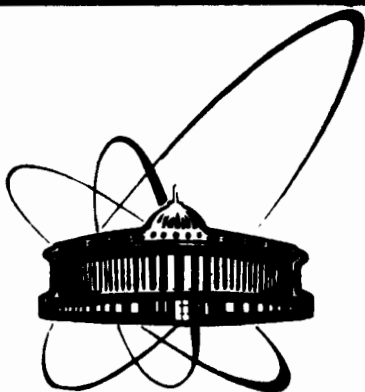


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T. Galbaatar ¹, N. M. Plakida, S. L. Drechsler ²

SUPERCONDUCTIVITY IN THE METASTABLE
PHASES OF TRANSITION METAL HYDRIDES

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¹On leave from Institute of Physics
and Technology, Ulaanbaatar-51, Mongolia

²Zentralinstitut für Festkörperphysik
und Werkstofforschung, AdW Dresden, DDR

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I. Introduction

Metal hydrides have been very exciting research objects from the basic as well as applied research aspects. The discovery of superconductivity in Th_4H_{15} [1] and subsequently in related transition metal hydrides as PdH, ZrH and HfH [2,3,4] gave it new stimulations. The superconducting transition temperatures T_c of the metal hydrides are roughly an order of magnitude higher than those of pure metals which do not exceed 0.6K. In the metastable $\text{Pd}_{1-x}\text{M}_x\text{H}_y$ (M=Cu,Ag,Au) alloy a remarkable high T_c -17K was achieved [5]. The outstanding feature of all these transition metal hydrides is the inverse isotope effect they exhibit upon substitution of deuterium (D) for hydrogen (H) which has been explained theoretically by anharmonic optical vibrations of H (D) (for PdH) [6] or low-lying tunneling modes (for ZrH and HfH) [7]. As for the PdMH alloys the anomalous isotope effect, namely the change of its sign at a critical M-concentration is still not satisfactorily settled. Meanwhile a new related superconducting metal hydride joined the family. Titanium hydride formerly known to be not superconducting is found to be so in the metastable δ' ($T_c=3.7\text{K}$) and ϵ ($T_c=4.3\text{K}$) phases exhibiting an inverse isotope effect ($T_c^0=5\text{K}$ for the ϵ phase) [8]. Inelastic neutron scattering (INS) study [9] (at KFA Jülich) has revealed additional inelastic intensities for these phases in the low frequency region (5-9 meV) in comparison with the non-superconducting δ -phase (Fig.1). This finding indicates that for TiH low-lying two-level systems (TLS) may be of importance in explaining the inverse isotope effect similarly to (Zr,Hf)-H systems [7]. A detailed investigation of TLS-contribution to superconductivity and

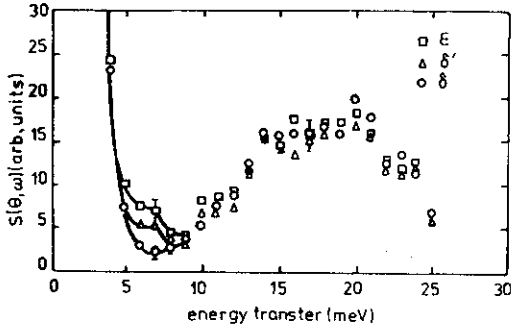


Fig.1 INS spectrum of TiH_{0.76} . After [9].

particularly to the isotope effect in the transition metal hydrides is therefore of great interest, also from the high- T_c point of view as there are now hints for the existence of TLS in the new cuprate oxide superconductors. Thus, their study in less complicated systems as the hydrides are is desirable.

In the present work we study the superconductivity in the metal hydrides within the anharmonic model [10] basing on new experimental data for titanium hydride.

II. Model and estimation of parameters

As neutron diffraction (ND) [11] investigations show H preferentially occupies octahedral (O) interstitial positions in the titanium matrix in the c -phase and tetrahedral (T) ones in δ' and δ phases.

