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ISOTOPE EFFECTS IN SUPERCONDUCTING TRANSITION METAL HYDRIDES

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Résumé.- Les effets isotopiques dans les hydrures des métaux de transition peuvent être reliés à une stabilisation différente du champ cristallin pour les atomes H et D aux sites interstitiels tétraédriques ou octaédriques. Les métaux avec une faible électronégativité ou travail de sortie montrent l'effet isotopique normal avec une température de transition de la supraconductivité plus basse pour le deutéride, une énergie d'activation plus élevée pour la diffusion et une température plus élevée pour la lacune de miscibilité de la phase α. Les métaux avec une électronégativité supérieure à 4,5 V montrent l'effet inverse. La dilatation volumétrique relative peut être reliée à l'électronégativité et est un peu plus petite pour l'échantillon deutérogéné.

Abstract.- Isotope effects in transition metal hydrides can be related to a different crystal-field stabilization for H and D atoms at tetrahedral or octahedral interstices. Metals with low electronegativity or electron work function exhibit the normal isotope effect with a lower superconducting temperature for the deuteride, a higher activation energy of diffusion and a higher temperature for the miscibility gap of the α-phase. Metals with an electronegativity larger than about 4.5 V exhibit the reverse behaviour. The relative volume expansion can be related to the electronegativity and is somewhat smaller for the deuterated sample.

Since the discovery of superconductivity in thorium and palladium hydride in 1970 /1/ and 1972 /2/ resp. many metal-hydrogen systems were investigated /3/ with the aim for a better understanding of superconductivity in such simple compounds. The major interest concentrated on the transition metal hydrides where hydrogen enters interstitial sites without major changes of the metal lattice structure but some variation of the average number of valence electrons with hydrogen content. In figure 1 part of the periodic table with the transition metals is shown.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	Tc-0.39	5.4							0.86
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
(2.7)	0.65	9.2	0.92	7.8	0.49				0.52
Lg	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
4.9	0.13	4.5	0.015	1.7	0.66	0.11			4.15
6.0									3.95

Fig. 1 : Superconducting temperatures of transition metals at 1 atm. or at high pressure (values in brackets) and ability for hydride formation (hatched fields).

The numbers below the elements indicate the critical temperatures of superconductivity of the pure metals with maximum values for the fifth and the seventh group. The hatched fields indicate those

metals which can form hydrides - that are the elements of the third, fourth and fifth group, chromium, nickel and palladium.

Two schematic phase diagrams are shown in figure 2 as an example for hydride formation.

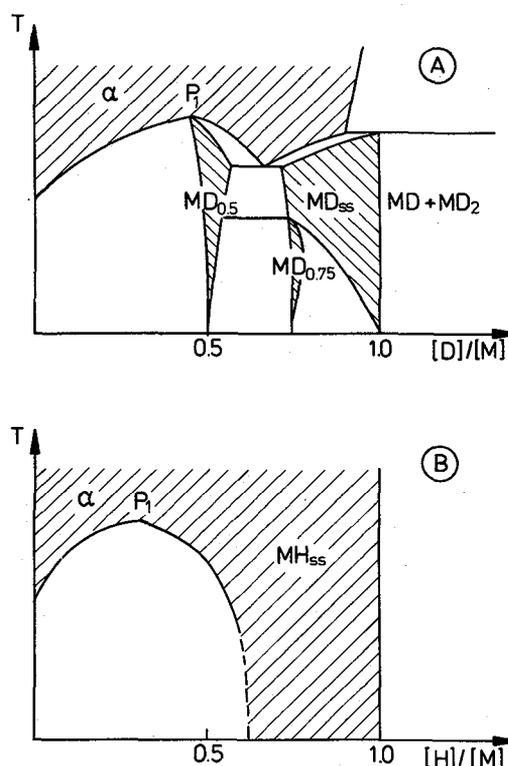


Fig. 2 : Schematic phase diagrams for hydrides at equilibrium conditions (a) VD and for a metastable non-stoichiometric solid solution (b) PdH.

