Crystal structure and superconductivity of high pressure hydrides and deuterides of HfRu and ZrRu compounds

V.E. Antonov, E.L. Bokhenkov, A.I. Latynin and V.I. Rashupkin

Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow District (Russian Federation)

B. Dorner*

Institute Laue-Langevin, 15X, F-38042 Grenoble Cedex (France)

M. Baier and F.E. Wagner

Physics Department, Technical University of Munich, W-85747 Garching (Germany)

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Abstract

The solubility of hydrogen and deuterium in HfRu and ZrRu was measured at 600 K and pressures up to 7 GPa. HfRuH(D)_{≈ 3.6} and ZrRuH(D)_{1.6-2.2} were synthesized. At ambient pressure these were shown to be superconductors with $T_c \approx 4.5$ and 3 K respectively. No difference between the T_c values of the hydrides and deuterides of the same compound was detected. X-ray diffraction at 100 K has shown the metal sublattices of HfRuH_x(D_x) and ZrRuH_x(D_x) to be base-centred orthorhombic with very similar unit cell parameters. The crystal structures of HfRuH_{3.6} and HfRuD_{3.6} determined by neutron diffraction at 120 K were of the ZrNiH₃ type. The observed superconducting and structural properties of HfRuH_x(D_x) and ZrRuH_x(D_x) agree with the predictions of the rigid d-band model. The applicability of this model to other high pressure hydrides is discussed.

1. Introduction

The technique of compressing gaseous hydrogen in macroscopic volumes to pressures of several gigapascals made it possible to synthesize bulk homogeneous hydrides of many transition metals which cannot be hydrogenated by standard procedures [1, 2]. In order to explain the observed dependence of the magnetic properties of the 3d metals and their alloys on the hydrogen content, the rigid d-band model was proposed [2]. Studies of the superconducting properties of high pressure hydrides of the 4d and 5d metals and their alloys led to the discovery of new superconducting hydrides [3, 4] and showed that, with proper corrections for the hydrogen-induced changes in the phonon spectra, the rigid d-band model could also be used to explain the observed superconducting phenomena [4].

The studies on superconductivity, however, were limited to the hydrides of group V–VIII metals and alloys. Since the rigid d-band model was the only guide allowing understanding and, under certain conditions, predicting the superconducting properties of hydrides of the alloys, it seemed worthy of investigation and, if possible, to

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extend the scope of its applicability. In the present work we used the high pressure technique to synthesize hydrides and deuterides of alloys of the group IV metals Hf, Zr and Ti with the group VIII metal Ru. According to the rigid d-band model, these hydrides were expected to be superconductors.

While single-phase samples of the TiRu hydride could not be obtained, the synthesized single-phase hydrides and deuterides of HfRu and ZrRu could be studied at ambient pressure, their superconducting temperatures could be measured and their crystal structures could be determined by X-ray and, for the hydride and deuteride of HfRu, by neutron diffraction.

2. Sample preparation and experimental details

Ingots of HfRu, ZrRu and TiRu compounds were melted from iodine Hf, Zr and Ti and ruthenium powder (99.97 wt.% Ru) in a levitation induction furnace under an argon atmosphere and then annealed in a vacuum of 10^{-4} Pa at 1473 K for 24 h, with subsequent cooling within the furnace. The samples were cut from these polycrystalline ingots with an abrasive wire saw. The damaged surface layer, about 0.02 mm thick, was then

^{*}Author to whom correspondence should be addressed.

removed by chemical etching. The final dimensions of the samples were $3 \times 3 \times 0.4$ mm³.

The samples were hydrogenated by a 24 h exposure to a hydrogen atmosphere at 600 K and pressures up to 7 GPa for HfRu and ZrRu and up to 9 GPa for TiRu, with subsequent cooling to 100 K. The method is described in more detail elsewhere [2]. The pressure was determined to an accuracy of about 5%, the temperature to within \pm 7 K. Samples of HfRuD_x and ZrRuD_x were prepared in a deuterium atmosphere using the same procedure and a pressure of 7 GPa.

At ambient pressure the obtained hydrides and deuterides began to rapidly lose hydrogen (deuterium) at temperatures between 170 and 200 K. All the apparatus used for their investigation permitted loading the samples without warming above 80 K. When not in use, the samples were stored in liquid nitrogen.

