

## 10-Physical and Chemical Properties of Materials in Relation to Structure (Superconductors, Fullerenes, etc)

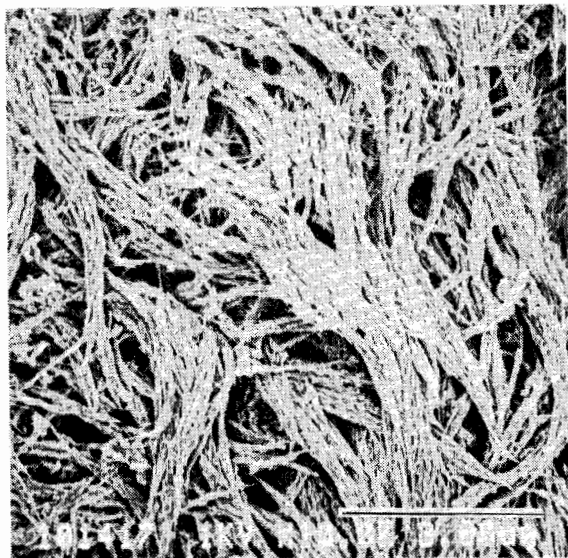


Fig. 1 A SEM image of the carbon nanotubes.

### PS-10.02.10 NEGATIVELY CURVED STRUCTURES:

**FLEXI-CRYSTALLOGRAPHY** By H. Terrones<sup>†</sup> and A. Mackay<sup>‡</sup>. Instituto de Física, UNAM, Apartado Postal 20-364, 01000 México, D.F. <sup>†</sup>Birkbeck College, University of London, Malet Street, London WC1E 7HX, England, U.K.

The discovery of  $C_{60}$ ,  $C_{70}$ , cylindrical graphite and other Fullerenes has opened the field of a new kind of materials with important properties. Starting from the concepts of 2-D manifolds or surfaces, negatively curved graphite structures are proposed. In  $C_{60}$  the positive Gaussian curvature is due to the presence of pentagonal rings of carbon. We have found that introducing rings with more than six carbon atoms, periodic graphite structures with the same topologies as triply periodic minimal surfaces can be constructed. Geometric properties and stability of these hypothetical structures are discussed. In general, the decoration of surfaces with different Gaussian curvatures (Flexi-crystallography) allows us to characterize structures already known and propose others waiting to be discovered.

**PS-10.02.11 XAFS STUDIES ON Rb-DOPED  $C_{60}$  SUPERCONDUCTORS.** By Y. Kubozono, I. Kimura, T. Fujimoto, A. Hirano, H. Maeda, S. Kashino, K. Oshima and H. Yamazaki, Faculty of Science, Okayama University, Japan, H. Ishida, College of General Education, Okayama University, Japan, T. Ishii, Faculty of Engineering, Okayama University, Japan, S. Emura, ISIR, Osaka University and K. Kato, Institute for Molecular Science, Japan.

The breakthroughs in synthesizing large amounts of Buckminster fullerene ( $C_{60}$ ) and other fullerenes have made it possible to study their structures and properties (W. Kratschmer, L.D.Lamb, K.Fostiropoulos and R.D.Huffmann, Nature, 1990, 347, 354-358). Since the discovery of superconductivity in alkali-metal-doped compounds of  $C_{60}$  molecule, a number of intensive studies concerning the crystal structures have been reported based on powder and

single crystalline X-ray diffraction and X-ray Absorption Fine-Structure (XAFS) methods (P.W.Stephens, L.Mihaly, J. B.Wiley, S-M.Huang, R.B.Kaner, F.Diederich, R.L.Whetten and K.Holczer, Phys. Rev., 1992, B45, 543-546). The purpose of the present work is to investigate the local structure around the Rb ions in  $Rb_3C_{60}$  in order to clarify the relation between the structure and superconducting phenomenon.

$C_{60}$  powder were prepared by arc-heating of graphite under a 200-Torr He atmosphere and were subsequently separated chromatographically using an activated alumina column with benzene/hexane developer. The purity of the  $C_{60}$  was confirmed to be at least 99% by UV-VIS and NMR spectra. The  $C_{60}$  (25 mg) was placed in a pyrex tube (6 mm diameter) together with Rb. The small amounts of Rb metal were measured in metal-filled glass capillary tubes (0.5 mm diameter), which were cut and handled under a nitrogen atmosphere in a glove-box. The pyrex tubes containing  $C_{60}$  and the Rb were degassed to  $10^{-2}$  Torr and sealed. These were then heated at 513 K for 64 hr. The transition temperature ( $T_c$ ) was confirmed to be 27 K by a SQUID magnetometer (SHE VTS900).

