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Rare Earth–Hydrogen Systems. IV. The Higher Hydride of Ytterbium, a New Type of Hydride[1]

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The higher hydride of ytterbium, $YbH_{2.55}$, is a black material which is fairly stable in air. It is face-centered cubic, $a = 5.192$ A. When decomposed at elevated temperatures (200–300°) it yields an fcc modification of YbH_2, which if quenched is metastable at room temperature ($a = 5.253$ A). On annealing, fcc YbH_2 reverts to the orthorhombic form. The magnetic susceptibility of $YbH_{2.55}$ is intermediate between that of YbH_2 (nearly diamagnetic) and that of Yb(III) compounds. The infrared spectrum of $YbH_{2.55}$ corresponds to that of a semiconductor, while the spectrum of orthorhombic $YbH_{1.94}$ resembles that of CaH_2. The evidence supports the view that $YbH_{2.55}$ contains Yb(II) and Yb(III) ions which are made equivalent through resonance, *i.e.*, through exchange by conduction electrons. Such a hydride is unprecedented, although parallels are found in oxide systems, as Fe_3O_4. The small paramagnetism and conductivity of YbH_2 are also attributed to the contribution of a small proportion of Yb(III) and conduction electrons to the resonance structure.

Introduction

The reaction of ytterbium or europium metal with hydrogen at atmospheric pressure and moderate temperatures yields only the dihydrides,[2] whereas all other rare earth metals can form trihydrides under these conditions. This occurrence of the Yb(II) and Eu(II) states is a manifestation of the stability associated with completely filled and half-filled 4f subshells. The rare earth hydrides formed in all cases are nonstoichiometric to some degree. Preparation of a ytterbium hydride with the atomic ratio H:Yb greater than 2 was successfully achieved by reaction of the metal with hydrogen at several atmospheres pressure and elevated temperatures in a high-pressure system.[3,4] The ytterbium hydrides thus prepared were then examined using various physicochemical methods.

Experimental Section

The materials and preparative techniques employed are described in the preceding paper.[4]

Analyses.—Since the rare earth hydrides can be quantitatively decomposed by acids, an analytical procedure was developed using a Schiff nitrometer (modified Dumas method) whereby the volume of hydrogen evolved from a known mass of sample could be measured. The analytical train consisted of a 30-ml nitrometer, a reaction flask in which the hydride could be decomposed, and a supply of very pure carbon dioxide as the carrier gas (prepared using marble chips and HCl in a Kipp generator following the method outlined by Johns[5]).

The procedure developed was briefly as follows. The apparatus, charged with the metal or hydride (the latter in an evacuated ampoule), was flushed with CO_2, and the ampoule was broken by a glass hammer. An excess of 6 *F* hydrochloric acid (previously saturated with CO_2) was pressured in, and the H_2 was collected in the nitrometer. The solution was boiled to ensure complete release of hydrogen and to oxidize Yb^{2+} to Yb^{3+}. A blank was determined, and corrections for the vapor pressure of water over the KOH solution were made, using the data of Milner and Sherman.[6] Analyses of several pure metals (Mg, Zn, Yb) yielded results accurate to ±1%.

In addition, samples were analyzed in a vacuum line, the hydride being decomposed either with acid or with heat, and the hydrogen released was transferred with a Sprengel pump to a calibrated section of the line. The compositions of the hydrides were calculated using the equation

$$YbH_x + 3H^+ \longrightarrow Yb^{3+} + \frac{3+x}{2} H_2$$

The moles of hydrogen released at STP were calculated from the observed volume, pressure, and temperature, and the moles of sample could be calculated from the mass of sample taken and a formula weight obtained by the method of successive approximations. Analysis of the first higher ytterbium hydride on the vacuum line gave the formula $YbH_{2.50\pm0.03}$, while analyses utilizing the nitrometer gave $YbH_{2.59\pm0.06}$. The average composition was considered to be $YbH_{2.55\pm0.05}$.

