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Introduction of Conductivity in Molecular Assemblies

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Diversity of electronic properties of molecular solids has been briefly summarized with special emphasis on the electrical conduction in the A_2B type charge transfer salts. It has been demonstrated that electrons in these systems are generally strongly correlated and that the characteristic features are systematically understood based on the extended Hubbard model on the basis of molecular orbitals.

Keywords: charge ordering; charge transfer; conductivity; DNA; electronic properties; molecular solids; Mott insulators; strong correlations

INTRODUCTION

The metallic and insulating states are the most remarkable characteristic features the condensed matter can show, where atoms and molecules are spatially arranged in a condensed form. However in molecular assemblies the introduction of metallic states has not been easy in general since the transfer integrals representing the quantum tunneling of electrons between atomic or molecular orbitals are relatively small.

Both intensive and extensive research activities on the pursuit of metallic molecular solids since early 70's have been based on charge transfer (CT) salts, where there exists transfer of electrons between different kinds of molecules [1]. In 1980 superconductivity has been discovered in such CT salts, TMTSF2PF6 [2]. These efforts have eventually resulted in the realization of single component molecular

The content of the present article is based on the various discussions with many experimental colleagues on one hand and the long term collaborations with H. Seo, H. Kino and C. Hotta on the other hand, to whom he thanks deeply.

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metals in 2001: a very important step in the progress of materials science [3].

For these experimental developments it has been crucially important that microscopic theoretical understanding of the electronic states in molecular solids has been established based on the molecular orbitals as first proposed by the group of Kobayashi [4] who developed these procedures even to the level of designing new types of CT salts. The validity of this approach has been later confirmed in $DCNQI_2M$ (M = Ag, Cu) by LDA calculations [5] and by deHaas-van Alphen experiment [6].

Encouraged by these developments of the understanding of one-particle states, we have tried to pursue coherent understanding of variety of ground states based on the effective Hamiltonian which takes into account of the effects of mutual Coulomb interaction not only on-site, U [7] but also inter-site, V [8,9]. The characteristic features of the electronic states (band structure) of each molecular solid are represented by the transfer integrals, t_{ij}, between molecules, which are usually very anisotropic. With this type of Hamiltonian, which may be called extended Hubbard model, general trends of the ground states of various molecular solids have been extracted first by the mean-field approximation and then, if necessary, more elaborated methods, field theoretical methods such as bosonization, numerical calculations etc., which take quantum fluctuations into consideration.

The powerfulness of such theoretical approach in molecular crystalline solids has naturally triggered the efforts toward the non-crystalline molecular assemblies based on the similar method, since such approaches based on the tight-biding approximation by use of molecular orbitals are suited for the concrete studies of local properties together with interaction effects. It is a personal view of the author that science and technology of bio-materials based on the understanding of electronic properties will be pursued along such procedures developed in condensed matter physics.

In this brief report, the present understanding of A_2B type of molecular crystals, which are typical examples of CT salts, will first be summarized with special emphasis on ET_2X (ET = BEDTTTF) family. Then, as an example of non-crystalline materials, issues of possible electrical conductivity of DNA will be briefly addressed to which there exist many but often contradicting reports.

PHASE DIAGRAM OF GROUND STATES OF ET_2X FAMILY

As a typical example of A_2B type charge transfer (CT) salts, we will consider the case of ET_2X, which has many polytypes depending on anions, X. In ET_2X, there exist holes in ET-HOMO band because of

