Mott insulating state in incommensurate molecular conductors

Hitoshi Seo\textsuperscript{1}, Hideo Yoshioka\textsuperscript{2} and Yuichi Otsuka\textsuperscript{3}

\textsuperscript{1} Synchrotron Radiation Research Center, Japan Atomic Energy Agency, SPring-8, Hyogo 679-5148, Japan
\textsuperscript{2} Department of Physics, Nara Women’s University, Nara 630-8506, Japan
\textsuperscript{3} CREST-JST, Department of Material Science, University of Hyogo, Hyogo 678-1297, Japan
E-mail: seo0@spring8.or.jp

Abstract. We theoretically investigate the possibility of a Mott insulating state in a class of molecular conductors where the composition ratio between two molecular species is incommensurate to each other, i.e., incommensurate molecular conductors. Although the band-filling becomes irrational and then metallic behavior would be expected, the on-site Coulomb repulsion among the valence electrons together with the potential from the closed-shell ions supplying the carriers can give rise to an “incommensurate Mott insulator”, which is characterized by the carriers being localized with a period incommensurate to the underlying lattice. First, we numerically confirm the existence of this insulating state in a simplified one-dimensional model by a clear opening of the charge gap within quantum Monte Carlo simulation. We also find an incommensurate antiferromagnetic insulating state as mean-field solutions in two-dimensional models, adopting the crystal structures of the actual materials showing insulating behavior experimentally, (MDT-TSF)\textsubscript{0.441}AuI\textsubscript{2} and \textsubscript{4}(BEDT-TTF)\textsubscript{4}X (X = Hg\textsubscript{2}Cl\textsubscript{8} and Hg\textsubscript{2}Br\textsubscript{8}), which correspond to the incommensurate Mott insulating states.

1. Introduction

Most of the molecular conductors are composed of two or more molecular species with charge transfer between them in order to generate carriers. Their composition ratio is usually rational expressed as, for example in the case of two-component systems, $A_xB_y$ having a rational combination of $x:y$. Typical examples are the intensively studied charge-transfer salts $A_2B_y$, i.e., the so-called 2 : 1 salts. Recently, compounds with irrational values of $x:y$ are attracting interest \cite{1}, since they can result in electronic bands near the Fermi energy with irrational fillings, due to the incommensurability between the lattice of the molecules where the carrier exists and the carrier number, $n$ (either in terms of electron or hole): carrier doping from commensurate fillings. In this paper we call such compounds as incommensurate molecular conductors.

Recently, a series of incommensurate molecular conductors composed of MDT-TSF (methyleneedithiotetraselenafulvalene) molecules and its analogs as donors and anions such as AuI\textsubscript{2} and I\textsubscript{3} were synthesized by Takimiya \textit{et al.} \cite{2, 3}, and intensively investigated by Kawamoto \textit{et al.} \cite{4, 5}. These compounds have compositions $AB_y$ ($A$: donor, $B$: anion) with $y \sim 0.44$, whose value slightly varies depending on each salt. Since the anions are monovalent there exist $y$ hole per molecule in the valence $\pi$-band of the donors; its carrier density is $n_{th} = y$ where $n_{th}$
is the hole concentration. Most of them are in fact intrinsically metallic as expected from the irrational filling and even superconductivity was found in several members. The exception is (MDT-TS)(AuI)\textsubscript{0.441} [3, 5] where a metal-insulator crossover is observed at ambient pressure, while the insulating state is suppressed under pressure and a superconducting phase arises next to the insulating phase.

The nature of the insulating phase was proposed by Yoshioka et al. [6], noticing the importance of the fact that the anions form a periodic lattice structure incommensurate to that of the donors. A novel type of Mott insulating state was predicted based on a simplified one-dimensional model, which is realized when the on-site Coulomb repulsion among electrons, $U$, in the donor lattice and the strength of the incommensurate potential from the anions, $\delta$, both exceed critical values. Note that in the 2 : 1 salts such a potential from the anions does not play an important role in most cases, since they situate at equal distance from the donors (at least approximately). This state is called as the “incommensurate Mott insulator” since the periodicity of the localized carriers (holes in the case of (MDT-TS)(AuI)\textsubscript{0.441}) is incommensurate to the donor lattice where the carriers exist.

