Charge ordering and sliding-induced instability in thiazyl-radical organic crystal of (NT)$_3$X

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Abstract. We examine exotic properties of the charge-ordered (CO) state which has been found even at room temperature in the 3:1 organic compound (NT)$_3$GaCl$_4$ (NT=naphtho[2,1-d:6,5-d']bis[1,2,3]dithiazole). First we analyze the band structure by using the extended Hückel method and reveal nontrivial bond modulations along the staking axis: a strong trimerization on one chain and a dimerization on another chain. Based on this lattice structure, we examine the origin of such a CO by using a two-chain extended Hubbard model. Within the mean-field approximation, it is shown that the CO pattern observed in the experiment is well reproduced by taking into account the intermolecular Coulomb repulsions. Furthermore we analyze the variation of the energy by shifting the phases of density-wave order parameters and find that the characteristic energy for the melting of the CO state is quite small, $\Delta E = 20$ meV. Based on these analyses, the anomalous non-linear conductivity found in the compound is also discussed.

1. Introduction

The charge-ordering phenomena is the recent topics in organic conductors not only for the insulating state but also for the connection to superconductivity [1]. The one-dimensional organic compounds (NT)$_3$X [2, 3], where $X = \text{GaCl}_4^-$ and $\text{FeCl}_4^-$ are monovalent counterions, have recently attracted significant attention, since these exhibit the remarkable features of the nonlinear conductivity and the negative-resistance effect, which have been observed in the room-temperature measurement of the current-voltage characteristics at low electric field [2, 3]. Even at room temperature, the systems exhibit semiconducting behavior and the charge-ordered (CO) state with a three-fold periodicity along the stacking direction, which stems from the strong intermolecular Coulomb repulsion, has been verified and characterized by the X-ray structure analysis [2]. It indicates that there are four kinds of crystallographically-independent NT molecules, namely, NT$_1$, NT$_2$, NT$_3$, and NT$_4$ [2]. The variety of the molecule gives the crystal structure consisting of two kinds of chains A and B along the stacking axis, which exhibit a three-fold periodicity of different kinds of molecules given by $[-\text{NT1}-\text{NT4}-\text{NT4}-]$ for chain A and $[-\text{NT2}-\text{NT3}-\text{NT3}-]$ for chain B [3]. The amounts of charges on the respective NT molecules are estimated as [2]

$$\langle n_{\text{NT1}} \rangle = +0.8, \quad \langle n_{\text{NT2}} \rangle = 0, \quad \langle n_{\text{NT3}} \rangle = +0.5, \quad \langle n_{\text{NT4}} \rangle = +0.1. \quad (1)$$

With decreasing temperature, the electric conductivities of (NT)$_3$X suggest the semiconducting behavior with an activation energy $\Delta E = 0.18$ eV both for (NT)$_3$GaCl$_4$ and for (NT)$_3$FeCl$_4$. The spin susceptibility of (NT)$_3$GaCl$_4$ at temperature lower than 20K indicates...
Figure 1. (a) The HOMO of the NT molecule where the red and blue colors denote signs of the molecular orbital. (b) Schematic view of the crystal structure of (NT)\textsubscript{3}X, and the experimentally-observed CO pattern along the a-axis (stacking axis), where the ellipses show the locations where charge becomes rich. (c) The schematic crystal structure on the b-c plane perpendicular to stacking axis. There are two kinds of sheets in this system: one consists of the NT\textsubscript{1} and NT\textsubscript{2} molecules (upper panel) and the other consists of NT\textsubscript{3} and NT\textsubscript{4} molecules (lower panel).

