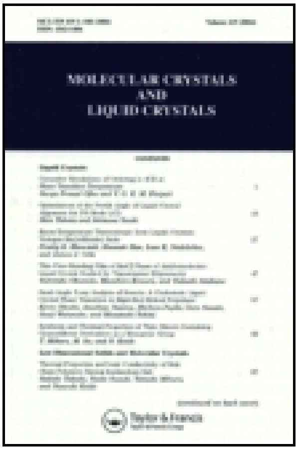

Molecular Crystals and Liquid Crystals

Reflectance spectra of θ-ET 2 MM′(SCN) 4 [MM′=RbCo, RbZn, CsZn]

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Version of record first published: 18 Oct 2010

To cite this article: Hiroyuki Tajima, Shinichi Kyoden, Hatsumi Mori & Shoji Tanaka (2003): Reflectance spectra of θ-ET 2 MM′(SCN) 4 [MM′=RbCo, RbZn, CsZn], Molecular Crystals and Liquid Crystals, 380:1, 215-220

To link to this article: http://dx.doi.org/10.1080/713738706

Mol. Cryst. Liq. Cryst., Vol. 380, pp. 215-220
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1058-725X/02 \$12.00 + .00
DOI: 10.1080/10587250290101603

REFLECTANCE SPECTRA OF θ-ET$_2$MM$'$(SCN)$_4$ [MM$'$ = RbCo, RbZn, CsZn]

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Temperature dependence of the polarized reflectance spectra have been measured on the single crystals of θ-ET$_2$MM$'$(SCN)$_4$ [MM$'$ = RbCo, RbZn, CsZn] salts. The reflectance spectra of RbCo and RbZn salts exhibit drastic change around 190 K for samples cooled down slowly ($dT/dt \sim -0.1$ K/min). This spectral change disappears for the samples cooled down rapidly ($dT/dt \sim -1$ K/min). The reflectance spectra of MM$'$ = CsZn salt exhibit Drude-like future down to 20 K. Charge-ordering patterns on these salts are deduced by the spectral analysis using mean-field calculations.

Keywords: reflectance spectra; charge order; ET salt

INTRODUCTION

Optical spectra of molecular conductors contain a lot of information such as electron-electron correlation effects, electron-phonon interaction, etc. However, the interpretation of the optical spectra is not straightforward. Among all, the coexistence of the metallic conduction and MIR band (electronic transitions in the mid-infrared region) in one-dimensional molecular conductors has puzzled many researchers [1]. In order to explain this phenomenon, the following hypotheses were recently proposed by the author (H. T.) and his group [2,3].

i) In some molecular conductors, the original crystal symmetry is broken even at room temperature due to spin polarization (or charge ordering) resulting from the Coulomb repulsion.

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ii) The symmetry breaking at around room temperature is followed by domain formation. Electric current is carried by charged domain walls rather than by single particles.
iii) The MIR band is essentially the inter-band transition within spin-polarized (or charge-ordered) domains.

On the basis of these hypothesis, the spectral analysis using the mean-field calculation was applied to several molecular conductors. The consistency between the observed and calculated spectra is satisfactory for both cases. In this paper we present the summary of our study for θ-$ET_2MM'(SCN)_4$ [4].

CONDUCTIVITY SPECTRA OF θ-$ET_2MM'(SCN)_4$

θ-$ET_2MM'(SCN)_4$ salts are a series of molecular conductors which afford a wide variety of electronic states, although they have similar crystal structures [5]. In our present study, we have measured reflectance spectra of θ-$ET_2MM'(SCN)_4$ ($MM' = RbCo$, RbZn, CsZn).

The RbCo and RbZn salts exhibit metal-insulator transition at 190 K, when they are cooled slowly—hereafter we call this state as relaxed state (R-state). The magnetic susceptibility below and above 190 K in the R-state is almost continuous and does not exhibit any anomalous feature related to the phase transition [5]. On further lowering the temperature, the salts fall into the spin-Peierls state below 20 K. Interestingly, these phenomena below 190 K disappear, when samples are cooled rapidly ($dT/dt \geq 1$ K/min) —hereafter we call this sate as quenched state (Q-state). The magnetic susceptibility in the Q-state exhibits the Curie-Weiss tail below 90 K and does not indicate any symptom of the spin-Peierls transition [6].

The CsZn salt exhibits metal-insulator transition at 20 K. An increase of susceptibility is observed below 20 K [5]. The principal axes of the EPR g-tensor are recently reported to rotate with lowering the temperature [7].

