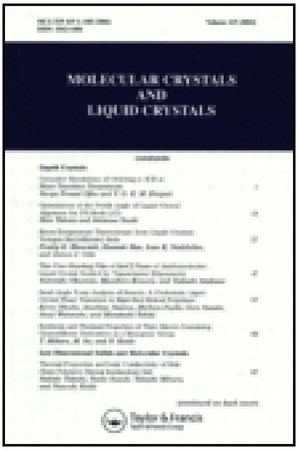
This article was downloaded by: [University of Haifa Library]
On: 22 August 2012, At: 10:10
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Effects of Pressure and Shear Stress on the Absorption Spectra of Thin Films of Pentacene

I. Shirotani [a], J. Hayashi [a], K. Takeda [a], H. Kawamura [b], M. Inokuchi [c], K. Yakushi [d] & H. Inokuchi [e]

[a] Muroran Institute of Technology, Mizumoto, Muroran, Japan

[b] Faculty of Science, University of Hyogo, Kamigohri, Hyogo, Japan

[c] Faculty of Science and Engineering, Tokyo University of Science, Onoda, Yamaguchi, Japan

[d] Institute for Molecular Science, Myodaiji, Okazaki, Aichi, Japan

[e] Japan Aerospace Exploration Agency, Tsukuba Space Center, Tsukuba, Ibaraki, Japan

Version of record first published: 31 Jan 2007

To cite this article: I. Shirotani, J. Hayashi, K. Takeda, H. Kawamura, M. Inokuchi, K. Yakushi & H. Inokuchi (2006): Effects of Pressure and Shear Stress on the Absorption Spectra of Thin Films of Pentacene, Molecular Crystals and Liquid Crystals, 461:1, 111-122

To link to this article: http://dx.doi.org/10.1080/15421400600914890

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [University of Haifa Library] at 10:10 22 August 2012

Mol. Cryst. Liq. Cryst., Vol. 461, pp. 111–122, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400600914890

Taylor & Francis
Taylor & Francis Group

Downloaded by [University of Haifa Library] at 10:10 22 August 2012

Effects of Pressure and Shear Stress on the Absorption Spectra of Thin Films of Pentacene

I. Shirotani
J. Hayashi
K. Takeda
Muroran Institute of Technology, Mizumoto, Muroran, Japan

H. Kawamura
Faculty of Science, University of Hyogo, Kamigohri, Hyogo, Japan

M. Inokuchi
Faculty of Science and Engineering, Tokyo University of Science, Onoda, Yamaguchi, Japan

K. Yakushi
Institute for Molecular Science, Myodaiji, Okazaki, Aichi, Japan

H. Inokuchi
Japan Aerospace Exploration Agency, Tsukuba Space Center, Tsukuba, Ibaraki, Japan

The absorption spectra in an oriented film of pentacene have been studied up to 10 GPa under hydrostatic conditions. The absorption bands of this hydrocarbon rapidly shifted to a longer wavelength region. The Davydov splitting of the 0-0 band in the oriented film abruptly increased with increasing pressure up to 1.2 GPa. However, this splitting disappeared at around 1.5 GPa. The absorption spectrum at this pressure is similar to that of the amorphous film. The molecular arrangements in the oriented film of pentacene changed to the amorphous state at around 1.5 GPa. When the pressure was increased further, the absorption peaks disappeared at pressures greater than 6.6 GPa. When the pressure is reduced from 10 GPa to the ambient pressures, we cannot find the original absorption spectra of the oriented film of pentacene. The irreversible optical property arises from the solid-phase reaction at higher pressures.

