

HYDROGEN ABSORPTION AND MAGNETIC PROPERTIES OF INTERMETALLIC COMPOUNDS  
BASED ON 3d ELEMENTS

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**Abstract** - A review is given of the various types of changes in magnetic properties due to hydrogen absorption observed in certain groups of intermetallic compounds. These comprise compounds of 3d transition metals in which the second component is one of the strongly hydrogen attracting metals such as Ca, Y, the rare earths, Sc, Ti, Zr, Hf or Th. The changes in magnetic properties do not only entail increases or decreases in transition metal moment but also changes from Pauli paramagnetism to ferromagnetism as well as changes in the reverse direction. It is discussed to what extent these changes can be explained in terms of changes in 3d band occupation and changes in 3d band exchange splitting. Particular attention is given to the changes in  $^{57}\text{Fe}$  isomer shift observed in several Fe compounds.

INTRODUCTION

The metals of group II, IIIa and IVa of the periodic table have a strong affinity for hydrogen. The hydrogen concentration in the corresponding binary hydrides (for example  $\text{AH}_2$  with  $A = \text{Ca}, \text{Y}$  or  $\text{Zr}$ ) is rather high. Unfortunately the hydrogen, once absorbed, is difficult to remove again because of the very low equilibrium hydrogen pressure associated with the reaction  $\text{AH}_2 \rightleftharpoons A + \text{H}_2$ . This precludes most technological applications of these materials. The equilibrium pressure can be brought into a more convenient range by combining these elements with metals that have only a very small or no affinity for hydrogen, such as the 3d transition metals. Pressure-composition isotherms observed in two such intermetallic compounds are shown in Fig. 1.  $\text{LaNi}_5\text{-H}_2$  is an example of systems in which the  $\text{H}_2$  take-up leads only to a single hydride phase ( $\text{LaNi}_5\text{H}_6$ ). Hydrogen absorption in  $\text{HfNi}$  leads to two hydride phases, viz.  $\text{HfNiH}$  and  $\text{HfNiH}_3$ . The equilibrium pressures pertaining to  $\text{LaNi}_5 + 3\text{H}_2 \rightleftharpoons \text{LaNi}_5\text{H}_6$ ,  $2\text{HfNi} + \text{H}_2 \rightleftharpoons 3\text{HfNiH}$  and  $\text{HfNiH} + \text{H}_2 \rightleftharpoons \text{HfNiH}_3$  appear as plateaus in the graph. The equilibrium and also the H/M ratio of the corresponding hydrides are temperature-dependent. The number of intermetallic compounds formed by combining (A) the alkaline earths, the rare earths or metals like Sc, Y, Ti, Zr or Hf with (B) either Ni, Co, Fe or Mn is of the order of 500. The equilibrium  $\text{H}_2$  pressure associated with the various compounds ( $\text{AB}_n$ ) and the corresponding ternary hydrides comprises a considerable range, meeting the requirements of most technological applications. This is the more so since the  $\text{H}_2$  pressure can be tailored to a given application by means of pseudobinary compounds like  $(A_{1-x}A'_x)_nB$  or  $\text{AB}_{n-x}B'_x$ . Roughly speaking one could say that the entropy of the  $\text{H}_2$  gas is lost when the hydrogen is absorbed into the intermetallic compound. For this reason the entropy change  $\Delta S$  in the reaction  $\text{AB}_n + m\text{H}_2 \rightleftharpoons \text{AB}_n\text{H}_{2m}$  is more or less the same in all intermetallics ( $30 \pm 10$  cal/mole  $\text{H}_2$  at 300 K) and equal to the entropy of pure  $\text{H}_2$  gas at room temperature. Since the equilibrium pressure can be expressed by means of the van 't Hoff relation as  $\ln p_{\text{eq}} = -\Delta S/R + \Delta H/RT$ , this means that differences in the tendency of the relevant compounds to absorb  $\text{H}_2$  can largely be understood on the basis of differences in the formation enthalpies of the corresponding hydrides. By means of a simple model (1,2) values of  $\Delta H$  can be estimated and the corresponding equilibrium pressure predicted. For fixed B and n in  $\text{AB}_n$  the equilibrium pressure is expected to increase in the series La to Lu, becoming about equal for A = Ti and Hf but lower for A = Zr. For fixed A the equilibrium pressure decreases in the direction Ni to Mn and for fixed A and B it increases with increasing n. There is good agreement between the model predictions and experimental observations. As required by experiment, it also follows from the model that under not too high pressures and at room temperature most of the ternary hydrides ( $\text{AB}_n\text{H}_{2m}$ ) are metastable (2) and decompose into the corresponding binary hydrides  $\text{AH}_2$  (or  $\text{AH}_3$ ) and a B-richer compound  $\text{AB}_p$  ( $p > n$ ). If a B-richer compound  $\text{AB}_p$  does not occur in the A-B phase diagram, pure B metal will be formed instead. The decomposition reactions like  $\text{AB}_n\text{H}_{2m} \rightleftharpoons \text{AH}_2 + n\text{B} + (m-1)\text{H}_2$ , are thermally activated processes and can be largely avoided in most cases by performing the charging with  $\text{H}_2$  gas under carefully controlled conditions. The absorption of hydrogen gas is in most cases accompanied by marked changes in magnetic properties. A discussion of these changes is presented in this paper.

