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Hydrogen-stabilized yttrium monoselenide*

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Abstract

Mild oxidation of YH_2 (from the elements) with selenium (1:1 molar ratio, 850 °C, 7 days; sealed tantalum capsule) yields black single crystals of $YSeH_x$ when some alkali chloride (*e.g.* NaCl) is used as a flux. Since $YSeH_x$ is *not* moisture sensitive, pure samples can be obtained on rinsing off the chloride with water.

$YSeH_x$ (hexagonal, $P\bar{6}m2$, $Z=1$, $a=383.33(2)$ pm, $c=388.76(4)$ pm, $R=0.041$, $R_w=0.034$) basically crystallizes with the WC-type structure: six Se^{2-} surround each Y^{3+} as trigonal prisms and vice versa. H^- is believed to occupy trigonal planar interstices within the yttrium monolayers, just as in the isoelectronic YBr_2H_x (MoS_2-type heavy atom structure).

In contrast to NaCl-type YSe, the electronic structure of WC-type YSe exhibits one band located slightly below the main d block, being occupied by one electron. Owing to the interaction with hydrogen in $YSeH_x$, this band splits into two, whereas the bonding combination is lowered in energy and occupied by two electrons.

Conductivity measurements show that $YSeH_x$ is an insulator. Therefore x should to be close to *one* according to salt-like $[(Y^{3+})(Se^{2-})(H^-)]$, and hydrogen combustion analyses really suggest a composition like $YSeH_{0.8(2)}$.

1. Introduction

AB compounds with the WC-type structure [1] are well known for carbides and nitrides of transition metals, especially for group 6b elements. Monochalcogenides adopt this simple arrangement so far only for members of group 4b, *e.g.* ZrS and HfS [2, 3], whereas most other transition metal monochalcogenides crystallize with the NaCl-, NiAs- or ZnS-type structure [4, 5] containing closest-packed arrangements of anions. Electronic arguments (such as the presence of one energetically lowered d band for d^2 systems) based on band structure calculations, *e.g.* for ZrS [2, 6], are well-accepted explanations for the different structural preferences.

The number of investigations on monosulphides and monoselenides of the rare earth metals is legion [7, 8], but structurally only the NaCl type (with a considerable phase width in some cases) has been reported [9, 10], except for thin layers of sputtered material of MSe (M ≡ Sm, Tb, Dy, Yb) with the hexagonal wurtzite structure of ZnS [11] or high pressure EuSe with the cubic CsCl structure [12].

Mild oxidation of (hydrogen-containing) yttrium powder with equimolar amounts of selenium in the presence of some alkali chloride as a flux (NaCl or CsCl) at 800–850 °C produced "yttrium monoselenide" which, for the first time, exhibited the WC-type heavy atom arrangement. Further investigations clearly revealed that a certain hydrogen content is responsible for the stabilization of this particular structure, whereas experiments under strictly hydrogen-free but otherwise analogous conditions yielded NaCl-type samples of YSe [13] as one would expect.

2. Experimental details

YCl_3 was prepared from Y_2O_3 (powder, 99.99%, Johnson–Matthey) via $(NH_4)_3YCl_6$ following the "wet variant" of the ammonium chloride route [14]. Conproportionation with appropriate amounts of yttrium (chips, 99.99%, Johnson–Matthey) and YH_2 (from the elements; H_2: 99.999%, Messer Griesheim) in silica-protected sealed tantalum containers [15] effected its conversion to $YClH_{0.67}$ [16]. Equimolar amounts of $YClH_{0.67}$ and selenium (shot, 99.999%, Johnson–Matthey) react to yield Sc_2S_3-type Y_2Se_3 [17, 18] and Na_3YCl_6 [19] when NaCl (suprapur, E. Merck) is present as a flux. Analogous reactions with molar ratios of $YClH_{0.67}$:NaCl:Se such as 3:3:2 result in the formation of $YSeH_x$ ($x \approx 0.8$) along with the above-mentioned ternary chloride. To secure the hydrogen contents in $YSe(H_x)$, yttrium and YH_2 respectively were reacted

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with selenium under analogous conditions (equimolar amounts of the components, tantalum capsule, NaCl flux, 850 °C, 7 days). While NaCl-type YSe [13] is the product of hydrogen-free experiments, YSeH$_x$ forms quantitatively through the reaction of YH$_2$ with selenium in 1:1 molar ratios. The bulk product of NaCl-type YSe looks black. Under the microscope small crystals show cubic or almost spherical habit and exhibit (brass- or bronze-coloured) metallic lustre under strong reflective illumination, as often reported previously [13, 20]. They are always well separated from the colourless flux crystals (NaCl). The same is true for the products of experiments involving hydrogen, but bluish-black single crystals of irregular, almost spherical shape and glassy lustre turned out to be the main product instead of NaCl-type YSe. Suitable crystals were selected under mineral oil and their quality was checked by X-ray film methods (oscillation, Weissenberg, precession). All information leads to a hexagonal primitive unit cell with high Laue symmetry (6/*mmm*) and small lattice dimensions ($a \approx 380$ pm, $c \approx 390$ pm), consistent with a WC-type heavy atom arrangement. A complete intensity data set was recorded with an automatic four-circle diffractometer. Further information on the data collection and the results of the structure determination and refinement are summarized in Table 1.

