Evaporation of a toluene solution of C_{60} 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 $I > 3\sigma(I)$. R=0.08.

Each C_{60} 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.
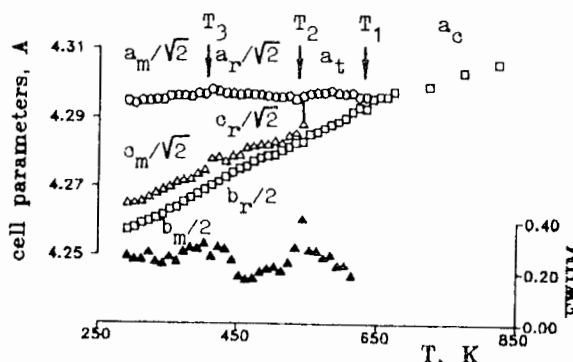
PS-10.02.13 STRUCTURAL PHASE TRANSFORMATIONS OF THE PROTOTYPIC CERAMIC SUPERCONDUCTOR BaPbO₃.

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, $2\theta=10\sim150°$, 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 $Pb^{2+}-Pb^{4+}$ 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	α (×10⁶)		
		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_{60} COMPARISON BETWEEN THEORY AND EXPERIMENT

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The isotropic Compton profile of C_{60} 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_{60}, or is it an effect related to the packing of C_{60} units?

In order to answer this question, an ab initio calculation has been undertaken for an isolated C_{60} unit, using the TURBOMOLE code, with a double zeta polarised 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_{60} 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.
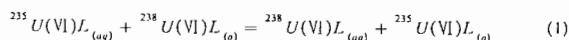
The isotope effects of isotopic exchange reactions between different molecules are directly related to the structure of these molecules. In recent years, many isotopic effects of uranium-crown ether systems were found. Further studies were carried out with single-crystal X-ray diffraction and infrared spectrometry. The experimental values obtained agreed with the quantitative estimates.

Crystals of $(DCH18C6.H_3O)_2UO_2Cl_4$ are triclinic with one formula per unit cell. The two cations $(DCH18C6.H_3O)^+$ surround one anion $UO_2Cl_4^{2-}$ 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

bending modes respectively. The asymmetric stretching of the U-Cl bond is at 262 cm^{-1}.

The isotopic exchange reaction for U(VI) extracted by crown ether can be written as:

$$^{235}U(VI)L_{(aq)} + {}^{238}U(VI)L_{(o)} = {}^{238}U(VI)L_{(aq)} + {}^{235}U(VI)L_{(o)} \qquad (1)$$

Quantum-mechanical treatment for isotope-exchange reactions (Bigeleisen and Mayer (1947). J. Chem. Phys. 15, 261.) shows that the reduced partition function (RPFR) calculates as:

$$f' = \Pi_i \frac{u_i}{2} sh\frac{u_i'}{2} / \frac{u_i'}{2} sh\frac{u_i}{2} \qquad (2)$$

Where

$$u_i = \frac{h v_i}{kT} \qquad (3)$$

The isotopic effect depends on the ratio α of RPFRs for the two compounds taking part in isotope exchange of U between organic and aqueous phases, i.e. α is the separation factor of a single stage of U isotope exchange. Computed values of α are 1.000746, 1.000688 and 1.000673 at 12°C, 25°C and 29°C respectively. The experimental values are 1.00010±0.0002 and 1.00012±0.0004 at 12°C and 29°C respectively. The single-stage factor α = 1.00066±0.00019 has been obtained by experimental measurement of extraction of U(VI) by DCH24C8 at 27°C. Experimental results basically agree with calculations.

In water, UO_2^{2+} exists as $UO_2^{2+}(5H_2O)$, in a coordination very different from the organic phase, and this contributes to the large isotope effect. Experiments indicate that extraction of UO_2Cl_4 and UCl_4 by DCH18C6 and DCH24C6 all have large isotopic effects.

PS-10.03.02 DESIGN OF LIGHT-SENSITIVE MATERIALS FROM MOLECULAR AND CRYSTAL STRUCTURES OF PHOTOTROPIC ORGANIC COMPOUNDS.