Table 1. The HOMO level energies for the respective NT molecules and the intermolecular overlap integrals $S$.

| HOMO level energies $W$ (eV) | Overlap integrals $S \times 10^3$ |
|-----------------------------|-------------------------------|
| $W_{NT1}$ | $W_{NT2}$ | $W_{NT3}$ | $W_{NT4}$ | $S_{a1}$ | $S_{a2}$ | $S_{a3}$ | $S_{a4}$ | $S_{p1}$ | $S_{p2}$ | $S_{p3}$ | $S_{p4}$ | $S_{p5}$ | $S_{p6}$ |
| -9.592 | -9.645 | -9.600 | -9.635 | 15.0 | 0.2 | 0.5 | 21.7 | 5.1 | -2.9 | -4.1 | -4.9 | 4.6 | 4.1 |

a transition into the nonmagnetic state with finite spin gap. As a possible origin of the nonlinear conductivity, the measurement on the electron-paramagnetic-resonance (EPR) spectra of (NT)\textsubscript{3}GaCl\textsubscript{4} suggests that it comes from the inhomogeneous formation of the high-conducting pathways made by the melting of the CO state [3]. In the transport phenomena of charge-density wave, the sliding motion is also possible [4] and this problem is still in controversy.

In the present study, we analyze the band structure of (NT)\textsubscript{3}GaCl\textsubscript{4} and examine the origin of the CO in this system, and further we demonstrate a possible mechanism of melting to discuss the nonlinear conductivity.

2. Band structure analysis
First, we examine the band structure of (NT)\textsubscript{3}GaCl\textsubscript{4} based on the extended Hückel calculation. The NT molecule is first synthesized by Barclay et al [5]. Even at the room temperature, this material shows the CO and the NT molecules are not equivalent. The X-ray crystal structure analysis at 173 K indicates [2] that there are total six NT molecules in a unit cell and the space group is triclinic P1, where there are four crystallographically-independent NT molecules:
Figure 2. (Left panel) The energy-level profiles of HOMO of NT1-NT4 and NT2-NT3 in the (NT)$_3$GaCl$_4$ crystal. Due to the large $S_{a1}$, the NT4-NT1-NT4 molecules form trimer, while the NT3-NT3 molecules form dimer due to $S_{a4}$. (Right panel) The three-dimensional band structure of HOMO of (NT)$_3$GaCl$_4$, as a function $(k_a, k_b, k_c)$. The two top bands come from the anti-bonding orbitals of NT4-NT1-NT4 and NT3-NT3.

we denote NT1, NT2, NT3, and NT4, by following the notation in Ref. [2]. We apply the extended Hückel method [6, 7] on the respective molecules. The highest-occupied molecular orbital (HOMO) of NT1 is shown in Fig. 1 (a). In this analysis, we focus only on the HOMO level of the respective NT molecules. The HOMOs for other molecules have almost same character, however, the energy levels of HOMO are sensitive to the detailed structure of the molecule and are summarized in Table 1. We also examine the overlap integrals between the molecules $S$. The definition of respective $S$'s are given in Fig. 1 and the corresponding magnitudes are summarized in Table 1. Within the b-c plane, the magnitude of overlap integrals between the same NT molecules (e.g., NT1-NT1, NT2-NT2, ...) are negligibly small. Here we listed only the overlap integrals along the stacking axis and within the b-c plane, but some of the diagonal overlap integral (e.g., between NT1 and NT3) takes the same order of $S_p$.

Along the stacking direction, we find large $S_{a1}$ and $S_{a4}$, while quite small $S_{a2}$ and $S_{a3}$. In addition, the overlap integrals between molecules on the b-c plane (the perpendicular plane to the stacking a-axis) are small compared with $S_{a1}$ and $S_{a4}$. Therefore these results indicate that the NT4-NT1-NT4 molecules form strong trimerization along the stacking direction, while the NT3-NT3 molecules form strong dimerization and the NT2 molecule is almost isolated. The HOMO energy levels for NT1 and NT3 are higher than those for NT2 and NT4. These features of overlap integrals and the HOMO level energies are compatible with the charge densities given in Eq. (1). Figure 2 shows the energy-level profile of HOMO of NT1-NT4 and NT2-NT3. The intermolecular overlap integral can be transformed into the transfer integral by $t = 10S$ [6, 7]. In the isolated limit, the HOMO energy levels of NT2 and NT4 are lower than those of NT1 and NT3. Due to the large transfer integral $t_{a1}$, one NT1 level and two NT4 level change into the bonding, nonbonding, and antibonding levels. Also due to the large transfer integral $t_{a4}$, two NT3 levels change into the bonding and antibonding levels. Since there are total ten electrons (i.e., two holes) per six NT molecules, the antibonding levels can attribute to the HOMO level. By further considering the small intermolecular hopping integral, the total band structure can be obtained (Fig. 2 (right panel)). It should be noticed the dispersion is very small and the two bands with the highest energy mainly comes from the anti-bonding orbitals. Because these two bands are very close, we can expect that the CO pattern estimated by experimental measurements can naturally be reproduced by taking into account the effect of Coulomb repulsion.
by and the chain (a). Our Hamiltonian is given by

