HYDROGEN IN METALS : APPLICATIONS OF THE MÖSSBAUER EFFECT

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Résumé. — On présente une revue des applications de l'effet Mössbauer pour l'étude de systèmes métal-hydrogène.
Les informations relatives aux variations de déplacement isomérique, d'effet quadrupolaire et de champ hyperfin résultant de la présence d'hydrogène sont analysées au terme de calcul de structure de bandes. Quelques nouvelles applications de l'EM, comme l'étude de la diffusion de l'hydrogène et de la distribution de l'hydrogène autour de l'atome résonnant, sont discutées en détail.

Abstract. — A review of the applications of the Mössbauer effect to the study of metal-hydrogen systems is given. The informations obtained on hydrogeninduced changes in isomer shifts, quadrupole splittings and hyperfine fields are reported in view of recent band-structure calculations. Some new applications of the ME, like the study of the hydrogen diffusion and the determination of the hydrogen distribution around the Mössbauer atom, are discussed in detail.

1. **Introduction.** — The properties of metal-hydrogen (M-H) systems, although investigated extensively for over more than a century, are still in the center of scientific interest [1, 2]. What are the reasons to-day for the impetus to study hydrogen in metals ? Three regions of interest may be pointed out here :

First, the aspects connected with the *metallic* properties of the M-H systems. Hydrogen behaves in many M-H systems like a metallic alloy component. Hydrogen can be alloyed to many metals quite simply by loading either from the gas phase or electrolytically or, in a more expensive way, by ion implantation. Some M-H systems retain their simple structure over a wide range of composition ; they often systematically change their properties as a function of hydrogen concentration. The Pd-H system may be named as the most famous example, since it varies its band properties from nearly ferromagnetic to diamagnetic and finally to superconducting [3, 4].

Second, the *technological* interest in M-H systems is still growing. This is connected with the future problems of energy generation in new ways. The fuel cell (cold oxidation of hydrogen) needs metallic catalysts ; further, the hydrogen can be best stored in those metallic matrices, which absorb considerable amounts of it and which contain more hydrogen per volume unit than liquid H_2 [5]. For conventional nuclear reactor design, the properties of hydrides (as neutron moderator or reflector materials) have been widely investigated [6]. For the fusion reactor, serious technological problems [7] are connected with the wall materials which must be resistant against the permeation of deuterium and tritium (and, of course, of other reaction products). Hydrogen embrittlement of steels is a phenomenon still in investigation [8].

The third point we may call the *theoretical* aspect. There are a variety of properties of M-H systems which

are still in discussion. The thermodynamic behaviour of M-H systems, the theory of the elastic H-H interactions and phase-transitions [9, 10], the diffusion process [11] at high and low temperature (*quantum diffusion* [12]) and the vibrational behaviour of the H or D atoms (local modes) in the lattice [13] may be named. One of the basic questions is connected with the electronic structure at the hydrogen interstitials and with the changes induced by the hydrogen in the band properties of the matrix. Recent experiments and bandstructure calculations have led to information now far beyond the rigid band model [14] which has been quite successfully applied for a long time to describe the properties of the M-H systems of the transition metals.

In section 2 some elementary properties of the M-H systems of the transition metals will be outlined. Some general aspects to the application of the ME to the M-H systems will be given in section 3. In section 4, the ME studies of hydrogen in d-metal systems will be reviewed. Section 5 will give an introduction to the properties of the rare-earths hydrides and a survey of the ME studies on them (including the actinides). Finally, conclusions will be drawn to future applications of the ME in this field.

2. **Properties of the metal-hydrogen systems of the d-transition metals.** — 2.1 HYDROGEN SOLUBILITY AND LOCATION, PHASE-DIAGRAMS. — In some d-transition metals (located at the beginning) and the end of the d-metal series, hydrogen can be absorbed exothermically in large quantities. The enthalpy of solution, ε, determines for the metal in question the amount of hydrogen absorption at a certain temperature and pressure. In figure 1, this parameter is plotted for the d-metals as a function of the number of outer electrons. For negative ε, the solubility of H is high and increases with decreasing temperature (for solubility isotherms
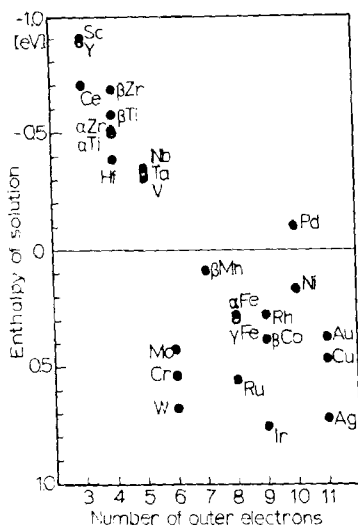
FIG. 1. — Enthalpy of solution for H in the transition metals (adapted from ref. [10]).

can be regarded as the best example for this concept (see Fig. 2a). In the α-phase, which corresponds to the gas phase, the hydrogen occupies the interstices statistically ; on increasing the concentration or lower-

(a)

(b)

(c)

FIG. 2. — Schematic phase diagrams for (a) Nb-H, (b) Pd-H and (c) Ta-H (adapted from ref. [15]).

see ref. [15]). For positive ε, the solubility of H is low and increases with increasing temperature. Hydrogen loading then requires large hydrogen pressures or the application of the electrolytical method. The hydrides of group 3, 4 and 5 (Fig. 1) are stable in air (either due to the formation of stable hydride phases or due to the fact that an oxid layer on the surface hinders the escape of the diffusing hydrogen). The Pd and Ni hydrides lose hydrogen continuously at room temperature and normal atmosphere. Static conditions can be obtained by cooling or by an external hydrogen pressure.

Hydrogen is in general dissolved into interstitials sites of the matrix. Into what kinds of interstitials (octahedral, tetrahedral, triangular, etc.) the hydrogen is placed was questionable for a long time. The answer has been given mainly from neutron diffraction and quasielastic neutron scattering experiments [16, 17]. It was found, for example, that in f. c. c. Pd and Ni, the octahedral interstices are occupied, whereas in b. c. c. Nb and Ta the tetrahedral sites are favoured (this result has been supported from recent channeling experiments [18]). For b. c. c. V, an occupation of both tetrahedral and octahedral sites has been suggested [19].

The interstitial hydrogen exhibits a very high mobility in some d-transition metals. The diffusion occurs via empty interstices with a diffusion rate up to 10^{12} jumps per second at room temperature (e. g. V [15]). This jump rate is 15-20 orders of magnitude larger than those for other interstitials like N or O. The jump rate increases over a wide temperature range exponentially with temperature. From this behaviour the activation energy of U of the jump process can be easily derived. Typical values are $U \approx 0.1$ eV (respectively $\sim 1\,000$ K). The high mobility of H and the similarities of the M-H phase diagrams with the gas-liquid-solid phase diagram of an one-component system have led to a description of the hydrogen as a *lattice gas* [10, 20]. The Nb-H system
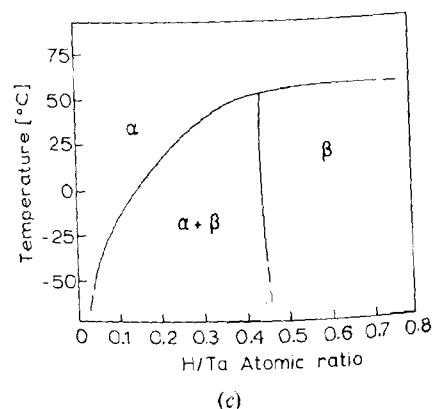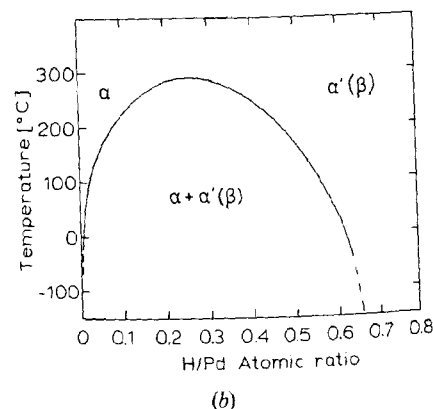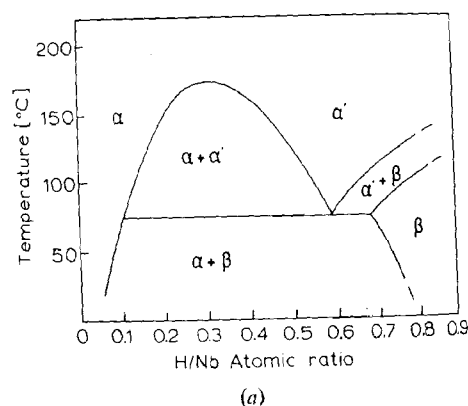
ing the temperature, the interaction amongst the hydrogen interstitials leads via a gas-liquid phase transition to the α'-phase. This transition is accompanied by an increase in the lattice constant (the lattice symmetry does not change) and by the onset of short-range order between the (still diffusing) H-atoms. The transition into the (solid) β-phase is characterized by a change of the host lattice structure to lower symmetries (e. g. from cubic to tetragonal or orthorhombic) and/or by

a periodic arrangement of the H-atoms (superstruc-
ture). Depending on H concentration, several β-phases
(then named β', γ, δ-phases) may occur ; it is also
possible that a second liquid phase exists [10]. It has
been further explained [10] why the phase diagrams of
Ta-H (Fig. 2b) and Pd-H (in the shown phase region
of Fig. 2c) miss either the liquid or the solid phase.
The broad miscibility gap (coexistence of α and α'-
phase) is an important feature of the Pd-H system (in
literature, the α'-phase in Pd-H is usually named
β-phase).

2.2 ELECTRONIC STRUCTURE OF HYDROGEN IN
d-TRANSITION METAL. — The electronic properties
of d-transition metal hydrides have been described for
a long period in the impressive picture of the rigid-
band model developed by Mott [14]. It was thought
that the dissolved hydrogen gives its electron to the
common band, which should retain its basic structure
on alloying. Therefore, the additional electrons must
fill up (at least partially) the empty band-states above
the Fermi level of the pure matrix. The hydrogen atoms
were considered as protonic, that means, as fairly
unscreened which, on the other hand, is very unlikely
in a metallic system with a high density of states.
However, susceptibility and specific-heat measure-
ments on Pd and Ni alloy systems with H, Ag and Cu
supported the rigid-band model and were used as text-
book examples for it [21] ; the transition from strong
paramagnetism to diamagnetism at typical alloy
compositions $PdH_{0.6}$ or $Ni_{0.40}Cu_{0.60}$ was explained
by the same mechanism of filling up the 0.6 Pd or Ni
d-band holes by the s-electrons of the added alloy
component. The inadequancy of the rigid-band model
for the characterization of a M-H system like Pd-H was
demonstrated by de Haas-van Alphen measure-
ments [22] and band-structures calculations [23], which
showed that pure Pd has only 0.36 holes in its d-band,
in contrast to 0.6 as predicted from the rigid-band
model. The break-through in the understanding of
M-H systems was attained 1971 by the work [24] of
Eastman, Cashion and Switendick, which proved by
photoemission (UPS) study and by APW bandstructure
calculations on Pd-H the existence of low-lying hydro-
gen band states and a considerable modification of the
Pd d-band (see Fig. 3). These findings have been
confirmed recently by the calculations of Zbasnik
and Mahnig [25] and Faulkner [26] as well as by XPS
photoemission studies [27, 28]. Even in the substitu-
tional alloys (e. g. PdAg) the rigid-band model is not
valid for describing the band properties [29, 30]. Since
we shall compare in the following M-H systems with
M-N systems (where N is a noble metal), the band-
structure of Pd-Ag is given in figure 4. Evidently, the
Pd d-bands in figures 3 and 4 remain by no way rigid
on H or Ag alloying (the decrease in the Pd d-band
width can be described phenomenologically as to be
due to the reduced d-d interaction and to the increase
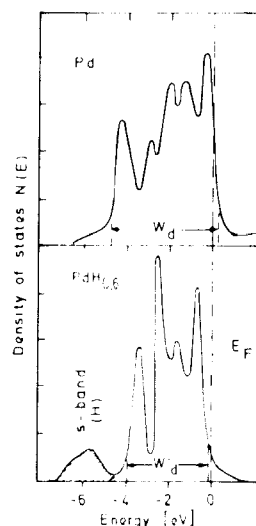in the lattice constant on alloying). The hydrogen

FIG. 3. — Density of states curves for Pd and PdH (from ref.
[24]).
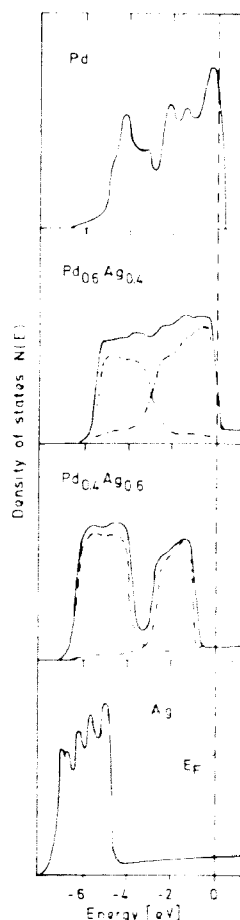

FIG. 4. — Density of states curves for $Pd_{1-x}Ag_x$ alloys (from
ref. [29]).

atoms establish their own band which is built up from
modified Pd s-p band states (for details see ref. [24, 25,
26]). The variation of $N(E_F)$ on alloying, however, is
very similar for the Pd-H and Pd-Ag systems and
in accordance with that proposed by the rigid-band

model [14, 21]. This behaviour is the reason for the success of the rigid-band model in describing correctly many properties of Pd alloys connected with $N(E_F)$.