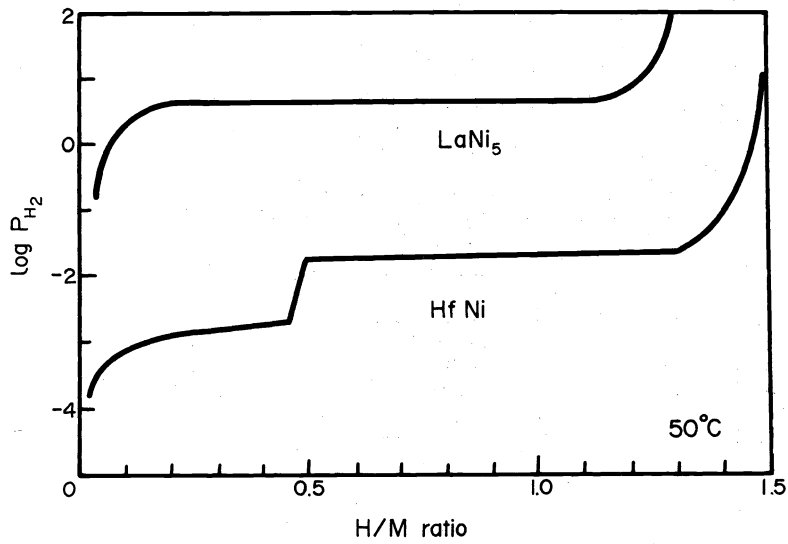


Fig. 1 Pressure composition isotherms of  $\text{LaNi}_5\text{H}_x$  and  $\text{HfNiH}_x$  at  $50^\circ\text{C}$ .

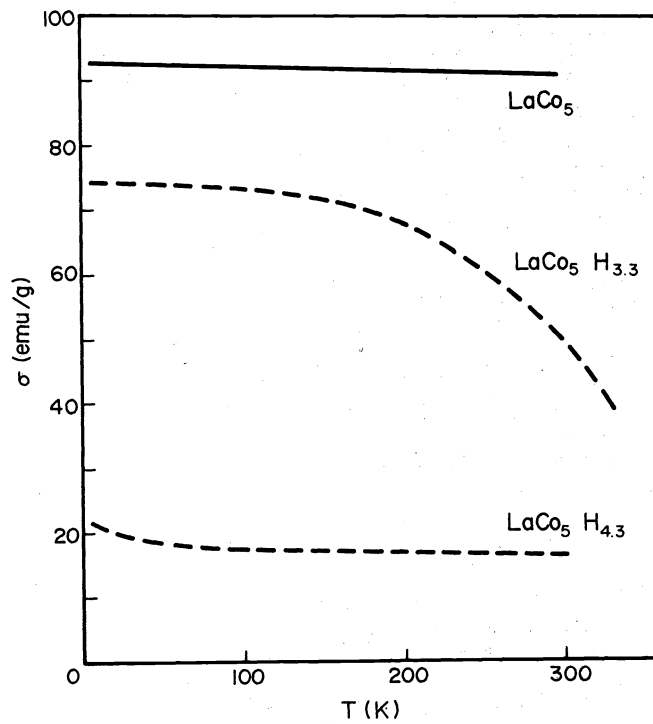


Fig. 2 Magnetic properties of  $\text{LaCo}_5$  before charging (full line) and after charging with  $\text{H}_2$  (Data are taken from Ref. 8).

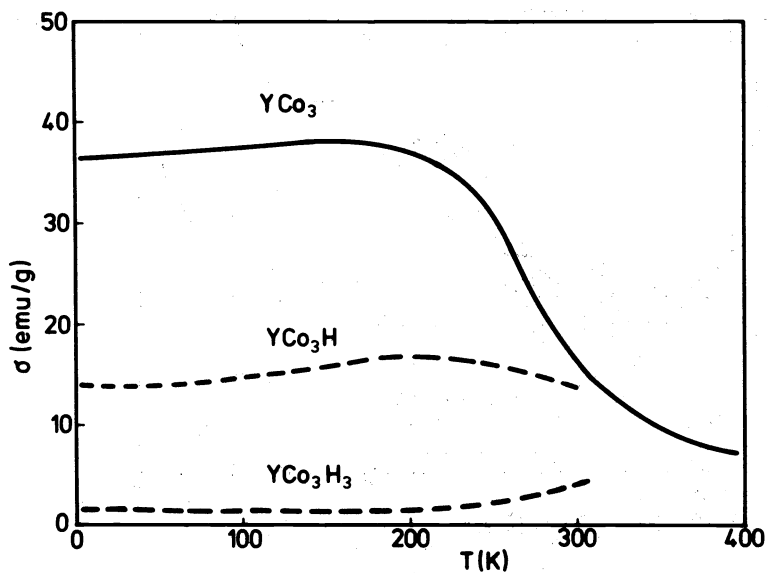


Fig. 3. Temperature dependence of the magnetization in  $\text{YCo}_3$  and two of its hydrides measured in a magnetic field of 9 kOe.

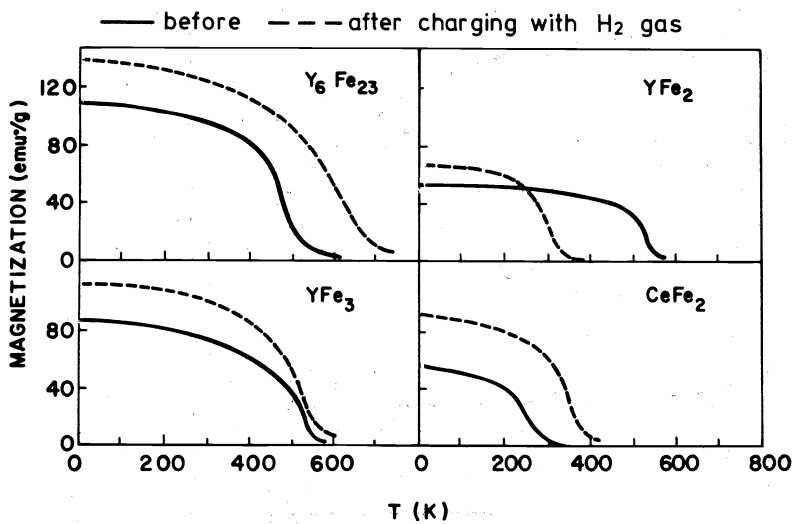


Fig. 4. Magnetic properties of various Fe compounds before (full lines) and after charging with hydrogen (broken lines). Details of the magnetic measurements are given in Refs. 11 and 16.

