# $Y_2HfS_5$ with Ordered $U_3Se_5$ Type Structure and Related Compounds

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$Y_2HfS_5$ crystallizes with space group *Pnma*, $a=11\cdot4585$ (3), $b=7\cdot7215$ (3), $c=7\cdot2207$ (2) Å. Its structure was determined from three-dimensional single-crystal X-ray counter data and refined with ellipsoidal thermal parameters to a conventional $R$ of $0\cdot072$ for 1082 reflections. It corresponds to that of $U_3Se_5$ with Y and Hf substituting for U in an ordered manner. The Y and Hf atoms are coordinated to eight and seven S atoms, respectively. Four independent S atoms are four or five coordinated by the metal atoms. The HfS polyhedra share edges with each other, thus forming a one dimensionally infinite $[HfS_3]^{6-}$ polyanion. The new compounds $La_2ThS_5$ and $La_2ThSe_5$ also crystallize with this structure, which derives from the $Rh_5Ge_3$ antitype structure by small atomic displacements and a doubling of the *b* axis.

## Introduction

Recently we reported on the preparation of a series of compounds with general composition $Ln_2TX_5$ where Ln = a rare-earth element, T = Zr or Hf, and X = S or Se (Donohue & Jeitschko, 1974). These compounds are black and semiconducting and crystallize with an orthorhombic unit cell. In the present paper we establish that they crystallize with an ordered version of the $U_3Se_5$ type structure which in turn can be regarded as a distorted $Rh_5Ge_3$ antitype structure. Isostructural $La_2ThS_5$ and $La_2ThSe_5$ are reported for the first time.

## Crystal structure of $Y_2HfS_5$

*Experimental*

Single crystals of $Y_2HfS_5$ were grown from the elemental components in evacuated silica tubes by a transport reaction with iodine, as previously described (Donohue & Jeitschko, 1974). They were examined in a Buerger precession camera with Mo $K\alpha$ radiation. Lattice constants were obtained through least-squares refinement of Guinier–Hägg powder data with high-purity KCl ($a=6\cdot2931$ Å) as standard (Table 1). Intensity data were collected from a prismatic crystal with rhombic cross section, $50 \times 50$ $\mu$m, and a height of 35 $\mu$m in an automated four-circle diffractometer with Zr-filtered Mo radiation. Scans were along $2\theta$ with a scan angle of $0\cdot8°$ plus the angular $\alpha_1-\alpha_2$ separation and a scan speed of $0\cdot4°$ $2\theta$ min$^{-1}$. Background was counted for 20 s at both sides of each scan. The intensity of a standard reflection varied $\pm 1\%$ during the data collection. All reflections within one asymmetric quadrant up to 70° $2\theta$ were measured. The usual Lorentz–polarization correction was applied. An absorption correction was made assuming spherical

crystal shape ($\mu r=0\cdot8$). Maximum errors in $F$ values due to deviations from spherical crystal shape were calculated to be about 10%.

Table 1. *Lattice constants of ordered* $U_3Se_5$ *type compounds*

Standard deviations (in the least significant digits, given in parentheses) obtained in the least-squares refinements do not reflect any possible homogeneity ranges.

|  | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ (Å³) |
|---|---|---|---|---|
| $Y_2HfS_5$ | 11·4585 (3) | 7·7215 (3) | 7·2207 (2) | 638·87 (3) |
| $Gd_2ZrSe_5$ | 12·0636 (8) | 8·1379 (7) | 7·6029 (5) | 746·39 (7) |
| $La_2ThS_5$ | 12·081 (2) | 8·371 (2) | 7·607 (1) | 769·3 (2) |
| $La_2ThSe_5$ | 12·562 (3) | 8·648 (3) | 7·937 (2) | 862·2 (3) |

*Structure determination*

Single-crystal diffraction photographs of $Y_2HfS_5$ show *mmm* symmetry with extinctions (0*kl* observed only with $k+l=2n$, *hk*0 only with $h=2n$) characteristic of space groups *Pnma* and *Pn2₁a*. The centrosymmetric group was found to be correct during the structure refinement.