We have observed in situ *shear stress effects on the oriented film of pentacene in the sapphire-anvil cell under the microscope. After the pressure is increased up to 2 GPa, one sapphire-anvil is rotated by applied force to generate shear*

Address correspondence to I. Shirotani, Muroran Institute of Technology, 27-1 Mizumoto, Muroran 050-8585, Japan. E-mail: sirotani@mmm.muroran-it.ac.jp

stress at this pressure. The color of the thin film changed remarkably from blue to yellow at the outer part on the anvil, but the color at the center was blue, insensitive to shear stress. The absorption intensity of the visible bands sharply decreased, and the width vastly broadened in the outer part. The amorphization of the oriented film is accelerated under shear deformation. On the other hand, the intensity of the absorption band below 400 nm increased in the outer part. After shear stress was reduced, the original spectrum of pentacene did not recover completely. The conjugated system in pentacene is partly broken by shear stress. Thus, the solid-phase reaction is also induced by shear stress for the thin film.

Keywords: absorption spectrum; amorphization; high pressure; pentacene; shear stress; solid-phase reaction

Downloaded by [University of Haifa Library] at 10:10 22 August 2012

INTRODUCTION

The effects of pressure on an electrical resistivity of aromatic crystals have been studied; the resistivity rapidly decreases by several orders of magnitude at high pressures. This behavior is closely associated with an increase in the amount of overlap between adjacent molecules. The band calculations at high pressure have been carried out for aromatic crystals by several authors [1,2]. *p*-Iodanil and tetraselenotetracene have the low resistivity of ca. 10^{-1} Ω cm at around 20 GPa [3]. An insulator-to-metal transition in *p*-iodanil is found at around 30 GPa. Further, this compound shows the superconductivity at about 2 K at pressures greater than 52 GPa [4]. This is the first observation of the superconductivity in simple organic molecular crystals.

Pentacene ($C_{22}H_{14}$) is a five-ring polyacene molecule. The crystal structure of this compound is triclinic, with two molecules in a unit cell [5,6]. The resistivity of pentacene abruptly decreases from 10^{15} Ω cm at normal pressure to 10^{-1} Ω cm at 16 GPa [7,8]. A single crystal of pentacene shows a metallic behavior at around 19 GPa, and further, the solid-phase reaction is induced at very high pressures [7]. The phase transition in pentacene is found at around 0.2 GPa [6]. We have already studied the absorption spectra of oriented and amorphous films of tetracene and pentacene up to 0.6 GPa [9,10]. The absorption bands of both films rapidly shift to a longer wavelength region at high pressures. The Davydov splitting in the oriented film markedly increases with increasing pressure. This behavior is explained by the theory of molecular excitons [9–11]. Pentacene shows interesting physicochemical properties at high pressures.

Downloaded by [University of Haifa Library] at 10:10 22 August 2012

We have prepared new sapphire-anvil type and diamond-anvil cells to generate shear stress at high pressure. Using these cells, shear stress effects on the absorption spectra and X-ray diffraction of the one-dimensional metal complexes have been studied under high pressure [12,13]. It has been found that the electronic states of these complexes essentially change by applying shear deformation.

We have studied in detail the pressure effect on the absorption spectra in the oriented film of pentacene under hydrostatic conditions. Further, the electronic spectra in the oriented film of pentacene have been investigated under applied shear deformation and nonhydrostatic conditions. In this report, pressure and shear stress effects for the thin films of pentacene are discussed.

EXPERIMENTAL

The absorption spectra in thin films of pentacene were measured in detail with a sapphire-anvil cell in the 0- to 2-GPa region [14], and with a diamond-anvil cell in the 3- to 10-GPa region under hydrostatic conditions [4]. The optical system comprised a standard microscope and a spectrophotometer with an associated photodetection system. A fourier transform infrared spectrometry (FT-IR) (Nicolet MAGNA-IR760) was used for the measurement of the absorption spectra in the near infrared region. An oriented film of pentacene was prepared by evaporation onto the surface of an anvil in high vacuum. The thickness of the evaporated films is about 1500 Å. Fluorinert was used as the pressure medium.

