

Properties of »Perfect« and »Imperfect« Solid State Materials

Inorganic solid state chemistry has been an innovative field of research for quite some time. The development, modification, and characterization of inorganic solids are, more and more, providing new materials for diverse areas of applications. Solid state chemistry covers an infinite number of aspects, not only the goal of obtaining new crystalline solids with a perfect structure, but also solids with highly distorted structures that are very reactive. In the case of very ordered solids, interest lies in structure motifs determined by single crystal analysis and the corresponding physical properties of this solid. The reactivity of these ordered solids is low, however »imperfect« solids, which have a degree of disorder, are often used in chemical reactions as reactive components, for example for applications in the field of heterogeneous catalysis.

The aesthetics of single crystal inorganic solids

Our studies on selected classes of compounds, such as metal hydrogen chalcogenates, microporous phosphate fluorides, and halogen metallates, have shown that structure motifs in inorganic solids are not only interesting for their material properties, but also have an aesthetic quality to them. Special materials properties observed have been protonic conductivity, ferroelectricity, ion exchange, and in particular magnetic properties.

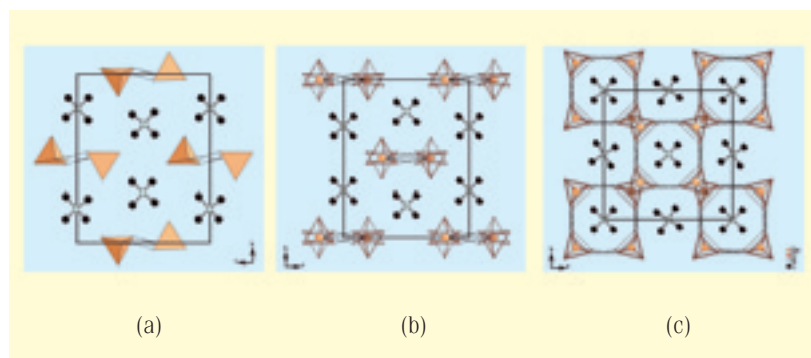


Fig. 1
(NMe₄)HSeO₄ structure before and after two phase transitions from a) the ordered structure over b) a slightly disordered dimeric structure to c) a strongly disordered »superprotonic« phase.

Acid oxosalts and hydrogen bond systems

In the last decade, we have synthesized and structurally characterized more than 80 new acid oxosalts to understand their hydrogen bonding and their principles. New phase transitions lead to phases with high protonic conductivity. The main structural aspects of acid oxosalts

Festkörperchemie

Schon lange hat sich die anorganische Festkörperchemie als innovatives Forschungsgebiet etabliert. Entwicklung, Modifizierung und Charakterisierung anorganischer Feststoffe münden immer häufiger in die Bereitstellung neuer Materialien für verschiedenste Anwendungsgebiete. Dabei umfasst die Festkörperchemie eine Vielzahl von Aspekten, ihr Ziel besteht sowohl in der Darstellung neuer kristalliner Festkörper mit perfekter Struktur als auch solcher mit hochgradig gestörten Strukturen, die sehr reaktiv sind. Im

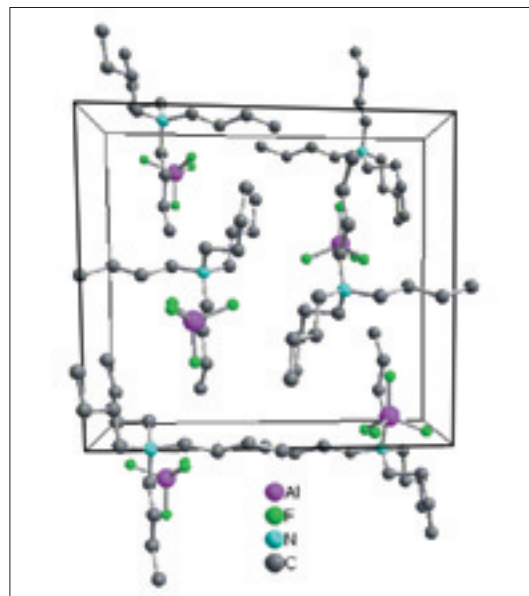


Fig. 2
Crystal structure of [N(C₄H₉)₄](AlF₄).

have been reviewed [1]. The following groups of acid oxosalts have been investigated systematically:

- Alkali metal hydrogen chalcogenates (sulfates and selenates)
- Bivalent metal hydrogen chalcogenates
- Alkali metal hydrogen chalcogenate phosphates
- Mono and bivalent metal hydrogen phosphites
- Metal hydrogen fluorophosphates (including salts with N donor organic cations).

