of these guidelines for the prediction of new europium(II) oxide phases, providing the proposed phase has an Sr^{2+} analog and the lattice energy of the phase is favorable. In fact the lattice energy often favors the existence of a complex phase, as in $EuMoO_4$, $EuWO_4$, and various Eu–M–W–O phases, where it is sufficient to overcome unfavorable redox thermodynamics.

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Registry No. $Eu(Mg_{0.5}W_{0.5})O_3$, 53881-32-6; $Eu(Mn_{0.5}W_{0.5})O_3$, 53182-85-7; $Eu(Mg_{0.33}Ta_{0.67})O_3$, 51912-62-0; $Eu(Mg_{0.33}Nb_{0.67})O_3$, 53973-48-1; $Eu(Mn_{0.33}Ta_{0.67})O_3$, 51912-63-1; $Eu(Mn_{0.33}Nb_{0.67})O_3$, 53973-49-2; $Eu(Al_{0.5}Ta_{0.5})O_3$, 51846-03-8; $Eu(Ti_{0.5}Ta_{0.5})O_3$, 53973-50-5; $Eu(Ti_{0.5}Nb_{0.5})O_3$, 53992-02-2; $Eu(V_{0.5}Ta_{0.5})O_3$, 53973-51-6; $Eu(V_{0.5}Nb_{0.5})O_3$, 53973-52-7; $Eu(Cr_{0.5}Ta_{0.5})O_3$, 51912-44-8; $Eu(Cr_{0.5}Nb_{0.5})O_3$, 53973-53-8; $Sr(Ti_{0.5}Ta_{0.5})O_3$, 53992-01-1.

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Preparation and Some Properties of Ytterbium Carbide Hydrides

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Equilibria in the ytterbium–carbon–hydrogen system have been investigated for various carbon to metal ratios at 900° and 0.5 atm of hydrogen. Samples were prepared by reaction of the dihydride and graphite in molybdenum containers. Two ytterbium carbide hydride phases have been identified by X-ray diffraction and chemical analysis; hexagonal $YbC_{0.5}H$ ($a = 3.575 \pm 0.002$, $c = 5.786 \pm 0.004$ Å) and fcc $YbCH_{0.5}$ ($a = 4.974 \pm 0.001$ Å) are observed. Magnetic, electrical, and hydrolysis data have been obtained and employed in describing these phases on the basis of ionic models. Structures which account for the observed nonstoichiometry and phase equilibria of the carbide hydrides are proposed. In the presence of oxygen, metastable fcc products with lattice parameters in the range 4.85–4.96 Å have been observed between the $YbO_{0.5}C_{0.5}$ and $YbCH_{0.5}$ compositions; this quaternary phase appears to be the metal-rich carbide reported for the composition range $YbC_{0.30}$–$YbC_{0.65}$. Attempts to prepare the analogous carbide hydrides of europium were unsuccessful; however, the previously reported metal-rich europium carbide, EuC_x, has been identified as EuO.

Introduction

Several investigations of the ytterbium–carbon system have been described;[1-4] however, conflicting reports have appeared on the composition and properties of the most metal-rich carbide, the so-called hypocarbide. The existence of a nonstoichiometric fcc phase ($a = 4.993$ Å) near $YbC_{0.33}$ was first reported by Spedding, *et al.*,[1] who prepared their product by direct combination of the elements. By treating ytterbium dihydride with graphite, Lallement[2] also obtained an fcc phase of variable composition ($YbC_{0.3}$ to $YbC_{0.65}$) with lattice parameters which ranged from 4.88 to 4.96 Å at the carbon-rich and metal-rich boundaries, respectively. Haschke and Eick,[3] who investigated the composition range from Yb to YbC_2 by direct reaction of the elements, obtained a dimorphic phase near the $YbC_{0.5}$ composition; an ordered anti-$CdCl_2$-type rhombohedral Yb_2C phase ($a = 6.176$ Å, $\alpha = 33.33°$) was found to coexist with a disordered fcc $YbC_{0.5\pm z}$ phase ($a = 5.001$ Å) of variable composition. Laplace and Lorenzelli[4] repeated the procedures of Lallement and found a similar fcc phase with a between 4.85 and 4.97 Å. Their investigation was also extended to the europium–carbon system for which an analogous fcc phase ($a = 5.141$–5.145 Å) was observed. The noticeable differences between results obtained in the presence and absence of hydrogen led Haschke and Eick[3] to suggest that the phase reported by Lallement is a carbide hydride of variable composition.

