

A recent determination¹³ of the heat of formation of calcium oxide is in good agreement with the value listed by the National Bureau of Standards.¹² Taking an average of -151.85 kcal. mole⁻¹, the heat of formation of water as -57.80 kcal. mole⁻¹, and an average heat of dissociation of 26.06 kcal. mole⁻¹ gives the standard heat of formation at 298°K . of calcium hydroxide as -235.71 ± 0.10 kcal. mole⁻¹. With entropies of the elements

(13) E. J. Huber, Jr., and C. E. Holley, Jr., *J. Phys. Chem.*, **60**, 498 (1956).

listed by Stull and Sinke,¹⁴ the standard free energy of formation at 298°K . is -214.77 ± 0.10 kcal. mole⁻¹. The chemical thermodynamic properties from 298.15 to 1000°K . have been calculated using these selected values and are given in Table IV. These values lead to a calculated dissociation pressure of one atmosphere at 784°K .

(14) D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," Advances in Chemistry Series No. 18, American Chemical Society, 1956.

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Precise Lattice Parameters of Selected Rare Earth Tetra- and Hexa-borides¹

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RECEIVED APRIL 2, 1959

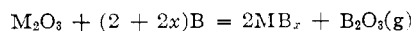
The refractory tetraborides and hexaborides of seven of the rare earth elements have been prepared by heating intimate mixtures of the sesquioxide and boron in a high vacuum in tantalum, molybdenum or graphite crucibles. The samples were analyzed by chemical and X-ray diffraction procedures. Precise lattice parameters, obtained by analytical extrapolation using a digital computer, indicate a pronounced difference between the tetraborides and the hexaborides in the trends of their lattice parameters. The former show a nearly linear decrease in lattice parameters through the series, while the latter show an irregular decrease. The results generally confirm earlier values of Post, Moskowitz and Glaser.

The rare earths form two groups of refractory borides. The tetraborides are gray and have a tetragonal structure belonging to space group $D_{4h}^5-P_4/mbm$. The hexaborides are blue with a cubic structure, space group $O_h^1-Pm\bar{3}m$.

Many investigators²⁻⁷ have examined various facets of the rare earth-boron systems. The crystal structure and lattice parameters of CeB_4 were reported by Zalkin and Templeton,³ while the lattice parameters of PrB_4 , Gd_2B_6 , SmB_6 and YbB_6 were reported by Post, *et al.*⁶ Neshpor and Samsonov⁷ have recently published lattice parameters for the hexa- and tetraborides of Dy, Ho and Lu which differ drastically from the values that would be predicted from the data of Post, *et al.*⁶ This investigation was undertaken to determine which of the reported values were correct and to establish more nearly accurate parameters for the compounds.

Materials.—99.9% pure Nd_2O_3 and Sm_2O_3 were obtained from Ames Laboratories, Ames, Iowa. Similar purity Sm, Gd, Tb, Dy, Ho, Er and Yb sesquioxides were obtained from Heavy Minerals Corporation, Chattanooga, Tennessee. The 99.11% boron containing 0.5% Fe and 0.2% C was obtained from Fairmont Chemical Company, Inc., Newark 5, New Jersey.

Preparation.—Samples were prepared in the form of wafers $1/8''$ to $1/4''$ high and $1/4''$ in diameter by pressing at about 500 p.s.i. mixed powders of sesquioxide and boron in the proportions to give MB_4 or MB_6 according to the equation



(1) Data included herein were presented at the 134th meeting of the American Chemical Society at Chicago, September, 1958.

(2) J. M. Lafferty, *J. Appl. Phys.*, **22**, 299 (1951).

(3) M. V. Stackelberg and F. Neumann, *Z. physik. Chem.*, **19B**, 314 (1932).

(4) P. Blum and F. Bertaut, *Acta Cryst.*, **7**, 81 (1954).

(5) A. Zalkin and D. H. Templeton, *ibid.*, **6**, 269 (1953).

(6) (a) B. Post, D. Moskowitz and F. W. Glaser, *THIS JOURNAL*, **78**, 1800 (1956); (b) E. J. Felten, I. Binder and B. Post, *ibid.*, **80**, 3479 (1958).

(7) (a) V. S. Neshpor and G. V. Samsonov, *Dopovidi Akad. Nauk Ukr. R.S.R.*, 478 (1957); (b) V. S. Neshpor and G. V. Samsonov, *Zhur. Fiz. Khim.*, **32**, 1328 (1958).

The wafers were heated separately by induction from 5 min. to 12 hr. at 1000 to 2100° .

Considerable care was taken to obtain pure samples; to reveal any possible reaction with crucible materials, graphite, Mo and Ta were used. The wafers were placed on edge to minimize contact. Samples obtained from all types of crucibles were identical in all respects, thus indicating freedom from contamination.

