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Pressure dependence of the photoluminescence of polyparaphenylene

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The photoluminescence and optical-absorption spectra for polyparaphenylene (PPP) and I_2-doped PPP are measured. The photoluminescence of PPP can be attributed to bipolarons by comparing the luminescence and the absorption spectra for PPP and I_2-doped PPP. The photoluminescence spectrum of PPP has been studied as a function of hydrostatic pressure, in the range of 0–6.0 GPa. We find a redshift and then a blueshift of the spectrum with an increase in pressure. We can therefore draw the conclusion that the band gap of PPP decreases and then increases as the interchain coupling increases because of the quite small confinement energy due to the interchain coupling compared to that of a bipolaron due to the energy difference between nondegenerate ground states. We suggest that the variation of the band gap with interchain coupling arises from the dependence of the interchain coupling on both the dimerization amplitude and the energy bandwidth. As a result, the decrease and then increase of the band gap of one-dimensional polymers with interchain coupling can, in principle, be expected. In addition, resolved structures that are observed in the luminescence spectrum decrease in magnitude and broaden at high pressure.

I. INTRODUCTION

For one-dimensional polymers with delocalized π electrons, the π band is half filled, and metallic properties would be expected in these systems. It is well known that these polymers are insulated when the temperature is low enough, due to the fact that one-dimensional systems tend to be dimerized. This dimerization opens an energy gap, which is called the Peierls gap, at the Fermi surface, if such a break in the energy band coincides exactly with the edge of the Fermi distribution. The states that are displaced downwards in energy are then occupied, and the states that are raised are empty.[1,2] The competition between the decrease in the electronic energy and the increase in the elastic energy among atoms on the chains (caused by the distortion) leads to an equilibrium bond-length alternation (i.e., the dimerization amplitude), which is approximately 0.03 Å in polyacetylene (PA).[3] Various other calculations on both *trans*- and *cis*-polyacetylene support the idea that the larger dimerization amplitude corresponds to the larger Peierls gap.[4]

In one-dimensional polymers, the anisotropy of the compressibility tensor is large, due to weak van der Waals interaction between chains compared with the covalent bonds along the chain. Consequently, the interchain-coupling effect of the band gap and the dimerization can be investigated by the application of hydrostatic pressure, which brings about a significant decrease in interchain distances. For *trans*- and *cis*-PA, Moses *et al.*[5] have studied the interchain-coupling effect on the band gap; the large redshift of the optical-absorption edge with hydrostatic pressure from 0 to 1.3 GPa has been found, indicating a reduction in the band gap as a function of increasing pressure in both isomers. This result has been interpreted in terms of the simplified tight-binding calculation, which implies that interchain coupling will lead to a broadening of the energy band (and the dimerization amplitude is considered to be interchain-coupling-independent).

In this paper, we have measured the photoluminescence spectra of PPP under various hydrostatic pressures from 0 to 6.0 GPa at room temperature. The main observation of this experiment implies that the band gap decreases and then increases with applied pressure. We believe that the dimerization amplitude is not interchain-coupling-independent, and that the interchain coupling will affect both the dimerization amplitude and the width of the energy band. The interchain-coupling dependence of the dimerization amplitude as well as that of the bandwidth have been discussed.

In Sec. II, we give a brief description of the experimental apparatus and samples. In Sec. III, we develop a theory about the interchain-coupling dependence of the dimerization amplitude and that of the bandwidth. In Sec. IV, the experimental results are described and analyzed using the theory in Sec. III.

II. EXPERIMENTAL APPARATUS AND SAMPLES

High pressures were obtained in a diamond-anvil cell using a mixed fluid of methanol and ethanol as the pressure medium. The diamond-anvil cell is sketched in Fig. 1. The pressure calibration was confirmed by measuring the photoluminescence of ruby. The photoluminescence spectra of PPP were measured with a JY-T800 Raman spectrometer.

Two kinds of samples of PPP, namely powder and film, were used in the measurement of the luminescence and absorption spectra. PPP powder was synthesized by the Kovacic method, and the PPP film was electrochemically polymerized.

