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Electrical Conductivity and Photoresponse in Tetracyanoquinodimethan

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Abstract—Dark and photoconductivity in tetracyanoquinodimethan have been measured in the temperature range of 170 °C to − 35 °C. The majority carriers are electrons with hopping activation energy of 0.48 (± 0.05) eV. The band gap is estimated to be 2.05 eV and 2.31 eV from photoconductivity and transmission data respectively, with a temperature coefficient of 1.7×10^{-8} eV K^{-1}.

1. Introduction

Electrical conduction in charge transfer complexes and ion radical salts of tetracyanoquinodimethan (TCNQ) has become a subject of considerable interest during the past decade. It has been felt that besides being chemically stable, their electrical conductivity could possibly be controlled by combining suitable cations to the anion TCNQ radical. Absorption edge and photoconductivity

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spectra in these salts appear to greatly depend upon whether the cation is metallic or organic and whether the anion is represented by $TCNQ^-$ or $(TCNQ^-)$ $(TCNQ^\circ)$. A similar dependence is observed for electron spin resonance signal in different complexes which arises out of variable exchange coupling of charge carriers.

It is possible to probe into the physical nature of the TCNQ complexes by investigating the pure TCNQ itself, about which relatively little is known from the literature. Aust *et al.*[1] have studied the effect of pressure on its optical absorption and have concluded that increase in pressure causes cross-linking between different TCNQ molecules. The transition responsible for this absorption band arising out in the visible region has been identified by Mookherji *et al.*[2] using transmission and reflection techniques. It is believed to be a direct allowed transition with an activation energy of about 2.3 eV.

To have a better understanding of the above observation the present investigations were undertaken on dark and photoconductivities of pure TCNQ crystals. These results were further supplemented by optical transmission data.

2. Experimental

Crystals of pure TCNQ were supplied by duPont Company. The purity of the material was determined by chromatographic method and differential thermal analysis. The DT analysis was made using duPont Model 900 analyzer and the results are shown in Fig. 1. Although the origin of the peaks in this curve is not understood, the sharpness of these peaks and the gradual, smooth slope of the base line at lower temperatures fairly indicates the purity of the material.

The crystals were orange and their typical dimensions were $0.3 \times 0.1 \times 0.1$ cm^3. Silver paste was used to make electrical contacts. The ohmicity of the contacts was checked by studying the current–voltage characteristics. The maximum applied field was about 100 V/cm, and it was observed that the contacts were

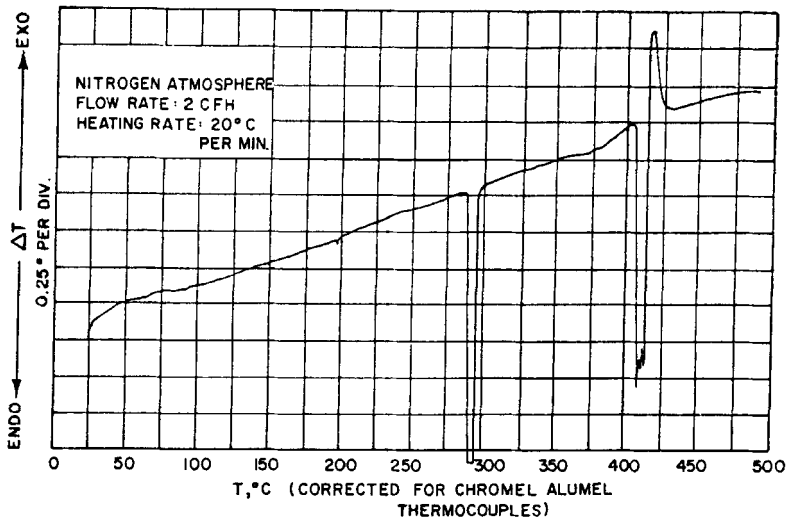

Figure 1. Differential thermal analysis of TCNQ.

perfectly ohmic throughout the experimental temperature range.

