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Infrared study on pressure-induced charge delocalization in Cs_2TCNQ_3

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Abstract

Pressure dependence of several molecular vibration modes in Cs_2TCNQ_3 has been observed through infrared absorption measurements. The behaviour of the C–CN and C–H stretching modes suggests that a phase transition takes place at around 3.6 GPa. The π^* -electrons, which are localized on TCNQ^- molecules in the low-pressure phase, are delocalized significantly in the high-pressure phase. However, the radical-like and neutral-like molecules still coexist in the high-pressure phase indicating that the electrons are not completely delocalized. The electron–molecular-vibration coupled mode disappears in the high-pressure phase in coincidence with the disappearance of the inter-radical charge-transfer band S_1 , proving the strong coupling between them.

1. Introduction

Cs_2TCNQ_3 crystallizes into a columnar structure consisting of a periodic stack of $\text{TCNQ}^0/\text{TCNQ}^-/\text{TCNQ}^-$ [1], where TCNQ^0 and TCNQ^- are neutral and anion radical molecules, respectively, resulting in a semiconductor with the lowest optical energy gap of 0.3 eV [2]. The radicals TCNQ^- are dimerized, so the uppermost valence band is formed by the π^* -orbit of spin singlet. Since the on-site repulsion energy $U \approx 1.2$ eV of the π^* -electrons is much higher than the transfer integral $t \sim 0.12$ eV [3] Cs_2TCNQ_3 may be regarded as a charge-transfer semiconductor of the one-third-filled Hubbard system [4]. Its optical spectra suggest that the π^* -electrons are not uniformly distributed along the TCNQ molecular stack, but are localized on certain sites, i.e., the TCNQ^- radicals [5]. The high degree of localization is responsible for the low electrical conductivity in this crystal, which is $\sim 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at room temperature [3].

High-pressure electric resistivity measurement has shown that this material undergoes a phase transition to a metallic state at around 3 GPa [6]. However, the optical energy gap remains unclosed throughout the phase transition indicating that the metallic state in this material

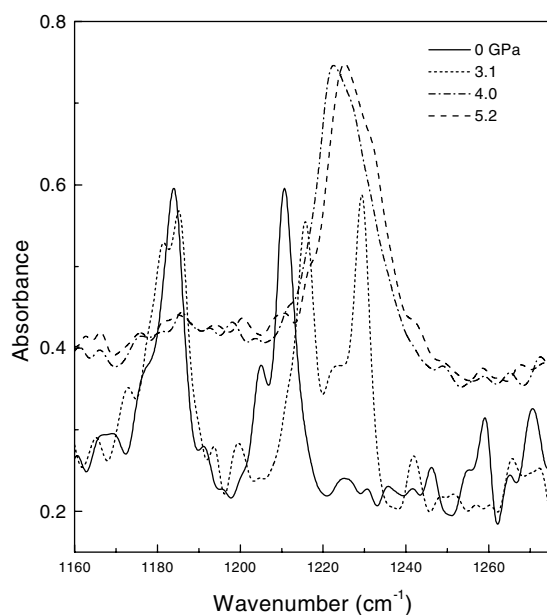


Figure 1. Absorption spectra in the C–CN stretching region at several pressures.

should be considered different from those of ordinary metals [2]. The results from a high-pressure Raman scattering experiment suggest that the electrons are completely delocalized from TCNQ^- radical molecules at high pressure resulting in a homogeneous distribution of charge along the TCNQ molecular stack [7].

The purpose of this work is to study the electronic mechanism underlying the aforementioned phase transition in Cs_2TCNQ_3 . We have measured the pressure dependence of the infrared absorption due to molecular vibration. Infrared spectroscopy gives information on the charge distribution along the TCNQ stack complementary to that from Raman spectroscopy. In particular, infrared spectroscopy allows us to observe the electron–molecular–vibration (emv) coupled modes, which are unobservable in Raman spectroscopy.

2. Experimental details

The Cs_2TCNQ_3 salt is synthesized from the reaction of TCNQ with an excess of CsI, and the single crystals of this material were obtained by recrystallization of the salt from acetonitrile–ether solution. The as-grown single crystals of Cs_2TCNQ_3 , about $10\ \mu\text{m}$ thick, are used as the samples. The pressure is generated using a DAC. Daphne oil is used as the pressure-transmitting medium. The unpolarized infrared absorption is measured using a spectrometer system (Jasco FT/IR-410) equipped with a microscope. The ruby fluorescence method is used for calibrating the pressure.