In an effort to resolve the differences in the data for the metal-rich carbides and to investigate the possible existence of carbide hydrides of europium and ytterbium, an investigation of the phase equilibria in the metal–carbon–hydrogen systems of these elements was initiated.

Experimental Section

Preparative Procedures. Phase equilibria in the Yb–C–H system were examined at constant temperature and constant hydrogen pressure with various C:Yb ratios, x, according to eq 1. The dihydride

$$YbH_2(s) + xC(s) \rightarrow YbC_xH_y(s) + [(2-y)/2]H_2(g) \qquad (1)$$

was prepared from the elements (Yb, 99.9%, distilled, Rare Earth Research Corp.; H_2, prepurified, Matheson) by procedures similar to that described previously,[5] and oxygen-free samples were prepared by a vapor-transport procedure. Samples of YbH_2 or Yb metal were placed in a Mo tube (6.4-mm o.d. × 150 mm) under 0.5 atm of H_2. The dihydride was transported and single crystals were grown under a temperature gradient of 900–600°. The powdered dihydride was combined with finely divided graphite (spectrographic grade rod, Ultra Carbon) in the desired stoichiometric ratios; the components were mixed throughly and placed in reaction containers fashioned of 6.4-mm o.d. × 40-mm length molybdenum tubing. The capsules were welded at one end and were closed at the other with a snugly fitting plug which

Table I. Lattice Parameters for the Equilibrium Phases of the Yb System at 900° and 0.5 atm of H_2

C:Yb ratio	Condensed	Lattice parameters,[a] Å		
x	equilibrium phase	a	b	c
$x < 0.5$	Orth YbH_2	5.902 (7)	3.583 (3)	6.794 (8)
	Hex $YbC_{0.5}H$	3.577 (2)		5.773 (3)
$0.5 < x < 1.0$	Hex $YbC_{0.5}H$	3.578 (2)		5.797 (3)
	Fcc $YbCH_{0.5}$	4.963 (1)		
$x > 1.0$	Fcc $YbCH_{0.5}$	4.975 (1)		
	Hex C[b]			

[a] Uncertainties in the last digit appear in parentheses. [b] Graphite could not be detected directly by X-ray methods.

allowed communication with the atmosphere but minimized the loss of metal vapor during reaction. Samples with $0.3 < x < 2.0$ were heated for 2–10 hr at 900° in a nitrogen-trapped Vycor vacuum system (10^{-6} Torr residual pressure) which had been back-filled to 0.5 atm with hydrogen. The above procedures and conditions were employed for investigation of the europium system and for reactions involving stoichiometric addition of ytterbium or europium oxide to the respective dihydride plus carbon mixtures.

Samples prepared according to eq 1 were also allowed to react at hydrogen pressures other than 0.5 atm and with container materials other than molybdenum. Reaction capsules of both Mo and Ta were heated under He at a static pressure of 0.5 atm, and Ta capsules were heated in evacuated sealed quartz ampoules. Tantalum containers were constructed of 6.4-mm o.d. tubing and were crimped shut to restrict the loss of gaseous metal. Since hydrogen pressures varied as a function of gaseous diffusion rates for the Mo capsules and also as a function of the H:Ta ratio, *i.e.*, scavenger capacity of the container, for Ta capsules, hydrogen fugacities for these experiments are not known. During sealed-ampoule experiments in which the quantity of product hydrogen greatly exceeded the scavenger capacity of the Ta container, several glass ampoules exploded and use of this preparative method was discontinued.

All products were quenched from their reaction temperatures and removed to a glove box in which the recirculated nitrogen atmosphere was purged of both water and oxygen.

