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Hydrogen storage properties and characteristics of rare earth compounds

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Résumé. — Les caractéristiques des composés intermétalliques de terres rares qui absorbent suffisamment d'hydrogène pour présenter un intérêt pour le stockage de l'énergie sont passées en revue et l'état de la technologie de ces matériaux ainsi que leurs applications potentielles exposés. L'ensemble des propriétés nécessaires à un stockage efficace de l'énergie sont discutées. L'hydrogène apparaît de plus en plus comme étant un nouveau vecteur d'énergie avantageux, le stockage par les hydrures étant l'élément clé dans l'étude des systèmes. Plusieurs des applications actuelles ou prévues à court terme sont répertoriées. La contribution industrielle devient effective et promet de s'étendre. Les composés et alliages de terres rares jouent un rôle important dans cette évolution. Les critères de formation des hydrures sont décrits et les connaissances actuelles dans les tentatives de prévision mentionnées. Les terres rares par leurs possibilités d'ajustement et de modification des propriétés de stockage des composés intermétalliques et donc de l'hydrure offrent de grands espoirs. La corrélation établie dans notre laboratoire entre la dimension des trous interstitiels et la stabilité des hydrures a montré qu'elle était un moyen très utile et important dans ce domaine.

Abstract. — The characteristics of rare earth intermetallic compounds that absorb sufficient hydrogen to be of interest for energy storage purposes were surveyed, and the status of the materials technology and their application's potential reported. All of the properties pertinent to viable hydrogen energy storage are discussed. Hydrogen appears more and more to be an attractive alternative energy carrier with hydride storage as a key element in systems approaches. Some of the current and projected near-term applications are catalogued. Industrial participation is beginning to emerge and shows good potential for expansion. The rare earth compounds and alloys are playing an important role in this evolutionary process. The criteria of hydride formation are described, and the current knowledge of predictive approaches are outlined. The rare earths show promise in adjusting and modifying storage properties of intermetallic compounds that hydride. The interstitial hole size-stability correlation developed in our laboratories has demonstrated itself to be a very useful and important tool in this respect.

1. Introduction. — Hydrides of metals, inclusive of the alkali metals, the alkaline-earth metals, and the transition metals, have been known, investigated and used for industrial applications for scores of years in both commercial and government applications. Almost without exception, these metal hydrides were characterized by their highly stable condition. The uses of these hydrides ranged from reducing agents, generation of hydrogen with water, drying agents, deoxidation and desulfurization of molten ferrous metals, and high energy fuels. The most notable application was that for nuclear purposes.

More recently another class of hydrides emerged from studies during the latter 1960's at the Brookhaven National Laboratory [1, 2, 3] and at Philips [4, 5] in Eindhoven, The Netherlands. These hydrides have been termed less-stable hydrides, or *unstable* hydrides. They absorb and desorb hydrogen reversibly with rapid kinetics at ambient temperatures and at pressures slightly greater than ambient. The enthalpies of formation are low. They consist of one component metal systems in some cases, such as V or Nb, or, more commonly, they are binary metal systems of specific intermetallic compounds, such as Mg_2Ni , $FeTi$, or $LaNi_5$. Their hydrogen

occlusion characteristics are such that they make excellent storage media, having hydrogen densities approaching twice that of liquid hydrogen. They saturate to a range of about 1.5 to 4 weight percent hydrogen. They have stimulated many new applications and the development of an alternative energy approach employing hydrogen as a versatile and useful secondary fuel.

2. Discussion. — **2.1 GENERAL PREDICTIVE THEORIES.** — Since the discovery in the late 1960's of *unstable* hydrides and their hydrogen storage properties for energy applications, much progress has been made to elucidate their fundamental properties. Some of the more general criteria and patterns of formation are presented as follows (principally applicable to the transition metal intermetallic compound hydrides) :

1. It is necessary that at least one of the elemental components for binary or ternary intermetallic compounds be a stable hydride former.

