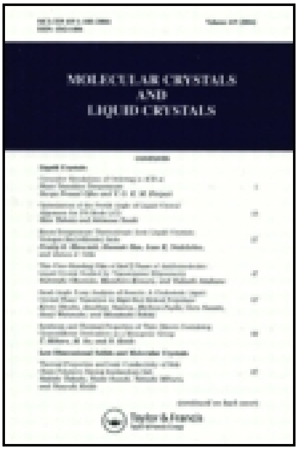

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Anomalous Temperature Dependence of Low-Enercy-Electron Transmission Spectra of Thin Films of Tetrakis(Nonylthi 0)-Tetrathiaful Valene (TTC$_9$-TTF)

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ANOMALOUS TEMPERATURE DEPENDENCE OF LOW-ENERGY-ELECTRON TRANSMISSION SPECTRA OF THIN FILMS OF TETRAKIS(NONYLTHIO)-TETRATHIAFULVALENE (TTC_9-TTF)

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Abstract Temperature dependence of low-energy-electron transmission spectra was measured for thin films of a molecular fastener, tetrakis(nonylthio)tetrathiafulvalene. 10 spectral features, which can be ascribed to the structure of the conduction bands, were observed in the energy region of incident electron of 0 - 15 eV. They showed a large temperature dependence of the energy position as well as of the sharpness and the intensity. The energy positions shifted ~0.6 eV to high-energy side by cooling from room temperature to -124°C. Such a large energy shift was not observed for other thin films consisting of long-alkyl molecules, and is considered as a result of the molecular fastener effects.

INTRODUCTION

Tetrakis(alkylthio)tetrathiafulvalenes (TTCn-TTF's) form a series of tetrathiafulvalene (TTF) derivatives with four alkylthio substitutional groups, in which good electrical conduction was observed.[1] Through the measurements of electrical conductivities, crystal structure, ionization threshold energies and thermal properties for the series of TTCn-TTF's, Inokuchi and his coworkers found a new function named as "molecular fastener effect" in the compounds with long alkyl chains.[1-7] The physical meaning of the fastener effects is that intermolecular interactions between side alkyl chain groups work as attractive force to reduce the interplanar distance between adjacent TTF parts.[1,2] As a result, high electrical conductivity is realized along the stacking direction of conjugated π-systems.[1,2,8] In fact, TTC_9-TTF and TTC_{10}-TTF have unique crystal structures with strong S-S atomic contacts of 3.57 Å between molecules and a short interplanar distance of 3.49 Å,[1,4,5] and show the extraordinarily low ionization threshold energies of 4.7 eV in the crystalline state.[1,2,6] These anomalous features are considered to be realized by a concurrence between the intermolecular repulsive and attractive forces which respectively exist at TTF and TTCn parts.

On the other hand, we observed for thin films of long alkyl molecules using low-energy electron transmission (LEET) technique that the thermal excitations of molecular vibrations significantly perturb the conduction band structure.[9] Further it has been known that the intermolecular distance in the crystals of polyethylene[10] and long chain alkanes[11] are highly temperature dependent due to the thermal excitations of molecular vibrations. We thus expect that the molecular fastener effects depend on temperature to produce changes of the intermolecular distance of crystalline TTC_9-TTF[12] and electronic structure due to the thermal excitations of molecular vibrations of the alkyl parts.

In this paper we report the temperature dependence of low energy electron transmission (LEET) spectra of thin films of TTC_9-TTF and demonstrate that an extraordinarily large temperature dependence of the conduction bands exists in this material.

EXPERIMENTAL

In the LEET experiment, a monoenergetic electron beam impinges perpendicularly on a thin film deposited on a metal substrate and the electron current transmitted through the film (I_t) is measured at the substrate as a function of incident electron energy (E_i). The transmitted current $I_t(E_i)$ is in general dependent on the crystal structure and electronic states of the film through both electron elastic and inelastic scattering, and hence the $I_t(E_i)$ curves (LEET spectra) give information on these factors.[9,13,14]

The experiments were performed using the LEET spectrometer described in the previous papers.[13,14] In the present measurements, the incident electron current (I_i) was 1×10^{-11} ($\pm$ 3×10^{-13}) A and the number density of the incident electron at the sample surface was estimated to be 3-8×10^{-8} Å^{-2}s^{-1} by measuring the beam diameter with the method described in a previous paper.[13] The ultralow density of the incident electron at the film surface enabled us to measure the spectra of organic thin films without radiation damage. The energy resolution was measured to be 0.3 eV from the energy width of the rising part of the $I_t(E_i)$ spectrum at E_i=0 eV. The vacuum condition during the measurements was ~2×10^{-9} Torr for low temperature measurements and 5×10^{-9} Torr for room temperature measurements.