An X-ray study of the samples was performed at 100 K by a photographic technique using a DRON-2.0 diffractometer with Cu K α and Fe K α radiation. The crystal structures of the initial HfRu compound (with a mass of 1 g) at 300 K and of the HfRuH_{3.6} and HfRuD_{3.6} samples (about 0.1 g each) at 120 K were studied using the D20 neutron powder diffraction instrument at the ILL, Grenoble, with neutrons of wavelength $\lambda = 0.1295$ nm. The powder diffraction patterns were scanned in steps of 0.1° (2 Θ) and both fixed time and monitor counting schemes were employed. To avoid texture effects, the samples were ground at low temperature.

The superconducting transition temperatures were determined by the induction method from the location of the step midpoint in the temperature dependence of the signal of unbalance of an a.c. bridge. The hydrides and deuterides were studied at temperatures down to 1.5 K obtained by pumping on a ⁴He bath, while the initial compounds were studied at temperatures down to 0.34 K obtained by pumping on ³He.

The H and D content of the samples was determined from the amount of hydrogen liberated during their decomposition at temperatures up to 780 K. The ZrRuH_x(D_x) and HfRuH_x(D_x) samples were brittle and crumbled to a fine powder in the process of decomposition, the powder of HfRuH_x(D_x) being pyrophoric. The relative accuracy of the determination of x was $\pm 2\%$, $\pm 5\%$ and $\pm 10\%$ for the hydrides and deuterides of TiRu, ZrRu and HfRu respectively.

3. Experimental results

The X-ray examination showed that the initial HfRu, ZrRu and TiRu samples contained only a single phase with a CsCl-type crystal structure. The structure type and the lattice parameters (Table 1) agree with the

TABLE 1. Hydrogen content (x), structure type and unit cell parameters of the metal sublattice at 100 K, volume per metal atom (V_a) and superconducting transition temperature (T_c) of the HfRu, ZrRu and TiRu compounds and their hydrides

Sample	x	Metal lattice	<i>a</i> (nm)	b (nm)	c (nm)	$V_{a} \times 10^{3}$ (nm ³)	Т _с (К)
HfRu	_	CsCl	0.3225	_	_	16.78	1.18
Hf-	3.8	CrB	0.3655	1.058	0.4462	21.56	4.5
RuH,	_	CsCl	0.3249	-	_	17.15	< 0.34
ZrRu	2.2	CrB	0.3668	1.065	0.4509	22.01	3.0
ZrRuH <u>,</u> TiRu	-	CsCl	0.3068	-	-	14.44	1.07

literature data [5] for the equiatomic compounds in these binary systems. As for the literature data on superconductivity of these compounds, TiRu was shown to have $T_c = 1.07$ K, ZrRu was not studied and no superconductivity was found in HfRu above 1.02 K [5]. As one can see from Table 1, the latter disagrees with our result of $T_c = 1.18$ K for HfRu, which is not surprising if one takes into account that the T_c values of intermetallic compounds often depend strongly upon the prehistory of the samples.

As can be seen from Fig. 1, at 600 K the hydrogen solubility in the CsCl-type lattice of HfRu, ZrRu and TiRu is very low until, at pressures of about 2, 0.7 and 6 GPa respectively, hydrides with a different structure of the metal lattice begin to form. The hydrogen content of the single-phase hydrides of HfRu was $x=3.6\pm0.4$ and did not depend on the pressure. That for the ZrRu hydrides monotonically increased with pressure from $x \approx 1.6$ at 1 GPa to $x \approx 2.2$ at 7 GPa. No single-phase samples of TiRu hydrides were obtained at pressures up to 9 GPa.

At T>1.5 K no superconducting transition was observed in the TiRu-H samples. Both HfRu and ZrRu hydrides turned out to be superconductors (Fig. 2) with a rather broad superconducting transition, presumably due to internal stresses in the samples caused by the large volume expansion accompanying the hydride formation (about 28% according to the structural data). Within experimental error the T_c values of the hydrides were independent of the pressure of the synthesis and, in the case of the ZrRu hydrides, of the hydrogen content. The T_c values of the deuterides did not differ from those for the hydrides.

The X-ray diffraction patterns of the TiRu-H twophase samples contained only a small number of weak lines attributable to the hydride, which did not permit the crystal structure of the hydride phase to be determined.