\[ H = \sum_{l,\sigma} \left[ -t_{11}(c_{A,1,l,\sigma}^\dagger c_{A,2,l,\sigma} + c_{A,2,l,\sigma}^\dagger c_{A,1,l+1,\sigma}) + H.c. \right] - t_{13}(c_{B,1,l,\sigma}^\dagger c_{B,2,l,\sigma} + c_{B,2,l,\sigma}^\dagger c_{B,1,l+1,\sigma}) + H.c. \]

\[ - t_{14}(c_{B,1,l,\sigma}^\dagger c_{B,2,l,\sigma} + c_{B,2,l,\sigma}^\dagger c_{B,1,l+1,\sigma}) + H.c. \]

\[ + \sum_{\alpha=A,B} \sum_l \left( W_{\alpha,1} n_{\alpha,1,l} + W_{\alpha,2} n_{\alpha,2,l} + W_{\alpha,3} n_{\alpha,3,l} \right) \]

\[ + U \sum_{\alpha=A,B} \sum_{i,l} n_{\alpha,i,l} n_{\alpha,i,l+1} + V_\parallel \sum_{i,l} n_{A,i,l} n_{B,i,l} \]

\[ + V_\parallel \sum_{\alpha=A,B} \sum_l \left( n_{\alpha,1,l} n_{\alpha,2,l} + n_{\alpha,2,l} n_{\alpha,3,l} + n_{\alpha,3,l} n_{\alpha,1,l+1} \right), \]

where the hole picture is introduced. In the unit cell, there are 6 = (3 × 2) sites and two carriers (holes). \( c_{\alpha,i,l,\sigma} \) is the annihilation operator of the hole with spin \( \sigma (= \uparrow, \downarrow) \) at the site \( i (= 1, 2, 3) \) and the chain \( \alpha (= A, B) \) in the \( l \)th cell \( (l = 1, 2, \cdots, N_L) \). The density operators are given by \( n_{\alpha,i,l,\sigma} = c_{\alpha,i,l,\sigma}^\dagger c_{\alpha,i,l,\sigma} \) and \( n_{\alpha,i,l} = n_{\alpha,i,l,\uparrow} + n_{\alpha,i,l,\downarrow} \). The correspondences between each site and the NT molecule are given as follows: \( (\alpha, i) = (A, 1) \) and \( (B, 1) \) are for NT1 and NT2, while \( (A, 2), (A, 3) \) and \( (B, 2), (B, 3) \) are for NT4 and NT3, respectively (see Fig. 3 (a)). We impose the periodic boundary condition, \( c_{\alpha,i,l+N_L,\sigma} = c_{\alpha,i,l,\sigma} \). For simplicity, the on-site repulsive interaction \( U \) is set identical for respective molecules. \( V_\parallel \) and \( V_\perp \) are the repulsive interactions between nearest-neighbor sites for intrachain and interchain, respectively. The overlap integrals