Additional support for the above formula came from further experiments with the $YbH_{2.55}$. A weighed specimen of the $Yb_{2.55}$ was placed in a Pyrex tube in the calibrated vacuum line, evacuated, pressured to 0.8 atm of hydrogen (more easily to control the decomposition), and then heated with a small resistance furnace. At approximately 300° the pressure rise clearly indicated that hydrogen was being evolved from the sample. After cooling and measuring the amount of hydrogen, the formula of the resulting hydride was calculated to be $YbH_{1.98\pm0.04}$. Analyses of samples of this material using the nitrometer gave the composition as $YbH_{1.97\pm0.04}$.

X-Ray Diffraction Experiments.—Numerous ytterbium hydride samples were studied by X-ray diffraction techniques in order to characterize and identify the phases present in coordinating with the other experimental results. The procedures, computations, and corrections were described earlier.[4,7]

Magnetic Susceptibility Measurements.—In an attempt further to characterize the phases in the ytterbium–hydrogen system, magnetic susceptibility measurements were carried out. The gram susceptibilities were determined by the Gouy method. The apparatus consisted of a semimicrobalance and an electromagnet and power supply capable of producing fields up to 15,000 gauss. The metal hydride specimen was tightly packed into a 1.7-mm i.d. glass tube, 17 cm in length and fitted with a ground-glass cap or torched off to protect the hydride. The tubes were filled in a glove box containing carbon dioxide, using a glass rod to compact the hydride uniformly. The tube was then suspended by a thread fastened to one of the balance pans, and the change in weight of the sample for various magnetic field strengths was measured. It was not possible with the existing apparatus to

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[1] Based in part on the Ph.D. dissertation of K. I. Hardcastle, University of Southern California, Aug 1961.

[2] W. L. Korst and J. C. Warf, *Acta Cryst.*, **9**, 452 (1956).

[3] J. C. Warf and K. I. Hardcastle, *J. Am. Chem. Soc.*, **83**, 2206 (1961).

[4] K. I. Hardcastle and J. C. Warf, *Inorg. Chem.*, **5**, 1728 (1966).

[5] I. B. Johns, "Laboratory Manual of Microchemistry," Burgess Publishing Co., Minneapolis, Minn., 1942, p 6.

[6] R. T. Milner and M. S. Sherman, *Ind. Eng. Chem., Anal. Ed.*, **8**, 331 (1936).

[7] W. L. Korst and J. C. Warf, *Inorg. Chem.*, **5**, 1719 (1966).

measure the susceptibility as a function of temperature. The sample temperature was not critically controlled during the measurements, but was always 22–25°.

The increase in weight of each sample was measured for three or four different field strengths. The values calculated for the gram susceptibilities were found to be dependent upon the field strength. Indeed, the first sample of $YbH_{2.55}$ examined was found to be attracted sufficiently so as to rest against one of the pole pieces.

Results and Discussion

The ytterbium hydrides (H:Yb > 2) prepared from the high-pressure experiments were black powders. Subsequent stability experiments showed them to be essentially unaffected upon exposure to the atmosphere; *e.g.*, a 94-mg sample increased less than 1 mg after 7 months and did not noticeably change in appearance.

The Higher Hydride of Ytterbium.—The initial powder diffraction photographs of the hydrides removed from the bomb showed the major phase to have a face-centered-cubic unit cell (this is with respect to the Yb atoms only, and this holds true for all of the diffraction results presented in this paper) with a lattice constant of approximately 5.19 A.

The unit-cell constant for the fcc phase was determined from a number of X-ray diffraction photographs of specimens containing various proportions of hydrogen. The results are listed in Table I. The $YbH_{2.42}$ and $YbH_{2.04}$ were obtained by thermal decomposition of samples of $YbH_{2.55}$. The standard errors listed were obtained from the least-squares method and are all possibly low by a factor of 2.