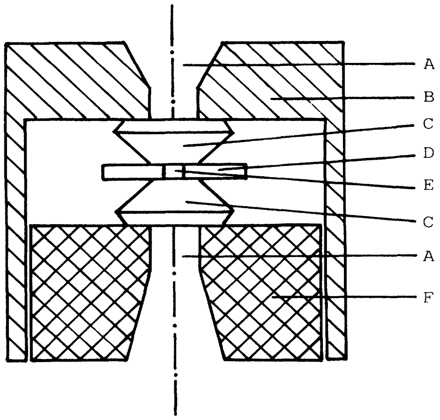

FIG. 1. High-pressure cell for the photoluminescence measurement. *A*, optical window; *B*, steel cylinder; *C*, diamond; *D*, steel gasket; *E*, a hole in which the sample, ruby, and pressure medium are loaded; *F*, steel piston.

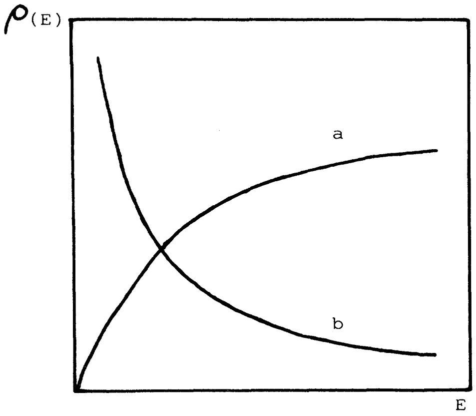

FIG. 2. Density of electronic states for one- and three-dimensional systems. Curve *a*, three-dimensional systems; curve *b*, one-dimensional systems.

III. THEORY OF THE INTERCHAIN-COUPLING EFFECTS ON THE BAND GAP

A. Interchain-coupling effects on the dimerization

It is well known that the dimerization amplitude depends on the competition between the decrease in the electronic energy and the increase in the elastic energy among atoms on the chains caused by the distortion of the one-dimensional crystal lattice.

The dimerization amplitude U for one-dimensional systems can be obtained by calculating the following equation:

$$\frac{\partial E}{\partial U}=0 , \tag{1}$$

where $E=E_1+E_2$, (E_1 and E_2 are the total electronic and the elastic energy, respectively). U is the distortion of the one-dimensional crystal lattice due to dimerization. Note that the dimerization amplitude could be changed only if the variation of the electronic or elastic energy to the distortion U varies.

It is also well known that the average electronic energy can be written as

$$\bar{E}_1=\frac{\int \rho(E)f(E)dE}{\int \rho(E)dE} , \tag{2}$$

where $\rho(E)$ is the density of electronic states and $f(E)$ is the distribution function of electrons.

It should be pointed out that for a real one-dimensional polymer, as the interchain distance decreases, the density of electronic states may have more or less the character of a three-dimensional system, although the van der Waals interaction between one-dimensional polymer chains is still rather weak. We know that the density of electronic states of a three-dimensional system is proportional to $\sqrt{E}$ and that of an ideal one-dimensional system is proportional to $1/\sqrt{E}$, as shown in Fig. 2. Having considered the interchain coupling, we suggest that the density of electronic states of a one-dimensional system under high pressure can be given by the following form:

$$\rho(E)\propto a\frac{1}{\sqrt{E}}+b\sqrt{E} . \tag{3}$$

The parameters a and b in Eq. (3) are defined as

$$a=\frac{I}{I+I'} , \quad b=\frac{I'}{I+I'} , \tag{4}$$

where I and I' are the intrachain and interchain electronic transfer integral, respectively. Figure 3 shows the density of electronic states of the one-dimensional system with or without the consideration of the interchain coupling according to Eq. (3). To combine Eqs. (3) and (2), we find that interchain coupling will increase the total electronic energy of a one-dimensional polymer.

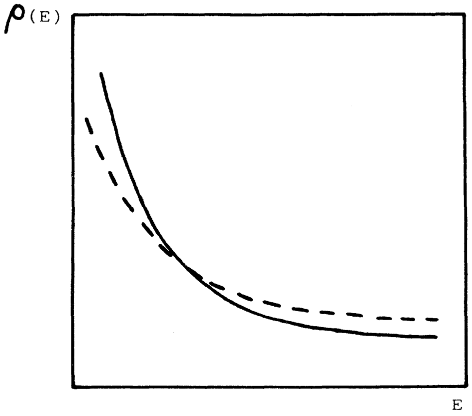

FIG. 3. Density of electronic states for one-dimensional systems at ambient (solid line) and hydrostatic pressure (dashed line), respectively.

