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High pressure electrical transport behavior in organic semiconductor pentacene

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The high pressure electrical transport behavior of pentacene has been investigated by alternating current impedance techniques and direct current resistivity measurement in a diamond anvil cell (DAC). The resistance decreases with increasing pressure below 17.4 GPa, while it increases above 17.4 GPa, which is caused by the transition of pentacene from an ordered state to the disordered state under higher pressure. From the Raman spectra under various pressures, pentacene becomes amorphous above 17.3 GPa, which is consistent with the impedance results. The charge transport operates in the hopping regime with charges jumping between interacting molecules, and the hopping mechanisms are related to the vibration modes. Above 17.4 GPa, the pressure dependence of the relaxation activation energy is 21.7 meV/GPa and pentacene keeps semiconductor characteristics up to 28.3 GPa.

Keywords: diamond anvil cell; impedance; resistivity; hopping mechanism; activation energy

1. Introduction

Organic semiconductors have attracted considerable attention because of their abundant properties in electronics, optics and magnetism. They have been widely applied as functional materials to flexible large-area displays, light-emitting diodes and solar cells.[1–5] By doping with alkaline metals, the organic molecular compounds can display novel physical properties, such as metallic behavior and superconductivity.[6–9]

High pressure may not only lead to structural and electronic phase transformations and consequently change the properties accounting for conductivity of a material, but also introduce gradual modulation of the band gap, the concentration of charge carrier and the mobility of a carrier.[10,11] Pressure-dependent electrical transport measurement would allow a more precise understanding of the role of intermolecular interactions on electronic bandwidth, carrier delocalization and relaxation process, shedding further light on the transport mechanisms responsible for charge mobility in organic materials. The charge transport properties of pentacene under high pressure have been investigated previously in several works. For example, Rang et al.

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*Corresponding authors. Emails: cailong_liu@jlu.edu.cn, cxgao599@aliyun.com observed a linear increase in field-effect mobility with increasing pressure in pentacene.[11,12] Aust et al. concluded that pentacene becomes “metallic” at 27 GPa by the electrical resistance measurements.[13] The purpose of this work is to investigate the pressure-dependent electrical transportation behavior of pentacene by *in situ* alternate current impedance spectroscopy and direct current (DC) electrical resistivity measurements in a diamond anvil cell (DAC). Raman spectra under high pressure were also conducted for understanding the effect of vibration modes on the electrical properties.

2. Experimental conditions

High pressure measurements were performed in a DAC with the anvil culet of 400 μm in diameter. In preparation of a gasket for the measurements, a sheet of T-301 stainless steel was pre-indented to a thickness of 30 μm, on which a hole of 250 μm in diameter was laser drilled. After filled and compacted with the mixture of diamond powder with epoxy, a new hole of 170 μm in diameter was drilled to serve as a sample chamber. The pressure was determined from the pressure shift of the $R1$ ruby fluorescence line.[14] The electrodes were made by the microcircuit fabrication process in the configuration described in [15,16]. No pressure medium was used to assure that the impedance spectroscopy reflects the information of the pure pentacene. The impedance spectroscopy was measured with a Solartron 1260 impedance analyzer equipped with a Solartron 1296 dielectric interface by introducing 0.1 V sine signal into the sample in the frequency range of 0.1–10^7 Hz under a controlled stable room temperature. The temperature dependence of resistivity was measured with the DAC heated in a tropical drying cabinet 10 min after temperature of the system became stable.[17] The sample thickness under pressure used for resistivity calculation was determined by a micrometer of 1 μm precision with the diamond deformation being taken into account.[18] Raman spectra at various pressures were recorded using a Jobin Yvon T64000 Raman spectrometer. A 532 nm laser line was used to irradiate the powdery samples. The sample was introduced to the DAC in a nitrogen-filled drying glove box to prevent the effect of absorbed water during the loading. No pressure medium was used. For both experiments, the sample was saved and introduced to the DAC in a nitrogen-filled drying glove box to prevent the effect of absorbed water during the loading.