2. The formation of an *unstable* hydride proceeds at relatively low temperatures (ambient and slightly

above). Thus, the appearance of a new crystal structure as a result of the hydrogen absorption is accompanied by very small diffusional changes in the positions of the metal atoms. The hydride structure is essentially derived from the intermetallic compound structure by sub-lattice movements of the metal atoms.

3. The binary metallic system acts more like a two- rather than three-component system when it absorbs hydrogen. As a result, the phase stability of the system may not be in its most favored thermodynamic configuration.

4. When the system is heated to an elevated temperature, the atoms are free to diffuse more readily. The ambient temperature hydride phase then tends to decompose into a more stable thermodynamic configuration. The formation of the hydride of the one component which is a stable hydride former is likely.

5. Many binary systems which contain more than one intermetallic compound demonstrate hydride stabilities of the respective compounds as a function of composition in proportion to the weighted average of stabilities of the elemental hydrides of the component metals. This phenomenon has been observed by various investigators such as Clinton *et al.* [6] in the Pr-Co system, Buschow *et al.* [7], in Th-base binary systems, and Busch *et al.* [8], in the La-Ni system. The best example is that of Reference [8] for the La-Ni-H system. A good linear plot of the heat of formation of hydrides of the respective hydride compounds : LaH_2 , $\text{La}_7\text{Ni}_3\text{H}_{19}$, $\text{LaNiH}_{3.9}$, and LaNi_5H_6 , as a function of increasing nickel composition was observed.

6. Along with the diluent effect on enthalpy-of-hydride-formation by the non-hydride former atoms in a binary series of intermetallic compounds, the saturation capacity (or H/M) is generally observed to decrease with increasing non-hydride former content. Examples of this effect are observed in references [6, 7] and [8].

7. It has been proposed that the number of available equivalent interstitial positions in the AB_n (where $n > 1$) intermetallic compound are involved in determining the total hydrogen saturation. The studies of Lakner *et al.* [9] are the best evidence for this. An additional third plateau for the LaCo_5 -H system was discovered by the application of ultra-high pressure (1 250 atm) bringing the stoichiometry to LaCo_5H_9 . The maximum number of equivalent interstitial positions is reported to be nine. Studies in our laboratory [10] also indicate a correlation of the saturation of AB_2 and AB_5 hydrides with the number of certain types of tetrahedral holes in the lattice. Also, the size of the A atom has been hypothesized as being determinative of hydrogen absorption capacity. This assumption stems from the model

of van Mal *et al.* [11] from which they formulate the *Rule of Reversed Stability*. This will be discussed more fully later. In the model for the formation of AB_nH_{2m} , a geometric configuration is required in which the hydrogen separates the A and B atoms. Thus, the larger the A atom, the more the number of H atoms is required to separate A and B atoms.

There are three additional predictive approaches which have been proposed with a more analytical basis from which one can arrive at relative stability or semi-quantitative stability information. These are as follows :

a) The Hildebrand-Scott solubility parameter was developed for the prediction of intermetallic compound hydride storage materials by Lawson *et al.* [12]. Lawson postulates that the solubility of one material, such as hydrogen, in another, such as an intermetallic compound, depends on the matching of their solubility parameters. He calculates the solubility parameter by means of the following equation :

$$\delta^2 = \frac{\Delta H_s - RT}{V}$$

where δ = the solubility parameter,
 ΔH_s = the heat of sublimation,
 V = the atomic volume,
 T = the absolute temperature,
 R = the gas constant.

Lawson calculates the solubility parameter (δ) of hydrogen by considering it a metal. He obtains reasonably good agreement between the δ of hydrogen and that of the currently more attractive compounds such as LaNi_5 and FeTi .

b) One of the best known predictive approaches is the Rule of Reversed Stability. This was developed by Miedema [13, 14, 15] and van Mal *et al.* [11]. It states that the more stable the intermetallic compound, the less stable is its hydride. It employs the heats of formation of the various components which contribute to formation of a ternary hydride. The heat of formation of a ternary hydride is obtained as follows :

$$\Delta H(\text{AB}_n\text{H}_{2m}) = \Delta H(\text{AH}_m) + \Delta H(\text{B}_n\text{H}_m) - \Delta H(\text{AB}_n).$$

The equation is applicable for any transition metal intermetallic compound, AB_n , with $n > 1$. This rule was developed initially for lanthanum compounds, AB_n , but it has been generalized and applies to the other transition metals as well. The model requires that the metal A form a stable binary hydride, as in the case of lanthanum. The rule is not only one which can be employed to screen candidate intermetallic compounds for the appropriate and desired stability range. It can also be employed for tailoring or adjust-

ing the pressure-composition plateaus to lesser or greater stability for a binary intermetallic compound by ternary additions to either component of the AB_n compound.

