Charge order and possible bias-induced metastable state in the organic conductor \( \beta-(\text{meso-DMBEDT-TTF})_2\text{PF}_6 \): effects of structural distortion

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Abstract
We theoretically investigate charge order and nonlinear conduction in the quasi-two-dimensional organic conductor \( \beta-(\text{meso-DMBEDT-TTF})_2\text{PF}_6 \) (DMBEDT-TTF = dimethylbis(ethylenedithio)tetrathiafulvalene). Within the Hartree–Fock approximation, we study the effects of structural distortion on the experimentally observed checkerboard charge order and its bias-induced melting by using an extended Hubbard model with Peierls- and Holstein-types of electron–lattice interactions. The structural distortion is important in realizing the charge order. The current–voltage characteristics obtained by a nonequilibrium Green’s function method indicate that a charge-ordered insulating state changes into a conductive state. Although the charge order and lattice distortions are largely suppressed at a threshold voltage, they remain finite even in the conductive state. We discuss the relevance of the results to experimental observations, especially to a possible bias-induced metastable state.

(Some figures may appear in colour only in the online journal)

1. Introduction
Organic conductors offer intriguing examples of low-dimensional correlated electron systems in which various electronic states emerge at low temperatures [1, 2]. In addition to the origin of such phases in thermal equilibrium conditions, nonequilibrium properties induced by external stimuli have attracted much attention recently [3, 4]. For example, photoinduced phase transitions [5–7] and nonlinear conduction phenomena [8–11], which have been observed mainly in Mott insulators and charge-ordered compounds, have been intensively studied.

In the quasi-two-dimensional organic conductor \( \beta-(\text{meso-DMBEDT-TTF})_2\text{PF}_6 \) [12] (abbreviated as \( \beta-(\text{DMeET})_2\text{PF}_6 \) hereafter), nonlinear conduction has been observed in a charge-ordered insulating phase [13]. The conduction layer of \( \beta-(\text{DMeET})_2\text{PF}_6 \) consists of a weakly dimerized pair of neighboring donor molecules (figure 1(a)) and forms a 3/4-filled band. This compound shows a second-order metal–insulator transition at 90 K, where the peculiar checkerboard charge order (CCO) occurs [14, 15] (figure 1(b)). This transition accompanies a structural distortion. Under pressure, the CCO is readily suppressed and superconductivity with \( T_C \sim 4 \) K appears [12, 16, 17]. Theoretically, Yoshimi et al [18] have investigated the superconductivity by using the random phase approximation for an extended Hubbard model with on-site and nearest-neighbor Coulomb interactions. They show that the CCO does not appear when they consider values of the Coulomb interactions that are determined from the intermolecular distances and the effective molecular sizes. Since their model has only electronic degrees of freedom, their result suggests that electron–lattice (e–l) interactions play an important role in stabilizing the CCO. In fact, it is experimentally known
In this paper, we study the equilibrium and nonequilibrium properties of \(\beta\)-(DMeET)\(_2\)PF\(_6\). We use an extended Hubbard model with two kinds of e–l couplings that are deduced from the experimental observations. The CCO becomes the ground state due to these lattice distortions since the Coulomb interactions basically do not favor the checkerboard charge pattern. This state is similar to the (1100) charge order that has been discussed in quasi-one-dimensional systems by Clay et al. [20]. In two dimensions, a concept of the paired-electron crystal [23, 24] that consists of pairs of charge-rich sites separated by pairs of charge-poor sites, has been proposed in order to understand the ground state of interacting quarter-filled systems with e–l couplings and frustration. We investigate nonlinear conduction by applying a bias to the CCO insulating state. The bias induces a conductive state possessing a weak CCO and partial lattice distortions, which is distinct from the insulating ground state. This indicates the appearance of a metastable state different from the metallic phase at high temperatures.

This paper is organized as follows. In section 2, the model Hamiltonian for \(\beta\)-(DMeET)\(_2\)PF\(_6\) and the methods of calculations are presented. In section 3, we show the results and their relevance to the experimental observations is discussed. Section 4 is devoted to a summary and conclusions.