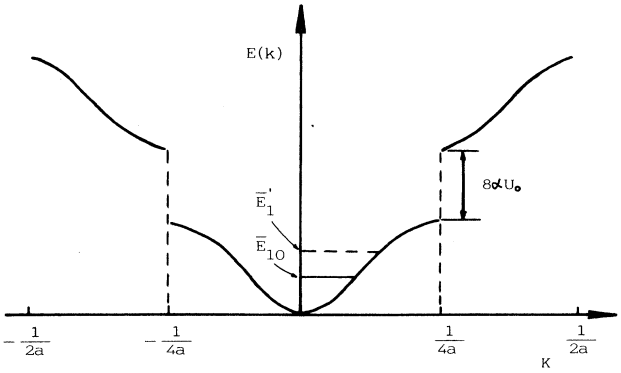

FIG. 4. Electronic energy at ambient ($\bar{E}_{10}$) and hydrostatic pressure ($\bar{E}_1'$), respectively, before the energy-band structure varied.

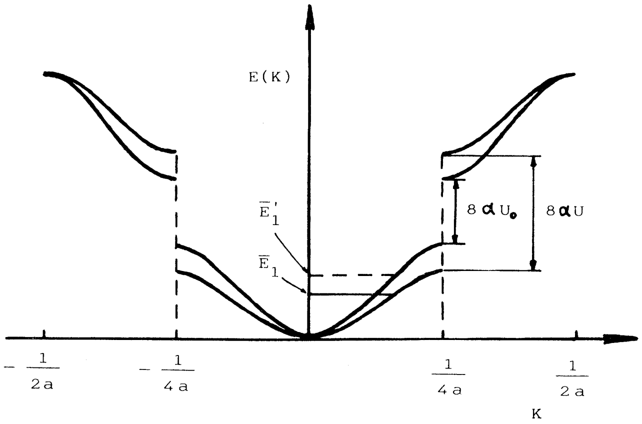

FIG. 5. Variation of electronic energy with the dimerization amplitude.

In fact, interchain coupling will increase the average energy of electrons in occupied band. We use $\bar{E}_{10}$, I_0', U_0, $\bar{E}_1$, I', and U to represent the average energy of electrons, interchain coupling, and the dimerization amplitude for a one-dimensional polymer at ambient and hydrostatic pressure, respectively. We assume that the increase in the average energy of electrons with interchain coupling is linear. Therefore, if the dimerization amplitude is considered not to be changed, when the interchain coupling is I', then the average energy of electrons is labeled $\bar{E}_1'$, which can be written as follows:

$$\bar{E}_1' = \frac{I'}{I_0'} \bar{E}_{10} \; . \tag{5}$$

$\bar{E}_1'$ and $\bar{E}_{10}$ are shown in Fig. 4. Figure 4 clearly shows the increase in the electronic energy with interchain coupling. On the other hand, the elastic energy of a one-dimensional polymer results from the interaction between localized σ electrons, and should therefore be interchain-coupling-independent in the range of the pressure that we applied.

Consequently, the total energy E for one-dimensional polymers will increase when the hydrostatic pressure is applied, due to the increase in the electronic energy. Then the original equilibrium bond-length alternation depending on the competition between the lowering of the electronic energy and the increase in the elastic energy is broken by the increase of the electronic energy. In order to decrease the total energy of polymers under pressure, it is expected that the dimerization amplitude will be changed, reaching a new equilibrium bond-length alternation. As discussed above, the energy bandwidth will be affected by the variation of the dimerization amplitude. If the energy band becomes narrower, the average energy of electrons will decrease (see Fig. 5). We assume the dimerization amplitude is varied from U_0 to U, and then the average electronic energy will be $\bar{E}_1$ instead of $\bar{E}_1'$, as shown in Fig. 5.

Once the linear relationship between the variation of the average energy of electrons and the shift of the band is assumed, $\bar{E}_1$ can be written as

$$\bar{E}_1 = \frac{\frac{1}{2}W - 4\alpha U}{\frac{1}{2}W - 4\alpha U_0} \bar{E}_1' = \frac{\frac{1}{2}W - 4\alpha U}{\frac{1}{2}W - 4\alpha U_0} \frac{I'}{I_0'} \bar{E}_{10} \; , \tag{6}$$

where W is the width of the π band and α is the electron-phonon coupling constant.