Characterization. Reaction products were analyzed by both chemical methods and powder X-ray diffraction procedures. Although changes in the initial C:Yb ratios from vaporization of metal were determined by mass loss of the samples during heating, the products were analyzed microchemically for metal, carbon, hydrogen, and oxygen. Samples (0.2–0.3 g) were ignited under a stream of high-purity oxygen at 950°; metal percentages were obtained from the oxide residue, while carbon and hydrogen contents were determined gravimetrically by collection of the product carbon dioxide and water on anhydrous magnesium perchlorate and Ascarite, respectively. Hydrothermally prepared lanthanum hydroxide carbonate, $LaOHCO_3$, was employed for calibration of the collection train. Oxygen percentages were determined by vaporization methods.[5] Unbound carbon contents were measured by collection of the acid-insoluble residues on aluminum oxide wool and subsequent ignition in the carbon analysis train. Powder X-ray diffraction patterns were obtained with a 114.6-mm diameter, forward-focusing Guinier-Haegg camera using Cu $K\alpha_1$ radiation and silicon (a = 5.43062 Å) as an internal standard. The flat-plate specimens were prepared by mounting the powdered samples on plastic tape and coating them with a thin layer of paraffin oil to prevent hydrolysis. During exposure, the diffraction chamber was maintained under dynamic vacuum. Relative intensities were estimated visually; lattice parameters were refined with the least-squares program of Lindqvist and Wengelin.[6]

Identification of carbon anions was attempted by vapor-phase hydrolysis in a vacuum line. The gaseous hydrocarbon products were separated from hydrogen and excess water and analyzed mass spectrometrically at 50–70 eV with an AEI Model 902 spectrometer.

Magnetic susceptibilities of samples sealed in glass tubes were measured by the Gouy method. Ytterbium sesquioxide with a median gram-susceptibility of 35×10^{-6} cgsu at room temperature[7,8] was employed as a reference material. Applicability of the Curie law was assumed for ytterbium.[9] Attempts to measure the temperature dependence of the susceptibility by the Faraday method were made but were discontinued after failure to prepare a sample container which would adequately prevent hydrolysis. Electrical resitivity measurements were made on polycrystalline samples pressed in Pyrex tubes between gold contact electrodes; samples of powdered graphite and silicon were employed as calibrating materials.

The vaporization behavior of selected product samples was investigated with molybdenum effusion cells at 700–750°. Solid residues were characterized by X-ray diffraction.

Results and Discussion

Ytterbium Carbide Hydrides. Preparative results obtained at various C:Yb ratios, x, show the existence of two intermediate phases at 900° and 0.5 atm of H_2. Monophasic products were obtained at the x = 0.5 and x = 1.0 compositions. The X-ray diffraction data for these materials are indexable on hexagonal and fcc symmetries, respectively. Elemental analysis of crystallographically pure hexagonal (a = 3.575 ± 0.002, c = 5.786 ± 0.004 Å) and fcc (a = 4.974 ± 0.001 Å) samples gave $YbC_{0.49\pm0.02}H_{1.05\pm0.09}$ and $YbC_{1.00\pm0.05}H_{0.47\pm0.08}$, respectively, which correspond closely with the compositions $YbC_{0.5}H$ and $YbCH_{0.5}$. The error limits are uncertainties in analysis and do not indicate composition limits of the phases. The observed two-phase fields and lattice parameters of the condensed equilibrium phases are presented in Table I; the X-ray data for the equilibrium carbide hydrides

Table II. Powder X-Ray Diffraction Data for Equilibrium Phases in the Yb–C–H system at 900° and 0.5 atm of H_2

Hexagonal $YbC_{0.5}H$				Face-centered cubic $YbCH_{0.5}$			
I[a]	hkl	d_{obsd},[b] Å	d_{obsd},[c] Å	I	hkl	d_{obsd},[d] Å	d_{obsd},[e] Å
w	001	5.793	5.804	s	111	2.866	2.873
m	100	3.098	3.098	m–s	200	2.481	2.489
m	002	2.893	2.902	m	220	1.754	1.759
vs	101	2.730	2.732	m	311	1.497	1.500
m–s	102	2.111	2.116	w	222	1.432	1.436
m–s	110	1.786	1.787	w	400	1.241	1.244
m	103	1.635	1.641	w–m	331	1.139	1.141
w	200	1.548	1.548	w–m	420	1.109	1.112
m	112	1.519	1.522	w–m	422	1.103	1.016
m	201	1.495	1.497				
w–m	202	1.364	1.367				
w	113	1.309	1.311				
m	203	1.206	1.208				
vw	210	Unobsd	1.170				
m–s	211	1.147	1.148				
m	212	1.086	1.087				
m	105	1.082	1.085				
w–m	300	1.032	1.033				
m	213	1.001	1.002				

[a] Key: w, weak; m, medium; s, strong; v, very. [b–e] The data are for the phase in equilibrium with (*b*) YbH_2, (*c*) $YbCH_{0.5}$, (*d*) $YbC_{0.5}H$, and (*e*) C, respectively.