3. Model Hamiltonian and mean-field approach

By taking into account the fact that there are two-kinds of chains in this system, we consider a 2-chain system as a minimal theoretical model to describe the CO state. Using the values obtained in the preceding section, we construct the 2-chain extended Hubbard model (Fig. 3 (a)). Our Hamiltonian is given by

\[ H = \sum_{l,\sigma} \left[ -t_{11}(c_{A,1,l,\sigma}^\dagger c_{A,2,l,\sigma} + c_{A,2,l,\sigma}^\dagger c_{A,1,l+1,\sigma}) + H.c. \right] - t_{13}(c_{B,1,l,\sigma}^\dagger c_{B,2,l,\sigma} + c_{B,2,l,\sigma}^\dagger c_{B,1,l+1,\sigma}) + H.c. \]

\[ - t_{14}(c_{B,1,l,\sigma}^\dagger c_{B,2,l,\sigma} + c_{B,2,l,\sigma}^\dagger c_{B,1,l+1,\sigma}) + H.c. \]

\[ + \sum_{\alpha=A,B} \sum_l \left( W_{\alpha,1} n_{\alpha,1,l} + W_{\alpha,2} n_{\alpha,2,l} + W_{\alpha,3} n_{\alpha,3,l} \right) \]

\[ + U \sum_{\alpha=A,B} \sum_{i,l} n_{\alpha,i,l} n_{\alpha,i,l+1} + V_\parallel \sum_{i,l} n_{A,i,l} n_{B,i,l} \]

\[ + V_\parallel \sum_{\alpha=A,B} \sum_l \left( n_{\alpha,1,l} n_{\alpha,2,l} + n_{\alpha,2,l} n_{\alpha,3,l} + n_{\alpha,3,l} n_{\alpha,1,l+1} \right), \]
taken in the present model are given by \([6, 7]\) \(t_{\parallel i} = 10S_{p1}\) \((i = 1, \cdots, 4)\) (eV) for the intrachain transfer integral, and \(t_{\perp 1} = 10S_{p2}\) and \(t_{\perp 2} = 10S_{p3}\) (eV) for the interchain transfer integral, where the coefficient is conventionally taken as \(-10\ eV\) \([6, 7]\) but we adopt \(10\ eV\) since the minus sign of \(t\) is put in the Hamiltonian. We note that other choice of the interchain transfer energy such as \(t_{\perp 1} = 10S_{p2}\) and \(t_{\perp 2} = 10S_{p6}\) gives essentially the same results. The quantity \(W_{\alpha i}\) represents the site potential which comes from the variation of the HOMO energy levels of the NT molecule. These energies are measured from the averaged value of HOMO energy, \(\bar{W} = -9.618\ eV, i.e., W_{A1} = -(W_{NT1} - \bar{W}) = -26\ meV, W_{A2} = W_{A3} = -(W_{NT4} - \bar{W}) = 27\ meV, W_{B1} = -(W_{NT2} - \bar{W}) = -18\ meV\) and \(W_{B2} = W_{B3} = -(W_{NT3} - \bar{W}) = 17\ meV\), where the negative signs arises from the hole picture.

The Hamiltonian is analyzed within the mean-field approximation where all the energies are taken in the unit of meV. The size of unit cell along the chain is set unity. For the lattice of the cell, we apply the Fourier transform, \(c_{\alpha i l;\sigma} = \frac{1}{\sqrt{NL}} \sum_k c_{\alpha i k;\sigma} e^{iql}\) and \(n_{\alpha i l;\sigma} = \frac{1}{\sqrt{NL}} \sum_q n_{\alpha i q;\sigma} e^{iql}\). We restrict ourselves to the case where the density modulations have three-fold periodicity along the stacking direction, i.e., \(q = 0\), which gives the same mean field on every unit cell. The mean-field Hamiltonian can be written as

\[
H_{\text{MF}} = \sum_{k, \sigma} \begin{pmatrix} c_{A1, k;\sigma} & e^{i\xi_{A1, \sigma}} t_{\parallel 1} & -t_{\parallel 1} e^{-i\xi_{A1, \sigma}} & -t_{\parallel 1} & 0 & 0 \\
-\xi_{A1, \sigma} & -t_{\parallel 2} & 0 & -t_{\parallel 2} & 0 & 0 \\
-t_{\parallel 1} e^{i\xi_{A2, \sigma}} & -t_{\parallel 2} & \xi_{A2, \sigma} & 0 & 0 & -t_{\parallel 2} \\
-t_{\perp 1} & 0 & -t_{\parallel 2} & \xi_{A3, \sigma} & 0 & -t_{\parallel 2} \\
0 & 0 & -t_{\perp 1} & 0 & -t_{\parallel 2} & -t_{\parallel 3} e^{-i\xi_{A1, \sigma}} \\
0 & 0 & 0 & -t_{\perp 2} & -t_{\parallel 3} e^{i\xi_{A1, \sigma}} & -t_{\parallel 4} e^{i\xi_{B1, \sigma}} \end{pmatrix} \begin{pmatrix} c_{A1, k;\sigma} \\
c_{A2, k;\sigma} \\
c_{A3, k;\sigma} \\
c_{B1, k;\sigma} \\
c_{B2, k;\sigma} \\
c_{B3, k;\sigma} \end{pmatrix}
\]

