

Fig. 1.—Axial crystal field splitting of the configuration p^4 . The zero of energy is the free ion ground state 3P_2 .

population of the $^3\Pi_2$ and $^1\Sigma$ states. Then the three observed transitions at 15,500, 20,000, and 24,400 cm^{-1} might be assigned to the excited states $^1\Pi$, $^3\Sigma$, and $^1\Delta$. The numerical fit is rather poor and is particularly dubious in view of the fact that the spectra then would require a $^3P-^1D$ term splitting of 15,500 cm^{-1} , while the gas phase value is 10,650 cm^{-1} ; experience with transition metal ions indicates that the free ion term splittings are invariably lowered in the crystal field.

We conclude that the crystal field model does not completely account for the spectra unless the possibility of more than a single chemical species is admitted.

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On the Existence of Erbium, Thulium, and Lutetium Hexaborides

Sir:

The hexaborides of all the lanthanons (except promethium), together with some of their physical properties, have been reported.¹⁻⁴ In recent work in which relatively pure samples of the lanthanons or their compounds have been employed, one finds only isolated reports concerning the preparations of the hexaborides of erbium, thulium, and lutetium.⁵⁻⁹

(1) B. Post, D. Moskowitz, and F. W. Glaser, *J. Am. Chem. Soc.*, **78**, 1800 (1956).

(2) E. J. Felten, I. Binder, and B. Post, *ibid.*, **80**, 3479 (1958).

(3) G. V. Samsonov, *Usp. Khim.* **28**, 189 (1959); translated by F. Hilton, U.K.A.E.A. Research Group, Harwell AERE-Trans 849.

(4) H. A. Eick and P. W. Gilles, *J. Am. Chem. Soc.*, **81**, 5030 (1959).

(5) V. S. Neshpor and G. V. Samsonov, *Dopovidi Akad. Nauk Ukr. RSR*, 478 (1957).

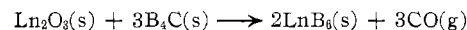
(6) V. S. Neshpor and G. V. Samsonov, *Zh. Fiz. Khim.*, **32**, 1328 (1958).

(7) G. V. Samsonov, Yu. B. Paderno, and T. I. Serebryakova, *Kristallografiya*, **4**, 542 (1959).

(8) N. N. Tvorogov, *Russ. J. Inorg. Chem.*, **4**, 890 (1959).

Furthermore, the data so far published as evidence for the preparation of these hexaborides have been minimal.

These three hexaborides were said to have been prepared by the high-temperature reaction of the lanthanon sesquioxide with boron carbide according to the equation



Earlier attempts by one of the authors to prepare erbium hexaboride had been unsuccessful and, as a result of these reports, efforts to prepare hexaborides of erbium, thulium, and lutetium in this Laboratory were intensified.

The respective sesquioxides were mixed with boron carbide in the molar ratio of 1:3, formed into pellets under a pressure greater than 3000 p.s.i., and then placed into a thoroughly out-gassed zirconium diboride crucible. The crucible was heated *in vacuo* to temperatures between 1100 and 1600°. The progress of the individual reactions was followed by quenching and observing the phases present after increasingly high temperatures had been attained. It was observed that the lanthanon boride phases grew in until finally no more carbon monoxide was produced and the sesquioxide phases had disappeared entirely. Invariably the predominant phase in the products of the complete reactions was the tetraboride, but, in addition, the face-centered cubic phase of the dodecaboride of the respective metal also was observed.

To assure that the presence of carbon was not affecting our results, similar reactions between the sesquioxides and elemental boron and the reactions of the metals with boron by the technique of arc-melting under an inert atmosphere were induced and resulted in the same two boride phases. Likewise, reactions conducted in a boron nitride crucible together with the arc-melting experiments demonstrated that our results were independent of the zirconium diboride crucible.

X-Ray diffraction methods were used to detect and identify the phases in the reaction products. In no case was even a trace of a cubic hexaboride phase detected. The d -values from a typical X-ray powder photograph are listed in Table I.

For a cubic hexaboride of erbium having $a_0 = 4.10$ Å, the three most intense reflections would have calculated d -values of 4.10, 2.90, and 2.37 Å. ($hkl = 100$, 110, and 111, respectively).

La Placa, Binder, and Post¹⁰ report that the stability of the dodecaborides of dysprosium, holmium, erbium, thulium, lutetium, and yttrium appears to be a function of the effective size of the metal atom; they were unable to prepare dodecaborides of those metals having atomic sizes larger than dysprosium or smaller than zirconium. This strongly suggests that a similar

(9) Yu. B. Paderno and G. V. Samsonov, *Zh. Strukt. Khim.*, **2**, 213 (1961).

