The Crystal Structure of the Deuterides of Ytterbium and Europium

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Ytterbium and europium have been found to form deuterides which are isostructural with the hydrides of the alkaline earth metals.

Introduction

X-ray powder photographs for the hydrides of lanthanum, cerium, and praseodymium were first reported by Rossi (1934). Dreyfus-Alain & Viallard (1953) have reported such photographs for lanthanum hydride. Holley, Mulford, Ellinger, Koehler & Zachariasen (1955) have reported the results of X-ray and neutron diffraction investigations of these hydrides, and in addition those of neodymium and samarium. All of these hydrides are face-centered cubic, and their formation is accompanied by an expansion in volume. Maximum compositions approaching MH_3 are attained. It has been found in this laboratory that the deuterides of ytterbium and europium are of a different nature.

Experimental

The ytterbium metal used was obtained through the courtesy of Dr F. H. Spedding, and its preparation was described by Daane, Dennison & Spedding (1953). It reacted with deuterium relatively slowly. The reaction was carried out on a quartz helix balance in a vacuum system, and in two experiments the maximum compositions attained were $YbD_{1.93}$ and $YbD_{1.98}$. A sample of somewhat lower deuterium content, which was annealed at approximately 540° C. for 8 hr. in a pyrex capillary, gave the most sharply defined pattern, and this sample was used for the structural determination.

Europium metal, prepared through the courtesy of Dr Spedding from salts graciously loaned by Mrs Herbert N. McCoy, was found to react similarly, attaining a maximum composition of $EuD_{1.95}$, as measured using a quartz fiber torsion balance.

Structure

The X-ray powder photograph for ytterbium deuteride was found to be similar to those for the alkaline earth metal hydrides (Zintl & Harder, 1935a). The same orthorhombic structure was assumed, and the lines were indexed considering the space group as *Pnma*,

with the origin at $\bar{1}$. With the metal atoms in positions $4(c)$, with $x = 0.240$ and $z = 0.110$, and provisional values of the reciprocal axial lengths, the intensities of all possible lines were calculated from the expression

$$I \propto |F|^2 p \, \frac{1+\cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

and indices were assigned to the lines observed. Some of the stronger lines of the body-centered cubic form of Yb_2O_3 were also present (Bommer, 1939). The axial lengths were determined by least squares to be as follows:

$$a = 5.871, \quad b = 3.561, \quad c = 6.763 \text{ Å}, \quad \text{each} \pm 0.005 \text{ Å}.$$

(λ for Cu $K\alpha$, 1.5418 Å; for lines with $\theta > 60°$, λ for Cu $K\alpha_1$, 1.5405 Å.)

The diameter of the europium deuteride sample was rather large, and few lines were observed at small values of θ using Cu radiation, because of absorption. More lines having smaller indices could be read on a film prepared using Mo radiation, though fewer lines could be read on the entire film than in the case of ytterbium deuteride, and accuracy of the cell constants is much less. These were found, using least squares, to be

$$a = 6.21, \quad b = 3.77, \quad c = 7.16 \text{ Å}, \quad \text{each} \pm 0.02 \text{ Å}.$$

(λ for Mo $K\alpha$, 0.7107 Å.)

Observed and calculated diffraction data for the two deuterides are presented in Table 1. Lines not observed have been omitted.

Discussion

The formation of dihydrides by ytterbium and europium is doubtless related to their electronic configurations, which make it possible for both these elements to exhibit divalent character in many compounds, besides the more stable trivalent character common to all the rare earth elements.

In contrast to the other rare earth metals, ytterbium and europium undergo contractions in volume in

forming the deuterides, of 13·5 and 12·5%, respectively. That the structure of these deuterides is the same as that of the alkaline earth metal hydrides also suggests that they may be predominantly ionic in character, rather than interstitial. This suggestion is further supported by the radii calculations which follow.

Zintl & Harder (1935a) calculated the average Sr–H distance to be 2·56 Å, having placed hydride ions in the largest holes. Use of Goldschmidt's value of 1·27 Å for the radius of Sr^{++} gave the radius of hydride ion as 1·29 Å. A similar calculation for metal–deuterium distances, and use of a value 0·01 Å smaller for the deuteride ion (Zintl & Harder, 1935b), gives radii for Yb^{++} and Eu^{++} of 1·07 and 1·21 Å, respectively. Senff & Klemm (1939) have stated that Yb^{++} should be considered as having approximately the same radius as Ca^{++}, namely Goldschmidt's value of 1·06 Å, on the basis of measurements of the lattice constants of the isostructural selenides and tellurides. Beck & Nowacki (1938) found EuS to be isostructural with the alkaline earth metal sulfides, with a cell dimension which gave the radius of Eu^{++} as 1·24 Å. This was confirmed by Klemm & Senff (1939), who studied the selenide and telluride, as well as the sulfide, and stated that the radius of Eu^{++} was approximately 0·03 Å less than that of Sr^{++}.