## MAGNETIC PROPERTIES

The main magnetic interaction in the uncharged intermetallic compounds is between the 3d moments (3). Next in importance comes the interaction between the 4f and 3d moments. The interaction between the 4f moments is rather weak. In order to be able to separate out changes in 3d electron magnetism we will first discuss results obtained upon  $H_2$  absorption in intermetallic compounds in which the 3d elements are combined with nonmagnetic metals like La, Y, Sc, Ti, Zr, Hf or Th. In a separate section we will discuss the changes observed in compounds where the partner element also carries a magnetic moment.

Ni compounds

Of these compounds, most of which are Pauli paramagnetic, only few examples were investigated. Magnetic measurements on the hydrides of  $La_7Ni_3$  and  $LaNi_5$  did not lead to quantitative information regarding the changes in 3d band magnetism (4). The first hydride was found to decompose into  $LaH_3$  and  $LaNi_5$  whereas the charging of  $LaNi_5$  usually leads to the presence of increasing amounts of Ni as a ferromagnetic impurity phase after repeated cycling (5). Busch and Schlapbach (6) were able to show, however, that the magnetic susceptibility had decreased after each charging operation, indicating a smaller susceptibility in  $LaNi_5H_6$  than in  $LaNi_5$ . This was explained in terms of a decreasing density of states. Similar conclusions were reached by Walsh et al., who performed EPR measurements on Gd doped  $LaNi_5H_6$  (7).

Co compounds

A relatively large number of the Co intermetallics forming a stable hydride are ferromagnetic. Neutron diffraction and bulk magnetic measurements in various hydrides of the  $RCO_5$  compounds show that the Co moment decreases upon  $H_2$ -absorption (8). The effect of  $H_2$  absorption in  $LaCo_5$  ( $T = 840$  K) is shown in Fig. 2. A reduction in Co moment upon hydrogen absorption has also been observed in compounds of lower Co content such as  $La_2Co_7$  ( $T = 450$  K) and  $YCo_3$  ( $T = 305$  K). Results of the magnetic measurements in  $YCo_2H_4$  are shown in Fig. 3. As in the case of  $LaCo_5H_3$ , the comparatively high equilibrium pressure hampers magnetic measurements in the hydrides at elevated temperatures. The compounds  $ZrCo$  and  $YCo_2$  are both Pauli paramagnetic. In these two compounds the absorption of  $H_2$  has been reported to lead to an increase of the magnetic susceptibility (9,10). These changes are of a different nature from those described above. Irvine and Harris (10) showed that charging  $ZrCo$  with hydrogen gas results in a structural change from cubic CsCl to orthorhombic CrB. After removal of the hydrogen, X-ray diffraction showed the reappearance of the cubic structure but with considerable deviations from perfect atomic order relative to the CsCl-type. Irvine and Harris therefore ascribe the increased susceptibility to the atomic disordering, leading to a certain fraction of Co atoms for which the number of nearest neighbour Co atoms has increased. In  $YCo_2$  as well, the increase in susceptibility after  $H_2$  absorption has been ascribed to atomic disordering (9) resulting from the metastable character of the ternary hydrides mentioned in the introduction. Disregarding these latter two examples, one may state that  $H_2$  absorption has the effect of lowering the Co moment in the intermetallic compounds. Some representative data have been collected in Table 1.

TABLE 1. Co moments in various intermetallics before and after charging with hydrogen.

Compound	$\mu_{Co} (\mu_B)$	Hydride	$\mu_{Co} (\mu_B)$
$LaCo_5$	1.5	$LaCo_5H_{3.3}$	1.1 (a)
		$LaCo_5H_{4.3}$	0.3 (a)
$La_2Co_7$	1.0	$La_2Co_7H_5$	0.6
$YCo_3$	0.8	$YCo_3H$	0.3
		$YCo_3H_3$	0.0

(a) Data taken from Ref. 8.

Fe compounds

Magnetic results on several rare earth iron compounds and their ternary hydrides are shown in Fig. 4. It is seen that in all compounds studied hydrogen absorption is accompanied by a substantial increase in Fe moment. In view of the results obtained with Co and Ni compounds this increase is rather surprising. The most drastic increase in Fe moment occurs in  $CeFe_2$ , where  $\mu_{Fe}$  changes from  $1.3 \mu_B/Fe$  to  $2.1 \mu_B/Fe$ . (Ce is not far from tetravalent and has no magnetic moment). Similar results were also obtained recently in  $ScFe_2$  where the formation of the hydride  $ScFe_2H_2$  leads to an increase in Fe moment from  $1.4 \mu_B/Fe$  to  $2.2 \mu_B/Fe$ , which is almost as high as in elemental Fe. An increase in Fe moment has been reported (11) in  $ThFe_3$  as well, while a change from Pauli paramagnetism to ferromagnetism has been observed in  $Th_7Fe_3$  (12) and  $Hf_2Fe$  (13). Representative data of the Fe moments in the compounds and their hydrides are given in Table 2.