The TTC_9-TTF samples used in the present measurements were described in the literature[5] (molecular structure is shown in Fig. 1). The crystalline thin films were prepared (1) by the spin coating of 2800 rpm from 0.2% (wt/vol) hexane solution onto Cu substrates and (2) by evaporating the crystals onto Cu substrates in the preparation chamber at a pressure below 1×10^{-8} Torr (deposition rate ~2.7 Å/min). Amorphous thin films were prepared onto Cu substrate kept at -137°C under a vacuum condition of less than 5×10^{-9} Torr during evaporation. The deposition rate was ~6 Å/min. The crystalline thin films evaporated on Cu substrate showed sharp X-ray diffraction pattern, indicating that the molecules can be evaporated to form thin crystalline film with little decomposition. This was also confirmed by mass spectra of the vaporized molecules using the method described in Ref. 15.

RESULTS AND DISCUSSION

The LEET spectra (I_t and dI_t/dE_i curves) measured at low temperature for the crystalline thin films prepared by the spin-coating and vacuum evaporation are shown in Fig. 1, together with the results for the amorphous thin film. The crystalline films prepared with different methods show similar LEET features. The $I_t(E_i)$ features are seen more clearly in $dI_t(E_i)/dE_i$ curves. The amorphous spectra are significantly different from those of the crystalline films. The fine features observed in the crystalline spectra are not observed in the amorphous spectra.

Structures observable in LEET spectra of condensed films may in general be broadly divided into two categories; the structures resulting from elastic electron interactions and the others originating in electron inelastic processes. For molecular solids, in which intermolecular interaction is very weak, the main LEET features due to electron inelastic processes occurs through the creation of localized molecular

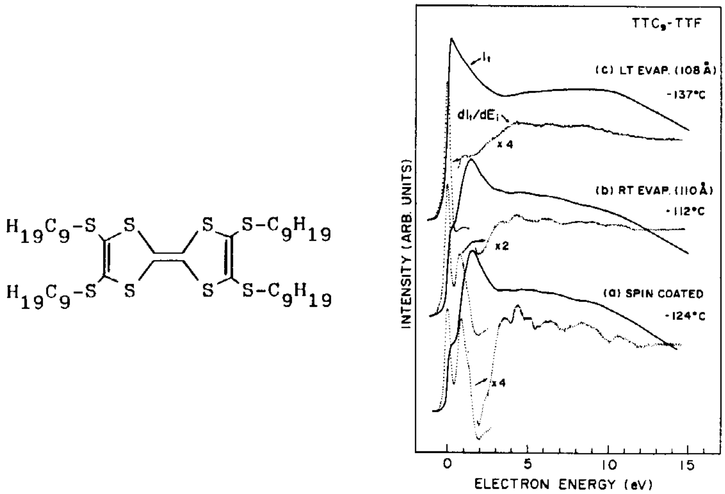

FIGURE 1 Molecular structure of TTC$_9$-TTF (left) and LEET spectra of crystalline and amorphous thin films of TTC$_9$-TTF (right). (a) Spin-coated crystalline film. (b) Evaporated crystalline film of 110 Å thick. (c) Evaporated amorphous film of 108 Å thick. All spectra were measured at low temperature (indicated in the figure). $I_t(E_i)$ and $dI_t(E_i)/dE_i$ curves are shown by solid and dotted curves, respectively.

exciton, and when this processes dominate the LEET spectra, the LEET features correspond to the electronic excitations of individual molecules.[16] These features are not so dependent on the crystal structure or the degree of crystallinity of the film. On the other hand, the LEET features which originate in the elastic electron interaction are highly dependent on the crystal structure rather than the molecular electronic states. In this case, the structure of the conduction bands is reflected in the spectra through the energy dependence of the injection of incident electrons at the film surface. The incident electrons are injected into the film depending on the density-of-states of the conduction bands which are determined by the crystal structure.[13, 14]

The results shown in Fig. 1 thus lead us to a conclusion that the LEET features appearing in the crystalline films do not originate in the creation of the molecular excitons, but in the structure of the conduction bands.

