Photoconductivity and optical absorption coefficients near the band edge of phenazine-tetracyanoquinodimethane

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The photoconductive technique of Moss and Hawkins is used to obtain the room-temperature optical absorption coefficients near the band edge of phenazine-tetracyanoquinodimethane. From the analysis of the results we deduced that this organic solid has a direct as well as an indirect gap whose values are 1.96 ± 0.01 eV and 1.78 ± 0.01 eV, respectively. We also found the energy of the phonon involved in the indirect transitions to be 0.063 ± 0.01 eV.

I. INTRODUCTION

In order to obtain additional information concerning the physical properties of the quasi one-dimensional organic compound phenazine-tetracyanoquinodimethane (TCNQ) some of the electrical and optical properties of this crystal are studied in this work. The electrical transport properties reported in a previous paper[1] were obtained once we were able to simulate a charge-carrier injector via a cw He-Ne laser. Due to the geometry of the single crystals (needlelike with the c axis along the axis of the needle; typical dimensions $5 \times 0.5 \times 0.2$ mm^3) we can measure the electrical and optical properties along the c axis of the sample. As a natural extension of the previous work we studied the photoresponse of the sample as a function of the wavelength for a fixed applied voltage; the spectral distribution of the photoconductivity follows qualitatively the phenomenolocal model of de Vore.[2] By means of the technique of Moss and Hawkins[3] it was possible to measure the optical absorption coefficient in the vicinity of the band edge along the c axis of the sample. It is found from the results that the sample has an indirect as well as a direct band gap, and we determined the values of the direct energy gap E_{gd}, indirect energy gap E_{gi}, and energy of the phonon involved in the indirect transitions E_{ph}. We identify this phonon as the one assigned to phenazine in the Raman scattering work done in phenazine-TCNQ by Kuzmany and Elbert.[4]

II. EXPERIMENTAL DETAILS

The single crystals of phenazine-TCNQ used in this work were grown in the same batch as those from Ref. 1. The electrical contacts were done by means of silver paste. The measurements were carried out in a normal environment and at room temperature. The experimental setup for both the photoconductivity and the absorption coefficient measurements consisted of a cell containing the sample in series with a Keithley 246 power supply and a PAR model No. 124A lock-in amplifier with a model No. 184 current preamplifier. The source of light was a halogen tungsten lamp monochromatized by a Zeiss M4QIII monochromator. The light was focused with conventional optics and the calibration of the light intensities was done using a standard silicon photocell. The slit of the monochromator was set at such a value as to give a resolution of 0.007 eV at 1.952 eV (635 nm).

III. RESULTS AND DISCUSSION

Figure 1 shows the photoresponse[5] of a sample which was illuminated uniformly perpendicularly to the c axis of the crystal. We can see that the spectral distribution of the photoconductivity follows qualitatively the model of de Vore.[2] We are not concerned in this paper with the quantitative study, this being a subject for a future work. In the same figure we also show the photoresponse of a crystal when it is illuminated along the c axis; that is, using the geometry of Moss and Hawkins.[3] We can see that the

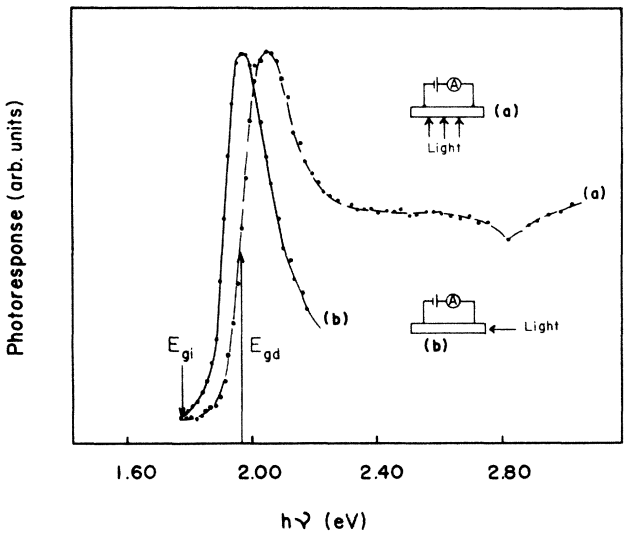

FIG. 1. Photoresponse as a function of the photon energy. Curve (a) illustrates the case of photoconductivity with uniform illumination of the sample as seen in the inset (a). Curve (b) shows the photoresponse for the case of illumination along the c axis as shown in inset (b). Applied voltage 200 V.