Above about 100 - 300°C the metal can absorb hydrogen or deuterium in the α -phase up to a concentration of about one hydrogen per metal atom with a random distribution of the hydrogen atoms at the interstices. At lower temperature several miscibility gaps occur between ordered phases. At very low temperatures, which are of particular interest for superconductivity, only certain stoichiometric compounds can exist at equilibrium conditions as it is shown in the schematic VD-phase diagram in figure 2a. In other systems like the palladium-hydrogen phase diagram a non-stoichiometric solid solution remains metastable within the approximate concentration range $\text{PdH}_{0.6}$ to PdH (figure 2b). In such metastable systems the superconducting behaviour changes continuously otherwise discontinuously.

There are four possibilities for such a change, as are outlined in figure 3 for some ternary compounds: the critical temperature can decrease with increasing hydrogen content or it increases at a certain composition and it also can have a maximum or a minimum value in between.

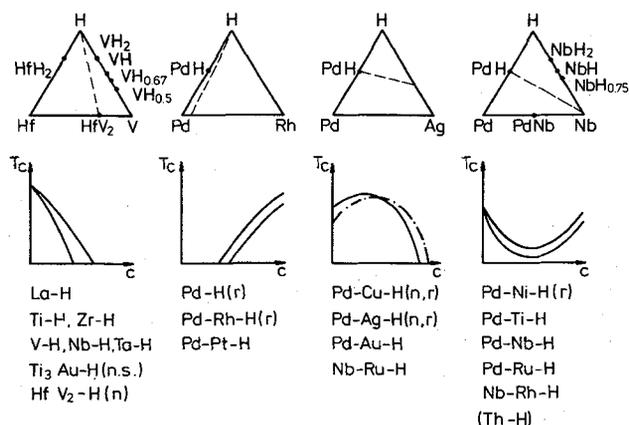


Fig. 3 : Superconductivity of binary and ternary hydrides and deuterides with normal isotope effect (n) or reverse isotope effect (r). Some examples of ternary systems with a change of T_c along the dashed lines are given in the upper part.

Some ternary systems are sketched with a change of T_c along the dashed line like Hf V_2 charged with H, PdRhH , PdAgH and PdNbH . Usually one obtains different values if hydrogen is replaced by deuterium. This is referred to as the normal isotope effect as indicated by a \underline{n} as for $\text{HfV}_2\text{-H}$, if T_c is lower for the deuterated sample. The reverse isotope effect is obtained if T_c is higher for the deuterated sample as indicated by a \underline{r} as for PdH system. In some systems like Pd-Ag-H and Pd-Cu-H , the isotope

effect changes from normal to reverse /3/. At low silver content of the alloy T_c of the deuterated sample is higher, at higher silver content it is lower than for the hydride. The actinide element thorium may also be included and exhibits a discontinuous change of T_c with a minimum. Thorium metal is superconducting below 1.4 K, ThH_2 is not superconducting above 1.2 K and $\text{ThH}_{3.75}$ becomes superconducting below about 8 K. No isotope effect was found for this compound within the experimental uncertainty /1/.

The theories for the superconductivity of hydrides were mainly developed for palladium alloys. One condition for obtaining superconducting hydrides seems to be the quenching of spin fluctuations. Palladium metal for example is paramagnetic. The susceptibility is decreased by addition of hydrogen and also by alloying with silver. At about the composition $\text{PdH}_{0.7}$ it becomes superconducting with a T_c increasing with hydrogen content to about 9 K in the binary and to a maximum value of about 15.6 K at the composition $\text{Pd}_{0.70}\text{Ag}_{0.30}\text{H}_{0.8}$ of the ternary system /3/. In the binary Pd-Ag alloy the spin fluctuations are also quenched above about 60 at% silver but it does not become superconducting. From this one might conclude that there should be an additional condition for superconductivity. From McMillan's formula for T_c in the form given by Dynes /4/ one might conclude that electron-phonon coupling with acoustical or optical phonons is important for superconductivity.

$$T_c = \frac{\langle \omega \rangle}{1.2} \exp \left(\frac{-1.04(1+\lambda)}{\lambda - \mu^* (1+0.62\lambda)} \right)$$