There are some other limitations to the rule. Thus, the first row transition metal compounds behave somewhat anomalously according to the reversed stability rule.

c) Another very useful predictive approach was developed by Lundin, Lynch, and Magee [16]. It can be applied to the screening of new compound candidates and for adjusting the stability of known compound hydrides to required specifications. The approach has been termed the size-stability correlation. The initial discovery of this effect in our laboratories many years ago [17] for pure elemental hydrides was first tested for these lesser stable hydrides in 1975 [18]. It was found to operate much more effectively for the *unstable* class of hydrides. The correlation more specifically states that the larger the interstitial hole size for hydrogen occupancy, the more stable is the compound. A separate correlation exists for each homologous series of compounds, each with the same structure type, AB_n , where $n \geq 1$. A plot of the logarithm of the pressure plateau at a consistent isotherm temperature *versus* the interstitial hole size yields a correlation line. Once established, this correlation line can be applied to adjust plateau pressures either up or down very conveniently with minor ternary metal alloy additions. The size of the metal solute atom addition can be smaller or larger than the A or B atom in the AB_n compound it replaces. This correspondingly adjusts the interstitial hole to a smaller or larger size, which results in the expected lesser or greater hydride stability, respectively. It has been the experience of the author that very few exceptions to this size-stability correlation have been noted. The original family of materials employed to develop this approach was the series of rare earth pentanickel and pentacobalt compounds. The correlation has also been quantitatively tested with AB intermetallic compounds of B2 type structures (TiFe, TiCo, TiNi and minor ternary solute additions) and AB_2 Laves phases. Qualitatively, it has been confirmed at our laboratory with many other structure types with a variety of stoichiometries. The size-stability correlation can be employed with several short cut modifications of the size factor. A good qualitative fit of the correlation can be had by substituting the atomic volume for interstitial hole size. The atomic volume can be conveniently calculated from the intermetallic compound lattice parameters. This approach has often been used for predictive screening studies in our laboratory, particularly when the structure is complex and the interstitial hole size calculation is difficult. It has likewise been employed by other investigators [19, 20, 21].

An even quicker technique which yields very good results is to employ the atomic size of the adatom

(solute atom) and compare it with the atomic size of the atom it is replacing, either partially or fully. For instance, the adatom can either fully replace the A or B atom in the compound, AB_n . If it is larger than A or B, the hydride is stabilized, and if it is smaller, the hydride is destabilized. In the case of the adatom partially replacing either A or B, the same stability correlation occurs. The adatom must be within the solubility limit so that the structure type does not change. This technique becomes more quantitative when one knows the stability (pressure plateau) from a specific isotherm of the compound. The advantage is that no lattice parameter data are required to make a prediction. One only needs a table of atomic sizes which is readily available from many texts or reference books.

The steep slope of the correlation line also is indicative of the sensitivity of these hydrides to minor changes in the size function. Different rare earths or solute additions thereto and different solute additions to replace the Ni will cause a rather large change in stability. The slope of the correlation line for the CsCl, AB compounds is even more steep. Certain solute additions can compound this sensitivity further. For instance, the addition of 0.5 or 1.0 atomic percent of aluminum to partially replace Ti in FeTi causes a distinct destabilization of the FeTi-hydrogen system. This modification is the only solute addition known to destabilize the hydride of FeTi and does so in a very powerful way. An alloy such as $FeTi_{0.98}Al_{0.02}$ will have a 25 °C first plateau at about 8 atm; and $FeTi_{0.99}Al_{0.01}$ at about 6 atm, compared to 3.75 atm for the FeTi first plateau [22]. No lattice or hole sizes parameters are required for the compound or its modification to make a prediction of the type of stability change.