On the other hand, the variation of the dimerization amplitude should cause a change of the elastic energy among atoms on a chain for a one-dimensional system. Considering all these factors, when the new equilibrium between the lowering of the electronic energy and the increase of the elastic energy is set up under hydrostatic pressure, the total energy E for a one-dimensional polymer can be written as

$$E = N \frac{\frac{1}{2}W - 4\alpha U}{\frac{1}{2}W - 4\alpha U_0} \frac{I'}{I_0'} \bar{E}_{10} + 2NKU^2 \; , \tag{7}$$

where K is the elastic coefficient among atoms in a chain and N is the number of atoms on a chain. By solving the extremum of Eq. (7) in terms of Eq. (1), the effect of the interchain coupling on the dimerization amplitude U can be presented by

$$U = \frac{\alpha}{(\frac{1}{2}W - 4\alpha U_0)K} \frac{I'}{I_0'} \bar{E}_{10} \; . \tag{8}$$

Using the original value $U = U_0$ when $I' = I_0'$, the following result can be obtained from Eq. (8):

$$U_0 = \frac{\alpha}{(\frac{1}{2}W - 4\alpha U_0)K} \bar{E}_{10} \; . \tag{9}$$

Substituting Eq. (9) into Eq. (8), we obtain

$$U = \frac{I'}{I_0'} U_0 \; . \tag{10}$$

Equation (10) indicates that the dimerization amplitude will increase under the applied external pressure. As a result, we can conclude that the interchain coupling will increase the dimerization amplitude, and this effect of interchain coupling on the dimerization amplitude will result in an increase of the Peierls gap for one-dimensional polymers.

The dependence of the pressure on the interchain coupling can be written as[5]

$$I'=I(0)\exp(CP)\ , \tag{11}$$

where C is a parameter, indicating the variation degree of the interchain coupling with the hydrostatic pressure. Then, Eq. (10) can be changed into the following:

$$U=U_0\exp[C(P-P_0)]\ . \tag{12}$$

B. Interchain-coupling effects on the bandwidth of one-dimensional polymers

It is well known that the energy levels for isolated atoms are separated, not successive. The energy band of a polymer chain can be interpreted as degenerate electronic states in energy for an isolated atom being split due to electronic Coulomb interaction from other atoms on a chain, and then leading to the energy band consisting of successive levels and the gap between the energy bands. Consequently, the stronger Coulomb interaction among atoms on a chain will give rise to the broader energy band or the smaller band gap.

On the other hand, for a chain with a fixed length, when the interchain coupling is taken into account, the energy band will be broadened by the electronic Coulomb interaction from other chains. The effect of the interchain electronic Coulomb interaction on the energy band is just like that of the chain length on the energy band.

As a result, one can conclude that the interchain coupling will decrease the band gap for one-dimensional polymers. The interchain-coupling dependence of the band gap is given by[5]

$$E_g=8\alpha U-8T\ , \tag{13}$$

where T can be assumed as $T=DP$, and D is a variable. Hence, it is obvious that another effect of the interchain coupling on the energy band is then to broaden the energy band or to decrease the Peierls gap.

To summarize, interchain coupling will give rise to two kinds of effects on the band gap for one-dimensional polymers, according to the discussion in Secs. III A and III B. One of the effects is that interchain coupling increases the dimerization amplitude or the band gap. Another is that interchain coupling broadens the energy band or decreases the band gap. Therefore, we finally obtain the interchain-coupling dependence of the band gap for one-dimensional polymers:

$$E_g=8\alpha U_0\exp[C(P-P_0)]-8DP\ . \tag{14}$$

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Absorption and luminescence of the polyparaphenylene

For one-dimensional polymers with nondegenerate ground states, the electron-hole pair will first be produced in a chain by the excitation light when its energy is greater than the energy gap of a chain, and then the electron-hole pair can decay into a polaron (or a bipolaron) by the crystal lattice relaxation. Two polarons can also form a bipolaron. As a result, the photoluminescence due to polarons (or bipolarons) for these polymers, such as *cis*-PA, PPP, and PT can be expected. In order to investigate the origin of the photoluminescence of PPP, we first studied the optical absorption of PPP. Polarons and bipolarons, which have been observed in the optical-absorption spectra of polythiophene[6] and polypyrrole,[7] are main excited states in these polymers, and give rise to three or two subgap transitions, respectively, as shown in Fig. 6.