The material was brittle and, consequently, it was difficult to make measurements down to liquid nitrogen temperature. It appears that the constraints imposed by the contacts caused the samples to crack at temperatures below about − 35 °C; hence, no reproducible measurement could be made below this temperature. The limit to the high-temperature measurements was placed by the sublimation point of the material, which is + 170 °C.

For the electrical measurements, conventional d.c. techniques were employed using a Cary vibrating reed electrometer Model 3810. Sapphire substrates were used to obtain good thermal transfer between the crystal and the cryostat cold finger. Temperature measurements were made by the use of copper-constantan thermocouple affixed to the top of the substrate and were recorded through a digital thermocouple thermometer Digitek Model 569.

Spectral response of photoconductivity and transmission was recorded by scanning the Perkin-Elmer spectrophotometer Model 112U equipped with a Gier-Dunkle integrating sphere between the

wavelengths 0.29 to 2.1 microns. A special variable temperature cryostat assembly had to be built to fit suitably at the exit slit of the monochromator for the measurement of photoconductivity.

3. Results

Prior to making any measurement, the samples were kept under vacuum of 10^{-5} torr for several hours to remove any adsorbed gases on the surface of the samples. Measurements on temperature dependence of the dark conductivity of TCNQ are shown in Fig. 2. All the curves yielded only one slope at temperatures above about 10 °C and the calculated average activation energy from $\rho \sim \exp(E/kT)$ was found to be 0.48 (± 0.05) eV. Between the temperature range of 10 °C to − 35 °C, however, the activation energies were different from sample to sample and varied between the limits 0.08 and 0.60 eV. It was difficult to make any reasonable deduction from these low temperature measurements.

The plots of conductivity versus temperature during continuous irradiation with white light were similar to the one obtained in dark, although the net conductivity of the samples in this case was almost double its value in dark. Attempts to measure Hall voltages in TCNQ were highly unsuccessful even under constant illumination of the sample with intense white light. It could, therefore, be suggested that the mobilities of the charge carrier are quite small (less than 10^{-3} cm²/V-sec). We determined the sign of these carriers by thermoelectric measurement; it appears that the electrons are the majority carriers in the conduction process. This observation is further confirmed by the g-value from ESR absorption, which is of the order of 1.9916.[3]

To find the concentration of the magnetic electrons, we made use of our unpublished room temperature magnetic susceptibility data, which is + 0.1348 emu/gm. The spin concentration thus calculated is of the order of 2×10^{17} per cm³. This electron concentration was calculated assuming a spin of $\frac{1}{2}$ and a g-value of 1.9916. The former assumption seems valid from our temperature variation studies of ESR[3] in which we did not observe any triplet