ω is the phonon frequency, λ the phonon induced attractive electron-electron coupling and μ^* the pair breaking Coulomb pseudopotential which is usually about 0.1 for superconductors. The optical and the acoustical branch of the phonon spectra are well separated in hydrides because of the different masses of the metal and hydrogen atoms. The optical phonons can be related to the metal hydrogen bonding the acoustical to metal-metal interactions. Roughly speaking there are three kinds of explanations for the superconductivity of hydrides : At the first possibility mainly the acoustical phonons are considered to be enforced by the introduction of hydrogen into the metal lattice, - that is either that the metal-metal distance decreases by introducing small metallic hydrogen /5/ or by coupling between acoustical phonons and d-electrons /6/ or sp electrons /7/, or - considering the isotope exchange of H by D - the volume could change

because of a smaller zero point motion /8/, or - considering alloys like the ternary system PdAgH - a volume change could lead to different oscillations of hydrogen atoms /9/. However there are several reasons that indicate that the acoustical phonons are not so important in hydride systems. One major point is the negative pressure effect of PdH - that means with increasing pressure the volume decreases and the metal-metal interaction should increase. T_c however decreases instead of increasing /3/.

Another possibility is the coupling between optical phonons and the electrons. Because of the relation between optical phonons and metal hydrogen bonding Ganguly /10/ reduced the formula of Dynes to the expression

$$T_c \approx \sqrt{\frac{f}{M}} \exp\left(\frac{-1}{\frac{C}{f}}\right)$$

where f is the force constant, M the effective mass and C is an electronic factor which is considered to be constant by Ganguly. A high T_c should be obtained for small f values because of the exponential function. The higher T_c of the deuterated palladium sample was related to a smaller force constant due to anharmonic vibrations /10/. An anharmonicity was also postulated for the ternary system PdAgH with an asymmetric neighborhood of the hydrogen atoms /11/. The negative pressure effect was explained by the stiffening of the force constant /3/. For PdH an anharmonic potential along $[110]$ direction was found experimentally /12/.

Other authors relate a change of f to different electronic properties. Miller and Satterthwaite /13/ concluded for the isotope effect of PdH that the smaller motion of deuterium causes a smaller overlap of wave functions between Pd and D. The additional electrons increase the Fermi energy and cause a higher T_c . For PdAgH system an increasing electron density at the hydrogen atom was considered for increasing H or Ag content /14/. In PdD a higher electron density than in PdH was found by NMR /15/.

The latter two groups of theories can explain well the superconductivity and the isotope effect of PdH but there are some difficulties for ternary systems where T_c has a maximum or a minimum and for those systems where the reverse isotope effect changes to normal with the composition of the alloy.

At the LT 15 conference in Grenoble a simple model was presented which can be correlated to these theories but has some new aspects, which can be summa-

rized shortly in two theses :

- (1) Hydrides with small thermal stability have small force constants and are favourable for superconductivity.
 - (2) There exists a qualitative relation between free energy of hydride formation and the electronegativity or electron work function of the metal.
- The first point might be explained by figure 4, where the hydride formation is considered in three steps of a theoretical process /16/.

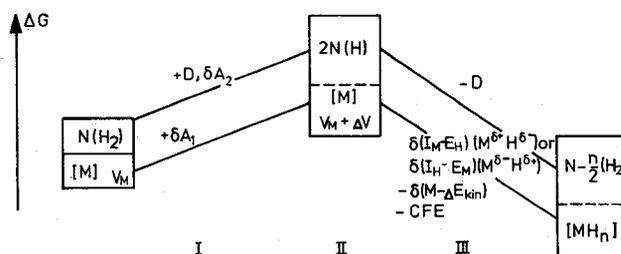


Fig. 4 : Theoretical process of transition metal hydride formation (D dissociation energy of H_2 , δA volume work of the metal and the gas phase, δ (I-E) partial contribution of ionisation energy and electron affinity, M Madelung lattice energy, ΔE_{kin} kinetic energy of H atoms).

