Recent studies on electrical and magnetic properties of molecular solids

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Abstract. Recent progress in studies on electrical and magnetic properties of some typical molecular solids is described, focussing on research in Japan. Especially we focus on two recent topics, organic semiconductor BTQBT and organic superconductors. Two types of compound are discussed, $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ and M_3C_{60} ($\text{M} = \text{K}$ or Rb). Finally, two kinds of molecular ferromagnet, nitronyl nitroxide radicals and $\text{C}_{60}(\text{TDAE})$, are briefly introduced.

Keywords. Molecular solids; electrical conductivity; Molecular ferromagnetism; organic superconductors; fullerenes.

1. Electrical properties of organic molecular solids

1.1 Organic semiconductors and conductors

The first observation of electrical conduction in organic solids was most confidently presented as a concept of “organic semiconductors” by Akamatu and Inokuchi (1950). Typical organic semiconductors at that time were such polycyclic aromatic hydrocarbons as anthracene, perylene or violanthrone. The essentially important feature in these substances is that they consist of π -electron systems, and it has been known that a variety of functionalities of organic materials are caused by these π -electron systems.

A breakthrough from semiconductors to organic metallic conductors was also opened by Akamatu *et al* (1954) as the discovery of very high conductivity of perylene–bromine complexes. The first observation of metallic conductivity was reported by Coleman *et al* (1973) for tetrathiafulvalene-tetracyano-quinodimethane (TTF-TCNQ). The one-dimensional structure causes inherent instability in the electronic band structure and makes an energy gap at the Fermi-energy level. This electronic phase transition is accompanied by a lattice distortion through an electron–phonon coupling which stabilizes a charge-density-wave (CDW) insulating state. This type of metal–insulator transition usually occurs at a finite temperature, e.g. 53 K for TTF-TCNQ.

In order to stabilize metallic phases at low temperatures, the increase of dimensionality has been pursued by introducing intercolumnar interactions or heteroatom–heteroatom interactions in plane-parallel directions between TTF-type molecules. Replacement of sulphur atoms in TTF moiety with selenium atoms which have larger interaction radius and smaller ionization potential is effective in increasing dimensionality. High-pressure application is physically effective in increasing dimensionality and in suppressing the metal–insulator transition.

Electron–electron repulsive correlation is another crucial factor in realization of a metallic state in narrow electron energy band systems. Especially, the on-site (on-one-molecule) Coulomb repulsive energy (U) relative to the bandwidth (W) is a very important measure in determining if the material will be metallic or insulating. If the ratio U/W is much greater than unity, the material is a Mott-type insulator. In

order to reduce U , various strategies have been attempted, such as to use larger-size, twin-type or multi-valency molecules. The former approach was very successful, that is, to use (*bis*)ethylenedithio-tetrathiafulvalene(BEDT-TTF) as an electron donor (Saito *et al* 1982).

1.1a BTQBT: Relatively highly conductive single-component organic semiconductors were recently realized by Yamashita *et al* (1991). A typical example is *bis*[1, 2, 5]thiadiazolo-*p*-quinobis(1,3-dithiole) (BTQBT), which was synthesized with the strategy to realize much stronger intermolecular interactions in single-component molecular crystals. This novel molecule has electron-withdrawing heterocycles which are fused to the skeleton of a very strong electron donor, 2,2'-*p*-quinobis(1,3-dithiole) (QBT) (figure 1). In addition to the advantage of the strong intermolecular interactions (heteroatom–heteroatom contacts), relatively extending π -conjugation on the molecular plane of BTQBT may reduce the on-site Coulomb repulsion. Furthermore, this molecule is highly polarized because of intramolecular charge transfer, and accordingly it is expected to have a relatively small HOMO–LUMO gap. All these features may contribute to high electrical conductivity of this material.

BTQBT single crystals actually exhibited an unusually high conductivity of $1 \times 10^{-3} \text{Scm}^{-1}$ at room temperature with a thermal activation energy of 0.21 eV. Hall effect and its temperature dependence were successfully observed by Imaeda *et al* (1992). The Hall mobility with positive sign is $2.4 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ at 330 K and $6.3 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ at 175 K, and it changes with temperature $T^{-1.6}$.

1.1b (DMe-DCNQI)₂Cu complex: The molecular structure of this compound is shown in figure 2. DMe-DCNQI is an electron-accepting molecule. The coordination to Cu ion is at the nitrogen atoms of cyanide groups. The DMe-DCNQI molecular planes overlap each other to form one-dimensional column structure in the crystal and copper ions connect these one-dimensional columns to form three-dimensional networks as shown in figure 3. The copper ions are in mixed valence state of $4/3 +$ average valence charge, which indicates that the copper *d*-orbitals are interacting with the π -orbitals (LUMO) of DMe-DCNQI molecules.

