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Electrical conductivity and thermoelectric power of highly graphitizable poly(p-phenylene vinylene) films

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The electrical conductivity and thermoelectric power of poly(p-phenylene vinylene) films have been studied as a function of heat-treatment temperatures (HTT's) up to 2900 °C. The electrical transport is found to turn from a three-dimensional variable-range-hopping mechanism to metallic conduction by heat treatment above 800 °C. The electrical properties of the films with HTT's higher than 2900 °C are shown to be those of well-graphitized carbon.

I. INTRODUCTION

Conducting polymers with highly conjugated π-electron systems have attracted much interest in both fundamental and practical points of view since the discovery of novel properties of AsF_5-doped polyacetylene.[1]

Intensive studies on polyacetylene with the simplest molecular structure have been performed. However, the chemical instability of this substance in air limits its practical application. This limitation promotes interest in air-stable conducting polymers such as poly(p-phenylene)[2,3] and polythiophene.[4]

From this point of view, graphitic materials such as polyacenic material,[5,6] are also very interesting as a new type of conductor. The graphitic materials are very air stable and are expected to show the metallic properties due to the suppression of the Peierls distortion characteristic to one-dimensional materials, by the formation of two- or three-dimensional conjugated system.

One of the preparation methods of graphitic materials is a heat treatment (pyrolysis) of the insulating polymer. The properties of pyrolysis polymers based on polyimides,[7,8] phenolformaldehyde resin,[9] etc., have been studied. The physical properties of pyrolyzed polymers are dependent upon the starting polymer.

Very recently, Murase *et al.* reported that high-quality films of poly(p-phenylene vinylene) (PPV) can be prepared by casting the precursor film[10] and heat-treated PPV films indicate high electrical conductivity,[11] comparable to that of highly oriented pyrolytic graphite (HOPG)[12] or highly ordered benzene-derived graphite fiber (BDF).[13] However, detailed electrical properties like temperature dependence of electrical conductivity and thermoelectric power have not been reported.

In this paper, we will report the results of electrical conductivity and thermoelectric power measurements for the heat-treated poly(p-phenylene vinylene) films prepared by Murase's method,[10] and will discuss a conduction mechanism in comparison with graphite.

II. EXPERIMENT

Poly(p-phenylene vinylene), PPV, films were prepared by the method of Murase *et al.*[10] Namely, a polyelectrolyte was derived by adding an ion-exchanging resin into p-xylene (diethylsulphonium bromide) dissolved in water. A precursor film was then prepared by casting from the aqueous solution of the polyelectrolyte and then it was subjected to a heat treatment at 200 °C for 1 h under vacuum. By this procedure, an unstretched PPV film was obtained, and stretching of the films was effected at the same time with the heat treatment. In this study, unstretched films and fourfold stretched films were used.

The pristine films (unstretched and fourfold stretched film) were sandwiched between two graphite blocks and then were heat treated at various temperatures between 600–2900 °C for 1 h in an Ar atmosphere. For the low-temperature heat treatment ($\leq$1000 °C), we used an electrical furnace with SiC resistance, and for the heat treatment at temperatures above 1000 °C, a graphite-tube resistance furnance with a high-purity argon atmosphere was used.

The samples for electrical measurements were cut out into a small rectangular chip (about 1×10 mm^2) and the electrical properties were measured along the film surface. The electrical conductivity was measured by a conventional two- or four-terminal method. The electrical contacts between the sample and lead wire were made using silver paint or carbon-containing paste (Electrodag).