At the time the structure was determined, the exact composition of the crystals had not been established. Symmetry considerations and densities, determined for the isostructural phase in the system Sm–Hf–S (Donohue & Jeitschko, 1974), led us to assume the presence of four Hf atoms per unit cell. The positions of the Hf atoms were deduced from a three-dimensional Patterson synthesis. Subsequent difference syntheses, computed with a program by Fritchie & Guggenberger (1967) revealed the Y and S positions.

The structure was refined with a full-matrix least-squares program by Finger (1969). Atomic scattering factors for neutral atoms were used (Cromer & Mann, 1968), corrected for anomalous dispersion (Cromer & Liberman, 1970). The sum over all differences $w(KF_o - |F_c|)^2$ was minimized, where $w$ is the weight based

on counting statistics and $K$ is a scale factor. An extinction correction in the form of $I_{corr}=I_{uncorr}/(1-cI_{uncorr})$ was applied (Zachariasen, 1963) where $c$ was $0.18 \times 10^{-5}$. Reflections for which this correction amounted to more than 15% and reflections which were measured smaller than 3 standard deviations were given zero weight in the final least-squares refinements. They are marked with an asterisk in the list of observed and calculated structure factors.* The structure was refined only in the centrosymmetric space group *Pnma* and the normal behaviour of the thermal parameters (Table 2) indicates that this assignment is correct.

Since the exact composition of the sample was not known, occupancy factors were also refined. With the occupancy of the Hf and S atoms held at 1, the occupancy of the Y position refined to $1.040 \pm 0.006$. With full occupancy of both metal positions, occupancy factors of the sulfur atoms refined to 0.93, 1.07, 1.00, and 1.00 for S(1), S(2), S(3), and S(4) respectively, with standard deviations of about 0.02. We believe that these small deviations from full occupancies are related to systematic errors in the data (due to not fully accounting for absorption effects) and should not be taken as an indication of nonstoichiometry. Final conventional $R$ values (on $F$'s) for the refinements with full

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* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30954 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

occupancies and anisotropic thermal parameters are 0.072 for 1082 reflections with nonzero weight and 0.120 for the total of 1488 reflections. For the 520 strongest reflections (but excluding those where the extinction correction was more than 15%) $R=0.040$.

## Discussion

A stereo view and near-neighbor coordinations of the structure are shown in Figs. 1 and 2. Yttrium is coordinated to eight S atoms forming a slightly distorted 4,4-bicapped trigonal prism with Y–S distances varying between 2·81 and 2·96 Å. Seven S atoms, forming a distorted four-capped trigonal prism, surround Hf at distances between 2·51 and 2·70 Å. The S(1) atoms are in very distorted (Table 3) tetrahedral coordination of two Y and two Hf atoms; the other three independent S atoms are five-coordinated, each with four Y atoms at the base and one Hf atom at the apex of a distorted tetragonal pyramid.

In rare-earth (Ln) sulfides the coordination number CN of the Ln atom varies from 6 to 8, and in accord with the lanthanoid contraction CN 8 and 7 occur for the light Ln elements while CN 6 and 7 predominate among the heavy rare-earth sulfides (Carré, Flahaut, Khodadad, Laruelle, Rodier & Vo Van Tien, 1973). We have found the $Y_2HfS_5$ structure (CN 8 for Ln) with Zr or Hf as third component for light and heavy Ln elements. Of the corresponding selenides only the large early Ln elements form this structure (Donohue

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Table 2. *Positional and thermal parameters of* $Y_2HfS_5$

Numbers in parentheses are e.s.d.'s in the least significant digits. Thermal parameters ( $\times 10^5$) are of the form $T = \exp(-\sum\sum h_i h_j b_{ij})$. The last column contains equivalent isotropic $B$ values.