The hydrogen bonding of acid oxosalts depends on the H/XO₄ ratio. Low H/XO₄ ratios, such as 0.5, yield dimeric units of [H(XO₄)₂] typically connected by a bridging H atom. In some M^IH XO₄ and M^{II}(HXO₄)₂ salts, closed dimers with two bridging H atoms are present, whereas other structures contain infinite zigzag (LiHSeO₄) or screw-like chains (Mn(HSeO₄)₂). As the H/XO₄ ratio increases, the hydrogen bond systems become two or three dimensional because of the larger number of bridging H atoms. Flat or wave-like layers of H-bonded XO₄ units are present in the structures with the H/XO₄ ratio of 1.33 for M^I₂(H₂SO₄)₂(H₂SO₄) and 1.5 for M^I(H₂XO₄)(H₂XO₄), respectively. The main feature of the metal hydrogenfluorophosphate structures is the nonparticipation of the fluorine atoms in the hydrogen bonding system.

Fälle der Festkörper hoher Ordnung besteht ein Interesse in ihren mittels Einkristallanalyse ermittelten Strukturmotiven und den korrespondierenden physikalischen Eigenschaften dieser Festkörper. Während die Reaktivität dieser »perfekten« Feststoffe mit geordneter Struktur relativ gering ist, werden dagegen »imperfekte« Festkörper, die ein bestimmtes Maß an Unordnung aufweisen, häufig als reaktive Komponenten in chemischen Reaktionen genutzt, beispielsweise für Anwendungen in der heterogenen Katalyse.

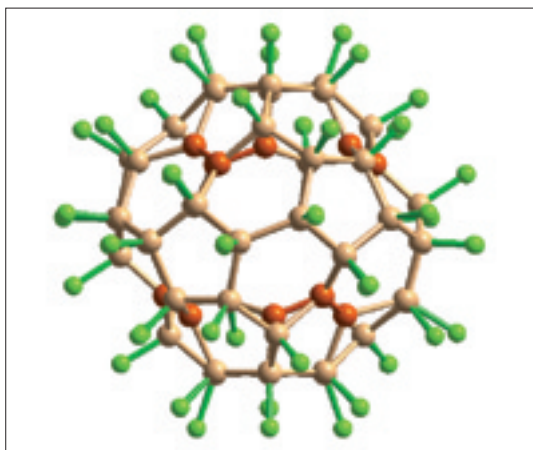


Fig. 3
Structure of the D_3 isomer of the indented fluorofullerene, $C_{60}F_{48}$.

Recently, phase transitions in $(NMe_4)HSeO_4$ at 354 and 371 K were investigated by X-ray and neutron diffraction (Fig. 1). The first phase transition leads to slight disorder in the monoclinic structure containing closed dimeric $(HSeO_4)_2$ units. The second one results in the formation of a »superprotonic« tetragonal phase with a strong disorder of the $HSeO_4$ groups combined into tetramers connected by disordered hydrogen bonds [2].

Halogen metallates and halogenated fullerenes

Halogenometallates and fullerenes have been of scientific interest, because of their unusual structures, coordinations, and bonding properties. Therefore, the chemical structures of these innovative materials with useful properties is being developed.

Fluoroaluminates

According to textbooks, aluminum fluorides and their complex salts, the fluoroaluminates, occur as inorganic polymers, consisting of corner shared Al-F octahedra forming chains and layers. Like AlF_3 , the three dimensional frameworks have a great variety of connectivity.

