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Effect of Pressure on Electrical and Optical Behaviour of Quaterrylene, $C_{40}H_{20}$

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The temperature dependence of the electrical resistance of the compressed quaterrylene was studied over the temperature range from 300°K to 1000°K under high pressure. The intrinsic energy gap and also the extrinsic energy gap, which is formed by oxygen adsorbed onto the organic crystals, decreased with an increase in the pressure. These changes were dependent linearly on the pressure. The pressure effect on the absorption spectra of the evaporated film and that on the spectra of the solid solution of quaterrylene were observed. It was found that the value of the peak-shift, 8—9×10^{-6} eV/bar, is comparable to the contraction of the thermal energy gap, 9×10^{-6} eV/bar, determined from the temperature dependence of the electrical resistance.

The effect of pressure on the electrical resistance of the organic semiconductors has been studied:(1,2) The variation in the resistance of the various polycyclic aromatic crystals with pressure can be interpreted to show that the energy gaps between the valence and conduction bands of these compounds decrease with an increase in the pressure at the rate of approximately 2—9×10^{-6} eV/bar.(3,4)

Quaterrylene ($C_{40}H_{20}$), used in this study, is a very stable compound and has a high electrical conductivity under atmospheric pressure.(5) Recently, Maruyama has reported that the semiconductive character of the quaterrylene film is an extrinsic one at an atmospheric pressure at which adsorbed oxygen forms an acceptor level.(6) Further, he assumed that the intrinsic energy gap, observed under a high vacuum, is 1.7 eV; this corresponds with the absorption band at ~760 mμ of the quaterrylene film.

In this report, we will discuss the pressure dependence of the intrinsic and also the extrinsic

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1) H. Inokuchi, This Bulletin, **28**, 570 (1955); H. Inokuchi, I. Shirotani and S. Minomura, *ibid.*, **37**, 1234 (1964).

2) G. A. Samara and H. G. Drickamer, *J. Chem. Phys.*, **37**, 474 (1962).

3) Y. Harada, Y. Maruyama, I. Shirotani and H. Inokuchi, This Bulletin, **37**, 1378 (1964).

4) I. Shirotani, H. Inokuchi and S. Minomura, *ibid.*, **39**, 386 (1966).

5) Y. Maruyama, H. Inokuchi and Y. Harada, *ibid.*, **35**, 1559 (1962).

6) Y. Maruyama and H. Inokuchi, *ibid.*, **39**, 1418 (1966).

behaviour of the energy bands and of the optical absorption spectra of quaterrylene.

Experimental

A tetrahedral anvil-type high-pressure apparatus similar to those described by Hall was used for this study.[7] The present apparatus consisted of four 250 mm hydraulic rams with 20 mm triangular tungsten carbide anvils, which were driven together simultaneously on a pyrophyllite-tetrahedron sample assembly with an edge length of 25 mm. Figure 1 illustrates the sample assembly used for the electrical resistance measurements. A tublar graphite furnace bounded by graphite end plugs was placed nearly at the centre of gravity of the pyrophyllite-tetrahedron and was used for heating the sample. The electric power was applied to the graphite furnace through molybdenum tabs which made contact with the face of a pair of anvils. The abrupt changes in the electrical resistances of Bi(I–II), Tl(II–III), and Ba(II–III) at their phase transitions were used to calibrate the pressure applied to the pyrophyllite-tetrahedron. The sample was studied as a powder which was fused into flat plotelets by the applied pressure. The details of the experimental technique have already been reported.[8]

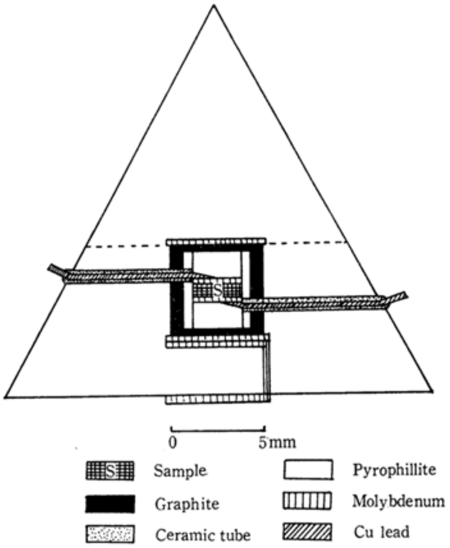

Fig. 1. The sample assembly.

The measurement of the absorption spectra was carried out at room temperature with a hardened-steel optical vessel, which had two sapphire windows.[9] A hydrostatic pressure was applied by means of a pressure-transmitting medium, kerosene, up to 7 kbar.

The thin quaterrylene films were grown on a NaCl single crystal plate by sublimation in a vacuum. The quaterrylene-polystyrene solid solution was prepared by the polymerization of purified monomer styrene, in which a trichlorobenzene solution of quaterrylene was mixed at an elevated temperature.