3. Results

The oxidation of YClH$_{0.67}$ with selenium (1:1 molar ratio) in the presence of equimolar amounts of NaCl results in the formation of (almost black) Y$_2$Se$_3$ (and colourless Na$_3$YCl$_6$ [19]) according to

$$3\mathrm{YClH}_{0.67} + 3\mathrm{Se} + 3\mathrm{NaCl} = \mathrm{Y}_2\mathrm{Se}_3 + \mathrm{Na}_3\mathrm{YCl}_6 + \mathrm{H}_2 \qquad (1)$$

This is not unexpected, since the corresponding system with sulphur (YClH$_{0.67}$/S/NaCl) behaves likewise under analogous conditions (850 °C, 7 days, tantalum capsule) [25]. While the D-Y$_2$S$_3$ forms in the latter case, Y$_2$Se$_3$ proves to crystallize with the Sc$_2$S$_3$-type structure [17, 18] in brownish-black, almost octahedral beads. Substoichiometric amounts of selenium, however, favour

$$3\mathrm{YClH}_{0.67} + 2\mathrm{Se} + 3\mathrm{NaCl} = 2\mathrm{YSeH}_{0.8} + \mathrm{Na}_3\mathrm{YCl}_6 + 0.2\mathrm{H}_2 \qquad (2)$$

to become the major reaction. YSeH$_x$ ($x \approx 0.8 \pm 0.2$ from several hydrogen combustion analyses) crystallizes with the WC-type heavy atom arrangement according to the results given in Table 1. Since it is not sensitive to water, the chloride can be rinsed off easily to leave pure YSeH$_x$ behind. Moreover, the direct reaction of YH$_2$ (better, YH$_{1.7(2)}$, according to hydrogen combustion analysis) with equimolar amounts of selenium in the presence of some NaCl as a flux gives access to pure (and large) samples of (WC-type) YSeH$_{0.8}$, while the oxidation of (hydrogen-free) yttrium chips yields (NaCl-type) YSe under otherwise analogous conditions:

$$\mathrm{YH}_{1.7} + \mathrm{Se} = \mathrm{YSeH}_{0.8} + 0.45\mathrm{H}_2 \qquad (3)$$

but:

$$\mathrm{Y} + \mathrm{Se} = \mathrm{YSe} \qquad (4)$$

The two distinct products resulting from reactions (3) and (4) may serve as further important proof for the presence of hydrogen within the WC-type arrangement of YSe.

TABLE 1. YSeH$_x$: crystallographic data and their determination

Lattice parameters (pm), *molar volume* V_m(cm^3 mol^{-1})
Guinier powder data [21] (Enraf–Nonius FR 552, eight reflections):
$a = 383.28(3)$, $c = 388.82(5)$, $V_m = 29.789(7)$
diffractometer powder data (Huber G 645, 13 reflections):
$a = 383.33(2)$, $c = 388.76(4)$, $V_m = 29.792(5)$
four-circle diffractometer single-crystal data (20 reflections):
$a = 382.71(2)$, $c = 388.90(3)$, $V_m = 29.707(4)$

Crystal system: hexagonal, *space group*: $P\bar{6}m2$ (no. 187), $Z = 1$

Data collection: four-circle diffractometer Siemens–Stoe AED 2, Mo Kα radiation, graphite monochromator, $\lambda = 71.07$ pm, ω scan, scan width and speed: variable ("learnt profile" [22]), $2° \leqslant \Theta \leqslant 35°$, $F(000) = 73$, $\mu = 467.18$ cm^{-1}

Data corrections: background, polarization and Lorentz factors; absorption: Ψ scan for 20 reflections

Data statistics: 874 reflections measured, of which 114 were symmetrically independent ($R_{int} = 0.076$) and used for refinement

Structure determination and refinement: program SHELX-76 [23], scattering factors from Cromer and coworkers [24], direct methods (Y, Se) and successive difference Fourier syntheses, full-matrix least-squares refinement, $R = 0.041$, $R_w = 0.034$ ($w = 0.464\ \sigma(F_o)^{-2}$)