Table 1. *Observed and calculated diffraction data*

	Ytterbium deuteride				Europium deuteride		
hkl	$(\sin^2 \theta)_o$	$(\sin^2 \theta)_c$	I_o	I_c	I_o	$(\sin^2 \theta)_o$	$(\sin^2 \theta)_c$
011	0·0606	0·0599	m	480	m	0·01197	0·01135
200	0·0701	{ 0·0690	vs	{ 480	vs	0·01349	{ 0·01312
102		0·0692		945			0·01314
111	0·0779	0·0771	s	1000	s	0·01510	0·01463
211	0·1296	0·1288	m	326	w	0·02489	0·02447
013	0·1650	0·1638	m	214	—	—	—
113	0·1823	0·1811	w	119	m	0·03516	{ 0·03435
020	0·1884	0·1875	w	111			0·03555
302	0·2086	{ 0·2072	m	{ 180	w	0·03947	{ 0·03937
004		0·2079		85			0·03943
311	0·2156	0·2150	m	208	—	—	—
104	0·2262	0·2252	vvw	23	—	—	—
213	0·2339	0·2328	m	242	vw	0·04474	0·04419
220	0·2573	{ 0·2564	s	{ 5	s	0·04862	{ 0·04867
122		0·2567		260			0·04869
400	0·2778	{ 0·2759	m	{ 56	w	0·05313	{ 0·05247
204		0·2769		102			0·05255
313	0·3192	0·3190	w	42	—	—	—
411	0·3355	0·3357	w	66	—	—	—
015	0·3722	{ 0·3717	vvw	{ 7	—	—	—
223		0·3734		2	—	—	—
115	0·3891	0·3890	m	121	—	—	—
322	0·3952	{ 0·3946	m	{ 123	m	0·07457	{ 0·07492
024		0·3954		56			0·07498
124	0·4154	0·4126	vvw	17	—	—	—
413	0·4399	{ 0·4397	m	{ 82	w	0·08294	{ 0·08354
215		0·4407		11			0·08363
131	0·4514	0·4520	w	64	—	—	—
420	0·4641	{ 0·4633	m	{ 50	w	0·08771	{ 0·08802
224		0·4644		90			0·08810
502		⎧ 0·4830		⎧ 44			⎧ 0·09184
404	0·4833	⎨ 0·4838	w	⎨ 40	w	0·09234	⎨ 0·09190
106		⎩ 0·4850		⎩ 35			⎩ 0·09201
230		⎧ 0·4908		⎧ <1	—	—	—
511	0·4894	⎨ 0·4909	w	⎨ 53			
132		⎩ 0·4910		⎩ <1			
231	0·5034	0·5038	w	38	—	—	—
315	0·5275	0·5269	m	80	—	—	—
206	0·5375	{ 0·5368	w	{ 12	—	—	—
033		0·5388		34	—	—	—
133	0·5562	0·5560	vvw	20	—	—	—
331	0·5874	0·5900	w	48	—	—	—

Table 1 (cont.)

hkl	Ytterbium deuteride				Europium deuteride		
	$(\sin^2\theta)_o$	$(\sin^2\theta)_c$	I_o	I_c	I_o	$(\sin^2\theta)_o$	$(\sin^2\theta)_c$
233	0·6076	0·6077	w	61	—	—	—
600	0·6230	0·6207	w	17	—	—	—
306		0·6230		29	—	—	—
522		0·6705		70			0·1274
424	0·6697	0·6712	m	66	w	0·1268	0·1274
126		0·6725		58			0·1277
611	0·6841	0·6806	vw	29	—	—	—
017		0·6836		41	—	—	—
333	0·6951	0·6939	vvw	18	—	—	—
431	0·7094	0·7107	vw	32	—	—	—
226	0·7232	0·7242	vvw	24	—	—	—
406	0·7441	0·7436	vvw	12	—	—	—
040	0·7518	0·7487	w	21	—	—	—
217		0·7516		80	—	—	—
135	0·7619	0·7628	w	78	—	—	—
613	0·7806	0·7832	w	59	—	—	—
515	0·8002	0·8016	w	76	—	—	—
620		0·8068		41			0·1536
326	0·8085	0·8093	w	65	w	0·1533	0·1538
433		0·8133		77			0·1546
240	0·8154	0·8175	m	49	—	—	—
142		0·8178		96	—	—	—
531	0·8614	0·8644	vw	63	—	—	—
702	0·8920	0·8953	vw	53	—	—	—
506		0·8975		44			0·1707
208	0·8996	0·8994	m	36	w	0·1706	0·1709
711		0·9032		68			0·1720
342	0·9527	0·9555	s	205	—	—	—
044		0·9563		96	—	—	—
417	0·9569	0·9581	s	211	—	—	—
244	—	—	—	—	w	0·1946	0·1947

s: strong; m: medium; w: weak; v: very.

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