To study the electron-phonon and electron-TLS interactions for the systems under consideration we write the Eliashberg function in the quite general form

$$\alpha^2 F(\omega) = S(\omega) = \sum_i^4 \alpha_i^2 F_i(\omega) = \sum_i^4 \frac{\lambda_i \omega_i}{2} \delta(\omega - \omega_i) \quad (1)$$

Here $i=1$ stands for the TLS contribution, $i=2$ for the usual acoustic phonon part (vibration of the metal ions) and $i=3,4$ for the high frequency optical vibrations of H in octahedral and tetrahedral coordinations, respectively, and we approximate the

peaks by δ -functions, for the sake of simplicity. The effective electron-phonon coupling constants (i.e. $i=2,3,4$) are given as usually by

$$\lambda_i = \eta_i \frac{1}{m\omega_i^2} \quad (i=2,3,4) \quad (2)$$

Owing to the very high frequency of the optical vibrations of T-coordinated H (150 meV) any essential contribution of it in Eq.(1) can be excluded, i.e. we set throughout the paper $\lambda_4=0$.

Now we consider the TLS contribution.

The unique feature of the TiH_x system is that one can alter its superconducting properties by changing the state of H for a constant overall content x of H. Consequently, the acoustic part of the phonon spectrum will not be affected by the $\epsilon \rightarrow \delta' \rightarrow \delta$ phase transitions. Thus, we argue that the low frequency INS intensity found for TiH_x is not of acoustic phonon anomaly origin. Instead, we propose that it is caused possibly by lattice strains and distortions, (e.g. increase of Ti-H interatomic distances upon the $\alpha \rightarrow \epsilon$ transition in TiH_x or instability of H induced by substitution of noble metals for Pd in the PdMH alloys (see Fig.3)) the vibrational potential of H(D) at some O-sites would be changed into a double-well one. In fact, the occurrence of a double-well potential after shifting a light ion from a highly symmetric point to a less symmetric one can be often observed. Recently it has been reported for the anharmonic oxygen (O3) ion in the high- T_c superconductor $TlBaCaCuO$ [12] a situation similar to the above proposed one.

We use a x^4 -model potential to describe the double-well potential (see Fig.2)

$$V(x) = \frac{A^2}{4B} - \frac{A}{2} x^2 + \frac{B}{4} x^4 \quad (3)$$

where $V_0 = \frac{A^2}{4B}$ is the central barrier height and $x_0 = \pm \sqrt{A/B}$ are the positions of the potential minima. Introducing $\xi = \frac{x}{x_0}$ we write the

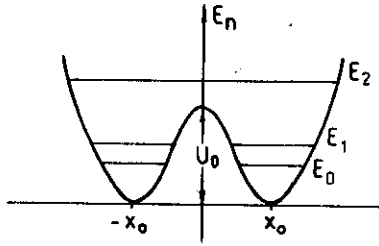


Fig.2 The shape of the model potential.

Schrödinger equation as

$$\left\{ -\beta^2 \frac{\partial^2}{\partial \xi^2} + (1-\xi^2)^2 \right\} \phi_n(\xi) = \epsilon_n \phi_n(\xi) \quad (4)$$

with $\epsilon_n = E_n/V_0$ and $\beta = \frac{\hbar\omega_0}{4V_0}$. $\omega_0^2 = 2A/m$ is a characteristic harmonic frequency in one potential well and m - the mass of H (D). In what follows we set $\hbar=1$.

Thus, we study the vibrational spectra by adjusting β , only. Solving numerically (2) we obtain the eigenvalues $E_n = V_0 \epsilon_n$ and the transfer matrix elements between the eigenstates n and m

$$x_{nm} = x_0 \langle m | \xi | n \rangle \quad (5)$$

to discuss the isotope effect.

In terms of our model, we ascribe the experimentally observed peak at 7 meV to the transition $E_0 \rightarrow E_1$, i.e.

$$\omega_{\text{TLS}} = \omega_1 = E_1 - E_0 = 7 \text{ meV} \quad (6)$$

The high frequency (75 meV) broad optical peak in the INS spectrum of TiH_x , which does not exhibit any pronounced anharmonicity may be identified with the vibration of H either in the regular O-site or the distorted site with the double-well potential. Its large width (44 meV) would support the second possibility if the matrix elements of higher order transitions are finite as our calculations show for

$$x_{02} = x_0 \langle 2 | \xi^2 | 0 \rangle,$$

giving rise to the broadening. The absence or a very weak intensity of this peak in the δ' phase may be caused by the lower concentration of distorted sites with double-well potential. We assign this frequency to the transition $E_1 \rightarrow E_2$ and the broadening is due to the second order transition $E_0 \rightarrow E_2$, i.e.

$$\omega_{op} = \omega_3 = E_2 - E_1 = 75 \text{ meV} \quad (7)$$

Thus, our model adjusting parameter β and the barrier height V_0 can be fixed uniquely by (6) and (7). The ratio ω_{op}/ω_{TLS} is reproduced for $\beta^H=0.5$ and $V_0=20$ meV, a value physically quite reasonable. Assuming that the substitution of D for H would not affect the electronic structure (i.e. $V_0=\text{const}$) we have $\beta^D=0.3536$ and from Eq.(2) we obtain the frequency shifts

$$\omega_{TLS} = 2.3 \text{ meV and } \omega_{op} = 60 \text{ meV,}$$

which are used in our discussion of the isotope effect.