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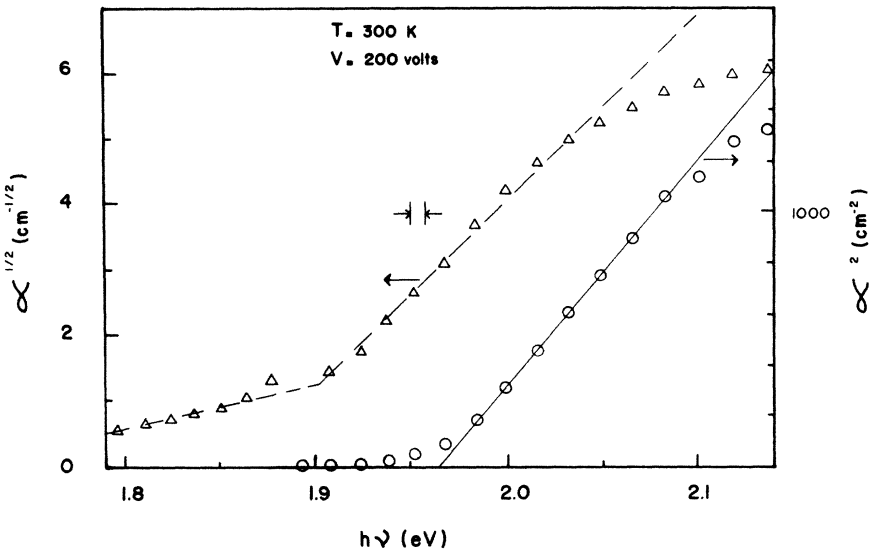

FIG. 2. Dependence of $\alpha^{1/2}$ vs $h\nu$ for the case of photoconductive measurements using the (b) geometry of Fig. 1. The applied voltage was 200 V, the full and the interrupted lines are the least-squares fit to $\alpha^2 = Ah\nu + B$ and $\alpha^{1/2} = Ah\nu + B$, respectively.

photoresponse is sharper than in the previous case of uniform illumination, and also that there is an energy shift in the position of the maximum of photoresponse. This is due to the fact that now there is a competition between the generation of carriers in the sample and the absorption of light along the length of the sample. As we can see from the equation giving the photoresponse in the Moss-Hawkins geometry,[3] the energetic position of the maximum of the photoresponse is a function of the difference $t_2 - t_1$ of the electrical contacts along the c axis.

Following Moss and Hawkins[3] we analyze the photoconductivity results using the analytical expression for the calculation of the absorption coefficient

$$\frac{\beta^\beta S(h\nu)}{\gamma^\gamma S_{\max}} = (e^{-\alpha t_1} - e^{-\alpha t_2}) , \tag{1}$$

where $S(h\nu)$ is the photoresponse at the energy $h\nu$, $S_{\max}$ is the maximum photoresponse, t_1 is the position of the contact near to the light entrance to the crystal, t_2 the position of the contact along the c axis, and α is the optical absorption coefficient, $\gamma = t_2/(t_2 - t_1)$ and $\beta = t_1/(t_2 - t_1)$. We solve Eq. (1) numerically for the range of energies used and find the absorption coefficient as a function of the energy of the photon. Figure 2 shows the plot of $\alpha^{1/2}$ vs