The three-dimensional electronic structure stabilizes the metallic state down to low temperatures without metal–insulator transition. However, the metallic state is transformed to insulating state under relatively low pressure (> 100 bar), and around the critical pressure region the “metal–insulator–metal” reentrant behaviour was observed with decreasing temperature (Tomic *et al* 1988). Similar metal–insulator transition

Figure 1. Molecular structures of some derivatives of TTF (a), BTQBT (b), and QBT (c).

Figure 2. Crystal structure of $(\text{DMe-DCNQI})_2\text{Cu}$.

and also reentrant behaviour were discovered with the substitution of hydrogen atoms in DMe-DCNQI with deuteriums or ^{12}C of cyanide groups with ^{13}C (figure 4). The isotope exchange may cause qualitatively similar effect to the pressure effect, i.e. chemical pressure effect.

The theoretical details of the strongly correlated electron systems of $(\text{DMe-DCNQI})_2\text{Cu}$ crystal have been studied by Fukuyama (1993).

1.2 Organic superconductors

In order to stabilize metallic states at low temperatures, enhancement of low dimen-

Figure 3. Reentrant metal-insulator transition by isotope substitution in (DMe-DCNQI)₂Cu.

Figure 4. Molecular structure of R_1, R_2 -DCNQI.

sionality and reduction of on-site Coulomb repulsion energies have been pursued. The first organic superconductor discovered by Jerome *et al* (1980) is (TMTSF)₂X (X = PF₆, $T_c = 0.9$ K at 12 kbar) (figure 5). TMTSF complex forms quasi-one-dimensional columnar structure and the intercolumnar Se-Se interaction is essential to stabilize the metallic state. Although in the case of X = PF₆ compound some pressure is necessary to suppress the metal-insulator transition, X = ClO₄ compound was found to be superconducting at 1.4 K under ambient pressure due to the stronger intercolumnar interactions in this case.

1.2a (BEDT-TTF)₂X: (BEDT-TTF)₂X compounds (figure 5) investigated by Saito *et al* (1982) have given much more successful results. The larger size of π -electron conjugation of BEDT-TTF may reduce the on-site Coulomb repulsion and the two-dimensional (not quasi-one-dimensional) crystal structure (figure 6) is advantageous for metallic phase.

The structure and function of the insulating layer X in (BEDT-TTF)₂X are also important for two-dimensional metallic character of these compounds. In the cases of X = Cu(NCS)₂, Cu(CN)[N(CN)₂], Cu[N(CN)₂]Br and Cu[N(CN)₂]Cl the superconducting critical temperatures T_c are relatively high, 10.4, 12.3, 11.2 and 12.5 K, respectively. The highest T_c is 13.1 K under 0.3 kbar for X = Cu[N(CN)₂]Br. The pressure dependence of T_c for X = Cu(NCS)₂ is, however, rather negative. The isotope

Figure 5. Molecular structures of the components of typical organic superconductors.

Figure 6. Crystal structure of (BEDT-TTF)₂Cu(NCS)₂.

effect for T_c is also negative for $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ when the peripheral hydrogen atoms are substituted by deuterium atoms. On the contrary, substitution of ^{12}C atoms in inner TTF core with ^{13}C exhibited almost no isotope shift in T_c . The magnetic field effects for metallic states have been very extensively studied to reveal the two-dimensional nature and Fermi-surface structures of these materials. $(\text{BEDT-TTF})_2\text{X}$ compounds may be classified to type II superconductors, and the magnetic behaviours below T_c are not sufficiently clarified yet.

1.2b Fullerenes: The discovery of such new cage-type carbon-atom clusters as C_{60} or fullerenes has opened a new horizon in the field of molecular materials (Kroto *et al* 1985). After the development of mass-production method for fullerenes by carbon contact arc discharge (Kratschmer *et al* 1990), the discovery of superconductivity at 18 K in K_3C_{60} (Hebard *et al* 1991) has strongly accelerated the study of fullerenes.

The electrical conductivity of C_{60} single crystal is strongly and negatively dependent on the ambient oxygen pressure, and it is believed to be around 10^{-5}S cm^{-1} at 295 K in the most oxygen-free pure C_{60} single crystals. The thermal activation energy of conductivity is 0.26 eV, which indicates that pure C_{60} crystal is a molecular semiconductor. The charge-carrier mobility in pure C_{60} single crystals was measured by two methods, time-of-flight (Frankevich *et al* 1993) and Hall effect (Arai 1994). The drift mobilities obtained by the former method were $1.7\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for holes and $0.5\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for electrons which are temperature-independent below (50–250 K) and above (260–300 K) the phase transition point, around 260 K. At this temperature the mobility increased stepwise by 1.7 times with decreasing temperature. It is known that the changes in the molecular rotational freedom and accordingly in the crystal structure take place at this temperature, which suggests that transporting electrons or holes may couple with molecular rotations. The Hall mobility with positive sign is reported to be $0.15\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and it is again almost temperature-independent between 290 K and 570 K.

Figure 7. Correlation between T_c and a_0 in alkali metal- C_{60} superconductors.