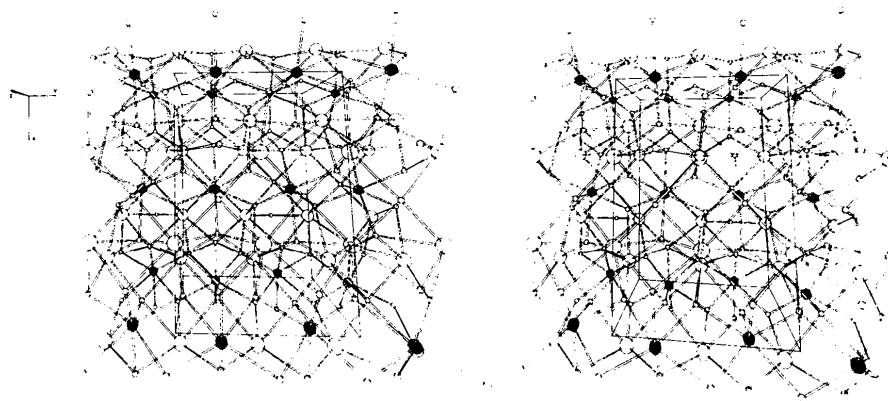| | Pnma | x | y | z | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ | $B$ (Å²) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Y | 8(d) | 0·1778 (1) | 0·9974 (2) | 0·0251 (2) | 156 (9) | 170 (16) | 233 (18) | −10 (11) | −30 (9) | 75 (18) | 0·57 (2) |
| Hf | 4(m) | 0·0060 (1) | ¼ | 0·5742 (1) | 165 (6) | 253 (10) | 219 (12) | 0 | −4 (7) | 0 | 0·64 (2) |
| S(1) | 8(d) | 0·4081 (3) | 0·0367 (4) | 0·1630 (4) | 169 (20) | 231 (41) | 230 (47) | 22 (26) | 81 (25) | 33 (36) | 0·64 (5) |
| S(2) | 4(m) | 0·1822 (4) | ¼ | 0·3331 (7) | 121 (28) | 156 (57) | 313 (73) | 0 | 53 (39) | 0 | 0·55 (7) |
| S(3) | 4(m) | 0·5032 (4) | ¼ | 0·5522 (6) | 142 (27) | 283 (56) | 213 (70) | 0 | 4 (42) | 0 | 0·62 (7) |
| S(4) | 4(m) | 0·2921 (4) | ¼ | 0·8125 (6) | 168 (31) | 166 (59) | 185 (68) | 0 | −44 (37) | 0 | 0·55 (7) |



Fig. 1. Stereo drawing of the $Y_2HfS_5$ structure prepared with Johnson's (1965) program. Hf atoms are shown with filled spheres, Y and S with large and small open spheres, respectively.

& Jeitschko, 1974). The corresponding heavy rare-earth selenides do not form apparently because CN 8 is too large for these compositions.

Although seven-coordination is known for Zr and Hf in oxides (*e.g.* $ZrO_2$, McCullough & Trueblood, 1959) and fluorides (*e.g.* $K_3ZrF_7$, Zachariasen, 1954; $Na_5Zr_2F_{13}$, Herak, Malčič & Manojlovič, 1965) the isostructural compounds $Ln_2(Zr, Hf) (S, Se)_5$ are the first sulfides or selenides with CN 7 for Zr and Hf. CN 6 and 8 do occur in binary and other ternary Zr and Hf sulfides and selenides.
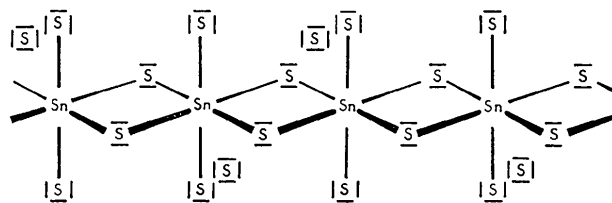
*Bonding*