As for the acoustic phonon frequency we take for it (because of the large width) the corresponding logarithmic frequency

$$\omega_{ac} = \omega_2 = 12.5 \text{ meV.}$$

From the unit cell geometry given in [8] for the ϵ and δ phases one may estimate $x=0.2 \div 0.4 \text{ \AA}$.

The effective electron-TLS coupling constant (i.e. λ_1 in Eq.(1)) is given in the anharmonic model [10] by

$$\lambda_{TLS} = \lambda_1 = c n_{TLS} \frac{2x_{01}^2}{\omega_{TLS}} \tanh \frac{\omega_{TLS}}{2T_C} \quad (8)$$

where c denotes TLS concentration.

In order to estimate the Hopfield parameters one has to take into account some essential features of the electronic structure of the metal hydrides near the Fermi energy E_F . Many energy band calculations for various hydrides show that it is determined by metal d-states and antibonding s-p states of H. Two typical cases can be considered;

(1) E_F is within the bands with nearly d-character (probably

realized for TiH_x). In this case one obtains relatively large partial-density of states (DOS) with d-character and a Hopfield parameter at the transition metal sites $\eta_{ac}^d \approx 2 + 3 \text{ eV/\AA}^2$, i.e. values typically for transition metals. (The superscript d means that the Fermi energy lies within the d band) The corresponding partial DOS with s-p character at H site and the resulting Hopfield parameters $\eta_{op}^d \approx \eta_{TLS}^d$ are smaller by several orders of magnitude [13]. The magnetic susceptibility $\chi > 0$ is dominated by the paramagnetic Pauli-part.

(2) E_f is located within the s-p antibonding bands of H (realized for $\text{Pd}_{1-x}\text{M}_x\text{H}_y$ provided x+y is not too small ($\geq 0.1-0.2$) [14]) leading to $\chi < 0$ which has been measured for $\text{Pd}_{1-x}\text{M}_x\text{H}_y$. This results in enhanced values for the Hopfield parameters at H sites

$$\eta_{op}^{s-p} \gg \eta_{op}^d$$

and in somewhat reduced ones at the M-sites i.e.,

$$\eta_{ac}^{s-p} \leq 1 \text{ eV/\AA}^2 \leq \eta_{ac}^d$$

As an illustration we refer to the work of Papaconstantopolous et al. [13] for PdH (see also [14])

$$\eta_{op}^{s-p} \leq 0.4 \text{ eV/\AA}^2 \text{ and } \eta_{ac}^{s-p} \leq 0.9 \text{ eV/\AA}^2.$$

Due to the similar electronic structure and acoustic phonon spectra of the hydrides and the parent metals one can estimate for the first case $\lambda_{ac}^d \approx 0.3 + 0.5$.

Thereby a somewhat enhanced value of the Coulomb pseudopotential

$$\mu^* = 0.17$$

is assumed ($\mu^* = 0.17$ for e.g. Zr [15]). Thus, the absence of superconductivity or a very low T_c of $\delta\text{-TiH}_x$ is quite naturally. For the second case we estimate

$$\lambda_{ac}^{s-p} \approx 0.2$$

reflecting the reduced d-partial density of states at the transition metal site. It should be pointed out that while λ_{ac} and λ_{op} do not depend on the H(D) mass λ_{TLS} depends (Eq.(8)) on the mass via ω_{TLS} being therefore of special interest for the

discussion of the isotope effect. Our calculation scheme is as follows; We use $S(\omega)$ (see Eq.(1)) which is essentially an effective Hopfield parameter as an adjusting parameter. That is, we start from the experimentally observed T_c^H and compute the corresponding $S(\omega)$ by means of the Eliashberg equation. Then using this $S(\omega)$ we calculate T_c^D for the frequencies ω_{TLS}^D which are obtained from Eq.(2) (in the case of PdH the frequencies are taken from experimental data).