3. Mössbauer spectroscopy on metal-hydrogen systems.

— Mössbauer spectroscopy has been applied since 1965 [31] to the study of M-H systems. The basic idea of the first works was a proof of the rigid-band concept by the information obtained on hydrogen-induced variations of the hyperfine interactions ; especially the isomer shift was thought to provide valuable information on the electronic structure of M-H systems which could not be obtained from other spectroscopic methods. In the meantime, the applications of the ME to the study of M-H system have reached a wider scope. Before discussing the ME works in detail, some remarks on the facilities and limitations of the ME to the study of M-H systems will be made.

First, the ME informs microscopically on the properties of an M-H system. It is obvious that a Mössbauer isotope, which belongs to the matrix per se, would be the best choice for the investigation of a distinct M-H system. From the d-metals which can absorb large quantities of hydrogen only Ni, Hf and Ta possess Mössbauer isotopes, and the ME has been applied so far only to Ta-H as a *pure* system (see Fig. 5). In most of
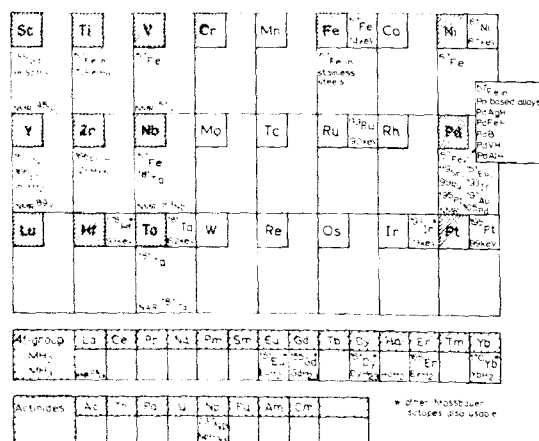

FIG. 5. — Chart of d-transition metals, rare-earth and actinides. Shadowed metal symbols indicate exothermic hydrogen solution, half-shadowed symbols indicate some metal wich can be H-charged, for instance, electropytically in their elemental form or in alloys. ME isotopes are named for the d-metals beside the metal symbols when they have been applied to M-H system. In the rare-earths and activides region. ME isotopes are given only when applied to M-H systems. ME isotope symbols below a metal symbol indicate an ME study on the M-H system of this metal. ME studies on alloys or hydrides are also indicated. Finally, some NMR isotopes, which has been applied to the M-H systems in question, are given.

the ME works on d-transition M-H systems, the Mössbauer atom is itself an impurity and any interpretation of these results must consider the fact that the probe atom may have quite a different electronic structure and surroundings than the matrix atoms. It is well-known that impurities in an M-H system show attrac-

tive or repulsive interactions with the hydrogen interstitials [32, 33]. Therefore, it is questionable whether an [57]Fe or [197]Au atom, for instance, has the same number of H atoms in its nearest neighbourhood as an atom (e. g. Pd) which belongs to the hydrogenated matrix.

Secondly, the absorption of hydrogen in metals is accompanied by an expansion of the host lattice; especially the transitions to phases with higher H concentrations show a considerable increase in the volume of the unit cell (e. g. by $\sim 11\ \%$ in the α-β phase transition of Pd-H). Therefore, an interpretation of hydrogen induced changes of hyperfine parameters should always start with a consideration of the contributions arising solely from the changes in volume. This information is usually obtained from pressure experiments [34].

Thirdly, many ME studies (using gamma transitions of high energy) must be performed at rather low temperatures where some of the special properties of the M-H systems disappear, for instance, the diffusion of the hydrogen and the existence of hydrogen-rich α and α'-phases. It must be further emphasized that the resolution power of some Mössbauer resonances is too small to distinguish between different phases and, therefore, the data analysis may be complicated in cases where different phases coexist. In some ME studies the determination of the H content (either by volumetric, gravimetric or X-ray diffraction methods) is small in precision ($\pm$ 10 %) which limits the interpretation of the data and the comparison with other studies.

The information obtained in M-H systems by the ME can be classified into the following six topics ; the group number will be used in the appendix which lists the Mössbauer works for the different host systems for a short characterization :

(1) *Isomer shifts* (*IS*) : the most important information which is obtained in most works on d-transition metal systems, also on some rare-earths and one actinide system.

(2) *Magnetic ordering and hyperfine fields* : the magnetic ordering potential of magnetic materials is drastically lowered on hydrogenation ; most of the works were performed on Pd-Fe, Ni and the rare earths.

(3) *Quadruple interactions* (*QI*) : little is known on the QI produced by a single H atom ; in some ordered M-H phases a QI is observed.

(4) *Crystalline electric field* (*CEF*) *ground states* of rare earth atoms in the dihydrides ; *Debye temperatures* and *recoil-free fractions*.

(5) *Hydrogen distribution around impurities* ; *short-range order* : a promising application of the ME for impurity and pure systems.

(6) *Diffusional behaviour of hydrogen* : a new spectroscopic tool introduced by the high-resolution resonance of [181]Ta.

For the investigation of many peculiar properties of M-H systems, other microscopic methods may be more suitable than the ME ; this is especially true for all methods using the hydrogen (deuterium or tritium) atoms as probe. The nuclear magnetic resonance (NMR) on ^1H and ^2H has been widely used for the study of the dynamical behaviour of the hydrogen and the phase transitions [35]. NMR studies on matrix atoms may also provide valuable information on the microscopic electronic structure from the observed Knight shifts and quadrupole broadenings [36]. The nuclear acoustic resonance (NAR) has been recently applied to the Ta-H system [37]. Since these results are closely related to the ME, some NMR (NAR) studies are listed in Table 2 of the appendix. Neutron diffraction, inelastic and quasi-elastic neutron scattering experiments are well suited, as mentioned previously for studying the location and the jumping and vibrational behaviour of hydrogen or deuterium. For macroscopic methods, e. g., the study of the transport properties, the reader is referred to recent conference proceedings [1, 20] which may also inform comprehensively on the present state of the investigations of M-H systems.

4. Review of ME work on d-transition metal hosts.

— 4.1 ^{57}Fe IN Ni-H. — One of the first ME works performed on M-H systems shows almost all typical features which one can observe on hydrogenation of a d-metal. Wertheim and Buchanan [38, 39] loaded a $^{57}CoNi$ electrolytically source with hydrogen ; the ME patterns display dramatically the occurrence of a new and unmagnetic phase ($NiH_{0.6}$) ; its amount increases proportional to the loading time (Fig. 6). Since the Ni-H system behaves similar to the Pd-H system (Fig. 2c), the α-phase corresponds to the (almost) pure Ni matrix which is magnetically ordered and characterized by the typical ^{57}Fe six line pattern. The β-phase ($NiH_{0.6}$) is magnetically unsplit down to 4.2 K and exhibits a single (somewhat broadened) line which is considerably shifted in comparison to the $^{57}FeNi$ spectrum (by 0.5 mm/s towards lower electron densities). This increase in the isomer shift exceeds largely the variation expected from the volume expansion which accompanies the formation of the β-phase, $\Delta V/V \approx 0.10$ [39]. Using $(\partial(IS)/\partial \ln V)_r = 1.1$ mm/s observed in pure Ni [40], a volume dependent increase of the IS by 0.11 mm/s can be derived. This strongly indicates that the electronic structure on the Fe atoms has changed on hydrogenation. The results were discussed in terms of a d-band filling of the Ni matrix which is accompanied by an increase in the d-electron number at the Fe atoms [39].

Besides these illustrative results on the isomer shifts, Wertheim and Buchanan [39] demonstrated that the ^{57}Fe atoms retain a magnetic moment in the diamagnetic $NiH_{0.6}$ matrix, a behaviour quite similar to the $^{57}FeCu$ and $^{57}FeAg$ systems [41]. The line broadening in the β-phase found to be due to the nonhomege-
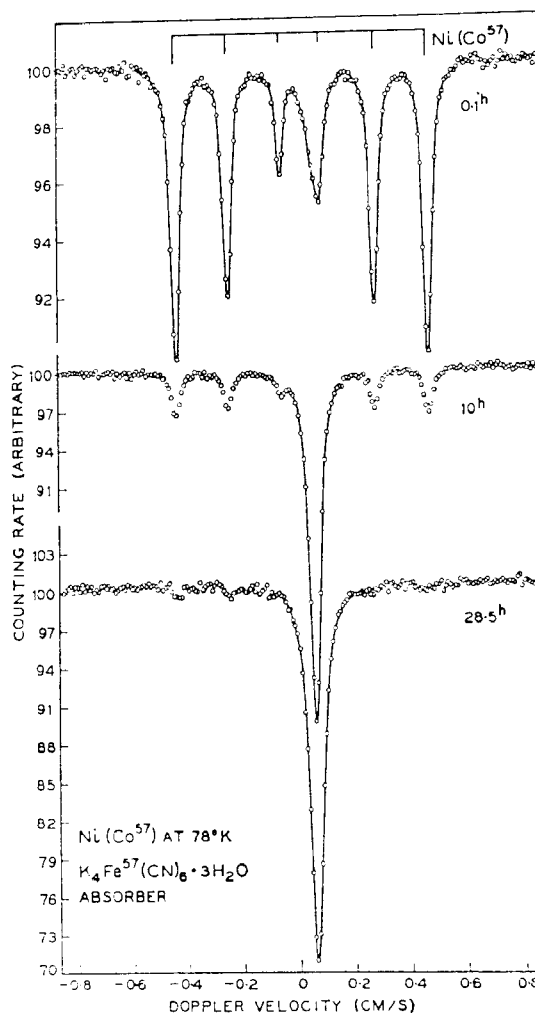
FIG. 6. — ^{57}Fe Mössbauer spectra of ferromagnetic Ni indicating the formation of the nonmagnetic $NiH_{0.7}$ phase as a function of the electrolytic-loading time (from ref. [39]).

neous distribution of hydrogen atoms around the Fe atom which causes a scatter in both the IS and the QI.

4.2 MÖSSBAUER ISOMER SHIFTS OF ^{57}Fe, ^{119}Sn, ^{151}Eu, ^{99}Ru, ^{193}Ir, ^{195}Pt AND ^{197}Au IN THE Pd-H SYSTEM. — The Pd-H system has attracted most interest from Mössbauer spectroscopists. Due to the striking changes in the electronic properties of the Pd matrix on hydrogenations, one might expect a correspondingly strong variation in the isomer shift of the Mössbauer probe atoms, even when they are present as impurities in the matrix. Unfortunately, there exists no Pd Mössbauer isotope and, due to the lack of this, almost all commonly used Mössbauer isotopes have been incorporated into the Pd-H system (see Fig. 5).