For the thermoelectric power measurement, a rectangular sample was mounted between two copper blocks using conductive paste. The temperature difference of both ends of the sample was set to ±1.0 °C by alternatively heating one of the copper blocks. The thermoelectric power at temperature T was measured by taking an average for the two cases of inverse temperature differences. The measurements of ambient temperature and temperature difference were performed utilizing an Alumel-Chromel differential thermocouple. Detailed procedures of thermoelectric power measurement have already been reported in our previously written paper.[9]

III. RESULTS AND DISCUSSION

A. Electrical conductivity

Figure 1 shows the room-temperature electrical conductivity of unstretched PPV films as a function of heat-treatment temperature (HTT). The room-temperature conductivity of the films is remarkably enhanced at

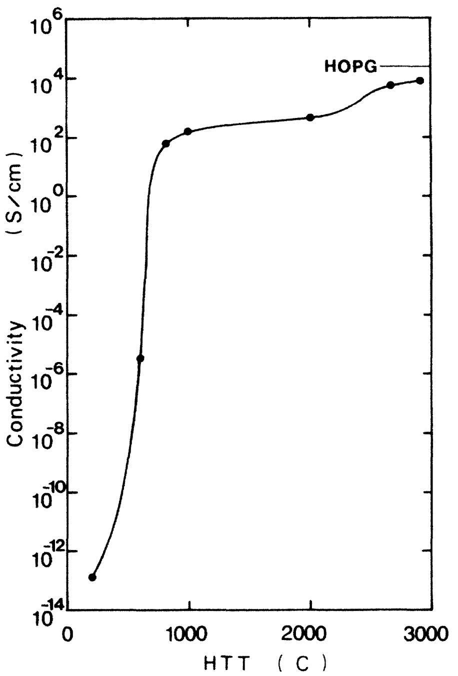

FIG. 1. Room-temperature conductivity of PPV film as a function of HTT.

around 600 °C. This remarkable enhancement seems to originate from the increase of carrier density due to the carbonization by reduction of hydrogen. The next flat region for the HTT between 1000 and 2000 °C, which is observed in most of soft carbon, results from the compensation effect between the crystalline growth and the decrease in carrier density. The third region for a HTT higher than 2000 °C, which is characterized by a rapid increase of the conductivity, corresponds to the development of the three-dimensional graphite structure. This behavior is consistent with that of soft carbon.[14]

Ohnishi *et al.*[11] reported such behavior in biaxial threefold stretched PPV film. And they indicated that the room-temperature conductivities of unstretched and biaxial threefold stretched films for a HTT of 3000 °C are as high as 1.4×10^{3} and 1.6×10^{4} S/cm, respectively, which are comparable to those of HOPG[12] and BDF.[13] In this study, the unstretched film for a HTT of 2900 °C exhibited room-temperature conductivity of 8100 S/cm. It is surprising that such high conductivity can be obtained from unstretched PPV film by high-temperature treatment.

Temperature dependences of electrical conductivity in the pristine film and films heat treated below 1000 °C are indicated in Fig. 2. The activation energies at room temperature are 540 and 3 meV for the pristine and 1000 °C-treated films, respectively.

Figure 3 shows the plots of $\log\sigma$ and $T^{-1/4}$ in the films heat treated below 1000 °C. It is seen from Fig. 3 that the behaviors of $\sigma(T)$ of all samples are well fitted by the $T^{-1/4}$ function. These linearities suggest that the carrier transport by the three-dimensional variable-range hopping (3D VRH) process[15] is working in these materials as it is in the cases of amorphous carbon[16] and the pyrolyzed insulating phenolformaldehyde resin.[9]

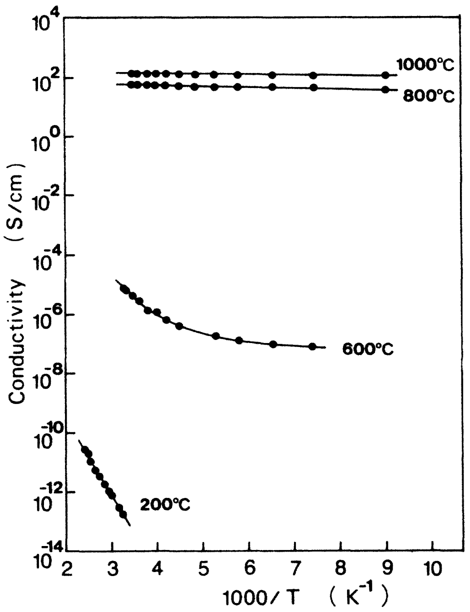

FIG. 2. Temperature dependences of electrical conductivity for the pristine and heat-treated PPV films.