The new sapphire-anvil cell designed to generate shear stress has already been prepared [12]. Figure 1 shows the schema to generate shear stress under high pressures. After two anvils are pressurized, shear stress is generated by the rotation of one anvil at high pressure. A radius (r) of the anvil top is 0.50 mm. The flat film of pentacene with the thickness of 1500 Å was prepared by evaporation onto one sapphire-anvil. The electronic absorption spectra of the thin film on the anvil were measured at several points along the radial direction under shear deformation. In this case, the gasket was not used in order to observe the remarkable shear stress effect. Thus, it is very difficult to determine the pressure by the ruby fluorescence method because the ruby is a very hard material. The pressure *vs*. wavelength curve for pentacene was studied under hydrostatic conditions. In a previous article, we reported that the absorption band around the center of the anvil is insensitive to shear stress [12]. Thus, the pressure in the cell under nonhydrostatic conditions was determined from the pressure *vs*. wavelength curve of pentacene [12,13].

Downloaded by [University of Haifa Library] at 10:10 22 August 2012

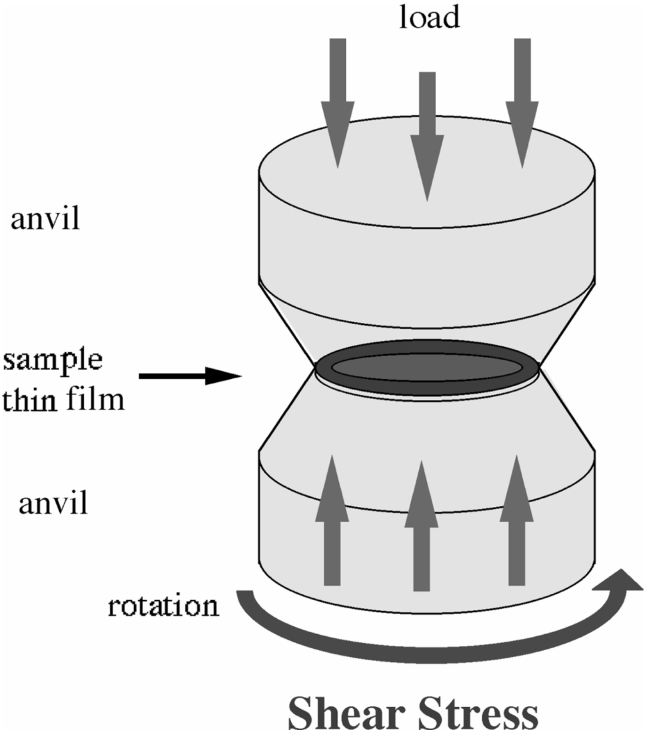


FIGURE 1 Schema to generate shear stress under high pressures.

RESULTS AND DISCUSSION

Pressure Effects on the Absorption Spectra in the Oriented Film of Pentacene

The orientation of pentacene and tetracene molecules in evaporated thin films is sensitive to the substrate temperature [10,15]. When the temperature on the substrate is greater than room temperature, the oriented film is easily grown. On the other hand, the amorphous film is prepared on the substrate cooled by liquid nitrogen. The interesting absorption bands in the oriented film of pentacene are observed at around 630 and 670 nm [10,15]. Both bands are the Davydov components of the 0-0 band. The magnitude of this splitting is about 920 cm^{-1}. This value is much larger than that of ordinary aromatic hydrocarbons. The sublimation energy of pentacene is largest among aromatic crystals with 22 carbon atoms [10]. The large value of the Davydov splitting arises from the strong intermolecular interactions between adjacent molecules at ambient pressure. On the other hand, the Davydov splitting is not observed in the amorphous film of pentacene [15].