However, only two optical-absorption bands have been observed at low doping in PPP,[8] indicating that bipolarons are the primary excited states induced by doping in PPP.

We also measured the optical-absorption spectra for primary and I_2-doped PPP film, as shown in Fig. 7. Only one subgap transition (at $\sim$2.5 eV) in the absorption spectrum of I_2-doped PPP films was observed in the range 300–900 nm, which is in good agreement with the predicted optical-absorption features for bipolarons, similar to the experimental result in Ref. 8. The peak at 2.5 eV corresponds to absorption due to the electron transition from the valence band to the antibonding bipolaronic levels [see transition 2′ in Fig. 6(b)]. The energy difference between the bonding bipolaronic level and the valence band is about 0.5 eV, and the absorption band at 3.10 eV is then attributed to the electronic transition between the valence band and the conduction band (see Ref. 8). The broader absorption edge in Fig. 7 implies an extensive distribution in molecular chain length.

We then measured the photoluminescence spectra for primary and I_2-doped PPP film. Both the luminescence spectra for primary and I_2-doped PPP film consist of a broad band (around 2.2 eV) with some resolved weak peaks, as shown in Fig. 8. The interval among the resolved peaks is about 1200 cm^{-1}. Figure 8 shows a slight blueshift of the broad emission band of PPP with

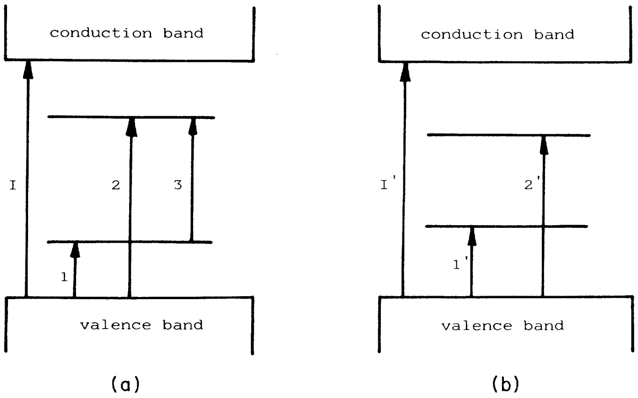

FIG. 6. Energy-level diagram for (a) a polaron and (b) a bipolaron, showing all allowed optical transitions.

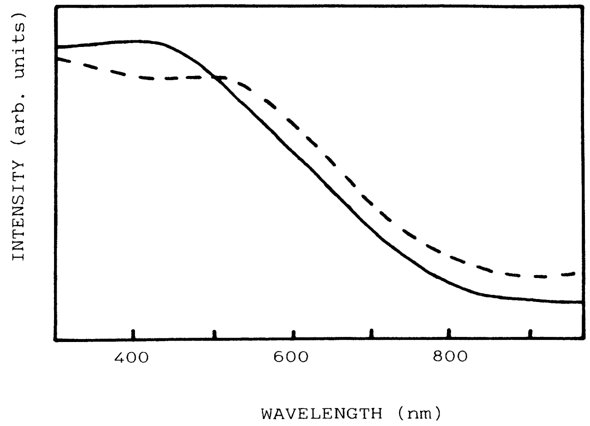

FIG. 7. Optical-absorption spectra for I_2-doped (dashed line) and undoped (solid line) PPP films, respectively.

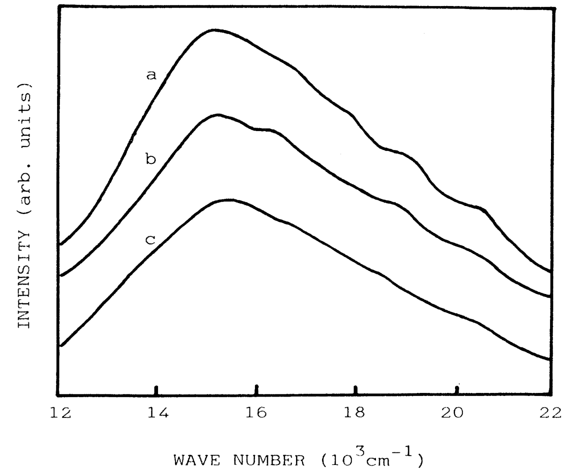

FIG. 9. Emission spectra for an (a) undoped, (b) lightly I_2-doped, and (c) heavily I_2-doped PPP powder; $\lambda_{ex}=488$ nm.