The patterns of the HfRu and ZrRu hydrides and deuterides were very much alike. In the case of the HfRu hydride 28 unambiguous reflections were selected for indexing. The nearly exhaustive index variation



Fig. 1. Hydrogen-to-metal ratio n=x/2 of the (a) TiRuH_x, (b) ZrRuH_x and (c) HfRuH_x samples produced by a 24 h exposure at 600 K and the hydrogen pressures indicated on the abscissa: filled circles, hydrogen primary solutions with CsCl-type metal lattice; open circles, hydrides; half-filled circles, two-phase samples.

method proposed by Taupin and implemented in the computer program POWD [6] was applied to obtain the lattice parameters from the measured interplanar distances. The solution proposed by the program was a C-centred orthorhombic lattice with the refined unit cell parameters given in Table 1. The reliability of the unit cell and indexing is indicated by de Wolf [7] and Smith-Snyder [8] figures of merit $M_{20} = 19.4$ and $F_{28} = 8.2(0.041, 84)$. All lines of the diffraction pattern could be indexed for the proposed unit cell. The observed reflections satisfied the restrictions h + k = 2n (hkl), l = 2n (0kl) and h + l = 2n (h0l). The possible space groups are therefore Cmcm and Cmc.

The X-ray powder patterns obtained from $ZrRuH_{2,2}$ were processed in the same manner. In this case 24 lines were involved in the indexing procedure. The reliability of the indexing of the X-ray patterns is



Fig. 2. Superconducting transition temperature T_c of the (a) ZrRuH_x and (b) HfRuH_x samples produced by a 24 h exposure at 600 K and the hydrogen pressure indicated on the abscissa: filled circles, hydrogen primary solutions with CsCl-type metal lattice; open circles, hydrides; half-filled circles, two-phase samples. Symbols with arrows stand for samples exhibiting no superconductivity above 1.5 K. Error bars indicate the 10%–90% widths of superconducting transitions.

characterized by $M_{20}=21.8$ and $F_{24}=13.8(0.029, 60)$. The refined values of the lattice parameters are given in Table 1.

Several equiatomic compounds of elements of groups IV and VIII (HfNi, HfCo, ZrNi, ZrCo) are known to form hydrides with the orthorhombic *Cmcm* metal sublattice, a structure of the CrB type [9]. The complete crystal structure was first determined for ZrNiH₃ [10] and is therefore referred to as the ZrNiH₃ structure type. The intensities of X-ray diffraction lines for the HfRu and ZrRu hydrides with the ZrNiH₃-type structure calculated with the LAZY PULVERIX [11] computer program agreed rather well with the experimental data.

Since X-ray studies provide information only on the metal sublattice of the hydrides, neutron diffraction measurements were performed and the data were analysed using the Rietveld profile refinement technique implemented in the DBWS-9006PC computer program [12].

The analysis of the neutron powder diffraction pattern from the initial HfRu confirmed that the HfRu equiatomic compound possesses a completely ordered CsCl structure. The experimental data and calculated profile are presented in Fig. 3(a).

At the beginning of the structure refinement procedure for the HfRu deuteride the atoms were placed on the positions of the $ZrNiH_3$ structure given in ref. 10. The procedure involved 17 fitting parameters: five atomic coordinates, three isotropic temperature pa-



Fig. 3. The final Rietveld difference plots for the neutron diffraction patterns of (a) HfRu (300 K), (b) HfRuD_{3.6} (120 K) and (c) HfRuH_{3.6} (120 K). The experimental data are shown by dots, the calculated profile by the solid lines. Differences are plotted in the lower parts of the figures.

rameters, a scale factor, a zero-shift parameter, three cell parameters, one asymmetry and three halfwidth parameters. The refinement converged to $R_{\rm F} = 6.48$, $R_{\rm B} = 8.53$ and $R_{\rm wp} = 8.83$. The neutron diffraction pattern

TABLE 2. Positional parameters and Debye–Waller factors (B) for HfRuD_{3.6}

Atom	Site	Coordinates			в	Occupancy	
Hf	4(c)	0,	0.125,	0.25	0.11	0.74	
Ru	4(c)	0,	0.427,	0.25	0.10	0.74	
D	4(c)	0,	0.903,	0.25	1.2	1.00	
D	8(f)	0,	0.301,	0.520	1.2	1.00	

for HfRu_{3.6} and the profile fit are shown in Fig. 3(b). The final atomic parameters are given in Table 2. The χ value, *i.e.* the ratio of R_{wp} to the expected value R_{exp} , for the analysed portion of the spectrum is 2.21. Ideal structural models generally refine to values $\chi \leq 2$ [13]. The rather large values of the R factors can mainly be attributed to poor statistics of the experimental data caused by the small mass (about 100 mg) of the sample.

