Ultrafast THz response of photo-induced insulator to metal transition in charge ordered organic conductor $\alpha$-(ET)$_2$I$_3$

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Abstract. Photo-induced insulator to metal transition in a two-dimensional charge-ordered (CO) organic salt $\alpha$-(ET)$_2$I$_3$ (ET: [bis(ethylenedithio)]tetraethylenedithio) was investigated using near-IR-pump and terahertz(THz)-probe spectroscopy. Electronic properties and electron-phonon (e-p) coupling of the photo-induced metallic state were discussed based on the excitation intensity and temperature dependences of transient absorption spectrum. Long-lived (ca. ns) induced absorption with large spectral weight at $<5$ meV is detected for strong excitation at $T-T_{\text{CO}}$ ($T_{\text{CO}}=135$ K), which is attributable to the photo-induced macroscopic metallic state. On the other hand, short-lived transient absorption, reflecting generation of the microscopic metallic state, shows relatively small spectral weight for $<5$ meV at $20$ K $<T_{\text{CO}}$.

1. Introduction

Ultrafast photo-induced insulator to metal (I-M) transitions (PIMTs) have attracted considerable interest for application to switching devices and basic research on non-equilibrium phase dynamics in solids [1, 2]. Actually, PIMTs have been demonstrated in organic and inorganic highly correlated systems using various ultrafast detection methods. Among them, pump-probe spectroscopy in the terahertz (THz) region is a powerful technique for revealing the electronic nature of the photo-induced metallic state [1, 3-5] because the I-M transition is characterized by low energy ($<100$ meV) spectra. To date, however, few THz spectroscopic studies of the photo-induced I-M transition for organic compound have been reported. For this study, ultrafast spectral responses reflecting the I-M transition in THz region were investigated using near-infrared (NIR) pump and THz-probe spectroscopy in a typical layered organic salt $\alpha$-(ET)$_2$I$_3$ (ET = BEDT-TTF: [bis(ethylenedithio)]-tetraethylenedithio) [6].

$\alpha$-(ET)$_2$I$_3$ shows a metallic nature at room temperature, but it transforms to a charge-ordered (CO) insulator at temperatures below $T_{\text{CO}}$ (transition temperature to CO state=135 K). The I-M transition in $\alpha$-(ET)$_2$I$_3$ is a first-order transition, but the lattice effect is not crucial: the CO in this compound can be

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described by the Wigner crystallization. Very recently, this type of 3/4 filled organic salt has demonstrated its potential for application to organic devices [7, 8]. Photo-induced melting of the CO state and generation of the metallic state have been studied using near-mid infrared (IR) pump-probe spectroscopy in this compound [9–11]. For strong excitation at $T = T_{CO}$, photo-induced metallic state shows a long lifetime (ca. 1 ns), whereas rapid decay as fast as 1 ps is detected for the weak excitation at $T < T_{CO}$. It is noteworthy that the temperature dependence of the fast and the slow decay times show different critical behaviors. Therefore, possible origins of the fast and slow decaying photo-induced metallic states, being different in the thermodynamic nature, are microscopic and macroscopic metallic states [9–11] respectively. However, electronic property and electron-phonon (e-p) coupling of these photo-induced metallic states have not been clarified. We employed ultrafast optical pump-THz probe transient absorption spectroscopy to elucidate this problem.

For this study, we performed steady state and transient THz absorption measurements for organic conductor $\alpha$-(ET)$_2$I$_3$. Slow decaying photo-induced transient absorption with a lifetime of nanoseconds exhibits large spectral weight at <5 meV at $T < T_{CO}$, whereas short-lived transient absorption observed at $T << T_{CO}$ shows small low energy spectral weight. Such spectral difference in THz region indicates that the electronic property and/or the e-p coupling of the photo-induced macroscopic metallic state are different from those of the microscopic metallic state.

2. Experimental setup
For NIR-pump (0.89 eV) and THz-probe (1.5–13 meV) spectroscopy, a 1 kHz Ti: Al$_2$O$_3$ regenerative amplifier system (Hurricane; Spectra-Physics) was used as the light source. Output from the amplifier is divided into two beams: one is used for generating a NIR pump in a handmade optical parametric amplifier. The THz probing pulse was generated using a residual amplified beam by differential frequency generation in a ZnTe crystal with thickness of 1 mm, and focused in a pumped area of 1.5 mm diameter on the single crystal of $\alpha$-(ET)$_2$I$_3$ ($2 \times 2 \times 0.025$ mm$^3$). The transmitted THz light was detected using an EO sampling method. The time resolution is ca. 1 ps.