The 3D VRH mechanism is represented by the following equation

$$\sigma(T)=\sigma_0\exp\left[-\left[\frac{T_0}{T}\right]^{1/4}\right], \tag{1}$$

where σ_0 and T_0 are a constant and an exponential factor, respectively. The exponential factor T_0 in Eq. (1) is

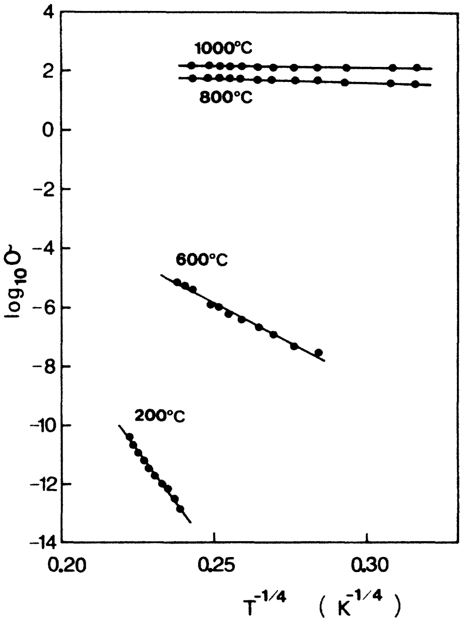

FIG. 3. The plots of $\log\sigma$ versus $T^{-1/4}$ for the pristine and heat-treated PPV films.

decomposed into

$$T_0=\frac{16\alpha^3}{k_B N(E_F)}\ , \tag{2}$$

where α^{-1}, k_B, and $N(E_F)$ are the radii of the localized states wave function, Boltzmann's constant, and density of states at Fermi level, respectively.

For the estimation of the density of states at Fermi level $N(E_F)$, we used a value of 10 Å for α^{-1} as a typical value as in the case of sputtered amorphous carbon film.[16] The exponential factor T_0 and the density of states at Fermi level $N(E_F)$ in the heat-treated films evaluated by these procedures were summarized in Table I.

The values of $N(E_F)$ in the pristine and 600 °C-treated films are 1.8×10^{16} and 1.1×10^{18} states/eV cm^3, contrasted with 10^{18} states/eV cm^3 of sputtered amorphous carbon film.[16] On the other hand, the values of $N(E_F)$ in heat-treated films for HTT's higher than 800 °C, are in excess of 10^{22} states/eV cm^3, which is unreasonable, resulting in the interpretation that the 3D VRH mechanism is not at work in the films heat treated at higher than 800 °C.

Assuming both strongly scattering metallic conduction and a 3D VRH process for these films, temperature dependence of conductivity is fitted by the following relation:

$$\sigma(T)=\sigma(0)+\sigma_0\exp\left[-\left[\frac{T_0}{T}\right]^{-1/4}\right]\ , \tag{3}$$

where $\sigma(0)$ represents zero-temperature-limit conductivity. In this analysis, $\sigma(0)$ was obtained from extrapolation of $\sigma(T)$ versus the T plot. The value of T_0 obtained from $\log[\sigma(T)-\sigma(0)]$ versus the $T^{-1/4}$ plot and $N(E_F)$ were evaluated to be in the order of 10^4–10^5 K and 10^{21}–10^{22} states/eV cm^3, contrasted with 10^5 K and 10^{20} states/eV cm^3 of pyrolytic poly(p-phenylene-1,3,4-oxadiazole).[17]

From these results, it can be considered that the 3D VRH process is not the activator in these samples heat treated at higher than 800 °C, but the metallic conduction is likely the mechanism. However, the temperature dependence indicates that the activated type of conduction is still working. This dependence should originate from the carrier hopping process among the conducting carbonized metallic fragments. This interpretation is similar to that of pyrolyzed phenolformaldehyde resin.