TABLE I

UNIT-CELL CONSTANT OF THE HIGHER YTTERBIUM HYDRIDE

H:Yb	a, A
2.42	5.1948 ± 0.0007
2.2	5.1921 ± 0.0013
2.04 (annealed)	5.1914 ± 0.0006
2.04 (after 1 month)	5.1907 ± 0.0021
2.55	5.1914 ± 0.0005

a (av) = 5.1921 ± 0.0012 A

A set of weak diffraction lines in addition to those of orthorhombic YbH_2 also appeared in some of the photographs. These corresponded to those of Yb_2O_3 or YbN and presumably arose from the adventitious presence of air. Only in a single specimen, $YbH_{1.73}$, prepared for magnetic susceptibility measurements, was the presence of fcc ytterbium metal detected.

Face-Centered-Cubic Ytterbium Dihydride.—During the preparation of ytterbium hydrides in the composition range 2 < H:Yb < 2.5 by decomposing $YbH_{2.55}$, one specimen, $YbH_{2.42}$, was quenched from 450° to room temperature by removing the furnace and blowing air on the reaction tube. Its X-ray diffraction pattern showed the presence of two fcc phases in roughly equal amounts. One was identified as the previously described phase with a = 5.192 A, and the second fcc phase was found to have a lattice constant of approximately 5.25 A. An additional portion of $YbH_{2.55}$ was decomposed at 350–400° to $YbH_{2.04}$ and quenched; it also contained this novel fcc phase. The lattice constants from three separate films are listed in Table II.

TABLE II

UNIT-CELL CONSTANT OF FCC YbH_2

H:Yb	a, A
2.42	5.2537 ± 0.0010
2.04	5.2528 ± 0.0005
2.04 (after 1 month)	5.2532 ± 0.0012

a (av) = 5.2532 ± 0.0009 A

The possibility that this fcc phase with a = 5.253 A could be the nitride or a suboxide was considered. The lattice constant was much too large to be YbN, a = 4.785 A,[8] or even YbO, a = 4.86 A.[9] Moreover, a Kjeldahl analysis showed no detectable nitrogen.

The sample of $YbH_{2.04}$ was examined by X-ray diffraction immediately after preparation and then again after standing for 1 month at room temperature. After standing for this period, a small portion of the fcc phase (a = 5.25 A) had been converted to the fcc phase with a = 5.192 A and to orthorhombic YbH_2. It was also possible to effect complete conversion of this phase by annealing the original sample by slowly cooling from 400°. This new phase was thus metastable at lower temperatures with respect to orthorhombic YbH_2 and the original fcc phase. The experimental evidence showed that this new phase was an fcc modification of ytterbium dihydride. Additional evidence is presented below in the section on the magnetic susceptibility measurements.

Orthorhombic Ytterbium Dihydride.—During the course of these investigations, another determination of the cell constants of orthorhombic YbH_2 was made. The lattice constants were determined using Cohen's[10] method of least-squares from an X-ray diffraction photograph of $YbH_{1.96}$ and found to be: a = 5.904 A, b = 3.580 A, and c = 6.794 A. These agreed well with those obtained earlier:[2] a = 5.905 A, b = 3.561 A, and c = 6.790 A.

Magnetic Susceptibility Measurements.—The values obtained for the gram susceptibility, χ_g, of the various hydrides examined are listed in Table III. These are values of χ_g at infinite field strength (H_∞) obtained from an extrapolation of the χ_g *vs.* $1/H$ data.

TABLE III

MAGNETIC SUSCEPTIBILITY DATA

H:Yb	$10^6\chi_g$ for H_∞, cgs/g
2.55	23.6
2.42	19.4
2.04 (quenched)	5.0
2.04 (annealed)	3.3
1.90	2.0
1.90 (annealed)	1.87
1.88	1.50
1.96 (prepared from metal and hydrogen at <1 atm)	1.83

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(8) H. A. Eick, N. C. Baenziger, and L. Eyring, *J. Am. Chem. Soc.*, **78**, 5987 (1956).

(9) J. C. Archard and G. Tsoucaris, *Compt. Rend.*, **246**, 285 (1958).

