VIII-P Syntheses of Fullerene-Based New Materials with Novel Physical Properties

Fullerene-based new materials are synthesized, and the structures and physical properties are studied in wide temperature and pressure regions. The structures and transport properties of pressure-induced superconducting fulleride, Cs_3C_{60}, are studied by X-ray powder diffraction, ESR, Raman, AC susceptibility and resistivity measurements, in order to clarify the mechanism of pressure-induced superconductivity. The structures and transport properties of metallofullerenes are also studied by X-ray diffraction and resistivity. The field-effect transistors (FET's) with thin-films of fullerenes are fabricated and their transport properties are studied in wide temperature region. STM studies on metallofullerenes adsorbed on Si(111)-(7×7) surface are performed under high vacuum condition.

VIII-P-1 Pressure and Temperature Dependences of the Structural Properties of Dy@C_{82} Isomer I

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Crystals of Dy@C_{82} isomer I are studied by x-ray powder diffraction with synchrotron radiation in wide temperature and pressure regions. The isomer I of Dy@C_{82} shows a simple cubic structure with lattice constant, *a*, of 15.85(3) Å at 298 K, while the isomer II shows a face-centered cubic structure with *a* of 15.75(4) Å. The structural phase transition of the second-order is indicated for the isomer I at 300–310 K by the temperature dependence of x-ray diffraction and differential scanning calorimetry. Further, the pressure dependence of the lattice constant is studied for the isomer I up to 60 kbar, which can be fitted by a Murnaghan equation of state.

VIII-P-2 Ferromagnetism and Giant Magnetoresistance in the Rare-Earth Fullerides $Eu_{6-x}Sr_xC_{60}$

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[*Phys. Rev. B* **65**, 134431 (2002)]

We have studied crystal structure, magnetism, and electric transport properties of a europium fulleride Eu_6C_{60} and its Sr-substituted compounds, $Eu_{6-x}Sr_xC_{60}$. They have a *bcc* structure, which is an isostructure of other M_6C_{60} (*M* represents an alkali atom or an alkaline-earth atom). Magnetic measurements revealed that magnetic moment is ascribed to the divalent europium atom with $S = 7/2$ spin, and a ferromagnetic transition was observed at T_c = 10–14 K. In Eu_6C_{60}, we also confirm the ferromagnetic transition by heat-capacity measurement. The striking feature in $Eu_{6-x}Sr_xC_{60}$ is very large negative magnetoresistance at low temperature; the resitivity ratio $\rho(H = 9\ T)/\rho(H = 0\ T)$ reaches almost 10^{-3} at 1 K in Eu_6C_{60}. Such large magnetoresitance is the manifestation of a strong π-*f* interaction between conduction carriers on C_{60} and 4*f* electrons of Eu.

VIII-P-3 Bridging Fullerenes with Metals

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[*Chem. Phys. Lett.* **359**, 177 (2002)]

The bonding nature between rare earth metals and fullerene molecules has been investigated. The electron density distribution for nominal Sm_3C_{70}, calculated by a maximum entropy method (MEM) based on the Rietveld analysis of synchrotron X-ray diffraction pattern, unambiguously demonstrated a covalent Sm···C bond, which is almost as strong as the interatomic bonding of crystal Si. Furthermore, the Sm bridges two C_{70} molecules, producing a C_{70}···Sm···C_{70} dimer structure.

VIII-P-4 Structure and Physical Properties of $Cs_{3+\alpha}C_{60}$ (α = 0.0–1.0) under Ambient and High Pressures

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[*Phys. Rev. B* **65**, 235425 (2002)]

The intermediate phases, $Cs_{3+\alpha}C_{60}$ (α = 0.0–1.0), have been prepared, and their structure and physical properties are studied by x-ray powder diffraction, Raman, ESR, electric conductivity and ac susceptibility measurements under ambient and high pressures. The x-ray powder diffraction pattern of $Cs_{3+\alpha}C_{60}$ (α = 0.0–

1.0) can be indexed as a mixture of the body-centered-orthorhombic (*bco*) and cubic (A15) phases. The A15 phase diminishes above 30 kbar. The broad ESR peak due to conduction electron (*c*-ESR) is observed only for the phases around $\alpha = 0.0$ in $Cs_{3+\alpha}C_{60}$. The resistivity of the $Cs_{3+\alpha}C_{60}$ ($\alpha \neq 0$) sample follows the granular metal theory and/or Sheng model even in the sample exhibiting a broad ESR peak. No superconducting transition is observed up to 10.6 kbar in $Cs_{3+\alpha}C_{60}$ ($\alpha \neq 0$). These results present that bco phase of $Cs_{3+\alpha}C_{60}$ ($\alpha = 0$) is a final candidate for a pressure-induced superconductor.