As one can see from Table 2, the sites in the metal sublattice of the HfRu deuteride are only partly occupied, which accounts for its "overstoichiometric" composition HfRuD_{3.6}. The goodness of this fit, however, is only slightly better than that for the composition HfRuD₃ with another set of thermal parameters. Owing to a strong correlation between the occupancy numbers and Debye–Waller factors, an accurate determination of these parameters would require a much better quality of the diffraction data.

At the same time, a good convergence of the fit with respect to the atomic coordinates enabled us to determine these with a rather high accuracy of ± 0.002 . As is seen from Table 2, the deuterium atoms occupy four octahedral $(0, y, \frac{1}{4})$ and eight tetrahedral (0, y, z)interstices formed by the metal atoms. A schematic drawing of the structure is given in ref. 14.

The neutron diffraction spectrum from the HfRuH_{3.6} sample was fitted in the same way (Fig. 3(c)). The atomic positions in HfRuH_{3.6} and HfRuD_{3.6} were found to be close to each other and to those in NiZrH₃, the differences being less than 0.02. The fact that the neutron diffraction patterns of both HfRuD_{3.6} and HfRuH_{3.6}, despite being quite different in appearance, can be described by the same structure model is good evidence in favour of the correctness of this model.

4. Discussion

4.1. Superconductivity

As was shown earlier [4], the rigid d-band model principally explains the available data on superconducting properties of hydrides of the group V-VIII transition metals and their alloys. In accord with the predictions of this model, the present study has revealed that the hydrides of HfRu and ZrRu become superconducting. This shows that the rigid d-band model takes into account one of the main effects hydrogenation has on the superconducting properties of a rather large variety of transition metals and their alloys.

The rigid d-band model takes into account the specific changes in the band structure of transition metals on hydrogen uptake first outlined by Switendick [15] and then confirmed by many other calculations for various d-metals, namely that the hydrogen leaves the upper part of the d-band of the host metal nearly unaffected, but noticeably decreases the energy of the s-states. The latter lowers the rate η of d-band filling with the electrons supplied by the hydrogen to a value of the order of $\eta = 0.5$ electrons per H atom (varying from about 0.3 to about 1 for different metals and alloys). This concept implies that those properties of the metal which essentially depend on the d-band occupation should vary with the increasing hydrogen concentration as if the hydrogens were merely donors of a fractional number of $\eta \approx 0.5$ electrons per hydrogen atom into the otherwise unchanged metal d-band. This is the very approximation that we call a rigid d-band model for brevity.

To apply this model, one needs to know how the property of interest depends upon the degree of dband filling for the specific material to be hydrogenated. The necessary information is easily attainable for the 3d metals, which form broad ranges of continuous solid solutions with many properties, in particular the magnetic ones, well described by the rigid band model. As for the superconducting properties of transition metals, there is a correlation, known as the Matthias rule, between the T_c values and the electron concentration N^e , *i.e.* the average number of outer d+s electrons per alloy atom.

The correlation suggests [16] that over rather wide concentration ranges these properties for many different alloys are satisfactorily represented by the rigid band model, *i.e.* the alloys have approximately the same conduction band and their T_c values are largely determined by its electron occupation. The density of dstates at the Fermi level of transition metals and alloys is usually much higher than that of s-states, so it is actually the degree of d-band filling that governs the T_c behaviour.

In contrast with alloys of 3d metals, the applicability of the rigid band model to alloys of 4d and 5d metals is usually limited to intervals of a few atomic per cent. The available data make it possible, however, to specify at least two kinds of alloys with superconducting properties obeying the rigid band model. These are (i) primary solid solutions of neighbouring elements in the periodic table and (ii) $A_{1-y}(B, C, ...)_y$ alloys or intermetallic compounds with fixed y, where the elements B, C, etc. are close neighbours, whereas element A is positioned far from them in the periodic table. In such systems replacing, for instance, element B by element C or varying their relative concentrations produces only minor changes in the band structure of the alloy. Wherever data are available, the Matthias plots of T_c vs. N^e for both kinds of alloys exhibit a large broad peak centred at $N^e \approx 6.3-6.7$ e atom⁻¹ [5, 16, 17].