Because of the relatively high electropositivity of the Ln component, the Ln–S(Se) interaction is predominantly ionic. Zr and Hf are less electropositive and also carry a larger formal charge. Therefore the Zr(Hf)–S(Se) interactions may be considered as predominantly covalent. Thus $Y_2HfS_5$ can be formulated as an yttrium polythiohafnate $Y_2^{3+}[HfS_5]^{6-}$. The anion is linear and infinite, parallel to the $y$ axis, and of the form
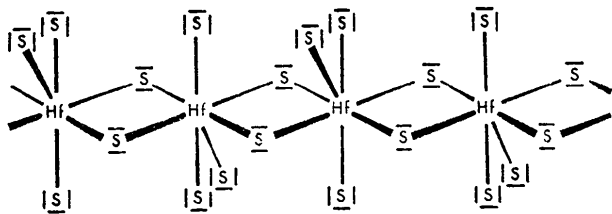
where each line represents two valence electrons. This description is also consistent with the semiconducting behaviour of the compounds.

The recently determined structure of $La_2SnS_5$ (Jaulmes, 1974) with anti-$Rh_5Ge_3$ type structure (Fig. 3), is very similar to that of $Y_2HfS_5$. There the Sn is octahedrally coordinated by sulfur and one fifth of the S atoms have only four La neighbors in a square planar coordination. In $Y_2HfS_5$ these sulfur atoms have a Hf atom as fifth neighbor at the apex of a square pyramid. By analogy with the above description for $Y_2HfS_5$ the anions in $La_2SnS_5$ may be represented by

Thus the two structures differ essentially only in one metal–sulfur distance which is a bonding distance for
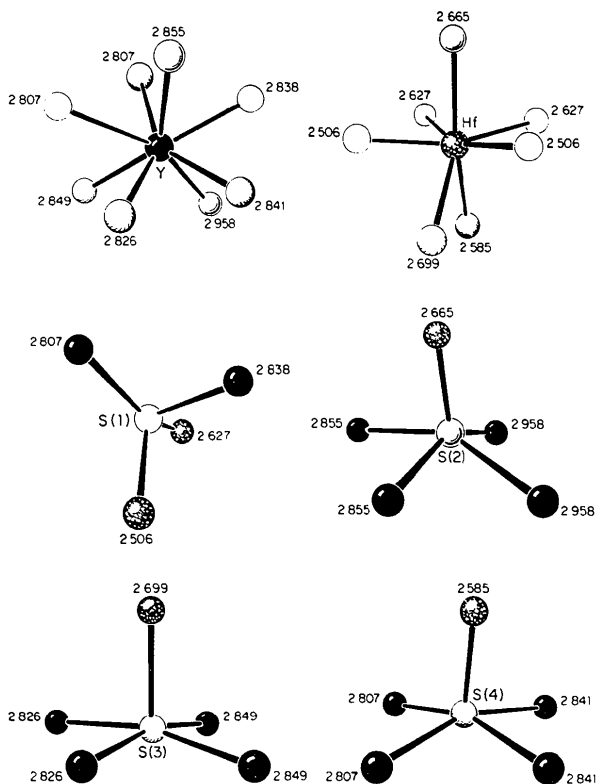


Fig. 2. Near neighbor coordinations in $Y_2HfS_5$. Standard deviations in interatomic distances are all less than 0·005 Å. All metal–sulfur distances shorter than 3·7 Å are shown. Shortest sulfur–sulfur distances are 3·064 Å; no metal–metal distances are shorter than 3·8 Å.

