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The hydride fluoride crystal structure database, HFD

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Abstract

HFD is a new data base containing crystal structure information on more than one thousand metal hydrides and fluorides. It includes space group, cell parameters, standardized atom positions, site occupancies and references. The compilation is critical as only refined crystal structures are considered and the data are checked for internal consistency. It is comprehensive as structural information is extracted from all major scientific journals, and it is continuously updated. HFD can be searched according to various criteria such as symmetry, chemical elements, composition etc. The primary motivation for creating HFD was to predict new metal hydrides and to study their structural analogies with metal fluorides. However, HFD can also be used for other applications such as the simulation of diffraction patterns and the drawing of crystal structures.

Keywords: Data base; Crystal structures; Fluorides; Structure data

1. Introduction

During our work on ternary alkaline earth hydrides [1] we have noticed pronounced structural analogies between this new class of saltlike compounds and the ternary metal fluorides. All ternary alkaline earth hydrides known so far crystallize with structures also found among ternary fluorides. This analogy was very useful for the characterization of new metal hydrides such as orthorhombic $Ba_6Mg_7D_{26}$ [1], which was found to be closely related to monoclinic $Ba_6Zn_7F_{26}$ [2]. In view of the large number of ternary fluoride structures known (more than one thousand) compared to the small number of ternary hydride/deuteride structures characterized (about two hundred), we decided to look at this analogy in a more systematic way in order to use it as a tool for the search of new metal hydrides. This motivated us to create *the Hydride Fluoride Crystal Structure Database, HFD*, presented in this paper.

2. Selection criteria

The crystal structures included in HFD have been selected according to the following criteria:

- The hydrides must contain hydrogen atoms bonded to metal atoms. Compounds containing hydrogen atoms bonded to non-metal atoms only, such as hydroxides, hydrocarbons, ammonium compounds, compounds containing H_2O, NH_3, PH_3 etc. are not included.
- The fluorides must contain fluorine atoms bonded to metal atoms. A few exceptions have been made by including compounds containing $[SF_3]^+$, $[NF_4]^+$, $[PF_6]^-$ ions, the structures of CF_4 and ClF_3 and a few Xe fluoride structures.
- The structure models must be complete, i.e. include space group, cell parameters and refined atom positions for all atoms, including hydrogen. For hydrides this means that neutron diffraction data on deuterated samples should generally be available. Hydride structures characterized by X-ray diffraction only are not included, unless their precision is sufficient. This favorable situation may occur for single crystal data collected on hydrides containing light metals only.

3. Creation and content of data base

Before entering the structure data into HFD, they were subjected to the following checking procedure:

1. The data were standardized by using a program that combines the features of STRUCTURE TIDY [3] and MISSYM [4]. The former program transforms non-standard space-group settings into standard ones and produces a set of so-called *standardized* atomic coordinates which are unique for each structure type, i.e. corresponding atomic coordinates in two isostructural

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compounds have identical or similar values. This procedure allows one to recognize isotypic structures more easily. The latter program checks for the presence of additional symmetry or pseudo-symmetry elements which are not described by the space group. The entries showing such features were flagged with an asterisk in the space-group record **SPCG**, and the symmetries found were stated explicitly in records labeled **MISS** (see below).

2. The standardized data were checked for internal consistency by testing the presence of abnormally short distances. Among the over thousand entries checked so far, six misprints of atomic coordinates or cell parameters were detected, and two cases were found which showed a mismatch between unit cell setting and set of atomic coordinates. The corrections made were documented by a **RMRK** record (see below).

The selected structure data were then entered into several direct access files and tables. Each data set consists of various records which were identified by a four-letter symbol. Their information content can be summarized as follows:

TYPE structure type, data base entry number
COMP compound formula, number of formula units per cell, standardization parameter Γ, center of gravity CG (for details see [3])
AUTH names of authors
JRNL reference of publication
TITL title of publication
CELL cell parameters (without standard deviations)
SPCG * mark for additional symmetry elements detected during standardization (optional), space-group number, space-group symbol, Wyckoff sequence (the complete sequence of the Wyckoff positions as they appear in the standardized structure data including the number of times each Wyckoff position is occupied)
PCOD Pearson code [5], indicating crystal system, Bravais lattice type and number of atoms/cell (negative numbers following this code indicate the number of missing atoms/unit cell in case of partially occupied sites); number of atoms of each type per cell
DEFI (optional) definition of atom sites with mixed occupancy
ATOM atom label, fractional atomic coordinates (without standard deviations), occupancy (optional), site multiplicity, Wyckoff symbol, atom identifier as given in the original literature
STAN (optional) remarks concerning the standardization procedure (e.g. shift of origin, transformation of axes, etc.)
RMRK (optional) general remarks, e.g. concerning the diffraction method used (SC = single crystal, P = powder, X = X-rays, N = neutrons), experimental conditions (temperature, pressure), crystal quality (twinning), correction of misprints or other errors detected during standardization etc.
MISS (optional) remarks containing the symmetry elements in a structure, only if additional symmetry was detected by MISSYM
OTHR remarks preceding a second standardization with similar standardization parameters (when applicable)

An example that illustrates the information content of HFD is shown in Fig. 1. The list shows the data stored for the ternary fluoride β-$RbAlF_4$ (entry no. 479). Its structure has body-centered tetragonal symmetry and contains 120 atoms/cell. The atoms are listed in the order of general to special Wykoff sites and are sorted for each site according to increasing *x, y, z* coordinates, regardless of the atom type. The atom labels are displaced sidewise according to the compound formula in order to allow isostructural compounds to be recognized more easily. The latter two features can be suppressed. Since the atoms were renumbered by the standardization procedure, the original atom identifiers are given at the end of each **ATOM** record. The asterisk in the **SPCG** record indicates that additional symmetry was detected (see **MISS** records). The **STAN** record states that the atomic coordinates were shifted by the vector 0, 1/2, 1/4 during standardization. The structure was refined on single-crystal X-ray data (Molybdenum radiation).

HFD is updated continuously. At present (October 1996), it contains 1063 entries, of which 787 concern fluorides, 207 deuterides and 11 hydrides. The remaining ones concern oxides, oxofluorides, chlorofluorides, chlorohydrides, sulfates, silicates etc. which were included because they denote structure types. 78 entries exhibit additional symmetry elements.

4. Data retrieval and use

The data retrieval program allows users to search for compounds or groups of compounds by the following criteria or combinations thereof:

- database entry number
- compound or structure type formula (or part of formula)
- number of elements in a compound
- types of elements
- Pearson code or range of Pearson codes
- Wyckoff sequence (complete or partial)
- cell dimensions (exact values or range of cell parameters or parameter ratios)

```
TYPE   Rb Al F4  beta                                              entry    479
COMP   Rb Al F4  beta                                      Z=20    3.7991 0.3209
AUTH   Fourquet J.L., Plet F., de Pape R.
JRNL   Acta Crystallographica B36 (1980) 1997-2000
TITL   RbAlF4: Structure of its beta Metastable Form and Description of
TITL   the Mechanism of its Irreversible and Topotactic Phase Transition
CELL         11.6660 11.6660 12.5510    90.      90.      90.
SPCG*  (120) I -4 c 2   - i6 f e d a
PCOD   tI120           Rb 20.    Al 20.    F  80.
ATOM      F1      .00110 .15550 .24850       16(i)                        1
ATOM      F2      .06670 .35810 .24880       16(i)                        2
ATOM     Rb1      .15960 .15850 .06190       16(i)                        2
ATOM      F3      .20610 .42230 .11150       16(i)                        3
ATOM      F4      .41990 .21110 .11000       16(i)                        4
ATOM     Al1      .42370 .20740 .24930       16(i)                        2
ATOM      F5      0      0      .11210       8(f)                         6
ATOM      F6      .28160 .28160 1/4          8(e)                         5
ATOM     Rb2      0      1/2    0           4(d)                         1
ATOM     Al2      0      0      1/4         4(a)                         1
STAN   Origin  0 1/2 3/4
RMRK   SC X(Mo)
MISS The Structure implies the following Symmetry Elements ( * = new)
MISS * [ 1 1 0]  Perpendicular Mirror Plane through 0.000 0.000 0.000
MISS * [ 0 0 1]  Fourfold Axis through 0.000 -0.500 0.000
MISS * [ 1 -1 0] Perpendicular Mirror Plane through 0.500 -0.500 0.000
MISS   [ 1 0 0]  Perpendicular Glide Plane through 0.000 0.000 0.000
MISS             Glide = 0.000 0.000 0.500
MISS   [ 0 1 0]  Perpendicular Glide Plane through 0.000 0.250 0.000
MISS             Glide = -0.500 0.000 0.000
MISS * Inversion Center at -0.250 0.250 -0.002
```

Fig. 1. Crystal structure data for β-RbAlF4 (entry no. 479) as stored in HFD; for a description see text.