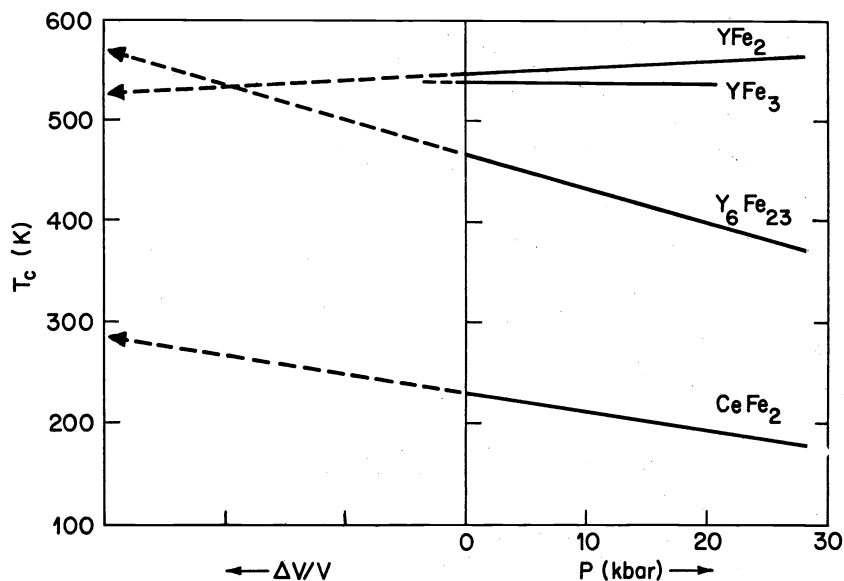


Fig. 5 Effect of external pressure on the Curie temperature of various Fe compounds.

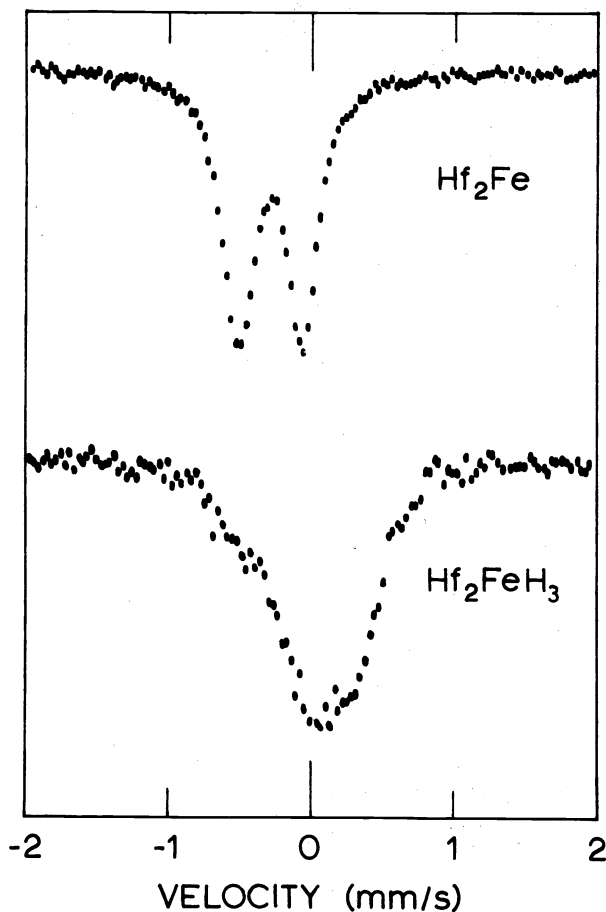


Fig. 6.  $^{57}Fe$  Mössbauer spectrum of  $Hf_2Fe$  and  $Hf_2FeH_3$  at room temperature ( $T_c = 73$  K). In the uncharged compound a well-defined quadrupolar splitting is observed. In the spectrum of the hydride the absorption peak is considerably broadened while also the quadrupole splitting can no longer be resolved. (See Ref. 13).

TABLE 2. Fe moments in various intermetallics before and after charging with hydrogen.

Compound	$\mu_{\text{Fe}} (\mu_{\text{B}})$	Hydride	$\mu_{\text{Fe}} (\mu_{\text{B}})$
ScFe <sub>2</sub>	1.4	ScFe <sub>2</sub> H <sub>2</sub>	2.2
CeFe <sub>2</sub>	1.3	CeFe <sub>2</sub> H <sub>4</sub>	2.1
YFe <sub>2</sub>	1.4	YFe <sub>2</sub> H <sub>4</sub>	1.8
LuFe <sub>2</sub>	1.3	LuFe <sub>2</sub> H <sub>4.2</sub>	1.7
Y <sub>6</sub> Fe <sub>23</sub>	1.7	Y <sub>6</sub> Fe <sub>23</sub> H <sub>21</sub>	1.9
Hf <sub>2</sub> Fe	0	Hf <sub>2</sub> FeH <sub>3</sub>	0.9
Th <sub>7</sub> Fe <sub>3</sub>	0	Th <sub>7</sub> Fe <sub>3</sub> H <sub>30</sub>	1.4 <sup>(a)</sup>

(a) data taken from Ref. 12

At first sight there seems to be no uniform behaviour regarding the changes in magnetic ordering temperatures accompanying the hydrogen take-up. It was mentioned on several occasions that H<sub>2</sub> absorption leads to a large expansion of the crystal lattice. If the changes in interatomic distances were to be held mainly responsible for the changes in T<sub>c</sub>, published data (14,15) on the pressure dependence of T<sub>c</sub> in the uncharged intermetallics could be used to analyse the T<sub>c</sub> changes observed. In Fig. 5 some of the data obtained with external pressure are reproduced. As indicated by the broken lines, one expects no change of T<sub>c</sub> in YFe<sub>2</sub>, an increase of T<sub>c</sub> in Y<sub>6</sub>Fe<sub>23</sub> and CeFe<sub>2</sub> and a decrease of T<sub>c</sub> in YFe<sub>2</sub>. The agreement with experiment (Fig. 4) is satisfactory.