\[
- NL \left\{ U \sum_{\alpha i} \langle n_{\alpha i, \downarrow} \rangle \langle n_{\alpha i, \downarrow} \rangle + V_{\parallel} \sum_{i} \langle n_{\alpha i} \rangle \langle n_{\alpha i} \rangle + V_{\parallel} \sum_{i} \langle n_{\alpha i} \rangle \langle n_{\alpha i} \rangle \right\},
\]

where the diagonal terms \(\varepsilon_{\alpha i, \sigma}\) are

\[
\varepsilon_{\alpha i, \sigma} = W_{\alpha i} + U \langle n_{\alpha i, \overline{\sigma}} \rangle + V_{\parallel} \sum_{j \neq i} \langle n_{\alpha j} \rangle + V_{\parallel} \langle n_{\alpha i} \rangle,
\]

and \(\overline{\sigma} = \downarrow (\uparrow)\) when \(\sigma = \uparrow (\downarrow)\), and \(\overline{\alpha} = B(A)\) when \(\alpha = A(B)\). We diagonalize numerically the Hamiltonian (3) represented by \(6 \times 6\) matrices where the eigenvalues and eigenvectors are written as \(E_{r \sigma}(k)\) and \(\langle F_{r A1 \sigma}(k), F_{r A2 \sigma}(k), F_{r A3 \sigma}(k), F_{r B1 \sigma}(k), F_{r B2 \sigma}(k), F_{r B3 \sigma}(k) \rangle^\dagger\) \((r = 1, 2, \cdots, 6)\), respectively. The density \(\langle n_{\alpha i, \sigma} \rangle\) can be calculated self-consistently by

\[
\langle n_{\alpha i, \sigma} \rangle = \frac{1}{NL} \langle n_{\alpha i, q = 0, \sigma} \rangle = \frac{1}{NL} \sum_{rk} |F_{r A1 \sigma}(k)|^2 f(E_{r \sigma}(k)),
\]

where \(\langle \cdots \rangle\) is calculated by the Hamiltonian (3), and \(f(E_{r \sigma}(k)) = 1/(1 + e^{(E_{r \sigma}(k) - \mu)})\). The chemical potential \(\mu\) is determined so as to satisfy the condition \(\sum_{\alpha i, \sigma} \langle n_{\alpha i, \sigma} \rangle = 2\). The ground state is described by a linear combination of several density waves where the magnitudes of charge and spin on the respective sites can be obtained from Eq. (5).

In addition to the ground state, we also examine the energy change, by shifting the phase of the order parameter of the CO state. We examine these states within the three-fold periodicity on the each chain. Consequently the charge density \(\langle n_{\alpha i, \downarrow} \rangle + \langle n_{\alpha i, \uparrow} \rangle\) and the spin density
Figure 4. The $U$ dependence of the charge density (a) and the spin density (b) for $V_\parallel = V_\perp = 0$. NT1 and NT2 correspond to (A, 1) and (B, 1), respectively, while NT3 is for (B, 2) and (B, 3) and NT4 is for (A, 2) and (A, 3).