The absorption spectra in the oriented film of pentacene were measured with the sapphire-anvil type cell up to 2 GPa under hydrostatic conditions. Figure 2 shows the absorption spectra in the oriented film of pentacene at high pressures. The absorption bands in visible region for this compound rapidly shift to longer wavelength region with increasing pressure. Both bands indicated by the arrows are due to the Davydov splitting. Two bands with the Davydov components are observed at around 645 nm and 720 nm under 1.1 GPa. The magnitude of the Davydov splitting is 1615 cm^{-1} at this pressure. This splitting rapidly increases with increasing pressure at the average rate of 630 cm^{-1}/GPa. The Davydov splitting of tetracene is also sensitive to pressures [10]. The rate of the increase of the Davydov splitting for

Downloaded by [University of Haifa Library] at 10:10 22 August 2012

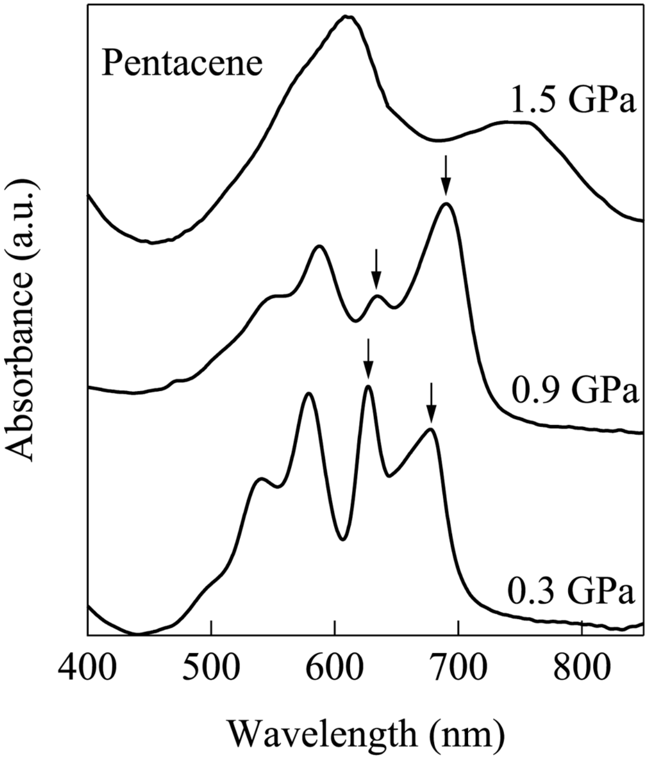


FIGURE 2 Pressure effects on absorption spectra for the oriented film of pentacene in 0- to 2-GPa region. Both bands indicated by the arrows are due to the Davydov splitting.

Downloaded by [University of Haifa Library] at 10:10 22 August 2012

pentacene is about two times larger than that of tetracene. The large value of the Davydov splitting and its pressure dependence for pentacene cannot be explained by the usual exciton theory in the weak coupling limit [10,11]. The intensity ratio of the both bands changes sharply with increasing pressure greater than 0.6 GPa. This mainly may be due to the rotation of the molecular plane in the unit cell at high pressures [9]. Two bands with the Davydov components becomes one at around 1.5 GPa. The Davydov splitting disappears at around this pressure. As mentioned previously, the 0-0 band in the amorphous film does not indicate the Davydov splitting [10,15]. The absorption spectrum at 1.5 GPa is similar to that of the amorphous film.

The absorption spectra in the oriented film of pentacene were measured with the diamond-anvil cell up to 10 GPa at room temperature. Figure 3 shows the absorption spectra of the thin film of pentacene in