III. Results and discussion

Titanium hydride. Let us first consider the δ -phase which is not superconducting down to 0.6K. Due to our assumption, in the δ -phase all H(D) are located on T-positions i.e., there are no TLS, thus

$$\lambda_{TLS}=0$$

Because $\omega_{op} \gg \omega_{ac}$ and correspondingly $\lambda_{op} \ll \lambda_{ac}$ we omit the optical phonon contribution and deal with the acoustic phonon contribution. Assuming that δ -TiH_x becomes superconducting around 0.5K we have $\lambda_{ac} \approx 0.5$. Now we turn to the ϵ phase. With the following parameters

$$\omega_{TLS} = 7 \text{ meV}, \omega_{ac} = 12.5 \text{ meV and } \lambda_{ac} = 0.5$$

the Eliashberg equation reproduces the nearly experimental value of $T_c \approx 4.36K$ for $\lambda_{TLS} = 0.4$. Replacing ω_{TLS} by $\omega_{TLS}^D \approx 2.3 \text{ meV}$ and repeating the computation we obtain for the deuteride

$$T_c \approx 5.0K,$$

i.e., the experimentally observed inverse isotope effect is very well reproduced.

Consider now the δ' -phase.

From Fig.1 we deduce crudely a decrease of 30-50% in the TLS concentration in the δ' -phase, that results in decreasing of $\lambda_{TLS}(\delta') \approx 0.3$. The Eliashberg equation delivers then the experimentally observed $T_c \approx 3.6K$.

Assuming $x_0 = 0.3 \text{ \AA}$ we obtain from Eq.(7) for the Hopfield parameter at the H(D) site
$$c\eta_{\text{TLS}} = 1.4 \cdot 10^{-2} \text{ eV/\AA}^2$$
 being consistent with the above given discussion on the Hopfield parameters.

Hydride of PdM alloys (M=Cu,Ag,Au).

Turning to the $\text{Pd}_{1-x}\text{M}_x\text{H}_y$ alloys (M=Cu,Ag,Au) we notice that in these systems H(D) usually occupies O-positions, only. In PdH the optical phonon ($\omega^{\text{H}} \approx 60\text{meV}$) exhibits some anharmonicity in the force constant which is the main contribution to the inverse isotope effect (for a more detailed discussion of the origin of the IIE in this system see e.g.[16]). We propose that doping with noble metal brings about some deformation at some H(D) sites (see Fig.3) similar to the case considered in the previous section. That is, we have an increasing number of H sites with a double-well potential, which are responsible for the TLS contribution and the remaining ones for the usual optical phonon

$$\lambda_{\text{TLS}} = c\lambda_{\text{TLS}}^{(1)}, \quad \lambda_{\text{op}} = \lambda_{\text{op}}^0(1-c)$$

where c denotes again the TLS concentration being proportional to the noble metal content. This can be understood as follows; due to the disturbance brought in by doping with noble metals a part of regular O-positions goes over to some metastable state resulting

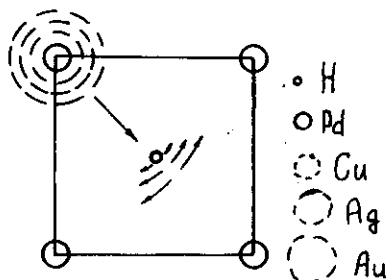


Fig.3 Schematic representation of the substitution of noble metals (Cu,Ag,Au) for Pd and its impact on the state of hydrogen (deuterium) possibly leading to the double-well potential.