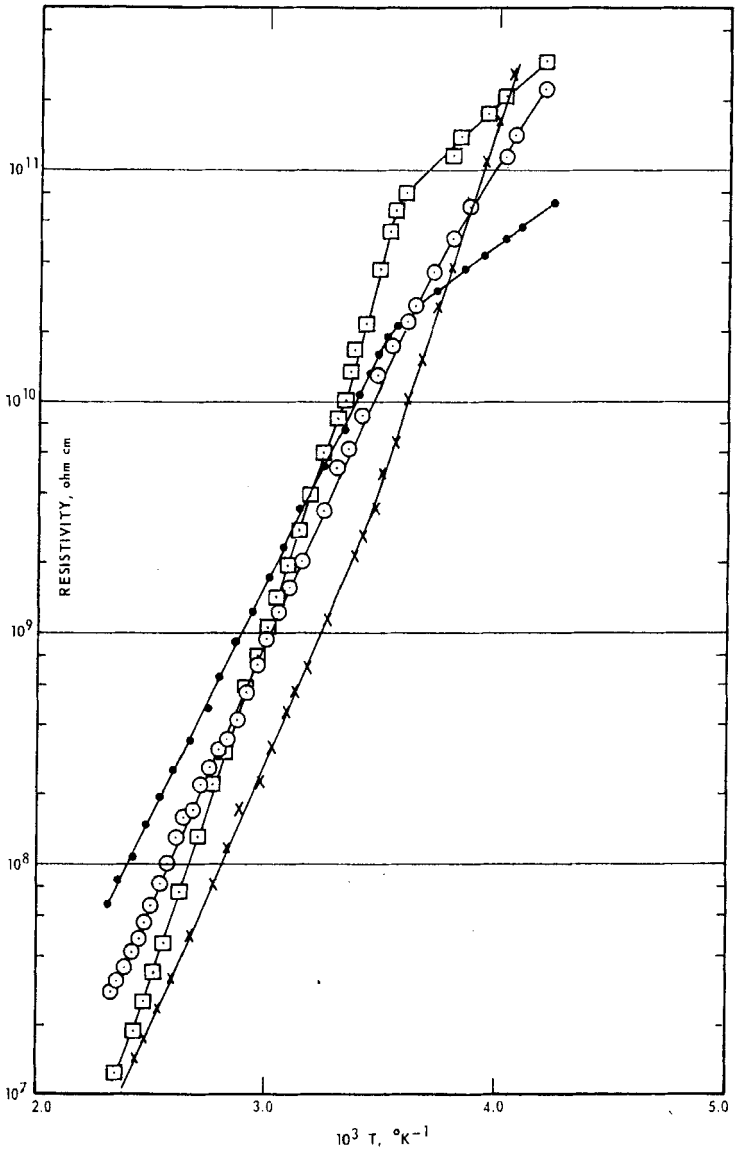

Figure 2. Temperature dependence of dark conductivity for four samples of TCNQ.

state in TCNQ. If we now assume that all these electrons participate in the conduction process, the mobility for a sample with resistivity 10^9 ohm cm should be of the order of 10^{-7} cm^2 volt^{-1} sec^{-1}. However, it may be argued that only a part of the above calculated electron concentration participates in the conduction process. In such case, the mobility will be more than 10^{-7} cm^2 volt^{-1} sec^{-1} but in no case will exceed 10^{-3} cm^2 volt^{-1} sec^{-1}, as was concluded earlier. With such low values of mobility, it seems reasonable that the charge carriers are localized on particular lattice sites, so that the orbitals of one molecule are relatively isolated from that of the other. The conduction process in this case could then be explained by means of the well-known hopping model.[4] A similar process was suggested for TEA-TCNQ from theoretical calculations, which states that conduction proceeds by excitation from the lowest and most populated level into the upper level followed by subsequent hopping from one group of TCNQ to another.[5]

As mentioned earlier, although the activation energies determined from the temperature dependence of conductivity remain essentially the same for crystals in dark and under illumination, the net value of conductivity increases in the latter case. This increase is due to the excitation of carriers from valence to the conduction band. The invariance of the activation energies in the two cases and the small magnitude of the mobility lead to the conclusion that these energies arise due to the temperature variation of mobility and not that of carrier concentration. The temperature dependence of conductivity in TCNQ is, therefore, essentially the temperature dependence of mobility. The observed high temperature activation energy of 0.48 eV could be expected to be the energy needed by a π-electron to hop from a particular molecular site to its nearest neighboring site.

The spectral response of photoconductivity is shown in Fig. 3. The threshold of photoconductivity has been determined on the basis of Moss' criterion,[6] according to which it is the wavelength for which the response towards the long wavelength side has fallen to one-half of the maximum. From this theory we find that

