# IV-F Electronic and Magnetic Properties of π-Electron-Based Molecular Systems

π-electrons are an interesting building block in architecting functionalized electronic and magnetic molecular systems. We have focused on nano-sized graphite and TTF-based organic charge transfer complexes, in which π-electrons play an important role, in developing new types of molecular electronic systems. In nanographene, single layer nanographite, which is defined as flat open π-electron system have edges and contrasted to closed π-electron systems of fullerenes and carbon nanotubes, non-bonding π-electronic state appearing around the Fermi level generates unconventional nanomagnetism. We have found an interesting electronic wave interference effect in finite-sized graphite with distortion-network structures and anisotropy of the Raman spectra of nanographite ribbons. A combination of TTF-based π-electron donor and counteranion having localized spins is a useful way in producing molecular magnetic conductors, which are expected to have properties different from traditional metal magnets featured with s-d interaction. Under this scheme, we have developed a new class of TTF-based organic magnetic conductors. The interaction between the conducting π-electrons of donors and the localized d-electrons of magnetic anions are found to show interesting interplay between magnetism and electron transport.

## IV-F-1 Metal-Insulator Transition in Iodinated Amorphous Conducting Carbon Films

**KUMARU, Latha[1]; SUBRAMANYAM, S. V.[1]; ETO, Soichiro[2]; TAKAI, Kazuyuki[2]; ENOKI, Toshiaki**
*([1]Indian Inst. Sci.; [2]Tokyo Inst. Tech.)*

[*Carbon* **42**, 2133–2137 (2004)]

In this work, the effect of iodine incorporation on the electrical conductivity, magnetic susceptibility ($\chi$) and magnetoresistance (MR) of amorphous conducting carbon (a-C) films has been discussed. Variation in conductivity of a-C films depends on the sample preparation conditions and iodine concentration. Evidence of metal–insulator (M–I) transition as a function of pyrolysis temperature is observed for iodinated (a-C:I) samples. The temperature dependent magnetic susceptibility of a-C:I sample shows a Curie behavior at low temperatures. The positive magnetoresistance is observed for all the samples irrespective of the conduction regimes. This is accounted by the electron–electron interaction in the a-C:I system.

## IV-F-2 Magnetic Resonance Study of Nanodiamonds

**SHAMES, Alexander I.[1]; PANICH, A. M.[1]; KEMPIŃSKI, W.[2]; BAIDAKOVA, M. V.[3,4]; OSIPOV, V. Yu.[3]; ENOKI, Toshiaki; VUL', A. Ya.[3]**
*([1]Ben-Guiron Univ. Negev.; [2]Polish Acad. Sci.; [3]Ioffe Phys.-Tech. Sci.; [4]Tokyo Inst. Tech.)*

[NATO Science Sries, D. M. Gruen, O. A. Shenderova, A. Ya. Vul', Eds., Springer; Dondrecht/Boston/London, pp.271 (2005)]

Magnetic resonance techniques, namely Electron Paramagnetic Resonance (EPR) and solid state Nuclear Magnetic Resonance (NMR), are powerful non-destructive tools for studying electron-nuclear and crystalline structure, inherent electronic and magnetic properties and transitions in carbon-based nanomaterials. EPR allows to control purity of ultradispersed diamond (UDO) samples, to study the origin, location and spin-lattice relaxation of radical-type carbon-inherited paramagnetic centers (RPC) as well as their transformation during the process of temperature driven diamond-to-graphite conversion. Solid state NMR on $^{1}$H and $^{13}$C nuclei provide one with information on the crystalline quality, allows quantitative estimation of the numbers of different allotropic forms, and reveals electron-nuclear interactions within the UDO samples under study. Results of recent EPR and $^{13}$C NMR study of pure and transition metal doped UDD samples, obtained by detonation technique, are reported and discussed. In addition to characteristic EPR signals, originated from para- and ferromagnetic impurities and doping ions, the UDD samples show a high concentration of RPC (up to $10^{20}$ spin/gram), which are due to structural defects (dangling C–C bonds) on the diamond cluster surface. *In-situ* EPR sample's vacuumization experiment in conjunction with precise SQUID magnetization measurements allowed concluding that each UDD particle carries a single spin (dangling bond) per each from 8 crystal (111) facets bounded the particle.

## IV-F-3 *d*-Electron-Induced Negative Magnetroresistance of π-*d* Interaction System Including Brominated-TTF Donor

**NISHIJO, Junichi[1]; MIYAZAKI, Akira[1]; ENOKI, Toshiaki; WATANABE, Ryoji[2]; KUWATANI, Yoshiyuki[3]; IYODA, Masahiko[3]**
*([1]Indian Inst. Sci.; [2]Tokyo Inst. Tech.; [3]Tokyo Metropolitan Univ.)*

[*Inorg. Chem.* **44**, 2493–2506 (2005)]

A new π-d interaction system (EDT-TTFBr$_2$)$_2$FeBr$_4$ (EDT-TTFBr$_2$ = 4,5-dibromo-4',5'-ethylenedithio-tetrathiafulvalene) and its nonmagnetic anion analogue (EDT-TTFBr$_2$)$_2$GaBr$_4$ based on a brominated TTF-type organic donor are investigated. The salts featured by quasi-1D π-electronic systems are metallic with metal-insulator transitions taking place at about 20 and 70 K for the FeBr$_4^-$ and GaBr$_4^-$ salts, respectively, where the low-temperature insulating state is associated with charge ordering or a Mott insulator followed by an antiferromagnetic transition at lower temperatures. The