3. Results

Figure 1 illustrates the Nyquist plotting of the impedance response in pentacene under different pressures at room temperature. Below 5.5 GPa, the impedance spectra includes two parts: the circle at high frequency (left) is considered due to the conduction process from the grain interior, while the arc at the lower frequency is from the grain boundary. Above 5.5 GPa, the low-frequency arc disappeared, indicating that the grain boundary effect weakened and the conduction through grains in pentacene is dominant. According to the Raman spectra measurements by Farina et al., a pressure-induced phase transition of pentacene from the C structure to the denser H phase occurred at 0.2 GPa, while completed above 5 GPa.[19] The significant impedance variation at 5.5 GPa is thus related to this structural phase transition. The phase transition results in a large number of defects (such as the vacancies and dangling bonds) at the grain boundary, which affects the carrier scattering in the grain boundary conduction process, leading to the change on the microstructure of grain boundaries. At higher pressures, there exists a tail in the low-frequency region, which is due to the space charge depletion at grain boundaries.[20] For powder samples, the equivalent circuit method is a reliable approach to describe the impedance

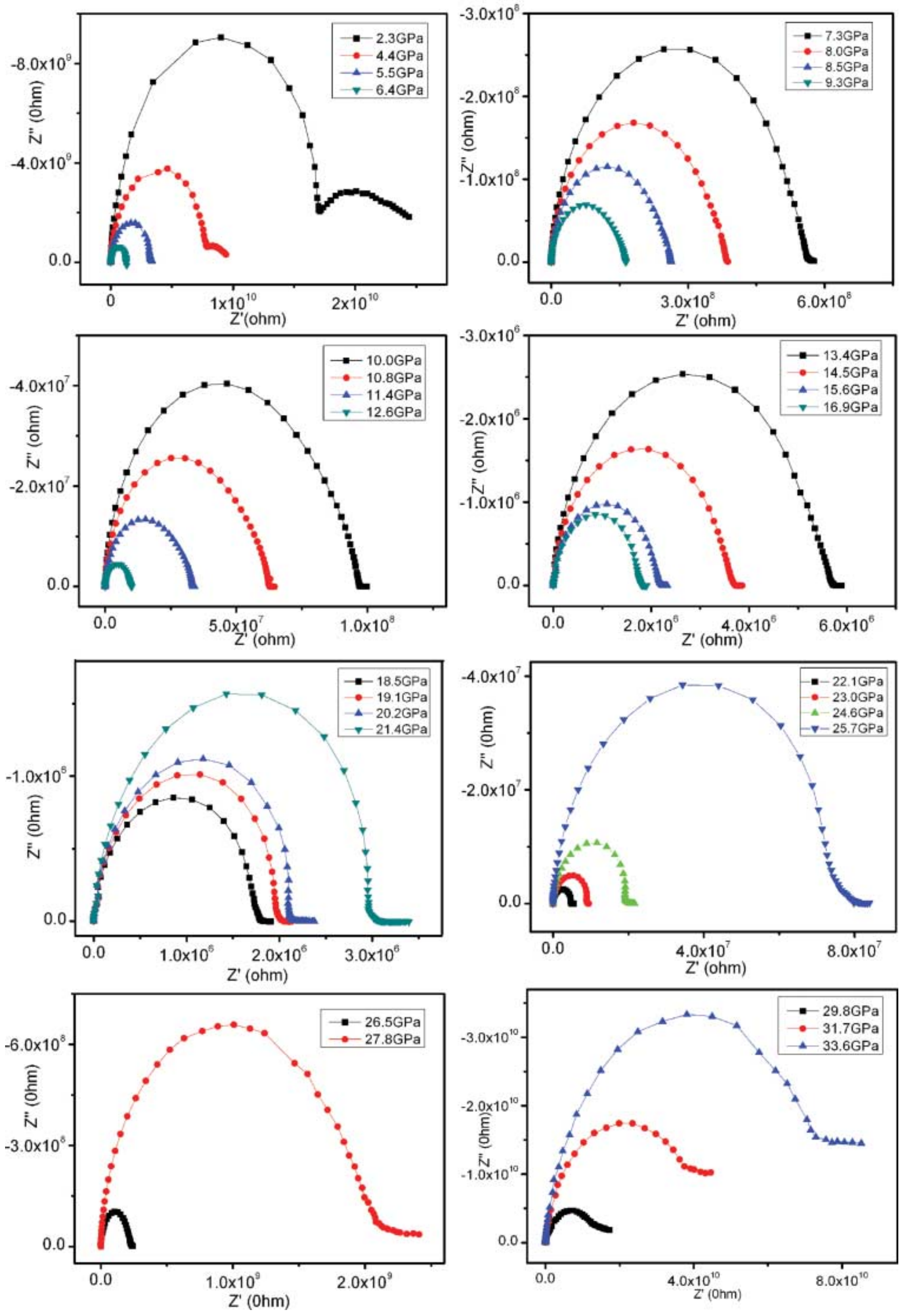

Figure 1. (color online) Nyquist impedance plots of pentacene under pressures.