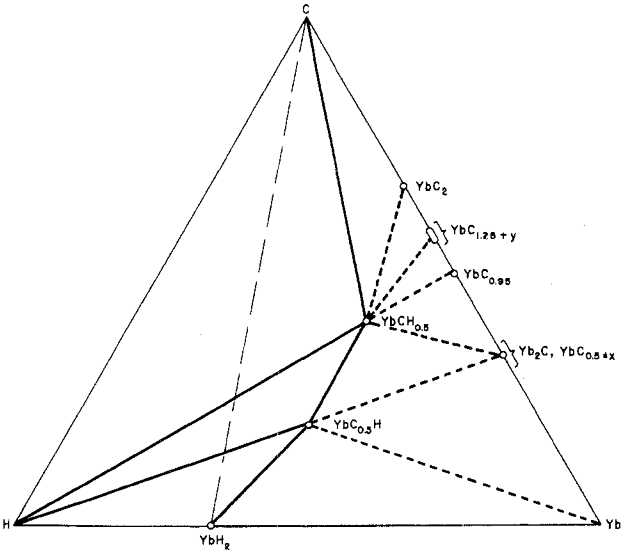

Figure 1. Phase diagram for the Yb–C–H system at 1173 K and 0.5 atm of hydrogen. (Equilibria in the binary Yb–C and Yb–H systems were obtained from ref 3 and 5, respectively.)

appear in Table II. For $x < 0.5$, all reflections were assignable either to $YbC_{0.5}H$ or to orthorhombic YbH_2.[10] For $x > 1.0$, only the diffraction pattern of the fcc carbide hydride was observed. The coexistence of graphite and $YbCH_{0.5}$ in this composition range was established by chemical and X-ray analysis of acid-insoluble residues. The diffraction data contain no unassignable reflections which might indicate either the presence of extraneous phases or the existence of substructure–superstructure relationships. The X-ray intensity data for $YbC_{0.5}H$ (Table II) are consistent with a NiAs-type structure, and the compound appears to belong to the same general class of hexagonal closest packed carbide hydrides as the analogous phases of Ti, Y, Zr, La, Hf, and Th.[11,12] The fcc $YbCH_{0.5}$ appears to be a new type of carbide hydride.

The crystallographic data which are presented for the equilibrium carbide hydrides in Tables I and II indicate that these phases have homogeneity ranges due to variable carbon content. Diffraction data for hexagonal $YbC_{0.5}H$ prepared under different hydrogen pressures show larger variations in lattice parameters with a ranging from 3.574 to 3.593 Å and c ranging from 5.723 to 5.852 Å. The largest values are observed under conditions of low hydrogen pressure, *i.e.*, Ta containers with static pressures of 0.5 atm of He. The rupture of quartz ampoules during heating indicates that hydrogen pressures may have approached 50 atm during some experiments. Composition limits for the $YbC_{0.5}H$ phase have not been determined, but data for the hexagonal thorium analog show variation from $ThC_{0.5}H_{0.9}$ to $ThC_{0.5}H_{1.0}$.[12] Under similar variations in hydrogen pressure, parameters for fcc $YbCH_{0.5}$ in equilibrium with hexagonal $YbC_{0.5}H$ varied slightly with observed values as low as a = 4.954 Å.