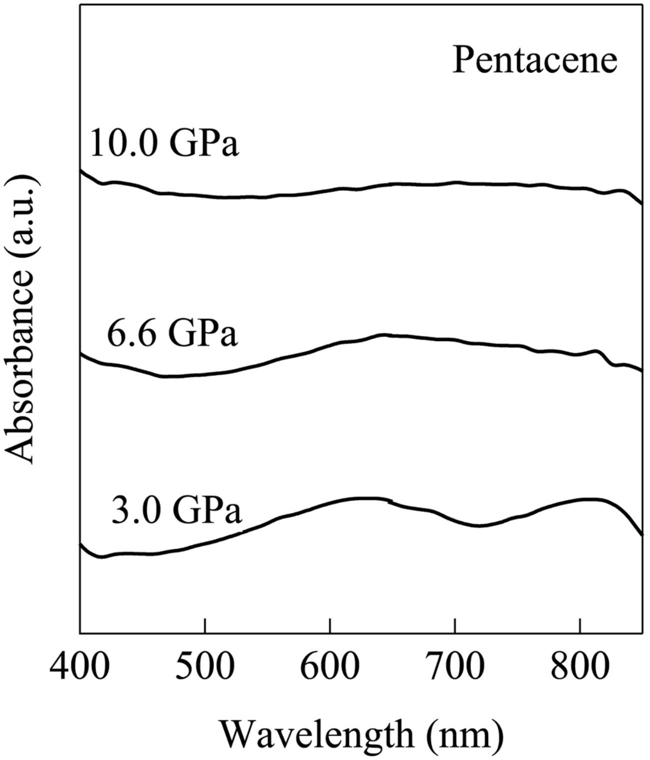


FIGURE 3 Pressure effects on absorption spectra for the oriented film of pentacene in 3- to 10-GPa region. There are small peaks in the 800- to 900-nm region in the figure. These are due to the light source (xenon lamp).

Downloaded by [University of Haifa Library] at 10:10 22 August 2012

the 3- to 10-GPa region. The absorption spectra become broader at higher pressures. The Davydov splitting is not found at around 3.0 GPa. The molecular arrangements in the oriented film of pentacene change to the amorphous state at around 1.5 GPa. When the pressure is increased further, the absorption peaks disappear at pressures greater than 6.6 GPa. When the pressure is reduced from 10 GPa to the ambient pressure, we cannot find the original absorption spectra in the oriented film of pentacene. The irreversible optical behavior is observed for this compound. The visible peaks in the absorption spectra of pentacene are due to the lowest energy transition of the π electrons. The disappearance of these bands at high pressure arises from the disturbance of the conjugated system. The resistivity of the polycrystalline pentacene abruptly decreases from $10^{15}\,\Omega\,\mathrm{cm}$ at normal pressure to $10^{-1}\,\Omega\,\mathrm{cm}$ at 16 GPa. However, the resistivity rapidly increases with time above 16 GPa [7,8]. This electrical behavior suggests that the solid-phase reaction is induced at high pressures. Bastron and Drickamer have reported that the solid-phase reaction may be due to the pressure-induced polymerization [16]. The disappearance of the absorption peaks observed for the thin film of pentacene occurs at around 6.6 GPa. This value is much lower than the pressure (16 GPa) observed in the polycrystalline pentacene. In general, the reactivity of thin films is much higher than that of the polycrystals. Thus, the solid-phase reaction is easily induced for the thin film of pentacene in the low-pressure region.

We have already reported the amorphization and the solid-phase reaction for the one-dimensional palladium complex, α-Pd(bqd)$_2$ at high pressures [17,18]. The powder X-ray diffraction of this complex has been studied with synchrotron radiation at high pressures. The intensity of many diffraction lines rapidly decreases and the width markedly broadens at pressures greater than 3.5 GPa; the amorphous patterns are observed. Many diffraction lines disappear at pressures greater than 6.8 GPa. When the pressure is reduced to ambient pressure, the original pattern is not recovered. The X-ray behavior is irreversible. The absorption band based on the 4d–5p transition fades out at higher pressures. The electrical resistivity increases rapidly with time at high pressure [17]. These electrical, optical, and structural properties at high pressure arise from the pressure-induced amorphization and solid-phase reaction. A molecule of Pd(bqd)$_2$ is the long molecule with the length of more than 10 Å. Thus, the crystal structure of α-Pd(bqd)$_2$ is anisotropic at ambient pressure. The structural anisotropy becomes remarkable at high pressures. We suggest that the amorphization and solid-phase reaction for α-Pd(bqd)$_2$ are induced by the increase of asymmetric intermolecular interactions at higher pressures [18].

