximately 0.7 and 1.0 V/cm, are relatively low compared to those found in other samples of $(TaSe_4)_2I$.[10,12] The temperature dependencies of ϵ_0 and E_T are presented in Fig. 2. Other samples we studied with higher threshold fields displayed higher ω_0's as has also been observed for the $K_{0.3}MoO_3$ bronzes.[7]

Figure 3 presents the temperature dependence of the mean CDW relaxation time τ_0. In the temperature range 90—170 K the relaxation times fit an excellent Ahrrenius behavior over more than three decades of times. Linear regression analysis of the data finds the slope of $\tau_0 = \tau_0^0 \exp(-\Delta/T)$ to be 1436 K (0.124 eV). Such Ahrrenius behavior of τ_0 has been observed over various regions of temperature for pure and doped bronzes and orthorhombic TaS_3. The surprising result for $(TaSe_4)_2I$, however, is that the activation energy for CDW relaxation is the same as that for the normal resistivity (ρ_0). This is not observed in other materials, where the temperature dependences of ρ_0 and τ_0 are of the same order of magnitude but not equivalent. The temperature dependence of the normal resistivity between 90 and 180 K is presented in Fig. 4 and is fit in a linear regression analysis by an Ahrrenius law with a slope of 1434 K (0.124 eV) over
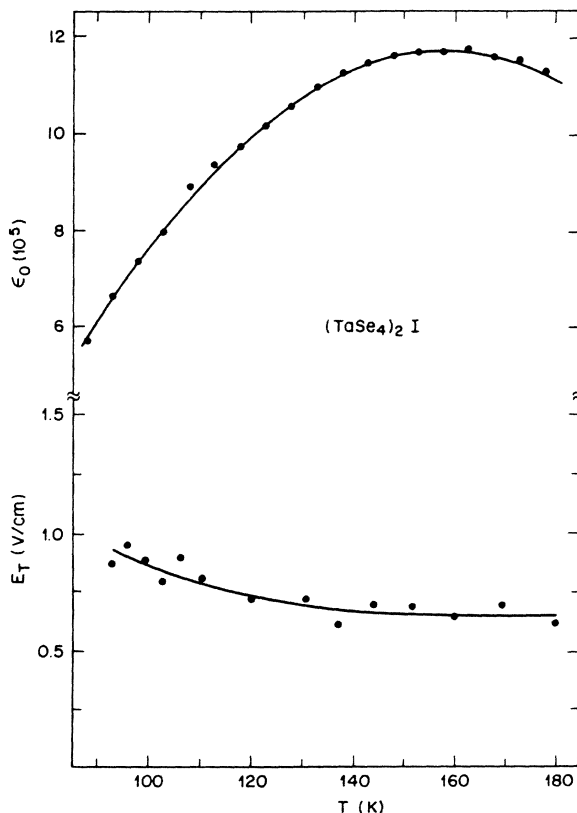

FIG. 2. Temperature dependence of the static dielectric constant (ϵ_0) and the threshold field for nonlinear conductivity (E_T) in $(TaSe_4)_2I$.