(10) S. La Placa, I. Binder, and B. Post, *J. Inorg. Nucl. Chem.*, **18**, 113 (1960).

TABLE I

INTERPLANAR d -SPACINGS (\AA) OF AN ERBIUM SESQUIOXIDE-BORON CARBIDE REACTION PRODUCT									
d_{obsd}	ErB ₁₂ d_{calcd}	ErB ₁₂ (hkl)	ErB ₄ d_{calcd}	ErB ₄ (hkl)	d_{obsd}	ErB ₁₂ d_{calcd}	ErB ₁₂ (hkl)	ErB ₄ d_{calcd}	ErB ₄ (hkl)
5.019			5.000	110	1.670 ^a	1.673	420	1.666	330
4.326	4.321	111			1.577			1.576	411
4.011			4.000	001	1.539			1.538	331
3.750	3.742	200			1.527	1.528	422		
3.538			3.536	200	1.490			1.490	312
3.161			3.162	210	1.440	1.440	333/511		
2.646	2.646	220	2.648	201	1.334			1.333	431
2.479			2.480	211				1.332	003
2.259	2.257	311			1.324	1.323	440		
2.236			2.236	310	1.312			1.313	520
2.161	2.160	222						1.310	511
2.121			2.120	221	1.302			1.301	412
2.000			1.999	002	1.280			1.280	332
1.952			1.951	311	1.265	1.265	531		
1.871	1.871	400			1.248	1.247	600	1.247	203
1.762			1.761	321	1.212			1.213	530
1.741			1.740	202	1.184	1.183	620		
1.714	1.716	331	1.715	410	1.161			1.160	531
1.689			1.689	212	1.142	1.141	533		

^a Diffuse.

relationship between the stabilities of the hexaborides and the size of the metallic atom or ion might well exist.

Preliminary data seem to indicate that a correlation exists between the electronegativity of the lanthanon metals and the ease or difficulty encountered in the preparation of the corresponding hexaboride.

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Book Reviews

Regular Solutions. By JOEL H. HILDEBRAND, University of California, Berkeley, California, and ROBERT L. SCOTT, University of California, Los Angeles, California. Prentice-Hall, Inc., Englewood Cliffs, N. J. (Prentice-Hall International Series in Chemistry), 1962. x + 180 pp. 15 × 23 cm. Price, \$7.00.

Hildebrand published his first paper on solutions over four decades ago and since that time he and his collaborators have made outstanding contributions to our knowledge of solubility and of the properties of solutions. The results of the research from Hildebrand's laboratory have appeared in scientific journals and in three books, the most recent of which was entitled, "Solubility of Nonelectrolytes" (1950). The present monograph is a new book, quite different from the book written in 1950. The reader who compares the present volume with "Solubility of Nonelectrolytes" will find such topics as hydrogen bonding, high polymer solutions, and metallic solutions missing; the authors point out that the topics which are omitted are discussed adequately elsewhere.

The present volume, as the title states, is concerned only with regular solutions and is not concerned with the entire field of non-polar solutions. The authors define the term "regular solution" on p. 4 thus: "A regular solution is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged."

The monograph brings together under one cover the quantitative aspects of regular solutions. After a brief chapter explaining

the regular solution concept, a short chapter on thermodynamic relations follows. The next eight chapters of the monograph deal with the topics of entropy of mixing, heat of mixing, volume changes on mixing, regular solutions of gases in liquids, regular solutions of solids, liquid-liquid mixtures, the liquid state, and intermolecular forces. The last chapter gives an appraisal of the present state of the regular solution theory; the chapter focuses attention on the conclusions which are based on substantial evidence and those problems still awaiting answers. Appendices contain tables of data and a supplement to the subject of solubility parameters.

The reader is struck with the wisdom of the senior author as he writes out of a background of a half-century of research and teaching; one is always aware of the care taken by the authors in testing a postulate or theory against the experimental evidence and that they are not led astray by the elegance of theory alone. It is a pleasure to read a book written by authors who have been major contributors to the subject about which they write and who have the gift of presenting their material clearly and concisely.

The monograph is well organized and the topics are developed in a logical sequence. The printing is of high quality and there are relatively few typographical errors or defective type. On p. 30, spacings in the words "hexadecane" and "degree" are imperfect; the abbreviation for *Comptes rendus* (e.g., p. 12) is not in harmony with *Chemical Abstracts*; the abbreviation for *Chemical Reviews* is incorrect on p. 90. Figure 2.3 has no label on the ordinate. On p. 24, footnote number 13 is not referred to in the text. Hamann's name is misspelled in reference 15 on p. 74.