The first ME work of this type has been performed by Bemski, Danon, de Graaf and da Silva on the ^{57}Fe (Pd-H) system [31]. An increase of the IS of ~ 0.1 mm/s was observed on a hydrogenation of about 40 at %. Chekin and Naumov [42] used for a similar study the ^{119}Sn resonance. They further compared the variation of IS in the Pd-H system (up to

22

40 at %) with that in the Pd-Ag alloy series and found a close agreement. The small increase in electron density was discussed in terms of the rigid-band model as a filling up of band states with s-electron character by the diamagnetic alloy components. It was shown, however, two years later by a pressure study on a PdSn (12 at %) alloy [43] that in this matrix the s-electron density at ^{119}Sn nucleus increases with the volume of the unit cell ; the observed variation of IS on Ag or H alloying can be, therefore, explained within the error bars of both experiments alone by the volume expansion.

In PdFe (0.3 and 9 at %) and PdSn (5 and 10 at %) alloys Mahnig and Wicke [44] were the first observing a steep increase in the ^{57}Fe and ^{119}Sn isomer shifts when the added hydrogen content exceeds a critical value. This characteristic kink in the IS versus H-concentration curve was thought to indicate the filling-up of the Pd d-band. In accordance with susceptibility [45], specific heat [46] and hydrogen solubility [47] measurement, it was pointed out that the ^{57}Fe and ^{119}Sn isomer shifts can be plotted on a common curve for all alloy compositions, when the additional electron concentration, n_e, is used as abscissa. n_e is defined for an alloy of the composition $(Pd_{1-x}M_x)H_n$ as

$$n_e = xZ_M + nZ_H . \qquad (1)$$

Here x is the atomic ratio $M/(Pd + M)$ and n is the atomic ratio $H/(Pd + M)$. Z_M is the valency of the substitutional metal atoms (e. g., $Z_{Fe} = 3$) and Z_H is the valency of the interstitial H atoms $(Z_H = 1)$. In the picture of the rigid-band model, the valency numbers are equal to the number of electrons which are donated by the alloy components to the matrix. For the ^{119}Sn isomer shifts, a « valency » number of $Z_{Sn} = 3.5$ [47] has been applied.

The investigation of Pd-based alloys was continued in the Münster group by Wanzl [48]. The ^{57}Fe isomer shifts in binary and ternary alloy systems of Pd with Fe, V, Ag, Al with various H contents were investigated in great detail at 35 °C. It was also demonstrated that boron can be used instead of hydrogen as interstitial alloy component. Part of these results is discussed in the work of Obermann, Wanzl, Mahnig and Wicke [49]. In particular, it was definitely shown [48] that in all alloy systems (except for $(Pd_{1-x}V_x)H_n$ at $x > 0.05$ [48, 49]) the isomer shifts increase sharply when the characteristic value $n_e \approx 0.55$ is reached ([1]). The eq. (1) for n_e can be simply extended to additional alloy components by summing over all substitutional and all interstitial

components. For Ag, Al, B and V, the valency numbers 1, 3, 3 and 5, respectively, were used (together with the numbers for Fe and H given above) for an uniform representation of the isomer shifts in all Pd-based M-H systems. The measurements with interstitial B atoms yielded important information on the quadrupole interactions and screening conditions in Pd-based alloys. At room temperature, the hydrogen jump rates of $\sim 10^{11}$ s^{-1} and $\sim 10^{-9}$ s^{-1} in the α- and β-phases, respectively, average out the H-induced isomer shifts and quadrupole interactions at the Fe atoms, and no H-induced line broadenings of the ^{57}Fe resonance line have been observed. The interstitial boron atoms, however, can be regarded as static when investigated by means of the ME. Indeed, the spectra of $(Pd_{1-x}Fe_x)B_n$ show an unresolved quadrupole structure up to $n_e < 0.55$ and at $n_e > 0.55$ a resolved quadrupole dublett [48, 49]. A similar increase of the experimental linewidth at $n_e > 0.55$ has been observed by Longworth [50] in the substitutional alloy series $Pd_{0.98-x}Au_xFe_{0.02}$ (which also parallels with a steeper increase of the ^{57}Fe isomer shift, see Fig. 7). This behaviour has been explained in both cases as being due to the reduced screening of the impurity potential by the matrix electrons when the band-filling is reached [51, 52], since the screening length λ depends critically on $N(E_F)$: $\lambda \propto (N(E_F))^{-1/2}$.
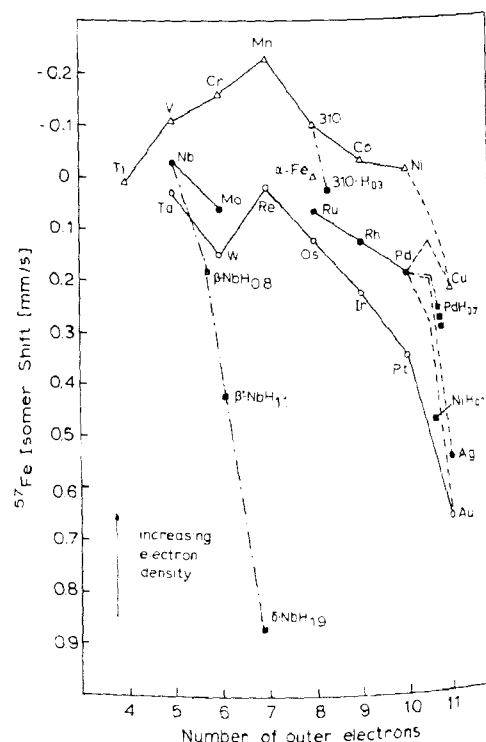

FIG. 7. — ^{57}Fe isomer shifts in the d-transition metals and alloys : The full lines connect the IS obtained on ^{57}Fe as dilute impurity in the pure metals of the 3d, 4d and 5d series. The dashed lines between Pd (or Ni) and the noble metals N describe the *variation* of the IS of ^{57}Fe in $Pd_{1-x}N_x$ alloys. The dashed-dotted line connects different hydride phases of a metal. In this case the abscissa was varied by n_e, the number of electrons introduced by the hydrogen (see text). The isomer shift data were adapted from ref. [50, 75, 92, 106] ; for M-H systems see text.

([1]) This increase of the IS (its slope is indicated in Fig. 7) is observed in the region of the homogeneous β-phase. It clearly exceeds the volume dependent part of the IS by a factor of ~ 5. In $(Pd_{1-x}Ag_x)H_n$ alloys (with 0.3 at % ^{57}Fe) some short range order effects have been deduced from a steeper increase of IS. The value of n_e at the band filling point is somewhat smaller than the one given in other papers, e. g. ref. [60] ; this may be due to the different temperatures, at which the experiments were performed.

The variation of the electron density $\rho(0)$ at a rare-earth atom in the Pd-H system (with 2.5 at % Eu) was studied by Meyer, Friedt, Iannarella and Danon [53] using the ^{151}Eu resonance. They could explain the observed decrease of $\rho(0)$ at the Eu^{3+} atoms by the volume expansion alone ; the volume dependence of the Eu isomer shifts was derived from pressure data [54]. In the region of co-existing α- and β-phases, a slight increase of the resonance line was observed.

A first account on studying the Pd-H system by use of the Mössbauer resonances of ^{99}Ru, ^{193}Ir, ^{195}Pt and ^{197}Au was given by Iangarella, Wagner, Wagner and Danon [55]. The isomer shifts of the above isotopes (which were alloyed in small concentrations into the Pd matrix) in hydrogen-saturated β-phases ($PdH_{0.7-0.8}$) were compared with those obtained as dilute impurities in pure Pd and Ag [56]. In all cases, the electron density $\rho(0)$ was smaller in $PdH_{\sim 0.8}$ than in Pd.

The d-metal isotopes ^{99}Ru, ^{193}Ir and ^{195}Pt exhibited larger (or almost equal) values of $\rho(0)$ in $PdH_{0.8}$ than in the Ag matrix. For the noble-metal isotope ^{197}Au, however, a smaller value of $\rho(0)$ was found in $PdH_{\sim 0.8}$ than in Ag.

This work has been continued by a detailed study of the Pd-Ag and Pd-H alloy series with the ^{197}Au resonance [57]. For the $(Pd_{1-x}Ag_x)_{0.99}Au_{0.01}$ system, the IS decreases from 2.2 to 1.8 mm/s between $x = 0$ and 0.6 ; from $x = 0.6$ (which corresponds to the bandfilling point) to $x = 1.0$, however, the IS increases to 2.0 mm/s ([2]). The increase of the IS (and of $\rho(0)$) from the bandfilling point to the pure Ag matrix is an unique behaviour of the ^{197}Au resonance in the Pd-Ag series and indicates that the number of s-conduction electrons increases at the noble-metal Mössbauer isotope when the matrix approaches to a noble metal itself ([3]). In contrast, for the d-metal Mössbauer isotopes ^{57}Fe, ^{99}Ru, ^{193}Ir and ^{195}Pt [56], a strong decrease in $\rho(0)$ is observed when going from the d-transition matrices to the noble metals which exceeds largely the volume effects on $\rho(0)$ [58]. The variations of the ^{57}Fe isomer shifts in the Ni-Cu, Pd-Cu, Pd-Ag and Pd-Au systems which are schematically shown by the dashed lines in figure 7 are characteristic for this behaviour and show clearly a kink towards lower electron densities at the band-filling point.

In the $(Pd_{0.99}Au_{0.01})H_n$ system, a linear decrease of the ^{197}Au isomer shifts till $n \approx 0.65$ was observed (from 2.2 to 1.4 mm/s) ; then up to $n = 0.8$ the IS remains unchanged. It has been stressed [57] that the *linear* variation of the IS in the concentration range $n < 0.6$ is an artifact resulting from fitting only one Lorentzian line to the unresolved resonance pattern of the coexisting α and β-phases. Therefore, it can be

([2]) All ^{197}Au isomer shifts are given relative to an Au absorber.

([3]) A similar behaviour but masked by the volume effect may be deduced from the variations of the ^{197}Au isomer shifts in Ni-Cu [59].

stated that ^{197}Au exhibits in the β-phase of $(Pd_{0.99}Au_{0.01})H_n$ with $n = 0.65 ... 0.80$ an IS of 1.4 mm/s which lies definitely below the Pd-Ag alloy series.

The coexistence of the α- and β-phase in (nonmagnetic) Pd-H alloys is strikingly demonstrated by the ^{99}Ru resonance which has a better resolution power for isomer shifts than the ^{197}Au resonance. In figure 8, the
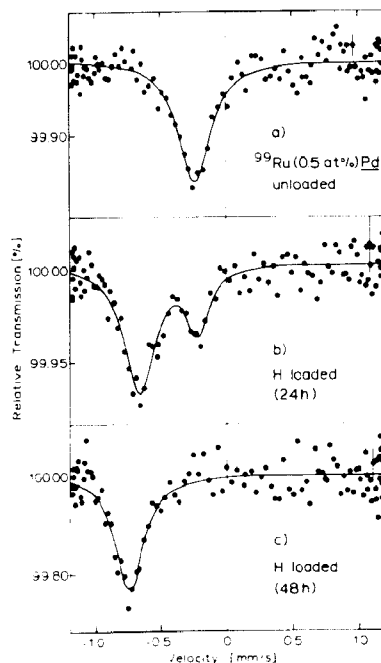

FIG. 8. — ^{99}Ru Mössbauer spectra on $(Ru_{0.995}Pd_{0.995})H_n$ as a function of hydrogen-loading time (from ref. [57]). The measurements were performed as source experiments (versus a Ru metal absorber) ; the velocity scale, however, is given in the absorber convention.