Meanwhile, Kanoda [7] have pointed out the possibility of a similar insulating state in another incommensurate molecular conductor system $\kappa$-(BEDT-TTF)$_4$X ($X = \text{Hg}_{2.78}\text{Cl}_8$ and Hg$_{2.89}$Br$_8$). These materials were synthesized by Lyubovskaya et al. [8, 9] in the 1980s and recently have been investigated by several groups [10, 11]. The incommensurability in the Hg$^{2+}$ ions gives rise to carrier doping in the BEDT-TTF layer, where the average valence of the BEDT-TTF molecule is $(1 + z)/2$, with $z = 0.22$ for $X = \text{Hg}_{3.2}\text{Cl}_8$ and $z = 0.11$ for Hg$_{3.2}$Cl$_8$; due to the strongly dimerized $\kappa$-type structure, they are 22% and 11% hole-doped system compared to the 1/2-filled $\kappa$-(BEDT-TTF)$_2$X system. They are intrinsically metallic consistent with the irrational carrier concentration, in spite of the calculated large value of effective strength of electron correlation which should have resulted in a Mott insulating state at 1/2-filling. Interesting properties are found in their phase diagrams by applying pressure, such as a crossover from non-Fermi liquid to Fermi liquid behavior and a non-monotonic behavior in the superconducting phase transition temperature. However, at high pressure region an insulating behavior in the resistivity is observed in both of these compounds [9, 11]. This is again apparently not expected by means of carrier concentration of the system if the nesting instability is not present.

In this paper, we show results of several model calculations to investigate the possible Mott insulator in the incommensurate molecular conductors mentioned above. We will first introduce the simplified one-dimensional model in section 2 and confirm the existence of the incommensurate Mott insulating state by numerical simulations. Then we show mean-field calculations on two-dimensional models for (MDT-TS)(AuI)$_{0.441}$ (section 3) and for $\kappa$-(BEDT-TTF)$_4$X (section 4), concentrating on the antiferromagnetic insulating solutions. Details of the calculations will be published elsewhere [12].

2. One-dimensional model

The simplified one-dimensional model [6] for (MDT-TS)(AuI)$_{0.441}$ is schematically drawn in Fig. 1. The Hamiltonian is written as

$$\mathcal{H} = t \sum_{i,s} (c_{i+1,s}^\dagger c_{i,s} + h.c.) + U \sum_i n_i \downarrow n_i \uparrow + \sum_i v_i n_i,$$

(1)

where $t$ and $U$ are the transfer energy between the nearest-neighbor donor sites and the on-site repulsive interaction, respectively; the creation and number operators at the $i$-th site with spin $s=\uparrow/\downarrow$ are denoted as $c_{i,s}^\dagger$ and $n_{i,s} = c_{i,s}^\dagger c_{i,s}$, while $n_i = \sum_s n_{i,s}$. We consider the anion potential from the fully ionized anions, which form a regular lattice, as $v_i = \delta \cos(2\pi/\lambda \times x_i)$, where $\lambda$ is the period of the anions which is related to the hole density $n_h$ of the donor sites as $\lambda/a = 1/n_h$. 

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Next, we extend the model in the previous section and include the transverse transfer integrals adopting the crystal structure of (MDT-TS)(AuI$_2$)$_{0.441}$, as schematically drawn in Fig. 2. The Hamiltonian has the form same as eq. (1) but the first kinetic term modified as $\sum_{(i,j),s} t_{i,j} \left[ c_{i,s}^\dagger c_{j,s} + h.c. \right]$, with three kinds of transfer integrals, $t_{i,j} = \{ t_a, t_{p1}, t_{p2} \}$. Now the site indices run over the lattice sites in the two-dimensional plane. The anion potential $v_i$ is chosen as in section 2 along the $a$ direction as $v_i = \delta \cos(2\pi/a \times i)$ ($x_i$ : coordinate along the $a$-direction), while the phase between chains is set as shown in Fig. 2. We apply mean-field approximation to the on-site Coulomb interaction as $n_{i,\uparrow} n_{i,\downarrow} \rightarrow \langle n_{i,\uparrow} \rangle \langle n_{i,\downarrow} \rangle + \langle n_{i,\uparrow} \rangle \langle n_{i,\downarrow} \rangle - \langle n_{i,\uparrow} \rangle \langle n_{i,\downarrow} \rangle$, and seek for self-consistent solutions of $\langle n_{i,s} \rangle$ for all the sites within the supercells. In the calculation, since the supercell size should be finite, the period of the anion potential cannot be set to irrational values therefore rational values close to them are chosen. For example, in Fig. 2, we show the case of $\lambda/a = 1/5$ and $\delta/\lambda = 5/4$.