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Based on crystal-chemical studies of organic compounds with intra- (Aldoshin & Atovmyan (1984) Khim. Fyzika 3, 915 (Russian)) and intermolecular (id. et al. (1988). Izv. Akad. Nauk., Ser Khim. pp. 1312, 1319, 1773, 2301 and 2308; (1989) pp. 598, 602; (1990) p. 567 (Russian)) proton transfer, we have demonstrated the possibility of creating light-sensitive crystals, and of controlling this property by the specific organization of their molecular and crystal structure. Crystal-chemical factors favouring proton phototransfer for different classes of organic compounds have been evaluated by analysis of structural data and of results of quantum-chemical calculations on model compounds. The role of cooperative hydrogen bonding, with formation of linear polar chains, has been shown for intermolecular proton transfer. Light sensitivity in these crystals increases sharply with formation of hydrates where water molecules participate in chains of intermolecular hydrogen bonds, and where the dipole moment of water molecules coincides with that of the tautomeric molecules in the chains. The concept of crystal-chemical design of tautomeric crystalline systems with intermolecular proton phototransfer has been introduced, and possible structural modifications aiming at the improvement of photochemical properties have been proposed.

PS-10.03.03 STRUCTURAL STUDY OF INTERCALATION COMPOUND Fe_xTiS_2.

By Y. Kuroiwa*, M. Nishimura and Y.Noda, Faculty of Science, Chiba University, Yayoi, Chiba 263, Japan.

The transition metal dichalcogenides with layered structures are intercalated with various ions and molecules between chalcogen layers which are connected by weak Van der Waals interaction. These intercalation compounds are of interest because the physical and chemical properties are different from those of the host materials, and the intercalant atoms form two dimensional system. Among them, the iron metal intercalate Fe_xTiS_2 shows three magnetic ordered phases, which depend on the Fe concentration. When x less than 0.2, a spin-glass phase appears below $T_g \sim 40K$, while a ferromagnetic phase establishes at $x \geq 0.4$. On the other hand, in $0.2 \leq x \leq 0.4$, so called cluster-glass phase appears. Concerning the atomic structures of the intercalated Fe atoms, it is reported that the Fe metals are in octahedral sites between the TiS_2 layers and form the $2a \times 2a$ and $\sqrt{3}a \times \sqrt{3}a$ in-plane superlattice at the characteristic concentrations x=1/4 and 1/3 respectively.

We report the results of X-ray measurements on the atomic structure in the spin-glass phase. The diffuse scattering whose maxima are at the (1/2,0,1/2), (0,1/2,1/2), (1/2,1/2,1/2) and their equivalent positions were observed. However, the temperature dependence of these diffuse scattering was not observed even below T_g, as shown in Fig.1. The lattice parameters for a and c axes become smaller with decreasing temperature, and no discontinuous change was found at T_g, as shown in Fig.2. The Arrangements of Fe atoms was investigated by X-ray anomalous scattering at the Photon Factory of National Laboratory for High Energy Physics. The arrangements of Fe atoms which have hexagonal symmetry are discussed.
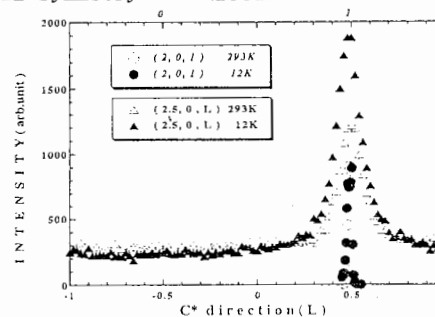

Fig.1. The temperature dependence of the profiles of diffuse scattering and Bragg reflection along c* direction.
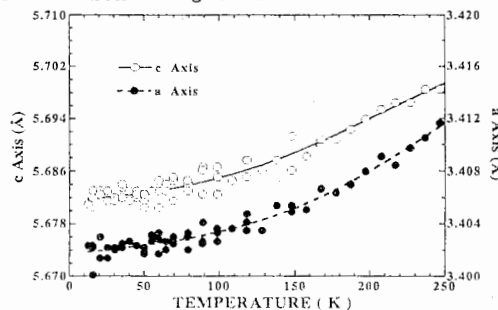

Fig.2. The temperature dependence of the lattice parameters for a and c axes.