the transfer of electrons form ET to anions, X, and the amount of these holes is 1/2 per ET molecule as an average resulting in a quarter-filled band if all ET molecules are equivalent. In such quarter-filled bands there exist two interesting limiting cases for the possible types of ground states in the presence of strong Coulomb interaction; the charge ordered states (Wigner crystals on lattices) in the absence of (or in the presence of weak) dimerization and Mott insulators in the presence of strong dimerization, as shown schematically for the case of one-dimensional lattices in Figure l, where the degree of the dimerization is parametrized by Δ_d. The former is due to the long range part of Coulomb interactions (inter-site V), while the latter can be understood as follows: a dimer can be taken as a unit where there is one hole per dimer and then the energy band of anti-bonding state of ET HOMO-dimer is half-filled resulting in possible Mott insulating states in the presence of strong correlations. In two-dimensional ET_2X family, typical examples of these two are the θ-type for the former and the κ-type for the latter, respectively, as seen in Figure 2, where the spatial arrangement of ET molecules and resultant energy band structures are schematically shown. Due to the anisotropy of transfer integrals there is another interesting feature characterized as those on anisotropic triangular lattices as seen in Figure 3, where circles stand for ET molecules in the case of the θ-type, while for a dimer in the case of the κ-type. Hence the essence of electronic properties of θ and κET2X are characterized by those of anisotropic triangular lattices at 1/4 filling and half-filling, respectively.

In κ-type, interesting competition between antiferromagnetic Mott insulator and superconductiviy together with realization of spin-liquid state have been observed experimentally [10,11], while in the θ-type charge orderings with various spatial patterns of charge

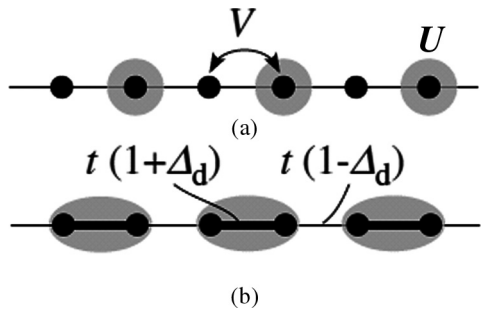

FIGURE 1 Schematic representations of two limiting cases in quarter-filled system; (a) the charge ordered state and (b) the dimer-Mott insulating state.

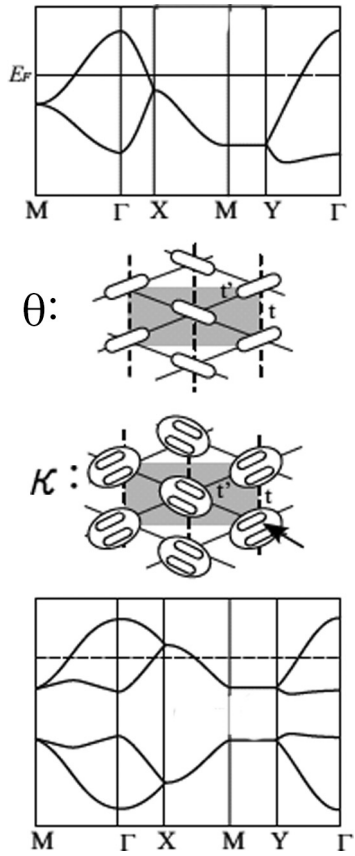

FIGURE 2 Spatial arrangement of ET molecules and resultant energy band structures of θ- and κ-ET_2X types.

disproportionation have been confirmed. In the latter, various intriguing phenomena associated with charge ordering have been experimentally observed, such as superconductivity [12], T^3-dependences of the resistivity [13], existence of low energy excitations probed by NMR [14], which await detailed analysis and theoretical understanding.

In ET_2X family, there is yet another complexity due to the fact that values of transfer integrals do not always have high symmetry (as in the cases of β- and λ-types), leading the splitting of the energy bands along XMY in the Brillouin zone in Figure 2.