spectra. The equivalent circuit of pentacene (inset of Figure 2) consists of an RC subcircuit, where the capacitor is represented by constant phase element (CPE). The impedance of the CPE

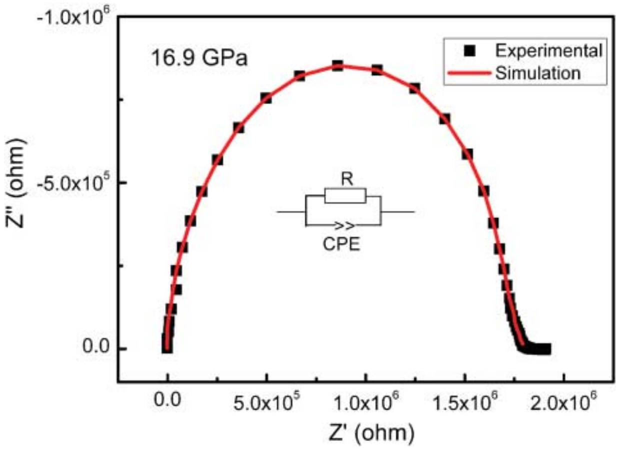

Figure 2. (color online) Simulation results at 16.9 GPa of the impedance spectra obtained from the equivalent circuit shown in the inset. Black square symbols and red solid curves are the experimental and calculated results, respectively.

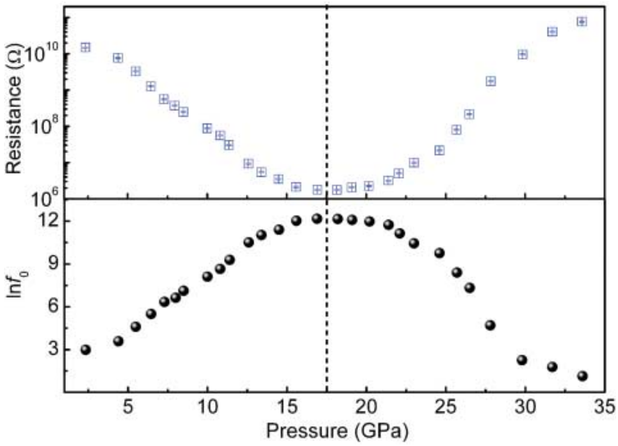

Figure 3. Variation in the resistance and relaxation frequency of pentacene with pressure.

is given by $Z_{\mathrm{CPE}} = B^{-1}(\mathrm{j}\omega)^{-n}$, where B is a constant that is independent of frequency. The simulation data of the real and imaginary parts of the impedance spectra at 16.9 GPa, according to the equivalent circuit, are shown in Figure 2.

The variation of resistance with increasing pressure is shown in Figure 3. The resistance of pentacene decreases with increasing pressure below 17.4 GPa, while it increases with increasing pressure above 17.4 GPa. This result is consistent with the change in the absorption edge energy from the optical measurements by Farina et al. and the abnormal change at 17.4 GPa is attributed to the amorphous state of pentacene due to the formation of saturated C···C bonds.[21] The amorphous character in pentacene at higher pressure is related to the presence of static disorder through the charge transport process. The increasing amount of disorder at higher pressure localizes more and more of the states in the band, until all states become localized in the case of strong disorder. Transport then operates in the hopping regime with charges jumping between interacting molecules.[10]

The amorphous character of pentacene at higher pressure can also be found from the Raman spectra. The typical Raman spectra of pentacene under various pressures are shown in Figure 4.

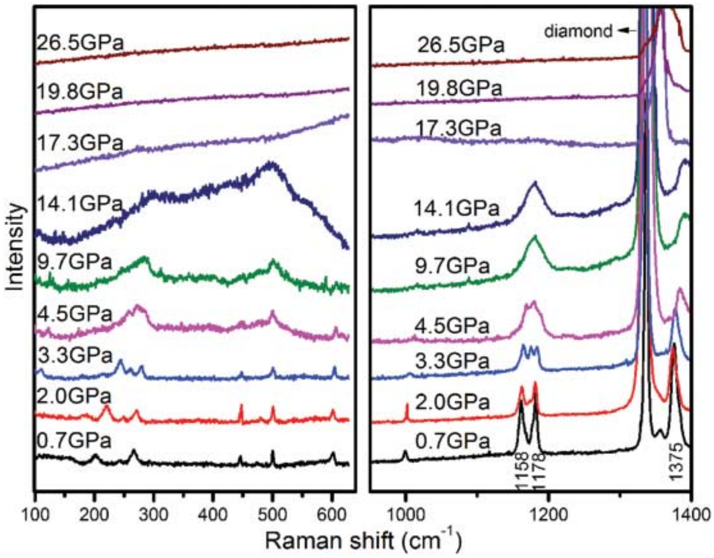

Figure 4. (color online) Raman spectra of pentacene at selected pressures.

