

# High pressure optical absorption in Cs<sub>2</sub>TCNQ<sub>3</sub> complexes grown under the influence of magnetic field

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## Abstract

Crystals of the organic semiconductor Cs<sub>2</sub>TCNQ<sub>3</sub> have been grown under the influence of magnetic field of 5 T and their optical properties have been compared with the crystals grown without magnetic field. The magnetic field effect manifests itself as the enhancement of the intradimer charge transfer band S<sub>1</sub>, which appears at around 1.3 eV in the E//a polarization. The high-pressure optical absorption measurements have shown that the S<sub>1</sub> band of the crystal grown at 5 T contains a new component, which is significantly intensified with increasing pressure up to 1 GPa, but diminishes as pressure increases further up to 4 GPa, and remains constant at higher pressures. This new component is additional to the component of S<sub>1</sub> band which has similar properties to that of the crystals grown without magnetic field, which continuously grows up to 3 GPa and abruptly broadens out at higher pressures. The new component of S<sub>1</sub> is strongly linked to the ferromagnetism in this substance.

## Keywords:

Organic semiconductor, crystal growth under magnetic field, high pressure, optical properties.

## INTRODUCTION

$\text{Cs}_2\text{TCNQ}_3$  is a 1:2  $\text{TCNQ}^0/\text{TCNQ}^-$  mixed organic semiconductor, where TCNQ is tetracyanoquinodimethane. It crystallizes into a columnar structure consisting of a periodic stack of  $\text{TCNQ}^0/\text{TCNQ}^-/\text{TCNQ}^-$ , where  $\text{TCNQ}^0$  and  $\text{TCNQ}^-$  are neutral and anion radical molecules, respectively [1], resulting in a semiconductor with the lowest optical energy gap of 0.3 eV [2]. The  $\text{TCNQ}^-$  are dimerized, so that the uppermost valence band is formed by the  $\pi^*$  orbit of spin singlet. Since the on-site Coulomb repulsion energy  $U$  of  $\approx 1.2$  eV of the  $\pi^*$  electrons is higher than the transfer integral  $t$  of  $\sim 0.2$  eV [3],  $\text{Cs}_2\text{TCNQ}_3$  may be regarded as a charge-transfer semiconductor of the 1/3-filled Hubbard system [4].

A very weak but definite ferromagnetism with a coercive force of about 100 Oe has been observed in this substance at room temperature [5]. Such behavior is remarkable since most of the  $\pi^*$  electrons of radicals are in the magnetically silent state of singlet spin. In addition, this substance undergoes a pressure-induced phase transition to a metallic state at around 3 GPa [6] although the energy gap remains unclosed [2]. This metallic state is suggested to arise from the delocalization of the  $\pi^*$  electrons of radicals [7,8].

Properties of the crystals of this material grown under high magnetic field are of current interest. Despite the morphological properties, the space symmetry of the crystal structure and its lattice constants are almost unaffected by the field, it has been found that the crystals grown under the influence of magnetic field show remarkable effects in the electric, magnetic, and optical properties [9]. In this work we report on the results of the high-pressure optical absorption measurement for those crystals.

## EXPERIMENTAL PROCEDURES

The single crystals are grown by basically the same mixed-solvent method as that without magnetic field. We encapsulate the glass bottle containing the nearly saturated acetonitrile solution of  $\text{Cs}_2\text{TCNQ}_3$  into a larger bottle together with diethylether, while opening the inner bottle. This dual container system is placed on the central position of the magnetic field of a cryogen-free superconducting magnet, which can generate magnetic field up to 11 T. The temperature of the system is regulated at 20 °C. As the vapor of diethylether recondenses to mix with the solution, the  $\text{Cs}_2\text{TCNQ}_3$  crystals precipitate as needles or thin plates. After 2~3 days a half amount of the dissolved material recrystallizes but the precipitation rate tends to be suppressed by magnetic field.

The as-grown plate crystals, which are approximately 10  $\mu\text{m}$  thick, are used as the samples. The plate has the  $ab$  surfaces of the monoclinic crystal structure. The optical absorption is measured using a spectrometer system equipped with a microscope; the probe-light is incident normal to the surface of the sample. In the high-pressure measurements pressure is generated with the diamond anvil cell. The daphne oil is employed as the pressure-transmitting medium.