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The data are shown graphically in Figure 1. The values of χ_g for $YbSO_4$,[11] $YbCl_2$,[12] Yb_2O_3,[11,13] and Yb[14] metal obtained by other investigators are included for reference. A reasonably smooth curve can be drawn through the plotted points, except for the unannealed sample of $YbH_{2.04}$ which contained a large proportion of the fcc ytterbium dihydride phase.

The quenched sample of composition $YbH_{2.04}$ in a sealed tube was examined. The susceptibility was measured before and after annealing the hydride by cooling from 450°. Ths susceptibility of the annealed $YbH_{2.04}$ was considerably smaller (Table III). An X-ray powder photograph showed that the annealing also resulted in the conversion of the fcc phase (a = 5.253 A) to a mixture of orthorhombic YbH_2 and the fcc phase (a = 5.192 A).

X-Ray evidence indicated that most of the ytterbium hydride examined in the magnetic susceptibility experiments contained traces of Yb_2O_3, a highly paramagnetic substance To attempt to correct for its presence, estimates as to the amount of oxide present were made by comparing powder photographs of the hydrides before and after addition of a few weight per cent of Yb_2O_3. It was estimated by this technique that the samples contained approximately 3 or 4% Yb_2O_3. Corrections of the data were then made using Wiedemann's additivity law

$$\chi = \chi_1 p_1 + \chi_2 p_2 + \ldots + \chi_n p_n$$

where χ is the susceptibility of the mixture and χ_n and p_n are susceptibilities and weight fractions, respectively, for the components. The corrected curve is shown as a dashed line in Figure 1. The samples of ytterbium hydride examined which had H:Yb equal approximately to 2 were still slightly paramagnetic, even after these corrections were made.

Susceptibility measurements by Klemm and Schüth[12] on $YbCl_2$ and by Hughes and Pearce[11] on $YbSO_4$ indicated that these compounds, supposedly containing only Yb^{2+} ions, were slightly paramagnetic. However, there is some doubt as to the purity of the rare earth compound used and also as to whether or not all the Yb^{3+} was reduced in the preparation of the $YbCl_2$ from Yb_2O_3. The measurements in this laboratory indicate that the orthorhombic ytterbium dihydride is slightly paramagnetic and that the susceptibilities of the stable hydrides with H:Yb above 2 but below 2.55 can be interpreted as being composed of mixtures of orthorhombic YbH_2 and a strongly paramagnetic higher hydride phase. Wallace, *et al.*,[15] have recently reported that measurements on YbH_2 showed that it was weakly paramagnetic and even possibly diamagnetic.

A future study is indicated from these results wherein the magnetic susceptibility of small pieces of very pure ytterbium metal could be measured during the absorption of hydrogen. A different method of measurement would be desirable, perhaps one similar to the Faraday procedure. There would be much less possibility of contamination of the sample since no transfer would be necessary, and also the range 0 < H:Yb < 2 could be studied. Attempts in this laboratory to prepare $YbH_{<1.7}$ from $YbH_{\sim 2}$ were unsuccessful. Thermal decomposition of $YbH_{1.7}$ resulted only in volatization of the ytterbium from the sample to form a mirror on the walls of the vessel. Low-temperature magnetic studies, to determine at which point ferro- or antiferromagnetism commences, would also be illuminating, as Wallace, *et al.*,[15] have shown with the hydrides of terbium and other metals.