The general trend of the ground state phase diagram of ET_2X, with such diversity has now been explored by the mean filed approximation

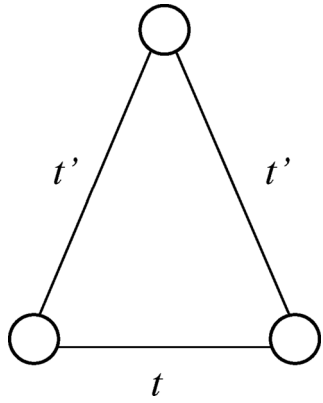

FIGURE 3 Anisotropic triangular lattice with transfer integrals, t and t'.

taking these features into account. However the understanding of effects of quantum fluctuations in such geometrically frustrated systems is far from complete at present.

POSSIBLE CARRIER DOPING INTO DNA

The carrier doping into band insulators is the basic of present semiconductor technology. The carrier doping into molecular assemblies has also historical examples such as perylene:Br by Akamatsu, Inokuchi and Matsunaga [15], and polyacetylene:I_3 by Shirakawa *et al*. [16]. Even without intention of doping, carriers may be doped into insulators. In this context it is interesting to observe many experimental reports on the possible electrical conduction in DNA reporting from solid insulators to superconductivity! [17]. In addressing to this issue, we note that any transport measurement on solids should pay attention to 1) sample quality and 2) the measurement procedures, especially electrical contact between metallic leads and molecules. In the case of DNA the above 2) has been seriously addressed by Zhang *et al*. [18], who concluded that DNA is insulators, while Kino *et al*. [19] addressed to the question of possible carrier doping by the cations always present in solvent. By taking a dimer of particular bases into consideration in electronic structure calculations, we found that some divalent cations like Mg^{++} can dope holes into guanines if sufficiently dehydrated. This result may indicate that holes can be doped in some cases without intention, which can be, at least, one of the causes of diverse contradicting experimental reports. If this is the case, there

will be a way to dope enough carriers into DNA, which make this material attractive as unique conductors with special morphology.

CONTACT PROBLEM

As mentioned in the previous section, the electrical contact between the lead and material to be measured is a very important subject technologically, since local electronic properties at the interfaces play decisive roles when any materials are to be used and electrons have to move through different regions. At the same time, there are many interesting and important questions await serious studies as basic science including the identification of the local atomic (molecular) arrangement including the orbital states and resultant local electronic spectroscopy. These problems associated with interfaces and contacts may symbolically be called "contact problem".

In contact problem, there exist two characteristic aspects to be addressed, the mechanical stability governed mainly by the deep levels and the transport properties associated with levels near the Fermi energy, both of which are governed by the orbital orientation just at the interface as schematically shown in Figure 4. Hence the

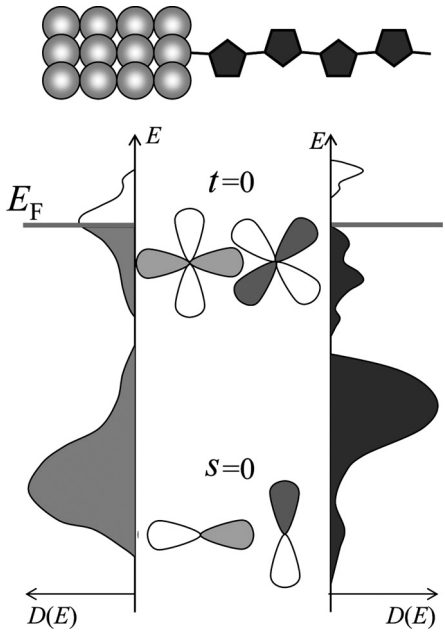

FIGURE 4 A symbolic representation of electronic states at the contact.

atomic scale local structure and resultant spectroscopy at the interface are scientific questions of contact problem.

FUTURE CHALLENGES IN MATERIAL SCIENCE

As has been briefly touched, a route for the systematic understanding of electronic properties of molecular solids is now opened naturally leading to research efforts on those of non-crystalline molecular assemblies, where the contact problem between molecules and metals inevitably emerges. This is precisely the same situation in heme-protein, where Fe is surrounded by the molecular π-orbitals in proteins, whose electronic states will be interesting scientific targets.

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