Results

Figure 2 shows the relation between the logarithm of the electrical resistance and the reciprocal temperature for the compressed quaterrylene at 50 kbar. The behaviour of the curve was reproducible against the applied pressure and also the temperature, even over 600°C; this suggests that no chemical change occurred as a result of this treatment.

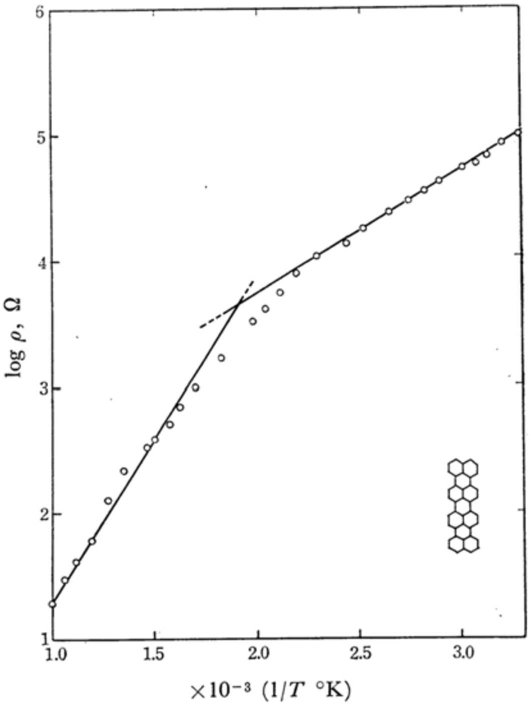

Fig. 2. The electrical resistance of quaterrylene as a function of temperature at 50 kbar.

Under 50 kbar, the energy gap calculated from the temperature dependence of the conductivity over the temperature range of 300—500°K, 0.39 eV, is, on the basis of previous work,[6] assumed to be an extrinsic one, the energy depth of the acceptor level measured from the top of the valence band. This is denoted as E_A. On the other hand, the energy gap estimated from the temperature-conductivity relation, in Fig. 2, at 550—1000°K was 1.24 eV under the same pressure. This gap, E_g, may be the intrinsic one.[6] Both gaps decreased with an increase in the pressure: Figure 3 shows the plots of E_g and E_A as functions of the pressure. These relations were linear, at least up to 50 kbar.

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[7] F. P. Bundy, "Modern Very High Pressure Techniques," ed. by R. H. Wentorf, Butterworth, London (1962), p. 1.

[8] S. Akimoto and H. Fujisawa, *J. Geophys. Res.*, **70**, 443, 1969 (1965).

[9] H. Ohigashi, I. Shirotani, H. Inokuchi and S. Minomura, *J. Chem. Phys.*, **43**, 314 (1965).

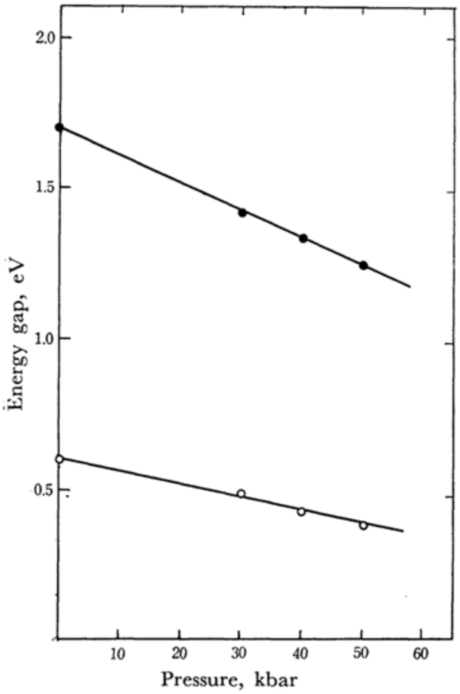

Fig. 3. The pressure dependence of the energy gap.

Table 1 shows the values of E_g and E_A and also the values of the electrical resistivity under high pressure.

TABLE 1. THE PRESSURE DEPENDENCE OF THE SEMICONDUCTIVITY OF QUATERRYLENE

Pressure (bar)	E_g (eV)	E_A (eV)	ρ (Ωcm)
1	1.7	0.6	10^{10} (powder) 10^6 (single)
30×10^3	1.4_2	0.4_9	9.9×10^5
40×10^3	1.3_3	0.4_2	8.7×10^5
50×10^3	1.2_4	0.3_9	5.4×10^5

The electronic absorption spectra of the evaporated microcrystalline film and of the solution of quaterrylene have already been reported.[5,6] These absorption bands revealed a red-shift with an increase in the pressure except for the large peak at 540 mμ; this peak did not depend on the pressure, at least up to 7 kbar. Similar phenomena have been observed in the evaporated film of violanthrone ($C_{34}H_{16}O_2$). The experimental results concerning this optical bahaviour will be reported and discussed in detail elsewhere.[10] In Fig. 4, the changes in the wave number of the absorption band are plotted as a function of the applied pressure. The energy shifts are approximately proportional to the applied pressure.