<sup>57</sup>Fe Mössbauer effect spectroscopy was performed on several of the ternary hydrides, such as YFe<sub>2</sub>, CeFe<sub>2</sub> and ThFe<sub>3</sub> (11, 16). In all cases the onset of hyperfine splitting was found to agree with the magnetic ordering temperatures derived from the magnetization measurements. Although the hyperfine splitting in the hydride of YFe<sub>2</sub> was found to be larger than in uncharged YFe<sub>2</sub>, a quantitative analysis of the hyperfine spectra of the hydrides below T<sub>c</sub> could not be made because of an extremely strong line broadening. This broadening reflects the presence of atomic disorder brought about by the tendency towards phase separation (2,9). Recently it has been possible to prepare ternary hydrides of DyFe<sub>2</sub> and ErFe<sub>2</sub> (17,18) and of ScFe<sub>2</sub> (19) in which the Mössbauer effect spectra did not show large line broadening. In these hydrides the H atoms occupy highly ordered atomic positions and the onset of phase separation had apparently not yet taken place. In ScFe<sub>2</sub>H<sub>2</sub> the hyperfine splitting at 4.2 K was found to have increased by about 60% relative to ScFe<sub>2</sub>. This compares favourably with the results of the magnetic measurements and seems to suggest that there is no drastic change in the relative magnitudes of the various hyperfine field contributions (such as core polarization and transferred hyperfine field).

In most of the compounds investigated by means of <sup>57</sup>Fe Mössbauer effect spectroscopy the H<sub>2</sub> absorption was found to be accompanied by quite a marked change of the isomer shift (IS). As an example we show in Fig. 6 the results obtained in Hf<sub>2</sub>Fe before and after charging with hydrogen. It is seen that the IS in the hydride takes more positive values than in uncharged Hf<sub>2</sub>Fe. Similar changes of the IS towards more positive values have also been observed in various other compounds. This can be inferred from the IS data collected in Table 3. In order to make a quick comparison possible we have transformed the various IS values reported into values relative to  $\alpha$ -Fe.

TABLE 3. The <sup>57</sup>Fe isomer shift observed in several intermetallic compounds (in mms<sup>-1</sup> relative to  $\alpha$ -Fe) before and after charging with H<sub>2</sub> gas.

Hydride	x	$\frac{\Delta V}{V}$	IS(x≠0)	IS(x=0)	Ref.
Hf <sub>2</sub> FeH <sub>x</sub>	3	0.2	+ 0.28	- 0.12	13
TiFeH <sub>x</sub>	1.7	0.2	+ 0.27	- 0.14	20
ScFe <sub>2</sub> H <sub>x</sub>	2	0.2	+ 0.19	- 0.18	19
YFe <sub>2</sub> H <sub>x</sub>	4	0.2	+ 0.32	- 0.12	16
GdFe <sub>2</sub> H <sub>x</sub>	4	0.2	+ 0.28	- 0.12	16
ErFe <sub>2</sub> H <sub>x</sub>	3.65	0.25	+ 0.31	- 0.14	17
Th <sub>7</sub> Fe <sub>3</sub> H <sub>x</sub>	14.2	0.3	+ 0.08	- 0.22	21
ThFe <sub>3</sub> H <sub>x</sub>	2	---	+ 0.37	- 0.16	11

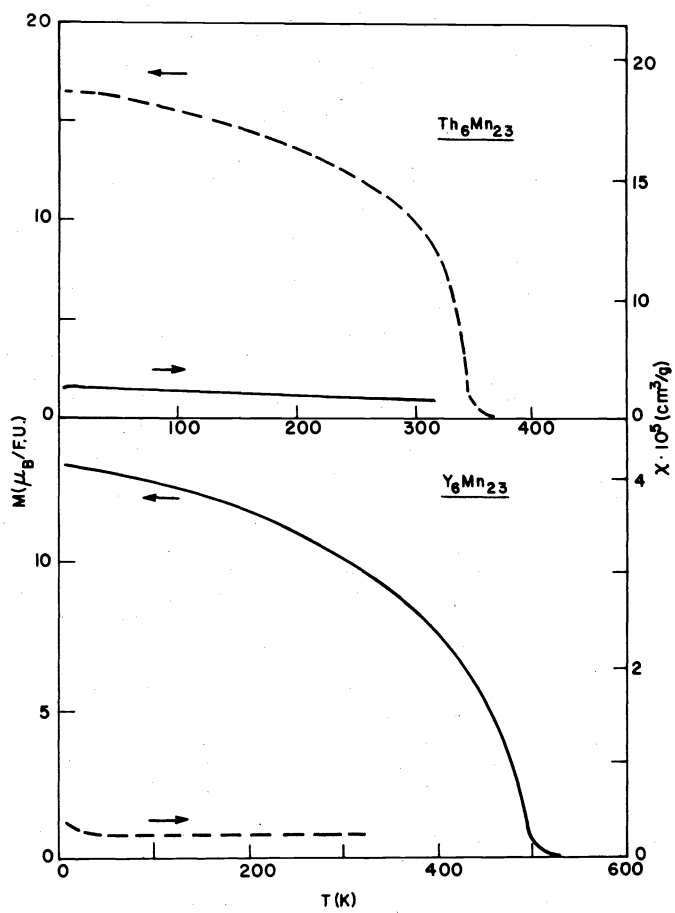


Fig. 7. Magnetic properties of  $\text{Y}_6\text{Mn}_{23}$  and  $\text{Th}_6\text{Mn}_{23}$  before (full line) and after charging with hydrogen (broken lines). Details of the magnetic measurements can be found in Ref. 25.