The bands at 1158 (A_g) and 1178 (A_g) cm^{-1} are related to C–H in-plane bending modes, and the 1375 (B_{3g}) band belongs to the aromatic C–C stretching vibration along the short molecular axis in the molecular plane. Indeed, in such a flexible molecule as pentacene, some intramolecular modes are expected to overlap in energy and be therefore strongly coupled with lattice phonons.[22] Due to the limit of the Raman experimental conditions, we cannot choose a lower energy excitation to avoid the strong background and the low-frequency intramolecular modes in the region of 20–100 cm^{-1} cannot be observed. According to density functional theory calculations,[23] the 1178 cm^{-1} band is the strongest C–H in-plane vibrational mode. From the Raman spectra under high pressure, pentacene shows an amorphous state above 17.3 GPa, which is consistent with the impedance results.

Due to the fluctuations at room temperature, the electrons can be considered localizing on a single molecule and its transportation can be regarded as the hopping process between molecules. Due to the flexible characteristic in organic molecules, the geometry structures of molecules are different between the neutral and electriferous states. The electrons will be subjected to a strong scattering during each skip from one molecule.[24] From the view of chemical reaction, the charge self-exchange occurs between the two nearest molecules. Taking one molecule as the starting point, the charge hops from this molecule to all the neighboring molecules. Assuming that the molecule has enough relaxation time from neutral conformation to electriferous conformation at each hopping, the charge transfer process in pentacene can be then described by the Marcus charge transport theory.[25] Irrespective of the electronic or energy transfer process, the hopping mechanisms in the reaction coordinate from reactant to product (as shown in Figure 5) are inseparable from the vibration effect.

During the carrier transfer process, the total free energy of the reaction could contribute to the full-width at half-maximum (FWHM) of the vibronic bands that involve the excitation process and lead to an unsymmetrical shape.[26] The degree of asymmetry of the bands can be quantified using an asymmetry ratio that is described as the ratio of the blue half to the red half of the FWHM.[27] Because the crystalline environment causes a shift of vibrational frequencies and possible splitting, the vibration modes generally have a higher asymmetry ratio in a disordered region than in an ordered region, which generates a higher impedance of pentacene above 17.4

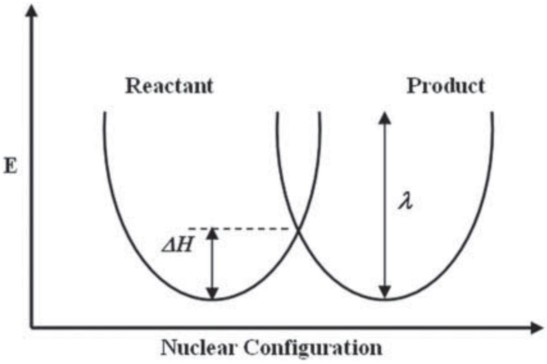

Figure 5. Schematic process of the self-exchange charge transfer. λ is the reorganization energy of the reaction. ΔH is the relaxation activation energy.

GPa. According to the Marcus equation, the reorganization energy λ of reaction represents the energy change in the process that electriferous molecules become neutral ones and the structural relaxation of adjacent neutral molecules to electriferous ones. Thus, λ is a measure of the strength of the hole–phonon or electron–phonon interaction and provides a direct link between the geometric and electronic structure and the transport properties of the material. The characterization of charge carrier coupling to molecular vibrations, which modulate on-site energies, has been investigated by theoretical and experimental studies.[28] The potential barrier of the reaction can be described by the relaxation activation energy ΔH.

