Role of electron-lattice couplings on charge order in quasi-two-dimensional organic conductors

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Abstract. Charge ordering with structural distortion in quasi-two-dimensional organic conductors \( \theta-(ET)_2RbZn(SCN)_4 \) (ET=BEDT-TTF) and \( \alpha-(ET)_2I_3 \) is investigated for an extended Hubbard model with Peierls-type electron-lattice interactions within the Hartree-Fock approximation. It is found that the lattice effects stabilize the experimentally observed charge order substantially in \( \theta-(ET)_2RbZn(SCN)_4 \), whereas the energy gain by a lattice distortion is small and its band structure and Coulomb interactions play an important role to realize the charge order in \( \alpha-(ET)_2I_3 \). The results are consistent with experimental observations and show contrastive roles of lattice degrees of freedom on charge orders in these compounds.

The family of quasi-two-dimensional organic conductors \( (ET)_2X \) (ET=BEDT-TTF) show a variety of low-temperature phases such as superconductivity, magnetism and charge order (CO). \( (ET)_2X \) consist of stacking layers of ET donor molecules and monovalent X anions. CO phenomena in several members of \( (ET)_2X \) with a \( 3/4 \)-filled \( \pi \)-electron band have been studied intensively since the electron correlation effects are realized to play an important role on their physical properties.

In this paper, we discuss the roles of electron-lattice couplings in \( \theta-(ET)_2RbZn(SCN)_4 \)\(^{1,2}\) and \( \alpha-(ET)_2I_3 \)\(^{3,4}\) which are typical compounds that are known to exhibit CO. \( \theta-(ET)_2RbZn(SCN)_4 \) shows a first-order metal-insulator transition at \( T_c = 200\text{K} \) and a spin gap behavior at low temperatures much below \( T_c \)\(^{5}\). The transition is accompanied by lattice distortion which changes its structure from the \( \theta \)-type in the metallic phase to the so-called \( \theta_d \)-type in the insulating phase. Several experiments such as X-ray scattering\(^6\) measurements show that the horizontal-type CO is formed in this compound. On the other hand, \( \alpha-(ET)_2I_3 \) shows a CO transition at \( T_c = 135\text{K} \)\(^7\), and the magnetic susceptibility measurement\(^8\) indicates a spin gap behavior below \( T_c \). Although the compounds \( \theta-(ET)_2RbZn(SCN)_4 \) and \( \alpha-(ET)_2I_3 \) have COs with very similar spatial patterns, the natures of the CO transitions are quite different. In \( \theta-(ET)_2RbZn(SCN)_4 \), the transition is of first order and accompanied with a large lattice distortion and large discontinuity, whereas the lattice distortion in \( \alpha-(ET)_2I_3 \) is relatively small. Theoretically, several authors have studied CO phenomena by using an extended Hubbard model which includes on-site (U) and intersite (V) Coulomb interactions\(^9,10,11\). However, the lattice effects in the above compounds are not fully understood so far.

In order to take account of lattice degrees of freedom explicitly, we consider an extended
The Hubbard model with Peierls-type electron-lattice couplings which is written as,

\[ H = \sum_{\langle ij \rangle \sigma} (t_{i,j} + \alpha_{i,j} u_{i,j}) (c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{\langle ij \rangle} V_{ij} n_{i\uparrow} n_{j\downarrow} + \sum_{\langle ij \rangle} \frac{K_{ij}}{2} u_{ij}^2, \tag{1} \]

where \( \langle ij \rangle \) represents the summation over the pairs of neighboring sites, \( c_{i\sigma}^\dagger c_{j\sigma} \) denotes the creation (annihilation) operator for an electron with spin \( \sigma \) at the \( i \)th site, \( n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma} \), and \( n_i = n_{i\uparrow} + n_{i\downarrow} \). The electron density is fixed at 3/4 filling. The electron-lattice coupling constant, lattice displacement and elastic constant are denoted by \( \alpha_{i,j}, u_{i,j} \) and \( K_{i,j} \), respectively. We further rewrite the parameters for the lattice degrees of freedom by introducing new variables as \( y_{i,j} = \alpha_{i,j} u_{i,j} \) and \( s_{i,j} = \alpha_{i,j}^2 / K_{i,j} \).