We start on the left side with N moles of H_2 gas and a piece of metal with the volume V_M . In a first endothermic step of this theoretical process the metal lattice gets expanded by ΔV . Hydrogen dissociates and the volume is changed in such a way that the volume of the gas and the metal phase are those of the hydride after the reaction. In a second step the hydrogen atoms are allowed to diffuse into the channels of the expanded metal lattice similar as in the Gay-Lussac experiment for ideal gases with no interactions with the metal. In a third step the interaction between hydrogen and the metal is considered, which is an exothermic process. The hydrogen atoms can gain electron density or can lose it. For both processes partial contributions to the ionisation energy and electron affinity must be considered. The hydrogen and the metal atoms change their effective charge which leads to a gain of Madelung lattice energy and crystal field energy. By these interactions between the H atoms and the metal lattice the hydride gets stable with a negative value for the free energy of formation. This contribution is considered further on figure 5, where the electron density for metals with different electronegativities is sketched. The electronegativity or the electron work function of the

elements give qualitatively the tendency to exchange electrons from the hydrogen to the metal atoms.

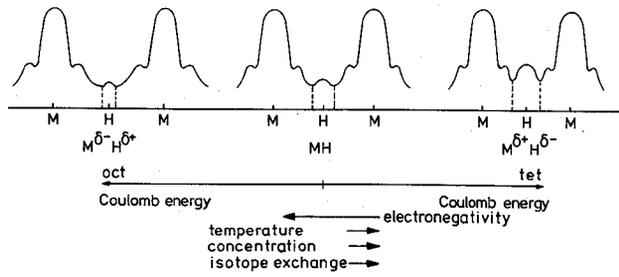


Fig. 5 : Schematic drawing of the electron density distribution in transition metal hydrides at different electronegativity, H concentration, temperature and at an isotope exchange.

There is very few exchange at about equal electronegativity values of hydrogen and the metal, only a little Coulomb energy is gained. In that case, the bonding between metal and hydrogen is weak and has a small force constant, which is supposed to be favourable for superconductivity. At large electronegativity values of the metal the hydrogen atoms loose some charge δ , at low values they gain some. In both cases the Coulomb energy increases. Because of the non-spherical distribution of the d orbitals of transition metals, crystal field energy is also gained. The electron density of the metal d-orbitals is higher at octahedral interstices than at tetrahedral interstices as was discussed in a former investigation /17/. Therefore octahedral sites are preferred by hydrogen atoms with a partial positive charge, otherwise hydrogen with a partial negative charge is repelled to tetrahedral sites. The electronegativity however is no constant value but depends slightly on temperature, concentration and isotope exchange. With increasing temperature, increasing hydrogen concentration or by exchange of H by D the effective positive charge at the hydrogen atoms decreases and/or the electron concentration nearby the D atoms increases because of the smaller thermal motion. Both lead to the same effect as a smaller electronegativity of the metal (figure 5).

At figure 6 the relation between free energy of hydride formation and electronegativity is shown. Metals with small electronegativity like La, Zr, Hf, Ti, Nb, Ta have $H^{\delta-}$ at tetrahedral sites. The stability decreases with increasing electronegativity of the elements. At high electronegativity like for Cu, Cr, Mo, Ni and Pd $H^{\delta+}$ occupies octahedral sites. The stability of the hydride increases

with increasing electronegativity.

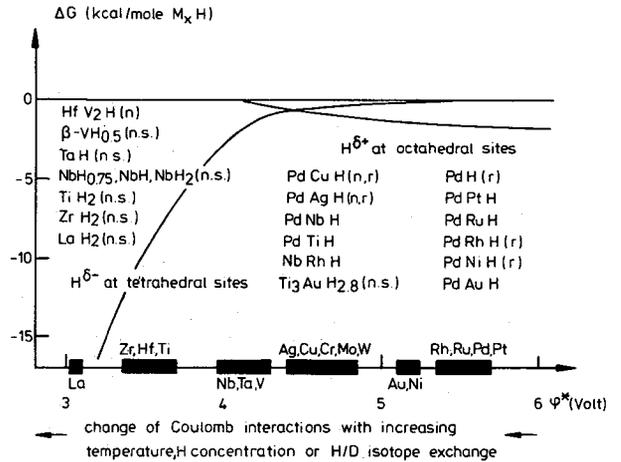


Fig. 6 : Variation of the free energy of hydride formation for transition metals with different electronegativities ϕ^* correlated to a reverse isotope effect of superconductivity (r) for metals with high ϕ^* and normal isotope effect (n) at low ϕ^* , (n.s. = not superconducting).