We have found that an antiferromagnetic insulating solution is stabilized over the paramagnetic metallic state at the large $U$ region; a typical charge and spin pattern of the solution is shown in Fig. 3. One can see that the charge disproportionation occurs due to the on-site Coulomb interaction as

$$\sum_{i,j} U_{ij} n_{i,\uparrow} n_{j,\downarrow}$$

while the phase between chains is set as shown in Fig. 2. We apply mean-field approximation in section 2 along the $a$-direction as $v_i = \delta \cos(2\pi/a \times i)$ ($x_i$ : coordinate along the $a$-direction), since each anion provides 1 hole. Here we do not consider the nearest-neighbor Coulomb interaction included in the model treated in Ref. [6], since it does not play an essential role whereas it should be important in quantitative analysis.

Using the bosonization technique combined with the renormalization group method, it was predicted that the ground state of this model turns from a metallic (Tomonaga-Luttinger) state to the incommensurate Mott insulating state when both $U$ and $\delta$ exceed a critical value; for a fixed value of $\delta$, the value of the critical on-site Coulomb repulsion $U_c$ is smaller for larger $\delta$. We note that this result is nontrivial in a sense that, in previous theoretical studies on “commensurate” one-dimensional Hubbard models, the Mott insulating state appears at infinitely small value of $U$; the critical value is $U = 0$.

We have investigated this model by a quantum Monte Carlo technique called the stochastic-series-expansion method [13] in the operator-loop-update scheme [14, 15]. The stochastic-series-expansion calculations fully include thermal and quantum fluctuations and give unbiased and high-precision data. We have added the chemical potential term, $-\mu \sum_j n_j$, to eq. (1) and calculated the carrier density $n$ as a function of $\mu$. The results for $a/\lambda = 0.441$, taken from the actual compound (MDT-TS)(AuI$_2$)$_{0.441}$, as well as $a/\lambda = 4/9 = 0.444$, which will be investigated in the next section, both show a clear plateau in the $\mu - n$ curve at $n = a/\lambda$ when $U$ and $\delta$ are large. This indicates that the system is indeed a Mott insulator state there, confirming the prediction in Ref. [6]. We note that there is no symmetry breaking in the system, which is characteristic of the Mott transition.

3. Two-dimensional model for MDT compounds

Next, we extend the model in the previous section and include the transverse transfer integrals adopting the crystal structure of (MDT-TS)(AuI$_2$)$_{0.441}$. We have investigated this model by a quantum Monte Carlo technique called the stochastic-series-expansion method [13] in the operator-loop-update scheme [14, 15]. The stochastic-series-expansion calculations fully include thermal and quantum fluctuations and give unbiased and high-precision data. We have added the chemical potential term, $-\mu \sum_j n_j$, to eq. (1) and calculated the carrier density $n$ as a function of $\mu$. The results for $a/\lambda = 0.441$, taken from the actual compound (MDT-TS)(AuI$_2$)$_{0.441}$, as well as $a/\lambda = 4/9 = 0.444$, which will be investigated in the next section, both show a clear plateau in the $\mu - n$ curve at $n = a/\lambda$ when $U$ and $\delta$ are large. This indicates that the system is indeed a Mott insulator state there, confirming the prediction in Ref. [6]. We note that there is no symmetry breaking in the system, which is characteristic of the Mott transition.
Figure 2. Schematic view of the two-dimensional model for (MDT-TS)(AuI₂)₀.₄₄₁. The donor lattice structure is shown where the unit cell is indicated as a rectangle. The minima of the incommensurate anion potential are schematically shown as the gray area.