From the relationship of imaginary part Z'' versus frequency (as shown in Figure 6), the relaxation frequency of pentacene at different pressures can be obtained (Figure 3). The appearance and nature of the peaks at a characteristic frequency provide information on the type and strength of the relaxation phenomenon occurring in the material. By fitting the pressure dependence of the relaxation frequency to the Arrhenius equation,

$$\frac{\mathrm{d}\,(\ln f_0)}{\mathrm{d}P} = -\left(\frac{1}{k_\mathrm{B}T}\right)\left(\frac{\mathrm{d}H}{\mathrm{d}P}\right), \tag{1}$$

where H represents the relaxation activation energy, k_B is the Boltzmann constant and T represents room temperature, the pressure dependence of the activation energy can be obtained. Below 17.4 GPa, the pressure dependence of the relaxation activation energy is -19.1 meV/GPa, indicating that the charge exchange in the reaction becomes easier with increasing pressure. Above 17.4 GPa, the pressure dependence of the relaxation activation energy is 21.7 meV/GPa, indicating that the barrier of charge exchange increases with increasing pressure. It should be noted that the reaction of the relaxation activation energy to pressure in pentacene also reflects the intermolecular close contacts.[29] The increase in relaxation activation energy at higher pressure results in an increased π-stacking in pentacene molecules. As mentioned above, the reorganization energy essentially corresponds to the sum of the relaxation energies when going from the neutral-state geometry to the charged-state geometry. Thus, a major contribution to the relaxation energy is provided by high-frequency modes.[28] It is important to note that the hole-vibrational coupling, which is inversely proportional to the number of atoms along the π-stacked backbone,[30] should be considered in pentacene because this interaction has a significant effect on the charge transport process in oligoacene systems.[28]

In order to determine whether or not pentacene becomes metallic under high pressure, we carried out the temperature dependence of DC electrical resistivity measurements at pressures. The results are plotted in the Arrhenius format and shown in the inset of Figure 7. The resistivity