A section of an idealized Yb–C–H phase diagram for T = 1173 K and $P(H_2)$ = 0.5 atm is given in Figure 1. Dark solid lines show equilibrium-phase fields defined in this system; the dashed line connecting YbH_2 and C describes the experimental variation of x according to eq 1. Because the equilibrium conditions involve excess hydrogen, the phase fields to the right of the solid line connecting dihydride with the carbide hydrides and graphite are experimentally inaccessible. The dashed tie lines indicate a set of possible phase fields which are consistent with the phase rule and the assumption that additional carbide hydrides do not exist. In an alternate diagram, the tie line connecting $YbCH_{0.5}$ with $YbC_{0.5}$ is replaced by one connecting $YbC_{0.5}H$ with $YbC_{0.95}$. The free energy relationships are unknown, and attempts to clarify the hydrogen-deficient regions by vaporization of the carbide hydrides were unsuccessful. Both phases vaporize incongruently with the loss of metal and hydrogen; the residues gave diffuse X-ray patterns which could not be identified as those of known carbide hydride or carbide phases.

Properties and Reactions of the Carbide Hydrides. The ytterbium carbide hydride products are reactive polycrystalline materials. Hexagonal $YbC_{0.5}H$ is dark gray or black, and fcc $YbCH_{0.5}$ is a silver-gray material with a slight metallic luster. Both compounds react rapidly with mineral acids and hydrolyze readily in moist air; however, the fcc phase is noticeably more reactive than the hexagonal material.

The preparation of pure carbide hydrides is complicated by several factors. These include slow reaction of graphite and composition changes from the loss of metal by vaporization. The attainment of products which do not contain unreacted carbon requires the use of finely divided graphite and reaction times greater than 5 hr.

A major difficulty with preparation of the carbide hydrides and with the elucidation of the ternary system is the facile introduction of oxygen into the reaction products. X-Ray diffraction data for the equilibrium products prepared from dihydride which had not been purified by vapor transport show the coexistence of a second fcc phase (a = 4.85 ± 0.01 Å) with each of the diphasic mixtures listed in Table I. The ubiquitous nature of the phase and the close correspondence of its lattice parameter with that of $YbO_{0.5}C_{0.5}$ (a = 4.857 Å)[13] suggested the involvement of oxygen. At 1000° and under high vacuum, vaporization of the triphasic mixtures to constant mass in molybdenum boats produced a nonvolatile residue of C-type Yb_2O_3, which constituted 5–10 mass % of the samples. Although reaction of YbH_2 with the atmosphere is not visibly evident, the products from dihydride which had been exposed to air for extended periods contained significantly higher levels of oxygen contamination. The formation and stability of the oxide carbide at 900° and under 0.5 atm of H_2 were verified by stoichiometric reaction of the hydride, carbon, and the oxide according to eq 2. The condensed products included fcc

$$4YbH_2(s) + Yb_2O_3(s) + 3C(s) \rightarrow 3Yb_2OC(s) + 4H_2(g) \qquad (2)$$

$YbO_{0.5}C_{0.5}$ with a = 4.850 ± 0.002 Å and a small amount of C-type Yb_2O_3.

The formation of an unusual single-phase region has also been observed in the oxygen-containing systems. X-Ray diffraction data for carbide hydride compositions from reaction containers which had been exposed to air at 800–900° for several minutes after rupture of their quartz ampoules show the formation of fcc products with lattice parameters in the range bounded by those of $YbCH_{0.5}$ (a = 4.963 Å) and $YbC_{0.5}O_{0.5}$ (a = 4.850 Å). A peculiar phenomenon, the existence of continuous diffraction bands, has also been observed in the X-ray patterns of several products quenched after 2 hr at 900°. These bands, which vary in width as a result of shifts in the low-angle boundary of the band, correspond to a fcc pattern with a range of lattice parameters extending from 4.85 Å for the high-angle boundary to a maximum of 4.96 Å for the low-angle boundary. The appearance of these bands, which have been observed only in samples with oxygen contamination, and the formation of fcc products in air are consistent with the existence of miscibility between fcc $YbCH_{0.5}$ and fcc $YbO_{0.5}C_{0.5}$. However, extended heating of these intermediate products results in separation of the diffraction bands into lines near the maximum and minimum boundaries, a result which indicates that the products are nonequilibrium materials which disproportionate into $YbCH_{0.5}$ and $YbC_{0.5}O_{0.5}$ at equilibrium. The nonequilibrium nature of these products is further evidenced by hysteresis effects in their formation. Intermediate products have been observed only in reactions of dihydride samples with homogeneously