Whether one uses the interstitial hole size, the atomic volume (based on lattice parameters) or the comparative atom size approach, the results are similar because all of them shrink or expand in proportion (to a good approximation). The interstitial hole size is felt to be the most satisfying, fundamentally, if one is sure of the type of occupancy. The B-rich, close-packed structures usually have about three types of tetrahedral interstitial holes; AB_3 , A_2B_2 , and B_4 . The B_4 hole is not expected to fill. Octahedral holes also have the possibility for filling, but from neutron diffraction data, the initial filling of tetrahedral holes is more likely for many intermetallic compound structure types. Sequential or even mixed filling of tetrahedral and octahedral holes has also been noted. The presence of two or more plateaus might also be attributable to sequential filling from one type of hole to another, but no correlation has been determined.

The correlation employing the interstitial hole size using the hard sphere model is an assumption, but probably not a bad assumption. One knows that the hydrogen is not a hard sphere nor are the metallic atoms which surround it. The fine details of stability

are better represented by the interstitial hole, because the filling of one of the types AB_3 , A_2B_2 , or the octahedral hole, will each present a different bonding characteristic. Actually, the hole type, the size, and the type of coordination are contributors to the bonding. Obviously, the geometric factor is not totally determinative of the stability since the electronic structure of metallic atoms and their interaction with each other and the hydrogen are also important.

Other effects such as residual mechanical strain or impurity content from interstitial contamination or from metallic impurities will cause minor stability changes because of the extreme sensitivity of the stability to hole size. Thus, different commercial sources of metal components, the type of or care in melting, the atmosphere and temperature of heat treatment, the residual strain from mechanical processing, and other processing variables in the history of handling these materials will cause small stability variations.

d) A more fundamental approach to predictive capability is the theoretical modeling of Switendek [23, 24]. Band structure calculations were employed for a series of the transition metal hydrides. He found that hydrogen contributes S-like states in a band at rather low energy levels below the Fermi level and d-band. The energy level of this band is determined by hydrogen-hydrogen separation. A small separation causes the band to increase in energy. A nominal distance of 2.1 Å or less of the H-H distance is thought to cause instability. The electrons associated with the hydrogen are not accepted if the band energy is too high. A large separation will result in a low lying band which can more readily be filled with the electron from the hydrogen. Thus, the hydrogen is accepted in the lattice. As the lattice fills with hydrogen, the spacing will decrease and the structure will saturate. The band calculations are difficult and have limited practical application to the screening of new hydride candidates.

e) Another rather cursory and still unreliable technique that has been proposed for prediction of total hydrogen saturation is that of electron concentration effects. Evidence does exist that the larger the electron-to-atom ratio for the compound, the less the total solubility for hydrogen. This effect was discussed earlier for the Pr-Co [6] and the La-Ni [8] systems. The early work of Pebler and Gulbransen [25] indicated the same relationship for Laves phases of Zr and the first row transition metals; V, Cr, Mn, Fe, and Co. Recent studies by Shaltiel *et al.* [26] on Laves phase intermetallic compounds of pseudobinary systems between $Zr(Co_xM_{1-x})_2$ and $Zr(Fe_xM_{1-x})_2$ where $M = V, Cr, \text{ and } Mn$ demonstrated that the hydrogen capacity decreased as a function of an increase of the 3d electron occupation across the 3d transition metal series.

f) Although not a stability or hydrogen absorption criteria, per se, a study by Lundin and Lynch [27] of the hysteresis effects observed in these *unstable* intermetallic compound hydrides is useful for understanding hysteresis in these systems. A model is proposed based on induced lattice strains during hydrogen absorption and its relief on desorption. The strain and its reversal cause a hysteresis in the interstitial hole size which can be correlated with the size-stability criterion. Hysteresis was proposed to be an irreversible process rather than just metastability. Using the relationship $\ln(P_2/P_1) = \text{constant}$ where P_2 is the absorption plateau pressure and P_1 is the desorption plateau pressure, for any one temperature, the hysteresis can be calculated for any other temperature within reasonable error.