At temperatures of about 1400° a deposit which was primarily iron, an impurity in the boron, sublimed from the samples, indicating in effect that the boron probably could now be considered as greater than 99.6% pure. After the heating, the sample was carefully broken and examined visually and by X-ray diffraction for homogeneity. Many preparations were reheated when two-phase regions were apparent.

Although enough boron was added to form B_2O_3 , it is not known whether this was the actual species evolved at the temperatures of the reaction. Possibly some $B_2O_3(g)$ was formed, and, if so, the product was deficient in boron. Such a situation was not harmful because the excess sesquioxide could be removed easily.

An X-ray powder diffraction study made of the products which resulted when Sm_2O_3 and boron were heated at various temperatures in a graphite and a Mo crucible indicated that the reaction proceeded first to give SmB_6 plus an unknown phase "Y"; then phase "Y" subsequently reacted with SmB_6 to form SmB_4 . This phase was not the same as that reported by Post, *et al.*⁶

The tetraborides free from diffraction lines of other phases were prepared both in graphite and Ta despite unsuccessful previous attempts.⁶ With Gd, Tb, Dy, Ho and Er, one hr. at 1900 – 2100° was required, while with Nd and Sm, 2–12 hr. at 1600° was required. All attempts to produce YbB_4 yielded YbB_6 and Yb.

The hexaborides of Nd, Sm and Yb were prepared in 1–6 hr. at 1800 – 1900° , but for Gd, Tb, Dy and Ho, 15–60 min. at less than 1500° were satisfactory. Ho and Tb hexaboride were never prepared free from the tetraboride, and the results are necessarily for metal saturated material. Erbium hexaboride could not be prepared in any manner, perhaps because too much boron was lost during the heating. A new, unidentified phase appeared in preparations designed to give HoB_6 and ErB_6 .

X-Ray and Analytical Procedures.—When X-ray examination revealed that a pure sample had been prepared, it was ground carefully in an Alundum mortar and washed twice with concentrated HCl to remove the sesquioxide. Unreacted boron presumably was not removed. The incompletely reacted sample was quite hard, but the final

TABLE I
PRECISE LATTICE PARAMETERS FOR THE RARE EARTH BORIDES (Å.)

Rare earth	No. of samples	MB ₄ tetragonal parameters				MB ₆ cubic parameters		
		<i>a</i> ₀		<i>c</i> ₀		No. of samples	<i>a</i> ₀	Prev. wk.
		This work ±0.001	Prev. wk.	This work ±0.0005	Prev. wk.		This work ±0.0005	
La			7.30 ^b		4.17 ^b			4.153 ^b
Ce			7.205 ^a		4.090 ^a			4.141 ^c
Pr			7.20 ^b		4.11 ^b			4.130 ^b
Nd	4	7.219		4.1020		3	4.1260	4.128 ^c
Pm								
Sm	2	7.174	7.12 ^b	4.0696	4.07 ^b	3	4.1333	4.129 ^b
Eu								4.178 ^b
Gd	4	7.144	7.12 ^b	4.0479	4.05 ^b	3	4.1078	4.110 ^b
Tb	2	7.118		4.0286		1	4.1020	
Dy	3	7.101	7.23 ^c	4.0174	4.09 ^c	2	4.0976	4.13 ^c
Ho	3	7.086	7.15 ^c	4.0079	4.099 ^c	1	4.096 ^f	4.12 ^c
Er	5	7.071		3.9972				4.11 ^d
Tm								
Yb			7.01 ^b		4.00 ^b	2	4.1468	4.140 ^b
Lu			7.15 ^c		4.045 ^c			4.11 ^c

^a Zalkin and Templeton.⁵ ^b Post, *et al.*⁶ ^c Neshpor and Samsonov.⁷ ^d Work quoted in Kiessling.¹⁰ ^e Blum and Bertaute.⁴ ^f Obtained from least squares extrapolation against erf as described in text.

product was soft and easy to grind. The sample was dried and then divided for X-ray and chemical analysis. A portion was weighed, dissolved under reflux with dilute HNO₃, and analyzed gravimetrically for metal content. Boron content was determined spectrophotometrically using the method developed by Professor Reynolds.⁸ All analytical work was performed on a micro scale, duplicate analyses being run whenever possible.

The analyses were not excellent but verified the composition of the phases and gave values of the B/M ratio for revealing a variation of the lattice parameters with sample composition.

