VI-T 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 two-dimensional polymeric fulleride, Na_4C_{60}, is also studied in order to clarify the novel physical properties which are expected from its low-dimenionality. The structures and electronic properties of solid metallofullerenes are first clarified under high pressure, and the first evidence has been obtained for the endohedral structure and electron transfer from a metal atom to the C_{60} cage in metal endohedral C_{60}.

VI-T-1 Structure and Raman Scattering of Cs_3C_{60} under High Pressure

FUJIKI, Satoshi; KUBOZONO, Yoshihiro; EMURA, Shuichi[1]; TAKABAYASHI, Yasuhiro; KASHINO, Setsuo[2]; FUJIWARA, Akihiko[3]; ISHI, Kenji[3]; SUEMATSU, Hiroyoshi[3]; MURAKAMI, Yoichi[4]; IWASA, Yoshihiro[5]; MITANI, Tatsuoki[5]; OGATA, Hironori
([1]Osaka Univ.; [2]Okayama Univ.; [3]Univ. Tokyo; [4]KEK-PF; [5]JAIST)

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Raman scattering is studied for a pressure-induced superconductor Cs_3C_{60} in a pressure region from 1 bar to 62 kbar. The center frequency ω_0 for $H_g(1)$ and $H_g(2)$ Raman peaks increases by applying pressure, but the increase shows a saturation in the high-pressure region. On the other hand, the ω_0 for $A_g(1)$ and $A_g(2)$ modes increase monotonically in all pressure regions. The electron-phonon coupling constant for Cs_3C_{60} shows a rapid decrease up to 30 kbar and an increase above 30 kbar. This result may be associated with a transformation from a multiphase (body-centered orthorhombic and A15 phases) to a single phase around 20 kbar. X-ray powder diffraction pattern at 11 K under a pressure of 40 kbar shows that a superconducting phase for Cs_3C_{60} is body-centered orthorhombic.

VI-T-2 Structure and Physical Properties of Na_4C_{60} under Ambient and High Pressures

KUBOZONO, Yoshihiro; TAKABAYASHI, Yasuhiro; KAMBE, Takashi[1]; FUJIKI, Satoshi; KASHINO, Setsuo[1]; EMURA, Shuichi[2]
([1]Okayama Univ.; [2]Osaka Univ.)

[*Phys. Rev. B* **63**, 45418 (2001)]

The structure and physical properties of two-dimensional polymeric Na_4C_{60} (body-centered monoclinic, space group *I*2/*m*) are studied in a wide temperature region from 12 to 300 K at 1 bar, and in a pressure region up to 53 kbar at 300 K. The temperature dependence of lattice constants suggests a structural anomaly below 100 K where the variation of spin susceptibility is observed from electron spin resonance. The thermal expansion of the unit-cell volume V is smaller than that of monomeric Rb_3C_{60} and K_3C_{60}. The compressibility of *c* is larger than that of *a* and *b*, which can be well explained by the repulsion between Na ions. The compressibility of the center-to-center distance in the $(10\bar{1})$ plane is ~ 1/3 times smaller than that in the (101) plane, which can be well explained by the formation of the polymer chains. Further, a possibility of a three-dimensional polymerization is discussed on the basis of the pressure dependence of $C_{60}\cdots C_{60}$ distance.

VI-T-3 Structure of $La_2@C_{80}$ Studied by La K-Edge XAFS

KUBOZONO, Yoshihiro; TAKABAYASHI, Yasuhiro; KASHINO, Setsuo[1]; KONDO, Masahiro[2]; WAKAHARA, Takatsugu[2]; AKASAKA, Takeshi[3]; KOBAYASHI, Kaoru[4]; NAGASE, Shigeru; EMURA, Shuichi[5]; YAMAMOTO, Kazunori[6]
([1]Okayama Univ.; [2]Niigata Univ.; [3]Univ. Tsukuba; [4]Tokyo Metropolitan Univ.; [5]Osaka Univ.; [6]Power Reactor and Nuclear Fuel Department Corporation)

[*Chem. Phys. Lett.* **335**, 163 (2001)]

The structure of $La_2@C_{80}$ is studied by La K-edge XAFS from 40 to 295 K. The distances between the La atom and the first nearest C atoms have been determined to be 2.42(1) Å at 40 K and 2.44(2) Å at 295 K, and those between the La atom and the second nearest C atoms to be 2.97(2) Å at 40 K and 2.98(3) Å at 295 K. The La–La distance has been determined to be 3.90(1) Å at 40 K and 3.88(2) Å at 295 K. The temperature dependence of the mean-square displacement of La–C is also studied to get an insight into the dynamical behavior of two La atoms in the C_{80} cage.

VI-T-4 Structure and Electronic Properties of $Dy@C_{82}$ Studied by UV-VIS Absorption, X-Ray Powder Diffraction and XAFS

IIDA, Satoru[1]; KUBOZONO, Yoshihiro; SLOVOKHOTOV, Yuri[2]; TAKABAYASHI, Yasuhiro; KANBARA, Takayoshi; FUKUNAGA, Takeo[1]; FUJIKI, Satoshi; EMURA, Shuichi[3]; KASHINO, Setsuo[1]
([1]Okayama Univ.; [2]Russian Acad. Sci.; [3]Osaka Univ.)

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Two isomers of Dy@C_{82} were separated by high performance liquid chromatography (HPLC), and their UV-VIS absorption spectra were measured to characterize these isomers. The crystalline powder of Dy@C_{82} was obtained by removing solvent (toluene) at 250 °C under vacuum. The X-ray diffraction pattern can be indexed with fcc crystal lattice, as that in La@C_{82}. The lattice constant *a* at 298 K, 15.86(1) Å, is close to that of La@C_{82}, 15.78 Å. The distances between Dy and the first and second nearest C atoms are determined to be 2.52(2) and 2.86(2) Å, respectively, on the basis of Dy L_{III}-edge EXAFS. The XANES shows that the valence of the Dy atom in Dy@C_{82} is +3.

VI-T-5 Dy@C_{60}: Evidence for Endohedral Structure and Electron Transfer

KANBARA, Takayoshi; KUBOZONO, Yoshihiro; TAKABAYASHI, Yasuhiro; FUJIKI, Satoshi; IIDA, Satoru[1]; HARUYAMA, Yusuke[1]; KASHINO, Setsuo[1]; EMURA, Shuichi[2]; AKASAKA, Takeshi[3]
([1]Okayama Univ.; [2]Osaka Univ.; [3]Univ. Tsukuba)

[*Phys. Rev. B* **64**, 113403 (2001)]

In view of the lack of information on the structure of M@C_{60} (M: alkaline earth and lanthanide metal) because of its instability and difficulties in purifying it, we have carried out and report here some structural investigations of Dy@C_{60}. We obtained a pure sample of Dy@C_{60} by high performance liquid chromatography with aniline as an eluent, and studied it by Dy L_{III}-edge XAFS and Raman scattering. Our results show conclusively that the structure is endohedral (with the metal inside the C_{60} cage) and that electron transfer takes place between Dy and C_{60}. The Dy in Dy@C_{60} is located at an off-center position, 1.25–1.30 Å, from the center of the C_{60} cage. The valence of the Dy is shown to be + 3 on the basis of a Dy L_{III}-edge XANES study. The $A_g(2)$ Raman peak also shows that three electrons have been transferred from Dy atom to the C_{60} cage. The UV-VIS-IR spectrum suggests that the HOMO-LUMO gap is small.