C_{60} crystals doped with alkali metals or alkaline-earth metals, M_xC_{60} , have realized a new family of molecular metals and superconductors which have much higher T_c than organic superconductors known so far. The dominant stoichiometry which yields metallic state is $x = 3$ and the corresponding ones for alkali metal-doped complexes, fullerides, make a systematic family of molecular superconductors (figure 7). The highest T_c in this family is 33 K for Cs_2RbC_{60} . However, it was very recently reported that Cs_3C_{60} stabilized under pressure may have ~ 40 K for T_c . The intrinsic nature of the metallic state and the mechanism of superconductivity in fullerides are not yet clarified. In the BCS regime a probable theoretical approach based on intramolecular-vibration-mediated Cooper pairing was proposed taking into account a strongly correlated electron system and relevant phonons and Coulomb energy windows (Ivanov and Maruyama 1995). However, such different approaches as charge-transfer pairing could be more general and relevant to molecular superconductors.

2. Magnetic properties of organic molecular solids

A very important subject in this field is to create or synthesize molecular ferromagnets. We focus on this subject in this section.

2.1 Molecular ferromagnetism

As radical molecules—neutral or charged—have unpaired electrons and show paramagnetism, they could be candidates for ferromagnetic materials. However, once these paramagnetic species are in the solid state, as a rule they are Curie–Weiss paramagnets. If the interactions between spins in different molecules are strong enough to order at some temperatures, the anti-ferromagnetically ordered states usually overcome the ferromagnetic states, since the bonding states between molecules are usually more stable than the antibonding states. Therefore the next strategy is how to make the bonding states unstable, or to make two unpaired spin states orthogonal.

Figure 8. Molecular structures of nitronyl nitroxide radicals.

Figure 9. Spontaneous magnetization in $C_{60}(TDAE)$.

2.1a Nitronyl nitroxide radicals: Nitronyl nitroxide radicals are the successful examples in this line (figure 8) (Kinoshita *et al* 1991). In the crystal unpaired spin states on $-NO$ groups are rather localized and located very far from each other due to crystal stability. Thus, nearly orthogonal relation between two unpaired spin states in neighbouring molecules is fulfilled in this case. Further, large on-site Coulomb repulsion may contribute to stabilize the triplet or ferromagnetic states in this system. This compound shows ferromagnetic ordering below 0.65 K.

2.1b $C_{60}(TDAE)$ ferromagnet: $C_{60}(TDAE)$ complex, where TDAE means tetrakis-diamino-ethylene, could be a different approach for a molecular ferromagnet in the charge transfer mechanism (Allemand *et al* 1991). Although extensive studies of this system have revealed aspects of its magnetic behaviour, such as the spontaneous

magnetization below 13 K or the hysteresis curve in the isothermal magnetization (figure 9) (Suzuki *et al* 1994), the nature of the magnetism, whether really ferromagnetic or spin-glass-like, is still unclear. The quest for itineracy of ferromagnetic spins is almost known to be negative through the recent experiments by two groups (Maruyama and Blinc).

References

- Akamatsu H and Inokuchi H 1950 *J. Chem. Phys.* **18** 810
Akamatsu H, Inokuchi H and Matsunaga Y 1954 *Nature* **173** 168
Allemand P M, Khemani K C, Koch A, Wudl F and Thompson J D 1991 *Science* **253** 301
Arai T 1994 *Electrical properties of C₆₀ single crystals*, Doctor Thesis, University of Tokyo, Tokyo
Coleman L B, Cohen M N, Sandman D J, Yamagishi F F, Garito A F and Heeger A J 1973 *Solid State Commun.* **12** 1125
Frankevich E, Maruyama Y and Ogata H 1993 *Chem. Phys. Lett.* **214** 39
Fukuyama H 1993 *J. Phys. Soc. Jpn* **62** 1436
Hebard A F *et al* 1991 *Nature* **350** 600
Imaeda K, Yamashita Y, Li Y, Mori T, Inokuchi H and Sano M 1992 *J. Mater. Chem.* **2** 115
Ivanov V and Maruyama Y 1995 *Physica C* (in press)
Jerome D, Mazaud A, Ribault M and Bechgaard K 1980 *J. Phys. Lett.* **41** L95
Kinoshita M *et al* 1991 *Chem. Lett.* 1225
Kratschmer W, Lamb L D, Fostiropoulos K and Huffman D R 1990 *Nature* **347** 354
Kroto H W, Heath J R, O'Brien S C, Curl R F and Smalley R E 1985 *Nature* **318** 162
Maruyama Y and Blinc R (Two groups)
Saito G, Enoki T and Inokuchi H 1982 *Chem. Lett.* 1345
Suzuki A, Suzuki T, Whitehead R J and Maruyama Y 1994 *Chem. Phys. Lett.* **223** 517
Tomic S, Jerome D, Aumuller A, Erk P, Hunig S and von Schulz J U 1988 *Synth. Met.* **27** B281
Wudl F and Thompson J D 1992 *J. Phys. Chem. Solids* **53** 1499
Yamashita Y, Tanaka S, Imaeda K and Inokuchi H 1991 *Chem. Lett.* 1213