Table III. Magnetic Data for Various Ytterbium Phases

Compn	Lattice, type	Lattice parameter, Å *a*	*c*	μ,[a] BM
$YbC_{0.5}O_{0.5}$	Fcc	4.850		4.5 (1)
$YbC_{0.65}$[b]	Fcc	4.88		4
$YbCH_{0.5}$	Fcc	4.974		4.4 (1)
$YbC_{0.30}$[b]	Fcc	4.96		1.8
$YbC_{0.5}H$	Hex	3.577	5.785	4.5 (1)

[a] Uncertainties in the last digit appear in parentheses. [b] Data from ref 14.

dispersed oxygen contamination or in processes, *e.g.*, reaction with air, which allow for homogeneous dispersion of oxygen. Reaction of samples prepared from oxygen-contaminated dihydride which has been segregated into $YbH_2 + Yb_2O_3$ by extended annealing or prepared by addition of Yb_2O_3 to the carbide hydrides apparently proceeds directly to a mixture of $YbCH_{0.5}$ and $YbC_{0.5}O_{0.5}$ without formation of intermediate products. The continuous diffraction bands are indicative of continuous composition variation and apparently arise because of gradients in oxygen concentration across the sample particles. The close correspondence of the lattice parameter ranges for these metastable products with those of the $YbC_{0.30}$ to $YbC_{0.65}$ phase[2,4] suggests that the hypocarbide is a metastable quaternary oxide carbide hydride. Variation of the $YbCH_{0.5}$ lattice parameter presented in Table I may result in part from oxygen inclusion. Although gross miscibility between $YbC_{0.5}H$ and $YbO_{0.5}C_{0.5}$ apparently does not exist, the extent of oxygen solubility in the hexagonal phase and its effects on lattice parameter ranges is not known.

Magnetic data for the carbide hydride and oxide carbide phases and those reported for the ytterbium hypocarbide phase[14] appear in Table III. Since the expected magnetic moments of Yb(III) and Yb(II) are 4.5 and 0.0 BM, respectively,[9] ytterbium is clearly trivalent in $YbC_{0.5}H$, $YbCH_{0.5}$, and $YbO_{0.5}C_{0.5}$. Although the crystallographic data for the $YbCH_{0.5}$–$YbO_{0.5}C_{0.5}$ intermediate products correspond closely with those of the $YbC_{0.30}$–$YbC_{0.65}$ phase, the magnetic data do not. A possible explanation for these differences is that the hypocarbide samples were prepared at 1100° under argon and may have contained divalent ytterbium in the form of free metal or unreacted dihydride.

Mass spectrometric analyses indicate similar hydrolysis products for both $YbC_{0.5}H$ and $YbCH_{0.5}$. The spectra show major quantities of CH_4, C_2H_6 (including C_2H_4 and C_2H_2), and C_3H_8 (including C_3H_6 and C_3H_4); a trace of C_4H_{10} was also observed in the product from the hexagonal phase. The presence of a strong CH_4 parent peak shows that methanide ion is a major anionic species in both solids. Hydrocarbons containing three or four carbons apparently originated from association of lower species during the hydrolysis process. Interpretation of spectra and the identification of anions with multiple bonds are further complicated by the ready availability of hydrogen and the extensive protonation occurring during hydrolysis.

Proposals concerning the types of ionic species present in the carbide hydrides are possible by combination of the resistivity data with the analytical, magnetic, and hydrolysis results. An immeasurably large resistivity was found for the hexagonal phase, and a value of 10^{12} ohm cm was observed for the fcc phase. Although electrical measurements on pressed polycrystalline phases are of questionable reliability, neither of the phases appears to be highly metallic, and charge-balance restrictions may be applied. The data for hexagonal $Yb^{III}C_{0.5}H$ are consistent with the presence of methanide and hydride ions in a 1:2 ratio. The situation for fcc $Yb^{III}CH_{0.5}$ is more complicated. Stoichiometry and charge balance are most simply satisfied by a mixture of methanide, acetylide, and hydride ions in a 2:1:2 ratio. Identification of C_2H_2 as a direct-hydrolysis product has not been possible, but its occurrence in the more carbon-rich binary lanthanide carbides is well known. It is interesting to note that the simultaneous application of stoichiometry and charge restrictions for $YbC_{0.5}H$ forbids the occurrence of any carbide ion other than methanide.