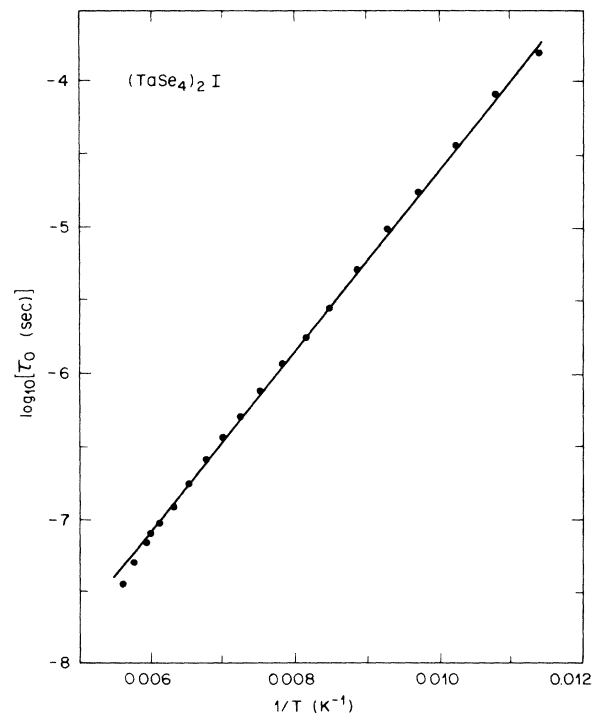FIG. 3. Temperature dependence of the mean CDW relaxation time τ_0 in $(TaSe_4)_2I$. Solid line fit to the data with $E_a = 1436$ K.
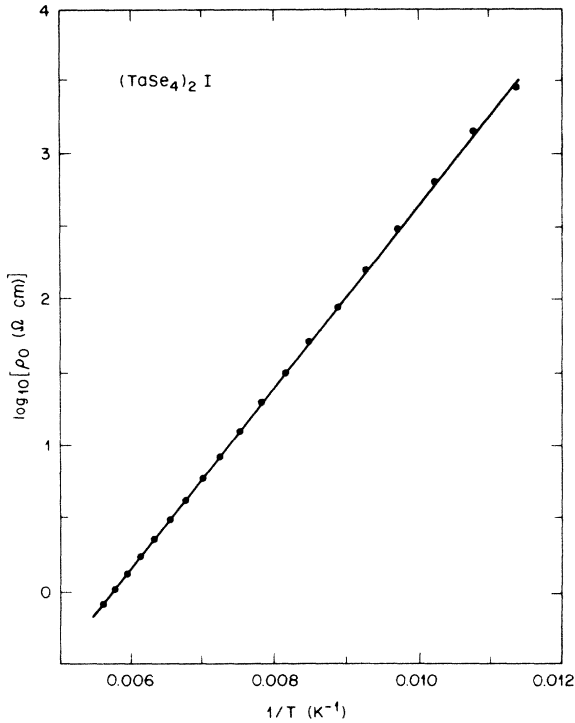
FIG. 4. Temperature dependence of the normal resistivity ρ_0 in $(TaSe_4)_2I$. Solid line fit to the data with $E_a = 1434$ K.

three and a half decades of resistivity. This resistivity is in excellent agreement with that reported in the literature for $(TaSe_4)_2I$. We have also measured the temperature dependence of the (inverse of the) CDW current in this sample[11] and found it to follow a similar temperature dependence as for ρ_0 and τ_0, but with a somewhat higher activation energy, 1741 K (0.15 eV).

DISCUSSION

We have found that the dielectric response of the CDW in $(TaSe_4)_2I$ in the audio frequency range is described very well by the dielectric relaxation of a system with a (relatively broad) distribution of characteristic times which is only slightly assymmetric ($\beta \approx 1$) about the mean times. The mean relaxation times are long for $(TaSe_4)_2I$ compared to other materials we have studied. We have also found the dielectric constant for times much longer than the mean time (ϵ_0) to be low relative to other materials that have been studied. In addition, there is a relatively large dielectric constant (ϵ_{HF}) at times much shorter than the mean relaxation times, suggesting that there may be another relaxation process present that is related to CDW dynamics at higher frequencies than are accessible in our experiment.

The surprising result is that the mean relaxation time of the CDW follows the same temperature dependence as the normal resistivity. The static dielectric constant and threshold fields for nonlinear conduction change only by a factor of 2 at most in the temperature range where the resistivities and relaxation times change by over 3 orders of magnitude, indicating that the CDW response is dominated by dynamic rather than static effects.