The crystal structure of pentacene is triclinic, with two molecules in a unit cell. This structure resembles that of anthracene. In particular, the molecular arrangements along the a- and b-axes are very similar to those of anthracene. The pressure dependence of the lattice parameters for anthracene has been investigated at room temperature [19]. The a- and b-axes of this hydrocarbon are easily compressed with increasing pressure; on the other hand, the c-axis is less compressible. The similar lattice constant *vs.* pressure curves are also expected for pentacene though the X-ray diffraction has not been studied at high pressure. Thus, the intermolecular interactions in the a–b plane for pentacene increase remarkably with increasing pressure. The molecular arrangements along the c-axis are composed of long molecules of about 12.3 Å. The compressibility of the c-axis for pentacene would be smaller than that of anthracene. The structure of pentacene must become more anisotropic at higher pressures. As mentioned previously, this behavior is similar to that of α-Pd(bqd)$_2$ [18]. The asymmetric intermolecular interactions for pentacene would also be expected at higher pressures. Thus, we suggest that the asymmetric intermolecular interactions are closely related to the amorphization in the pentacene film at high pressures. Recently, Bustingorry and Jagla have discussed the mechanism of the pressure-induced amorphization [20].

Downloaded by [University of Haifa Library] at 10:10 22 August 2012

Effect of Shear Stress on the Absorption Spectra in the Oriented Film of Pentacene

The shear stress effect on absorption spectra in the thin film of one-dimensional bis(diphenylglyoximato)platinum(II), Pt(dpg)$_2$, have been studied under high pressure [12,13]. After one sapphire-anvil is rotated by applied force to generate shear stress at 0.4 GPa, the color of the thin film changes remarkably from green to yellow at the outer part on the anvil, but the color at the center is green, insensitive to the shear stress. Absorption spectra at the outer part change markedly, the intensity of the d–p band decreases sharply, and this peak abruptly shifts to the near-infrared region. The shear stress effect on the Raman spectra of Pt(dpg)$_2$ has also been studied at high pressure. The Raman shift is sensitive to shear stress at the outer part [21]. Powder X-ray diffraction profiles of the thin film of Pt(dpg)$_2$ at center (green) and outer (yellow) parts have been studied under shear deformation. The 110 and 200 lines at the outer part shift to the lower d-value region [13]. This behavior corresponds to the shift of the absorption peak at the outer part.

Downloaded by [University of Haifa Library] at 10:10 22 August 2012

PLATE 1 a) Photographs of the thin film of pentacene at ambient pressure; b) photographs of the thin film of pentacene applying shear stress of less than 2 GPa.

We have observed *in situ* shear stress and pressure effects on the oriented film of pentacene in the sapphire-anvil cell under the microscope. The pressure in the cell is increased up to 2 GPa. Then, as shown in Fig. 1, one sapphire-anvil is rotated by applied force to generate shear stress at this pressure. We can see the region changed by shear stress with the naked eye. Plate 1 shows photographs of the thin film of pentacene by applying shear stress of less than 2 GPa. The color of the thin film changes remarkably from blue to yellow at the outer part on the anvil, but the color at the center is blue, insensitive to shear stress. The yellow region at the outer part is remarkably observed at around about 80% of the radius (0.8 r). The value of the shear deformation can be estimated by the formula [22]

$$\gamma = \frac{\varphi \mathrm{r}}{\mathrm{h}}, \tag{1}$$

where γ is the shear deformation, φ the angle of the anvil-rotation in rad, r is the radius of the sample in micrometers, and h the thickness of the sample in micrometers. The shear stress effects become stronger at the outer part of the anvil. Thus, the boundary based on the color change appears under the shear deformation.