The structures of \( \theta-(ET)_2 \text{RbZn(SCN)}_4 \) and \( \alpha-(ET)_2 \text{I}_3 \) in the high-temperature metallic phase are shown in Figs. 1(a) and 1(b), respectively. Let us consider the case of \( \theta-(ET)_2 \text{RbZn(SCN)}_4 \) first. In the metallic phase of this compound, there are two kinds of transfer integrals \( t_p \) and \( t_c \) for diagonal and vertical bonds. For the lattice degrees of freedom, we consider three kinds of electron-lattice couplings, \( s_{i,j} \): \( s_c, s_a \), and \( s_\phi \) that originate from the \( c- \) and \( a- \)axis molecular translations and molecular rotation, respectively. They have been deduced by the X-ray experiment[6] and introduced in [13, 14]. The modulations due to these electron-lattice couplings are denoted by \( y_c, y_a \), and \( y_\phi \), respectively. On the other hand, \( \alpha-(ET)_2 \text{I}_3 \) has a more complex structure with four molecules in the unit cell. According to the X-ray structural analysis[12], sites A and D are equivalent to each other owing to the inversion symmetry in the metallic phase, while the symmetry breaks below the CO transition temperature. Sites A and B (C and D) become hole-rich (hole-poor) in the horizontal CO state. It also indicates that there is a structural distortion at the transition. Here we investigate the effects of the modulations in \( t_{b1} \) and \( t_{b2} \) which are observed experimentally[12]. We do not consider the modulations in smaller transfer integrals than the above for simplicity. The electron-lattice coupling constants for the corresponding modulations are denoted by \( s_{b1} \) and \( s_{b2} \), as in the \( \theta \)-type salt.

We apply the Hartree-Fock approximation to eq. (1) and the obtained Hamiltonian is diagonalized in \( k \)-space by assuming unit cells of various mean-field order parameters. For the intersite Coulomb interactions \( V_{i,j} \), we consider nearest neighbor interactions \( V_c \) for the vertical direction and \( V_p \) for the diagonal direction, as shown in Fig. 1(a). In the calculations for \( \theta-(ET)_2 \text{RbZn(SCN)}_4 \), we use \( t_p = 0.1(\text{eV}) \) and \( t_c = -0.04 \) for \( t_{i,j} \) in eq. (1), whereas the values listed in Fig. 1(b) are used for the case of \( \alpha-(ET)_2 \text{I}_3 \). We consider four types of order parameters according to the alignment of hole-rich molecules, namely, the 3-fold, diagonal, horizontal and vertical COs which are schematically shown in Fig. 1(c). The ground-state energy is calculated by solving the mean-field equation self-consistently together with the lattice displacements, which are determined by the Hellmann-Feynman theorem.

The ground-state energies as a function of \( V_p/V_c \) for the case of \( U = 0.7 \) are compared in Fig. 2. In the figure, the energy of the 3-fold CO without electron-lattice couplings is set at zero. We have shown only the lowest energy state for each CO pattern among different spin configurations. In the absence of electron-lattice couplings, the 3-fold CO is the most favorable in the nearly isotropic region, \( V_p/V_c \sim 1 \), for both compounds.

In the case of \( \theta-(ET)_2 \text{RbZn(SCN)}_4 \), the diagonal CO is stable when \( V_p/V_c \) is small, \( V_p/V_c < 0.7[11, 14] \). Without electron-lattice coupling, the energy of the horizontal CO cannot be the lowest in any region. However, the electron-lattice couplings stabilize the horizontal CO considerably as can be seen in Fig. 2(a). The diagonal CO is not affected by electron-lattice couplings, then the horizontal CO becomes more stable than this state. The values of the electron-lattice couplings are chosen to be \( s_c = 0.08, s_a = 0.17, \) and \( s_\phi = 0.11 \), which give resultant lattice displacements comparable to the experimentally observed values[14]. The 3-fold CO also has energy gain from the lattice modulations due to \( s_c \) and \( s_\phi \). The 3-fold CO is
Figure 1. Schematic structures of (a) \( \theta \)-(ET)\(_2\)RbZn(SCN)\(_4\) and (b) \( \alpha \)-(ET)\(_2\)I\(_3\) in the high-temperature phase. The values of transfer integrals in (b) from the extended Hückel method\[12\] are \( t_{a1} = -3.5 \), \( t_{a2} = -4.6 \), \( t_{a3} = 1.8 \), \( t_{b1} = 12.7 \), \( t_{b2} = 14.5 \), \( t_{b3} = 6.2 \), and \( t_{b4} = 2.5 \) (10\(^{-2}\)eV). (c) Order parameters used in the Hartree-Fock calculations. The solid and open circles indicate the hole-rich and -poor sites, respectively.