Under conditions that prevent fluorine from acting as a bridging atom by bulky substituents, discrete fluoroaluminate species can be obtained. The above structures of fluoroaluminates critically depend on specific ratios of cation and metal-metal distances. Interestingly enough, the introduction of larger cations into the crystal establishes a stability criterion and yields discrete structures. Thus, large cations, i.e.,

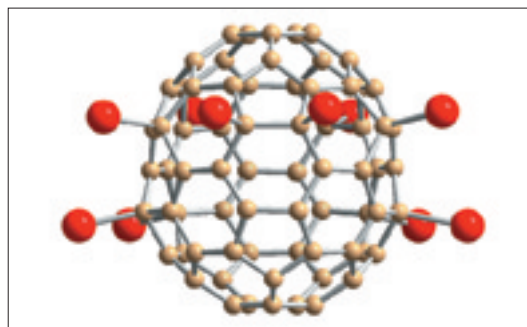


Fig. 4
Molecular structure of the first halogenated higher fullerene, $C_{70}Br_{10}$.

$N(CH_3)_4^+$, force the formation of isolated non-octahedral Al-F species. A compound with tetrahedral AlF_4^- ions were thus prepared and their single crystal structures were recently reported. The structure of this ion was determined with IR and Raman spectroscopy and with solid state ^{27}Al MAS NMR. The T_d X-ray structure for the tetrafluoroaluminate has been solved with $N(C_4H_9)_4^+$ as the counterion. (Fig. 2)

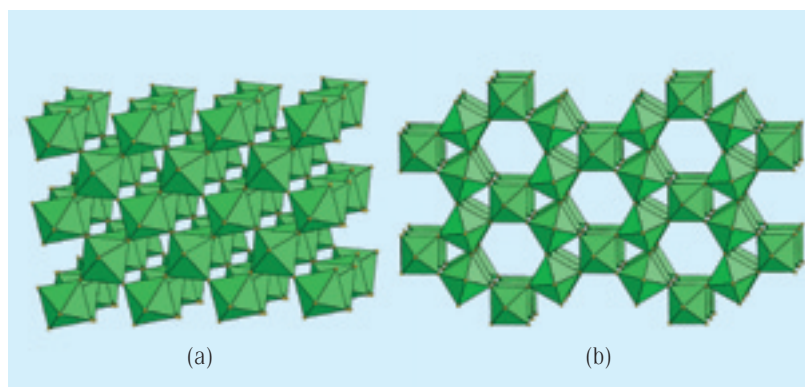


Fig. 5
Connectivities of AlF_6 -octahedra displayed for a) $\alpha-AlF_3$ and b) $\beta-AlF_3$

The novel pentafluoroaluminate ion, AlF_5^{2-} , was synthesized under non-aqueous conditions using a tetrafluoroaluminate salt and tetramethylammonium fluoride, which is a very strong Lewis base. Single crystals could not be obtained due to very poor compound solubility in apolar solvents, yet the structure has been postulated based on IR- and Raman measurements and ab-initio calculations. These measurements and calculations can be assigned to a trigonal bipyramide geometry with D_{3h} symmetry [3]. The ^{27}Al -MAS spectrum confirms the highly symmetrical structure of the ion with an unusually small signal line width of only about 127 Hz.

Halogenated fullerenes

The chemistry of fullerenes has developed rapidly in the last 10–15 years since their discovery. Many adducts of C_{60} and C_{70} , the two most stable fullerenes, have been prepared and structurally characterized