## RESULTS

Figure 1 shows the polarized optical absorption spectra of the crystals grown under 0 and 5 T. The measurement is performed at ambient conditions for  $E//a$  and  $E//b$ , where  $E$  is the electric field of light. In the spectral range of the present experiment there appear three absorption bands,  $S_1$ , B and C. The  $E//a$  and  $E//b$  spectra of the 0 T crystal are in good agreement with the previously reported results [10]. Compared with the 0 T crystals, the spectrum of 5 T crystals shows no significant difference for  $E//b$ , but shows a remarkable difference

for  $E//a$ . The difference occurs primarily upon the relative strength of the bands  $S_1$  and C. The former is assigned to the charge-transfer of the  $\pi^*$  electron of dimerized TCNQ $^-$  radicals, whereas the latter is known to be due to the transition of an electron of the doubly-occupied  $\pi$  state of TCNQ $^-$  to the vacant  $\pi^*$  state of TCNQ $^0$  [11]. We note that the  $S_1$  band, being barely observed in 0 T crystals, is enhanced in the 5 T crystals to be as intense as the C band. Similar enhancement is also observed in the electron-molecular-vibration (emv) coupled modes in the infrared region although their frequencies remain unaffected [9]. It should be noted that these magnetic field effects can only be observed for the crystals grown under the influence of magnetic field higher than 4 T.

The unpolarized optical absorption spectra of the 0 and 5 T crystals under several pressures are shown in Fig. 2 and 3 respectively. In the 0 T crystal, the  $S_1$  band continuously grows and blue-shifts with increasing pressure. At around 3.5 GPa it abruptly diminishes and broadens out at higher pressures. In the 5 T crystal, on the other hand, the behavior of the  $S_1$  band is different. It emerges that the  $S_1$  band of 5 T crystal seems to consist of two components. The first component, is strongly enhanced while continuously blue-shifted with increasing pressure up to 1 GPa. When pressure increases further it diminishes while abruptly blue-shifts, to become constant at around 4 GPa. The second component has almost the same pressure dependence with the  $S_1$  of the 0 T crystal. This component becomes clearly observable as the low-energy shoulder of the major peak when the latter abruptly blue-shifts at pressures higher than 1 GPa. Fig. 4 shows the comparison of the pressure dependence of the intensity of the  $S_1$  band between the 0 and 5 T crystals. It noteworthy that both components are coupled with the previously mentioned emv modes.

## DISCUSSION

The properties of the  $S_1$  band described above clearly show that the electronic structure, particularly the  $\pi^*$  state of the TCNQ $^-$  radicals, is significantly modified in the 5 T crystals. Such remarkable effect is very difficult to be ascribed to impurities or defects. It is then reasonable to interpret that a new electronic state at around 1.3 eV has been created by the field throughout the 5 T crystals. This electronic state is suggested to be strongly linked to the ferromagnetism in this material [9].

We have previously reported that the 0 T crystals undergo a pressure-induced phase transition at about 3.5 GPa, in which  $S_1$  disappears in the high-pressure phase [2]. In fact, although the pressure dependence of the intensity of  $S_1$  is different, similar phase transition seems to occur in the 5 T crystal, as well. The constant intensity of  $S_1$  at around 4 GPa and higher pressures is considered to correspond with the disappearance of  $S_1$  in the 0 T crystal. In addition, the emv coupled mode observed in the infrared region also disappears at high pressure as it does in the 0 T crystal [8].

Our experimental results have clearly shown that the ground state of the present substance has been radically reformed by the field. To the best of our knowledge such radical reformation has never been reported before.

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Figure captions.

Figure 1. Polarized optical absorption spectra in the 0 and 5 T crystals at room temperature and ambient pressure.

Figure 2. Unpolarized optical absorption spectra in 0 T crystals at several pressures.

Figure 3. Unpolarized optical absorption spectra in 5 T crystals at several pressures.

Figure 4. Pressure dependencies of the intensity of  $S_1$  band in 0 and 5 T crystals. The solid line is the guide for the eye.

Figure 1.