Figure 4 shows the temperature dependence of electrical conductivity in the films heat treated at higher than 800 °C. The temperature dependences of the film heat treated at higher than 1000 °C are very small, but the conductivity of most of them decreases slightly with decreasing temperature. Only the 2900 °C-treated film indicated the slight increase of conductivity at higher temperature and the maximum was observed at around 230 K. This behavior is similar to that of pyrolytic graphite[18] heat-treated at higher than 2750 °C or 2800 °C-treated BDF.[13] These temperature dependences suggest that the heat-treated PPV film is well graphitized carbon and the 2900 °C-treated sample is a highly conductive graphitelike film.

TABLE I. Exponential factor T_0 and density of states at Fermi level $N(E_F)$ evaluated from $T^{-1/4}$ dependence of conductivity.

HTT (°C)	T_0 (K)	$N(E_F)$ (states/eV cm^3)
200 (pristine)	1.0×10^{10}	1.8×10^{16}
600	1.7×10^{7}	1.0×10^{18}
800	2.4×10^{3}	7.8×10^{22}
1000	1.3×10^{1}	1.4×10^{24}

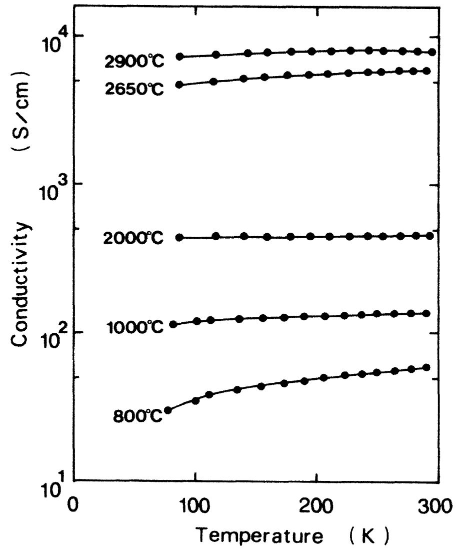

FIG. 4. Temperature dependences of electrical conductivity for the films heat-treated at temperatures higher than 800 °C.

B. Thermoelectric power

Figure 5 shows the room-temperature thermoelectric power (TEP) for the heat-treated unstretched PPV film as a function of the HTT. All the samples showed small TEP's, but the sign of thermoelectric power changed from

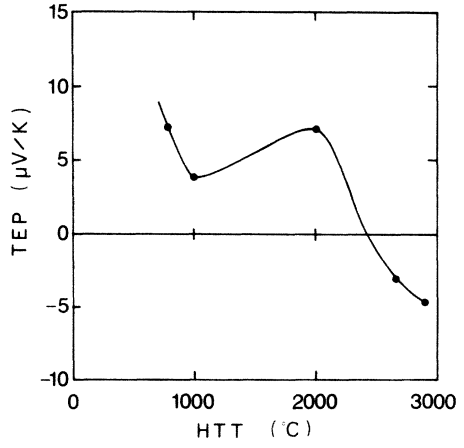

FIG. 5. Room-temperature thermoelectric power of heat-treated PPV film as a function of HTT.