3. Results and discussions
Figure 1 portrays polarized absorption spectra of $\alpha$-(ET)$_2$I$_3$ for $E//b$. The absorption spectra for $T = 200$ K (metallic) and 25 K (CO) are represented respectively as solid and dashed curves in Fig. 1(a). Marked change in the absorbance (metallic, OD ca. 5 at 200 K; CO, OD ca. 0.1 at 25 K) reflects the I-M transition. A differential spectrum $\Delta$OD$_m$–$\Delta$OD$_t$, in which $\Delta$OD$_m$ and $\Delta$OD$_t$ respectively represent the optical density of the metallic and the CO insulator phases, is displayed in Fig. 1(b). Transient absorption ($\Delta$OD) spectra measured at 20 K are presented in Fig. 1(c). The absorption increase at $t_d$ (time delay after excitation) = 0.1 ps in a whole spectral region suggests photo-induced melting of the CO state and generation of the metallic state. The photo-induced absorption change ($\Delta$OD of ca. 0.15) is apparently less than that for the thermal I-M transition ($\Delta$OD$_{th}$ of ca. 4). However, considering that
The time constants, reflecting the relaxation time of the photoinduced metallic state, are approximately equal to those of the photo-induced reflectivity change measured at near-IR and mid-IR regions [9–11]. The solid curve marks the time evolution of the transmitted THz amplitude $E_{\text{THz}}$, which is normalized as $E'(t)=A(1-E_{\text{THz}}(t)/E_0)$, where $E_0$ and $A$ respectively represent the amplitude before photo-excitation and the normalized coefficient. The time evolution of $E'(t)$ is approximately in agreement with that of $\Delta\text{OD}(t)$.

Figures 2(a) and 2(b) respectively depict transient absorption spectra for excitation intensity $I_{\text{ex}}$ of 0.01 mJ/cm$^2$, at 20 K(a) and 124 K(b). At 20 K, a major spectral weight exists at the high-energy side (5–10 meV). On the other hand, at 124 K the spectral weight exists at the low energy region (<5 meV). Figure 2(c) portrays $E'(t)$, reflecting the relaxation dynamics of the metallic state for various temperatures $T<T_{\text{CO}}$ ($I_{\text{ex}}=0.01$ mJ/cm$^2$). Relaxation times $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$ in THz region are shown as a function of reduced temperature, represented by large filled diamonds in Fig. 3(a). $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$ are obtained by fitting of the time profiles (Fig. 2(c)) with the three-component exponential decay with a time constant $\tau_{\text{fast}}$, $\tau_{\text{middle}}$ and $\tau_{\text{slow}}$. Of the three components, however, $\tau_{\text{middle}}$ (fraction<10%) is independent of temperature, indicating that $\tau_{\text{middle}}$ does not concern I-M transition. It is noteworthy that $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$ increase with temperature for $T<T_{\text{CO}}$. Such temperature dependence is analogous to the result of mid-IR pump-probe spectroscopy, as shown by the filled and white circles, rectangles, triangles, and crosses in Fig. 3(a) [9, 11]. The increase of the decay time near $T_{\text{CO}}$ has been ascribed to critical slowing down (CSD), as portrayed in Fig. 3(a) [9, 11]. Two kinds of decay time, $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$, are respectively attributable to the short-lived microscopic metallic state and the long-lived macroscopic metallic state. Possible origins for the different CSD behaviors are the efficient and
inefficient e-p coupling for the photo-induced metallic states (Figs. 3(b) and 3(c)), respectively. Therefore, large spectral weight at <5 meV (Fig. 2(b)) with long decay and the low-energy weight (Fig. 2(a)) indicating a fast decay are respectively attributable to the macroscopic and microscopic metallic states.

The reason for the difference between the transient THz spectra for the macroscopic metallic state at 124 K (Fig. 3(b)) and that for the microscopic metallic state at 20 K (Fig. 3(c)) can be discussed as follows. Large low-energy spectral weight for the macroscopic metallic state might be simply interpreted as the Drude-like metallic state. However, further discussion on this interpretation is difficult because of the narrow detection range of our measurement. Another possible interpretation is efficient coupling between the photo-induced macroscopic metallic state and the low-energy phonon modes. It is natural to consider that the low-energy spectral weight is ascribed to efficient coupling between the metallic state and the low-energy phonons, because the corresponding low-energy phonon modes such as intermolecular libration modes effectively modulate transfer integral [9, 11]. On the other hand, such e-p coupling can not be expected for the short-lived microscopic metallic state, because the lifetime is too short to interact with such low frequency phonons.

Summary

We measured the transient THz absorption spectra of the photo-induced metallic states in charge ordered organic salts α-(ET)$_2$I$_3$. Transient absorption spectrum for the macroscopic metallic domain (124 K) differs from that for the microscopic metallic domain (20 K): the transient absorption for the macroscopic domain exhibits a large spectral weight in the low energy (<5 meV) region and slow decay, but that for microscopic domain is characterized by the small spectral weight at low energy and fast decay. Such differences are ascribed to the electronic properties of the photo-induced metallic states and/or the coupling between the photo-induced metallic state and the low-energy phonons.

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