Atomic positions:		*x/a*	*y/b*	*z/c*
Y	(1*a*)	0	0	0
Se	(1*f*)	2/3	1/3	1/2
neither detected nor refined:				
H	(1*c*)	1/3	2/3	0

Coefficients of the "anisotropic" thermal displacement factors: exp $[-2\pi^2(a^{*2}h^2U_{11} + \ldots + b^*c^*kl2U_{23} + \ldots)]$, U_{ij} (pm^2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Y	50(9)	U_{11}	87(13)	0	0	$\frac{1}{2}U_{11}$
Se	120(13)	U_{11}	161(19)	0	0	$\frac{1}{2}U_{11}$

4. Crystal structures of YSe and YSeH$_x$

According to the structure determination (Table 1) and in perfect agreement with Guinier and powder diffractometer patterns, the WC-type heavy atom arrangement is present for the compound under consideration ("yttrium monoselenide"). However, the appearance of this structure (hexagonal, $P\bar{6}m2$, $a = 383.33(2)$ pm, $c = 388.76(4)$ pm, $Z = 1$, $V_m = 29.792(5)$ cm^3 mol^{-1}, $D_x = 5.64$ g cm^{-3}) seems to be rather unusual in comparison with the well-established NaCl-type structure of YSe (cubic, $Fm\bar{3}m$, $a = 570.56(3)$ pm, $Z = 4$, $V_m = 27.963(4)$ cm^3 mol^{-1}, $D_x = 6.00$ g cm^{-3}). Although both structures offer a coordination number of six for both cations and anions, there are striking differences. The NaCl-type structure of YSe consists of a cubic closest-packed arrangement of selenium where yttrium occupies all available octahedral interstices and vice versa (see Fig. 1, left, for a view of the layer-like arrangement along [111]). The most important internuclear distances are 285.3 (Y–Se or Se–Y, 6×) and 403.4 pm (Y–Y or Se–Se, 12×) (see Table 2). WC-type "YSe" (see Fig. 1, right, for a comparable view along [00.1]) exhibits a more than 6% larger molar volume owing to the (non-closest-packed) hexagonal primitive arrangement for both cations and anions. Yttrium is located at the centre of a trigonal prism consisting of six selenium atoms (and vice versa), which is obviously the reason for the more than 3% larger distances Y–Se or Se–Y (294.6 compared with 285.3 pm, in the NaCl-type case). The distances between identical atoms are 383.3 (6×) and 388.8 pm, (2×), which means that four next neighbours of the same species are missing compared with closest-packed NaCl-type YSe. Since sterical reasons highly favour the NaCl- over the WC-type arrangement of YSe and electronic arguments for pure WC-type "YSe" remain unsatisfying as well, only interstitial stabilization by hydrogen can be the reason for its existence.

All experiments are consistent in proving that WC-type "YSe" only forms when hydrogen is present. The only possibility to put hydrogen into the structure is to place it into trigonal planar voids within the yttrium monolayers in order to realize an arrangement as suggested in Table 1 and shown in Fig. 2. In one plane, hydrogen is surrounded by three yttrium atoms (d(H–Y) = 221.3 pm, 3×) and the coordination polyhedron of Y^{3+} expands to a tricapped trigonal prism with three capping H^-, in addition to the six prismatically arranged $Se^{2-}$from the basic WC-type structure. As for several rare earth dihalide hydrides MX_2H_x ($X \equiv Br$, I) [28] with MoS_2-type heavy atom arrangements, hydrogen in trigonal planar coordination of M^{3+} is not uncommon. From neutron diffraction data both the position and the fractional occupation of deuterium were refined for $CeI_2D_{0.96}$ [28, 29]. Moreover, YBr_2H_x could serve as an isoelectronic model for $YSeH_x$ and even the structures (MoS_2 *vs.* WC type) are highly related. Unfortunately, exact data for YBr_2H_x are not yet available, but x is believed to be somewhat smaller than 1.0 and markedly higher than 0.5, at least for the lanthanide dibromide hydrides so far investigated [28, 29]. The same seems to be true for $YSeH_x$, where hydrogen combustion analyses hint at a value $x \approx 0.8$. The reliability of these analyses is not too high, but parallelly analysed samples of YH_2 roughly verify the expected composition ($YH_{1.7(2)}$). At any rate, x should range at the upper phase boundary, since all investigated samples were prepared according to reactions ((2) and (3)) that provide sufficient hydrogen at least for the stoichiometric $YSeH_{1.0}$ composition.