2. Model and methods

We consider the extended Hubbard model with Peierls and Holstein type of e–l interactions written as

\[
H = \sum_{\langle ij \rangle \sigma} \left\{ (t_{ij} + \alpha u_{ij}) c_i^\dagger \sigma c_j \sigma + \text{h.c.} \right\} + U \sum_i (n_i \uparrow - N_c/2)(n_i \downarrow - N_c/2) + \sum_{\langle ij \rangle} V_{ij} (n_i \uparrow - N_c)(n_j \downarrow - N_c) + \beta \sum_i V_i (n_i - N_c) + \sum_{\langle ij \rangle} K_a \frac{\kappa_{ij}^2}{2} + \sum_{\langle ij \rangle} K_\beta \frac{\kappa_{ij}^2}{2},
\]

where \(\langle ij \rangle\) represents a pair of neighboring sites, \(c_i^\dagger \sigma c_j\sigma\) denotes the creation (annihilation) operator for an electron with spin \(\sigma\) at the \(i\)th site, \(n_{i\sigma} = c_i^\dagger \sigma c_i\sigma\), \(n_i = n_i \uparrow + n_i \downarrow\), and the average electron density is \(N_c = 1.5\). We write the transfer integrals as \(t_{ij}\), the on-site repulsion as \(U\), and the nearest-neighbor Coulomb interactions as \(V_i\). The coupling strength, the lattice displacement, and the elastic constant for the Peierls-type e–l interaction are denoted by \(\alpha, u_{ij}\), and \(K_a\), respectively, whereas those for the Holstein-type e–l interaction are written as \(\beta, V_i\), and \(K_\beta\). We introduce the new variables given by

\[
y_{\alpha}^{ij} = \alpha u_{ij},
\]

\[
u_{\sigma} = \alpha^2 K_a,
\]

\[
y_{\beta}^{ij} = \beta V_i,
\]

\[
s_{\beta} = \beta^2 K_\beta.
\]

For simplicity, we consider only one mode of displacement for each type of e–l interaction. The definition of
the actual modulation of the transfer integrals and on-site potentials is given below.

A schematic illustration of the high-temperature metallic phase of $\beta$-(DMeET)$_2$PF$_6$ is shown in figure 1(a). The unit cell contains two molecules. The charge density per molecule is uniform in this phase. The transfer integrals $t_{R1}$ and $t_{R2}$ are alternating in the vertical direction. The weakly dimerized molecules are connected by $r2$ bonds on which the magnitude of the transfer integrals is the largest.

In the CCO phase, there are four molecules in the unit cell as shown in figure 1(b). The transfer integrals are modulated by the structural distortion. The modulation in the vertical bonds is larger than that in the diagonal and horizontal bonds. In particular, $r1$ bonds in the high-temperature phase change into $R1$ and $R3$ bonds, which are inequivalent ($t_{R1} > t_{R3}$). According to x-ray diffraction measurements [14, 15], we have $d_{R2} = d_{R4} < d_{R3} \simeq d_{R1}$, where $d_i$ denotes the distance between the neighboring molecules connected by the bond $i$. The intermolecular distance within a dimer is the shortest. For the diagonal and horizontal directions, the intermolecular distances are larger than $d_{R1}$ and $d_{R3}$. With these facts, we expect that $V_{i2} > V_{i1} > V_{p}$, $V_{q1}$, $V_{q2}$ in figure 1(a), where $V_{i}$ represents the nearest-neighbor Coulomb interaction between the two sites connected by the bond $i$. In fact, it has been pointed out [14, 15] that, if it were not for $e$--$l$ interactions, the charge order along the vertical bond should be of $r$--$p$--$r$--$p$ type, where $r$ and $p$ represent hole-rich and hole-poor sites, respectively. This is because the charge pattern of the intradimer pair should be $r$--$p$, and that of the second-nearest interdimer pair should also be $r$--$p$ if we consider only the Coulomb interactions that are determined by the intermolecular distances. However, the CCO is of $r$--$r$--$p$--$p$ type, in which the two molecules connected by $R3 (R1)$ bonds become hole-rich (hole-poor). These considerations suggest that lattice effects are the key to understanding the CCO.