positive to negative at the HTT between 2000 and 2650 °C, indicating hole conduction for the samples heat-treated below 2000 °C and electron conduction for the films heat-treated at higher than 2650 °C. The decrease of the positive TEP with an increasing HTT from 800 to 1000 °C was observed at first and then the TEP increased with an increasing HTT. This decrease of the positive TEP is explained by an increase in the concentration of excess holes. The increase of the positive TEP for the sample of a HTT higher than 1000 °C should originate from the decrease of hole concentration because of the growth in crystallinity. The fact that the electrical conductivity was enhanced in the sample with lowered hole concentration by the HTT above 1000 °C should suggest that the carrier mobility increased in this sample. Furthermore, at a HTT$>$1000 °C, the TEP of the present film shows the similar HTT dependence to that in graphitized carbon.[14] The TEP increases to a peak value of 7 μV/K at a HTT of 2000 °C, and subsequently decreases. The sign inversion takes place between 2000 and 2650 °C, and at a HTT$\geq$2650 °C, the negative value increases. The TEP of the film for a HTT=2900 °C is -4.7 μV/K, which should be contrasted with -4 μV/K of Kish graphite.[19]

The temperature dependences of TEP in PPV films for various HTT's are shown in Fig. 6. The nearly linear dependence is known to be characteristic of near-filled-band metallic systems.[20] The TEP's of p-type near-filled-band metallic systems is usually analyzed by the following formula:

$$S(T)=\frac{\pi^2}{3}\frac{k_B}{|e|}k_BT\frac{N(E_F)}{n(E_F)}=\frac{\pi^2}{3}\frac{k_B}{|e|}k_BT\eta(E_F)\ , \tag{4}$$

where $n(E_F)$ is the carrier density at Fermi level and $\eta(E_F)$ is the density of states at Fermi level per carrier.

However, the observed temperature dependence of TEP slightly deviates from linear dependence. Therefore, assuming that both near-filled-band metallic conduction and hopping processes are working in the films obtained by heat-treatment at temperatures lower than 2000 °C, the temperature dependence of TEP is represented by the following equation:

$$S(T)=AT+BT^{1/2}\ , \tag{5}$$

where A and B are the temperature-independent constants. In comparison with Eq. (5), A can be expressed as the following:

$$A=\frac{\pi^2}{3}\frac{k_B^2}{|e|}\eta(E_F)\ . \tag{6}$$

The temperature dependences of TEP in these samples were examined with Eq. (5). From the obtained A values and Eq. (6), $\eta(E_F)$ in these films were evaluated to be 1.88, 0.82, and 1.56 states/eV carrier for a HTT of 800, 1000, and 2000 °C, respectively. The negative TEP's for the films heat-treated at temperatures higher than 2650 °C decrease with decreasing ambient temperature, as is evident from Fig. 6, and this dependence is very similar to that of graphitized coke.[21] However, in these films, a sign change from negative to positive was not observed within the temperature range studied in this experiment (300–200 K), contrary to Kish graphite in which sign reversal was observed at around 200 K.[19]

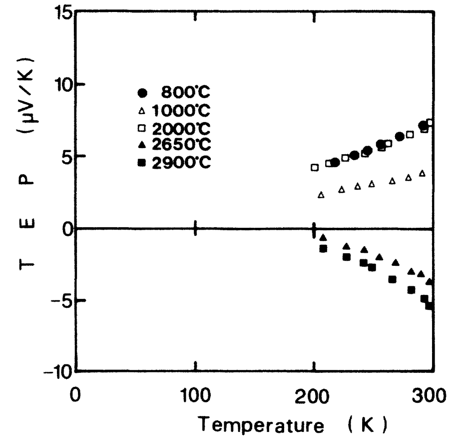

FIG. 6. Temperature dependences of thermoelectric power for the heat-treated PPV films.

From these TEP measurements, the three-dimensional graphite structure is considered to be well developed in PPV film by the high-temperature heat-treatment (HTT=2900 °C), so that we can expect to observe a phonon-drag effect in TEP for the 2900 °C-treated film in a lower-temperature range.