If the $T_c(N^c)$ dependence is known, the rigid d-band model allows one to estimate the contribution from the increasing d-band occupancy to the change in T_c on hydrogenation:

$$T_{\rm c}(n) = T_{\rm c}(N^{\rm e} + \eta n) \approx T_{\rm c}(N^{\rm e} + 0.5n) \tag{1}$$

where N^{e} is the electron concentration of the alloy and n is the hydrogen-to-metal atomic ratio of its hydride. The HfRu and ZrRu alloys with $N^{e} = 6 e$ atom⁻¹ studied in the present work belong to the type (ii) alloys ($A \equiv Hf$, Zr; B, C, $\dots = Ru$, Rh, Pd, Pt, \dots). The "effective" electron concentration of their hydrides is $N_{\rm eff}^{\rm e} \approx N^{\rm e} + 0.5n \approx 6.9$ and 6.4–6.55 e atom⁻¹ respectively if n = x/2. These values fall into the peak region of the Matthias plot. T_{c} is therefore expected to increase on hydrogenation of the alloys, which is indeed observed (Table 1). The equality of the T_c values for the hydride and deuteride of HfRu as well as ZrRu indicates that another mechanism that might affect the superconducting properties, namely the interaction of the conduction electrons with optical vibrations of the hydrogen or deuterium respectively, is hardly at work in the present case. Such an interaction has been found to play a major role in the dependence of T_c on the hydrogen or deuterium content of palladium [18], where it gives rise to a substantial isotope effect.

Formula (1) semiquantitatively describes the experimental $T_c(n)$ dependences for hydrogen solid solutions in h.c.p. Re, Ru [3] and Tc [19] and accounts for the absence of superconductivity in the f.c.c. Rh hydride [3] with $N_{eff}^e \approx 9.5$ e atom⁻¹ and for its presence in the h.c.p. Mo hydride [20] and the f.c.t. dihydride of the Nb₈₈Rh₁₂ alloy [21] with $N_{eff}^e \approx 6.5$ e atom⁻¹. On the other hand, in the hydrides based on b.c.c. and related metal lattices the d-band filling is not an unconditionally dominating mechanism.

The analysis [4] of the experimental $T_c(n)$ dependences for hydrogen solid solutions in the Nb₃Me (Me = Os, Ir, Pt, Au) compounds with the A15 structure and b.c.c. Nb-Ti alloys has shown that, along with the changes caused by the d-band occupation, there is also a steady decrease in T_c at a rate τ of the order of -5 to -10 K per hydrogen atom. This is presumably due to a hardening of the acoustic phonon modes of the host metal (note that the dissolved hydrogen causes an increase in the mean frequency of acoustic vibrations in b.c.c. Nb and Ta, but a decrease in the f.c.c Pd and Ni hydrides and h.c.p. Mn hydride [22, 23]). With both

contributions taken together, the $T_c(n)$ dependence for the alloys with b.c.c. and related structures may be written as

$$T_{\rm c}(n) \approx T_{\rm c}(N^{\rm e} + 0.5n) - \tau n \tag{2}$$

This formula also explains why the T_c value of the Nb₈₈Rh₁₂-H solutions with a D_{8b}-type metal lattice (another b.c.c.-related structure) hardly changes with the hydrogen concentration at $n \le 0.8$ [21] instead of increasing at a rate of approximately 5 K per hydrogen atom in accord with eqn. (1).

4.2. Crystal structure

The above discussion of the rigid d-band model would be unnecessarily thorough if the only result of the paper were the finding of superconducting transitions in the HfRu and ZrRu hydrides. Another interesting observation, however, was the CrB-type metal lattice structure of the hydrides. This is the structure of the HfPt and ZrPt compounds [24], whose electron number, $N^e=7$ e atom⁻¹, is close to the N_{eff}^e of the HfRu and ZrRu hydrides. This fact indicates that effective electron numbers near 7 e atom⁻¹ favour this structure.

There are indeed more and more indications (see e.g. refs. 16 and 25 and references cited therein) that the crystal structures of transition metals and alloys, with the possible exception of ferromagnetic Fe, Co and Ni, are to a large extent determined by the d-band occupation and, as a consequence, by the electron concentration N^{e} . In particular, because of a strong dependence of the superconducting properties of the metals upon their crystal structure, the existence of the Matthias rule implies by itself such a correlation.