As can be seen in Table 3, a fairly consistent picture emerges from these results, the IS values being shifted in all cases to more positive values. We will first discuss the effect of  $\Delta V/V$  on the isomer shift. From the review published by Kalvius et al. (37) an estimate of this effect can be obtained: An increase in volume of 10% leads to a value of IS being shifted by about  $0.15 \text{ mms}^{-1}$  in the positive direction. Taking account of the  $\Delta V/V$  values listed in the table, the volume correction of IS would approximately be equal to  $+0.4 \text{ mms}^{-1}$ . It is doubtful, however, whether one is justified in applying such volume correction. The volume increase accompanying the hydrogen absorption is mainly due to the additional space required by the H atoms. If more space becomes available to the Fe atoms after  $\text{H}_2$  take up it will, at best, be only a small fraction of  $\Delta V/V$ . For this reason we will leave the volume effect out of consideration.

Using the data listed by Walker et al. (38) the small positive change of IS observed would correspond to an increase in d-character of about 0.4 electron. In order to explain the changes of  $\mu_{\text{Fe}}$  in  $\text{ScFe}_2$ ,  $\text{Hf}_2\text{Fe}$  and  $\text{Th}_7\text{Fe}_3$ , a decrease in 3d electron character seems to be required that this is of the order of 1 electron per Fe atom. This large decrease in 3d character would only be compatible with the observed change in IS if simultaneously there were a decrease in s character of at least the same order of magnitude. The total amount of charge transferred from the Fe atoms, in for instance  $\text{ScFe}_2\text{H}_2$ , would then be more than 2 electrons per Fe (or H) atom. It is clear that this is an unreasonable high number. This shows already that explanations of the moment changes based exclusively on band filling and charge transfer are rather unsatisfactory. We will return to this point later on.

Finally we wish to mention that quite a different type of change in magnetic behaviour has been observed upon hydrogen absorption in  $\text{TiFe}$  (22,23). The uncharged compound is Pauli paramagnetic. Hydrogen absorption leads to the formation of Fe-rich microprecipitates that mainly determine the magnitude of the magnetic susceptibility (22,23).

#### Mn-compounds

Quite spectacular changes in magnetic properties occur when hydrogen is absorbed by rare earth manganese compounds (24, 25). As seen in Fig. 7, these entail changes from Pauli paramagnetism to ferromagnetism as well as changes from ferromagnetism to Pauli paramagnetism. The compounds  $\text{LuMn}_2$  and  $\text{YMn}_2$  are both Pauli paramagnetic. In these cases, too, ferromagnetism is observed after hydrogen take-up. In these latter two compounds in particular, it was found that very often the temperature dependences of the magnetization is as shown by the lines in Fig. 8. When the samples, before the magnetization measurements, were cooled to 4.2 K without the presence of a magnetic field, a maximum was observed in the  $\sigma$  versus T curves. On the other hand a more or less normal ferromagnetic type of  $\sigma$  versus T curve was obtained, if the sample prior to the measurements was cooled to 4.2 K in the presence of a magnetic field. The occurrence of these features in the temperature dependence of the magnetization are rather well known in systems in which there is a partially crystallographic disorder of the atoms carrying the magnetic moment (26, 27). We note that it was found by X-ray diffraction that long-range order is preserved after hydrogen absorption. Indications of the presence of local atomic disorder were obtained from the small broadening of the reflection lines observed in the X-ray diagrams of the hydrides of  $\text{YMn}_2$  and  $\text{LuMn}_2$ . In regions where the atomic disordering is relatively high, ferromagnetic ordering can be destroyed and the magnetic interaction of these regions with those in which ferromagnetism is preserved may be responsible for the peculiar  $\sigma$  versus T behaviour observed. For more details we refer to Ref. 25. Changes in magnetic behaviour, such as the ferromagnetic - Pauli paramagnetic transitions and vice versa mentioned above, do not occur in all R-Mn compounds. For instance  $\text{ThMn}_2$  and  $\text{ZrMn}_2$  remain Pauli-paramagnets after hydrogen absorption and  $\text{Lu}_6\text{Mn}_{23}$  remains a ferromagnet. In these compounds the changes in magnetic properties are only gradual ones (25).

Inspection of all of the magnetic data available at present on R-Mn compounds and the corresponding ternary hydrides suggests that the presence or absence of a magnetic moment on the Mn atoms is not correlated with the presence or absence of hydrogen (25). It is interesting to note that a correlation seems to exist between the presence of a Mn moment and a critical distance between the nearest neighbour Mn atoms. In keeping with this view are the results obtained on various hydrides of the type  $\text{YMn}_2\text{H}_x$ , shown in Fig. 8. X-ray diffraction showed that the cubic C15 structure is preserved and that increasing H concentration corresponds to an increasing lattice constant. It is seen that the magnetic moment disappears again when the lattice becomes too much expanded. Alternatively, in terms of a local moment description and assuming the persistence of magnetic moments, the disappearance of the magnetization in hydrides with a relatively large separation between the Mn atoms could equally well be ascribed to the occurrence of antiferromagnetic order or to a breaking down of the magnetic coupling between the Mn moments.