In order to take account of the structural distortion, we introduce modulation of the transfer integrals on the $r1$ bonds as

$$t_{R1}^d = t_{R1} + y_\alpha,$$

$$t_{R3}^d = t_{R3} - y_\alpha,$$  

where $t_{R1}^d (t_{R3}^d)$ is the modified transfer integral located on $R1 (R3)$ bonds in the low-temperature structure (figure 1(b)). When $y_\alpha > 0$, we have $t_{R1}^d > t_{R3}^d$, which is consistent with the relation $t_{R1} > t_{R3}$ in figure 1(b), which is derived from the experimental result. Experimentally, the thermal contraction makes the averaged $|t|$ larger at low temperatures, thus $|t_{R1}^d|, |t_{R3}^d| > |t_{R1}|$. In essence, the modulation given by equations (6) and (7) stabilizes the $r$--$r$--$p$--$p$ type charge pattern in the CCO. We do not consider modulation of the other transfer integrals since they are relatively small compared to the above. In our calculations, the values of the transfer integrals $t_{ij}$ in equation (1) are fixed at those in the high-temperature phase. We use $t_{12} = -0.0824, t_{22} = -0.226, t_p = 0.0475, t_{q1} = -0.0438, \text{and } t_{q2} = -0.115$.

For the Holstein-type $e$--$l$ coupling, we assume

$$y_\beta = \begin{cases} y_\beta & \text{for } i \in A, B, \\ -y_\beta & \text{for } i \in A', B'. \end{cases}$$  

Experimentally, it is known that in the CCO phase the hole-poor molecules are slightly bent, whereas the hole-rich molecules are almost flat [14]. This indicates that the modulation of the on-site potential is accompanied by the CCO.

We apply the Hartree–Fock approximation to the electron–electron interactions in equation (1). In the equilibrium case, we calculate the ground-state energies for several kinds of possible charge-order patterns with a $2 \times 4$ or $4 \times 2$ unit cell and the periodic boundary condition for much larger systems. The stability of the CCO due to the $e$–$l$ couplings is examined. The lattice distortions $y_\alpha$ and $y_\beta$ are self-consistently determined by the Hellmann–Feynman theorem. In the nonequilibrium case, we calculate physical quantities such as the current–voltage ($J$–$V$) characteristics by using the nonequilibrium Green’s function method [25, 26], which treats nonequilibrium steady states and contains the definitions of $J$ and $V$. This method has been used to study the suppression of rectification [25] and the dielectric breakdown [26] in one-dimensional interacting electron systems. The results are basically consistent with those obtained by other numerical approaches which take account of the effects of quantum fluctuations [27, 28]. Although the Hartree–Fock approximation generally overestimates the stability of ordered states, the present approach is expected to capture the essential physics of nonequilibrium phenomena in $\beta$-(DMeET)$_2$PF$_6$. As shown in figure 2, we attach left and right semi-infinite metallic electrodes to the CCO system, which is referred to as the central part. We choose the $y$-axis in figure 1(a) as the conduction direction, but the qualitative results are unaltered if the bias is applied along the $x$-axis. We assume that the electrodes are one-dimensional and the electrons in them are noninteracting. We do not consider work-function differences at the interfaces for simplicity. For the electrodes, the wide-band limit is applied so that the retarded self-energies due to the electron transfers between the electrodes and the central part are independent of energy [29].

For finite $V$, we introduce the chemical potential $\mu C = \mu L + \mu R / 2$ [25] and adjust it such that the electron density of the central part is fixed at 3/4-filling. Here $\mu_L = \mu C + V / 2$ and $\mu_R = \mu C - V / 2$ are the left and right chemical potentials, respectively. Throughout the paper, we set $\gamma_L = \gamma_R = 0.1$. 