The best superconductor should be found at small thermal stability with small interaction between metal and hydrogen and small force constants. An exchange of hydrogen by deuterium should decrease the force constant for the elements at the right side leading to a reverse isotope effect which is indicated by a r. For metals with low electronegativity the isotope exchange leads to a stronger force constant where the normal isotope effect can be expected as for HfV_2-H . If the Coulomb interaction is too large with stronger force constants the hydrides are not superconducting like LaH_2 , ZrH_2 , TiH_2 , niobium hydrides, TaH and $\beta-VH_{0.5}$. In between are listed those alloys containing a metal with low electronegativity and one with a high value like Ti_3Au , Nb-Rh etc. Usually the electronegativity of an alloy changes with the composition and should cause an inversion of the isotope effect. Only for $PdCuH$ and $PdAgH$ the isotope effect was measured. For both systems T_c has a maximum and the isotope effect changes from normal to reverse. In the system Pd-Cu-H the highest T_c of hydride systems was found by Stritzker with about 16.6 K /3/.

Because of these relations between small Coulomb interactions and superconductivity we had searched for new superconducting hydrides at the middle of the field and had found VH_2 with a T_c (midpoint) of 3.9 K /18/. In VH_2 the vanadium atoms form a fcc lattice similar as palladium, the H atoms however are at tetrahedral sites, VD_2 exhibits a

smaller room temperature lattice constant of $a = 4.215 \text{ \AA}$ compared to $a = 4.236 \text{ \AA}$ for VH_2 because of the increased Coulomb interaction and had no superconducting transition above 1.5 K.

In table I some force constants are listed which were calculated with the two mass model because of weak coupling at large mass differences /16/. There are small values for PdH with a reverse isotope effect and for $\beta\text{-VH}$ and larger values for the other elements. These values show that there is only a qualitative relation and that the force constants for example might also depend on crystal structure.

Table I : MH-force constants from $f = 0.59 \mu_{\text{MH}} (\nu/1000)^2$

	$f \text{ (mdyn/\AA)}$
PdH	0.09
PdD	0.08
$\beta\text{-VH}$	0.09
$\beta\text{-VD}$	0.17
$\alpha\text{-VH}$	0.39
$\alpha\text{-VD}$	0.48
$\alpha\text{-TaH}$	0.80
$\beta\text{-NbH}$	0.85
NbH_2	0.85
$\text{TiH}_{1.6}$	0.74
TiH_2	0.68
ZrH_2	0.74

There are other similar relations for the mean square amplitude of hydrogen oscillation, for the activation energy of diffusion and the volume expansion as it is outlined in figure 7 /16/. In hydrides with small force constants the hydrogen atoms usually have a large mean square amplitude of oscillation. If there are small Coulomb interactions between the metal and the hydrogen atoms the activation energy of hydrogen diffusion is small. VH_2 and PdH have the smallest activation energy of fcc metals, $\alpha\text{-VH}$ the smallest for a bcc lattice. The activation energies exhibit the same isotope effects as superconductivity. Metals with small electronegativity show the normal isotope effect with a higher activation energy for the deuterated sample like $\alpha\text{-VH}$, Ta and Nb hydrides, those with higher electronegativity than V like Cu, Ni and Pd exhibit the reverse isotope effect with a smaller value. At high temperatures of about 500 °C the isotope effect diminishes, probably because of the relatively small crystal field stabilization. The relative volume expansion has no maximum but can be related qualita-

tively to the electronegativity /19/. At high electronegativity the metal takes more electrons from the hydrogen atoms and expands more.