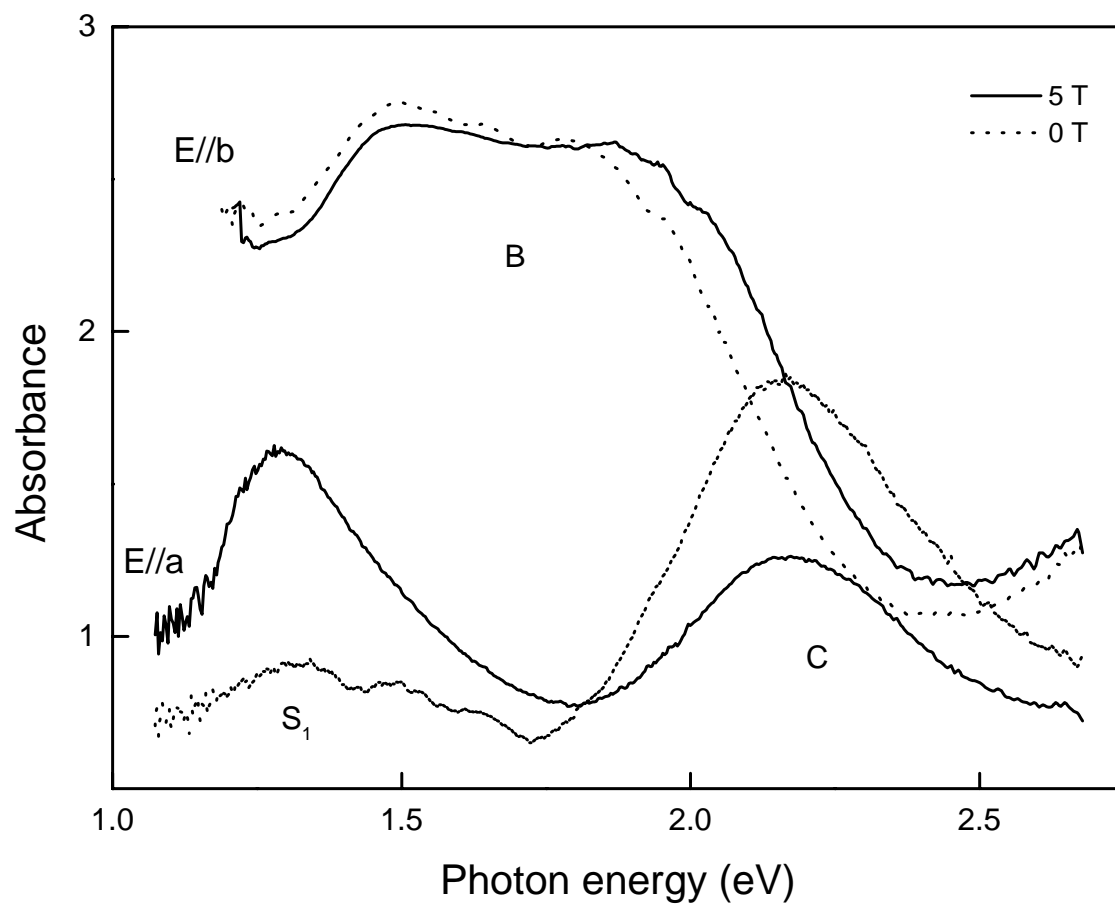


Figure 2.