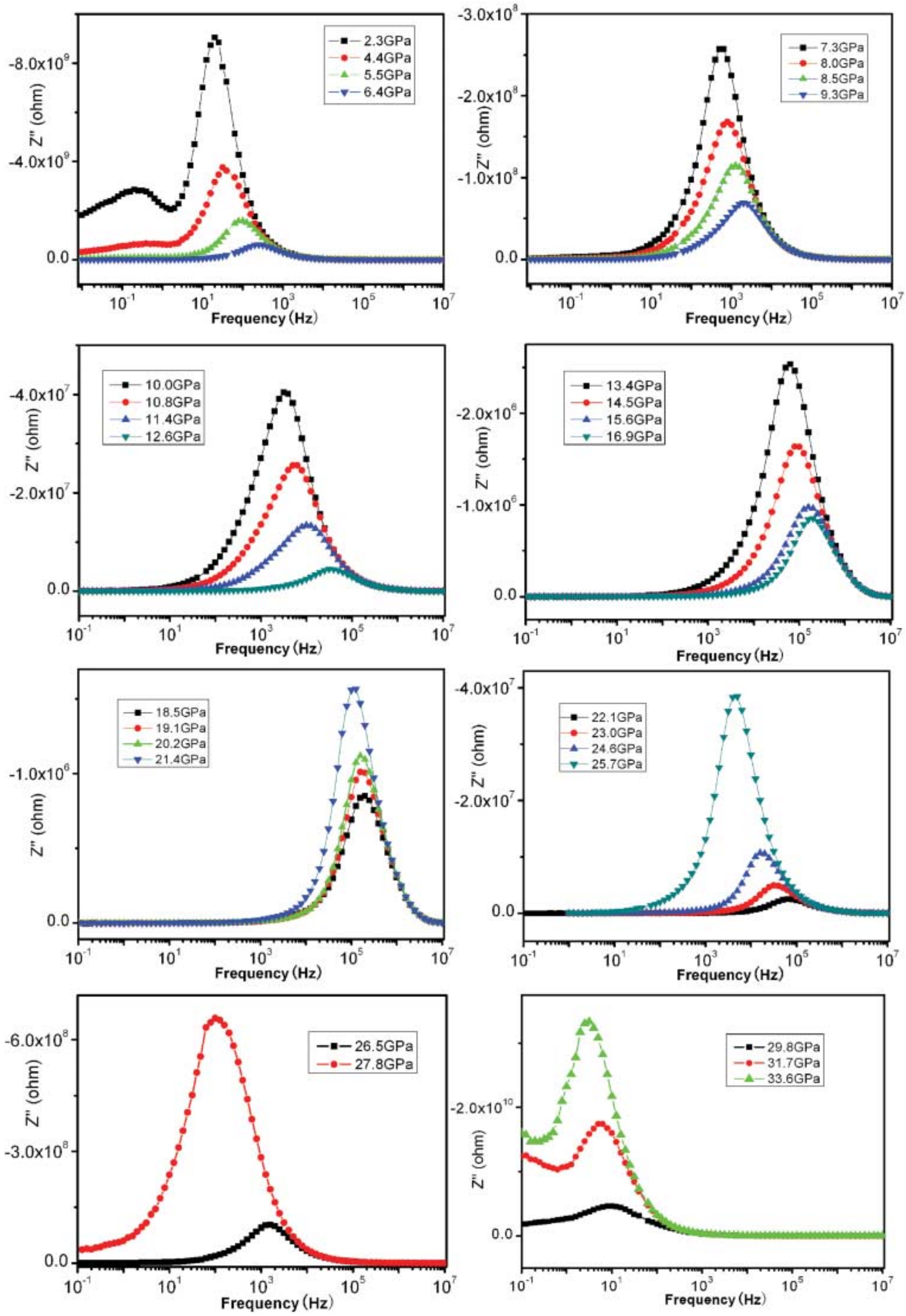

Figure 6. (color online) Variation of the imaginary part of impedance (Z'') as a function of frequency at pressures.

decreases with increasing temperature, indicating that pentacene shows a characteristic of semiconductor from ambient pressure to 28.3 GPa. To obtain more information about the electrical transport properties, we studied the transport activation energy of pentacene. The relationship

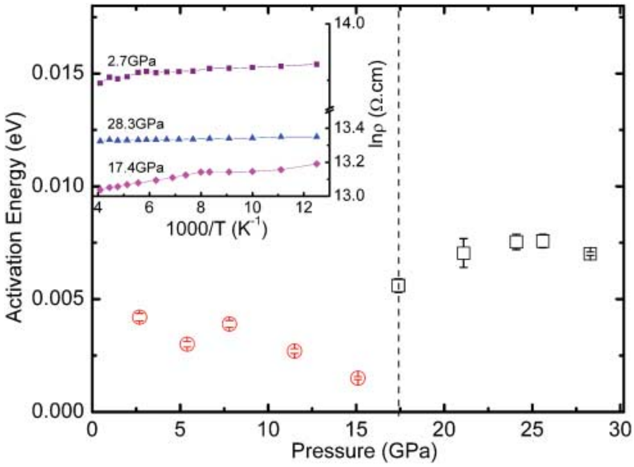

Figure 7. (color online) Pressure dependence of transport activation energy of pentacene. The inset shows the plots of lnρ versus 1000/T at 2.7, 17.4 and 28.3 GPa.

between the electrical resistivity and the temperature of semiconductor can be represented by the following equation:

$$\rho = \rho_0 \exp\left(\frac{E_t}{2k_B T}\right), \tag{2}$$

where ρ_0 is a constant; E_t is the transport activation energy; k_B is the Boltzmann constant and T is the temperature. Furthermore, E_t can be obtained by linearly fitting the plots of lnρ versus 1000/T. As shown in Figure 7, E_t initially decreases with increasing pressure, then it appears to discontinuously increase at 17.4 GPa. A similar trend was found in the variation of highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) band gap with pressure in pentacene.[29] The transport activation energy reflects the difference between HOMO edge and Fermi level and is determined by defect energy levels in the HOMO–LUMO band gap. The band gap continuously decreases as a function of applied pressure up to 17.4 GPa before subsequent expansion. The expansion of the band gap is due to the amorphous character at high pressure due to condensation reactions. It was evidenced again that pentacene still keeps its semiconductor characteristics up to 28.3 GPa.

4. Summary

In summary, we performed *in situ* high pressure impedance spectrum, resistivity and Raman measurements of pentacene. The resistance of pentacene decreased with increasing pressure below 17.4 GPa, while it increased above 17.4 GPa, corresponding to the transition from the molecular identity to an amorphous state, which was also proved by the Raman results. Pentacene showed lower impedance below 17.4 GPa due to the shift of vibrational frequencies and possible splitting. The amorphous character in pentacene at higher pressure was related to the presence of static disorder through the charge transport process. A major contribution to the relaxation energy is provided by high-frequency modes. Above 17.4 GPa, the pressure dependence of the relaxation activation energy is 21.7 meV/GPa and the barrier of charge exchange increases with increasing pressure. Pentacene shows a characteristic of semiconductor from ambient pressure to 28.3 GPa.

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