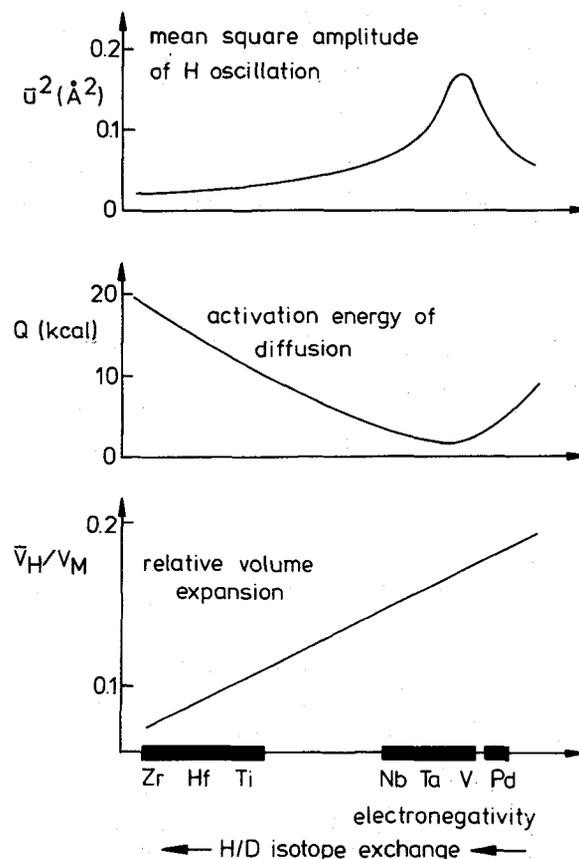


Fig. 7 : Sketch for the variation of the mean square amplitude of H oscillation, the activation energy of diffusion and the relative volume expansion with electronegativity and at an isotope exchange.

Deuterides usually have a smaller volume than hydrides. This relation shows that the occupation of H at tetrahedral or octahedral interstices of the metal lattice is no size effect but depends on crystal field stabilization.

Another isotope effect can be found by comparison of hydride and deuteride phase diagrams. Transition metals with low electronegativity like Nb and Ta exhibit a miscibility gap of the α -phase below P_1 (figure 2) at about 10 - 20°C higher temperatures for D than for H solid solution /20/. This can be attributed to the larger crystal field stabilization of ordered MD phases. Metals with high electronegativity like Pd and Ni show a reverse effect with a lower temperature value of P_1 for the deuterated sample, because of the decreased thermodynamic stability. The VH and VD systems exhibit different phase diagrams with different crystal structure

res, where H or D can occupy tetrahedral or octahedral sites /16/. At the composition $\text{VH}_{0.5}$ or $\text{VD}_{0.5}$ octahedral interstices are occupied in the ordered compounds, but change to tetrahedral in the α -phase with random distribution at about 440 and 405 K, resp. This large isotope effect can be explained by addition of two effects in the ordered and the disordered phase. $\beta\text{-VD}_{0.5}$ with octahedral occupancy has a lower crystal field stabilization than $\beta\text{-VD}_{0.5}$, the disordered $\alpha\text{-VD}$ however has a stronger crystal field stabilization than $\alpha\text{-VH}$. Therefore $\alpha\text{-VD}$ stays stable at lower temperatures than $\alpha\text{-VH}$. At higher deuterium concentrations deuterides with an occupancy of tetrahedral sites are formed at the composition $\text{VD}_{0.75}$, VD and VD_2 (figure 2a). In contrast to this hydrogen occupies octahedral sites in different phases with the composition $\text{VH}_{0.67}$ and probably VH and changes to tetrahedral occupancy only at the composition VH_2 /20/. The different behaviour of H and D in vanadium can be explained qualitatively by small changes of the crystal field stabilization which is leading to a preference of tetrahedral sites with increasing temperature, H or D concentration and at the exchange of H by D as it was outlined in figure 6 /16/.

It was the aim of this investigation, to show that there are some qualitative relations between different physical properties like superconductivity, thermodynamic stability, the activation energy of diffusion, optical phonons, mean square amplitude of H oscillation and the relative volume expansion. The isotope effect is a very sensitive indicator of this, if other factors like temperature, H-concentration and crystal structure remain unchanged. On the search for new superconducting hydrides materials with small Coulomb interactions seem to be favourable. A small Coulomb interaction can be estimated for materials with low thermodynamic stability, small activation energy of diffusion, large mean square amplitude of H oscillation and small optical phonon energies.

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