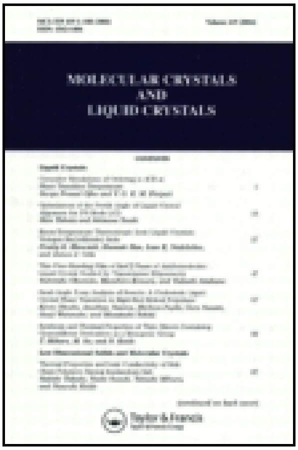

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Pressure dependence of the photoabsorption of polyacety-lene

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PRESSURE DEPENDENCE OF THE PHOTOABSORPTION OF POLYACETYLENE

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The optical absorption spectra of pure cis and trans-polyacetylene at various hydrostatic pressures, in the region 0–9 Kbar, are reported. We find a "red shift" of the absorption edge indicating a reduction of the energy gap as a function of pressure. At 9 Kbar, E_g is reduced by about 0.1 eV. In addition a decrease in the slope of $\alpha(\omega)$ is observed at high pressures. These changes result from an increase in the interchain transfer integrals, $t_\perp$. Comparison of the data with the results of tight binding calculations lead to estimates of $t_\perp \simeq 0.025 - 0.05$ eV (ambient) and $t_\perp/t_0 \simeq 10^{-2}$.

It is well known that a quasi-one-dimensional (1d) system possesses a Peierls gap , E_g, in its electronic band structure and is therefore a semiconductor below the Peierls transition temperature. For a strictly 1d system, the electronic density of states diverges at the top of the valence band and at the bottom of the conduction band. For real three-dimensional (3d) solids, however, the singularities in the density of states are removed by including the weak interchain transfer integrals transverse to the chain direction , $t_\perp$. In this paper we present a study of the "3d effects" on the electronic band structure of the quasi-1d conductor, $(CH)_x$. We have measured the optical absorption of trans and cis-$(CH)_x$ at ambient and various hydrostatic pressures. Application of external pressure is expected to increase the 3d interchain coupling since the interchain distances are reduced so that $t_\perp$ is enhanced. In particular, in $(CH)_x$, due to the anisotropy of the compressibility tensor ($\kappa_\perp \gg \kappa_\parallel$, Van der Waals interaction interchain as compared with covalent bonds intrachain), we expect that hydrostatic pressure will result in a significant decrease in the interchain distances while leaving the intrachain atomic spacing essentially unchanged.

The optical absorption coefficient is proportional to the joint density of states of the conduction and valence bands. At T = 0, where only vertical transitions are allowed, the optical absorption is directly proportional to the density of states $N(\varepsilon)$. At T > 0 there is a possibility of indirect gap absorption, which requires phonon absorption or emission; with a characteristic temperature dependence. We therefore present a comparison of the experimental results of the photoabsorption to the density of states obtained through a simple tight-binding band structure calculation. The calculated results agree with the experimental findings; the analysis yields a semi-quantitative estimate of $t_\perp$.

In Figure 1 and 2 we present the photoabsorption spectra of trans-$(CH)_x$ and cis-$(CH)_x$, respectively, at various hydrostatic pressures. We find a large "red shift" of the absorption edge, which indicates the pressure effect on the band structure of the polymer. The onset of the electronic interband transition shifts to lower energies. At a pressure of about 9 Kbar the energy gap is reduced, in both isomers, by about 0.1 eV. This is a relatively large effect considering that the estimated value of $t_\perp$ at ambient pressure is only about 0.4 eV. In addition, we observe a change in slope for the absorption edge as a function of pressure; the slope decreases at higher pressures.

The data in Fig. 2 for $\alpha(\varepsilon)$ of the cis-$(CH)_x$ indicates the existence of some trans-$(CH)_x$ in the measured film. We infer that from the lower "knee" in the absorption data located in the energy region which matches absorption of the trans isomer. This contribution from the trans-$(CH)_x$ is unavoidable since exposure of the film to room temperature results in partial isomerization of about 10-15%.