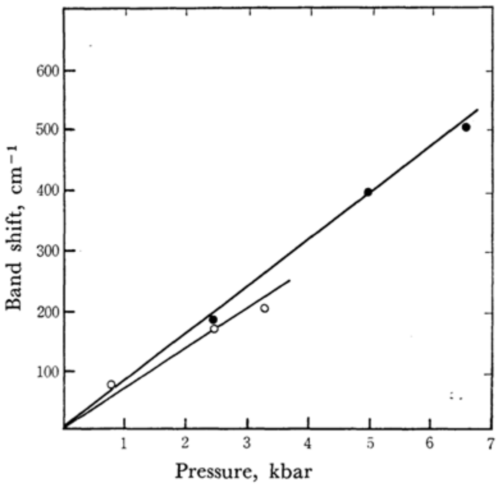

Fig. 4. The pressure dependence of the optical absorption band ○ for quaterrylene-polystyrene solid solution, ● for quaterrylene thin film.

Discussion

Certain types of impurities and imperfections may drastically affects the electrical properties of organic semiconductors. Recently, we found that an oxygen adsorbed onto organic crystals forms impurity levels[6,11]; the semiconductivity of the quaterrylene film is especially sensitive to oxygen. Under atmospheric circumstances, this compound is a p-type semiconductor due to an oxygen impurity level which lies 0.6 eV above the valence band.

From Fig. 3 we may find that the values of E_A and E_g decrease with an increase in the pressure at the rates of:

$$\left(\frac{dE_g}{dp}\right)_T = -9\times10^{-6}\ \mathrm{eV/bar} \qquad (1)$$

and

$$\left(\frac{dE_A}{dp}\right)_T = -4._2\times10^{-6}\ \mathrm{eV/bar} \qquad (2)$$

It is interesting to note that the pressure dependence of E_g is larger than that of E_A.*1

The average rate of the red-shift of absorption spectra for the polycyclic alternant hydrocarbons against the applied pressure was:

$$\left(\frac{d\nu_m}{dp}\right)_T = -8._5\times10^{-6}\ \mathrm{eV/bar} \qquad (3)$$

for the quaterrylene-polystyrene solid solution. For the adsorption band at 760 mμ of the evaporated film, on the other hands, the rate was about:

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[10] I. Shirotani, T. Kajiwara and H. Ohigashi, to be published.

*1 This difference seems to show that the interaction between quaterrylene molecules becomes stronger than that between oxygen and quaterrylene molecules with an increase in the pressure.

[11] G. H. Heilmeier and S. E. Harrison, *Phys. Rev.*, **132**, 2010 (1963).

$$\left(\frac{d\nu_s}{dp}\right)_T = -9._4 \times 10^{-6}\,\mathrm{eV/bar} \tag{4}$$

as is shown in Fig. 5.

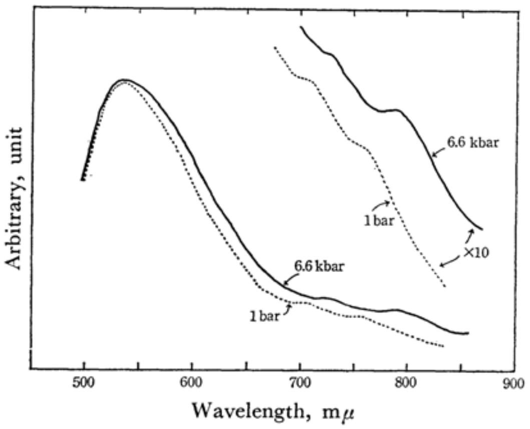

Fig. 5. The pressure dependence of the absorption spectra of the quaterrylene film.
---- at 1 bar, —— at 6.6 kbar.

Rice and Jortner proposed that the major part of the red-shift of the solid solution consists of the solvent shift which arises from a dispersion force.[12] In the crystal, not only the solvent shift but also the exciton shift must be considered.[9,12] Equations (3) and (4) show, however, that the exciton shift of the crystal can be neglected, for the values of the red-shift of the two samples, in solution and in the solid state, have similar values.

Further, as is shown in Eqs. (1) and (4), the red-shift of the peak at 760 mμ is similar in manner to those of the contraction of the energy gap, E_g. This behaviour will be useful in analyzing the mechanism of the carrier generation in the organic crystals.

The authors wish to thank Professor Shigeru Minomura for his helpful discussion, and also Dr. Hideyuki Fujisawa for his kind assistance throughout this work.

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12) S. A. Rice and J. Jortner, "Physics of Solids at High Pressures," ed. by C. T. Tomizuka and R. M. Emrick, Academic Press, New York (1966), p. 63.