Figure 4 shows absorption spectra of the center (blue) part and the outer (yellow) part in Plate 1b for the thin film of pentacene. The spectrum of the dotted line (blue part) is similar to that observed at around 1.5 GPa in Fig. 2. The solid line shows the absorption spectrum at the outer (yellow) part in Plate 1b. The intensity of the absorption band

Downloaded by [University of Haifa Library] at 10:10 22 August 2012

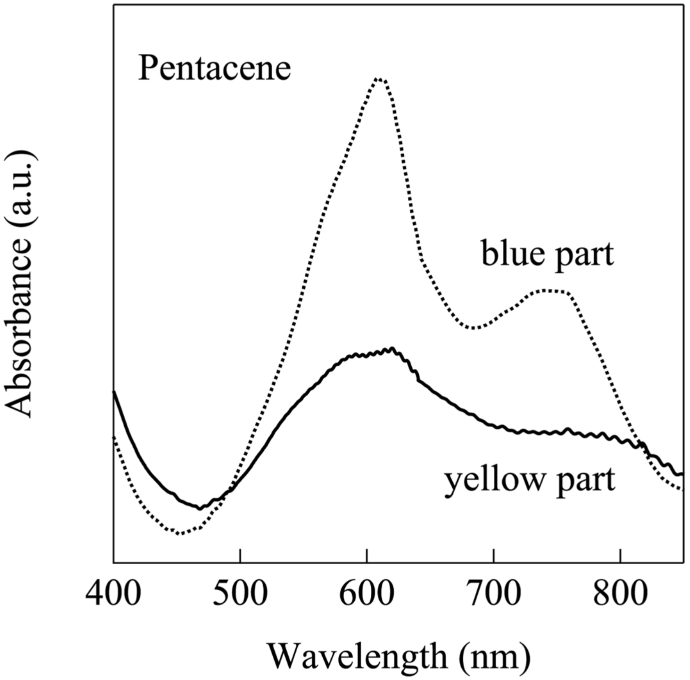


FIGURE 4 Absorption spectra of the center (blue) part and the outer (yellow) part in Plate 1b for the thin film of pentacene; dotted line: center (blue) part, solid line: outer (yellow) part.

sharply decreases and the width vastly broadens in the outer part. Amorphization of the oriented film is accelerated under shear deformation. On the other hand, the intensity of the absorption band below 400 nm increases in the outer part. The color at the outer part changes from blue to yellow. These results suggest that the conjugated system in pentacene is partly broken by shear stress. After shear stress is reduced, the original spectrum of pentacene is not recovered completely. The solid-phase reaction must be induced by shear stress for a part of the film. By applying shear stress, the amorphization and solid-phase reaction for pentacene occurs in low-pressure region. Pentacene is a long molecule of about 12.3 Å. The lattice constants of pentacene must show the anisotropic decrease by shear stress. Thus, physicochemical properties of pentacene are very sensitive to shear stress.

The shear stress effect on X-ray diffraction of GaSb with a diamond-anvil cell has been studied at room temperature [23]. The diffraction pattern of GaSb markedly changed from the crystalline state to the amorphous phase by applying shear deformation under high pressure. The stress-induced amorphizationis also observed for the inorganic material. Thus, the study of the shear stress effect on various materials under high pressure is an important goal for solid state physics and chemistry.

ACKNOWLEDGMENTS

This work was partly supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan: No. 17540310 (I. S.) and No. 17750186 (K. T.).