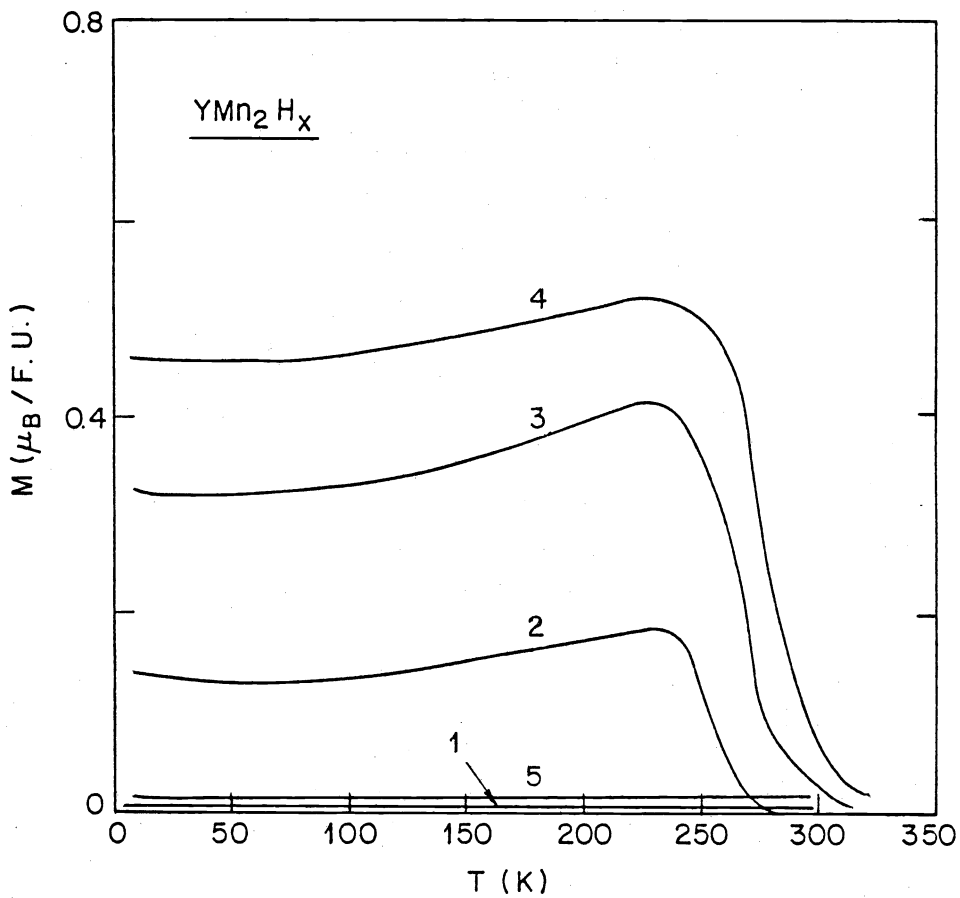


Fig. 8. Effect of increasing H concentration on the magnetic properties of  $YMn_2$ . Higher numbers correspond to higher H contents and to larger lattice constants of the hydride (In contradistinction to  $LaNi_5H_6$  the hydride  $YMn_2H_x$  has a homogeneity region so that the hydrogen content can continuously be varied within wide limits). Details regarding the magnetic measurements are given in Ref. 25.

### Compounds with a magnetic rare-earth component

Numerous investigators have reported on hydrogen-induced changes in magnetic properties of 3d compounds in which the partner (rare earth) element also carries a magnetic moment (8, 25, 28, 31).

In these cases one has to take into consideration that the introduction of hydrogen can lead to changes in magnetic coupling strengths not only between the 3d moments but also between the 4f moments and the 4f and 3d moments. This makes the information obtained from magnetic bulk measurements regarding the changes in 3d moment somewhat less conclusive. Considerably more revealing are results of investigations on several  $RFe_2$  compounds obtained by means of Mössbauer effect spectroscopy (17, 18) or neutron scattering (33). The results of all these investigations may be summarized as follows :

- (i) The antiferromagnetic coupling between the 3d moments and the 4f spin is preserved after hydrogen absorption. Indications have been obtained that the strength of the 4f-3d coupling becomes weaker.
- (ii) There exist more or less severe deviations from collinear ferrimagnetic spin ordering of the 4f and 3d moments. As a result the saturation magnetization does not represent the difference of the rare earth sublattice moment and 3d sublattice moment.

### 3d-BAND MODEL

In this paper we shall examine to what extent can the changes in 3d moment be understood in the framework of a band model. Unless self-consistent band calculations are performed for all the compounds under discussion such an analysis is bound to be rather speculative. However, the speculations being constrained by some known general features of the interactions and 3d band structures, there are limits to what can be reasonably accommodated within the band model. In particular, it is generally acknowledged that the most important interaction is the intra-atomic d-d Coulomb interaction. As this interaction is reduced, by the orbital antisymmetry of the wave-function required by the Pauli principle, for a parallel-spin pair of electrons, it can be said to be responsible for the ferromagnetism and enhanced paramagnetism of transition metal systems. Both of these phenomena are explained in the model by a contribution to the shift of the up-spin and down-spin subbands with respect to each other, which is proportional to the interaction parameter and to the resulting magnetic moment (molecular field approximation). In a discussion of the hydrogen absorption, where the possibility of electron transfer to or from d bands has to be considered, it is important to realize that the position of the d band with respect to the s-p band is also influenced by the d-d Coulomb interaction, because the energy of each d electron includes a Coulomb term that increases with increasing number of d electrons. There are three important implications of the band model and the above features of the Coulomb interaction, which will enter our discussion below : (I) large changes of the number of d electrons are counteracted by the Coulomb interaction, which raises (lowers) the d bands with respect to the s-p band if the number of d electrons increases (decreases); (II) any change in the magnetic moment will be enhanced by the exchange interaction, because the band splitting is proportional to the magnetic moment; (III) the effect of a changing number of d-electrons on the magnetic moment can be inferred from the fact that the occupancy of the two subbands changes in proportion to their density of states at the Fermi level. A consequence of the last observation is that (III') in a strong ferromagnet, where the majority subband is full, only the minority subband will change in occupancy, giving rise to a reduction of magnetic moment with increasing number of d electrons.