5. Electronic structures of YSe and $YSeH_x$

YSe usually adopts the NaCl-type structure and the appearance of the WC-type structure indeed would be surprising. The latter could be taken under consideration from the X-ray crystal structure determination (Table

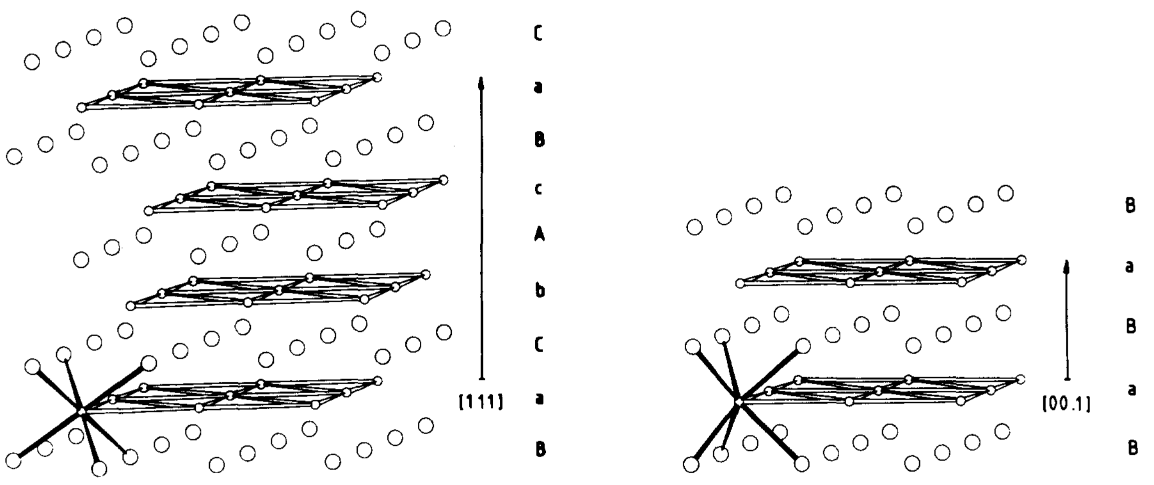


Fig. 1. Difference between the NaCl-type (left) and the (hypothetical) WC-type (right) structure of YSe (Y: small circles, Se: large circles; one octahedron (left) and one trigonal prism (right) of Se around Y are depicted by bold bonds).

TABLE 2. Important internuclear distances (pm) in WC-type $YSeH_x$ compared with those in NaCl-type YSe, CaF_2-type YH_2 and Mg-type Y

	$YSeH_x$ (WC type)	*YSe (NaCl type)*
Y-Se (=Se-Y)	294.6 (6×)	285.3 (6×)
Y-Y (=Se-Se)	383.3 (6×) 388.8 (2×)	403.4 (12×)
H-Y (=Y-H)	221.3 (3×)	
H-Se (=Se-H)	294.6 (6×)	
H-H	383.3 (6×) 388.8 (2×)	
	YH_2 (CaF_2 type) [26]	*Y (Mg type)* [27]
Y-Y	368.1 (12×)	355.7 (6×) 364.9 (6×)
Y-H	225.4 (8×)	
H-Y	225.4 (4×)	
H-H	260.3 (6×)	

1), since hydrogen cannot be localized in YSeH from an X-ray experiment. In this contribution we first study the electronic conditions for the NaCl- and WC-type structures of YSe respectively. Then we discuss the effects favouring the introduction of hydrogen into the WC structure, which sterically appears to be impossible for the NaCl structure.

The coordination environment for a WC-structured YSe is trigonal prismatic. From a simple molecular orbital (MO) calculation for a trigonal prismatic $[YSe_6]$ fragment we obtain a "one-below-two, below-two" splitting for the yttrium d levels, as shown in Fig. 3, together with the well-known energy splitting in an octahedral ligand field for the NaCl-structured YSe. With a local coordinate system with the z direction along the sixfold axis, the lowest level of the molecular $[YSe_6]$, with its geometry adapted from the $YSeH_x$ (WC-type) structure (see Table 1), is an **a** level (d_{z^2}), with an **e** level ($d_{x^2-y^2}$, d_{xy}) slightly higher in energy. The remaining **e** level (d_{xz}, d_{yz}) is destabilized by the local Se^{2-} ligand field.

