

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 K^{2+} and 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 F^- (Fig.1), while the oxygen of this water molecule has two 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.

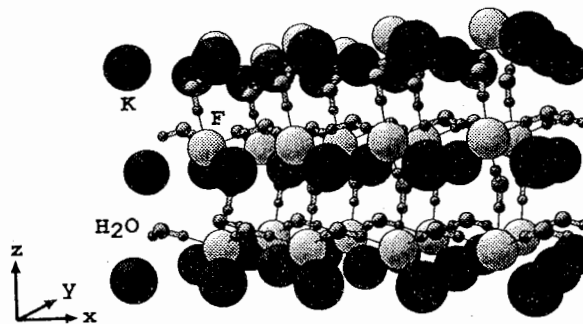


Fig.1 Crystal structure of $\text{KF}\cdot 2\text{H}_2\text{O}$

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 K^+ and 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 K^+ , but a reduced density near the hydrogen atoms which is caused by the hydrogen bonding to F^- . The interaction with K^+ is mostly electrostatic, while that with F^- has an additional covalent contribution.

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

By V. S. Goroshkoff and E. G. Noda, Department of Physics, Zaporozhye State University, Ukraine.

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.

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Angular parts of one-electron wave functions are simulated by linear combinations of spherical harmonics transformed on irreducible representations of point groups (solid or Cartesian harmonics). So each symmetrical association of electrons accompanies with the same radial orbital. Even use of one-determinant many-electron wave function permits to take into account a part of correlation energy.

Central ion orbitals are orthogonalized to ligand ones with the help of Lagrange multipliers by original procedure. In consequence, the contribution of ligand potential to self consistent field equations gets simplified. The expression for external potential field at the central d-metal ion was generated from Slater Type Orbitals of ligands. In order to simulate the environment of ligands in crystals a very simple physical model "ions in crystal" (E. Paschalis, A. Weiss, Theor. Chim. Acta, 1969, 13, 381) was used. This means that ligand is embedded in a hollow charged sphere with radius approximately equal to metal-ligand bond distance.

We have programmed DODAF formalism and applied it to several model systems such as Ni^{2+}/ZnO , Ni^{2+}/MgO , Cu^{2+}/CdO with satisfactory results. HF equations for transition metal ions were solved numerically (self consistency was reached up to 10^{-9}).

Some numerical aspects, especially the convergency properties of this method with respect to the number of ligands, their electronic structure and particular geometry, are discussed.

PS-09.01.12

SOME PRINCIPLES AND RESULTS OF HT-SUPERCONDUCTOR LIKE STRUCTURES DESIGN.

By S. F. Solodovnikov*. Russian Academy of Sciences, Siberian Branch, Institute of Inorganic Chemistry, Novosibirsk, Russia.

The crystal structures of cuprate superconductors and related compounds (more than 70 structure types) were analysed. The structures may be considered as sequences of plane square atomic nets of 9 types, 5 types of which being realized in HTSC structures. Based on the net approach to crystal chemistry and modelling of HTSC-related structures their maximum symmetry was shown to be within framework of 10 space groups: $I4/mmm$, $P4/mmm$, $P4/nmm$, $P4mm$, $Immm$, $Ammm$, $Bmmb$, $Bmm2$, $Pmmm$, and $Pnmb$. Proceeding from the building principles analysis of revealed HTSC structure types, empiric selection rules of the most probable structure models were formulated. Practically such structures contain no more than two different perovskite-like (involving copper-oxygen sheets) or additional (rock salt-, fluorite-type etc.) blocks with multiplicity for each of the blocks no more than three single sheets. Exceptions from this rule seem to be cuprates with only rock salt-type blocks which can include perovskite-like blocks with up to 6 copper layers, however, here again preparation of more than triple copper-layer compounds is rather complicated. Fluorite-like blocks in HTSC-related structures were assumed to be single because cuprates with a higher multiplicity of this block are not superconducting. It was also taken into account a rule of thumb that in mixed-layer compounds with different blocks of the same type (e. g. rock salt-type) their multiplicities may differ only by 1.

Using the formulated rules (some details for brevity omitted) the most probable models of HTSC-related structures were constructed. The total number of the models proved to be restricted to 73 variants (see Table), the biggest of which has 38 atomic nets in the unit cell corresponding to the "c" parameter value of 7.5 nm.

Table. Amounts of HTSC-like structures (N_i) vs net number (n) in unit cell

n	N_i			n	N_i		
	N_1	N_2	N_3		N_1	N_2	N_3
2	1	1	1	20	2	—	—
4	1	1	1	22	5	1	1
6	5	5	5	24	0	—	—
7	1	1	1	26	9	1	1
8	5	4	3	28	1	—	—
9	2	2	1	30	3	—	—
10	5	4	3	32	0	—	—
12	6	2	1	34	4	1	1
14	9	5	5	36	0	—	—
16	6	3	3	38	1	—	—
18	7	2	2	total	73	33	29

Notations: N_1 —the most probable models

N_2 —HTSC-related cuprates

N_3 —cuprate superconductors

PS-09.01.13 ENUMERATION AND IDENTIFICATION OF CRYSTAL-STRUCTURE TYPES BY A COMPUTER. By Masahiko HOSOYA* and Keiichiro TAKUSHI, Department of Physics, University of the Ryukyus, Japan

A computer program is presented to enumerate and identify crystal-structure types. If a chemical formula of contents in a primitive cell is given, the program enumerates all the possible structures for every space group, each of which is specified by the detailed arrangement of the atoms in the cell. Conversely, if a way of arrangement of the atoms is given, the legal name of the structure can be obtained uniquely in the present nomenclature. So any structure can be identified with another according to whether their names are reduced to the same legal one or not.

Example

Consider an intermediate step of the structure analysis of KH_2PO_4 . If the space group and the number of molecules in the primitive cell have been obtained, the program can answer all the possible types as far as the symmetry concerns. In the present case, the space group is $I42d(122)$, and the number of molecules in the cell is 2. First, the program requires the input of a genus. Input

A2B2C4D8

into the blank of a genus. It is given as follows.

$KH_2PO_4 \rightarrow K_2H_4P_2O_8 \rightarrow K_2P_2H_4O_8 \rightarrow A_2B_2C_4D_8$