$FeBr_4^-$ salt is featured with an antiferromagnetic transition of the anion d spins at a Néel temperature ($T_N$) = 11 K, which is significantly high despite its long anion-anion Br-Br contact, suggesting the importance of the π-d interaction in the magnetism. The surprisingly strong π-d interaction, *ca.* –22.3 K estimated from the magnetization curve, evidences the usefulness of the chemical modification of the donor molecule with bromine substitution to achieve strong intermolecular interaction. The antiferromagnetic state of the anion d spins affects the transport of the conducting π electrons through the strong π-d interaction, as evidenced by the presence of a resistivity anomaly of the $FeBr_4^-$ salt at $T_N$. Below $T_N$, the $FeBr_4^-$ salt shows negative magnetoresistance that reaches –23% at the highest magnetic field investigated ($B$ = 15 T), whereas only a small positive magnetoresistance is observed in the π-electron-only $GaBr_4^-$ salt. The mechanism of the negative magnetoresistance is explained by the stabilization of the insulating state of the π electrons by the periodic magnetic potential of the anion d spins in the $FeBr_4^-$ salt, which is modified by applying the external magnetic field.

### IV-F-4 Electronic and Mgnetic Properties of π-*d* Interaction System $(EDTDM)_2FeBr_4$

**OKABE, K.[1]; YAMAURA, J. -I.[2].; MIYAZAKI, Akira[1]; ENOKI, Toshiaki**
*([1]Tokyo Inst. Tech.; [2]Univ. Tokyo)*

[*J. Phys. Soc. Jpn.* **74**, 1508–1520 (2005)]

The crystal structure and electronic and magnetic properties of magnetic molecular conductor $(EDTDM)_2$ $FeBr_4$ are investigated. The material undergoes a SDW transition at $T_{MI}$ ~ 11 K and an antiferromagnetic transition of $Fe^{3+}$ *d*-spins at $T_N$ = 3 K. In addition to the appearance of an anomaly in the resistivity around $T_N$, a large magnetoresistance is observed below $T_N$, which diverges at the critical pressure ($P_c$ ~ 9.2 kbar) of the MI transition. The perturbation potential from the antiferromagnetic $Fe^{3+}$ spin arrangement stabilizes the SDW state, leading to the anomaly in the resistivity. The application of magnetic field reduces the potential of the $Fe^{3+}$ spins, which leads to the large negative magnetoresistance. This indicates that the π-*d* interaction plays an important role in the interplay between the magnetism and the electron transport.

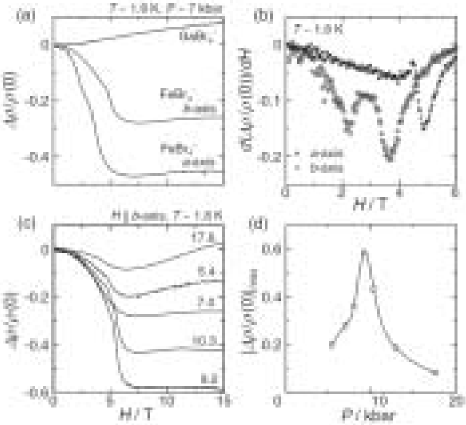

**Figure 1.** The field dependence of the magnetoresistance at $T$ ~ 1.9 K for $(EDTDM)_2MBr_4$ (M = Fe, Ga) under the pressure of 7.0 kbar. (b) The field dependence of the magnetoresistance at $T$ ~ 1.8 K for $(EDTDM)_2FeBr_4$ under pressures of 5.4, 7.0, 9.2, 10.3 and 17.6 kbar. (c) The numerical derivatives of the intra-layer magnetoresistance of $(EDTDM)_2FeBr_4$ at $P$ ~ 7.0 kbar as a function of applied field. (d) The pressure dependence of the maximum of the absolute value of the negative magnetoresistance of $(EDTDM)_2FeBr_4$.

### IV-F-5 Observation of Zigzag- and Armchair-Edges of Graphite

**KOBAYASHI, Yousuke[1]; KUSAKABE, Koichi[2]; FUKUI, Ken-ichi[1]; ENOKI, Toshiaki; KABURAGI, Yutaka[3]**
*([1]Tokyo Inst. Tech.; [2]Osaka Univ.; [3]Musashi Inst. Tech.)*

[*Phys. Rev. B* **71**, 193406 (4 pages) (2005)]

The presence of structure-dependent edge states of graphite is revealed by both ambient and ultra high vacuum (UHV) scanning tunneling microscopy and scanning tunneling spectroscopy observations. On a hydrogenated zigzag (armchair) edge, bright spots are (are not) observed together with a (√3×√3) *R*30° superlattice near the Fermi level ($V_S$ ~ –30 mV for a peak of the local density of states) under UHV (Figure 1), demonstrating that a zigzag edge is responsible for the edge states, although there is no appreciable difference between as-prepared zigzag and armchair edges in air. Even in the hydrogenated armchair edge, however, bright spots are observed at defect points, at which partial zigzag edges are created in the armchair edge.

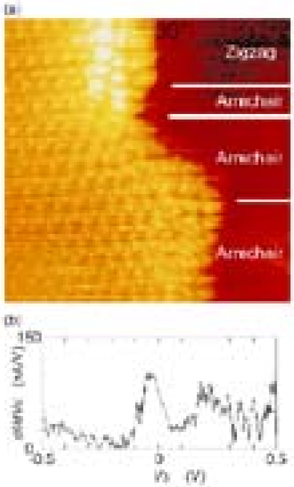

**Figure1.** (Color) (a) An atomically resolved UHV STM image of zigzag and armchair edges (9 × 9 $nm^2$). (b) Typical $dI/dV_S$ curve from STS data at a zigzag edge.