Table 3. *Interatomic angles in* $Y_2HfS_5$

All angles of the coordination polyhedra as shown in Fig. 2 are given in degrees of arc. Standard deviations are all less than 0·5°.

| | | | |
|---|---|---|---|
| S(1)–Y——S(1) | 131·6 | S(1)–Hf—S(1) | 77·4 (2 ×), 77·5, 124·2, 152·6 (2 ×) |
| S(1)–Y——S(2) | 69·5, 71·3, 73·7, 140·2 | S(1)–Hf—S(2) | 82·6 (2 ×), 84·1 (2 ×) |
| S(1)–Y——S(3) | 68·6, 75·1, 130·5, 136·9 | S(1)–Hf—S(3) | 75·5 (2 ×), 130·3 (2 ×) |
| S(1)–Y——S(4) | 71·6, 72·7, 73·7, 131·2 | S(1)–Hf—S(4) | 78·5 (2 ×), 106·9 (2 ×) |
| S(2)–Y——S(2) | 142·9 | S(2)–Hf—S(3) | 131·6 |
| S(2)–Y——S(3) | 73·1, 89·5, 114·1, 139·1 | S(2)–Hf—S(4) | 157·5 |
| S(2)–Y——S(4) | 80·6, 83·9, 86·4, 86·9 | S(3)–Hf—S(4) | 70·8 |
| S(3)–Y——S(3) | 87·8 | Hf—S(2)–Y | 96·1 (2 ×), 118·6 (2 ×) |
| S(3)–Y——S(4) | 65·5, 75·2, 133·6, 148·1 | Y——S(2)–Y | 82·6, 84·0, 86·2 (2 ×), 144·8 (2 ×) |
| S(4)–Y——S(4) | 144·1 | Hf—S(3)–Y | 94·5 (2 ×), 100·8 (2 ×) |
| Hf—S(1)–Hf | 102·6 | Y——S(3)–Y | 85·2, 86·3, 92·3 (2 ×), 164·7 (2 ×) |
| Hf—S(1)–Y | 100·4, 103·6, 107·0, 144·8 | Hf—S(4)–Y | 96·6 (2 ×), 105·6 (2 ×) |
| Y——S(1)–Y | 89·5 | Y——S(4)–Y | 84·6, 88·0, 89·4 (2 ×), 157·6 (2 ×) |

Hf–S (2·59 Å) and a nonbonding distance for Sn–S (3·96 Å).

*Structural relationships*

The structure of $Y_2HfS_5$ is an ordered version of the structures found for $U_3Se_5$ (Moseley, Brown & Whittaker, 1972) and $U_3S_5$ (Potel, Brochu, Padiou & Grandjean, 1972) where the Y and Hf atoms occupy the positions of the three- and four-valent U atoms, respectively. It has been shown earlier, through the formation of solid solutions, that the compounds $M_2^{III}U^{IV}S_5$ (where M = Gd, Pu, Ce; Marcon & Pascard, 1968), $M^{II}U_2^{IV}S_5$ (M = Pb, Eu), and $M^{II}U_2^{IV}Se_5$ (M = Ca, Sr, Ba, Eu, Pb; Brochu, Padiou & Prigent, 1972) crystallize with structures similar to $U_3S_5$, $U_3Se_5$ and $Np_3S_5$ (Marcon, 1967). It can be assumed that the order of the metal atoms in the $M_2^{III}U^{IV}S_5$ compounds corresponds to that of $Y_2HfS_5$. This is not necessarily true for
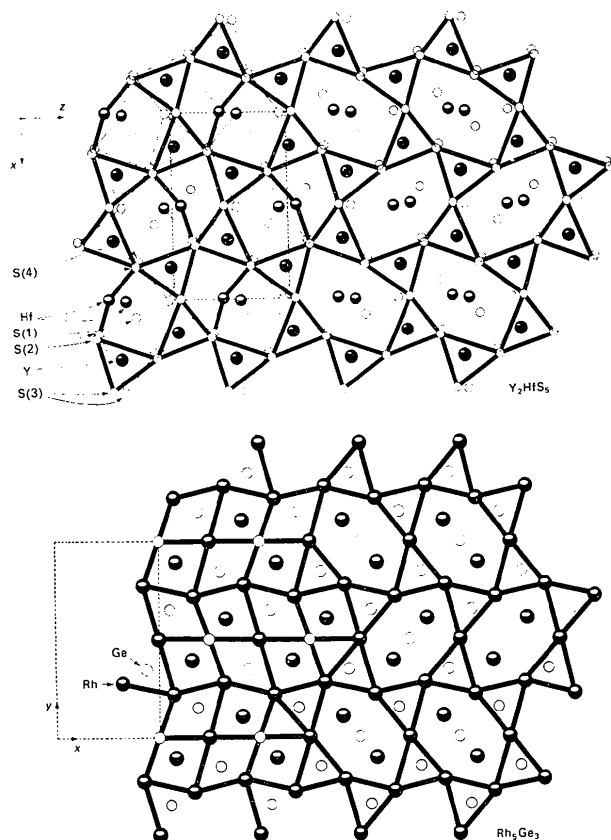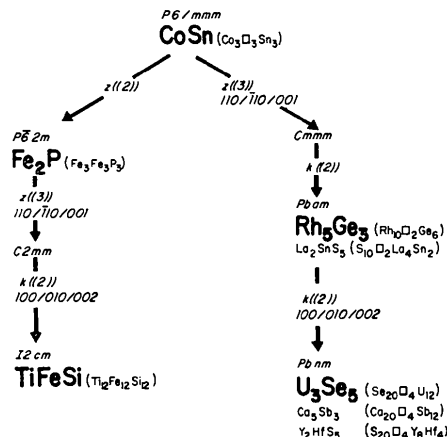
the $M^{II}U_2^{IV}(S,Se)_5$ compounds since then the bigger, more electropositive ion (*i.e.* $Ba^{2+}$) would need to occupy the site of the smaller, more covalent metal (Hf).