The depletion of the d band was assumed to be responsible for the reduction of the Co moment upon hydrogenation by Malik et al. (31). In view of the rule we have deduced above (III') this is a very unlikely explanation. The rather large value of  $\mu_{Co}$ , especially in  $LaCo_5$ , suggests a filled majority (say, spin-up) subband, in which case the depletion of the d band should lead to an increasing moment. One would have to assume a considerable number of d holes per Co atom to meet the condition  $N_{\uparrow}(E_F) > N_{\downarrow}(E_F)$ , which, according to III is necessary for the mechanism involved by Malik et al. to give the desired reduction of  $\mu_{Co}$ . As pointed out above (I), the number of d holes is not expected to deviate much in compounds from its value in pure Co, and the low electronegativities of Y and La make an increased number of holes especially unlikely in the compounds listed in Table I. Therefore, we are left with the conclusion of Kuijpers (8) that, if charge transfer plays a role in the reduction of  $\mu_{Co}$  upon hydrogen absorption, the d band must be assumed to become gradually filled. Because of the feedback mechanism (II) the change in the number of d electrons may be smaller than the change in  $\mu_{Co}/\mu_B$ .

We have seen that hydrogen absorption in Fe compounds, in contradistinction to Co compounds, leads to an increase in 3d moment (see Table 2). As the 3d moments quoted in Table 2 are by and large 1  $\mu_B$  higher than the ones given for  $\mu_{Co}$  in Table I, the same arguments can be used for the Fe compounds as for the Co compounds to show that  $N_{\uparrow}(E_F) < N_{\downarrow}(E_F)$  is more likely to hold than the opposite inequality. Therefore, III implies a depletion of the 3d band upon hydrogen absorption. This conclusion has been reached already before (12, 16). However, it should be pointed out again, that our explanation does not necessitate a charge transfer of d electrons of the order of  $\Delta\mu_{Fe}/\mu_B$ , because of the enhancement effect (II). It was mentioned already in the preceding section that the small positive change in IS implies that the transfer of charge has to be composed of about equal amounts of s and d

electrons. If the number of transferred d electrons is significantly below  $\mu_{Fe}/\mu_B$  the total number of electrons transferred can become of a magnitude that is in keeping with the redistribution of charge based on the electronegativity differences between the composing elements (34). In other words, because of the enhancement effect, the large change in  $\mu_{Fe}$  need not necessarily be in conflict with the small change of the corresponding IS. More difficult to understand is that if one wishes to ascribe a decisive rôle to d-band occupancy changes in the decrease of  $\mu_{Co}$  and increase of  $\mu_{Fe}$  upon hydrogen absorption, one has to assume that H donates electrons to the Co 3d band and accepts electrons from the Fe 3d band. Attempts have been made to explain this apparently contradictory situation in terms of electronegativities (35), the value for metallic H being lower than that of Co and higher than that of Fe (34).

Throughout our discussion we ignored the possibility that the d-d interaction parameter would change upon hydrogen absorption. This is not because such a possibility can be excluded, rather because of the uncertainties besetting any discussion of the effect. In fact, equally convincing arguments can be found for an increase or decrease of the interaction parameter upon hydrogen absorption. Presumably, the most important effect of the presence of a H atom near a Co or Fe atom is the hybridization of 3d states with the hydrogen 1s states, which leads to a reduction of the intraatomic Coulomb integral with respect to its value in the pure metals (36). However, in the compounds under consideration the 3d states are already hybridized with the 5d and 6s orbitals of the rare-earth atoms, and the Coulomb integral is already reduced. In general, it is impossible to tell whether the introduction of H atoms into the structure will lead to a further reduction, or whether it will restore the interaction strength to its original value.

#### CONCLUDING REMARKS

Whilst the hydrogen absorption in 3d intermetallics encompasses a wealth of changes in magnetic properties it does not seem possible at the moment to describe these by means of a unified model. The large increases in 3d moment in conjunction with only minor changes in isomer shift observed in the Fe compounds indicate that an increase in exchange splitting predominates over changes in 3d band occupation. If one extends this picture to the Co compounds one has to assume a decrease rather than an increase of the exchange splitting due to the hydrogen absorption. The failure to describe the changes in magnetic properties in terms of a simple band model becomes even more apparent if one wishes to include the results obtained on the Mn compounds. A point that deserves consideration is the tacit assumption made in the various investigations cited above, that the metallic character of the intermetallic compound is preserved after hydrogen absorption. This need not necessarily be so. Although there is a general lack of experimental information on this point, it has been shown by Walsh et al. (7) that charged  $LaNi_5$  has a quite low carrier concentration, reminiscent of semiconducting or barely metallic materials. Transitions from metallic to semiconducting are also well-known to occur in various binary hydrides (40). Further experimental studies on ternary hydrides to clarify this point would be welcome.

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