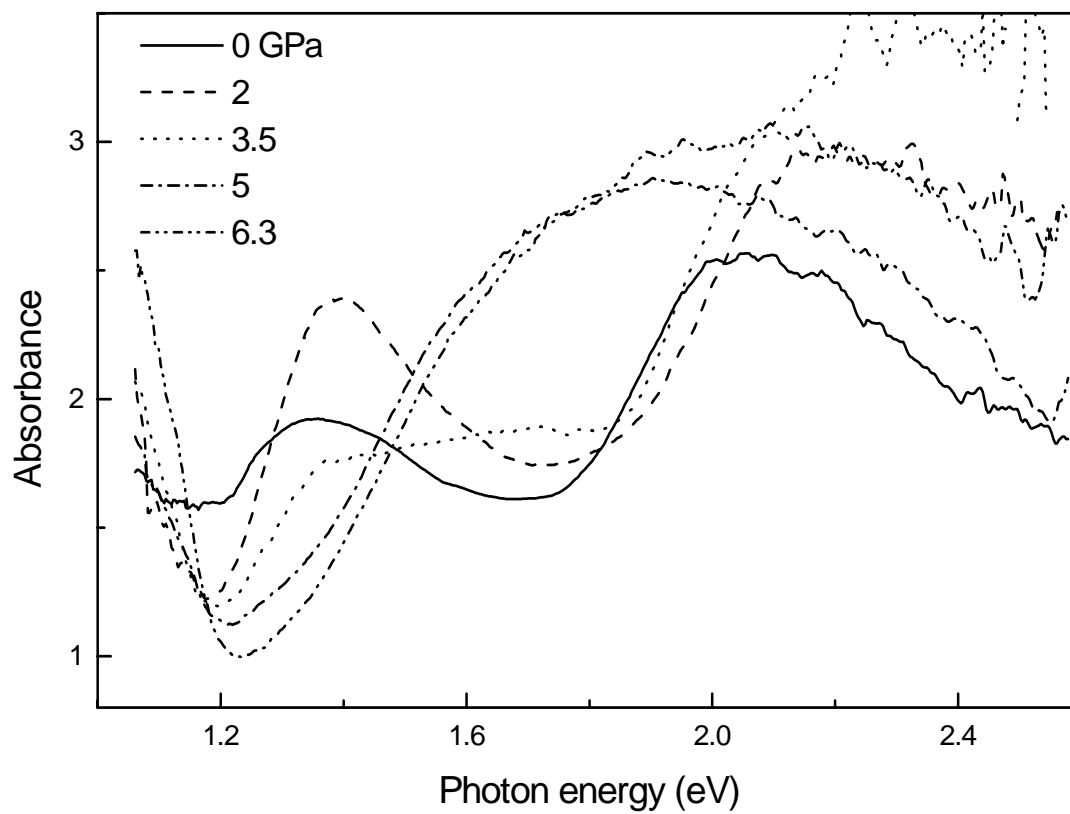


Figure 3.

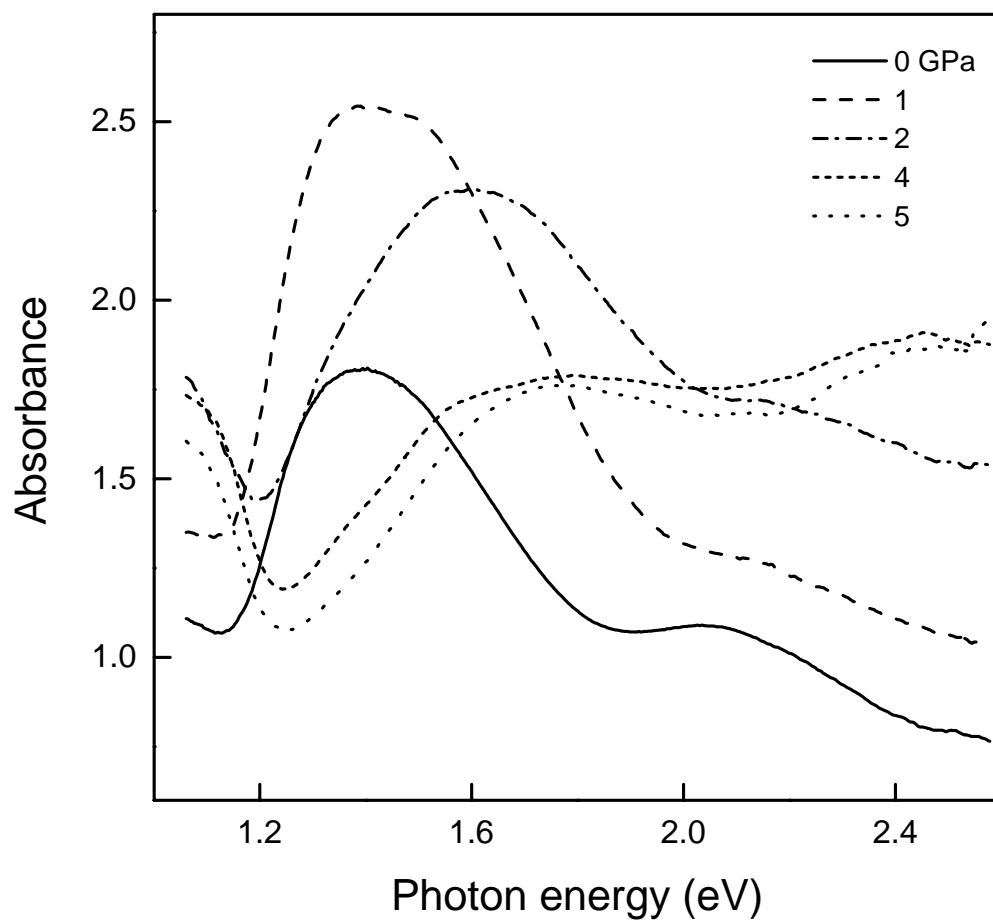




Figure 4.