^{99}Ru spectra of $(Pd_{0.995}Ru_{0.005})H_n$ (which should be regarded only as preliminary measurements [57]) are shown for various H contents. The results show that the β-phase (IS = $- 0.66$ mm/s) coexists with the α-phase (at $- 0.24$ mm/s) till $n = 0.65$ is reached. At further hydrogeneration, the β-phase line starts to move towards lower electron densities and lies at $- 0.75$ mm/s at $n = 0.8$.

An interpretation of the observed ^{57}Fe, ^{99}Ru, ^{197}Ir, ^{195}Pt and ^{197}Au isomer shifts must start with an estimation of the changes in $\rho(0)$ induced implicitly by the increase in the volume of the unit cell between the α- and the β-phase. For ^{57}Fe, the results from pressure experiments [40] on ^{57}FePd have been used [60] to demonstrate that the IS observed in the β-phase with minimum hydrogen content ($n_e \approx 0.6$) can be regarded to be induced alone by the volume expansion. For the other ME isotopes, no pressure experiments on Pd alloy systems have been performed so far ; in lack of such data, the volume coefficients of the ^{197}Au and ^{193}Ir isomer shifts observed in their pure metals may be used for an estimation. Taking $(\partial S_{IS}/\partial \ln V)_T = - 6.8(1.0)$ mm/s for ^{197}Au in Au [61], the volume increase

of ~ 11 % between the α- and β-phases accounts well for the observed isomer shifts ($\Delta IS = 0.8$ mm/s as cited above). For ^{193}Ir, similar conclusions can be drawn from the volume coefficient of the IS of ^{193}Ir in Ir metal,

$$(\partial S_{IS}/\partial \ln V)_T = -5.1(1.0) \text{ mm/s} \quad [62],$$

and the IS observed in PdH$_{0.8}$ [55]. By analogy, it might be concluded that also the ^{99}Ru isomer shifts in PdH$_n$ are mainly caused by the volume expansion.

Finally, some studies performed presently in the Munich group should be mentioned briefly. From the Mössbauer data on the Pd-H system presented so far in this review, it is by no means conclusive whether the Mössbauer probe atoms are surrounded by the same number of hydrogen atoms on the nearest (and next nearest) neighbouring interstices as the Pd atoms. This is due to the fact that the impurity atoms may have either attractive or repulsive interactions with the diffusing hydrogen which are caused by the electronic structure at the impurity and/or by lattice distortions induced by the impurity [32, 33]. For instance, a Pt atom which has about the same size as a Pd atom and the same electron number may see surroundings more similar to the Pd matrix than an Au atom which has a larger size and a different electronic structure. Preliminary results of Karger [63] show for the β-phase of Pd-H different ^{197}Au isomer shift when measured in a source experiment (1.1 mm/s) and in an absorber experiment (1.45 mm/s). This marked difference in the isomer shifts may be attributed to the fact that for source experiments performed at helium temperature on (^{197}PtPd)H$_n$, the mother isotope ^{197}Pt is responsible for the hydrogen distribution around the Mössbauer atom, since after the decay of ^{197}Pt to ^{197}Au no rearrangement of the surrounding H atoms is expected within the lifetime of the excited ^{197}Au nucleus ($T_{1/2} = 2 \times 10^{-9}$ s). The hydrogen mobility in β-Pd-H can be regarded as frozen out (in the time-scale of the ME) below 100 K (jump rate of 10^4-10^2 s^{-1} [64, 65]). Whether the different IS observed in the above source experiment results from more or less hydrogen atoms in the vicinity of the Mössbauer atom cannot be definitely stated at present. The observation of a broadened resonance line in the source experiment [63] may be an indication for the presence of H atoms on nearest-neighbour interstitial sites of the ^{197}Au atom. This would be in accordance with the arguments given above on the relationships between the Pd matrix and the impurity atoms Pt and Au, respectively. It is obvious that the comparison of ME data obtained from source and absorber experiments may be a new and promising method to the study of impurity interactions in M-H systems. The experiments will be continued including other Mössbauer-isotopes.

The ME can provide also useful information on the rigidity of the lattice of a M-H systems by the observing the recoil-free fraction f. In an (Pd$_{0.99}$Au$_{0.01}$)H$_n$ absorber, Karger [63] found a decrease of f by $\sim$

20 %, when going from the α-phase ($n = 0$) to the β-phase ($n = 0.74$). This result indicates that the Au modes soften considerably on hydrogenation. An extension of these studies to alloys with higher Au and H content may provide additional information on the lattice instabilities observed in these alloys in connection with their transitions to superconductivity [4]. The contributed paper of Kimball et al. [124] presents a first account on such a study for the Pd$_{0.99}$Sn$_{0.01}$H$_{0.96}$ system. A softening of the low energy tin modes and the appearence of a localized mode in the matrix was observed in this strong-coupled superconductor.

4.3 MAGNETIC PROPERTIES AND ^{57}Fe HYPERFINE FIELDS IN THE Pd-Fe-H SYSTEM.

— The PdFe system is characterized at low iron concentrations by the formation of localized (giant) moments around the Fe atoms which order ferromagnetically by a long-range coupling mechanism [66, 67]. This unique ordering potential is caused by the extreme polarization capability of the d-band electrons (because of their high density of states $N(E_F)$). The addition of non-magnetic alloy substitutes like Ag or of interstitials like H leads to a decrease of $N(E_F)$ (as shown in figures 3 and 4) and, therefore, to a strong reduction of the ordering potential. When the d-band of the Pd-matrix is filled, the Fe atoms should behave like in a noble metal. The ME on ^{57}Fe is a well-suited tool for the study of magnetic properties of such systems [41, 50, 60, 67].

The first work on Pd-Fe-H was performed by Jech and Abeledo [70] on alloys containing 11 and 15 at % Fe. They found a decrease of the Curie temperatures on hydrogenation (see Fig. 9) ; the ^{57}Fe hyperfine fields,
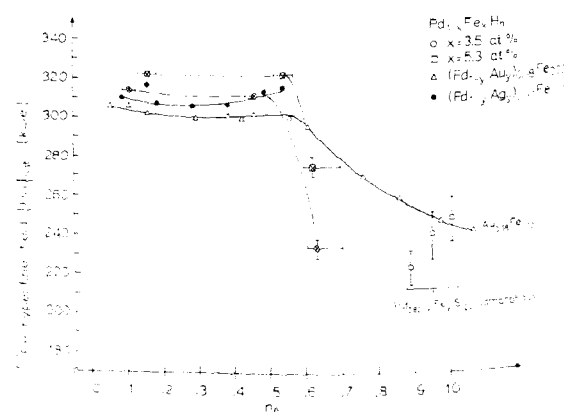
FIG. 9. — ^{57}Fe hyperfine fields in Pd-Fe-H- and Pd-Au(Ag)-Fe alloys. The solid lines show the variation of H_{hf} in substitutional alloy. The dashed-dotted line connects the H_{hf} values observed in different phases (from ref. [50, 60, 75]).

however, retained unchanged saturation values. The hydrogen content was estimated to be $n \approx 0.30$. Using the ternary phase diagrams of Carlow and Meads [60], the alloy formulae may be specified as (Pd$_{0.89}$Fe$_{0.11}$)H$_{\sim 0.3}$ and (Pd$_{0.85}$Fe$_{0.15}$)H$_{\sim 0.2}$.

Phillips and Kimball [70] performed a detailed

study on two Pd-Fe-H alloys with 2 and 5 at % Fe content. At these lower Fe concentrations, the formations of the α- and β-phases could be clearly distinguished by their different ordering temperatures and isomer shifts. The Curie temperatures decrease drastically from the α-phase (which is almost identical with the unhydrogenated matrix) to the β-phase (by about one order of magnitude, see Fig. 9). The ^{57}Fe hyperfine fields were measured down to 1.8 K. The 5 at % Fe alloy exhibits practically the same mean saturation value of H_{hf} in the α- and β-phase.

The 2 at % Fe sample exhibited a distribution of ordering temperatures (from 2.5-3.7 K) and, correspondingly, a spread in the hyperfine fields. Saturation values were not given, but an extrapolation leads to values near to the α-phase. An attempt was made to correlate the different hyperfine fields to different numbers nearest hydrogen neighbours around the Fe atoms. The applied model seems presently very questionable.

In the rather extensive work of Carlow and Meads [60, 71] on Pd-Fe-H alloys with Fe contents from 3.5-12.1 at %, a ternary phase diagram was established in close analogy with the Pd-Ag-H systems. The basic features are the following :

(i) Alloying of Fe to the Pd-matrix reduces the amount of maximum absorbable hydrogen. The α-phase can accept slightly more hydrogen and the β-phase is formed at considerably less hydrogen content. As a rule, one Fe atom corresponds to three H atoms, in accordance with n_e, the number of added electrons, in the picture of the rigid band model.

(ii) At room temperature, the two phase system disappeared at a Fe content > 11.5 at %.

(iii) The β-phase is formed with a value of $n_e \approx 0.55$ in the region of co-existing α- and β-phase. In this concentration range the saturation hyperfine fields of the α- and β-phase are identical, although the magnetic ordering temperature differ drastically (see Fig. 9

and 10). At higher hydrogen contents, $n_e > 0.65$, a new type of magnetic ordering behaviour appears in the β-phase characterized by considerably smaller saturation fields and by further reduced ordering temperatures. This change in the magnetic properties is coupled with the rapid increase in the isomer shift observed previously [44, 48].

The magnetic properties were discussed by Carlow and Meads [60] in terms of a model which describes conclusively the changes in the ordering by the filling up of two different types of d-holes at the Pd atoms. The ones have band character (t_{2g}-orbital) and are responsible for the long-range polarization of the Pd matrix, and the others are localized (e_g-orbitals) and carry an induced localized moment when they are nearest-neighboured to the Fe atoms. In the β-phase of Pd-Fe-H with $n_e < 0.65$, only the t_{2g} holes are filled up and the long-range ordering potential disappears. A further hydrogenation to $n_e > 0.65$ affects also the localized e_g holes in the vicinity of the Fe atoms leading to the reduced hyperfine fields and the increase in IS. The magnetic order then occurs between isolated Fe atom via the few s electrons in a random RKKY mechanism.

The properties of magnetic systems with random interactions have attracted considerable interest in the last few years. The AuFe system (with less than 8 at % Fe) has been described in terms of a new type of short range order without macroscopic polarization, the spin-glass behaviour (formerly also named as micto-magnetism or random antiferromagnet [68, 72]). Similar properties have been observed in Pd-based alloys, e. g., in $Pd_{0.99-x}Ag_xFe_{0.01}$ by low-field susceptibility measurements [73] and in $(Pd_{1-x}Fe_x)H_n$ by resistivity measurements [74]. The latter measurement demonstrates that the giant moment system of PdFe changes on hydrogeneration to a Kondo system (at Fe contents < 1 at %) and to a spin-glass system at higher Fe concentrations.

It should be noted that the ^{57}Fe Mössbauer study of Longworth [50] on the substitutional alloy series $Pd_{0.98-y}Au_yFe_{0.02}$ clearly reflects similar changes in the magnetic ordering properties. The ^{57}Fe hyperfine fields H_{hf} are shown for comparison in figure 9. $|H_{hf}|_{sat}$ remains nearly constant till the d-band filling is reached at $n_e \approx 0.6$: from this point a marked and continuous drop till the $Au_{0.98}Fe_{0.02}$ composition occurs. In $Pd_{1-x-y}Ag_yFe_x$ with $x = 0.03$ and 0.07 a similar variation of H_{hf} has been observed up to the bandfilling point [75]. On the same alloy system with $x = 0.01$ and $y = 0.50$, a distribution of hyperfine fields has been observed [76] which seem similar to that observed in $(Pd_{0.98}Fe_{0.02})H_n$ and which has interpreted in accordance with resistivity measurements [77], as due to a spin-glass behaviour.