C. Heat-treatment of stretched PPV film

Temperature dependence of electrical conductivity in the fourfold stretched PPV film for a HTT of 1000 °C is shown in Fig. 7. The fourfold stretched PPV film exhibited room-temperature conductivities parallel and perpendicular to the stretching axis of 420 and 130 S/cm. Furthermore, the conductivity parallel to the stretching axis ($\sigma_{\parallel}$) is three times as high as that of unstretched film, and the conductivity perpendicular to the stretching axis ($\sigma_{\perp}$) is just smaller than that of the unstretched film.

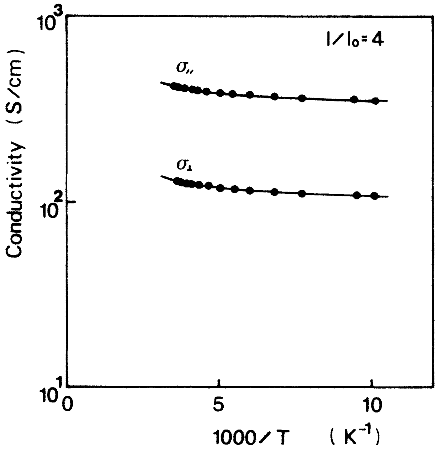

FIG. 7. Temperature dependences of electrical conductivity parallel ($\sigma_{\parallel}$) and perpendicular ($\sigma_{\perp}$) to the stretching axis in fourfold stretched PPV film for a HTT of 1000 °C.

However, temperature dependences of $\sigma_{\parallel}$ and $\sigma_{\perp}$ were much the same with that of the unstretched film, and the activation energies were in the order of meV in both directions.

Figure 8 indicates the temperature dependence of TEP for fourfold stretched PPV film heat-treated at 1000 °C. From Fig. 8, there seems to be no difference in TEP between parallel and perpendicular to the stretching direction at first appearance. However, from the analysis with Eq. (5) we find $A = 0.03$, $B = -0.24$ for the TEP perpendicular to the axis and $A = 0.02$, $B = -0.08$ for the TEP parallel to the stretching axis. Utilizing these A values and Eq. (6), the values of $\eta(E_F)$ were evaluated to be 0.82 and 1.23 states/eV carrier for the direction to parallel and perpendicular to the stretching axis.

The TEP perpendicular to the stretching axis originated from hopping process ($T^{1/2}$) was much larger than that parallel to the axis. This result suggests that heat-treated stretched PPV indicates well-ordered structure along the direction of stretching axis, so that carrier mobility parallel to the axis is larger than that of perpendicular to the axis. Therefore, the anisotropy of electrical conductivity should result from this difference of carrier mobility. It can be considered that the stretched film for a HTT of 1000 °C consists of the conducting carbonized metallic fragments, which are well ordered along the stretching axis, but the dc conductivity is limited by the carrier hopping process between these fragments.

IV. CONCLUSION

We have performed detailed electrical conductivity and thermoelectric power measurements in the poly(p-phenylene vinylene) films for the various heat-treatment temperatures. The results of this study can be summarized as the following:

(1) The heat-treatment temperature dependences of conductivity and thermoelectric power are similar to those of soft carbon. By the heat-treatment at 2900 °C, even the unstretched film is converted to the highly conductive graphitelike material. This interpretation is supported by the negative thermoelectric power at room temperature and temperature dependences of conductivity and thermoelectric power.

(2) The carrier transport process in the films heat-treated below 600 °C can be interpreted by the three-dimensional variable-range hopping mechanism. On the contrary, the electrical transport in the films for a HTT$\geqq$800 °C is found to turn into metallic conduction. However, the dc conductivity is suppressed by the carrier hopping among the metallic conducting fragments.