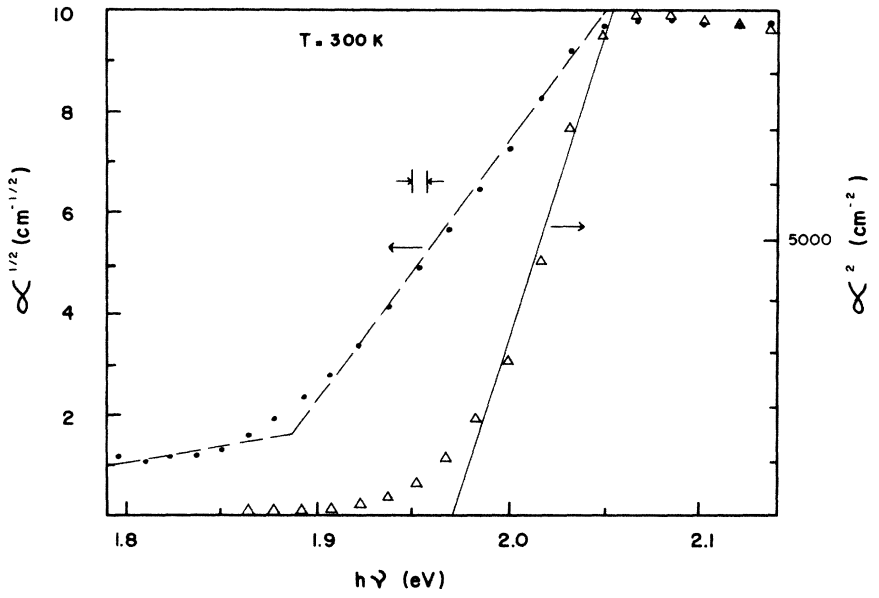

FIG. 3. The same as Fig. 2, but for the case of transmission measurements perpendicular to the c axis of the sample.

$h\nu$ and the plot of α^2 vs $h\nu$; as is usual in the analysis of the absorption coefficient versus energy we fit the low-energy part of the $\alpha^{1/2}$ vs $h\nu$ with one straight line and the high-energy part with another one, the intercepts with the energy axis giving $E_{gi}-E_{ph}$ and $E_{gi}+E_{ph}$, respectively. At the absorption edge the points of the α^2 vs $h\nu$ plot follow a straight line reasonably well and we find that the intercept of this line with the energy axis gives the value of E_{gd}. The values of the parameters found from the analysis are $E_{gi}=1.784$ eV, $E_{ph}=0.074$ eV, and $E_{gd}=1.96$ eV. For comparison purposes we also measured the absorption coefficient by the optical transmission technique but with the light impinging perpendicularly to the c axis. The results are displayed in Fig. 3. In this figure we have plotted $\alpha^{1/2}$ vs $h\nu$ as well as α^2 vs $h\nu$; the straight lines give the values $E_{gi}=1.75$ eV, $E_{ph}=0.105$ eV, and $E_{gd}=1.97$ eV. Though the values of the energy gaps drawn from the two different kinds of experiments differ very little, the values of the absorption coefficients for a given energy are systematically higher in the transmission measurements than in the photoconductivity measurements.

We summarize the results in Table I. With this information it is not possible for us to assign a position in the Brillouin zone to the conduction-band minimum in order to know the position of the indirect gap, due to the lack of phonon dispersion relations. Nevertheless, we can identify the phonon involved in the indirect transitions as follows: In the Raman scattering work of Kuzmany and Elbert[4] these authors assign the phonon with energy 502 cm^{-1} ($\sim$62 meV) as a mode due to phenazine in the phenazine-TCNQ compound. As it is well known, what one observes in first-order Raman scattering is the optical phonons, and usually the optical branches have a small variation with $\mathbf{k}$ in the vicinity of the Γ point ($\mathbf{k}=0$). Due to the similarity of the values of the phonons in our work and of that in Ref. 4, we think that it is very likely that this phenazine mode is the one involved in the indirect transitions.

TABLE I. Values of the parameters found with the two techniques.

Technique	E_{gd} (eV)	E_{gi} (eV)	E_{ph} (eV)
Photoconductivity parallel to c axis	1.96 ± 0.01	1.78 ± 0.01	0.063 ± 0.01
Transmission perpendicular to c axis	1.97 ± 0.01	1.75 ± 0.01	0.105

As a conclusion, we can say that the technique of Moss and Hawkins is very suitable for measuring optical absorption coefficients, and that in the case of the needlelike samples of phenazine-TCNQ it is almost the only one for measuring the absorption coefficient along the c axis. We were able to determine some values of the parameters involved in the optical absorption and we found that the one-dimensional compound phenazine-TCNQ has an indirect gap whose value is $E_{gi}=1.78\pm0.01$ eV, and that the value of the direct gap is $E_{gd}=1.96\pm0.01$ eV.

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[1]E. López-Cruz and B. Gómez-Reyes, Solid State Commun. **56**, 475 (1985).

[2]H. B. de Vore, Phys. Rev. **102**, 86 (1956).

[3]T. S. Moss and T. D. H. Hawkins, Phys. Rev. Lett. **1**, 129 (1958).

[4]H. Kuzmany and M. Elbert, Solid State Commun. **35**, 597 (1980).

[5]Photoresponse is used in the sense that the photocurrent is normalized to equal light intensities throughout the range of wavelength, as defined in Richard H. Bube, *Photoconductivity of Solids* (Wiley, New York, 1960).