As can be seen from Fig. 3 the $U_3Se_5$ type structure derives from the $Rh_5Ge_3$ (anti-) type structure (Geller, 1955) through small distortions which result in a doubling of the *b* axis of $U_3Se_5$ (or $Y_2HfS_5$). Thus no interchange of atomic positions is needed to go from one structural type to another, and diffusionless phase transitions between the two structural types seem possible. The transitions would be of the type *mmmFmmm* and therefore neither ferroelectric nor ferroelastic. Since the unit cell of $U_3Se_5$ is double that of $Rh_5Ge_3$, the phases with $U_3Se_5$ or ordered $U_3Se_5$ ($Y_2HfS_5$) type structure can be considered as low-temperature forms of the corresponding compositions with the simpler $Rh_5Ge_3$ type structure. The phase transformations do of course not need to occur, *i.e.* the compounds may melt before they transform. The powder patterns of the ternary phases described in this and our previous paper (Donohue & Jeitschko, 1974) all contain reflections with odd *k* values (Table 4) thus ascertaining the large $U_3Se_5$ type unit cell in all cases.

Table 4. *Space-group relationships of 'filled' CoSn type structures*

Chemical formulas in parentheses indicate the content of the unit cell. Vacant sites are indicated by squares. The operators *z* and *k* indicate whether the subgroup and supergroup have the same primitive cell (they are *zellengleich: z*) or whether they belong to the same point group (*klassengleich: k*) as discussed by Neubüser & Wondratschek (1966). The index of the transformation is given in parentheses and for the transformations where the cell changes, the transformation matrix is also listed.



Fig. 3. Comparison of the $Y_2HfS_5$ and $Rh_5Ge_3$ structures. On the left-hand side of the $Y_2HfS_5$ drawing, atoms at $y=\frac{1}{4}$ and $\frac{3}{4}$ are connected by thin and thick lines, respectively. Atoms at $y\sim0$ and $\sim\frac{1}{2}$ are superimposed and not connected. The right-hand side of that drawing emphasizes the relation of $Y_2HfS_5$ to the $Rh_5Ge_3$ anti-type structure which can be considered as an undistorted $U_3Se_5(Y_2HfS_5)$ type structure with half the translation period in the projection direction. In the left-hand side of the $Rh_5Ge_3$ drawing atoms at $z=0$ are connected by lines, atoms at $z=\frac{1}{2}$ are unconnected, thus emphasizing the relation of $Rh_5Ge_3$ to a cubic body-centered structure.