REFERENCES

[1] Harada, Y., Maruyama, Y., Shirotani, I., & Inokuchi, H. (1964). *Bull. Chem. Soc. Jpn.*, *37*, 1378–1380.
[2] Hummer, K., Puschnig, P., & Ambrosch-Draxl, C. (2003). *Phys. Rev.*, *B67*, 184105 (1–7).
[3] Onodera, A., Shirotani, I., Inokuchi, H., & Kawai, N. (1974). *Chem. Phys. Lett.*, *25*, 296–298.
[4] Shirotani, I., Hayashi, J., Yakushi, K., Takeda, K., Yokota, T., Shimizu, K., Amaya, K., Nakayama, A., & Aoki, K. (2001). *Physica B: Condensed Matter*, *304*, 6–11.
[5] Campbell, R. B., Robertson, J. M., & Trotter, J. (1961). *Acta Cryst.*, *14*, 705–711.
[6] Farina, L., Brillante, A., Della Valle, R. G., Venuti, E., Amboage, M., & Syassen, K. (2003). *Chem. Phys. Lett.*, *375*, 490–494.
[7] Aust, R. B., Bentley, W. H., & Drickamer, H. G. (1964). *J. Chem. Phys.*, *41*, 1856–1864.
[8] Shirotani, I., Inokuchi, H., & Minomura, S. (1966). *Bull. Chem. Soc. Jpn.*, *39*, 386–390.
[9] Ohigashi, H., Shirotani, I., Inokuchi, H., & Minomura, S. (1965). *J. Chem. Phys.*, *43*, 314–315.
[10] Shirotani, I., Kamura, Y., & Inokuchi, H. (1974). *Mol. Cryst. Liq. Cryst.*, *28*, 345–353.
[11] Davydov, A. S. (1961). *Theory of Molecular Excitons*, trans. M. Kasha & M. Opepenheimer, McGraw-Hill Book Company: New York.
[12] Shirotani, I., Hayashi, J., Hirano, H., Kawamura, H., Inokuchi, M., Yakushi, K., & Inokuchi, H. (2003). *Proc. Japan Acad. Ser., B 79*, 267–273.
[13] Shirotani, I., Hayashi, J., Takeda, K., Kawamura, H., Inokuchi, M., Yakushi, K., & Inokuchi, H. *Mol. Cryst. Lig. Cryst.*, in press.
[14] Takeda, K., Shirotani, I., & Yakushi, K. (2003). *Synthetic Metals*, *133–134*, 415–416.
[15] Kamura, Y., Shirotani, I., & Inokuchi, H. (1974). *Chem. Lett.*, 627– 630.
[16] Bastron, V. C. & Drickamer, H. G. (1971). *J. Solid State Chem.*, *3*, 550–563.
[17] Takeda, K., Shirotani, I., Yakushi, K., & Yamashita, M. (2000). In: *Science and Technology of High Pressure* (*Proceedings of AIRAPT-17*), Manghnani, M. H., Nellis, W. J., & Nicol, M. F. (Eds.), Universities Press: Hyderabad, India, vol. 2, pp. 998–1001.
[18] Takeda, K., Shirotani, I., Hayashi, J., Fukuda, H., & Ito, K. (2006). *Mol. Cryst. Lig. Cryst.*, *452*, 113–122.
[19] Oehzelt, M., Resel, R., & Nakayama, A. (2002). *Phys. Rev., B 66*, 174104 (1–5).
[20] Bustingorry, S. & Jagla, E. A. (2005). *Phys. Rev., B 71*, 224119 (1–12).

Downloaded by [University of Haifa Library] at 10:10 22 August 2012

[21] Inokuchi, M., Nagaoka, A., Yamamoto, M., Shirotani, I., Hayashi, J., Yakushi, K., Kawamura, H., & Inokuchi, H. (2005). *Synth. Metals*, *152*, 421–424.

[22] Eremets, M. I. (1996). *High Pressure Experimental Methods*, Oxford University Press, Oxford, p. 106.

[23] Aleksandrova, M. M., Blank, V. D., Golobokov, A. E., Konyaev, Y. S., Zerr, A. Y., & Estrin, E. I. (1988). *Phys. Stat. Sol.*, *105*, K29–K32.

Downloaded by [University of Haifa Library] at 10:10 22 August 2012