doping, and its intensity decreases with doping levels. Thereby, doping effects on the broad band in the luminescence spectrum, except its intensity, are not important for the PPP film, which is similar to the experimental result for polythiophene.[9] But the intensities of the resolved peaks decrease with doping, and the interval between the resolved peaks remains unchanged. By a comparison of the luminescence and absorption spectra for primary and I_2-doped PPP film, the broad emission band (at 2.2 eV) in the luminescence spectra can be attributed to the transition of electrons from the antibonding bipolaronic levels to the bonding bipolaronic levels. Therefore, it is not unreasonable to recognize that the broad band in the luminescence spectra for primary and I_2-doped PPP film is due to bipolarons. In other words, photoinduced bipolarons are the main stabilized excited states in primary and I_2-doped PPP film.

In addition, photoluminescence spectra for primary and I_2-doped PPP powder have been also measured. The spectra for both primary and I_2-doped PPP powder consist of a broad band (at ~2.0 eV) with some resolved peaks, as shown in Fig. 9. The interval among the resolved peaks is also about 1200 cm^{-1}. Figure 9 shows a blueshift of the broad emission band of PPP powder with doping, and its intensity decreases with doping. The intensities of the resolved peaks also decrease with the doping.

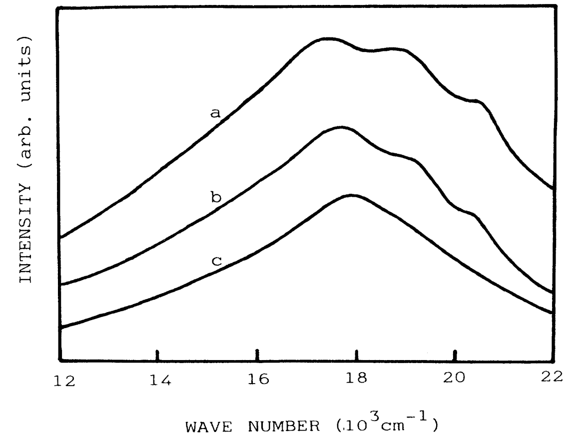

FIG. 8. Emission spectra for an (a) undoped, (b) lightly I_2-doped, and (c) heavily I_2-doped PPP film; $\lambda_{ex}=488$ nm.

By comparison between the luminescence spectra of PPP films and powder and that of I_2-doped PPP film and powder, we find that the main difference between the luminescence spectra for PPP film and PPP powder is that the broad emission band of PPP powder is different from that of PPP film in energy. But the effect of the doping on the broad emission band of PPP film is the same as that of PPP powder in energy and intensity. We know that the energy gap of a chain depends strongly on its length: a smaller energy gap for a longer chain, a larger energy gap for a shorter chain.[10] Thereby, the energy difference between the broad emission bands of PPP film and those of PPP powder could be attributed to the different distribution of chain length for PPP powder and film. The blueshift of the broad emission band of PPP film compared to that of PPP powder indicates the longer (shorter) chain length for PPP powder (film). The fact that the effects of doping on the behavior of the broad emission band of PPP powder are the same as those of PPP film and the formation and lifetime (~ns) of the excitation corresponding to the broad emission band suggests that the broad emission band of PPP powder arises from bipolarons. The photoinduced bipolarons are also primary stabilized excited states for PPP powder.[11]

B. Photoluminescence of PPP powder under hydrostatic pressure

In Fig. 10, we present the photoluminescence spectra of PPP powder at various hydrostatic pressures. The luminescence spectra of PPP powder at various pressures consist of a broad emission band with some resolved peaks. The broad emission band is just due to bipolarons (see Sec. IV A). A redshift of the broad emission band of PPP powder with pressure from 0 to about 3.5 GPa, and then a blueshift of the broad emission band with pressure from 3.5 to 6.0 GPa, are observed, as shown in Fig. 10. The variation of these resolved peaks with pressure in energy is very small, and the interval between the resolved peaks remains about 1200 cm^{-1}. However, these resolved peaks are broadened under high pressure, and finally disappear in the luminescence spectrum of PPP powder.