All X-ray powder diagrams were taken on a 114.6 mm. Debye-Scherrer powder camera using CuK_{α1} (K_{α1} = 1.54050; K_{α2} = 1.54434 Å.), Co (K_{α1} = 1.78890; K_{α2} = 1.79279 Å.), Fe (K_{α1} = 1.93597; K_{α2} = 1.93991 Å.), or Cr (K_{α1} = 2.28962; K_{α2} = 2.29352 Å.) radiation, whichever was necessary to give satisfactorily resolved lines of high quality in the back reflection region. Lattice parameters, with the exception of HoB₆, were obtained by a least squares extrapolation of the back reflection data according to the method of Hess.⁹ An IBM 650 digital computer equipped with floating point attachments was utilized to generate and solve the equations for both the tetragonal and cubic structures. The parameter for HoB₆ was obtained from an extrapolation against the function $(\text{erf})^{1/2}(\cos^2\theta/\theta + \cos^2\theta/\sin\theta)$ by a least squares technique. The standard error of the parameters was obtained from the least squares equations in all instances.

Results and Discussion.—The results of the lattice parameter measurements and computations are given in Table I along with the previously reported values. In the second and seventh columns are given the number of X-ray photographs of different preparations measured to obtain the results for the tetraborides and hexaborides, respectively. The third and fifth columns contain *a*₀ and *c*₀ for the tetragonal tetraborides, and the eighth contains *a*₀ for the cubic hexaborides as established by the present work. The values are for a temperature of about 23° and are not corrected for refraction. The other columns contain the previously reported values.

The computed standard errors were generally ±0.0003 for *a*₀ and ±0.0001 for *c*₀ in the tet-

ragonal systems and ±0.0002 for the cubic cases. The agreement between lattice parameters obtained for different samples of the same substance was not always as good as would be indicated by these calculated standard errors, probably because different individuals read the films; because, although the exposures were performed in an air-conditioned laboratory, the temperature of the specimen was not carefully controlled; and because the samples may have had slightly different compositions. Accordingly, the uncertainty reported is increased to ±0.001 for the tetragonal *a*₀ and to ±0.0005 for tetragonal *c*₀ and cubic *a*₀, thereby including practically all the observed values.

The results in general confirm the prior results of Post, *et al.*,⁶ but are in marked disagreement with those of Neshpor and Samsonov.⁷ A direct comparison of the results of Post, *et al.*, and the present ones for SmB₄, GdB₄, SmB₆, GdB₆ and YbB₆ shows that the agreement is within 0.01 Å. for tetragonal *c*₀ and hexaboride *a*₀. On *a*₀ for GdB₄ their value is 0.02 Å. lower than ours, but for SmB₄ their value is the same as theirs for GdB₄ and is considerably lower than ours, thus suggesting a misprint. The results of Neshpor and Samsonov⁷ are much higher than ours by about 0.03 Å. for the hexaborides, by 0.09 Å. for the tetragonal *c*₀ and 0.06–0.13 Å. for the tetragonal *a*₀, probably because their samples contained other elements.

The results show a pronounced difference in the behavior of the tetraborides and the hexaborides. Both tetragonal tetraboride parameters decrease nearly linearly with increasing atomic number. Superimposed on this trend is a slightly but significantly larger difference in the lattice parameters of the tetraborides between Gd and Tb than between other adjacent pairs. The differences show this effect to be attributable to Gd rather than Tb. On the other hand, the cubic hexaboride parameters show a much smaller over-all contraction with a slight rise at Sm and with a large rise at Eu and Yb superimposed.

(8) C. A. Reynolds, *Anal. Chem.*, **31**, 1102 (1959).

(9) J. B. Hess, *Acta Cryst.*, **4**, 209 (1951).

(10) R. Kiessling, *Acta Chem. Scand.*, **4**, 209 (1950).

Templeton and Dauben¹¹ used the lattice parameters of rare earth cubic sesquioxides and tetragonal oxychlorides to obtain a table of crystal radii for the trivalent rare earth ions. Their values show the same general smooth contraction as found here for the tetraborides, and the rate of contraction is the same. Post, *et al.*,⁶ have pointed out the similarity in the contraction, which is confirmed here, and they have suggested an "ionic" type of binding for the tetraborides.

Spedding, Daane and Hermann¹² have measured precise lattice parameters of the rare earth metals. The atomic volumes show a general decrease with abnormally high values for Eu and Yb and slightly high values for La, Gd and Lu. The slightly high value for GdB₄ may be associated with the slightly larger value of the parameter for Gd metal. The high value of the lattice parameter for YbB₆ when related to these results for the metals, sup-

(11) D. H. Templeton and C. H. Dauben, *THIS JOURNAL*, **76**, 5237 (1954).