The Europium System. Duplication of the preparative reaction with europium dihydride failed to produce analogous carbide hydrides; however, repetition of the procedures described by Laplace and Lorenzelli for the preparation of EuC_x[4] has led to its identification as EuO. Reaction of EuH_2–xC mixtures under vacuum proceeds with the loss of metal and hydrogen and the appearance of an fcc product (a = 5.143 ± 0.003 Å) even at $x = 0$. This result, the close correspondence of the reported lattice parameter range[4] with that of EuO (a = 5.1415–5.1437 Å),[15,16] and the reaction of EuH_2 with Eu_2O_3 to produce large quantities of the fcc product substantiate this conclusion. The failure to observe $Eu^{III}C_{0.5}H$ or $Eu^{III}CH_{0.5}$ phases is consistent with the high stability of divalent europium.

Conclusions

Reference to Figure 1 shows that $YbC_{0.5}H$ and $YbCH_{0.5}$ lie on lines of constant C:Yb ratio connecting known carbide compositions with hydrogen. These phase relationships suggest the possibility of preparing these and other carbide hydrides by hydrogen substitution into binary carbides. One interesting study would be the low-temperature hydrogenation of YbC_2, for which the expected product is YbC_2H, an acetylide hydride with the conduction electron bound as a hydride ion. If hydrogen substitution into the carbides occurs, structural similarities between the carbide and carbide hydride phases might be expected, and regions of nonstoichiometry might be observed.

Consideration of the structural relationships within the ytterbium system is instructive for explaining the wide occurrence and the properties of the hexagonal carbide hydrides and for predicting the existence of additional phases. Hexagonal $MC_{0.5}H$ phases are known for both lanthanum[14] and ytterbium and, with the exception of europium, probably exist across the lanthanide series. In addition, isomorphous $MC_{0.5}H$ phases are known for metals which have M(III) (M = Y, La) or M(IV) (M = Zr, Hf, Th) as their only stable valence state. Although these phases might be described as interstitial compounds, the data for the ytterbium phase are most consistent with an ionic model. Hydrogen in ytterbium dihydride is definitely anionic in nature.[9] For the $YbC_{0.5}H$ phase with a 2:1:2 Yb(III):methanide:hydride ratio, the anion to cation ratio is 1.5:1, and, therefore, the phase cannot exist in a simple NiAs-type structure. Two possibilities readily account for the hexagonal metal lattice indicated by the diffraction data. One involves hexagonal closest packing of anions, methanide plus hydride, with the metal ions randomly occupying two-thirds of the octahedral interstices. Numerous such metal-deficient NiAs-type phases with ordered metal vacancies are known for metal chalcogenide systems.[17] The second possibility is somewhat less pleasing from the standpoint of radius ratio considerations but is extremely attractive because of its usefulness in accounting for various experimental observations. In this model the metals occupy closest packed positions with half of the octahedral interstices occupied by methanide and half of the tetrahedral voids occupied by hydride, an assignment which is consistent with the tetrahedral-site preference of hydrogen.[18] This anion vacancy structure has been described for $TiC_{0.5}H$ and $ZrC_{0.5}H$ by Goretzki[19] using neutron diffraction. The existence of the hexagonal $MC_{0.5}H$ for both trivalent and tetravalent metals is compatible with this model if differences in electrical properties are considered. Presumably the compounds with M(III) are insulators, and those with M(IV) are conductors with the extra electron in the conduction band. The observations of Peterson and Rexer[12] indicate that $ThC_{0.5}H$ is metallic.

With the anion vacancy model, explanation of nonstoichiometry, compound formation, and structural relationships of the metal carbide hydrides is possible. In the hexagonal metal lattice, potential ionic processes include changes in the methanide to hydride ratio by ionic substitution, anion occupancy of available interstitial sites, and altervalent anion mechanisms such as acetylide replacement of methanide and hydrogen replacement of hydride. The first process, ionic substitution, appears to be operative in the thorium system;[12] at high H_2 pressures, a mixture of Th + $ThC_{0.5}H$ is unstable with respect to formation of $ThC_{0.33}H_{1.33}$ with hexagonal closest packed metals and apparent ordering of anion vacancies to give monoclinic symmetry.