2.2 PROPERTIES. — Many of the rare earth containing intermetallic compound systems have the ability to store large quantities of hydrogen. Nearly 60 atomic percent hydrogen, an N_H of hydrogen of 7.58 or a weight percent hydrogen of about 1.5 can be occluded in $LaNi_5$. The N_H represents an 30% increase in density of hydrogen in the hydride over liquid hydrogen. However, the density of $LaNi_5$ is rather high (8.25 g/cc). On a weight percent hydrogen basis, there are other hydrides which exceed that of $LaNi_5$ hydride, particularly the lightweight hydrides. Thus, where weight is not important, the rare earth (RE) Ni_5 -hydrides excel. One can begin to see from the above that the properties are important, and the hydride selection is based on the most optimum properties as dictated by the application. Many properties make up the composite of *best properties* for a certain application. These properties will be briefly enumerated in the subsequent discussions.

The properties of most importance are presented below (not necessarily in order of priority) :

1. Pressure - temperature - composition relationships.
2. Heat of formation of hydride.
3. Cost per unit of stored hydrogen.
4. Usable weight-percent hydrogen.
5. Density of hydride.
6. Kinetics of reaction in absorption and desorption.
7. Volume expansion on hydriding.
8. Hysteresis between absorption and desorption.
9. Contamination resistance.
10. Recyclability.
11. Safety.

The specific modifications of the $LaNi_5$ -H or $MM * Ni_5$ -H systems offer a large range of pressure-temperature-composition-relationships for a variety of applications. A thorough discussion of these types and their properties will not be made due to the limitations of scope of this paper. Only those which have commercial potential and whose family of

isotherms have been determined are to be considered. One is referred to the specific investigation (references are included) for further details. The individual types are listed below :

1. Ce-free, MMNi_5 [28].
2. $\text{Ca}_{1-x}\text{MM}_x\text{Ni}_5$ [29].
3. La- [30, 31] or $\text{MMNi}_{5-x}\text{Mn}_x$ [30].
4. $\text{Ca}_{1-x}\text{MM}_x\text{Ni}_{5-y}\text{Cu}_y$ [32].
5. La- [31, 33] or $\text{MMNi}_{5-x}\text{Al}_x$ [34].
6. $\text{MMNi}_{5-x}\text{Cu}_x$ [34].
7. $\text{MMNi}_{5-x}\text{Fe}_x$ [34].

The use of MM to replace La in selected systems can reduce the cost of the intermetallic compound considerably. The current price of La is about \$ 20/lb (\$ 44/kg), whereas MM is priced at about \$ 4/lb (\$ 8.93/kg). However, in some cases, only the LaNi_5 or some one of its modifications will have the required properties to match the application. Smaller cost savings will be realized on partial replacement of Ni by Mn, Cu, Al, and Fe when the properties are required.

The following table [34] presents the approximate costs, hydrogen capacities, stabilities at 25 °C of as-cast materials, and other pertinent information for the most commercially potential and available rare earth intermetallic compounds or their modifications.

2.3 APPLICATIONS. — The state-of-the-art of storage materials has reached the point where applications and hardware are beginning to evidence themselves in prototype systems. The storage of hydrogen as a hydride is a key link in the successful evaluation of the *Hydrogen Economy*. Certainly the rare-earth intermetallic compounds will make an integral and important contribution to the various applications that will be evolving. However, one cannot yet see a clear distinction in the role that the rare earth compounds will assume, since it is too early to anticipate trends. Currently for potential large scale uses FeTi-

base storage materials are predominating because of availability at the lowest cost. However, other smaller scale applications are currently being developed where rare earth compounds are employed due to certain more desirable properties.

The following list of applications and/or potential applications involving hydride storage is intended to give the reader a generalized compendium of the important hardware-, process-, or device-oriented uses.