Figure 1 shows the temperature dependence of the optical conductivity spectra for the RbCo salt. The spectra of the RbZn salt are similar to these spectra. The spectra exhibit a single-peaked feature around room temperature (290 K, 250 K, 200 K in Figure 1). When samples are cooled down slowly [0.1 K/min], the spectra exhibit drastic changes accompanying the phase transition into the R-state. The spectra in the R-state exhibit triple-peaked feature (150 K(R), 20 K(R) in Figure 1). On the other hand when the RbCo salt is cooled down slowly [1 K/min], this drastic change of the spectra is absent for samples cooled down rapidly (150 K(Q); 20 K(Q) in Figure 1).

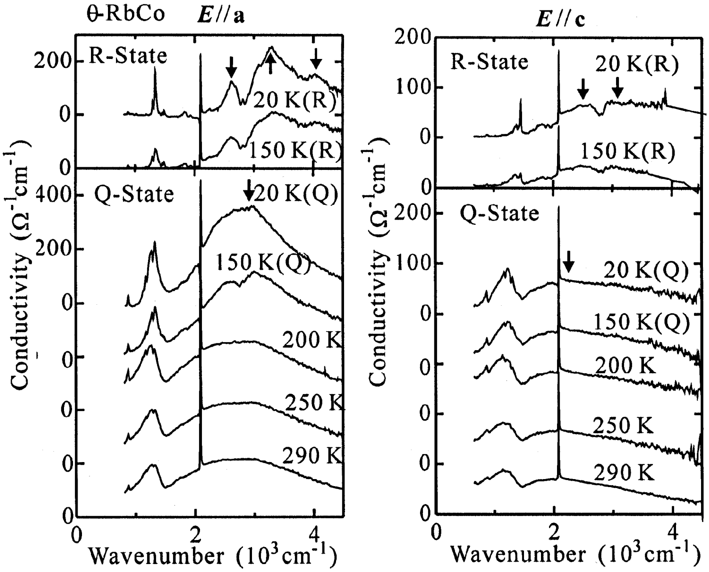

FIGURE 1 Temperature dependence of the optical conductivity spectra of θ-ET$_2$RbCo(SCN)$_4$. The arrows indicate the peak positions of the electronic transitions (MIR band). Sharp peaks which are not marked by arrows are associated with molecular vibrations.

Figure 2 shows the spectra of the CsZn salt. Although this salt is reported to undergo a metal-insulator transition at 20 K we could not cool the sample below 20 K in the present study. For this salt the spectra exhibit Drude-like feature from room temperature down to 20 K. The conductivity spectra exhibit broad absorption band around 2000 cm^{-1}. This band is obscure around room temperature and becomes intense with lowering the temperature. A similar absorption band is also observed in θ-ET$_2$I$_3$ [8].

DISCUSSION

We calculated the optical conductivity spectra on the basis of the mean-field approximation applied to the extended Hubbard model in order to analyse the results shown in Figures 1 and 2. In this calculation we assumed an extended Hubbard Hamiltonian and reduced it into the effective mean-field Hamiltonian in a similar manner reported by Seo [9]. Then we calculated optical conductivity spectra by using Kubo Formula. Figure 2

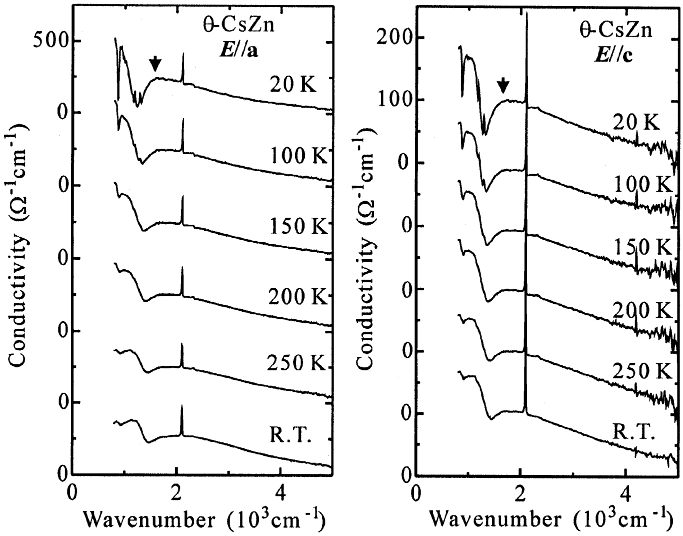

FIGURE 2 Temperature dependence of the optical conductivity spectra of θ-ET$_2$CsZn(SCN)$_4$. The arrows indicate the peak positions of the electronic transitions (MIR band). Sharp peaks which are not marked by arrows are associated with molecular vibrations.

