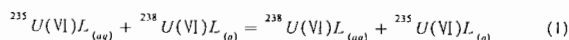


## 10-Physical and Chemical Properties of Materials in Relation to Structure (Superconductors, Fullerenes, etc)

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

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



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

$$f' = \prod \frac{u_i}{2} \frac{sh \frac{u_i}{2}}{sh \frac{u_i}{2}} \quad (2)$$

Where

$$u_i = \frac{hv_i}{kT} \quad (3)$$

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

In water,  $\text{UO}_2^{2+}$  exists as  $\text{UO}_2^{2+}(\text{5H}_2\text{O})$ , in a coordination very different from the organic phase, and this contributes to the large isotope effect. Experiments indicate that extraction of  $\text{UO}_2\text{Cl}_2$  and  $\text{UCl}_4$  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.** By S. Aldoshin, Institute of Chemical Physics (Chernogolovka), Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russia.

Based on crystal-chemical studies of organic compounds with intra- (Aldoshin & Atovmyan (1984) Khim. Fizika 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  $\text{Fe}_x\text{TiS}_2$ .** 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  $\text{Fe}_x\text{TiS}_2$  shows three magnetic ordered phases, which depend on the Fe concentration. When  $x$  less than 0.2, a spin-glass phase appears below  $T_g \sim 40\text{K}$ , 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  $\text{TiS}_2$  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.

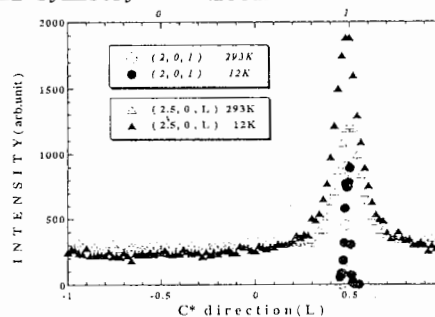


Fig.1. The temperature dependence of the profiles of diffuse scattering and Bragg reflection along  $c^*$  direction.

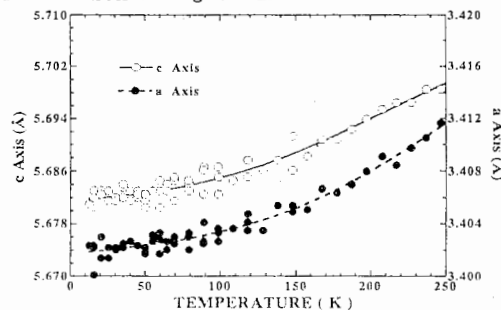


Fig.2. The temperature dependence of the lattice parameters for  $a$  and  $c$  axes.