3. Applications, potential and realized.

- Automobiles.
- Buses.
- Industrial Vehicles.
- Railroads.
- Storage of converted electrical off-peak energy from power plants.
 - Storage of converted wind, solar, or geothermal energy.
 - Storage of converted industrial waste heat energy.
 - Storage of feedstock for chemical, petrochemical, or other industrial uses.
- Fuel storage for industrial, home, farm or utility power applications.
 - Fuel storage for electrochemical systems.
 - Storage of hydrogen for and from coal gasification processes.
 - Storage for a power cycle working fluid.
 - Storage for fuel cell application.
 - Application for heat pumps for heating, air-conditioning, or refrigerative purposes.
 - Thermal compressor.
 - Chemical storage in solar power applications for home heating or air-conditioning.
 - Separation of hydrogen isotopes.
 - Hydrogen pump.
 - Source for high-purity hydrogen.
- Getters.

Table I.

Alloy	Density g/cm ³	Dissociation <i>P</i> at <i>H/M</i> = 0.5 atm	Wt % usable H ₂	Raw materials cost \$/g usable	
				\$/kg	H ₂
CeFree, MMNi_5	8.5	4.2	1.31	\$ 12.83	0.98
$\text{Ca}_7\text{MM}_{0.3}\text{Ni}_5$	7.2	3.8	1.11	4.98	0.45
$\text{MMNi}_{4.5}\text{Mn}_{0.5}$	—	4.3	1.15	5.77	0.50
$\text{MMNi}_{4.5}\text{Al}_{0.5}$	8.1	3.7	1.13	5.92	0.52
$\text{MMNi}_{3.5}\text{Cu}_{1.5}$	8.5	8.0	0.95	5.26	0.55
$\text{MMNi}_{4.0}\text{Fe}_{1.0}$	8.3	7.6	0.95	5.40	0.57
LaNi_5 (Present)	8.3	1.7	1.36	17.26	1.27
LaNi_5 (Future)	8.3	1.7	1.36	9.45	0.69
FeTi	6.5	4.2	1.24	3.05	0.25