The high pressures were achieved with a teflon cell. The pressure medium used was Flourinert, which was found through separate experiments to transfer hydrostatic pressures into the fibrillar $(CH)_x$ films. The monochromatic light from the spectrometer was coupled to the sample, which is located in the pressure cell, by optical fibers. The photodetector was placed behind the sample (in the pressure cell) for good efficiency of light collection. The $(CH)_x$ samples were thin films polymerized on thin glass slides (typical sample thick-

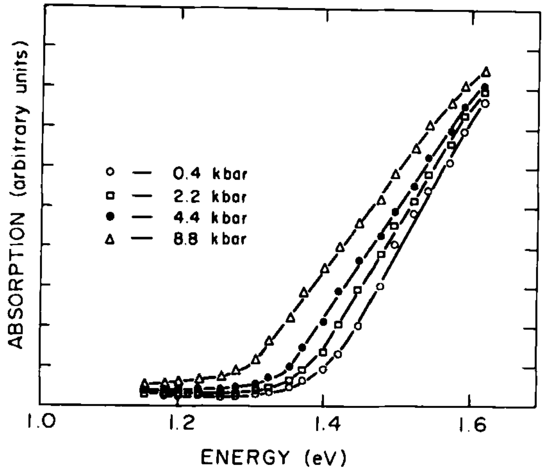

FIGURE 1 Photo-absorption spectra of trans-$(CH)_x$ at various hydrostatic pressures.

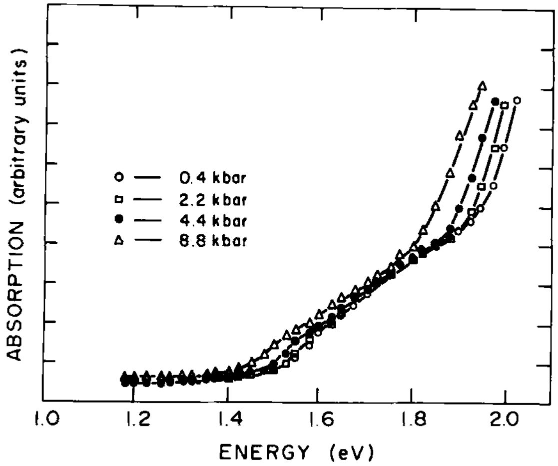

FIGURE 2 Photo-absorption spectra of cis-$(CH)_x$ at various hydrostatic pressures.

ness of ~ 2500Å). Rather thick samples were initially chosen for optimal sensitivity to the absorption coefficient, $\alpha(\omega)$ near the onset of the interband transition. With this thickness, the films become essentially opaque near the absorption maximum.

The data at each pressure were normalized to the source intensity measured by the detector without the sample. At the end of the pressure cycle, $\alpha(\omega)$ was remeasured at ambient pressure. The results were identical with those obtained before the application of high pressure. Thus the shift of the edge is a true indication of the pressure dependence, and does not arise from an irreversible charge in the sample.

In order to obtain estimates of the interchain transfer integrals, we calculated the joint density of states for model quasi-1d solids, including interchain coupling. The 1d dispersion relation is given by

$$\begin{aligned}\varepsilon_{\pm}(k) &= \varepsilon_0 \pm [2t_0^2 + 2t_1^2 + 2(t_0^2 - t_1^2)\cos 2kc]^{1/2} \\ &\equiv \varepsilon_0 + \varepsilon(k_z)\end{aligned} \qquad (1)$$

where c is the average distance between c-atoms along the chain, $t_0 + t_1$ is the transfer integral appropriate to the shorter c-c bond and $t_0 - t_1$ is the transfer integral appropriate to the longer c-c bond in the dimerized polyene chain. The total band width of the two energy bands is $W = 4t_0 \simeq 10$-12 eV, and the energy gap at $\pi/2c$ is $E_g = 4t_1$.

The solution for the energy bands[8] for a tetragonal array of chains with nearest chain coupling only is given by

$$\begin{aligned}\varepsilon(k_x, k_y, k_z) &= \varepsilon_0 \pm \Sigma(k_x, k_y) \pm [\varepsilon^2(k_z) + \Sigma^2(k_x, k_y) \\ &+ 8t_0\Sigma(k_x, k_y)\cos^2 k_z c + 8t_1\Sigma(k_x, k_y)\sin^2 k_z c]^{1/2}\end{aligned} \qquad (2)$$

where $\Sigma(k_x, k_y) = t_y \cos k_y b + t_x \cos k_x a$ and $\varepsilon(k_z)$ is defined in equation 1. Assuming $t_x = t_y \equiv t_\perp$, the minimum energy gap is given by

$$E_g = 4t_1 - 8t_\perp \qquad (3)$$

The joint density of states has been numerically calculated for the above 3d lattice. In Fig. 3 the results, for two values of $t_\perp$ are shown in the region of the onset of the interband transition. To match the 1d energy gap of <u>trans-</u>

(CH)$_x$, we have chosen t_1 = 0.4 eV. The value of $t_\perp$ are 0.02 and 0.04 eV, which we find to span the range of the experiments of pressures of 0-9 kbar.

