Thermoelectric power and Raman spectra of (Me₂DCNQI)₂CuₓLi₁₋ₓ

T. Yamamotoᵃ,⁎, H. Tajimaᵃ, R. Katoᵇ, M. Uruichiᶜ, K. Yakushiᶜ

ᵃInstitute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Japan
ᵇRiken, 2-1 Hirosawa, Wako, Japan
ᶜInstitute for Molecular Science, Myodaiji, Okazaki, Japan

Abstract

We measured thermoelectric power and Raman spectra for (Me₂DCNQI)₂CuₓLi₁₋ₓ. The ν₈ (quinoid C=N stretch) Raman line shifts downwards with an increase of copper contents (x), and exhibits a split for x ≤ 0.24. Temperature dependence of the thermoelectric power exhibits drastic change between x = 0.14 and x = 0.22. This behaviour is consistent with the phase diagram previously determined.

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1. Introduction

After the findings of CDW in TTF-TCNQ, physical properties of quasi-one-dimensional molecular conductors have been intensively studied. However “anomalous metallic state” in these conductors is still not well understood. This state is typically characterized by metallic behaviour of electrical conductivity around room temperature, by the “mid-infrared band” (an intense absorption band in the mid-infrared range), and by the constant thermoelectric power around room temperature. On lowering the temperature, a resistivity-temperature curve shows an upturn, and a conductor in this “anomalous metallic state” falls into an insulating state. In order to study this “anomalous metallic state” we are studying various properties of the quasi-one-dimensional conductors (Me₂DCNQI)₂CuₓLi₁₋ₓ. This system has the following features [1]:

(i) The DCNQI molecules form a regular one-dimensional column at room temperature. Consequently, the effect of lattice distortion is negligibly small in this system.
(ii) By substituting Cu for Li, the filling of the π-band changes from a quarter to approximately one-third.

Based on our previous study, we obtained an x–T phase diagram [1,2]. For x < 0.14, the ρ–T curve exhibits metallic behaviour around room temperature, a broad upturn at a temperature above ~200 K, and an inflection around 60 K. We revealed that this inflection is due to a phase transition from a paramagnetic state into a nonmagnetic state. For 0.17 ≤ x ≤ 0.29, the ρ–T curve exhibits an upturn between 200 and 80 K, but does not exhibit any inflection around 60 K. Magnetic susceptibility is paramagnetic down to 4.2 K. For 0.39 ≤ x, the ρ–T curve exhibits metallic behaviour down to 4.2 K.

In this communication, we report Raman spectra and temperature dependence of the thermoelectric power for (Me₂DCNQI)₂CuₓLi₁₋ₓ. On the basis of the Raman studies, we present direct evidence suggesting charge disproportion among the Me₂DCNQI molecules for x ≤ 0.22. We also show that the temperature dependence of the thermoelectric power drastically changes between x = 0.14 and x = 0.22.

2. Experimental

Raman spectra were measured by use of Ranishow microscope Raman system. A He–Ne laser was used for the light source of the excitation. All the spectra were measured in the backward scattering geometry. Thermoelectric power (S(T)) was measured by the two-probe method. Temperature gradient between the two electrodes was approximately 0.4 K.

3. Results and discussion

3.1. Raman spectra

Fig. 1 shows Raman spectra at room temperature and at 200 K for various contents of copper. On the basis of the
calculation by Lunardi and Pecile [3], we assigned the peak(s) shown by arrows in the figure to the \( v_8 \) mode (quinoïd C=N stretch) of Me₂DCNQI⁻. This mode shifts downwards with an increase of \( x \) and splits for \( x \leq 0.22 \). The frequency difference between the split peaks is approximately 10 cm⁻¹. We measured the polarization dependence of the Raman spectra. From the observed polarization dependence of the spectra, we concluded that the split is not that predicted by the factor-group analysis. Since the frequency of the \( v_8 \) mode is sensitive to the charge density on the Me₂DCNQI molecules, we concluded that the split is due to the charge disproportion among the Me₂DCNQI molecules.

3.2. Temperature dependence of thermoelectric power

Fig. 2 shows temperature dependence of thermoelectric power \( S(T) \). The \( S(T) \) curves below 60 K can be classified into two groups: \( S(T) \) exhibits semiconductive behaviour \( (S(T) \propto T^{1}) \) for \( 0 \leq x \leq 0.14 \) and metallic behaviour \( (S(T) \propto T) \) for \( x > 0.22 \). The boundary \( (0.14 < x < 0.22) \) is consistent with the phase boundary determined by resistivity and magnetic susceptibility measurements [1,2].

Thermoelectric power at 300 K, \( S \) (300 K), is almost constant \( (\sim -56 \mu V/K) \) for \( 0 \leq x \leq 0.24 \). For \( x \geq 0.29 \), \( S \) (300 K) increases with an increase of \( x \). Although \( S \) (300 K) at \( x = 0 \) is consistent with \( -k_B/e\ln 2 = 58.9 \mu V/K \) which is given by the large-\( U \) model at \( \rho = 0.5 \) [4,5], \( S \) (300 K) for \( x \neq 0 \) is not consistent with this model. More elaborate theory may be necessary.

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References