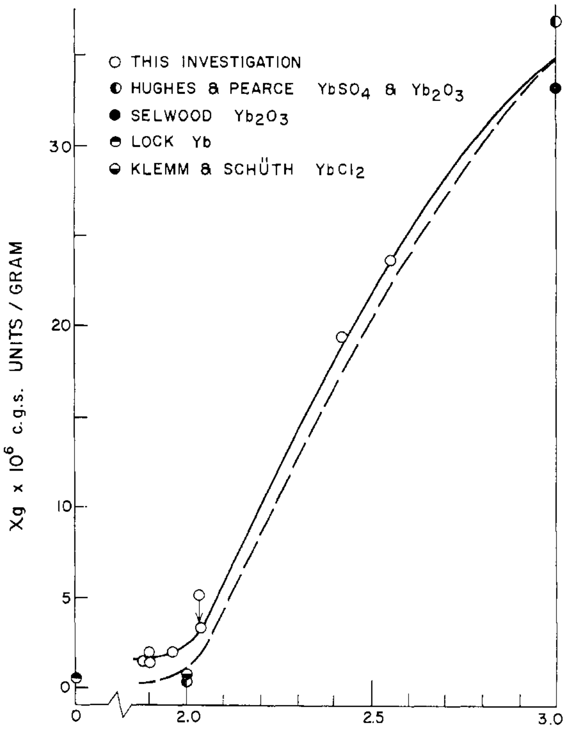

Figure 1.—Magnetic susceptibility *vs.* composition for the ytterbium–hydrogen system.

Infrared Absorption Studies.—To learn more about the higher hydrides of ytterbium and perhaps also to be able to distinguish between the structurally different types of hydrogen present, spectroscopic examination of samples of $YbH_{2.55}$, $YbH_{2.42}$, and $YbH_{1.90}$ was carried out using a Perkin-Elmer Infracord. The hydrides were finely pulverized in a drybox filled with CO_2, intimately mixed with Nujol mineral oil, and the mull was placed between KBr disks for examination.

The $YbH_{2.55}$ and $YbH_{2.42}$ spectra showed only a broad absorption region at the higher frequency end of the spectrum (Figure 2, upper curves). This was unenlightening except for comparison with the spectrum of a similarly examined sample of $LaH_{2.88}$ which was essentially the same. The broad absorption region is characteristic of semimetallic or conducting materials in which there are conduction electrons in the lattice to interact with the radiation over a large range of wavelengths.

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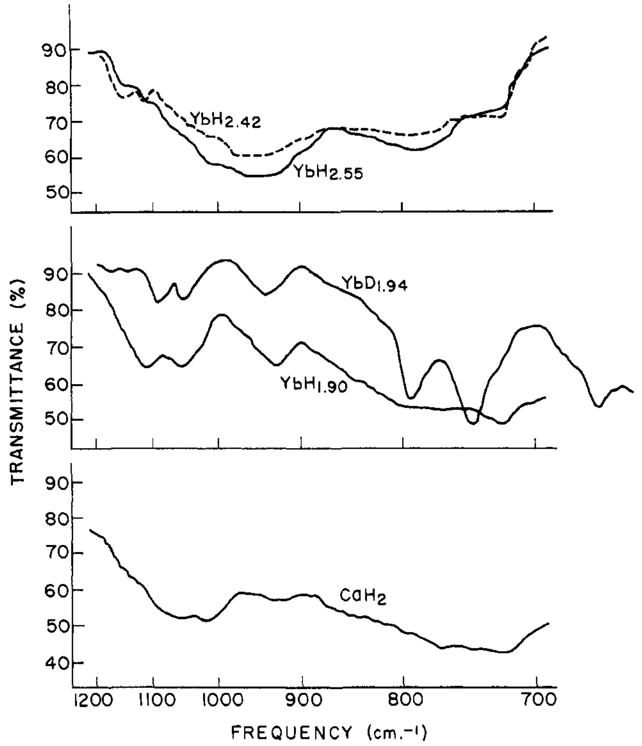

Figure 2.—Infrared spectra of CaH_2 and ytterbium hydrides.

The $YbH_{1.90}$ spectrum was of more interest in that three broad but definitely distinguishable absorption bands were observed (Figure 2, middle curve). These occurred at approximately 930, 1060, and 1115 cm^{-1}. They are qualitatively what one could expect from ytterbium–hydrogen stretching vibrations in an orthorhombic lattice (D_{2h}^{16}-Pnma). To check these interpretations a sample of CaH_2 which is isostructural with $YbH_{1.90}$ was examined (bottom curve). A similar spectrum was observed with the three broad absorption bands appearing at 920, 1030, and 1070 cm^{-1}.