The recent discussion of the Pd-Fe-H alloys in terms of a spin-glass behaviour demands a re-interpretation of some earlier Mössbauer results and may stimulate
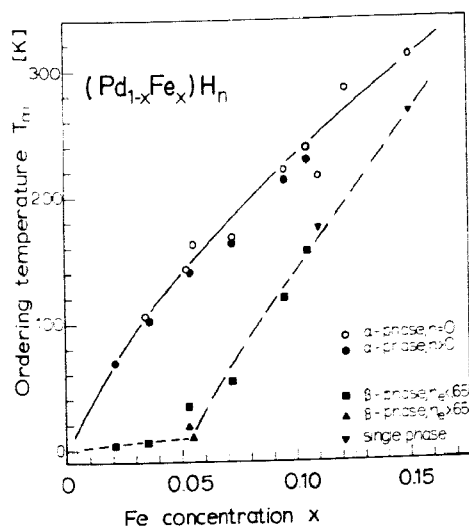

FIG. 10. — Magnetic ordering temperatures in the Pd-Fe-H system as obtained from ME studies (from ref. [60, 69, 70, 71]).

urther studies in the low Fe concentration range. It is evident even from the few Mössbauer data accumulated in figure 10 that around 5 at % Fe a change in the slope of magnetic ordering temperature of the β-phase occurs which is very similar to that observed in AuFe alloys and amorphous $Pd_{0.80-x}Fe_xP_{0.20}$ and $Pd_{0.80-x}Fe_xSi_{0.20}$ alloys [78]. It seems interesting to prove if there exists at low Fe concentrations a difference in the ordering mechanism of the β-phase with lower H concentration ($n_e < 0.65$) and with saturated H content ($n_e \approx 0.7$). A comparison of Mössbauer data with results from resistivity and low-field susceptibility measurements (obtained from identical samples with defined iron and hydrogen contents) is highly desirable.

4.4 INVESTIGATION OF OTHER d-METAL SYSTEMS BY THE ^{57}Fe RESONANCE.

— Beside the large amount of ME studies on Pd-based M-H systems, there are less ME studies on other d-metal systems. A comparison of these results with those obtained on the Pd-based systems may be very useful for the understanding of the behaviour of Fe atoms in different d-metal hosts. One of these ME studies (on the Ni-H system) has been already presented in the beginning of this chapter.

The study of Ableiter and Gonser [79] on the $(^{57}FeNb)H_n$ system with H concentrations up to $n = 1.9$ clearly demonstrates the occurrence of four different phases (α, β, β'' and δ) which can be directly visualized from the absorption spectra as partially-resolved lines with characteristic isomer shifts. Between the α-phase ($n < 0.05$) and the δ-phase ($n \approx 1.9$), a rather large change in the IS of ~ 0.9 mm/s is observed (see Fig. 7). These shifts exceed by far the changes of IS expected from the lattice expansion [40, 79]. The strong decrease of $\rho(0)$ at the Fe atoms was explained by a filling of the niobium d-band with the added hydrogen electrons. The ME data were used together with Hall-Effect and resistivity measurements to establish the Nb-H phase diagram towards high H concentrations. An indication for an H-induced localized moment at the ^{57}Fe was claimed from a study of the β-phase ($n = 0.76$) in an external magnetic field, although a positive internal hyperfine field was observed at the ^{57}Fe nucleus. The occurrence of a ^{57}Fe localized moment in $FeNbH_n$ alloys would be in accordance with such findings in $Fe_{0.01}(Nb_{1-x}Mo_x)_{0.99}$ alloys [80] and $(V_{1-x}Fe_x)H_n$ alloys [49]. The observation of an electric-quadrupole broadening of the β-phase line at low temperatures clearly indicates that H atoms have come to rest in the immediate vicinity of the Fe atom. The magnitude of the quadrupole splitting ($\Delta E_Q = 0.13$ mm/s at 77 K and 0.16 mm/s at 4.2 K) has been compared with model calculations on the electric field gradients produced by screened protons in tetrahedral nearest-neighbour sites [79].

An ME study on the $(^{57}FeV)H_n$ system has been reported by Simopoulos and Pelah [81]. The main information was obtained on the change of the recoil-free fraction f and of the second-order Doppler shift

in the temperature range from 100-700 K. The hydrogenated samples showed (independently on n varying from 0.11 to 0.43) an extremely high Debye temperature and a large f-factor ($f = 0.91$ at room temperature). From this behaviour it was concluded that hydrogen precipitates around the Fe impurities. No change in the line position on hydrogenation (within 0.1 mm/s) was observed. This may be due to a cancellation of electronic, volume and lattice strength effects.

The b. c. c. α-phase of iron does not dissolve hydrogen in amounts that would be necessary for ME studies (less than 10^{-3} at % at room temperature). A ME study on an electrolytically loaded Fe foil showed no change in the spectrum [39]. The f. c. c. γ-phase of iron can be investigated at room temperature only in Fe-rich alloys with other d-transition metals ; from these alloys the stainless steels (SS) are important subjects for a study of their properties with hydrogen. The first attempt has been reported by Wertheim and Buchanan [39] on the type SS 310 which has the non-magnetic austenite phase. An electrolytically charged foil exhibits an increase in the IS (0.25 mm/s) combined with a broadening of the experimental linewidth ($\Delta W = 0.17$ mm/s). The H content was determined as $n = 0.3$. The effect on the IS per H concentration is about one-half of the one observed in Ni, but still considerably larger than the one in Pd (see Fig. 7). Similar results, but more detailed, are reported on austenitic stainless steels by Fujita and Sohmura in a contributed paper to this conference [82]. These authors also report on measurements on ferromagnetic f. c. c. Fe-Ni alloys (with 45 and 75 at % Ni). The hydrogenated samples ($n = 0.24$) exhibit magnetically-split hyperfine pattern which could be decomposed into two subspectra belonging to different phases named γ' and β. The occurrence of these phases was confirmed by X-ray diffraction measurements. It is very interesting to note that isomer shifts, hyperfine fields and ordering temperatures of the two phases have many similarities with the ones observed in the Pd-Fe-H system. The γ'-phase of Ni-Fe-H corresponds to the α-phase of Pd-Fe-H, and correspondingly the β-phase of Ni-Fe-H to the β-phase of Pd-Fe-H with $n_e > 0.65$.

The $(Ni_{1-x}Fe_x)H_n$ system (with $x = 0.004$ and 0.01) was investigated in detail by use of the ^{57}Fe resonance by Janot and Kies [83]. The ME pattern were used to determine the time and temperature dependence of the H desorption process. The data suggest that the Fe atom has more H atoms in its surroundings than the matrix atoms at $n_e = 0.65$. It is interesting to note that systematically a smaller H-induced IS was observed than in the work [39] on $(^{57}CoNi)H_n$. Although a comparison between these to different studies is very hazardous, this may be an indication for effects similar to those observed on $(^{197}AuPd)H_n$ in source and absorber experiments.

First results of ME studies on $TiFeH_n$ have recently been announced by two groups [85, 86]. With increasing n, the occurrence of different phases with

increasing isomer shifts were reported [85]. No difference was found in spectra taken in normal transmission geometry and taken with back-scattered conversion electrons [86].

On the intermetallic compounds YFe_2 and $GdFe_2$, a decrease of the ^{57}Fe isomer shifts on hydrogenation has been reported [86]. The interesting properties of these compounds, where a decrease of the ordering temperature on hydrogenation is accompanied by an increase in the Fe moment, are described in ref. [87].

A final remark should be made on the various IS data of ^{57}Fe in the d-transition metals and alloys. In all cases (except vanadium), a decrease of $\rho(0)$ has been observed at the Fe atoms on hydrogenation which was, however, quite different in magnitude for different hosts. From this, and from the variation of the ^{57}Fe isomer shifts in related substitutional alloy systems (see Fig. 7), it must be concluded that the Fe atoms experience in some cases (especially Pd) only the lattice expansion, whilst in other cases (e. g. Nb, Ni) the hydrogen interacts directly with the Fe atoms. To elucidate the Fe-H interactions in the different matrices, source and absorber experiments similar to the ^{197}Au experiments reported previously seem very useful.

4.5 ISOMER SHIFTS OF ^{181}Ta IN THE α-PHASE OF Ta-H.

— Two properties characterize the ^{181}Ta Mössbauer studies on the Ta-H system reported recently by Heidemann, Kaindl, Salomon, Wipf and Wortmann [88, 89], when compared with the Mössbauer studies reviewed so far :

(i) The investigations were performed on a pure system.

(ii) The high resolution power of the 6.2 keV gamma transition of ^{181}Ta facilitated a precise study of isomer shifts and the hydrogen-induced line-broadenings within the α-phase as a function of H concentration and temperature.

This is demonstrated in figure 11a, where the room temperature spectra of hydrided Ta metal absorbers with various H concentrations are shown. The isomer shift S increases linearly with the H concentration c by $dS/dc = 57(6)$ mm/s (Fig. 11b). This is a very strong effect and corresponds to a shift of ~ 100 times the experimental linewidth $W_{c=0}$ for the spectra with the highest concentration ($c = 0.17$).

The strong shift is accompanied by a considerable hydrogen-induced line-broadening (Fig. 11a, b) which again increases linearly with c by $dW/dc = 6.3(7)$ mm/s (at 295 K). Besides this dependence on H concentration, the line-broadening exhibits a strong dependence on temperature which is demonstrated by the spectra of a hydrogen-loaded absorber with $c = 0.018$. At $T = 400$ K the line-width of this absorber is almost identical to that of an unloaded one ; the observed temperature dependence of the line-broadening is reversible (all experiments were performed in the α-phase of Ta-H, see Fig. 2c).
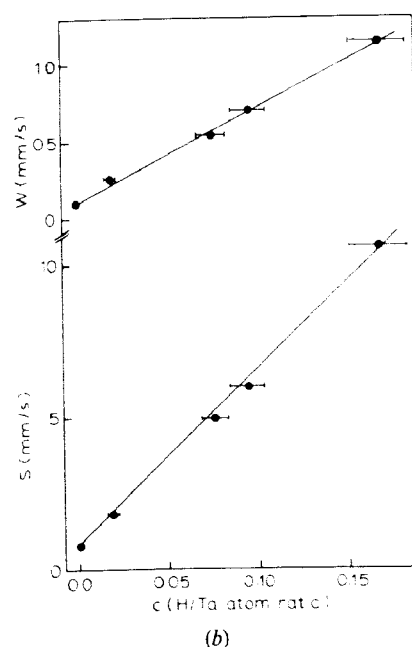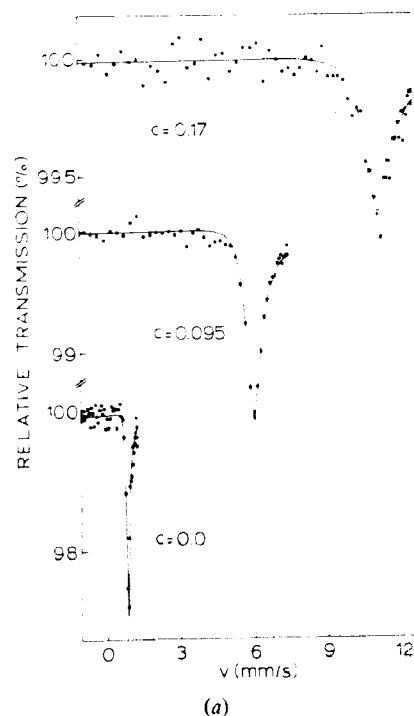
(a)

(b)

FIG. 11. — a) ^{181}Ta Mössbauer spectra of Ta-H absorbers at room temperatures for various H concentration c. The solid lines represent single lorentzians modified by a constant dispersion term, which is typical for the ^{181}Ta resonance [92]. (b) Results on the linewidth W and isomer shift S obtained from the spectra at room temperature (Fig. 11a) as a function of H concentration c.

The striking behaviour of the line-width of the ^{181}Ta resonance and its dependence on concentration and temperature will be used in the next section 4.6 to describe the dynamical behaviour of the diffusing hydrogen.

