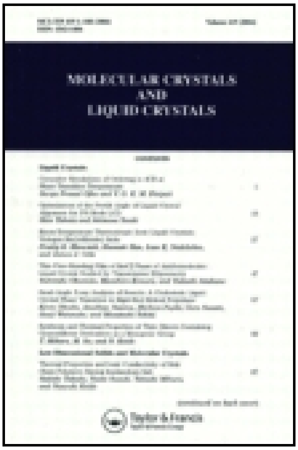

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Charge ordering patterns and their excitation spectra in two-dimensional charge-transfer compounds

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CHARGE ORDERING PATTERNS AND THEIR EXCITATION SPECTRA IN TWO-DIMENSIONAL CHARGE-TRANSFER COMPOUNDS

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We calculate optical conductivity spectra for various charge ordering (CO) states in the two-dimensional extended Hubbard model at quarter filling with the random phase approximation. The results are examined from a viewpoint of the atomic limit. We compare our results with the measured spectra for the θ-$(ET)_2X$ salts and discuss the CO patterns and their charge excitations realized in these compounds.

Keywords: charge ordering; θ-BEDT-TTF salts; extended Hubbard model; random phase approximation; optical conductivity

INTRODUCTION

The charge transfer salts, θ-$(\mathrm{BEDT\text{-}TTF})_2\mathrm{MM'(SCN)}_4$ ($\mathrm{M = Rb, Cs, M' = Zn, Co}$), are two-dimensional conductors at room temperature and show metal-insulator transitions depending on the temperature and the anion [1,2,3]. In the insulating phases, charge ordering (CO) states, in which the charge density is disproportionated and the spin degrees of freedom survive [4], are found by the X-ray structure analysis [5], ^{13}C-NMR measurements [6,7], EPR measurement [8], and Raman spectroscopy [9]. The degree of charge

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*Corresponding author. E-mail: morimich@ims.ac.jp transfer is estimated as about $0.36 \sim 0.40$ for the RbZn(SCN)$_4$ salt by the NMR measurement [6] and Raman spectroscopy [9].

By theoretical calculations, Seo [10] and T. Mori [11] have shown that CO states are caused by intersite repulsive interactions and that various charge ordering patterns are realized by different relative interaction strengths. Tajima et al. have measured the temperature dependence of the polarized reflectance spectra and studied the charge ordering patterns by comparing their experimental results with theoretical calculations based on the Hartree approximation [12].

In this paper, we calculate response functions in the random phase approximation (RPA) on the basis of the Hartree-Fock (HF) states and show features of the optical conductivity spectra characteristic of each CO state. If intersite interactions are essential, an excitonic effect should be significant to affect the peak positions and the lineshapes of the optical conductivity spectra. Such excitonic effect is included with the RPA. We will discuss difference between the RPA and HF results.

GROUND STATES OF EXTENDED HUBBARD MODEL

For the quarter-filled conducting layer in the hole picture, we adopt the two-dimensional extended Hubbard model including the nearest-neighbor interaction,

$$H = \sum_{\langle i,j\rangle,\sigma=\uparrow,\downarrow} (t_{ij}(c^\dagger_{i,\sigma}c_{j,\sigma} + H.c.) + U\sum_i n_{i,\uparrow}n_{i,\downarrow} + \sum_{\langle i,j\rangle} V_{ij}n_in_j, \qquad (1)$$

where $c^\dagger_{i,\sigma}(c_{i,\sigma})$ creates (annihilates) a hole with spin σ at site $i, n_{i,\sigma}$ is the hole number density, and $n_i = n_{i\uparrow} + n_{i\downarrow}$. The symbol $\langle i,j\rangle$ stands for nearest-neighbor sites. The transfer integrals t_{ij} and the inter-site repulsive interaction strengths V_{ij} are defined in the upper-right panel of Figure 1. We do not take account of lattice modulations in this paper.

Ground states obtained by the present HF calculations have three kinds of CO patterns: vertical, diagonal and horizontal patterns, as shown in Figure 1. We assumed that a unit cell contains four molecules, ignoring some HF solutions found by Seo for eight molecules per unit cell. Although the ignored solutions have different spin configurations, their CO patterns are similar to one of the above, so that we expect similar optical spectra.

We used the values of the overlap integrals calculated by H. Mori et al., [1] and chosen those values of U, V_c, V_p which reproduce the experimentally observed degree of charge transfer about 0.4 in the HF calculation for each CO pattern shown in Figure 1.