(12) F. H. Spedding, A. H. Daane and K. W. Herrman, *Acta Cryst.*, **9**, 559 (1956).

ports the view of Post, *et al.*,⁶ that the hexaborides exhibit some of the characteristics of metallic binding. The hexaborides are known to be good conductors also.²

As Table I indicates, several preparations of some of the samples were made. The lattice parameter was not found to change significantly with the conditions of preparation, the crucible material or the B/M ratio of the sample. For example, the three GdB₆ samples were analyzed and were found to have B/Gd = 5.39, 5.89 and 7.70. Thus, the limits of solid solution for these phases apparently are small.

Acknowledgments.—The authors wish to thank the Atomic Energy Commission for partial support of this work; Professor Charles A. Reynolds, Jr., and Mr. Frederick J. Luedders for the analytical work; Miss Diane Kerr for measuring the films; and Professor F. H. Spedding and the Ames Laboratory for some of the samples.

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The Role of Hydrogen in Raney Nickel Catalysts

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RECEIVED JANUARY 10, 1959

The physical properties of two samples of Raney nickel catalysts have been studied. It was found that the hydrogen content was 45 to 100 cc./g. catalyst. The evolution of hydrogen was an exothermic reaction but involved no phase changes and was substantially complete at 400°. X-Ray measurements indicated the predominant phase was face-centered-cubic and was presumably an aluminum-nickel alloy containing for one preparation 3% and for the second 8% aluminum by weight. The surface area of these two catalysts was 76 and 63 m.²/g. and was not reduced by heat treatment below 250 to 300°. Measurements of density and magnetic susceptibility were carried out at room temperature as a function of hydrogen content. These data led to the picture that the hydrogen in Raney nickel is present as atoms in a substitutional solid solution.

Introduction

Raney nickel catalysts prepared by leaching out with alkali the Al in NiAl alloys^{1,2} are substantially different from those prepared by the reduction of nickel oxides. For example, Raney nickel catalysts contain hydrogen in quantities too great to be ascribable to either adsorption or solution.^{3,4,5} This hydrogen participates to an extent in hydrogenations⁶ over this catalyst and although it is lost on aging it can be partially restored at high pressures.⁷ In addition, removal of this hydrogen is accompanied by a decline in the catalytic activity.^{3,4} Clearly, to understand the nature of Raney nickel we must first understand the role of this hydrogen. In this research we have attempted to shed some light on this question through studies, employing surface area measurement, differential thermal

analysis, X-ray diffraction and magnetic and density measurements as a function of the amount of hydrogen evolved.

Experimental

Two samples of Raney nickel were studied. The first of these was a commercial sample, Davison sponge nickel, supplied by the Davison Chemical Company. This sample, D-1 was stored under water for about one year prior to the studies reported here and, consequently, was probably fairly stable during the course of the experiments. The other sample of Raney nickel was prepared according to the W-6 procedure of Adkins and Billica² as modified by Smith, *et al.*,³ except that it was stored under water after its preparation.

Both samples were analyzed for Ni and Al⁸ after drying *in vacuo* at about 400°. The D-1 sample contained 0.8% acid (HCl) insoluble material, 91.0% Ni and 8.0% Al. The W-6 sample contained 0.3% acid insoluble (HCl) material, 77.3% Ni and 13.24% Al, the remaining 9.2% presumably being combined oxygen. In the case of the D-1 sample it is apparent that the Al is essentially all present as metallic Al and that the analysis as stated is substantially correct. In the W-6 sample it appears that a large fraction of the Al is not present as metallic Al but as the oxide. If it is assumed that the W-6 catalyst consists only of Ni, Al and Al₂O₃, the values 77.3% Ni, 19.8% Al₂O₃ and 3.0% Al are consistent with the above analysis and in reasonable agreement with those reported by Ipatieff and Pines.^{9,10}

(8) H. H. Willard and N. K. Tang, *Ind. Eng. Chem., Anal. Ed.*, **9**, 357 (1957).

(9) V. N. Ipatieff and H. Pines, *THIS JOURNAL*, **72**, 5320 (1950).

(10) G. W. Watt and S. G. Parker (*ibid.*, **74**, 1103 (1952)), have

(1) R. Mazingo, *Org. Syntheses*, **21**, 15 (1941).

(2) H. Adkins and H. Billica, *THIS JOURNAL*, **70**, 695 (1948).

(3) H. A. Smith, H. J. Chadwell and S. S. Kirdis, *J. Phys. Chem.*, **59**, 820 (1955).

(4) L. K. Freidlein and N. I. Ziminova, *C. A.*, **45**, 1836^a, 5029^b, 6031^a (1951).

(5) E. Lieber and F. I. Morritz, *Advances in Catalysis*, **5**, 417 (1953).

(6) N. A. Khan, *THIS JOURNAL*, **74**, 3018 (1952).

(7) H. L. Littman and B. Dew-Hughes, Paper presented at the 132nd meeting of the ACS at New York, September 1957.