The concentration dependence of the ^{181}Ta isomer shifts S reflects changes in the electronic structure of

the matrix atoms upon H loading and will be discussed following the arguments given in an earlier account on this work [90]. Again the two main sources for H-induced isomer shifts must be considered ; the first is the lattice expansion and the second is the explicit change of the electronic structure of the Ta atoms by the interstitially dissolved hydrogen. The influence of the lattice expansion on S is difficult to estimate in the present case since we are dealing with the α-phase where the hydrogen atoms induce mainly local distortions [91]. As a first approximation, these effects were considered by the averaged macroscopic volume expansion of the α-phase ; the corresponding contribution to S was derived from the known volume dependence of S in pure Ta metal (from pressure experiments [92]). It can account for, as an upper limit, one third of the observed variation of S with c. Therefore, the dissolved hydrogen induces an explicit change of $\rho(0)$. Since the mean-square nuclear charge radius is negative for the 6.2 keV gamma resonance, the observed increase of S corresponds to a decrease in $\rho(0)$ at the Ta nucleus with increasing c.

This decrease of s-electron density has been discussed [90] in terms of a rigid-band-like filling of the Ta band by the added H electrons. It was concluded that in this *protonic* picture about 50 to 100 % of the H electrons must fill up empty 5d states of tantalum to account for the observed decrease of $\rho(0)$ with c. Applying the more realistic picture developed for the Pd-H system [27, 25, 26] to the Ta-H system, the decrease of $\rho(0)$ can be more likely explained by a removal of s-p band states (from the bottom of the Ta band) from the Ta to the H atoms, thus making the band-states at Ta more d-like. This conclusion is supported by a recent photoemission study on the V-H and V-D systems [28], which reports on the observation of a low-lying H band in close analogy to the Pd-H system. Vanadium has a very similar band-structure to tantalum [93, 94]. Band-structure calculations on hydrides of group V metals are urgently needed. It may be interesting to note that an isomer shift of + 57(6) mm/s can be extrapolated for a stoichiometric TaH hydride from the slope of S given in figure 11*b*. This value is near to $S = + 71$ mm/s observed for TaC [92] which analogously has a metallic d band that has been investigated by photoemission studies and bandstructure calculations [95].

4.6 STUDY OF HYDROGEN DIFFUSION IN THE α-PHASE OF Ta-H BY THE MOTIONAL NARROWING OF THE ^{181}Ta RESONANCE LINES.

— The diffusional reduction of the line-width (motional narrowing) is a well-established phenomenon in the NMR spectroscopy and has been successfully applied in studies of diffusion, e. g. on metal hydrogen systems [35]. Mössbauer spectroscopy can yield similar information, as theoretically discussed [96] and observed in limited cases [97, 98], but motional-narrowing effects of Mössbauer lines have not been utilized so far for obtaining quantitative
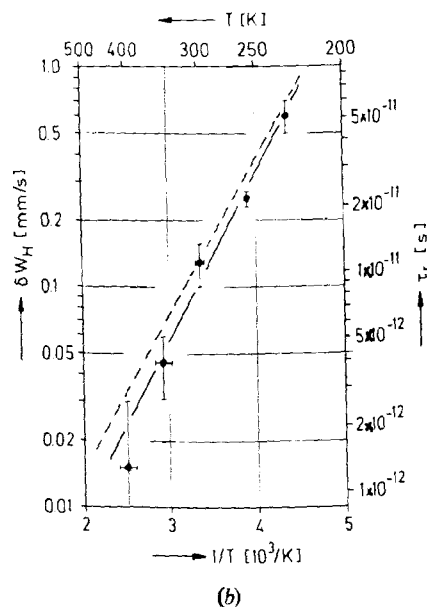

(a)

(b)
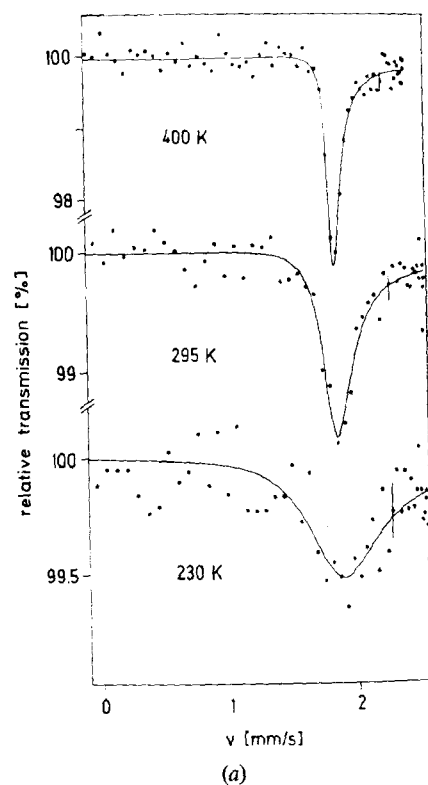
FIG. 12. — (a) ^{181}Ta Mössbauer spectra for a Ta-H absorber with $c = 0.018$ at various temperatures (the velocity scale is changed in comparison to Fig. 11a). (b) Semilogarithmic plot of the H-induced line broadening δW_H of the Ta-H absorber with $c = 0.018$ (Fig. 12a) versus the reciprocal temperature. The values of τ_r on the right-hand scale are calculated by use of the model described in the text. The dashed line indicates the values of τ_r as calculated from macroscopic diffusion measurements [15].

information on the diffusion process. From the experimental results on the isomer shift S and line-width W presented in figures 11*b* and 12*b*, Heidemann *et al.* [88] in a motional-narrowing approach were able to derive the activation energy and the jump frequency of the

diffusing H atoms. This opens a new microscopic method for studying the diffusion of H — and other interstitial atoms — in transition metal hosts. The method is complementarily related to usual NMR studies of diffusion, since here the probe atoms are not diffusing by themselves ([4]), but are subjected to fluctuating interactions with the diffusing interstitials ([5]).

The model applied to the analysis of the H-induced line-broadening makes two assumptions [88] :

(i) isomer-shift effects dominate electric-quadrupole effects and

(ii) only H atoms in nearest-neighbour interstitial sites contribute to the Ta isomer shifts.

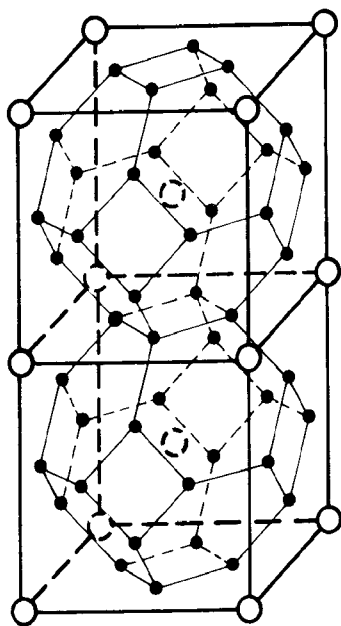The H atoms randomly occupy the tetrahedral interstitial sites in α-Ta-H (see Fig. 13) ; there are 6

FIG. 13. — Two unit cells of a b. c. c. metal (open circles) with tetrahedral interstices (filled dots). The course of the H diffusion can be best visualized when starting from a tetrahedral sites in the joint plane of the two unit cells.

tetrahedral sites per Ta atom and 24 interstitial sites in nearest-neighbour positions to a Ta atom ; therefore, the mean number of H atoms in all 24 nearest-neighbour atom around each Ta atom is $4\,c$. With ω_H as the isomer shift caused by one H atom on a neighbouring Ta atom, the mean H-induced isomer shift S_H can be written as

$$S_H = \omega_H \times 4\,c. \tag{2}$$

([4]) A diffusional behaviour of the Mössbauer atom leads to a line-broadening [99, 100] which increases with the diffusion rate.

([5]) The method is directly related to NMR and NAR studies on the matrix atoms [35, 36, 37], where the electric-quadrupole and magnetic dipole interactions with the diffusing interstitials lead to a line-broadening which narrows with increasing diffusion rate. On principle, the H-induced Knight shifts must also contribute to the line-broadening, when a microscopic picture of the H-induced changes of N(E$_F$) is applied.

From the observed variation of S_H with c, ω_H is found to be 14.2(1.5) mm/s. The modulation of the resonance energy by the diffusing hydrogen atoms is described by the two parameters $\varDelta$ and τ_c [101] where $\varDelta$ is the amplitude of the modulation and τ_c is the correlation time. In the limit of fast modulation ($\varDelta\tau_c \ll 1$), the H-induced increase δW_H of the line-width (FWHM) is given by [96, 101, 102]

$$\delta W_H = 2\varDelta^2\tau_c. \tag{3}$$

For low H concentrations, $\varDelta^2$ can be written as $\omega_H^2 \times 4\,c$ and represents the mean-square deviation of the isomer shift from its mean value S_H. The correlation time τ_c is proportional to the mean residence time τ_r of the H atoms on interstitial sites, $\tau_c = n\tau_r$. Here n is equal to the average number of times that a single H atom, starting from a nearest-neighbour interstitial site of a Ta atom will occupy anyone of the 24 nearest-neighbour interstitial sites of the same Ta atom in the course of its diffusion ([6]). This number has been calculated as $n = 12.6(5)$ with a Monte Carlo method [88] and as 12.65(5) by solving numerically the rate equation [103].

From the above equations, the line-broadening can be written as

$$\delta W_H = 8\,\omega_H^2\tau_r nc. \tag{4}$$

The linear dependence of δW_H on c is in agreement with the experimental results. The latter equation yields $\tau_r = (9.8 \pm 1.5).10^{-12}$ s (at room temperature), with the experimental values for δW_H and ω_H and the calculated value of n.

The observed temperature dependence of the line-broadening is contained in eq. (4) by the proportionality of δW_H with τ_r. Since $\tau_r \propto \exp(U/kT)$, where U is the activation energy of the diffusion process, a temperature dependence of $\delta W_H \propto \exp(U/kT)$ is expected. According to the Arrhenius plot of figure 12b, such a temperature dependence of δW_H has indeed been observed yielding $U = 0.14(1)$ eV [88]. The results for τ_r and U agree well, as shown in figure 12b, with values obtained from macroscopic diffusion measurements [15]. Particularly the result for τ_r strongly supports the assumptions made in this rather simple model, which completely neglects the effects of further-distant H atoms and of electric-quadrupole interactions. Recent NAR measurements on Ta-H [37] yielded valuable information on the H-induced quadrupole interactions at the Ta atoms [104]. From these results, the contribution of the electric-quadrupole interaction to the Mössbauer line-broadening has been estimated [88]. It accounts for about one-tenth of the observed line-broadening. This finding again supports the assumption that the observed line-broadenings

([6]) The isomer shift of the Ta atom is not changed as long as the hydrogen atom jumps from one nearest-neighour interstitial site to another one. It is easy to recognize from figure 13 that for 3 of the possible 4 jump direction, the H atoms remain on the nearest-neighbour shell of the Ta atom in question.

are mainly caused by isomer shift fluctuations. It should be noted that (in contrast to τ_r) U is obtained independently of the assumptions made in this model.

The studies of hydrogen diffusion in the Ta-H system are presently continued at lower H-concentrations and lower temperatures, where changes in the diffusional behaviour of H are expected [15]. Preliminary results on Ta-D absorbers [105] show a stronger line-broadening (by a factor of 2.5(8) at room temperature) than the one observed in Ta-H absorbers. This clearly reflects the slower diffusion rate of the heavier deuterium interstitials [15].