In the extended structure we could expect similar electronic features, because the yttrium atoms are relatively far from each other. Any interaction between the yttrium atoms, however, will affect the local ligand field splitting and thereby introduce additional orbital mixing. Interactions between the yttrium atoms occur within the metal monolayers (d(Y-Y) = 383.3 pm) and along [00.1] (d(Y-Y) = 388.8 pm ≡ c). If we consider metal-metal interactions, the d_{z^2} orbitals become more stabilized since they are required to be in phase at Γ, and the $d_{x^2-y^2}$ and d_{xy} orbitals are slightly raised in energy owing to interaction with orbitals of neighbouring yttrium atoms. Moving away from the Γ point, these orbitals are allowed to mix and the splitting off of one band becomes more significant in the density of states (DOS) calculation (Fig. 4, right) than in the MO of $[YSe_6]$. The major contributions to both DOS plots shown in Fig. 4 come from Se s, Se p and Y d orbitals with increasing energy. The lowest d block in the WC-type structure consists of approximately 37% $d_{x^2-y^2}$, 37% d_{xy} and 26% d_{z^2} orbitals. One electron per formula unit of YSe occupies the d block in both the NaCl- and the WC-type structure. This d^1 situation is known for the NaCl-type structure of YSe [30] and consequently leads to metallic conductivity ($\rho \approx 3$ mΩ cm at 25 °C and 10 mΩ cm at 650 °C [13]). Such an electronic situation, however, would be rather surprising for a WC-structured YSe. The ordering of states in the WC-type structure appears to gain maximum stability, with two electrons occupying the lowest d block, as known for *e.g.* ZrS [2, 6]. This is confirmed by the calculated crystal orbital overlap population (COOP) where the low-lying d block is bonding up to −9.7 eV, apt to accommodate two electrons. Thus we note that the WC structure is favoured for d^2 systems. For a one-electron system (YSe) a WC structure should therefore be susceptible to oxidation or electronic instability.

With hydrogen present in the structure, two electrons occupy the metal-hydrogen bonding level. A crystal

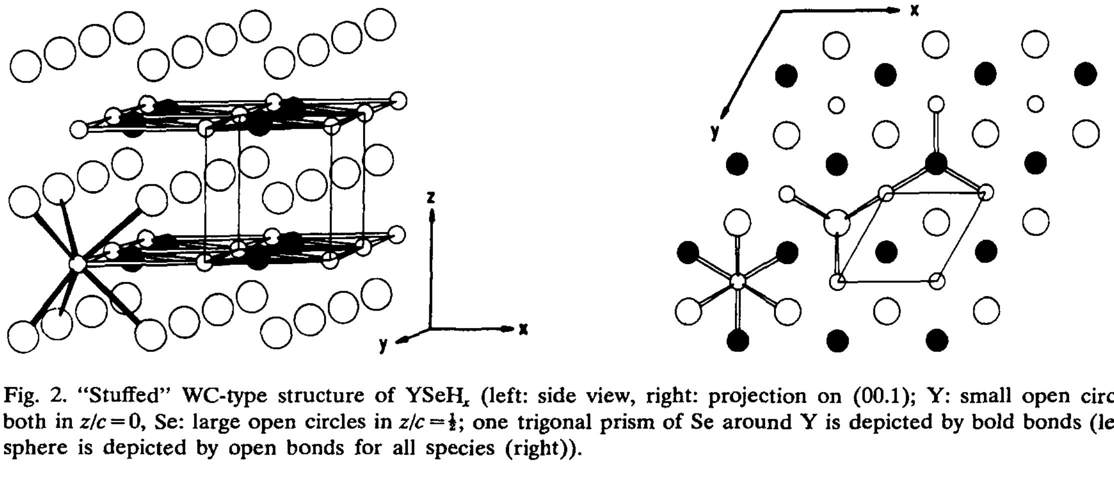


Fig. 2. "Stuffed" WC-type structure of $YSeH_x$ (left: side view, right: projection on (00.1); Y: small open circles, H: black circles, both in $z/c = 0$, Se: large open circles in $z/c = \frac{1}{2}$; one trigonal prism of Se around Y is depicted by bold bonds (left); one coordination sphere is depicted by open bonds for all species (right)).

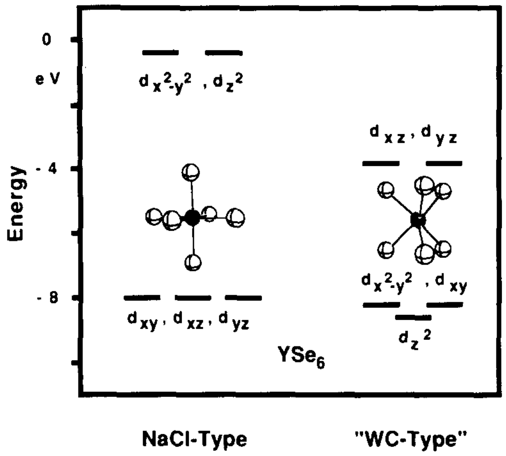


Fig. 3. Schematic d block splitting diagram of a $[YSe_6]$ cluster according to the NaCl- and the WC-type structure, with the geometry adopted from the YSe (left) and the YSeH (right) structure.