Consideration of the second mechanism, occupancy of interstitials, suggests interesting correlations between the structures of dimorphic $YbC_{0.5}$[3] and fcc $ThC_{0.5}H_x$[20] and the hexagonal $MC_{0.5}H$ phases.[11,12,19] The stoichiometric M_2C phases of Y and Yb exist in ordered rhombohedral (anti-$CdCl_2$-type) lattices[3,21] which involve cubic closest packed metal and carbide layers with alternate anion layers vacant; the nonstoichiometric fcc modification is disordered with random occupancy of octahedral sites in all anion layers. With the fcc modification of $MC_{0.5}$ as a starting point, hydride occupancy of tetrahedral interstices leads directly to the fcc $ThC_{0.5}H_{1.12}$ structure investigated by Makovec and Ban,[20] who found that in this phase 50% of the octahedral sites are filled by carbon and 52% of the tetrahedral and 8% of the octahedral sites are occupied by hydrogen. Occupancy of the remaining octahedral and tetrahedral voids by hydrogen essentially accounts for the wide composition range of $ThC_{0.5}H_x$; the analogous process is presumably operative in the hexagonal phase. The fcc form of $ThC_{0.5}H$ is metastable and transforms irreversibly into the hexagonal modification above 380°. Preparation of the fcc carbide hydrides of Y and Yb should be possible by low-temperature hydrogenation of the fcc $MC_{0.5}$ phases.

The observed increase in the hexagonal c parameter with increased C:Yb ratio is consistent with an altervalent process similar to that proposed for composition variations in $YbC_{1.25+y}$.[13] In this process, acetylide substitution for methanide on the octahedral sites readily accounts for the expansion of the lattice with increasing mole fraction of carbon.

It is interesting to examine the structural possibilities of the fcc $YbCH_{0.5}$ phase and to consider its weak electrical conductivity within the scope of an ionic model. For the proposed methanide acetylide hydride, the anion to cation ratio is 1.25:1. The X-ray data and the observed miscibility of $YbCH_{0.5}$ with NaCl-type $YbO_{0.5}C_{0.5}$ indicate that the carbide hydride also has a NaCl-type structure. Carbide ions presumably occupy three-fourths of the octahedral sites, and hydride ions fill one-fourth of the tetrahedral holes. This model is similar to that proposed for the hexagonal carbide hydride, and the same processes for nonstoichiometry are expected to be operative; however, their electrical properties are different. The most plausible explanation for conductivity is thermal population of the conduction band by electrons from hydride ions, a process which leaves the lattice partially occupied by neutral hydrogen. This assignment is consistent with the uncertain nature of hydrogen, *i.e.*, ionic *vs.* interstitial, in these compounds and with the low conductivity which could correspond to a maximum of 0.5 e/formula unit.

The present results clearly demonstrate that extreme care must be exercised with the preparative procedures for the lanthanide carbides. Although some carbides have been successfully prepared by the reaction of the hydride with graphite,[22] the analogous reactions apparently do not proceed for ytterbium. Ytterbium dihydride, which vaporizes congruently to the gaseous elements,[5] does not disproportionate on heating, and the formation of carbide hydrides is expected in the presence of carbon. The involvement of oxygen in both the europium and ytterbium systems is consistent with the results of Busch and coworkers,[23] who have found that the commercially available lanthanide metals of 99.9% purity contain several mole per cent impurity in the form of dissolved gases.

The complexities of the lanthanide–carbon–hydrogen–oxygen systems have been demonstrated, and some of the discrepancies in the metal–carbon systems of europium and ytterbium have hopefully been resolved.

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Registry No. $YbC_{0.5}H$, 54083-40-8; $YbCH_{0.5}$, 54083-39-5; YbH_2, 13598-40-8; $YbC_{0.5}O_{0.5}$, 12539-69-4; H_2, 1333-74-0; C, 7440-44-0; Yb, 7440-64-4; graphite, 7782-42-5.

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