Both the $U_3Se_5$ and the $Rh_5Ge_3$ type structures have been found recently as anti-types. $Ca_5Sb_3$ (Martinez-Ripoll & Brauer, 1974) crystallizes with $U_3Se_5$ type structure and $La_2SnS_5$ (Jaulmes, 1974) has an ordered $Rh_5Ge_3$ type structure. Thus the phase transitions discussed above could possibly be observed at room temperature in solid solutions, *e.g.* in the system $La_2HfS_5$ (ordered $U_3Se_5$ type) – $La_2SnS_5$ (ordered anti-$Rh_5Ge_3$ type), if they indeed form solid solutions.

The $Rh_5Ge_3$ structure may be considered as a distorted defect $Fe_2P$ ($= Fe_6P_3$) type structure where $\frac{1}{6}$ of the Fe positions are unoccupied (Schubert, 1964). The TiFeSi (distorted $Fe_2P$) type structure (Jeitschko, 1970; Jeitschko & Johnson, 1975) then corresponds to the $U_3Se_5$ (distorted $Rh_5Ge_3$) type structure. In terms of space-group relationships, however, the $Fe_2P$ and $Rh_5Ge_3$ type structures, as well as their distorted versions with lower symmetry and doubled pseudo-hexagonal axis (TiFeSi and $U_3Se_5$), represent different subgroups of $P6/mmm$. This space group is represented

by the CoSn type structure which may be considered as a higher symmetry defect structure of both the $Fe_2P$ and the $Rh_5Ge_3$ type structures with $\frac{1}{2}$ or $\frac{1}{6}$, respectively, of the metal positions unoccupied* (Bärnighausen, 1974). The structural and space group relationships of the various structural types are summarized in Table 4.

## $La_2ThS_5$ and $La_2ThSe_5$

The $4(m)$ metal position of the $U_3Se_5(Y_2HfS_5)$ type structure is seven-coordinated and usually occupied by a four-valent cation. Thus Th is well suited for this site. We have prepared the phases $La_2ThS_5$ and $La_2ThSe_5$ from the elements (all of purity $> 99.8$ at %) as described before (Donohue & Jeitschko, 1974). They have a structure corresponding to $Y_2HfS_5$. Lattice constants calculated from diffractometer data are given in Table 1. A powder pattern of $La_2ThS_5$ is shown in Table 5. These tables also contain data for the previously reported (Donohue & Jeitschko, 1974) phase $Gd_2ZrSe_5$ as an example for an ordered $U_3Se_5$ type structure with very different ratios of atomic scattering factors.

We thank D. M. Graham for contributing to the crystallographic work and D. W. Reutter for experimental help. We also acknowledge a very stimulating discussion with Professor H. Bärnighausen (Karlsruhe, Germany) on space-group relationships as a classifying principle in crystal chemistry.

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\* In this context the terms *defect* and *unoccupied* do not of course necessarily state anything about the actual density of these phases since the atoms surrounding the 'vacant' sites are much closer to the 'vacancy' in the defect structure than in the filled structure.

**Table 5.** *Powder patterns of* $Y_2HfS_5$, $Gd_2ZrSe_5$, *and* $La_2ThS_5$

The patterns of $Y_2HfS_5$ and $Gd_2ZrSe_5$ were recorded with a Guinier–Hägg camera and Cu $K\alpha_1$ radiation. The observed intensities of the $La_2ThS_5$ pattern are peak-height values measured from a diffractometer scan taken with Cu $K\alpha$ radiation. Intensities were calculated with the positional parameters of $Y_2HfS_5$ with a computer program (Yvon, Jeitschko & Parthé, 1969).