in the reduction of the optical phonon contribution and enhancement of that one of TLS. Actually, there is no experimental evidence for low lying excitations as yet. However, INS investigations on PdAgH [17] have revealed some broadening of the optical peak which could be of similar nature as discussed above for TiH_x . Furthermore we include a weak acoustic phonon part in accordance with many bandstructure calculations [13] i.e. $\lambda_{ac} = 0.175$ and assume for the sake of simplicity all other parameters independent on c . The Coulomb pseudopotential is chosen as usual $\mu^*(H) = 0.13$ and $\mu^*(D) = \mu^*(H) / (1 + \mu^*(H) \ln(\omega_{TLS}^H / \omega_{TLS}^D))$. Now we have to reproduce for $c=0$, $T_c^H = 9K$ and $T_c^D = 11K$. By solving the Eliashberg equation we obtain these values for $\lambda_{op}^0(H) = 0.35$ and $\lambda_{op}^0(D) = 0.505$ whereby $\omega_{op}^0 \approx 47meV$. According to the data of Stritzker [5] we set $T_c \approx 17K$ for $c=0.5$ and get $\lambda_{TLS}^{(0)} = 1.70$. This value corresponds to the case if 50% of the H(D) sites would be located in double-well potentials (i.e., $c=0.5$) while λ_{op}^0 accounts for purely optical phonon case. Here we have assumed the frequency of the TLS, due to lack of experimental data, in analogy to the TiH system around 7 meV. The results of our calculation of the

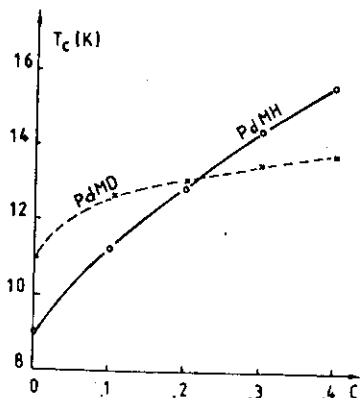


Fig.4 The calculated transition temperature versus the TLS-concentration c in PdMH and PdMD. For comparison with experimental curve see [5].

isotope effect are shown in Fig.4. As can be seen we have first an inverse isotope effect until some critical concentration of the noble metal content. Beyond this concentration the isotope effect changes its sign i.e., it becomes a normal one. We note that our calculations are in qualitative agreement with experimental data [5] (due to the arbitrariness of ω_{TLS} we are unable to give quantitative discussion). The physical reason for this change is that the influence of the TLS contribution starts to dominate at these concentrations. It has been demonstrated by us for a single mode that the isotope effect changes its sign when $\lambda_1 \approx 1.2$ i.e. at the intermediate to strong coupling crossover [18,19]. The maximum (of T_c) attainable for further increasing c is probably connected with the increasing distance of the double-well potential minima resulting in rapidly suppressed splitting energy (TLS frequency) ω_{TLS} . For the single mode case and the realistic parameters

$$c\eta_{\text{TLS}}x_{01}^2 \approx 1.6 \cdot 10^{-2} \text{ eV}$$

the dependence of T_c on the characteristic frequency is shown in Fig.5. At low frequencies the decrease of ω_{TLS} gives the most important influence.

For ever higher c the parameter x_0 increases correspondingly until some critical concentration where the fluctuations of $H(D)$ become so large that it can not be bound by the potential resulting in the dehydrogenation of the alloy and the complete suppression of the superconductivity at all. Due to the larger ionic radius this

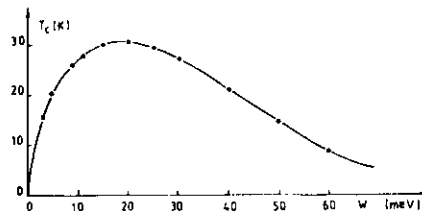


Fig.5 The dependence of T_c on the frequency of the
 TLS ω_{TLS} .

structural distortion is strongest for Au and gradually weaker for Ag and Cu at equal concentrations. Hence, the sign change of the isotope effect occurs for Au at the lowest concentration, for Cu at the highest and for Ag inbetween, correspondingly we have the highest T_C for Cu and lowest one for Au as observed.

IV Conclusion

We have shown that the superconductivity and the unusual isotope effects in metastable phases of transition metal hydrides can be well described by the anharmonic model. As for the hydrides of transition metal-noble metal alloys a combined TLS-phonon model is proposed. At lower noble metal content the contribution of the anharmonic optical phonons dominates and causes the inverse isotope effect as in pure PdH. With increasing metal content it is run out by the TLS contribution and the isotope effect becomes a normal one due to the crossover from the weak coupling to the intermediate/strong coupling.

As it was shown [20] within the anharmonic model the INS cross section is scaled by the factor $\tanh(\omega_{\text{TLS}}/2T)$. A careful investigation of the low frequency region at low temperatures is of great importance for the manifestation of the model as well as perspectives of further T_C -enhancement. Furthermore it should be cleared out whether the T_C -enhancement in PdMH(D) is limited by loss of hydrogen which, if so could be prevented by large pressure.

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