\[
\langle n_{\alpha,i,\uparrow} \rangle - \langle n_{\alpha,i,\downarrow} \rangle \text{ are written as}
\]
\[
\langle n_{\alpha,i,\uparrow} \rangle + \langle n_{\alpha,i,\downarrow} \rangle = D_\alpha \cos \left( \frac{\pi}{3} i + \theta_\alpha \right) + n_{c,\alpha},
\]
\[
\langle n_{\alpha,i,\uparrow} \rangle - \langle n_{\alpha,i,\downarrow} \rangle = S_\alpha \cos \left( \frac{\pi}{3} i + \phi_\alpha \right) + n_{s,\alpha},
\]

where $n_{c,\alpha}$ and $n_{s,\alpha}$ are mean values of the charge and spin densities:

\[
n_{c,\alpha} = \frac{1}{3} \sum_i \left( \langle n_{\alpha,i,\uparrow} \rangle + \langle n_{\alpha,i,\downarrow} \rangle \right),
\]
\[
n_{s,\alpha} = \frac{1}{3} \sum_i \left( \langle n_{\alpha,i,\uparrow} \rangle - \langle n_{\alpha,i,\downarrow} \rangle \right),
\]

and the quantities $\theta_\alpha$ and $\phi_\alpha$ represent the phase variables for the charge- and spin-density-wave order parameters, respectively, on chain $\alpha$ (= A, B). In order to analyze the phase dependence of the mean-field energy, the amplitudes, $D_\alpha$ and $S_\alpha$ (> 0), and the uniform part $n_{c,\alpha}$ and $n_{s,\alpha}$ are determined so as to minimize the total energy, while the phases ($\theta_\alpha, \phi_\alpha$) are not optimized. We will see that the case, $(\theta_A, \theta_B) = (4\pi/3, \pi/3)$, corresponds to the ground state where the charge densities on chain A and on chain B become [-Rich-Poor-Poor-] and [-Poor-Rich-Rich-], respectively, similar to the pattern found in the experiment.

3.1. Ground state
We examine numerically the ground state by solving Eq. (5) self-consistently and find the range of parameters, $U$, $V_\parallel$, and $V_\perp$, which can reproduce the charge densities similar to those found in the experiment.

Figure 4 shows the charge density $\langle n_{\alpha,i,\uparrow} \rangle + \langle n_{\alpha,i,\downarrow} \rangle$ and the spin density $\langle n_{\alpha,i,\uparrow} \rangle - \langle n_{\alpha,i,\downarrow} \rangle$ on respective molecules as a function of $U$ with the fixed $V_\parallel = V_\perp = 0$. For $U = 0$, the charge on NT3 becomes maximum since the site potential of NT3 is the lowest and the transfer energy between two NT3s is the largest. With increasing $U$, the charge on NT3 moves to the sites of NT1 and NT4 to avoid the increase of energy due to $U$. When $U$ becomes larger than 72 meV, there appears a magnetic state characterized by the up-spin on NT3 in the chain B and the down-spin on NT1 and NT4 in the chain A (see Fig. 4 (b)). By further increasing $U$ ($\gtrsim 200$
meV), one finds a clear separation of the up-spins and the down-spins between two chains, namely, two NT3 sites share one up-spin and the NT1 site is responsible for the down-spin with a small amount distributed on NT4 (see also Fig. 3 (b)). This magnetic state is reasonable by noting the characteristics of the transfer energy showing the dimerization between two NT3 sites and the trimerization for the bond connecting NT4-NT1-NT4. Actually, the increase of energy of the on-site repulsion $U$ is reduced by these bonds when the up-spin resides on the dimerization of NT3-NT3 and the down-spin does on the trimerization given by NT4-NT1-NT4. For large enough $U$, the charge density on the NT3 is 0.5 and that on the NT1 is 0.54, suggesting a qualitative agreement with the CO pattern found in the experiment. However, $U$ is not enough and $V_k$ and $V_\perp$ are needed for the quantitative comparison with the experiment.

**Figure 5.** (a) The charge density $\langle n_{NT1} \rangle$ on the plane of $V_\parallel$ and $V_\perp$ for $U = 500$ meV where the lines on the plane denote the contour of $\langle n_{NT1} \rangle$. (b) The energy band for $U = 500$ meV, $V_\parallel = 300$ meV and $V_\perp = 160$ meV. The solid lines denote the bands of the up-spin, and the dotted lines are for that of the down-spin.

