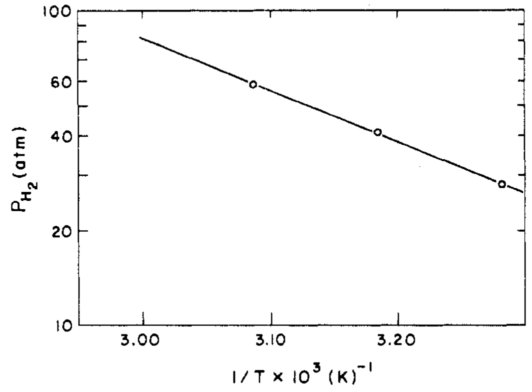

Figure 2. Semilogarithmic plot of P_{H_2} *vs.* reciprocal of the temperature in °K.

$GdCo_5$ have plateau pressures of the same order at room temperature,[3] and the lattice dimensions of the Y, Th, and Gd compounds are very close to each other. Lighter rare earth compounds have lower equilibrium pressure, and their lattice parameters are larger than those of $GdCo_5$, YCo_5, and $ThCo_5$.

Although these observations indicate that the stability of the hydride in a series (as, for example, the RCo_5-H series) is mainly controlled by the lattice dimensions, it is perhaps unwarranted to conclude that the mere size of the interstitial site available to hydrogen is the determining parameter. This undoubtedly would be the case were hydrogen anionic, but it seems unlikely that this is the situation since these intermetallics are primarily d transition metals. Hydrogen in these systems is probably not unlike that in the pure transition metals–*i.e.*, metallic.[6] The proton helps supply the field in which the delocalized electrons move. If so, the varying stability of the hydride in a series must be ascribed to the varying band structure of the parent intermetallic.

Acknowledgment. This work was assisted by a contract with the U. S. Atomic Energy Commission.

Registry No. YCo_5, 12017-71-9; $ThCo_5$, 12017-70-8; H_2, 1333-74-0.

(6) A. C. Switendick, *Ber. Bunsenges. Phys. Chem.*, **76**, 535 (1972).

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Solubility of Hydrogen in RCo_3 Compounds

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As pointed out in the preceding note, the RT_5 compounds (R is a rare earth metal and T is a d-transition metal Co or Ni) are prolific absorbers of hydrogen.[1] $LaNi_5$ is an example. It absorbs hydrogen at moderate pressure up to the composition represented by the formula $LaNi_5H_7$.[2] Buschow and van Mal have established[3] that $LaNi_5$ has a considerable range of compositional stability and, moreover, have shown that the equilibrium pressure of hydrogen diminishes as the composition of the phase deviates from ideal stoichiometry in the nickel-poor direction. This observation aroused our interest in RT_3 systems in regard to their capability as hydrogen host lattices and their potential for hydrogen storage.

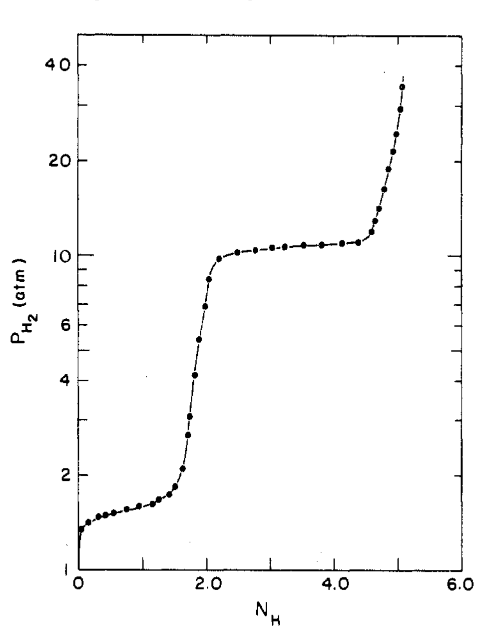

Figure 1. Pressure *vs.* composition for the $ErCo_3$-H system at 101°. Composition (N_H) is expressed as the gram-atoms of H per gram formula weight of $ErCo_3$.