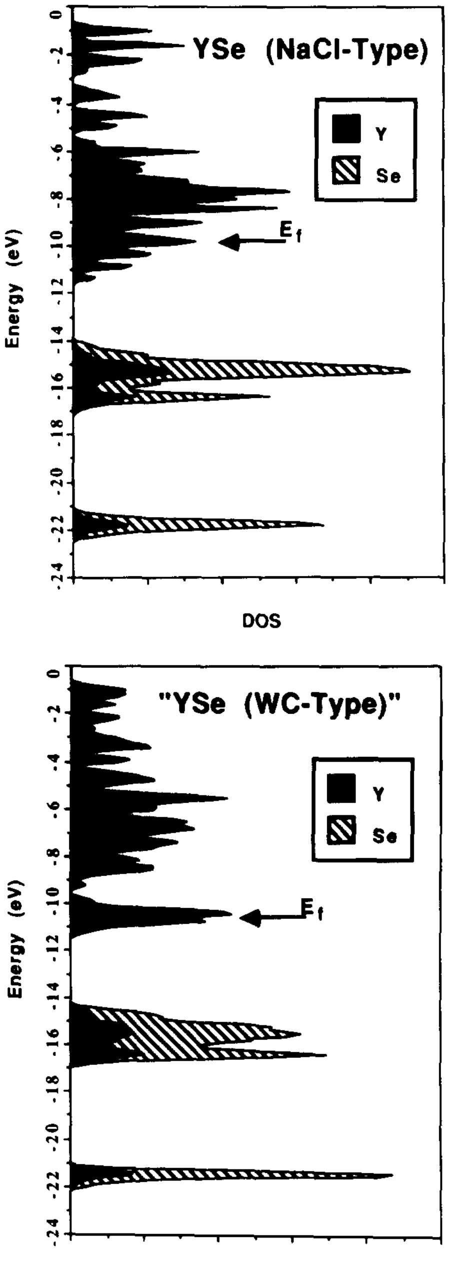


Fig. 4. Density of states (DOS) projection calculated for YSe adopting the NaCl- (above) and the (hypothetical) WC-type (below) structure.

orbital interaction scheme (at Γ) with hydrogen is provided in Fig. 5. When the metal–metal interactions are turned on, the d_{z^2} orbitals are strongly stabilized (compare Fig. 3) because they are required to be in phase at Γ. The metal–hydrogen interaction is restricted by symmetry to occur between the Y d_{z^2} orbitals and the H 1s orbitals (at Γ). The bonding interaction is lowered and the antibonding combination is pushed way up in energy. The stabilization of the d_{xz} and d_{yz} orbitals is meaningless here because they do not mix with the selenium orbitals at Γ.

In the extended structure only some symmetric combinations of the lowest d block interact with the H 1s level, namely the $d_{x^2-y^2}$, d_{xy} and d_{z^2} orbitals (also the Y 5s and 5p orbitals). This interaction leads to a major stabilization of the Fermi energy that would fall right above the Se p block. The states contributing to the bonding Y d–H block contain approximately 67% H, 27% Y and 6% Se orbitals. Thus hydrogen adopts the formal charge of $H^{-0.67}$. Going from WC-type YSe to YSeH, the low-lying metal–metal bonding block is converted into a metal–metal, metal–hydrogen bonding block. The larger amount of the former metal–metal bonding part (in YSe), however, is raised in energy and becomes the antibonding Y–H combination (in YSeH). The metal–metal overlap populations thereby decrease by 66% (from 0.12 to 0.04) within the metal layer and by 25% (from 0.08 to 0.06) for axial Y–Y contact. Part of the metal–metal interaction takes place within the layers of the trigonal metal arrangement just where the hydrogen atoms are believed to be situated (see Table 1). No matter if all the centres of metal triangles are occupied by hydrogen atoms, the bonding in these triangles is suggested to be formed by semi-localized three-centre orbitals of the metal arrangement and the H 1s orbital. The reader is referred to the work of Yee and Hughbanks [31] to see how such localization may be implemented in related systems such as MoS_2, $H_x(Nb,Ta)S_2$ or ZrS.