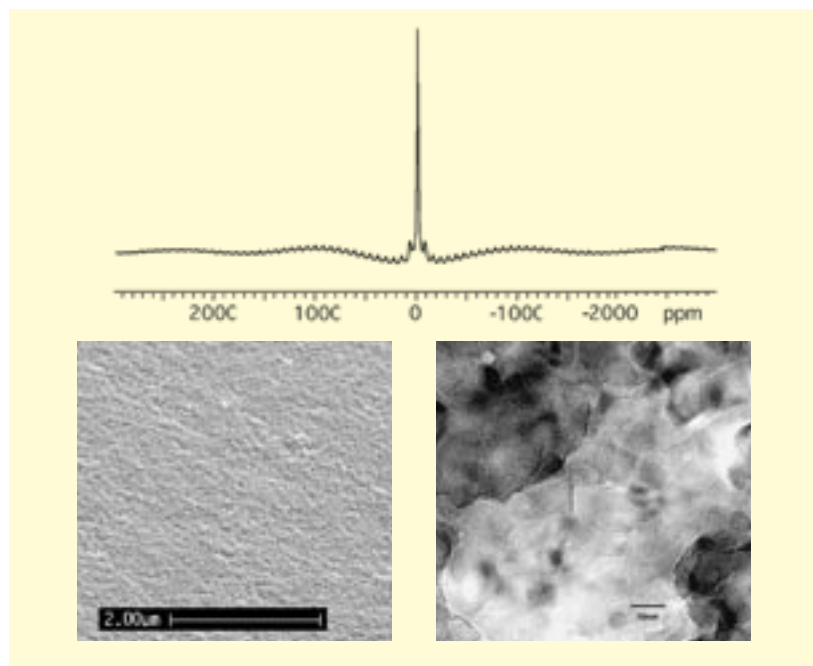
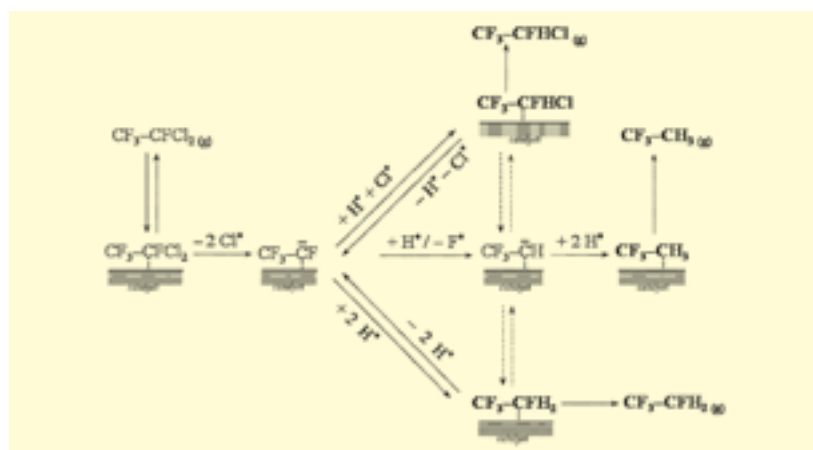


Fig. 6
The MAS-NMR spectra (upper) and SEM (lower left) and TEM micrographs of amorphous AlF_3 (lower right).

within a joint project between Humboldt-Universität zu Berlin and Moscow Lomonosov-University. Weak charge-transfer interactions are responsible for the formation of complexes, such as $\text{C}_{60}\cdot 3\text{TiCl}_4$, $\text{C}_{70}\cdot 2\text{TiCl}_4$, $\text{C}_{60}\cdot 2(1,2,4\text{-C}_6\text{H}_3\text{Cl}_3)$, and $\text{C}_{70}\cdot 2(1,2,4\text{-C}_6\text{H}_3\text{Cl}_3)$.

The molecular structures of fullerene fluorides and bromides have been determined. These halogenated fullerenes are important intermediates for further derivatization of fullerene. The $\text{C}_{60}\text{F}_{18}$ molecule only has one stable isomer, in which all 18 F atoms are

Fig. 7
Reaction path for the hydrodechlorination of CF_3CFCl_2 .



attached to one hemisphere of the C_{60} cage. The fluorinated hemisphere contains a flattened region with an aromatic six ring. A careful single crystal X-ray diffraction analysis of $\text{C}_{60}\text{F}_{48}$ revealed the presence of two very similar isomers in the same crystal [4]. Each isomer has six isolated C-C double bonds (Fig. 3). Three fullerene bromides, C_{60}Br_6 , C_{60}Br_8 , and $\text{C}_{60}\text{Br}_{24}$, were obtained in high yield by bromination of C_{60} in different solvents. The crystal and molecular structures were determined for the adducts of all three bromides with either solvent or Br_2 . The first crystal structure of the C_{70} bromide, $\text{C}_{70}\text{Br}_{10}$, determined has a very special arrangement of 10 Br atoms in the form of a belt in the equatorial region of the C_{70} cage (Fig. 4) [5].