| $Y_2HfS_5$ | | | | | $Gd_2ZrSe_5$ | | | | | $La_2ThS_5$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| hkl | $d_c$ | $d_o$ | $I_c$ | $I_o$ | hkl | $d_c$ | $d_o$ | $I_c$ | $I_o$ | hkl | $d_c$ | $d_o$ | $I_c$ | $I_o$ |
| 101 | 6.1989 | 6.1999 | 41 | vs | 101 | 6.4321 | 6.4462 | 3 | vw | 101 | 6.4372 | 6.4542 | 18 | 10 |

*Coincidence KCl

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# Structure Cristalline de l'Orthofluorobéryllate Co(NH4)2(BeF4)2.6H2O par Diffraction Neutronique

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The crystal structure of cobalt ammonium orthofluoroberyllate hexahydrate, $Co(NH_4)_2(BeF_4)_2.6H_2O$, has been refined by the least-squares method from three-dimensional neutron-diffraction data. With a total of 2086 reflexions ($2\theta_{max} = 100°$), the $R$ and $R_w$ values are 0·051 and 0·045 respectively. The structure is compared with that of the sulphate $Cu(NH_4)_2(SO_4)_2.6H_2O$ determined from three-dimensional neutron-diffraction data by Brown & Chidambaram. Both compounds exhibit the same hydrogen-bonding pattern. The distances $H \cdots F$ are systematically shorter than the $H \cdots O$ distances. Also the thermal parameters of the oxygen atoms differ in the $[Co(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ cations.

## Introduction

Les fluorobéryllates de formules $M^{II}M_2^I(BeF_4)_2.6H_2O$ sont connus depuis longtemps puisque Ray (1932) a préparé neuf composés avec $M^{II}$ = Ni, Co, Cu, Zn, Mn, Cd et $M^I$ = NH4, K, Rb. L'analogie de formule chimique et la formation de cristaux mixtes avec la série bien connue des sels de Tutton $M^{II}M_2^I(SO_4)_2 \cdot 6H_2O$, avaient conduit cet auteur à admettre l'isomorphisme de ces deux sels.

Les sulfates ont fait l'objet de nombreuses études par diffraction des rayons-X, mais les atomes d'hydrogène n'ont été approximativement localisés que dans le composé $Mg(NH_4)_2(SO_4)_2.6H_2O$, par Margulis & Templeton (1962). Seul le sel $Cu(NH_4)_2(SO_4)_2.6H_2O$, a été étudié par diffraction neutronique (Brown & Chidambaram, 1969), ce qui a permis aux auteurs de caractériser avec précision les différentes liaisons hydrogène.

L'isomorphisme des orthofluorobéryllates avec les sels de Tutton a été confirmé par Crouzet & Aléonard (1969). Ces auteurs ont donné les caractéristiques cristallographiques de quatorze composés. Ils ont également affiné les structures de $Co(NH_4)_2(BeF_4).6H_2O$ et $NiK_2(BeF_4)_2.6H_2O$ à partir d'observations obtenues respectivement sur un diffractogramme de poudre et sur des clichés de Weissenberg. Ces deux affinements n'ont pas permis de localiser les positions des atomes d'hydrogène.

Nous avons entrepris l'étude du sel $Co(NH_4)_2(BeF_4)_2.6H_2O$ par diffraction neutronique, en vue:

– de préciser les caractéristiques du tétraèdre $BeF_4$,

– de comparer les liaisons hydrogène $O-H \cdots F$ et $N-H \cdots F$ aux liaisons correspondantes $O-H \cdots O$ et $N-H \cdots O$ dans les sulfates,

– et d'étudier les vibrations thermiques des différents atomes d'oxygène du complexe $[Co(H_2O)_6]^{2+}$, dans la direction Co–O, car les amplitudes de vibration des atomes d'oxygène dans la direction de l'ion métallique du complexe $[Mg(H_2O)_6]^{2+}$ (Margulis & Templeton, 1962) diffèrent de façon inexpliquée de celles du complexe $[Cu(H_2O)_6]^{2+}$ (Brown & Chidambaram, 1969).

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