The temperature dependence of the LEET spectra is shown in Fig. 2a [$I_t(E_i)$ curves] and Fig. 2b [$dI_t(E_i)/dE_i$ curves]. The LEET features observed faintly in $I_t(E_i)$ curves can be seen more clearly in

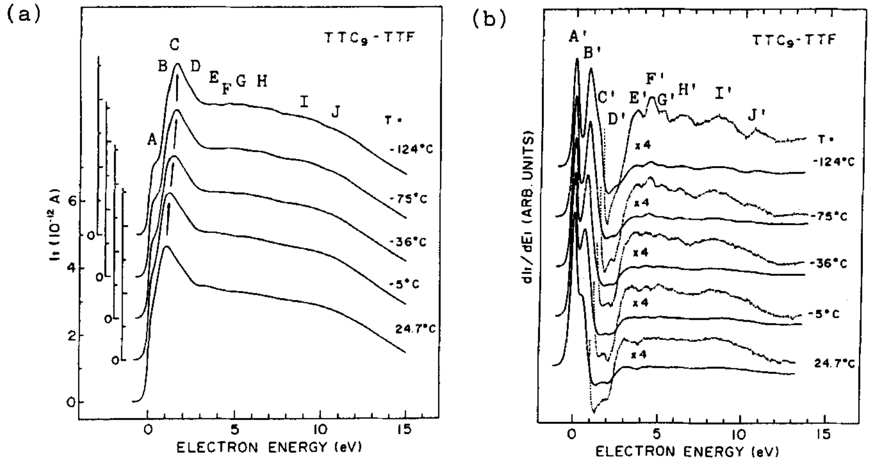

FIGURE 2 Temperature dependence of LEET spectra for spin-coated films of TTC$_9$-TTF. (a) $I_t(E_i)$ curves. (b) $dI_t(E_i)/dE_i$ curves.

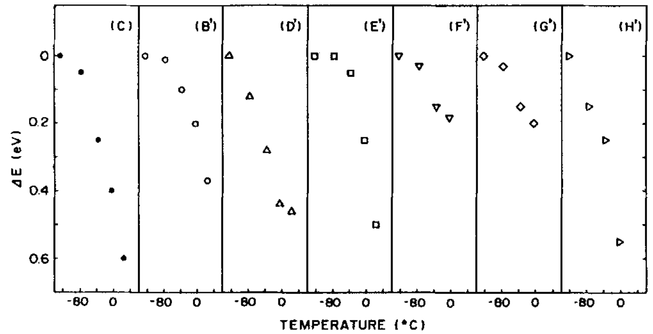

FIGURE 3 Temperature dependence of the energy positions of selected LEET features (B-H). The energy shift ΔE from E_i at the lowest temperature is shown. ΔE determined from the features in $dI_t(E_i)/dE_i$ curves are indicated by prime.

$dI_t(E_i)/dE_i$ curves. The spectra show diffused features at room temperature, and on cooling I_t increases and the features become very sharp. Such a sharpening of the LEET features as well as the increase in I_t on cooling were also observed for the thin films of organic molecular crystals which do not show the molecular fastener effects.[9]

The energy positions of the features shift to high energy side upon cooling and the energy shift (ΔE) was extremely large. For example, ΔE of the peak C in $I_t(E_i)$ is larger than ~0.6 eV for the temperature difference of ~150 K. The temperature dependences of the energy positions of some spectral features are shown in Fig. 3. Such large temperature dependences of the energy positions were not observed for organic molecular crystals which do not show the molecular fastener effects,[9,17] e.g. long chain alkanes and TTC_1-TTF.

So far, we know little about the quantitative expression and the temperature dependence of the fastener effects; the present result is considered to correlate closely with the fastener effects, and such a large temperature dependence of the electronic states must be a typical characteristic of the fastener effects.

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