- stoichiometry (different formats)
- authors (complete name or part of name)
- year(s) of publication

The results can be directed to screen or file as short or long listings. A separate program produces cross-reference tables ordered by space group, Pearson code, stoichiometry, compound formula, names of authors and entry numbers. An example of such a table is shown in Fig. 2. It gives a partial list of hydrides and fluorides that crystallize

S P A C E G R O U P - T A B L E

Space group	Wyckoff sequence	Pearson code		Compound formula	Type formula	Cell params
(198) P 21 3	- b a3	cP24	597	Sn2 F3 Cl	Sn2 F3 Cl	7.84
(198) P 21 3	- b a4	cP28	203	Yb Mg Ni D4	Ca Mg Ni D4	6.71
(198) P 21 3	- b a4	cP28	158	Ca Mg Ni D4	Ca Mg Ni D4	6.73
(198) P 21 3	- b a4	cP28	202	Sr Mg Ni D4	Ca Mg Ni D4	6.89
(198) P 21 3	- b5 a4	cP76	1002	K2 Mg2 Be3 F12	K2 Mg2 S3 O12	9.87
(198) P 21 3	- b5 a4	cP76	768	K2 Mg2 S3 O12	K2 Mg2 S3 O12	9.91
(198) P 21 3	- b5 a4	cP76	769	K2 Zn2 B3 F12	K2 Mg2 S3 O12	9.93
(198) P 21 3	- b5 a4	cP76	1003	Rb2 Cd2 Be3 F12	K2 Mg2 S3 O12	10.38
(198) P 21 3	- b5 a4	cP76	1004	Cs2 Ca2 Be3 F12	K2 Mg2 S3 O12	10.67
(199) I 21 3	- c2 b a3	cI84	599	Na2 Ca3 Al2 F14	Na2 Ca3 Al2 F14	10.25
(204) I m -3	- g2 e c a	cI70-30.00	199	Na4 Ba.84 Fe3.16 F	Na4 Ba.84 Fe3.16	8.07
(204) I m -3	- h g3 f e d a	cI162	833	Yb19 Mg8 D54	Yb19 Mg8 D54	12.06
(205) P a -3	- c a	cP12	780	Pd F2	Pd F2 HP	5.32
(205) P a -3	- c a	cP12	249	Cd Pd F4	Pd F2 HP	5.40
(206) I a -3	- e b a	cI64	93	Ag Sb F6	K Sb F6 II	9.85
(206) I a -3	- e b a	cI64	534	K Bi F6	K Sb F6 II	10.34
(206) I a -3	- e5 d2 c b a	cI320	369	Na4 Ba Cu3 F12	Na4 Ba Cu3 F12	16.15
(215) P -4 3 m	- i e2 a	cP21	21	Hf B4 H16	Hf B4 H16	5.82
(215) P -4 3 m	- h f e3 d	cP33-3.00	837	Yb4 Mg4 Co3 D19	Ca4 Mg4 Fe3 D22	6.65
(215) P -4 3 m	- h f e3 d	cP33	161	Yb4 Mg4 Fe3 D22	Ca4 Mg4 Fe3 D22	6.68
(215) P -4 3 m	- h f e3 d	cP33-3.00	836	Ca4 Mg4 Co3 D19	Ca4 Mg4 Fe3 D22	6.68
(215) P -4 3 m	- h f e3 d	cP33	160	Ca4 Mg4 Fe3 D22	Ca4 Mg4 Fe3 D22	6.70
(216) F -4 3 m	- i3 h6 f e3 c	cF652-250.56	457	Y.95 Ni2 D2.6	Y.95 Ni2 D2.6	15.11

Fig. 2. Space-group table for cubic hydride/deuteride and fluoride structures (space groups 198–216) as generated from HFD; for a description see text.

with cubic symmetry (space groups 198–216) by indicating the space-group number and symbol, the Wyckoff sequence, the Pearson code, the compound formula, the structure type and the cell parameter. Additional features of HFD are the possibility of computing interatomic distances and to create input files for application programs such as