5. The rare earths hydrides. — 5.1 PHASE-DIAGRAMS, STRUCTURE AND ELECTRONIC PROPERTIES OF RARE EARTH HYDRIDES. — Exposing rare earth (RE) metals to a hydrogen atmosphere at elevated temperatures (600-800 °C) leads to a rapid formation of two hydride phases of the basic formula RH_2 and RH_3 which exist over a wide range of stoichiometry. Solid solutions of hydrogen in the host lattice of α-phase type like in the d-metals V, Nb, Ta and Pd are not stable at room temperature due to the high heat of formation of the hydride phases. Figure 14 shows schematic phase-
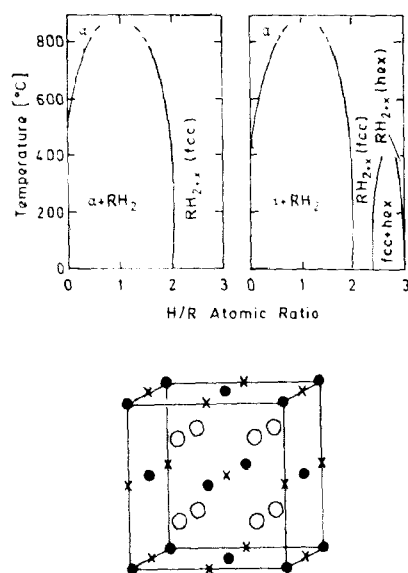

FIG. 14. — Upper part : Schematic phase diagrams of rare-earths hydrides. Left-hand side : Lighter rare-earths. Right-hand side : Heavier rare-earths. Lower part : CaF$_2$ structure of RE hydrides. Full circles : RE atoms ; open circles : H atoms on regular fluorite sites ; crosses : H atoms on octahedral interstitial sites.

diagrams of rare-earth hydrides, which also hold partially for Y, Lu and for some heavier actinides [107]. The RH_2 phase possesses the CaF$_2$ structure and exists over a wide range from considerable hydrogen deficiencies up to large excess hydrogen concentrations. In the RH_{2-x} range, some of the regular (tetrahedral) H lattice sites are not occupied ; the hydrogen atoms

are highly mobile at room temperature, jumping via the octahedral interstitial sites or via a direct process to the empty H sites (see Fig. 14). The jumping rate $(10^{11}\,s^{-1})$ is a function of x and decreases considerably when the stoichiometry RH_2 is approached [36]. Above the stoichiometric formula additional hydrogen is built into the octahedral interstitial sites, now being again more mobile (for small x) than the hydrogen in regular lattice sites. For the lighter RE (La, Ce, Pr, Nd) the RH_{2+x} phases can continuously accept hydrogen up to $x = 1$, now forming the f. c. c. RH_3 phase, in which all octahedral interstitial sites of RH_2 are occupied. For the heavier RE, the f. c. c. RH_{2+x} phase undergoes a transition to a hexagonal RH_{3-x} phase, coexisting with the f. c. c. RH_{2+x} phase over a wide composition range (see Fig. 14). Europium and ytterbium which are divalent in their metals form (divalent) dihydrides of orthorhombic structure [107]. The other RE are trivalent in both the di- and trihydrides.

The formation of the RE hydrides is connected with drastic changes in the electronic and magnetic properties, when compared with the unhydrided RE metals. While, for instance, the RH_2 phase remains metallic with no dramatic change in the conductivity, the high magnetic ordering temperatures generally observed in the RE metals drastically decrease in the dihydrides [108]. The trihydride phases show semi-conducting properties, indicating that all conduction electrons are trapped in hydrogen bonds. In addition, there is a complete lack of magnetic ordering in RH_3 systems down to 4 K.

The electronic structure of H-atoms in the dihydride phase was for a long time described by two contrary models which were named protonic and anionic (or hydridic) [5]. In the protonic model, the hydrogen was thought to give its electron to the matrix and to remain positively charged, where in the anionic model the hydrogen was thought as negatively charged by attracting an additional electron from the conduction band of the matrix.

Both the protonic and the anionic model of the dihydrides imply a splitting of the matrix d-band into a t_{2g} and an e_g sub-band due to the cubic crystalline electric field (CEF) ; in both models the metallic s-band lies above the lowest d-band. The difference between the models concerns the point that the CEF of the protonic hydrogen shifts the t_{2g} band towards lower energies, whereas in the anionic model the negatively charged hydrogen would repel the t_{2g} orbitals and raise them towards higher energies. It is obvious that band structure calculations may describe the properties of metal-hydrogen systems much better than the simple models cited above, which give no answer to the question how the hydrogen atom is actually bound into the matrix. As a first step of understanding, the models have proven quite useful and are still used for the discussion of electronic properties in the rare-earths hydrides.

Nowadays, most of the experimental results can be explained in the *anionic* (or *hydridic*) model, which can be brought in accord with bandstructure calculations [110]. Mössbauer spectroscopy has considerably contributed to the above findings. This is in part due to the fact that in the rare-earth region all investigations can be performed on pure systems because of the many well-suited Mössbauer isotopes (see Fig. 5).

5.2 REVIEW OF MÖSSBAUER WORKS ON RE HYDRIDES AND RELATED SYSTEMS. —

The first ME study on RE hydrides was concerned with a contamination effect. It was shown by Lounasma and Kalvius [110] that a previously reported anomaly in the specific heat of Eu metal at 16 K was due to the magnetic ordering of an impurity phase, which was identified as EuH_2.

A more detailed ME study on RE hydrides was reported by Abeles, Bos and Ouseph [111] using the [161]Dy resonance. The isomer shifts of DyH_2 and DyH_3 (obtained at room temperature) were compared with other compounds and Dy metal. A discussion in terms of the two contrary models was concluded in favour of the hydridic model and a covalent character of the metal-hydrogen bond was stated. The magnetic hyperfine fields of [161]Dy in $DyH_{2.05}$ were investigated by Hess, Bauminger, Mustachi, Nowik and Ofer [112]. The temperature variation of the hf fields taken at 0.23, 1.1 and 4.2 K could not be described in terms of a single CEF groundstate of Dy^{3+} when an ordering temperature of 8 K. as given in literature [108], was supposed. Therefore two nearly degenerate CEF doublets were assumed to fit the data. A recent specific-heat study on $DyH_{1.99}$ [125] reports on a considerably lower Néel temperature of 3.3 K from a λ-type anomaly and, in addition on a rather broad anomaly around 4.5 K. These findings may lead to a re-interpretation of the Mössbauer data.

Two recent works [113, 116] report on studies of Gd metal, GdH_2 and GdH_3 with the 86.5 keV resonance of [155]Gd. The one was performed in the course of an extensive investigation of nearly 50 Gd alloys and compounds by Cashion, Prowse and Vas [116]. The other study by Lyle, Walsh, Witts and Ross [113] was only concerned with the properties of the hydrides. The magnetic hyperfine field in GdH_2 was found to be ~ 20 °₀ smaller than that in the metal. The nonmagnetic and hexagonal GdH_3 phase exhibited a resolved quadrupole splitting. An electric field gradient of 5×10^{17} V cm^2 was derived. These properties were discussed together with the isomer shift results and found in fair agreement with the anionic model [113].

In EuH_2 and YbH_2 the rare-earth atoms are divalent like in their metals. Because of the reduced electrical conductivity (by 5 orders of magnitude) an almost empty conduction band can be assumed. [151]Eu and [170]Yb Mössbauer studies performed by Mustachi [114] on EuH_2 and YbH_2 yielded valuable information on their electronic structure. In particular, the observed quadrupole splittings could be explained by point-

charge calculations only in terms of the hydridic model. The isomer shift and the magnetic hyperfine field in EuH_2 can be used to derive the degree of covalency of the metal-hydrogen bond. It is interesting to note in this connection that the metal-hydrogen bonds must play an essential role for the magnetic ordering mechanism in EuH_2 ($T_c = 16$ K). Since conduction electrons are absent, which normally cause the exchange between the localized 4f moments in the rare-earth metals and dihydrides the ferromagnetic exchange must occur via the covalent hydrogen bonds.

Initiated by a search for Mössbauer source and absorber materials which exhibit unbroadened emission or absorption lines, the properties of some dihydrides of the rare-earths and of Sc and Y have been investigated in the last few years. For the [155]Gd resonance, Prowse, Vas and Cashion [115] prepared a single-line absorber by adding small amounts of isotopically enriched [155]Gd to ScH_2. Similar single-line absorber or source materials for the [166]Er and [160]Dy resonance were investigated recently by Stöhr and Cashion [117] and by Shenoy, Dunlap, Westlake and Dwight [119].

The rare-earths hydrides were found [115, 117, 119] as well-suited for single-line matrices because of the following properties :

(i) RH_2 can be produced from the metallic state quite simply by hydrogenation and forms a stable compound with a reasonable Debye temperature (which is higher than in the metal). Small deviations from stoichiometry do not influence the linewidth.

(ii) The crystal structure and point symmetry is cubic.

(iii) With respect to their metals and most intermetallic compounds the dihydrides show low ordering temperatures, so that some of them can be used even at helium temperatures (e. g. ErH_2, TmH_2) as single line absorber or source materials. For the others (e. g. DyH_2, HoH_2) a magnetic dilution with diamagnetic Sc or Y lowers the respective ordering temperatures well below 4.2 K and due to the fast spin-spin relaxation rates. unsplit resonance lines were observed at helium temperature (see also [131]).

Beside these aspects which are of great benefit for the Mössbauer spectroscopy in the rare earths region. Stöhr and Cashion for the first time applied the ME to the determination of the CEF groundstate of the RE ion in a dihydride matrix. They determined from the resolved paramagnetic hyperfine splitting of highly dilute [160]Dy and [166]Er impurities in YH_2 an Γ_7 Kramers doublet for both ions. From this result they conclude that the hydridic model must account for the electronic properties of the hydrogen.

This interpretation of the Mössbauer data [117] (which has been applied earlier to susceptibility and EPR measurements [5] is based on the fact that the

CEF groundstates of 4f ions in cubic surroundings have characteristic features, which depend on the properties of the CEF and which have been described and tabulated by Lea, Leask and Wolf [118]. According to the point charge model, the sign (and the order of magnitude) of the crystal field parameters A_4 and A_6 [118] is determined by the nearest neighbour shell of the 4f ion. Therefore the sign of A_4 and A_6 is fixed by the sign of the charge at the hydrogen atoms, which in turn is described as positive by the protonic model and as negative by the anionic model. It was shown in ref. [117] (and also in ref. [119]) that the observation of a Γ_7 or Γ_6 doublet as groundstate instead of a $\Gamma_8^{(3)}$ quartett (which has a completely different hyperfine splitting) favours the hydridic model.

The work of Stöhr and Cashion on RE dihydrides has been recently continued by Shenoy, Dunlap, Westlake and Dwight [119] by an investigation of the CEF and the magnetic properties of ErH_2 (by use of the ^{166}Er resonance). A magnetic ordering at 2.4(1) K was found. From the magnitude of the hyperfine fields observed with and without an external magnetic field and from magnetization measurements a Γ_6 groundstate and a $\Gamma_8^{(1)}$ first excited state (separated by about 125 K) was derived. The observation of the Γ_7 groundstate of Er in YH_2 was confirmed : the change from Γ_6 to Γ_7 between ErH_2 and YH_2, which have rather similar lattice constants ($a_0 = 5.123$ Å and 5.205 Å, respectively) was explained by a small change in the ratio of A_4 and A_6 (see ref. [125]).

The same authors (Shenoy et al., contributed paper to this conference [120]) have investigated $ZrH_{1.5}$ (the δ-phase of the Zr-H system) which has also the CaF_2 structure of the RE dihydrides with a considerable hydrogen deficiency (only 6 of the 8 regular hydrogen sites are occupied). The Mössbauer nucleus was again ^{166}Er which can be easily produced by neutron irradiation of Zr metal containing 0.2 at % of Ho metal. In spite of the large deviation from stoichiometry in $ZrH_{1.5}$ a basically cubic environment of the Er atom was concluded from the observation of an (almost undistorted) Γ_7 CEF groundstate (therefore all regular H sites around the Er ion should be occupied). For details see the original paper, which promises a sensitive spectroscopic tool for the study of the attractive or repulsive interactions of hydrogen with an impurity atom.