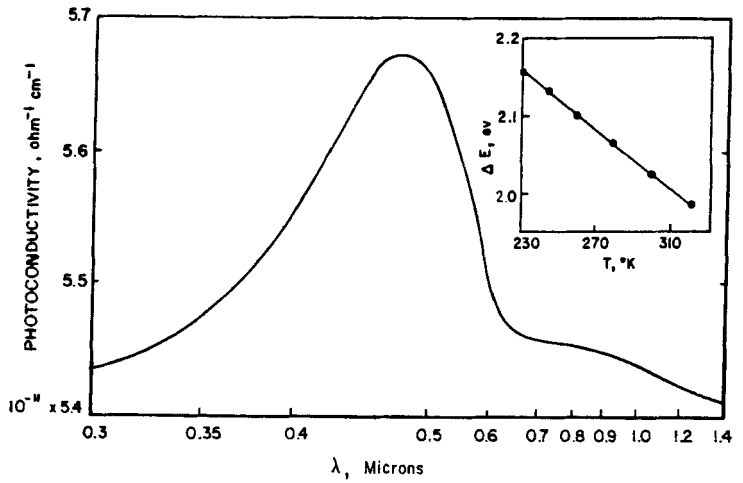

Figure 3. Spectral response of photoconductivity.

the energy gap ΔE is 2.05 eV at room temperature. It increases upon cooling the sample and varies as 1.7×10^{-3} eV $^{\circ}K^{-1}$ in the experimental range of temperatures, as shown in the insert of Fig. 3.

From our optical transmission measurements, shown in Fig. 4, the energy gap appears to be 2.31 eV which is about 10% higher than the value obtained from the photoconductivity data. We do not find this energy in the conductivity versus temperature plot which is quite evident as its value is comparatively large. Thus, it may be concluded that the above energy represents the band gap in TCNQ.

Besides the fundamental peak in the photoconductivity and transmission spectra, one could also observe one small peak at energy approximately 1.3 eV. We have not yet been able to explain the nature of this activation energy; however, we think that it could be due to some dislocations or defects present in the crystal.

4. Conclusion

We have investigated the dark conductivity, photoconductivity

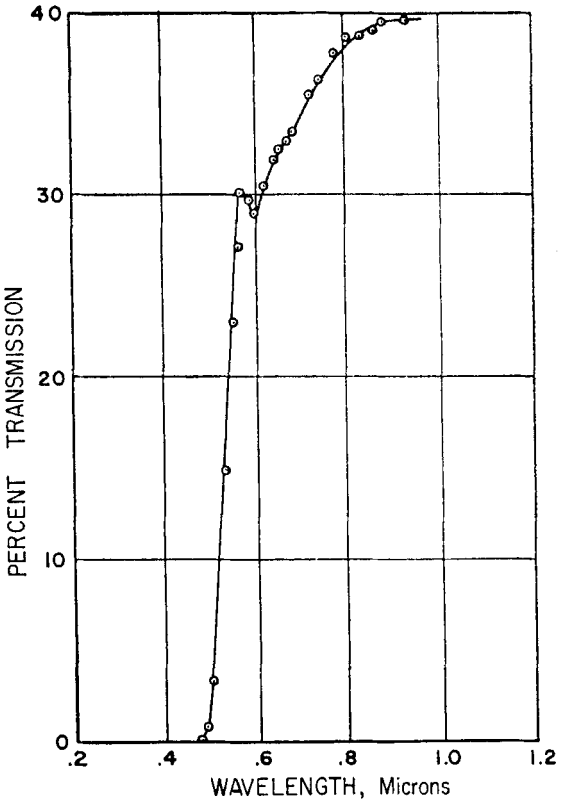

Figure 4. Spectral response of optical transmission.

and transmission spectra in pure TCNQ crystals. The majority carriers responsible for electrical conduction in TCNQ are found to be electrons with high temperature hopping activation energy of 0.48 eV. These carriers could be photo-excited directly from the valence band to the conduction band. The energy required for this excitation is 2.05 eV (from photoconductivity measurements) and 2.31 eV (from transmission measurements) at room temperature. The temperature coefficient of the band gap is estimated to be 1.7×10^{-3} eV $°K^{-1}$. The activation energy of 1.3 eV in photoconductivity and transmission spectra could be attributed to some dislocation or defect center.

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