Figure 5 (a) shows the $V_\parallel$ and $V_\perp$ dependencies of the charge density $\langle n_{NT1} \rangle$ with fixed $U = 500$ meV. The increase of $V_\parallel$ gives the enhancement of difference in the charge densities between NT1 and NT4 and then the increase of $\langle n_{NT1} \rangle$. The increase of $V_\perp$ results in the decrease of the charge on NT4 because the repulsive interaction between NT4 and the NT3 gives the reduction of the charge on NT4. Consequently $V_\perp$ enhances the charge on $\langle n_{NT1} \rangle$. The pattern of charge densities obtained in the experiment can be reproduced by the condition, $V_\perp = -1.43V_\parallel + 592$ meV, which is shown in Fig. 5 (a) with a contour $\langle n_{NT1} \rangle = 0.8$. However, for large ($V_\parallel (> 350)$ meV), the charge density on two NT3 sites shows the different magnitude, and then becomes incompatible with the experimental findings. We note that the large amount of $\langle n_{NT1} \rangle (= 0.8)$ is obtained for $U/t_\parallel \simeq 3$, $U/t_\perp < 2$ and $V_\parallel, V_\perp < U$, i.e., the interaction is not strong enough compared with the transfer energy. This is ascribed to the fact that the difference between the anti-bonding energy of the NT3-NT3 dimer and that of the NT4-NT1-NT4 trimer is small (see the left panel of Fig. 1) and the transfer integrals between them are very small. Consequently the bandwidth becomes small i.e., the interaction effect is effectively enhanced.

Figure 5 (b) shows the energy band at $U = 500$ meV, $V_\parallel = 300$ meV and $V_\perp = 160$ meV, which gives the same CO magnitude as in the experiment. The energy gap is $\Delta E = 241.3$ meV which is slightly larger than the activation energy (180 meV) found in the experiment [3].

### 3.2. Energy variation by the sliding of CO state

The small variation of the density around the ground state may induce an excitation in the presence of the charge ordering. Such an excitation can be extended into a global
Figure 6. (a) The energy variation on the plane of $\theta_A$, $\theta_B$ for $U = 500$ meV, $V_\parallel = 300$ meV and $V_\perp = 160$ meV. (b) The variations of the amplitudes of the CO state, $D_A$ and $D_B$ as a function of $\theta_B$. The phase $\theta_A$ is determined so as to minimize the energy, where $|\theta_A - 4\pi/3| < \pi/2$. The charge density takes a maximum on NT1 and the variation of the amplitude is small.

one if the collective motion is induced by the the phase slippage of the CO state given by Eqs. (6) and (7). The excitation energy can be estimated from the total energy $E = E(D_A, D_B, \theta_A, \theta_B, n_{c,A}, n_{c,B}, S_A, S_B, \phi_A, \phi_B, n_{s,A}, n_{s,B})$, which are minimized with the fixed phases, $\theta_A$ and $\theta_B$. The other quantities including $D_A, D_B, \cdots$ are obtained by calculating the corresponding mean-field self-consistently. Thus the energy as a function of $\theta_A$ and $\theta_B$ are symbolically written as

$$E(\theta_A, \theta_B) = E \left( D_A^{\min}, D_B^{\min}, \theta_A, \theta_B, n_{c,A}^{\min}, n_{c,B}^{\min}, S_A^{\min}, S_B^{\min}, \phi_A^{\min}, \phi_B^{\min}, n_{s,A}^{\min}, n_{s,B}^{\min} \right), \quad \text{(10)}$$

where the energy $E(\theta_A, \theta_B)$ is minimized with respect to variables except for $\theta_A$ and $\theta_B$. For example, $D_A^{\min}$ denotes $D_A$ which gives the local minimum of the total energy. Note that, we fix the transfer energies and the site potentials, for simplicity. If the electron-phonon coupling is taken into account, the sliding of the CO state might be accompanied by the lattice modulations. However, the analysis of such a possibility is beyond the scope of this paper and then we analyze the instability of the CO state by shifting the phase variables, $\theta_A$ and $\theta_B$.