Highly distorted, reactive solids for heterogeneous catalysis

Metal fluorides as heterogeneous catalysts

Metal fluorides, in most cases Lewis acids with different acidities, are known as effective heterogeneous catalysts in, e.g., the production of CFC alternatives, HFCs. In particular, modifications of aluminum fluoride, e.g., the meta-stable $\beta\text{-AlF}_3$, are convenient solid acids in similar gas phase reactions. The $\beta\text{-AlF}_3$ with a HTB-type structure (Fig. 5) and corner-shared Al-F octahedra consists of hexagonal channels with a more accessible surface.

Catalytic activity largely depends on the surface area of the solid catalyst. Large surface metal oxides syntheses, such as sol-gel and supercritical routes, are well-known and state of the art, however, no such synthetic methodologies exist for metal fluorides. Because of their high lattice energy, these solids tend to form regular crystalline structures. One breakthrough was our discovery of a method to obtain amorphous high surface area metal fluorides by an unconventional two-step non-aqueous route [6].

Fluorination under mild conditions of the metal alkoxides starting materials results in the formation of amorphous fluorides with unusual properties. AlF_3 , one of the most important representatives of the metal fluorides, has a surface area of about $200\text{ m}^2/\text{g}$ and exhibits outstanding catalytic properties in dimerization and isomerization reactions.

To understand the structural properties of amorphous AlF_3 , the solid was studied with IR, Raman, and ^{27}Al MAS NMR. The chemical shift of -13.8 ppm in the MAS NMR spectrum indicates an octahedral surrounding around the Al sites in the polymorphous solid with some co-ordinatively unsaturated Al-F species.

In addition, SEM micrographs show the AlF_3 porous surface of agglomerates of irregular size; lattice planes of regions are seen under the strong magnification of TEM. These regions are, however, too small to be detected by XRD. Principally, this »soft chemistry« method produces noncrystalline, highly distorted fluorides with unusually high surface areas. (Fig. 6)

Solid acids for acylation reactions and solid bases for the Michael addition

The use of classical acylation catalysts, such as inorganic mineral acids or AlCl_3 , presents serious environmental problems and urgently requires replacement. Solid acid catalysts offer an environmentally friendly and easier to handle alternative to the liquid acids used in the past. Surface modified ZrO_2 and TiO_2 are very strong solid acid, sometimes even stronger than zeolites and have been intensively studied in the last few years. We have prepared modified sulfated zirconia catalysts with different methods of solid state synthesis with cryogel, xerogels, or aerogels. The properties of these catalysts are then characterized with surface determination, acidity, catalytic, and thermal measurements. Phases have been obtained and patented [7], which are catalytically superior to zeolites and could replace the benzylation catalysts.

Using this knowledge of zirconia preparation, we have expanded our research to include the synthesis of base catalysts containing zirconia. The amphoteric oxide support is prepared similarly to that described above, but modified with agents to produce basic sites on the oxide's surface. These catalysts are characterized with a variety of methods including basicity measurements and tested in the Michael addition.

Temperature Programmed Isotope Exchange (TPIE)

The influence of the structural and surface properties on heterogeneous exchange and oxidation processes can be studied with temperature programmed isotope exchange (TPIE) on potential redox catalysts [8]. The solid oxide is reacted with a mixture of $^{18}\text{O}_2$ and a reagent, such as $^{16}\text{O}_2$, C_3H_8 , or CH_4 in Quartz reactor. The reactor is heated at a constant rate and the composition of the gas phase is analyzed with an online coupled mass spectrometer, to follow the progress of ^{18}O -IE and oxidation reactions.

Identical studies can be done on numerous oxide system for various reactions, to understand the mechanism of heterogeneously catalyzed oxidation reactions. Our current research concentrates on the study of vanadium doped ZrO_2 phases. This research is being carried out in a joint Special Form of DFG-

Funding-project. The catalysts are synthesized with different methods, i.e., coprecipitation, sol-gel, cryogel, aerogel, characterized with physico-chemical measurements, and tested in partial oxidation reactions with TPIE.

TPIE, however, can also be used to characterize other systems. One system, for example, is TPIE experiments with D_2 to obtain important mechanistic information on the dehydrochlorination of CF_3CFCl_2 , which seems to involve the formation of surface carbenes.

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