FULLPROF (powder pattern calculation) [6]

LAZY PULVERIX (intensity calculation of powder patterns) [7]

POWDERCELL 1.5 (powder pattern calculation and structure drawing) [8]

POLIEDRI (structure drawing) [9]

VIEW (structure drawing) [10]

XTAL (structure drawing, calculation of interatomic distances and angles) [11]

Examples for the use of HFD in conjunction with FULLPROF and POLIEDRI are given in Fig. 3, which shows the atom arrangement and a calculated neutron powder diffraction pattern of the ternary deuteride Mg_2FeD_6 (entry no. 57).

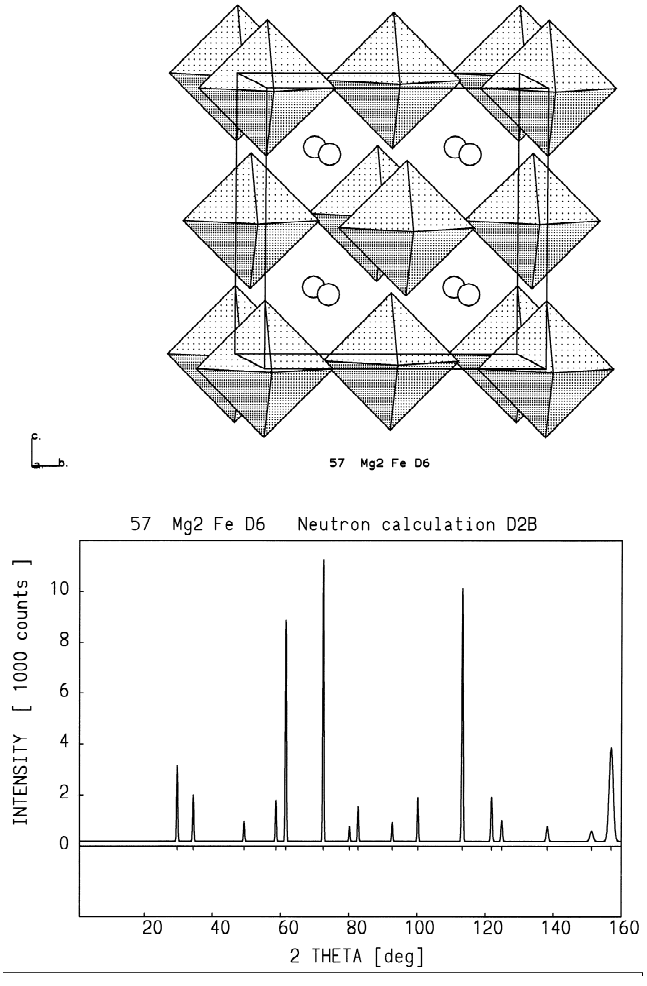

Fig. 3. Crystal structure (top; circles=Mg atoms; octahedra=FeD_6 groups; program POLIEDRI) and calculated neutron powder diffraction pattern (bottom; program FULLPROF) of cubic Mg_2FeD_6 as derived from the data stored in HFD.

5. Comparison with other crystal structure data bases

Major databases containing structural information on inorganic compounds are Pearson's Handbook and Atlas of Crystal Structure Types [5], ICSD [12] and TYPIX [13]. Pearson gives a comprehensive compilation of crystal structure data and crystal structure types for intermetallic compounds as they appeared in the literature up to 1991. They include hydrides but no fluorides. The data are not standardized and do not appear to have been checked for internal consistency. ICSD covers all inorganic compounds, including hydrides and fluorides, and lists all refinements (i.e. often more than one per compound). The compilation is critical and comprehensive, but the data are not standardized. TYPIX contains standardized data on crystal structure types for intermetallic compounds, including hydrides. The compilation is critical and comprehensive, but does not cover fluorides and does not list structure data for all representatives of a given series of isostructural compounds. Compared to all these databases, HFD is unique as it contains a critical and comprehensive up-to-date compilation of standardized structure data of all known metal hydrides (deuterides) and metal fluorides, i.e. also those of an isostructural series which usually change significantly from one representative to another.

6. Hardware requirements

The programs for this database were written in Fortran77 for an IBM compatible PC. A 386 processor and about 8 Mb disk space are required for optimal use of these programs and data files.

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