Figure 2. Ground-state energies for various CO states as a function of the ratio \( V_p/V_c \) at \( U = 0.7 \) for (a) \( \theta \)-(ET)\(_2\)RbZn(SCN)\(_4\) and (b) \( \alpha \)-(ET)\(_2\)I\(_3\). \( V_c/U \) is fixed at 0.35 in (a), while it is set at 0.4 in (b). The energy of the 3-fold CO is chosen to be zero. hr, dg, vt and pm denote the horizontal CO, diagonal CO, vertical CO and paramagnetic metallic states, respectively.

metallic even if the transfer integrals are modulated while the horizontal CO is insulating. In short, the horizontal CO with lattice distortion becomes stable for \( V_p/V_c < 0.7 \), while the 3-fold CO is favorable for \( 0.7 < V_p/V_c \sim 1 \).

Next, we consider the case of \( \alpha \)-(ET)\(_2\)I\(_3\). In this case, the horizontal COs are more stable than the other CO states even in the absence of electron-lattice couplings when the anisotropy in \( V_p/V_c \) is large, i.e., \( V_p/V_c < 0.65 \) as shown in Fig. 2(b). This has been pointed out within the Hartree approximation\[10\]. This is in contrast to the \( \theta \)-type salt where the horizontal CO does not become the ground state without electron-lattice couplings. Therefore, the band structure which comes from the asymmetric transfer integrals already in the metallic phase is considered...
to play an important role in stabilizing the CO in the α-type salt. In the presence of the electron-lattice couplings, the horizontal CO is further stabilized and it becomes the ground state for $V_p/V_c < 0.7$. No other state is affected by these electron-lattice couplings. As in the case of $\theta$-(ET)$_2$RbZn(SCN)$_4$, the electron-lattice couplings are chosen to be $s_{b1} = 0.08$ and $s_{b2} = 0.05$ so as to obtain lattice modulations consistent with the experimental values, i.e., $y_{b1} \sim 0.02$, and $y_{b2} \sim 0.01$[12, 15].

The contrastive roles of the lattice degrees of freedom in these compounds would explain the different natures of the CO phase transitions. In $\theta$-(ET)$_2$RbZn(SCN)$_4$, various COs compete with each other in the metallic phase because of its simple band structure with higher symmetry than that of $\alpha$-(ET)$_2$I$_3$. When the 3-fold CO fluctuations are dominant at high temperatures as suggested by the previous mean-field studies[11, 14], it is expected that the transition to the horizontal CO accompanies a large structural distortion since it requires the rearrangement of the charge patterns with different unit cells. This results in the first-order transition with large discontinuity as observed experimentally. On the other hand, for $\alpha$-(ET)$_2$I$_3$, the charge disproportionation exists even in the metallic state due to the asymmetry of transfer integrals[12]. In this phase, site B is hole-rich while site C is hole-poor, which is common to the charge disproportionation exists even in the metallic state due to the asymmetry of transfer integrals[12]. In this phase, site B is hole-rich while site C is hole-poor, which is common to the charge distribution in the horizontal CO. Therefore, the CO can be realized by merely breaking the equivalence of charge densities in sites A and D within the unit cell. This will lead to the first-order transition with small lattice distortion relative to that in $\theta$-(ET)$_2$RbZn(SCN)$_4$.

In summary, we investigated the lattice effects on the formation of CO in the quasi-two-dimensional organic conductors $\theta$-(ET)$_2$RbZn(SCN)$_4$ and $\alpha$-(ET)$_2$I$_3$. By explicitly taking account of Peierls-type electron-lattice couplings that cause the observed experimentally observed lattice modulation in each compound, we studied the relevant extended Hubbard model within the Hartree-Fock approximation. It is found that the electron-lattice couplings stabilize the horizontal CO for both compounds, which is consistent with the experimental observations. For $\theta$-(ET)$_2$RbZn(SCN)$_4$, the effect of the lattice distortion is crucial to realize the horizontal CO, while for $\alpha$-(ET)$_2$I$_3$, the horizontal CO is already stable if we consider the full band structure and the anisotropy in the nearest neighbor Coulomb interactions, although the electron-lattice couplings further lower the energy of this CO.

Acknowledgments

This work was supported by Grants-in-Aid and the Next-Generation Supercomputer Project (Integrated Nanoscience) from MEXT, Japan.

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