XAFS measurements were performed using synchrotron radiation from the Photon Factory (PF) at the National Laboratory for High-Energy Physics (KEK, Tsukuba). The rubidium K-edge XAFS spectra of a superconducting  $Rb_3C_{60}$  and reference sample rubidium hydrogen L-tartrate ( $RbHTr$ :  $C_4H_5O_6Rb$ ) were taken with the transmission mode at various temperatures from 10 to 300 K.

Figure 1 shows the Rb K-absorption spectra of (a) superconducting  $Rb_3C_{60}$ , (b) air exposed  $Rb_3C_{60}$  (non-superconducting) and (c)  $RbHTr$  at room temperature. The results of the EXAFS will be discussed in the presentation.

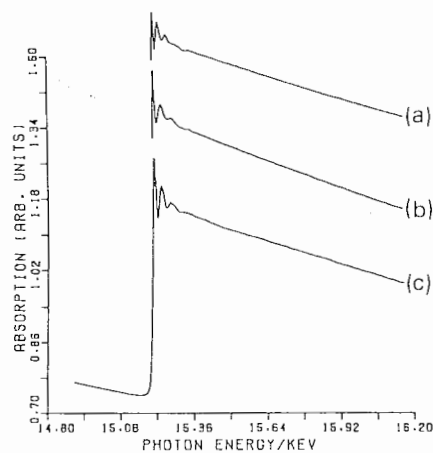


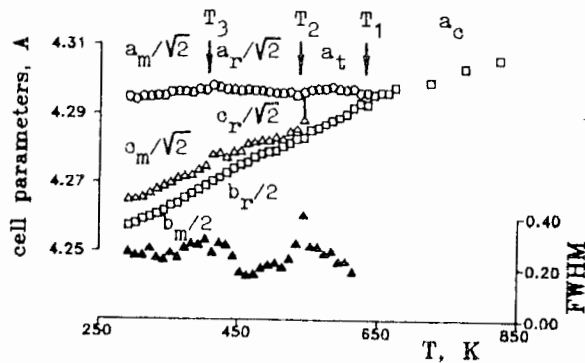
Fig. 1. Rubidium K-edge X-ray absorption spectra of (a) superconducting  $Rb_3C_{60}$ , (b) air exposed  $Rb_3C_{60}$  and (c)  $RbHTr$  at room temperature.

**PS-10.02.12 MOLECULAR PACKING AND DISORDER IN  $C_{60} \cdot 2C_{81}H_{68}O_4$  COMPLEX.** By B. Bachtel<sup>(a)</sup>, D. André<sup>(b)</sup>, H. Szwarc<sup>(b)</sup>, R. Céolin<sup>(c)</sup>, V. Agafonov<sup>(c)</sup>, R. Chiarelli<sup>(d)</sup>, C. Fabre<sup>(d)</sup> and A. Rassat<sup>(d)</sup>, (a) Lab. Cristallographie, Univ. Paris VI, F-75005 Paris, (b) CPMA, Univ. Paris XI, F-91405 Orsay, (c) Fac. Pharmacie, F-37042 Tours, (d) Lab. Activation Moléculaire, ENS, F-75005 Paris.

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Evaporation of a toluene solution of C<sub>60</sub> and Zephyrane (tetrakis triphenyl methoxy methyl methane) leads to transparent purple crystals. Tetragonal, I4/m, a=16.33 Å, c=32.61 Å, Z=4. The crystal structure has been solved by direct methods. Full matrix refinement. 744 independent reflections with I > 3σ(I). R=0.08. Each C<sub>60</sub> molecule is included between two Zephyrane ones and occupies four orientational positions at its site. It is likely that this results from dynamic orientational disorder.



PS-10.02.13 STRUCTURAL PHASE TRANSFORMATIONS OF THE PROTOTYPIC CERAMIC SUPERCONDUCTOR BaPbO<sub>3</sub>. By V.V.Zhurov, S.A.Ivanov\*, I.V.Ol'hovik, E.D.Politova, Karpov' Institute of Physical Chemistry, 103064 Moscow K-64, Russia.