By the processing of the luminescence spectra of PPP powder under various hydrostatic pressures, the dependence of the pressure on the broad emission band due to bipolarons is observed, as shown in Fig. 11. The variation of the broad emission band to the pressure is (in eV/GPa)

$$\frac{dE}{dP}=\begin{cases}-1.83\times 10^{-2}, & 0\text{–}3.5\ \text{GPa}\ ,\\ +1.50\times 10^{-2}, & 3.5\text{–}6.0\ \text{GPa}\ .\end{cases} \tag{15}$$

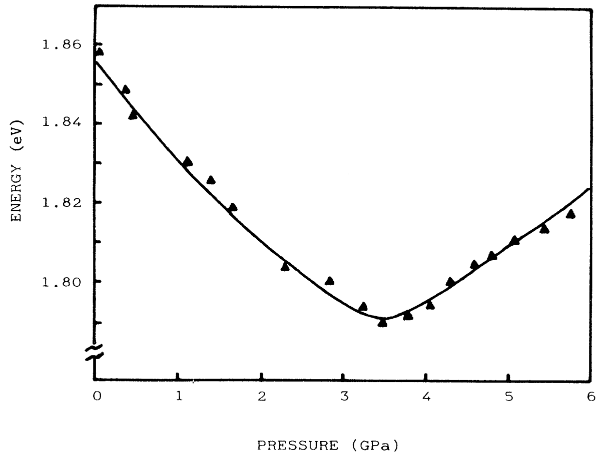

FIG. 11. Dependence of hydrostatic pressure on the broad emission band of PPP powder.

We know that the two localized levels of a bipolaron can be written as

$$\omega=\pm F(\gamma)\Gamma\ , \tag{16}$$

where F is a parameter (its value depends on the parameter γ), γ is the confinement parameter of a bipolaron, and Γ is half of the energy gap of a chain. So the dependence of interchain coupling on the luminescence of bipolarons originates from the effect of interchain coupling on both the confinement parameter γ and the energy gap in terms of Eq. (16). For polyacetylene, the confinement energy of a polaron in *cis*-PA is larger than that due to the interchain coupling in *trans*-PA by two to three orders of magnitude.[12] As a result, the confinement energy can only be thought of as resulting from the energy difference between nondegenerate ground states. The interchain coupling effects on the confinement energy of a bipolaron can be ignored, implying that the confinement parameter γ of a bipolaron is interchain-coupling-independent. Furthermore, we can draw the conclusion that the band gap of

FIG. 10. Emission spectra of PPP powder under various hydrostatic pressures. 0, 1.7, 3.5, 4.3, and 5.8 GPa from the bottom to the top, respectively; $\lambda_{ex}=514.5$ nm. For visual clarity only five representative pressure data are shown.

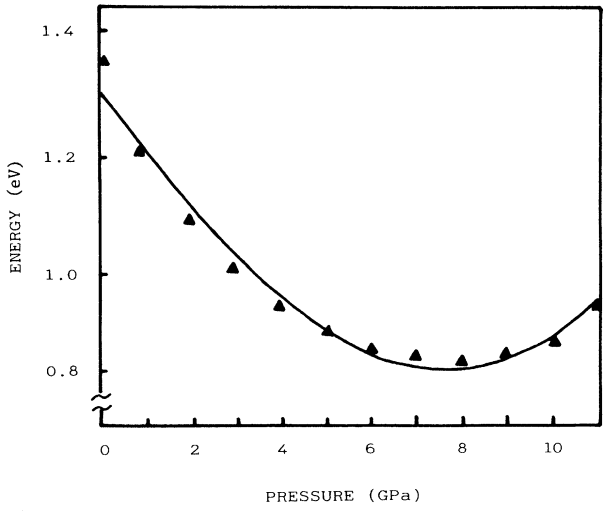

FIG. 12. Dependence of hydrostatic pressure on the energy gap of *trans*-PA. Solid triangles, experimental data from Ref. 13; solid line, fitting curve with Eq. (14).