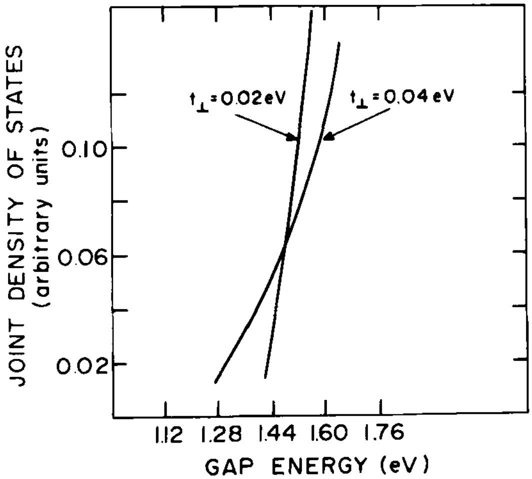

FIGURE 3 Results of tight-binding calculation of the joint density of states, for two different values of $t_\perp$, in the energy region near the onset of the interband transition.

There is a good agreement between the experimental results and the tight-binding model predictions. These latter results also indicate that upon increasing $t_\perp$ the energy gap decreases and that the slope of $\alpha(\omega)$ decreases as found in Figs. 1 and 2. The variation of the energy gap for trans-(CH)$_x$ as a function of pressure is shown in Fig. 4. The values for $E_g(P)$ were obtained by linearly extrapolating the experimental curves (Fig. 1 and 2) to $\alpha(\omega) \rightarrow 0$.

Finally we estimate the transfer integrals for trans-(CH)$_x$. From the shape of $\alpha(\omega)$ in comparison with the theoretical joint density of states we conclude that (for ambient pressure) t_1 = 0.4-0.45 eV and $t_\perp$ = 0.025 - 0.05 eV. Since the intrachain transfer integral, t_0, is about 3 eV, the band structure of polyacetylene is highly one-dimensional; $t_\perp / t_0 \sim 10^{-2}$.

If we assume the spatial dependence of $t_\perp$ (x) to be of the form

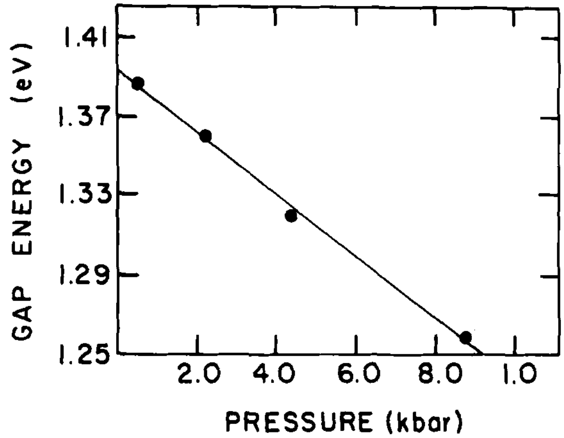

FIGURE 4 Pressure dependence of the energy gap of trans-$(CH)_x$

$$t_\perp = t_\perp(o)e^{-\Delta x(P)/a}$$

and if we assume that the applied pressure results in reducing only the interchain distances, $\Delta x/x = \frac{1}{3}K\ P$ where K is the compressibility[3] ($K \simeq 5 \times 10^{-3}$) then the slope of Fig. 4 gives a ~ 0.15 - 0.3Å. A more detailed analysis can be carried out in future using the known crystal structure and stacking of the $(CH)_x$ chains.

In summary, we find large pressure effects on the optical absorption spectra of polyacetylene. At high pressures the interchain distances are reduced and the transverse electronic transfer integrals are enhanced. Analysis of the data leads to values for the interchain coupling consistent with a highly anisotropic quasi-one-dimensional band structure.

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