

## 09-Engineering and Computer Simulation of Inorganic Crystal Structures

(Fe-S) ( S is an inorganic sulfur ) and (Fe-Sy) bonds, respectively. The  $k_{0,i}$ 's were allowed to dynamically fluctuate as a function of the clusters distortion.

The concept of fluctuating constant force was generalized to other atoms and could be used to predict the molecular structure of "small molecule" and mineral compounds, provided the topology of the structure was known. In the case of inorganic compounds the Lennard-Jones potential was replaced by Born-Mayer ( Born, M. and Mayer, J.E., Z. Phys. 75 1932, 1 ) or by Keating, P. N. (Phys. Rev. B2, 1966, 637 ) type potential. The contribution of electrostatic energy and Coulomb stress tensor which were omitted in the dynamic calculations were compensated by lattice energy (Evans, M., Ann. Phys., Leipzig, 64 (1921) 253; Bertaut, E.F., 1952, J. Phys. Rad. 13, 499-505 ).

Details of this method are described and results of two attempts of ab-initio structure determinations are also reported in this paper.

## PS-09.01.09 FLEXI-CRYSTALLOGRAPHY

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Nodal surfaces, defined by wave vectors in reciprocal space, equipotential surfaces, defined by point charges in real space, and periodic minimal surfaces, 'soap-film' elements lying smoothly across the asymmetric domains in given crystallographic symmetry groups, are exact mathematical objects which may be of physical significance and which can help with the visualisation of significant structure at a level above that of single atoms. They are two-dimensional manifolds, with local metrics different from the Euclidean metric of the planar sheets of orthodox crystallography, and are of use in the development of the flexi-crystallography of the 'soft matter' proposed by de Gennes and in crystal chemistry generally.

PS-09.01.10 CRYSTAL AND ELECTRONIC STRUCTURE OF  $\text{KF}\cdot 2\text{H}_2\text{O}$ . By A. Preisinger\*, M. Zottl, K. Mereiter, Ph. Dufek, K. Schwarz\* and P. Blaha, Technische Universität Wien, Austria. W. Paulus, CEN Saclay LLB, France.

Simple hydrates have been studied extensively in literature. We have chosen  $\text{KF}\cdot 2\text{H}_2\text{O}$  as a model system for a hydrate in an ionic solid in order to study the effects of hydrogen bonds. In this study we combine experiments and electronic structure calculations in order to investigate this system.

Single crystals were grown from solution and were investigated by X-ray and neutron diffraction. The crystal data are: space group  $\text{Pmc}2_1$  with  $Z=2$  and  $a=4.083(1)$ ,  $b=5.184(1)$ ,  $c=8.831(1)$  Å. Neutron refinement converged at  $R=0.020$  for 320 reflections.

Table 1. Positional and thermal parameters for  $\text{KF}\cdot 2\text{H}_2\text{O}$  from neutron diffraction data.

	$x/a$	$y/b$	$z/c$	$B_{eq}[\text{Å}^2]$
K	0.5000	0.3879(3)	0.0000	2.20(1)
F	0.0000	0.0969(2)	0.1093(2)	2.38(1)
O(1)	0.5000	0.2032(3)	0.7110(3)	2.76(1)
O(2)	0.0000	0.2918(3)	0.3969(3)	2.74(1)
H(1)	0.3127(3)	0.1003(3)	0.6804(3)	3.56(1)
H(2)	0.0000	0.2268(4)	0.2938(3)	3.58(1)
H(3)	0.0000	0.1414(4)	0.4616(3)	3.60(1)

The crystal structure consists of  $\text{K}^{(2+)}$  and  $\text{F}^{(2-)}$  octahedra. The water molecule with O(2), H(2) and H(3) lies in the (100)-plane and the two hydrogens point nearly towards the neighbouring  $\text{F}^-$  (Fig.1), while the oxygen of this water molecule has two  $\text{K}^+$  ions as nearest neighbours, where these four ions form a tetrahedron. The other water molecule has a similar coordination. The three types of distances K-F, K-O and hydrogen-bonded F-O are 2.72, 2.73-2.82, and 2.72-2.75Å, respectively.

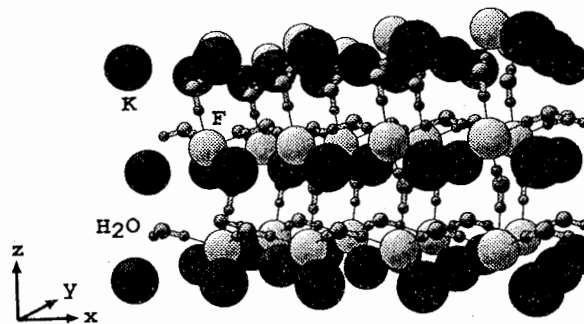


Fig.1 Crystal structure of  $\text{KF}\cdot 2\text{H}_2\text{O}$

In the theoretical study we determine the energy band structure by taking the structural data of the neutron experiments and perform full-potential linearized augmented plane wave (LAPW) calculations using the WIEN code (P. Blaha, K. Schwarz, P. Sorantin, S.B. Trickey, Computer Phys. Commun. 1990, 59, 399), where we treat exchange and correlation effects by the local density approximation. We obtain the density-of-states, which can be partly related to the corresponding MO diagram of a free water molecule by means of electron density plots. In order to study the polarization of the water molecule and its hydrogen bond, we calculate the density of a hypothetical reference system, in which we keep the water molecules in their positions as in the hydrate, but remove all  $\text{K}^+$  and  $\text{F}^-$  ions. The difference density between the true and the reference system indicates an increase of the lone pair densities due to a polarization by  $\text{K}^+$ , but a reduced density near the hydrogen atoms which is caused by the hydrogen bonding to  $\text{F}^-$ . The interaction with  $\text{K}^+$  is mostly electrostatic, while that with  $\text{F}^-$  has an additional covalent contribution.

## PS-09.01.11 DODAF SIMULATION OF ELECTRONIC STRUCTURE OF LOW SYMMETRY CRYSTALS DOPED WITH TRANSITION METAL IONS.

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In a contrast to the usual unrestricted Hartree-Fock (HF) method known as DODS, another variational "different orbitals for different angle functions" (DODAF) method is developed and used for calculations of electronic structure and spectra of transition metals in ionic crystals.