The discovery of high-T<sub>c</sub> superconductivity in Ba-Pb-Bi-O system has led to resurgence of interest in crystal structure of distorted perovskite phases. Although the underlying mechanism responsible for this phenomena still remains unclear, it is obvious that a detailed study of structural phase transitions may help to understand the nature of superconductivity. In connection with our earlier investigations on the structural mechanisms of phase transitions in high-T<sub>c</sub> superconductors we have examined precisely the temperature dependence of lattice constants in ceramic BaPbO<sub>3</sub> which was prepared using oxide synthesis technique. X-ray powder diffraction measurements were carried out on URD-63 and DRON-3 diffractometers (CuK<sub>α</sub> radiation, 2θ=10-150°, step width-0.02°, counting time-30s.) equipped with a special high-temperature chamber. Profile analysis and refinement procedures were performed using the local version of powder diffraction software package for IBM-PC. We have shown, that above 640K the structure of BaPbO<sub>3</sub> is cubic perovskite. As the temperature is lowered the results of thermal expansion measurements (see figure and table) indicate that BaPbO<sub>3</sub> undergoes a series of successive structural phase changes. There are three transitions, at about 630K to tetragonal phase, near 540K to orthorhombic phase and at about 420K to monoclinic one. It was found that the Pb<sup>2+</sup>-Pb<sup>4+</sup> valence fluctuations might occur in slightly oxygen deficient BaPbO<sub>3</sub> samples. The structure of BaPbO<sub>3</sub> has been also studied using the Rietveld method and the results will be presented. Although there are not enough data to establish quantitative trends of mechanisms of observed phase transitions, it has been shown that these structural transformations may be interpreted in terms of soft phonon modes.

Symmetry	ΔT, K	a (x10 <sup>6</sup> )		
		a	b	c
monocl.	300-420	5.69	25.68	22.05
orthor.	430-540	-3.42	23.06	16.70
tetrag.	550-630	-3.02	24.73	-
cubic	640-820	13.40	-	-

PS-10.02.14 COMPTON PROFILE OF C<sub>60</sub> COMPARISON BETWEEN THEORY AND EXPERIMENT

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The isotropic Compton profile of C<sub>60</sub> crystal has been measured at LURE DCI, and can be compared to that of graphite. It turns out that in fullerene, the momentum density is higher at small momentum transfer than the density of graphite. As a consequence, valence electrons seem to be more delocalized in fullerene than in graphite. Is this a consequence of the geometrical constraints in C<sub>60</sub>, or is it an effect related to the packing of C<sub>60</sub> units?

In order to answer this question, an ab initio calculation has been undertaken for an isolated C<sub>60</sub> unit, using the TURBOMOLE code, with a double zeta polarized basis set (900 basis functions). The wave function is then transformed into momentum space representation, in order to compute the momentum density and directional or average Compton profiles. The comparison with both the experiment and a similar calculation on graphite (with the same basis set) are under completion.

One striking difference with graphite, related to steric constraints, is that the bending of the structure of C<sub>60</sub> implies a partial s-p hybridisation of the π type electron states, the centre of charge is out of the average sphere, which increases the delocalization of those electron states.

10.03 - Defects, Microstructures and Textures

PS-10.03.01 COMPUTER CALCULATION OF ISOTOPIC EFFECTS IN URANIUM-CROWN ETHER COMPLEXES. By Y.D.Han, China Institute of Atomic Energy, Beijing 102413, PRC.

The isotope effects of isotopic exchange reactions between different molecules are directly related to the structure of these molecules. In recent years, many isotopic effects of uranium-crown ether systems were found. Further studies were carried out with single-crystal X-ray diffraction and infrared spectrometry. The experimental values obtained agreed with the quantitative estimates.

Crystals of (DCH18C6.H<sub>3</sub>O)<sub>2</sub>UO<sub>2</sub>Cl<sub>4</sub> are triclinic with one formula per unit cell. The two cations (DCH18C6.H<sub>3</sub>O)<sup>+</sup> surround one anion UO<sub>2</sub>Cl<sub>4</sub><sup>2-</sup> forming a 2:1 neutral sandwich compound. The U atom at a symmetry center bonds to two O and four Cl atoms giving a square pyramidal coordination with symmetry D<sub>4h</sub>. The vibration modes of the uranium group are at 912,836 (weak), 239 and 232 cm<sup>-1</sup> for asymmetric-symmetric stretching, and for two