

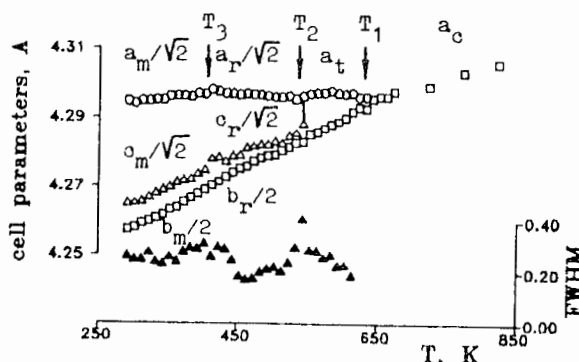
10-Physical and Chemical Properties of Materials in Relation to Structure (Superconductors, Fullerenes, etc)

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Evaporation of a toluene solution of C₆₀ 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 C₆₀ 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 BaPbO₃.

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_c 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_c superconductors we have examined precisely the temperature dependence of lattice constants in ceramic BaPbO₃ which was prepared using oxide synthesis technique. X-ray powder diffraction measurements were carried out on URD-63 and DRON-3 diffractometers (CuK_α 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 BaPbO₃ is cubic perovskite. As the temperature is lowered the results of thermal expansion measurements (see figure and table) indicate that BaPbO₃ 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 Pb²⁺-Pb⁴⁺ valence fluctuations might occur in slightly oxygen deficient BaPbO₃ samples. The structure of BaPbO₃ 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 ⁶)		
		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 C₆₀ COMPARISON BETWEEN THEORY AND EXPERIMENT

Oliver BECKERS, Pierre BECKER, Gilberte CHAMBAUD, Dominique BELLEMLILGA, Département Matériaux, Université de Marne la Vallée, 2 Allée Jean Renoir, 93160 Noisy le Grand, France

Genevieve LOUPIAS, Jacques MOSCOVICI, Laboratoire de Minéralogie et Cristallographie, Tour 16, 4 place Jussieu, 75252 Paris Cedex 5, France

The isotropic Compton profile of C₆₀ 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 C₆₀, or is it an effect related to the packing of C₆₀ units?

In order to answer this question, an ab initio calculation has been undertaken for an isolated C₆₀ 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 C₆₀ 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.H₃O)₂UO₂Cl₄ are triclinic with one formula per unit cell. The two cations (DCH18C6.H₃O)⁺ surround one anion UO₂Cl₄²⁻ 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_{4h}. The vibration modes of the uranium group are at 912,836 (weak), 239 and 232 cm⁻¹ for asymmetric-symmetric stretching, and for two