From a structural point of view the RT_3 compounds, which are rhombohedral, can be regarded as being derived from the hexagonal RT_5 by an ordered replacement of T with R, *viz.*, $2RT_5 - T + R = 3RT_3$. The structural details are set forth in a number of places, for example in a publication by Lemaire and Paccard.[4] Thus, the RT_3 phases could be regarded as T-deficient RT_5 phases, and, hence, on the basis of the observations of Buschow and van Mal, one might expect the RCo_3 phases to be more receptive to hydrogen than their RCo_5 counterparts. The present work was undertaken to verify this point, to provide information as to the maximum solubility of H_2 in the RCo_3 phases and to obtain pressure-composition-temperature data for RCo_3-H_2 systems. To date, the study has been limited to the systems with R = Dy, Ho, and Er. $TmCo_3$ and $YbCo_3$ have not been included because the volatility of these rare earth metals and the difficulty in preparing the RCo_3 compound as a single-phase material. The lighter rare earths were not used because of the low equilibrium pressures expected for them. Attention has instead been focused on systems with hydrogen vapor pressures exceeding 1 atm since these would be the only ones of use for hydrogen storage.

The procedure used in preparing the intermetallic compounds was identical with that used in the earlier study.[5] The hydrogenation procedure was also identical. The hydrogen absorbed or evolved was measured by standard gasometric means,[2] *i.e.*, measuring the pressure of the gas in a known volume and at a fixed temperature. Results obtained for the $ErCo_3$-H_2 system (Figure 1) are typical. The shape of the curve suggests the existence of two hydride phases in addition to the terminal solid solution phase based upon

(1) F. A. Kuijpers, Ph.D. Thesis, Technische Hogeschool, Delft, 1973.

(2) J. H. N. van Vucht, F. A. Kuijpers, and H. C. A. M. Bruning, *Philips Res. Rep.*, **25**, 133 (1970).

(3) K. H. J. Buschow and H. H. van Mal, *J. Less-Common Metals*, **29**, 203 (1972).

(4) R. Lemaire and D. Paccard, *Bull. Soc. Fr. Mineral. Cristallogr.*, **92**, 9 (1969).

(5) T. Takeshita, W. E. Wallace, and R. S. Craig, *Inorg. Chem.*, **13**, 2282 (1974).

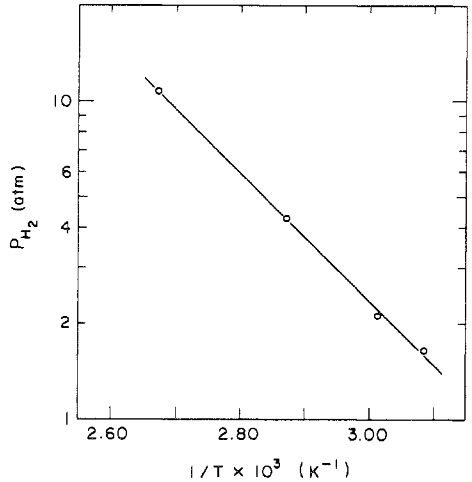

Figure 2. Semilogarithmic plot of P_{H_2} *vs.* reciprocal of the temperature in °K. The pressure plotted is that for the plateau between about $N_H = 2$ and $N_H = 4$ in Figure 1. Since the pressure is not constant in the "plateau region," the midpoint pressure is used.

Table I. Hydrogen Storage, H $cm^{-3} \times 10^{-22}$

Elemental H_2	
Gas (2000 lb/in.^{2}, 300°K)	0.65
Liquid	4.2
Solid	5.2
Metal hydrides	
$LaNi_5H_7$	~8.0
RCo_3H_5 (R = Dy, Ho, Er)	~7.2

$ErCo_3$. Details for the other two compounds will be published later in a full-length article. The equilibrium pressures between the two hydride phases are 3.0, 5.1, and 10.2 atm for $DyCo_3$, $HoCo_3$, and $ErCo_3$ at 100°, respectively. Thus, the trend of hydrogen-escaping tendency which has been observed in the RCo_5 and RNi_5 compounds, *i.e.*, increasing pressure with increasing atomic number of R at one temperature, is also observed in the RCo_3 compounds.