VIII-P-5 Complex-Plane Impedance Study on a Hydrogen-Doped Copper Coordination Polymer: *N*,*N*'-bis-(2-hydroxy-ethyl)-Dithiooxamidato-Copper(II)

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[*Mol. Cryst. Liq. Cryst.* **379**, 89 (2002)]

AC conductivity measurements with an impedance analyzer were carried out for a hydrogen-doped coordination polymer, *N*,*N*'-bis-(2-hydroxy-ethyl)-dithiooxamidato-copper(II), in order to estimate the protonic conductivity (σ_p). The log σ_p was linearly increased from 2.6×10^{-9} to 2.2×10^{-6} Scm^{-1} with relative humidity (RH) from 45 to 100% at 300 K. A slight hysteresis of protonic conductivity was observed upon increasing and decreasing RH, which implies that H_3O^+ is generated by a reaction between water molecule and acid-base polymer near RH ~ 100%.

VIII-P-6 Crystal Structure and Electronic Transport of Dy@C_{82}

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Crystal structure of Dy@C_{82} isomer I at 298 K has been determined by Rietveld refinement for X-ray powder diffraction with synchrotron radiation. The isomer I shows a simple cubic structure (sc: $Pa\bar{3}$) with a lattice constant, *a*, of 15.78(1) Å. The C_2 axis of a C_{2v}-C_{82} cage aligns along a [111] direction of this crystal lattice. The C_{82} cage is orientationally disordered to satisfy a $\bar{3}$ symmetry along [111] which is requested in this space group. The large thermal parameter for the Dy atom estimated from the X-ray diffraction probably reflects a large disorder caused by a floating motion of the Dy atom inside the C_{82} cage as well as a ratchet-type motion of the Dy@C_{82} molecule. The electronic transport of thin film of Dy@C_{82} shows a semiconducting behavior. The energy gap, E_g, is estimated to be 0.2 eV. Further, the variation of valence from Dy^{3+} to Dy^{2+} is found by metal-doping into the Dy@C_{82} crystals.

VIII-P-7 *N*-Channel Field-Transistors with Thin Films of Fullerenes

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[*Phys. Rev. B* submitted]

N-cannel field effect transistors (FETs) are fabricated with thin films of C_{60}, C_{70} and Dy@C_{82}, and an SiO_2 insulating layer. The transport properties of the C_{60} and C_{70} FET's are studied in a temperature region from 200 to 330 K. The typical FET properties are observed in C_{60} and C_{70} above 220 K. The hopping transport with activation energy of 0.3 eV is observed for the C_{60} and C_{70} FET's in this temperature region. Further, the condition of fabrication is studied in order to improve the FET property. The Dy@C_{82} FET is first fabricated and its property is studied at 295 K.

VIII-P-8 STM Study of Dy@C_{82} on Si(111)-(7×7) Surface

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[to be submitted]

Single-molecule image of Dy@C_{82} on Si(111)-(7×7) surface is observed by STM. The Dy@C_{82} molecules were deposited on the Si(111)-(7×7) surface under UHV chamber. The first layer of Dy@C_{82} is disordered, and no second layer islands are found before the complete formation of the first layer of Dy@C_{82}. A single-molecule image of Dy@C_{82} was clearly observed on the first layer. This image shows that the maximum height of the molecule is ~ 11.3 Å which corresponds to those of two long axes of Dy@C_{82} inclusive of van der Waals radius of C atom. The STS of the multilayer of Dy@C_{82} suggests a energy gap of 0.1 eV at 295 K, in consistent with that, 0.2 eV, determined by resistivity measurement for the Dy@C_{82} thin film. This shows that the Dy@C_{82} molecule is a small-gap semiconductor.