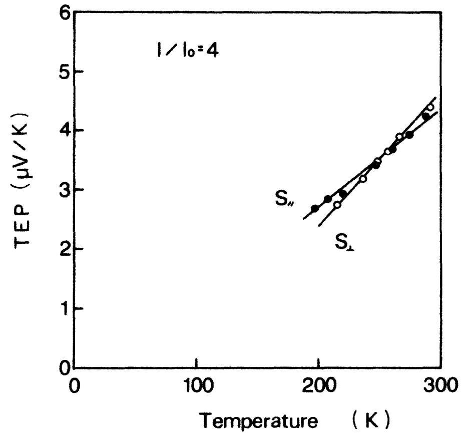

FIG. 8. Temperature dependences of thermoelectric power parallel ($S_{\parallel}$) and perpendicular ($S_{\perp}$) to the stretching axis in fourfold stretched PPV film for a HTT of 1000 °C.

(3) The fourfold stretched film heat treated at 1000 °C showed an anisotropy in the conductivity. This anisotropy can be explained by the difference of carrier mobilities parallel and perpendicular to the stretching axis, which should originate from the preferred orientation of crystallites by stretching.

From these findings, we can expect to observe the characteristic behavior of single crystal graphite in the PPV film heat treated at higher temperatures ($\geqq$3500 °C).

The electrical, magnetic, and structural properties in the pristine and intercalated graphitized PPV films are now under study.

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[1] J. B. Goldberg, H. R. Crowe, P. R. Newman, A. J. Heeger, and A. G. MacDiarmid, J. Chem. Phys. **70**, 1132 (1979).

[2] L. W. Shacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, Synth. Metals **1**, 307 (1979/80).

[3] M. Satoh, M. Tabata, K. Kaneto, and K. Yoshino, Polym. Commun. **26**, 356 (1985).

[4] K. Kaneto, K. Yoshino, and Y. Inuishi, Jpn. J. Appl. Phys. **21**, L567 (1982).

[5] T. Yamabe, K. Tanaka, K. Ohzeki, and S. Yata, Solid State Commun. **44**, 823 (1982).

[6] K. Tanaka, K. Ohzeki, S. Nankai, T. Yamabe, and H. Shirakawa, J. Phys. Chem. Solids **44**, 1069 (1983).

[7] H. B. Brom, Y. Tomkiewicz, A. Aviram, A. Broers, and B. Sunners, Solid State Commun. **35**, 135 (1980).

[8] E. K. Sichel and T. Emma, Solid State Commun. **41**, 747 (1982).

[9] K. Tanaka, S. Yamanaka, T. Koike, T. Yamabe, K. Yoshino, G. Ishii, and S. Yata, Phys. Rev. B **32**, 6675 (1985).

[10] I. Murase, T. Ohnishi, T. Noguchi, and M. Hirooka, Polym. Commun. **25**, 327 (1984).

[11] T. Ohnishi, I. Murase, T. Noguchi, and M. Hirooka, Synth. Metals **14**, 207 (1985).

[12] A. W. Moore, *Chemistry and Physics of Carbon*, edited by P. L. Walker, Jr. and D. A. Thrower (Dekker, New York, 1973),

Vol. 11, Chap. 2, p. 69.

[13] T. C. Chieu, M. S. Dresselhaus, and M. Endo, Phys. Rev. B **26**, 5867 (1982).

[14] E. E. Loebner, Phys. Rev. **102**, 46 (1956).

[15] N. F. Mott and E. A. Davis, *Electronic Process in Non-Crystalline Materials* (Clarendon, Oxford, 1979), Chap. 2.

[16] J. J. Hauser, J. Noncryst. Solids **23**, 21 (1977).

[17] M. Murakami, H. Yasujima, Y. Yumoto, S. Mizogami, and S. Yoshimura, Solid State Commun. **45**, 1085 (1983).

[18] C. A. Klein, J. Appl. Phys. **33**, 3338 (1962).

[19] T. Takezawa, T. Tsuzuku, A. Ono, and Y. Hishiyama, Philos. Mag. **19**, 623 (1969).

[20] J. M. Ziman, *Principle of the Theory of Solids* (Cambridge University Press, Cambridge, 1972), Chap. 7.

[21] Y. Hishiyama and A. Ono, Carbon **19**, 441 (1981).