The solubility of hydrogen in RCo_3 was established by exposing these materials to H_2 gas at 40 atm at room temperature. The system produced corresponded to the formula RCo_3H_5.

Kuijpers and Loopstra[6] determined the structure of fully deuterated $PrCo_5$, $PrCo_5D_4$, using neutron diffraction techniques. D was found to reside in portions of the octahedral and tetrahedral interstices; two-thirds of the former and one-third of the latter were filled. Were all of these sites filled, the fully hydrogenated material would correspond to $PrCo_5D_9$. Thus, only four-ninths of the sites are occupied at attainable pressures. In the RCo_3 phases complete hydrogenation, if hydrogen were confined to the tetrahedral and octahedral sites, would give RCo_3H_6. Subject to this assumption the available sites in RCo_3 are five-sixths filled whereas in the RCo_5 phases (if the results for $PrCo_5$ are general) the sites are only four-ninths filled. This higher fractional occupancy supports the initial supposition that the RCo_3 are better hosts for hydrogen than their RCo_5 counterparts.

There is linearity when $\log P_{eq}$ for the $ErCo_3$-H system is plotted against $1/T$ (Figure 2) corresponding to the expression

$$\log P(\text{atm}) = 5.67 - 2013/T$$

The heat of reaction corresponding with the slope in Figure 2 is −9.2 kcal/mol of H_2. This is somewhat more exothermal than the process for the RCo_5 systems, again indicating that RCo_3 is a better host for H_2 than RCo_5.

In Table I the hydrogen storage capability of the RCo_3 compounds is compared with that of $LaNi_5$. Also included are data for hydrogen in solid, liquid, and gaseous forms.

Acknowledgment. This work was assisted by a contract with the U. S. Atomic Energy Commission.

Registry No. $DyCo_3$, 12187-40-5; $HoCo_3$, 12140-00-0; $ErCo_3$, 12134-04-2; H_2, 1333-74-0.

(6) F. A. Kuijpers and B. O. Loopstra, *J. Phys. (Paris)*, 32, C1 (1971).

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Field Ion Mass Spectra of Boron Hydrides[1,2]

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Electron beam ionization of boron hydrides produces many fragments, and the parent ion minus two hydrogen atoms (p − 2) is often the highest mass which will yield a signal of significant intensity. Although parent ions are observable in hydrocarbon electron beam spectra, much fragmentation also occurs. In contrast, field ion spectra of hydrocarbons often consist of a parent ion signal only.[3,4] Consequently it was thought that this technique might be useful for obtaining simplified spectra of boron hydrides containing observable parent ion signals.

It is evident from the data in Tables I and II that parent ion signals of significant intensity can be obtained and fragmentation is clearly diminished. A feature not seen in the electron beam spectra is the presence of species with masses higher than the parent ion. These must result from ion-molecule reactions or proton-capture processes, effects which can readily occur under field ion conditions.[5] When interpreted in terms of ^{11}B, the heaviest mass in the B_4H_{10} spectrum is only p − 1. However, the parent ion at *m/e* 54 was seen sporadically and in the isotopic form $^{11}B_3{}^{10}B$ it would contribute to mass 53. The resolution at which the spectra were obtained (500 ppm) was lower than that necessary to identify monoisotopic signals (<200 ppm).

Calibration of the spectra in Table I was accomplished using acetone or bromobenzene as standards. Of the possible standards in the correct mass ranges, these were found to give the most reproducible signals. Bromobenzene had the added advantage of two isotopic parent ions for comparison. The "peak matching" technique allowed mass determination to the nearest whole mass number or better; the accuracy was dependent upon the degree of attendant "noise." Decrease or complete loss of sample signal intensity was observed for the spectra in Table II during calibration. This may have

(1) Support provided by NSF Grant GP-28928X.

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(3) J. Roboz, "Introduction to Mass Spectrometry Instrumentation and Techniques," Interscience, New York, N. Y., 1968.

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