Figure 2. Schematic model for nonequilibrium properties. The left and right electrodes are attached to the central part where the CCO is realized when the bias is absent. The $y$-axis ($x$-axis) is along (perpendicular to) the conduction direction.
where γ_L is the coupling constant between the central part and the left electrode and γ_R is the coupling constant between the central part and the right electrode. The interaction parameters U, V_1, s_a, and s_b are given in units of eV in the following.

3. Results

First, we discuss the ground state without the bias voltage. For the electron–electron interactions, we use U = 0.5, V_1 = 0.23, V_2 = 0.26, and V_p = V_q1 = V_q2 = 0.2. These parameter values are comparable to those obtained in recent ab initio calculations with the screening effects for typical organic compounds.

For V_1, we choose the values such that they satisfy the relation V_2 > V_1 > V_p, V_q1, V_q2 as discussed in section 2. In figure 3, we show the ground-state energy of the CCO for s_p = 0.45 as a function of s_a. The system size is L_x = L_y = 32, where L_x (L_y) is the number of sites in the x-direction (y-direction). In this figure, we also show the energies of three other phases, a paramagnetic metallic state with uniform charge density, a spin-density-wave (SDW) state and a diagonal CO, which are obtained without the e–l couplings, are also shown. The energy of the uniform state is chosen to zero. The inset shows the charge gap Δ in the CCO state as a function of s_a.

The ground-state energy per site of CCO as a function of s_a is shown in figure 3. In figure 3, we show the ground-state energy of the CCO for s_a = 0.055. This state with the bias on the CCO becomes the ground state for s_a > 0.055. This state has a charge gap Δ, as shown in the inset of figure 3. In figures 4 and 5, we show the electron density and the lattice distortions γ_a and γ_b. The electron density on sites A (A') is the same as that on sites B (B'). The CCO in figure 3 is nonmagnetic. In fact, a CCO with an antiferromagnetic order on the hole-rich sites, which has a slightly lower energy than the nonmagnetic CCO, is also obtained as a mean-field solution. The energy difference between the two CCOs is smaller than 10^{-3} eV/site for s_a = 0.06 and the difference decreases with increasing s_a. Because the antiferromagnetic order is an artifact of the Hartree–Fock approximation, hereafter we use the nonmagnetic CCO as the ground state when the bias voltage is applied. It should be noted that the spin configuration does not qualitatively alter the results. According to the experimental observations, the magnetic susceptibility for β-(DMeET)_2PF_6 shows a gradual decrease with decreasing temperature and abruptly drops around T = 80 K. Its temperature dependence below 80 K suggests that the system is nonmagnetic and a spin gap opens in the CCO state.

For finite bias voltage V, we set s_a = 0.075 so that the CCO becomes the ground state for V = 0. The effects of the bias on the CCO are investigated by the charge structure factor S_q(q), which is defined as

\[ S_q(q) = \frac{1}{N_w} \sum_{\mu, \nu} (\langle n_{\mu,1} n_{\nu,1} \rangle + \langle n_{\mu,2} n_{\nu,2} \rangle) e^{i q (R_{\mu} - R_{\nu})}, \tag{9} \]