5.3 FIRST APPLICATION OF MÖSSBAUER SPECTROSCOPY TO ACTINIDES HYDRIDES.

The hydrides of the actinides (like the Zr-H system) have attracted strong interest because of the technological aspects for nuclear reactor design [6]. The properties of the hydride systems of the lighter actinides are rather complex, whilst the heavier actinides form hydride systems similar to the heavier RE hydrides. The Np-H system, for instance, is well described by figure 14. The high resolution power of the 59.5 keV resonance of ^{237}Np has been applied recently to the study of the dihydrid phases NpH_{2+x}

(with $x = 0.1$, 0.3 and 0.5) by Mintz, Gal, Hadari and Bixon [121]. The spectra show drastical variations on hydrogen content (Fig. 15) and could not be explained by one uniform interaction for all Np sites. They were considered to result from different subspectra, which belong to Np with different number (and configuration) of excess hydrogen atoms at the 6 nearest-neighboured octahedral interstices (see Fig. 14). In a first attempt the spectra were analysed in terms of a random distribution of the excess hydrogen atoms (like in a *frozen* α-phase). Therefore, the relative inten-
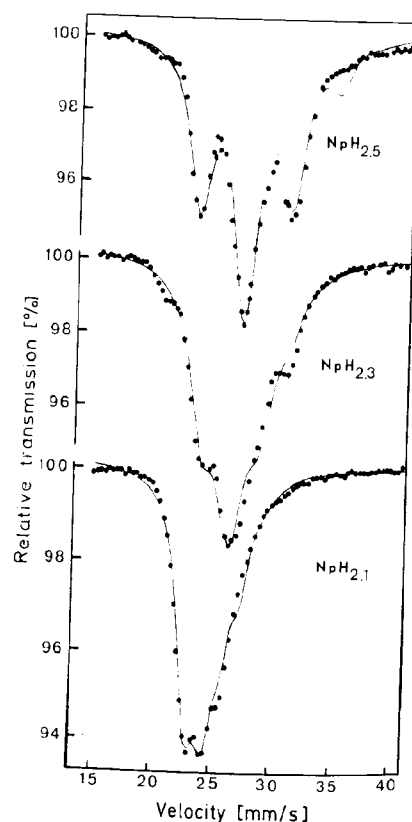

FIG. 15. — ^{237}Np Mössbauer spectra of NpH_{2+x} at 4.2 K. The solid lines represent a fit which assumes a random distribution of the interstitial H atoms, modified by nearest-neighbour interactions (from ref. [121]).

sities $P_m(x)$ of the subspectra of Np ions having m octahedral hydrogen neighbours were derived from the binomial formula. The IS (vs. $NpH_2^{(7)}$) of each subspectrum was assumed to be $m.\omega_{IS}(x)$, where $\omega_{IS}(x)$ is the isomer shift induced by one octahedral hydrogen neighbour. The quadrupole interactions of the different hydrogen configurations around the Np ions were described additively by $\omega_Q(x)$, the interaction with one H neighbour (the details are illustrated in the original paper). However, the spectra could not be fitted with the above assumption of a random hydrogen distribution. Therefore, an additional parameter E was introduced, which describes the repulsion (or the attraction) between two neighbouring interstitial

hydrogen atoms. With this assumption the spectra could be fitted satisfactorily (Fig. 15), although in all three spectra the right hand part of the resonance pattern was not well described by the theoretical curve.

The following results were derived within this model :

(i) The isomer shift $o_{I_S}(x)$ contributed from one hydrogen neighbour is 1.2, 2.3 and 3.6 mm s for $x = 0.1$, 0.3 and 0.5, respectively. This again corresponds to a decrease of $\rho(0)$ at the Np atom. [7]. The resonance line of almost stoichiometric dihydride ($NpH_{2.0.0}$) is located at 21.2 mm s when measured as above with an Am (6 ") Th source [126]. This corresponds to an IS of 15 mm s vs. $NpAl_2$ and 20 mm s vs. Np metal (towards lower electron densities).

(ii) One H neighbour produces a QI of

$$o_{I_Q} = e^2qQ = 1.7 \text{ mm s}.$$

This value is below the resolution power of the resonance lines and seems very small when compared with the theoretical value of an unscreened H^+ or H^- ion.

(iii) The H-H interaction parameter E yielded an attractive interaction at low concentrations ($x = 0.1$) and an increasingly repulsive interaction at higher concentrations ($x = 0.3$ and 0.5).

The model applied by Mintz et al. to the analysis of the ^{237}Np spectra may be regarded as too simple to describe the real properties in NpH_{2-x}. If there exists on the one hand a strong repulsive H-H interaction in the hydrogen-rich phases a lowering of the temperature must lead, on the other hand, to the formation of a short-range order and finally to the appearence of a superstructure. Indeed, superstructures have been observed in RH_{2+x} phases [122]. The $NpH_{2.5}$ spectrum could result from the same superstructure that has been observed in $CeH_{2.5}$, where three H-atoms are located in a planar arrangement around each metal atom (configuration number 10 of ref. [121]). In this case the symmetric spectrum of $NpH_{2.5}$ in figure 15 would result from a quadrupole splitting with an asymmetry parameter $\eta = 1$ [123] and an electric field gradient of $V_{zz} \approx 8 \times 10^{17}$ V cm^2 can be derived by visual inspection (^{7}).

The problems in analyzing the ^{237}Np hydride spectra may be solved in near future. In any case, the spectra presented by Mintz et al. clearly demonstrate the high resolution power of the ^{237}Np resonance for a study of interstitial hydrogen in the Np hydrides.

(^{7}) Since the 59.5 keV transition of ^{237}Np is of E1 type, a rather large dispersion term must occur in the absorption spectra (see, e. g., the similar case of ^{161}Dy [127]). Preliminary results [132] yielded a value of B_7 — 0.06 for the dispersion amplitude of ^{237}Np (as defined in [127]). Inclusion of such a term may considerably improve the fits of the NpH_{2+x} spectra.

6. Conclusion. — It is hoped that his review has demonstrated the wide range of applications of the ME to the study of hydrogen in metals. Beside the information obtained on the electronic structure of M-H systems from isomer shifts and quadrupole and magnetic hyperfine interactions, some applications of the ME reported in the last few years promise new sensitive tools for the study of e. g. the hydrogen diffusion, the phase transitions and analysis and the distribution of hydrogen around the matrix atoms and substitutional impurity atoms. Some fields which may be stressed in future studies may be listed here

(i) The general finding that hydrogen reduces the s-electron density of the matrix atoms should stimulate theoretical calculation on hydrogen-induced changes of $\rho(0)$ in dilute systems (e. g. d-metals) and phases (e. g. the RE dihydrides).

(ii) The information involved in the quadrupole interaction produced at a matrix atom by a neighbouring H atom may lead to a better understanding of the screening conditions in a metallic matrix, which is in turn strongly influenced by the presence of a H atom.

(iii) The Pd-Fe-H and Ni-Fe-H systems are well-suited candidates for further studies of the magnetic ordering behaviour in matrices where the hydrogen suppresses the long-range ordering potential.

(iv) The investigation of the RE hydrides has still proven as very successful. Future work may be concerned with phase transitions, investigation of near range order and diffusion. Investigations over a wider temperature range seem very useful.

(v) The ME can be successfully applied [128] to the investigation of strong-coupled superconductors. The M-H systems which exhibit superconductivity on hydrogenation are interesting candidates.

(vi) The investigation of hydrogen absorption and desorption in intermetallic compounds like $LaNi_5$ and TiFe which are considered as model substances for hydrogen storage materials is now in progress. This field is very important and very closely combines applied science with basic research.

Appendix

Table I

Compilation of ME studies, arranged for different host matrices (this compilation may be used in connection with Fig. 5). The subject numbers of the last column are defined in section 3.

Matrix	Isotope	Authors, year, reference	Subject number
Pd	^{57}Fe	Bemski et al. (1965) [31]	1
		Jech and Abeledo (1967) [69]	1, 2
		Phillips and Kimball (1968) [70]	1, 2
		Mahnig and Wicke (1969) [44]	1
		Carlow and Meads (1969, 1972) [71, 60]	1, 2
		Wanzl (1973) [48]	1, 3
		Obermann et al. (1976) [49]	1, 3
	^{119}Sn	Chekin and Naumov (1967) [42]	1
		Mahnig and Wicke (1969) [44]	1
		Kimball et al. (1976) [124]	1, 4
	^{151}Eu	Meyer et al. (1975) [53]	1
	^{99}Ru, ^{193}Ir ^{195}Pt, ^{197}Au	Iannarella et al. (1974) [55]	1
	^{197}Au	Iannarella et al. (1976) [57]	1
		Karger et al. (1976) [63]	1, 5
Ni	^{57}Fe	Wertheim and Buchanan (1966, 1967) [38, 39]	1, 2, 3
		Janot and Kies (1972) [83]	1, 2, 5
Ni-Fe	^{57}Fe	Fujita and Sohmura (1976) [82]	1, 2, 5
		Mizutani et al. [130]	1, 2, 5
Stainless Steels	^{57}Fe	Wertheim and Buchanan (1967) [39]	1
		Fujita and Sohmura (1976) [82]	1, 5
V	^{57}Fe	Simopoulos and Pelah (1969) [81]	1, 4
Nb	^{57}Fe	Ableiter und Gonser (1975) [79]	1, 2, 3, 5
	^{181}Ta	Heidemann (1976) [105]	1
Ta	^{181}Ta	Heidemann et al. (1974) [90]	1
	^{181}Ta	Heidemann et al. (1975, 76) [88, 89]	1, 6
TiFe	^{57}Fe	Swartzendruber and Bennet (1976) [84]	1, 5
		Ron et al. (1976) [85]	1, 5
YFe$_2$, GdFe$_2$	^{57}Fe	Buschow and van Diepen (1976) [86]	1, 2
EuH$_2$	^{151}Eu	Lounasmaa and Kalvius (1967) [110]	1, 2
EuH$_2$, YbH$_2$	^{151}Eu ^{171}Yb	Mustachi (1974) [114]	1, 2, 3
GdH$_2$, GdH$_3$	^{155}Gd	Cashion et al. (1973) [116]	1, 2, 3
		Lyle et al. (1975) [113]	1, 2, 3
ScH$_2$	^{155}Gd	Prowse et al. (1973) [117]	
DyH$_2$, DyH$_3$	^{161}Dy	Abeles et al. (1969) [111]	1
DyH$_2$		Hess et al. (1971) [112]	2, 5
DyH$_2$, ErH$_2$	^{166}Er	Stöhr and Cashion (1975) [117]	single line
HOH$_2$	^{160}Dy		substances
YH$_2$	^{166}Er ^{160}Dy	Stöhr and Cashion (1975) [117]	2, 4
ErH$_2$, YH$_2$	^{166}Er	Shenoy et al. (1976) [119]	2, 4
ZrH$_{1.5}$	^{166}Er	Shenoy et al. (1976) [120]	2, 4, 5
NpH$_{2+x}$	^{237}Np	M. H. Mintz et al. (1976) [121]	1, 3, 5

TABLE II

Compilation of NMR studies on M-H systems (which are listed in part in Fig. 5)

a) *NMR studies on matrix atoms* (Knight shift : subject number 7)

b) *Some recent NMR studies on* ^1H *and* ^2H (for literature up to 1972 see review article of Cotts [35]).

Matrix	Isotope	Authors, year, reference	subject number
a)			
Pd	^{105}Pd	Brill and Voitländer (1973) [133]	7
Pd-Ag	^{107}Ag	Brill and Voitländer (1975) [134]	7
V	^{51}V	Zamir (1965) [136]	6, 7
Nb	^{93}Nb	Zamir and Cotts (1964) [137]	6, 7
Ta	^{181}Ta	Ströbel et al. (1975) [37]	3, 5, 6 (NAR)
$LaH_{2,3}$	^{139}La	Schreiber and Cotts (1963) [36]	3, 6, 7
ScH_2	^{45}Sc	Schreiber (1965) [135]	3, 6, 7
YH_2	^{89}Y	Schreiber (1965) [135]	3, 6, 7
b)			
Pd	^1H	Seymour et al. (1975) [138]	6
Pd-Ag	^1H	Davis et al. (1976) [139]	6
Ta	^2H	Roenker et al. (1976) [140]	3, 5
$LaNi_5$	$^1H, ^2H$	Harper et al. (1976) [141]	3, 5, 6
PuH_x	^1H	Cinader et al. (1976) [142]	2, 5, 6, 7

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