shows the results of the spectral calculations for three SCF solutions denoted by vertical-stripe (V.S.), horizontal-stripe (H.S.), diagonal-stripe (D. S.), and antiferromagnetic (A.F.). The optical conductivity spectra exhibit single-peaked feature in the V.S. state, and triple-peaked feature in the H.S. and D. S. state. In the A.F. state, the spectra exhibit intra-band transition together with the weak MIR band.

By comparing the observed and calculated spectra, we concluded: i) for the RbCo and RbZn salts, the V.S. order exists in the conductive state above 190 K and in the Q-state below 190 K while the H.S. order exists in the R-state below 190 K: ii) the metal-insulator transition of the RbCo and RbZn salts at 190 K is accompanied by the change of charge-ordering patterns from the V.S. to the H.S.; iii) the charge disproportionation is absent or negligibly small in the CsZn salt above 20 K.

The difference between the calculated and observed spectra in the H. S. state may be attributable to the exciton effects, which have not been considered in this study. The conclusion ii) is consistent with that derived from the NMR experiments [10]. Although other conclusions have not been proved yet, they are explained if we assume the hypothesis ii) described in the introduction.

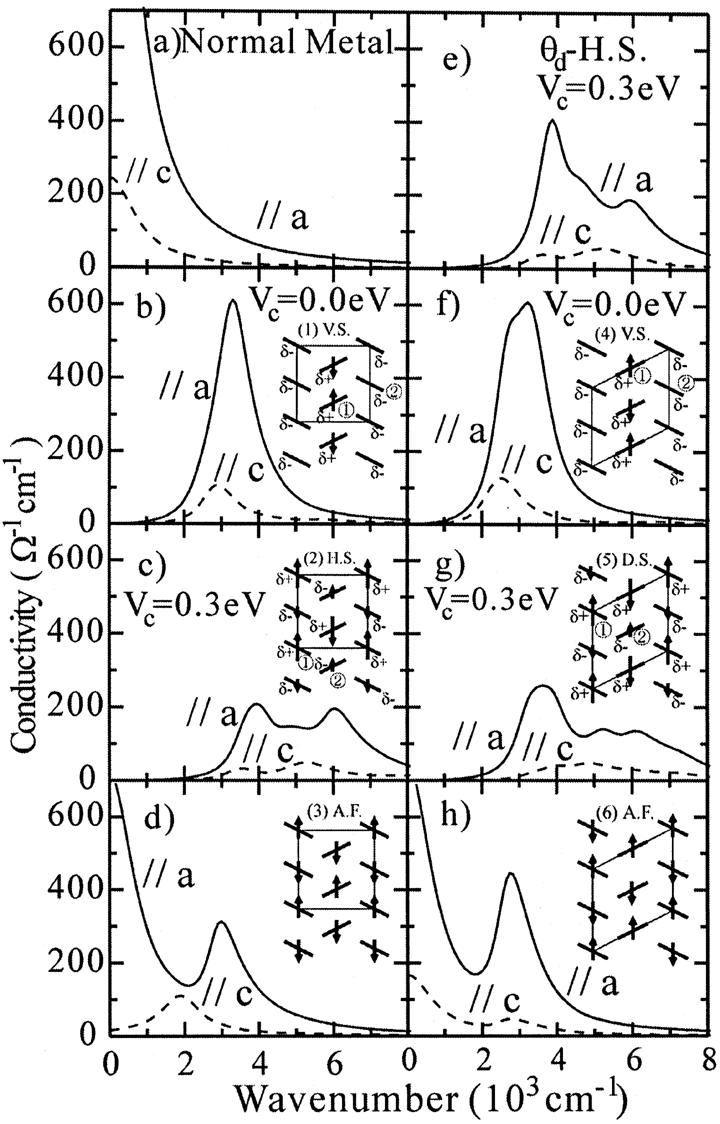

FIGURE 3 Optical conductivity spectra calculated on the basis of mean-field approximation applied to the extended Hubbard Hamiltonian. Abbreviations, V.S., H.S., D.S., A.F. indicate vertical-stripe, horizontal-stripe, diagonal-stripe, and antiferromagnetic, respectively.

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