The case of $(TaSe_4)_2I$ seems to be the first of the materials studied where the classical theory for CDW transport can by employed in a straightforward manner to understand the CDW relaxation and transport. Within the context of the classical model of the pinning of a CDW by impurities due to Lee and co-workers,[13,14] one considers the pinning of an incommensurate CDW of wave vector Q_z. If the effective pinning by disorder is weak, and the correlation length is long, only the effect of long-wavelength phase fluctuations in the CDW is considered. The electric field is assumed to couple to the full collective charge density ρ_c of the CDW. Within this picture, the dynamics is assumed to be given by an overdamped equation of motion.[15] The model can be used to estimate the relative magnitude of various quantities. A straightforward analysis[7] gives $\epsilon_0 \simeq \rho_c / Q_z E_T$, $\tau_0 \sim \lambda Q_z / \rho_c E_T$, and a value of the high-field CDW conductivity $\sigma_{CDW} \simeq \rho_c^2 / \lambda Q_z^2$, where E_T is the threshold field and λ is the damping factor. The values of ϵ_0 and E_T change little with temperature in $(TaSe_4)_2I$, and roughly inversely with each other. In addition, the wave vector of the CDW is incommensurate and independent of temperature.[16,17] The model then indicates that the CDW current and mean relaxation time are governed by the same dynamic damping factor, λ. Our measurements of σ_{CDW} and τ_0 indicate that this is approximately the case for $(TaSe_4)_2I$. Further, τ_0 follows the same temperature dependence as the normal conductivity, indicating a microscopic connection between the CDW relaxation and the CDW-induced band gap. This straightforward behavior is not observed in the bronzes and is complicated in orthorhombic TaS_3 by the complete disappearance of the low-frequency relaxation. The implication of this data is that in $(TaSe_4)_2I$ the viscous drag force $-\lambda v$ acting on a moving CDW is directly proportional to the normal resistivity ρ_0. This suggests that motion of the CDW involves CDW to normal carrier conversion in the bulk of the sample. (Contact effects could produce this behavior for a uniformly sliding CDW but would not affect the dynamic linear response.) At present there is no microscopic explanation of this unusual behavior. The dynamics of the CDW relaxation and transport in $(TaSe_4)_2I$ may be more straightforward than the other materials studied due to its long-wavelength incommensurate CDW with temperature-independent wavelength, and the relatively large CDW band gap (0.25 eV).

[1]P. Gressier, L. Guémas, and A. Meerschaut, Acta Crystallogr. Sect. B **38**, 2877 (1982).

[2]Z. Z. Wang, M. C. Sant Lager, P. Monceau, M. Renard, P. Gressier, A. Meerschaut, L. Guémas, and J. Rouxel, Solid State Commun. **46**, 325 (1983).

[3]M. Maki, M. Kaiser, A. Zettl, and G. Grüner, Solid State Commun. **46**, 497 (1983).

[4]See, for instance, Charge Density Waves in Solids, Vol. 217 of

Lecture Notes in Physics, edited by Gy. Hutiray and J. So'lyom (Springer-Verlag, Berlin, 1985).

[5]R. J. Cava, R. M. Fleming, P. Littlewood, E. Rietman, L. F. Schneemeyer, and R. G. Dunn, Phys. Rev. B **30**, 3228 (1984).

[6]S. Havrilak and S. Negami, J. Polym. Sci. C **14**, 99 (1966).

[7]R. J. Cava, L. F. Schneemeyer, R. M. Fleming, P. B. Littlewood, and E. A. Rietman, Phys. Rev. B **32**, 4088 (1985).

[8]R. J. Cava, R. M. Fleming, R. G. Dunn, and E. A. Rietman, Phys. Rev. B **31**, 8325 (1985).

[9]C. B. Kalem, N. P. Ong, and J. C. Eckert (unpublished).

[10]G. Grüner, in *Proceedings of the International Symposium on Nonlinear Transport and Related Phenomena in Inorganic Quasi-One-Dimensional Conductors* (Nokkaido University, Sapporo, Japan, 1983), p. 77.

[11]R. M. Fleming, R. J. Cava, E. A. Rietman, and R. G. Dunn (unpublished).

[12]P. Monceau, M. Renard, J. Richard, M. C. Saint-Lager, and Z. Z. Wang, in Ref. 4, p. 279.

[13]H. Fukuyama and P. A. Lee, Phys. Rev. B **17**, 535 (1978).

[14]P. A. Lee and T. M. Rice, Phys. Rev. B **19**, 3970 (1979).

[15]L. Sneddon, M. C. Cross, and D. S. Fisher, Phys. Rev. Lett. **49**, 292 (1982).

[16]H. Fujishita, M. Sato, and S. Hoshino, Solid State Commun. **49**, 313 (1984).

[17]K.-B. Lee, D. Davidov, and A. J. Heeger, Solid State Commun. **54**, 673 (1985).