If the hydrogen content in $YSeH_x$ is indeed somewhat less than *one* ($x \approx 0.8$ according to hydrogen combustion analyses), the electronic situation appears to be in between the DOS curves shown in Fig. 4 (right: YSe, WC type) and Fig. 6 (YSeH), meaning that not all of the low-lying d block in YSe is lowered in energy for $YSeH_x$ ($x < 1$). This, of course, has consequences for

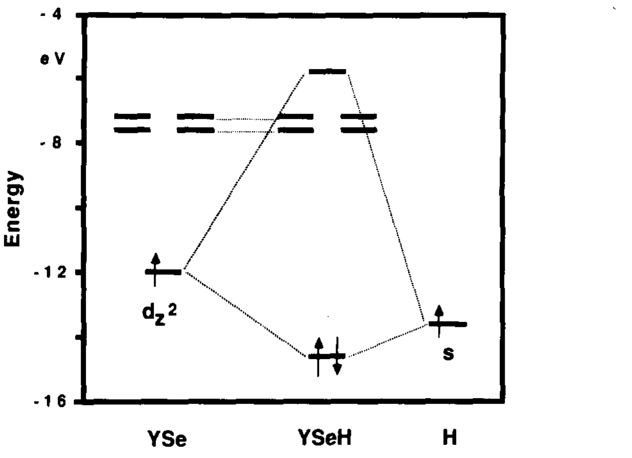


Fig. 5. Crystal orbital interaction diagram for d levels of (hypothetical) WC-type YSe and an H s orbital for YSeH at *Γ*.

the electronic conductivity. For the composition YSeH the Fermi level is at the upper edge of the main Se p block, leading to an insulating behaviour with a band gap of about 2.2 eV. In $YSeH_x$ ($x<1$) a portion of d levels will remain slightly below the main d block, being half occupied by electrons. Depending on the degree of localization of these electrons in three-centre bonds, this situation will lead to semiconducting (or weakly metallic) properties.

Interestingly, the electronic situation of $YSeH_x$ ($x \ll 1$) is not very different from that of the Li_xNbO_2 structure [32], containing trigonal prismatic $[NbO_6]$ units forming $[NbO_2]$ layers interconnected by lithium atoms, exhibiting superconductivity at low temperatures [33]. Conductivity measurements, however, show that $YSeH_x$ is an insulator. Therefore x should to be close to *one* according to a salt-like $[(Y^{3+})(Se^{2-})(H^-)]$. Several MoS_2-structured rare earth dihalides (*e.g* $LaBr_2$ [34]) have been recently found to be in fact dihalide hydrides, *e.g.* $LaBr_2H_x$ ($x \approx 0.9$) [28, 29]. Their electronic structures are quite similar to $YSeH_x$ (note that YBr_2H_x is even isoelectronic) and they are semiconductors.

The band structure of YSeH is shown in Fig. 6. The energy of the bands varies across the different directions of the Brillouin zone (Scheme 1). The lowest band in Fig. 6 is the Se s band. Going to higher energy, we note three Se p bands together with one bonding Y–H band, the four remaining Y d bands and the antibonding Y–H combination. The Y s and p levels are at higher energy. There are some degeneracies at special points, such as the p_x and p_y bands of selenium and the d_{xz} and d_{yz} as well as the $d_{x^2-y^2}$ and d_{xy} bands of yttrium at the zone centre. The p_x and p_y as well as the $d_{x^2-y^2}$ and d_{xy} bands are degenerate between *Γ* and A, parallel to the sixfold axis. One band of the original Y d block of the WC structure is lowered in energy owing to the interaction with hydrogen and now becomes the uppermost band situated in the Se p block. However, there are some antibonding interactions, mainly with the Se p_z band, broadening the Y–H bonding states by introducing additional orbital mixing. For this reason it may be unlikely to obtain the homologous YSH, since shorter Y–S distances could lead to an increased antibonding S–H interaction. Attempts to prepare YSH_x in analogy to $YSeH_x$ have failed so far: NaCl-type YS