where \( \mu \) and \( \nu \) denote indices for the unit cell shown in figure 1(a), 1 and 2 represent indices for the sites inside the unit cell, and \( R_{\mu} \) (\( R_{\nu} \)) is the position vector of the \( \mu \)th (\( \nu \)th) unit cell. \( N_w = L_x L_y \) is the total number of sites in the
central part. The wavevector that corresponds to the CCO is \( q = Q = (\pi, \pi) \). In figure 6, we show the \( J-V \) characteristics and the \( V \) dependence of \( S_c(Q) \) for \( L_x = L_y = 16 \). For comparison, we show the \( J-V \) curve obtained with \( L_x = L_y = 12 \), which gives qualitatively the same results. For small \( V \), the current \( J \) does not flow because the charge gap opens at \( V = 0 \) owing to the CCO. In this region, \( S_c(Q) \) is almost unchanged, so the CCO is robust against the bias. With increasing \( V \), \( J \) abruptly increases at \( V = V_{th} \sim 0.4 \), where the CCO changes into a conductive state. Although \( S_c(Q) \) largely decreases around \( V = V_{th} \), it remains finite even in \( V > V_{th} \), meaning that the CCO is not completely destroyed in the conductive state. In figure 7, we show the lattice distortions \( y_\alpha \) and \( y_\beta \) as a function of \( V \). Similar to the \( V \) dependence of \( S_c(Q) \), \( y_\alpha \) and \( y_\beta \) do not show noticeable changes for \( V < V_{th} \). At \( V = V_{th} \), both distortions are suppressed. In particular, the \( y_\alpha \)-distortion almost disappears for \( V > V_{th} \), whereas the \( y_\beta \)-distortion survives. In equilibrium conditions, the CCO has a finite gap \( \Delta \), as shown in figure 3. However, \( \Delta \) becomes very small when \( y_\alpha \) decreases. When the bias is applied, the initial insulating CCO switches to the conductive state by the suppression of the \( y_\alpha \)-distortion. The weak CCO survives owing to the partial \( y_\beta \)-distortion, so that the bias-induced state is different from the uniform phase or the CCO at \( V = 0 \). In figure 8, we show the density of states \( D(E) \) for different values of \( V \). For \( V = 0 \), there is no state around \( E = \mu_C \) because the charge gap opens. For \( V = 0.2 \), the gap structure in \( D(E) \) still exists since the CCO and the lattice distortions at \( V = 0 \) are robust against the bias for small \( V \). When \( V = 0.5 > V_{th} \), the gap at \( E = \mu_C \) disappears, which indicates that the weak CCO has the conduction property. In figure 6, the current \( J \) begins to decrease when \( V \) approaches half the bandwidth \( W = 1.29 \). This is because the number of one-particle states that have large contributions to the current \( J \) decreases for \( V > W/2 \) [26]. In other words, the tilting of the band by the applied bias becomes large, so that the ballistic transport is suppressed. The effects of the inelastic scattering in the central part, which are not considered in the present calculations, will modify the \( J-V \) curve in such a large-\( V \) region.
distortion. In this state, the values of $D(E)$ around $E = \mu_C$ are comparable to those at $V = 0.5$ in figure 8. The applied bias converts the insulating CCO into the conductive CCO. Our results may be related to the photoinduced structural changes in (EDO-TTF)$_2$PF$_6$, which exhibits the (1100) charge order at low temperatures. This charge order is triggered by displacements and bending of the EDO-TTF molecules, which corresponds to the Peierls- and Holstein-types of e–l couplings, respectively [20, 21]. The femtosecond electron diffraction study for (EDO-TTF)$_2$PF$_6$ has shown that the photoexcitation induces the metastable state mainly through the suppression of the molecular displacements, whereas the molecular bendings do not show noticeable changes [22]. More structural information such as x-ray diffraction data for the present material in the presence of the bias voltage may clarify the nature of this novel nonequilibrium phase.

4. Summary

We investigated the effects of the e–l couplings on the equilibrium and nonequilibrium properties of $\beta$-(DMeET)$_2$PF$_6$. We have shown that the CCO that is peculiar to this compound is obtained by the extended Hubbard model with two kinds of e–l interactions that originate from molecular displacements and deformations. The e–l couplings are important in stabilizing the CCO. The applied bias changes the initial insulating CCO into a conductive state with the weak CCO, which emerges on the disappearance of the Peierls-type distortion. This indicates the presence of a bias-induced metastable state different from the high-temperature metallic state. These results suggest that the lattice degrees of freedom play a key role in determining the conduction property in $\beta$-(DMeET)$_2$PF$_6$.

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