3. Results

Figure 1 shows the absorption spectra in the C–CN stretching region at several pressures. The features at 1205 and $1211\ \text{cm}^{-1}$ at ambient pressure arise from neutral and radical molecules, respectively. These features show a blue-shift with increasing pressure, while increasing their

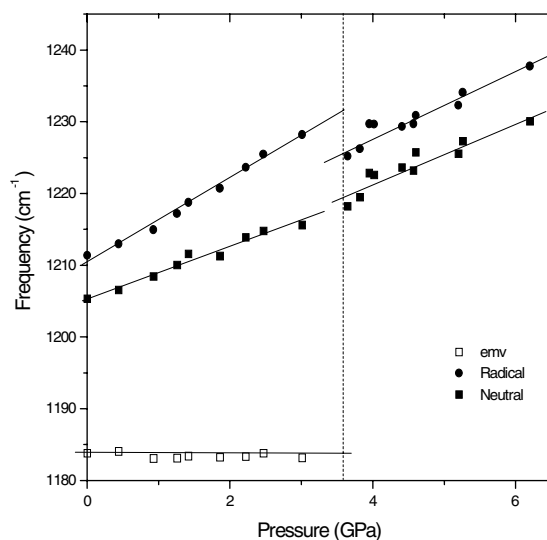


Figure 2. Pressure dependences of the frequencies of the molecular vibration modes in the C–CN stretching region.

energy spacing. At around 3.6 GPa they abruptly displace toward each other by about half the energy spacing. It is noteworthy that in the high-pressure phase the vibration modes arising from the radical-like and neutral-like molecules still coexist.

The feature at 1183 cm⁻¹ is the totally symmetric a_g mode. The a_g modes are originally infrared inactive in an isolated TCNQ molecule. They become infrared active as the result of the interaction of the molecular vibration with charge transfer, which is known as the emv coupling [8]. The frequency of the emv mode remains almost unchanged at low pressures. However, it disappears above 3.6 GPa, in coincidence with the disappearance of the electronic transition band S₁ [1, 9]. The pressure dependences of these modes are shown in figure 2.

The b_{2u}ν₁₈ modes arising from the C–H stretching relating to neutral and radical molecules observed at 3038 and 3054 cm⁻¹, respectively, at ambient pressure, exhibit similar properties to the aforementioned ones. It is also noteworthy that the absorption spectrum at ambient pressure after the compression is the same as the one before compression.

We intended to observe other modes such as C=C and C=N vibrations, but failed because of the strong absorption of the diamond and the pressure-transmitting medium.

4. Discussion

The results described above clearly show that a pressure-induced electronic phase transition occurs at around 3.6 GPa. The energy spacing between the neutral and radical modes of the two vibrations that abruptly decreases at high pressure indicates that the π*-electrons are significantly delocalized from radical to neutral molecules. However, in the high-pressure phase, radical-like and neutral-like molecules still coexist, indicating that the π*-electrons are not completely delocalized. This is significantly different from the findings from the Raman scattering measurement, which suggested that in the high-pressure phase TCNQ molecules have a homogeneous ionicity [7].

The delocalization of the π*-electrons in the high-pressure phase arises from the increasing of the transfer integral *t* as a result of the decreasing of the intermolecular distances in the TCNQ

stack. We have previously shown that at high pressure the bandwidth $4t$ becomes comparable to the Coulomb on-site energy U [2], which in the framework of the Hubbard model implies that the dimers tend to be unstable.

The disappearance of the emv coupled mode above 3.6 GPa in coincidence with the disappearance of the S_1 band is reminiscent of the results from temperature-dependent optical absorption measurement in $(\text{NMe}_4)_2\text{TCNQ}_3$ [9]. In $(\text{NMe}_4)_2\text{TCNQ}_3$ and the present crystal the TCNQ^- molecules are not perfectly eclipsed but is slightly displaced from each other along the short molecular axis, i.e., the a -axis at moderate temperatures in, as well [1, 10]. Consequently, the dipole moment of the charge transfer transition is not perfectly parallel to the b -axis but is slightly canted to have a weak component along the a -axis, and thus drives the S_1 and emv bands for the *Ella* polarization. As temperature is elevated the second order phase transition takes place at 338 K to have the TCNQ^- molecules be completely eclipsed [11], so that above 338 K both the S_1 and emv bands disappear for *Ella*. In this analogy, the present experimental result suggests strongly that the radical-like TCNQ^- molecules are eclipsed in the high-pressure phase of Cs_2TCNQ_3 .

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