Figure 6 (a) shows the total energy on the plane of $\theta_A$ and $\theta_B$, with fixed $U = 500$ meV, $V_\parallel = 300$ meV and $V_\perp = 160$ meV. The minimum value of $E(\theta_A, \theta_B)$ is found at $(\theta_A, \theta_B) = (4\pi/3, \pi/3)$, which leads to the same CO pattern as the experiment. The valley exists for $\theta_A = 4\pi/3$ and $\pi < \theta_B < 5\pi/3$, where the energy is higher than that of the ground state, by $\Delta E_B \approx 16.6$ meV. The variation of the amplitudes along this valley is shown in Fig. 6 (b). It turns out that the charge disproportionation on the chain B almost disappears, i.e., the charge density becomes uniform (1/3 per site), while the phase and amplitude of the CO state on the chain A hold their values as $\theta_A \approx 4\pi/3$ and $D_A > 0.4$, and there are no large change in this range. The rapid change of the amplitude in the chain B for $\theta_B = 0$ and $2\pi/3$ can be understood by considering the property of the transfer integrals: For $\theta_B = 0$ and $2\pi/3$, the maximum position of the CO state is located on the either site of the NT3-NT3 dimer. When the phase $\theta_B$ moves to the region $2\pi/3 < \theta_B < 2\pi$, the maximum position of the CO state is out of the NT3-NT3 dimer and the energy gain due to dimerization is reduced. Consequently the
amplitude $D_B$ is suppressed. One also finds another valley along $0 < \theta_A < 2\pi/3$ with $\theta_B = \pi/3$. On this valley, we find $D_A \approx 0$, i.e., $\langle n_{A,\lambda} \rangle \approx 1/3$ where the energy is higher than that of the ground state, by $\Delta E_A \approx 29.0$ meV. Further, the CO state itself becomes unstable in the square region around $(\theta_A, \theta_B) = (\pi/3, 4\pi/3)$, where both amplitudes vanish and then the energy takes maximum.

Finally, we show the $V_\parallel$ dependence of the energy difference, $\Delta E_A$ and $\Delta E_B$ in Fig. 7, where $V_\perp$ is set as $V_\perp = -1.43V_\parallel + 592$ meV which corresponds to the dotted line of the contour plot in Fig. 5 (a). We find $\Delta E_A < \Delta E_B$ for small $V_\parallel$, while $\Delta E_A > \Delta E_B$ for large $V_\parallel$. This can be explained as follows. For small $V_\parallel$, the energy of the CO state in chain B is much lower than that in chain A, due to the large energy gain of dimerization in chain B. For large $V_\parallel$, the energy of the CO state in chain B increases noticeably due to $V_\parallel$ between two sites of dimerization, while that in chain A remains almost unchanged. As for the uniform state, the energy of both A and B chains shows the similar increase.

4. Summary and discussion

We analyzed the band structure of (NT)$_3X$ based on the extended Hückel calculations and clarified the large bond modulation along the stacking axis. Using a model of two-coupled chain, we examined the exotic properties of the CO in (NT)$_3X$, which originates from the interplay of the variety of transfer energies and repulsive interactions. The charge rich site of NT3 is compatible with the property of the dimerization in chain B and the rich site at NT1 is also compatible with the trimerization in chain A. The pattern of the CO found in the experiment can be obtained by adding the intersite interaction, where this fact indicates the importance of the long range interaction.

Further we calculated the energy variation by shifting the phases of the CO state on chains A and B. The energy valleys are found where the corresponding CO state is unstable and the energy takes a local minimum with respect to the variation of the CO state on the opposite chain. These two kinds of valleys could be relevant to a pathways, in which the melting is suggested experimentally. If this is the case, it is of interest to determine which chain exhibits such a melting.

In the present analysis of the band structure, we focus only on the HOMO of each NT molecule. However, from the extended Hückel calculations, we recognize that the energy levels
of the lowest-unoccupied-molecular orbital (LUMO) are relatively close to those of HOMO. This means that the interband excitations may be relevant to the observed exotic properties. More detailed investigations focusing on the molecular orbitals are needed in order to clarify this problem.

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