A sample of orthorhombic $YbD_{1.94}$ (containing some YbH_2) was also examined using a Perkin-Elmer Model 421 to determine the frequency shifts due to replacement of the hydrogen atoms in the lattice with deuterium. The spectrum was similar to that observed for the $YbH_{1.90}$ except the absorption maxima occurred at 657, 751, and 794 cm^{-1}, respectively. These are all related by $\sqrt{2}$ to the observed maxima for the $YbH_{1.90}$ examined. This supports the hypothesis that these absorption maxima involve hydrogen and are probably three ytterbium–hydrogen stretching vibrations in the crystal lattice.

These results, although qualitative, do indicate that the fcc higher ytterbium hydride phase is structurally similar to the fcc rare earth trihydrides and that the ytterbium–hydrogen environments in the orthorhombic dihydride are different. A more exhaustive study is certainly indicated wherein, if one can correlate the actual absorption maxima with the hydrogen atoms in the lattice involved in these vibrations, one would be able to determine the directive-bond nature of ytterbium and perhaps any crystal field effect.

The Nature of the Hydrides of Ytterbium

An interpretation of the hydrides of ytterbium is as follows. Orthorhombic YbH_2 is made up essentially of Yb^{2+} and H^- ions, being isostructural with CaH_2. However, a small proportion of the metal ions lose an extra electron, and become Yb^{3+}, hence a slight paramagnetism. These electrons (*vide infra*) enter the conduction band, hence the metallicity (conductivity, wetting by mercury). On heating orthorhombic YbH_2 to 200–400°, it is transformed to a fcc modification, which can be quenched to a metastable compound (with respect to the orthorhombic form). This form also consists essentially of Yb^{2+} and H^- ions, arranged in a fluorite lattice, with a somewhat higher proportion of Yb^{3+} and magnetic susceptibility than in the case of the orthorhombic form.

An approximation of the cell constant of the cubic form of YbH_2 can be made by using 1.29 A as the radius of H^- and 1.05 A as the radius of Yb^{2+}. The latter value is computed from the cell constant of YbO (4.86 A, reported by Archard and Tsoucaris,[9] using 1.38 A for the radius of O^{2-}). These radii predict $a = 5.40$ A, somewhat greater than the observed 5.25 A. A high-temperature form of CaH_2 is known,[16] and we predict that this is fcc with a cell constant of approximately 5.32 A. Moreover, cubic modifications of SrH_2 and EuH_2 are expected, of cell constants 5.70 and 5.56 A, respectively. The high-temperature form of BaH_2 is evidently body-centered cubic.[17]

On heating fcc YbH_2 between 200 and 400° under elevated hydrogen pressures, a second unique fcc phase results. The coexistence of the two fcc phases is responsible for the plateaus in the phase diagram (Figure 9 of preceding paper[4]). The *P–T–C* data also suggest that at 280–300° a third type of solid phase appears; this might be a hexagonal, very hydrogen-deficient YbH_3. On cooling to room temperature, a mixture of YbH_2 and $YbH_{2.55}$ (each with fixed composition) always results, explaining the observed constancy of cell constants.

We regard $YbH_{2.55}$ as a substance in which the ytterbium ions are arranged in a face-centered-cubic lattice, with hydride ions in nearly all of the tetrahedral sites and in about 55% of the octahedral sites. It is considered that conduction electrons interconvert the two oxidation states of the metal, as is the case with a conducting oxide such as Fe_3O_4 (considering the iron atoms in octahedral sites only) above approximately 100°K, its transition temperature.[18] Gibb has suggested a similar phenomenon for TiH_2.[19] Accordingly, below a certain transition temperature, a relaxation time of perhaps 1 μsec for electron exchange between Yb(II) and Yb(III) might be detectable experimentally by esr, whereas above this temperature, we would be unable to distinguish between the ytterbium atoms

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which are formally Yb(II) and Yb(III). One difficulty in the proposed esr studies with $YbH_{2.55}$ might lie in finding an isostructural diamagnetic material with which to dilute it, if necessary, although lutetium hydride offers one possibility. Oxide systems offer a parallel.[20] In $YbH_{2.55}$, 55% of the ytterbium atoms are formally Yb(III) and the material exhibits a corresponding magnetic susceptibility.