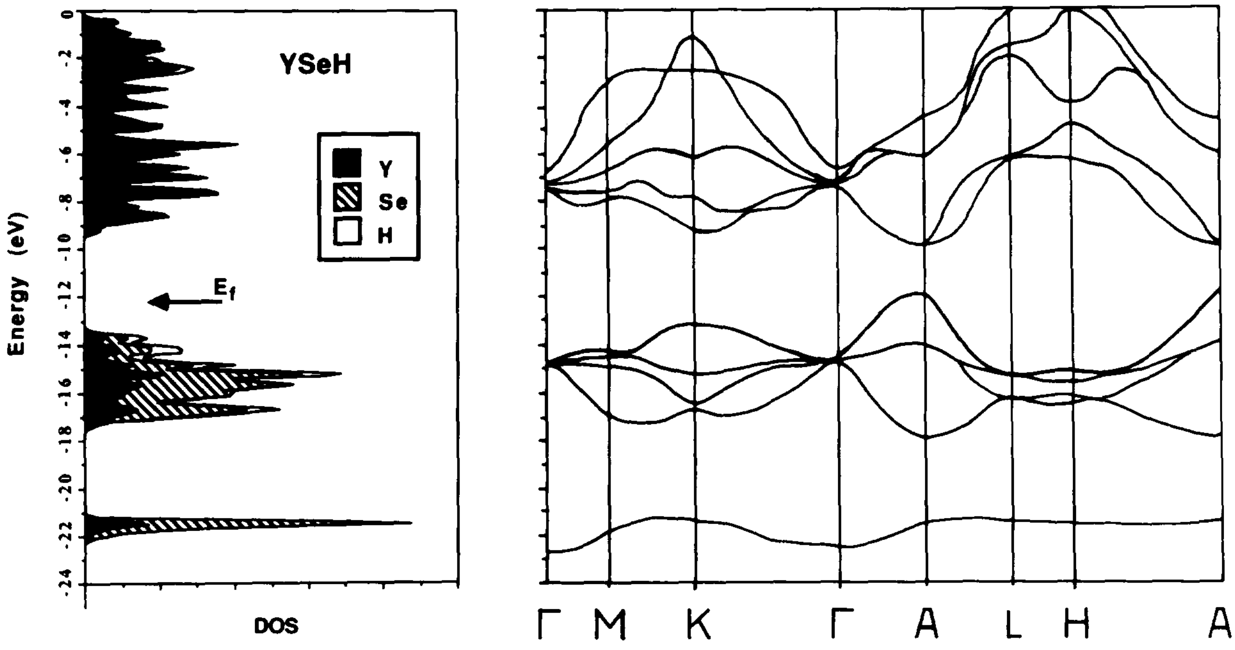
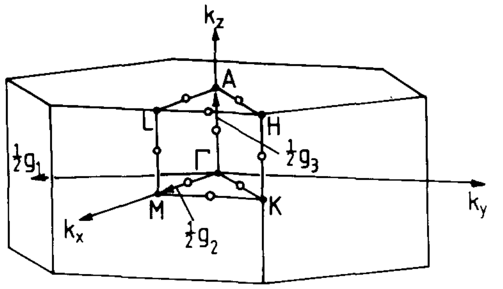


Fig. 6. Density of states (DOS) projection (left) and band structure (right) calculated for YSeH (*Γ*=0, 0, 0; M=0, $b^*/2$, 0; K=$-a^*/3$, $2b^*/3$, 0; A=0, 0, $c^*/2$; L=0, $b^*/2$, $c^*/2$; H=$-a^*/3$, $2b^*/3$, $c^*/2$; compare Scheme 1 for the Brillouin zone).



Scheme 1.

(with a considerable phase width [35]) forms instead. On the other hand, $YTeH_x$ [35], where these problems do not arise, has been obtained under similar conditions as described for the synthesis of $YSeH_x$.

6. Conclusions

Ubiquitous impurities have often turned out to be a problem in synthesis, also in understanding the unexpected physical properties of these compounds as long as the impurity is undiscovered. Hydrogen in particular provides a serious problem to solid state chemists (especially in rare earth metal compounds) since it usually can neither be detected nor localized by an X-ray crystal structure refinement. In this contribution we aimed to show that an investigation of the electronic structure can prove to be a useful tool to suspect the presence of such an impurity.

Hydrogen proves to be a rather simple example, because the interactions of the totally symmetric 1s orbital are limited. Such an interaction has been demonstrated for the hypothetical WC-type structure of YSe with a hydrogen atom. Owing to the trigonal prismatic environment of selenium around the yttrium atoms in a WC structure, the DOS exhibits one block (one band) to be split off below the main d block. This lower d block is bonding but contains only one electron instead of two. The interaction of an H 1s orbital with d states of appropriate symmetry can be demonstrated easily by a simple MO-like interaction diagram. A Y d^1 level and an H $1s^1$ level are converted into a Y–H bonding (mainly hydrogen character, at low energy) and Y–H antibonding combination (mainly yttrium character, at high energy), thereby decreasing the Fermi energy, to yield YSeH.

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Appendix

The extended Hückel tight-binding method [36] was used for the calculations of the band structure and DOS shown. H_{ii} values for yttrium were obtained from self-consistent charge iteration on Y_2Cl_3 (5s: -9.2, 5p: -5.9, 4d: -9.78 eV). Slater-type orbital exponents (coefficients in double-ζ expansion) used for yttrium are: 5s: $\zeta_1=1.74$, 5p: $\zeta_1=1.70$, 4d: $\zeta_1=1.56$ (0.8215), $\zeta_2=3.554$ (0.3004). Parameters for selenium and hydrogen were taken from the literature [37, 38]. DOS calculations were carried out using a set of 64 k points for the irreducible wedge of the Brillouin zone (see Scheme 1).