Figure 3. Antiferromagnetic mean-field solution for the two-dimensional model for (MDT-TS)(AuI₂)₀.₄₄₁ (see Fig. 2) at $U/t_a = 1.9$, $\delta/t_a = 0.7$. The charge (hole) density and the spin density on each site is shown as the diameter of the circle and the length of the arrow. The scale marks are taken in units of the lattice constants of the donor lattice.

to the existence of the anion potential. The spin arrangement can be interpreted as the antiferromagnetic ordering of the spins localized in the charge rich area, whose period matches the anion periodicity. This period is incommensurate to the donor lattice where the carriers exist, therefore we call this state as the “incommensurate antiferromagnetic insulator”. We note that there is no symmetry breaking in the charge degree of freedom similarly to the one-dimensional case above; there exists charge disproportionation even in the paramagnetic metallic state. Therefore this phenomenon should be distinguished with the charge ordering frequently observed in quarter-filled systems, which is accompanied with symmetry breaking in the charge degree of freedom. The critical value for the on-site Coulomb interaction, $U_c$, for the phase transition from the paramagnetic metallic state to the antiferromagnetic state depends on the value of $\delta$, i.e., $U_c$ is smaller for larger $\delta$ (for a fixed value of $\lambda$ and $n$), whose tendency is consistent with the critical value $U_c$ in the one-dimensional model [6] for the appearance of the incommensurate Mott insulating state.

4. Two-dimensional model for BEDT-TTF compounds
We have also investigated the two-dimensional model for $\kappa$-(BEDT-TTF)$_4X$ ($X = \text{Hg}_{2.78}\text{Cl}_8$, Hg$_{2.89}$Br$_8$), as schematically shown in Fig. 4, and applied the same theoretical method as in section 3. Here we adopt the transfer integrals calculated of the former Cl compound, while the latter compound show similar values [1, 10]. The anion potential $v_i$ is chosen as in section 2 and 3 along the $a$ direction as $v_i = \delta \cos (2\pi/\lambda \times x_i)$ ($x_i$ : coordinate along the $a$-direction),
**Figure 4.** Schematic view of the two-dimensional model for $\kappa$-(BEDT-TTF)$_4$Hg$_{2.75}$Cl$_8$. The donor lattice structure is shown where the unit cell is indicated as a rectangle. The minima of the incommensurate anion potential are schematically shown as the gray area.

**Figure 5.** Antiferromagnetic mean-field solution for the two-dimensional model for $\kappa$-(BEDT-TTF)$_4$Hg$_{2.75}$Cl$_8$ (see Fig. 4) at $U = 1$ eV, $\delta = 0.2$ eV. The charge (hole) density and the spin density on each site is shown as the diameter of the circle and the length of the arrow. The scale marks are taken in units of the lattice constants of the donor lattice.

while the phase between chains is set to be uniform along the $c$-direction as shown in Fig. 4. In the figure the periodicity of the anions is $\lambda/a = 3/4$ and the hole density is $n_h = 2/3$ (4/3 per dimer of BEDT-TTF: 33% hole doping), of which the results are shown in the following. Note that due to the two-dimensional structure of the BEDT-TTF layer and the one-dimensional nature of the anions, the relation $\lambda/a = 1/n_h$ does not hold here.

In Fig. 5, the charge and spin order of the self-consistent insulating solution we have obtained for $U = 1.0$ eV and $\delta = 0.2$ eV is shown. Similarly to the one-dimensional model and the two-dimensional model for (MDT-TS)(AuI)$_{0.441}$, charge disproportionation appears according to the anion potential, whereas the spin degree of freedom shows a complex two-dimensional ordering pattern. We have also found that for different values of $U$ and $\delta$, several different patterns can be stabilized, which show similar charge disproportionation but different spin order. This is probably due to the spin frustration inherent in the $\kappa$-type structure, as has been discussed in the 2:1 salt $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ [16]. In this case, the spin localizes on each dimer without charge disproportionation and the coupling between the spins forms a nearly isotropic triangular
lattice. The transfer integrals here also indicate isotropic values for the two inter-dimer couplings which give rise to spin frustration, and, moreover, the interplay between such frustration and the anion potential making the charge degree of freedom active provides an interesting spin-charge coupled situation of frustration, which requires more systematic investigations left for future studies.

5. Summary
We have theoretically investigated one-dimensional and two-dimensional Hubbard models with incommensurate one-particle potential and carrier concentration. When the period of the incommensurate potential and the carrier concentration is commensurate to each other, incommensurate Mott insulating states can be stabilized, which are incommensurate to the original lattice where the carriers exist.

Acknowledgments
We acknowledge T. Kawamoto for fruitful discussions. H. S. acknowledges A. Kawamoto, H. Taniguchi, and M. Watanabe for informative discussions on the $\kappa$-type BEDT-TTF compounds.

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