The CaF_2–YF_3 system[21] resembles the LaH_2–LaH_3 and YbH_2–YbH_3 systems with regard to the occupation of the octahedral sites. These sites are filled at random in the LaH_2–LaH_3 instance, but in an ordered manner in the YbH_2–YbH_3 case (*vide infra*). Considering a composition $YbH_{2.500}$, half of the octahedral sites are filled, and a superstructure is possible whose unit cell consists of eight of the smaller unit cells with $a = 5.19$ A. Such a superstructure, containing hydride ions in every other octahedral site, would be detectable by neutron diffraction. It would appear that a necessary consequence of the existence of plateaus in the pressure–composition isotherms, for the region richer in hydrogen than YbH_2, is that the hydrogen-rich phase has the ordered superstructure. In $YbH_{2.55}$, the hydrogen atoms beyond $YbH_{2.50}$ probably enter octahedral sites at random. Neutron diffraction techniques might also provide evidence on the equivalence of the ytterbium atoms in $YbH_{2.55}$, as in the case of certain oxides.[22] Crystal field deformations resulting from the Yb(III) are expected to be negligible.

Assuming a single phase containing ytterbium of average oxidation number 2.5, the calculated lattice constant would be 5.18 A if average radii of Yb^{2+} (1.05 A) and Yb^{3+} (0.868 A) are used, compared with the observed 5.19 A. When a one-phase material above 320°, of composition $YbH_{2.2}$, for example, is cooled, it disproportionates into fcc YbH_2 and another phase richer in hydrogen. This second phase is $YbH_{2.25}$ at 300°, $YbH_{2.46}$ at 260°, and $YbH_{2.55}$ at 25°. This material is formed rather than a hydrogen-deficient hexagonal YbH_3 because the resonance effects generate thermodynamic stability, relative to YbH_3. In pure YbH_2 also, the metal ions are all identical through resonance, or exchange *via* conduction electrons.

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Americium(III) Perxenate[1]

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Americium perxenate has been prepared by precipitation from basic solutions of americium(III). The compound is orange and shows the characteristic absorption bands of Am(III) in the visible and near-infrared regions, as well as the characteristic infrared absorption at 650–680 cm^{-1} for the Xe–O vibration in perxenate. The compound is highly hydrated and has the stoichiometric composition $Am_4(XeO_6)_3 \cdot 40H_2O$. Its solubility in water is 4.6×10^{-5} *M*. The compound dissolves in acid to form Am(VI) and Am(V).

Introduction

Am(III) in aqueous solutions can be oxidized by strong oxidants to the penta- or hexavalent state. In acid solutions, the formal oxidation potentials are 1.75 v for Am(III)–Am(VI) and 1.83 v for Am(III)–Am(V).[2] The oxidation potentials in basic solutions are unknown, but americium(III) hydroxide in suspension is readily oxidized by hypochlorite to americium(IV) hydroxide.[3] Ozone and persulfate oxidize Am(III) in hydroxide suspensions and in carbonate solutions to the penta- and hexavalent states.[3,4] It is of interest to examine the action of the new powerful oxidation agent, sodium perxenate,[5] which is effective in acid, neutral, or basic solutions. In acid solutions, indeed, plutonium(III) has recently been found[6] to be oxidized to Pu(IV) by "xenic acid," *i.e.*, hydrated XeO_3, quite rapidly, and Pu(IV) can be further oxidized to Pu(VI). The normal oxidation potentials in 1 *M* acid are 0.91 v for Pu(III)–Pu(IV) and 1.05 v for Pu(IV)–Pu(VI).[7] Oxidation of actinide ions in basic solutions by perxenate has not yet been reported. Sodium perxenate[5] is a white crystalline powder which exists as an anhydrous salt or may contain up to eight

[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission, presented in part at the XXXVth meeting of the Israel Chemical Society.

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