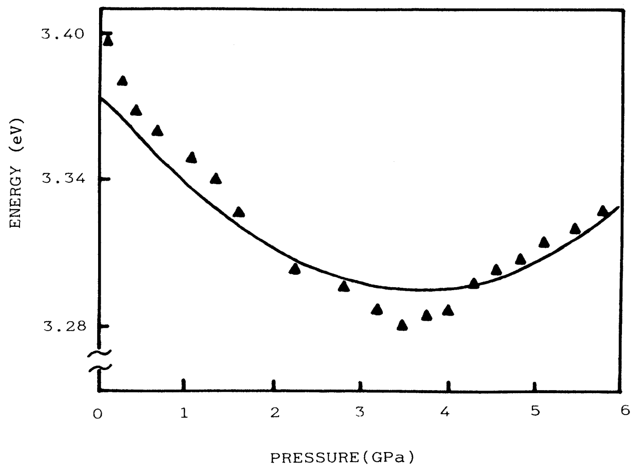

FIG. 13. Dependence of hydrostatic pressure on the energy gap of PPP powder. Solid triangles, experimental data; solid line, fitting curve with Eq. (14).

PPP decreases and then increases with the application of external pressure from 0 to 6.0 GPa, in terms of the pressure dependence of the broad emission band of PPP.

For *trans*-PA, the parameters $C=8.70\times10^{-2}$ (GPa)$^{-1}$ and $D=5.53\times10^{-2}$ eV/GPa could be obtained by fitting Eq. (14) to the experimental data of the pressure dependence of the energy gap in Ref. 13, as shown in Fig. 12. The pressure dependence of the interchain coupling can be written as[5]

$$I'=I(0)\exp[\Delta x(p)/l]\ , \tag{17}$$

where $\Delta x(p)$ is the change of the interchain distance due to the applied external pressure P, and l is a constant. $\Delta x(p)$ is given by

$$\frac{\Delta x(p)}{x_0}=\tfrac{1}{2}\kappa P\ , \tag{18}$$

where x_0 is the average interchain distance between two neighbor chains at ambient pressure, and κ is the interchain compressibility. To substitute Eq. (18) into Eq. (17), we obtain

$$I'=I(0)\exp\left[\frac{x_0}{2l}\kappa P\right]\ . \tag{19}$$

Using Eq. (19) together with Eq. (11), the constant l can be given by

$$l=\frac{\kappa}{2C}x_0\ . \tag{20}$$

Using $\kappa=5\times10^{-2}$ (GPa)$^{-1}$ in Ref. 14, we obtain $l=0.3x_0$.

For PPP, we have come to the conclusion that the band gap of PPP decreases and then tends to increase with pressure from 0 to 6.0 GPa because the effect of interchain coupling on the confinement energy of a bipolaron can be ignored, as discussed in Sec. IV B. The parameter F could be obtained to be 0.55 by using the band gap 3.4 eV of PPP.[15] Therefore, we obtain the dependence of the pressure on the band gap as shown in Fig. 13 by means of Eq. (16) in terms of the variation of the broad emission band due to bipolarons with the pressure for PPP. The parameters $C=5.72\times10^{-2}$ (GPa)$^{-1}$ and $D=5.98\times10^{-2}$ eV/GPa can be determined by fitting the data of the band gap with the pressure by means of Eq. (14), as shown in Fig. 13.

V. CONCLUSION

By comparison between the luminescence and absorption spectra for primary and I_2-doped isomers of PPP powder and film, there is every reason to believe that the broad emission band of PPP is due to bipolarons.

The photoluminescence spectrum of PPP has been studied as a function of hydrostatic pressure, in the range 0–6.0 GPa, in order to investigate the interchain-coupling dependence of the band gap. We have found a redshift and then a blueshift of the broad emission band of PPP as the pressure increases. We came to the conclusion that the shift of the broad emission band is due to the variation of the energy gap with pressure. We suggest that the interchain coupling increases the electronic energy and broadens the energy band, and then the dimerization amplitude increases to lower the total energy of one-dimensional polymers, leading to a new equilibrium bond-length alternation. As a result, the variation of the band gap for one-dimensional polymers with interchain coupling originates from the increase of the dimerization amplitude and the broadening of the energy band with the interchain coupling. This theoretical model is quantitatively consistent with the experimental results for PA and PPP, as shown in Figs. 12 and 13.

In conclusion, the decrease and then increase of the band gap of one-dimensional polymers with interchain coupling can, in principle, be expected.

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