References

- [1] REILLY, J. and WISWALL, R., *Inorg. Chem.* **6** (1967) 2220.
 [2] REILLY, J. and WISWALL, R., *Inorg. Chem.* **7** (1968) 2254.
 [3] REILLY, J. and WISWALL, R., *Inorg. Chem.* **9** (1970) 1678.
 [4] ZIJLSTRA, H. and WESTENDORP, F., *Solid State Commun.* **7** (1969) 857.
 [5] VAN VUCHT, J., KUIJPERS, F. and BRUNING, H., *Philips Res. Rep.* **25** (1970) 133.
 [6] CLINTON, J., BITTNER, H. and OESTERREICHER, H., *J. Less-Comm. Metals* **41** (1975) 187.
 [7] BUSCHOW, K., VAN MAL, H. and MIEDEMA, A., *J. Less-Comm. Metals* **42** (1975) 163.
 [8] BUSCH, G., SCHLAPBACH, L. and VON WALDKIRCH, Th., *Hydrides of Rare-Earth Nickel Compounds: Structure and Formation Enthalpies*, Proceedings Int. Symposium on Hydrides for Energy Storage, Geilo, Norway, August 1977.
 [9] LAKNER, J., STEWARD, S. and URIBE, F., Lawrence Livermore Laboratory, Dept. UCRL-52039 (1976).
 [10] LUNDIN, C., LYNCH, F. and MAGEE, C., 1st, 2nd and 3rd Quarterly Progress Reports, Denver Research Institute, Univ. of Denver, Contract No. 414771-S with Brookhaven Natl. Lab., 1977 and 1978.
 [11] VAN MAL, H., BUSCHOW, K. and MIEDEMA, A., *J. Less-Comm. Metals* **35** (1974) 65.
 [12] LAWSON, D., MILLER, C. and LANDEL, R., Proceedings 1st World Hydrogen Energy Conf., *A Simple Approach to Metal Hydride Alloy Optimization*, Miami Beach, Fla., 1976.
 [13] MIEDEMA, A., BOOM, R. and DE BOER, F., *J. Less-Comm. Metals* **41** (1975) 283; **45** (1976) 237; **46** (1976) 271.
 [14] MIEDEMA, A., DE BOER, F., CHATEL, P., *J. Phys. F* **3** (1973) 1558.
 [15] MIEDEMA, A., *J. Less-Comm. Metals* **32** (1973) 117; **46** (1976) 67.
 [16] LUNDIN, C., LYNCH, F. and MAGEE, C., *J. Less-Comm. Met.* **56** (1977) 19.
 [17] BECK, R., Denver Research Inst., Univ. of Denver, Report DRI 2059, AEC Contract 1962.
 [18] LUNDIN, C. and LYNCH, F., *Solid-State Hydrogen Storage Materials for Application to Energy Needs*, Denver Research Institute, Univ. of Denver, AFOSR-TR-76-1124, Final Report, Aug. 1976.
 [19] ACHARD, J., PERCHERON-GUEGAN, A., DIAZ, H., BRIANCOURT, F. and DEMANY, F., *Rare Earth Ternary Hydrides-Hydrogen Storage Applications*, Proc. Second Internatl. Congress on H₂ in Metals, Paper 1E12, Paris, 1977.
 [20] GRUEN, D., MENDELSON, M. and SHEFT, I., *Absorption of H₂ by the Intermetallics NdNi₅ and LaNi₅Cu and a Correlation of Cell Volume and Desorption Pressures*, Abstract No. 364, Proc. of Electrochem. Soc., Philadelphia, PA, 1977.
 [21] BUSCH, G., SCHLAPBACH, L. and SEILER, A., Proc. Int. Symp. on Hydrides for Energy Storage, Geilo, Norway, August 1977.
 [22] LUNDIN, C. and LYNCH, F., To be published.
 [23] SWITENDICK, A., *Solid State Commun.* **8** (1970) 1463.
 [24] SWITENDICK, A., *Int. J. of Quantum Chem.* **5** (1971) 459.
 [25] PEBLER, A. and GULBRANSEN, E., *Trans. AIME* **239** (1967) 1593.
 [26] SHALTIEL, D., JACOB, I. and DAVIDOV, D., *J. Less-Comm. Met.* **53** (1977) 117.
 [27] LUNDIN, C. E. and LYNCH, F. E., *A New Rationale for the Hysteresis Effects Observed in Metal-Hydrogen Systems*, Proceedings of International Symposium on Hydrides for Energy Storage, Geilo, Norway, Aug. 1977. To be published.
 [28] LUNDIN, C. and LYNCH, F., *Hysteresis Effects in Rare-Earth Research Conf.*, Oct. 1977, Ogelbay Park, West Va., Univ. of Pittsburgh. To be published (Plenum Press).
 [29] SANDROCK, G., *A New Family of Hydrogen Storage Alloys Based on the System, Nickel-Mischmetal-Calcium*, Proc. 12th IECEC, Vol. 1 (1977) 951.
 [30] LUNDIN, C. and LYNCH, F., *Modification of Hydriding Properties of AB₅ Type Hexagonal Alloys Through Mn Substitution*, Proc. Internatl. Conf. on Alternative Energy Sources, Miami Beach, FL, Dec. 1977. To be published.
 [31] PERCHERON-GUEGAN, A., ACHARD, J., SARRADIN, J. and BRONOEL, G., *Hydrogen Electrochemical Storage by Substituted LaNi₅ Compounds*, Proc. Internatl. Symposium on Hydrides for Energy Storage, Geilo, Norway, Aug. 1977. To be published.
 [32] SANDROCK, G., *A Survey of the Hydrogen Storage Properties of Ni-Cu-Mischmetal-Ca Alloys*, Proc. Internatl. Conf. on Alternative Energy Sources, Miami Beach FL, Dec. 1977. To be published.
 [33] MENDELSON, M., GRUEN, D. and DWIGHT, A., *Nature* **269** (1977) 45.
 [34] SANDROCK, G., *Development of Low Cost Nickel-Rare Earth Hydrides for Hydrogen Storage*, 2nd World Hydrogen Energy Conf., Zurich, Switzerland, Aug. 1978. To be published.