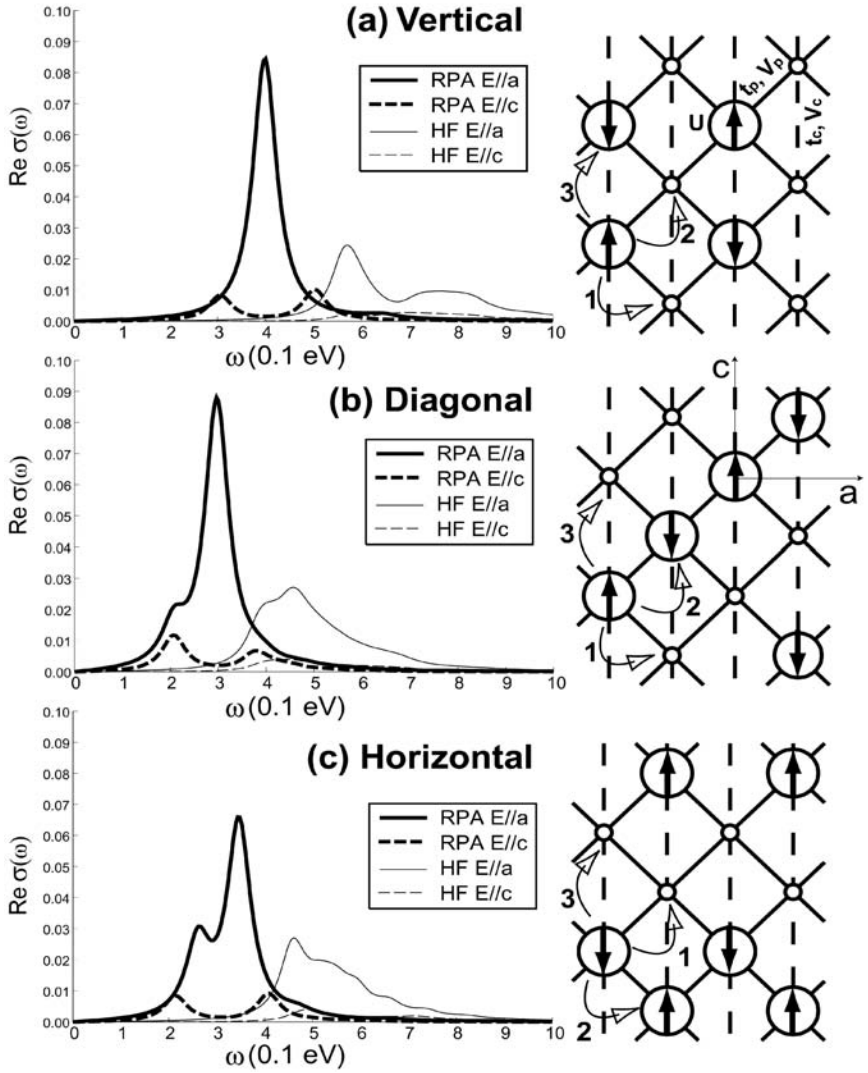

FIGURE 1 CO patterns and their optical conductivity spectra for (a) vertical, (b) diagonal, and (c) horizontal orders, with $t_c = 0.024\,\text{eV}$, $t_p = -0.094\,\text{eV}$ and $U = 0.7\,\text{eV}$. The values of V_c and V_p are $V_c = 0.30\,\text{eV}$, $V_p = 0.36\,\text{eV}$ for (a); and $V_c = 0.31\,\text{eV}$, $V_p = 0.29\,\text{eV}$ for (b) and (c).

OPTICAL SPECTRA IN CHARGE ORDERING STATES

We solve the linearized equation of motion for particle-hole pairs that describe quantum fluctuations around the HF ground state. Details of themethod are found in Ref. [13].

The optical conductivity spectra for polarization in the a and c directions are calculated within the RPA and HF approximation, and shown in Figure 1. In the RPA spectra for polarization in the a direction, the vertical order has one peak, while the diagonal and horizontal orders have two peaks. For reference, the excitation energies in the atomic limit where the RPA gives exact values are listed in Table 1. We find that E_1 and E_2 of the vertical order are degenerate. Meanwhile, E_1 of the diagonal and horizontal orders are different from their E_2. The excitation energies of the diagonal and horizontal orders are identical in the atomic limit. Since the E_3 process is not observed in the present polarization($//a$), it is reasonable that the vertical order has a single peak, while the diagonal and horizontal orders have two peaks. From these results, it is hard to distinguish the diagonal order from the horizontal one. The main peak by RPA appears narrower at a lower energy than the HF peak. It is due to the attractive nearest-neighbor interactions for the excited particle-hole pairs. If an intersite repulsive interaction is strong, such effect would be clearly observed.

The optical conductivity spectra for polarization in the a direction of the RbM′(SCN)$_4$ salts at 20 K [9,12] have two or three peaks. By comparing it with our results, the diagonal or horizontal order is considered to be realized in these salts. This conclusion from the RPA calculation is consistent with the Tajima et al.'s conclusion derived from theire experimental and theoretical studies based on the Hartree calculation [12]. However, the experimental data have no excitonic peak but rather broad peaks probably due to the inter-band transitions, which are actually calculated by Tajima et al. This fact indicates that the nearest-neighbor interaction

TABLE 1 Excitation Energies in the Atomic Limit with the RPA and HF Approximation. The Energies E_1, E_2 and E_3 Correspond to the Numbered Processes Shown in the Right Panels of Figure 1

		RPA	HF	RPA−HF
Vertical	E_1	$-2V_c+3V_p$	$-2V_c+4V_p$	$-V_p$
	E_2	$-2V_c+3V_p$	$-2V_c+4V_p$	$-V_p$
	E_3	$U-V_c$	U	$-V_c$
Diagonal and Horizontal	E_1	$2V_c-V_p$	$2V_c$	$-V_p$
	E_2	$U-V_p$	U	$-V_p$
	E_3	V_c	$2V_c$	$-V_c$

strengths are rather weak. The transfer integrals, obtained by the extended Hückel molecular orbital method together with the crystal structure analysis, have already included the Fock terms of the nearest-neighbor interactions. Then, the HF calculations with these transfer integrals may overestimate the intersite interactions to reproduce the experimentally observed degree of charge transfer. In the Hartree calculation by Tajima et al., the values of V_c and V_p to reproduce the degree of charge transfer are indeed 0.1 eV smaller than the present HF values. Although appropriate nearest-neighbor interaction strengths, which take account of the Fock term contribution to transfer integrals, may be a little smaller, they are still large enough to produce excitonic peaks. To compensate this contradiction, not only the intersite interactions but also other factors, e.g., electron-lattice interactions, would be needed.

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