With correlations of this kind existing in pure metals as well as their alloys and intermetallic compounds, one should also expect similar correlations between the crystal structures and $N_{\rm eff}^{\rm e}$ of the hydrides of transition metals and their alloys. There is indeed evidence for such correlations. For example, most hydrides with $6.1 \leq N_{eff}^{e} \leq 7.1 \text{ e atom}^{-1}$ have close-packed metal lattices (h.c.p., f.c.c. and their slightly distorted modifications) characteristic of most d-metals and alloys with N^e in the same range [1-3]. The model also accounts for the crystal structures of the hydrides of the 3d metals Fe, Co and Ni ($N^e = 8$, 9 and 10 e atom⁻¹) respectively. Iron hydride is d.h.c.p. [26] like Co metal doped with Fe [27], CoH is f.c.c. [2] like Ni, and NiH is f.c.c. [1] like Cu ($N^e = 11$ e atom⁻¹). It is interesting to note that the calculated crystal structures of ferromagnetic Fe, Co and Ni are notoriously incorrect because of a large magnetic contribution to the total energy of the crystals which is difficult to evaluate [25]. The rigid dband model describes the magnetic properties of the hydrides [2, 26] in a satisfactory way and thus takes this magnetic contribution into account automatically. For the 4d and 5d metals and alloys the most convincing observation is the above-mentioned CrB-type metal structure of the HfRu and ZrRu hydrides, but other examples can also be given. For instance, the metal lattice of the hydride of Rh ($N^e = 9$ e atom⁻¹) is f.c.c. [2] like that of Pd ($N^e = 10$ e atom⁻¹), and the metal lattice of the hydride of Pd ($N^e = 10$ e atom⁻¹) is f.c.c. [18] like that of Ag ($N^e = 11$ e atom⁻¹). In the case of the type (ii) Nb₃Me alloys (Me = Os, Ir, Pt, Au) with N^e ranging from 5.75 to about 6.5 e atom⁻¹, the hydrides all have the same A15 metal structure as the starting alloys [4]. The model predicts this at least for the cases with Me = Os, Ir and Pt.

The applicability of the rigid d-band model for the description of the crystal structures of hydrides is certainly much more limited than for the description of their physical properties, since there are many additional factors affecting the formation of hydrides. In particular, the interstices in the metal lattice of the hydride must be of a size appropriate for the accommodation of hydrogen atoms. Moreover, the structures with minimum specific volume are preferentially formed if the synthesis is done under high pressure. The success of the model thus shows that for many groups of alloys d-band occupation dominates over other mechanisms governing hydride formation. It is interesting to note that the dominating role of the increase in the electron concentration in the formation of interstitial phases has already been discussed long ago [28] for solid solutions of carbon in the d-metals of groups V and VI.

Concluding, we would like to demonstrate how the rigid d-band model can be used to predict the effect of hydrogen on crystal structure and superconducting properties. A good object for this purpose are the alloys with a σ phase (type D_{8b}) structure, which form in many transition metal systems and have been rather thoroughly studied.

In particular, niobium forms wide ranges of continuous solid σ solutions with the 5d metals Re, Os, Ir and Pt ($6 \le N^e \le 6.9$ e atom⁻¹). The T_c values of the alloys with $6 \le N^e \le 6.5$ e atom⁻¹ are close to 2 K and nearly independent of N^e . At higher electron concentrations they increase at an average rate of about 10 K per electron per atom, reach a maximum of about 5 K at $N^e \approx 6.7$ -6.8 e atom⁻¹ and then begin to decrease [16, 17].

The rigid d-band model predicts, correspondingly, that the hydrides with $N_{eff}^{e} \leq 6.9$ e atom⁻¹ will have metal lattices of the same D_{8b} type. This is a b.c.c. related structure, so the superconducting temperatures of the hydrides will follow eqn. (2). For example, the T_{c} value of the σ -type hydrides of the Nb₅₀Re₅₀ alloy ($N^{e} = 6$ e atom⁻¹) will decrease at the rate τ and vanish at $n \approx T_{c}(N^{e})/\tau \approx 0.2$ -0.4. The T_{c} value of the Nb₆₃Ir₃₇-H solid solutions ($N^{e} \approx 6.5$ e atom⁻¹) will remain approximately unchanged or slowly decrease at $n \leq (6.8-6.5)/0.5 \approx 0.6$ until $N_{\text{eff}}^{\text{e}}$ reaches the position of the maximum of the $T_{\text{c}}(N^{\text{e}})$ dependence and will then begin to decrease rapidly at higher hydrogen concentrations.

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References

- 1 B. Baranowski, in G. Alefeld and J. Völkl (eds.), *Topics in Applied Physics*, Vol. 29, *Hydrogen in Metals II*, Springer, Berlin, 1978, p. 157.
- 2 E.G. Ponyatovsky, V.E. Antonov and I.T. Belash, in A.M. Prokhorov and A.S. Prokhorov (eds.), *Problems in Solid-state Physics*, Mir, Moscow, 1984, p. 109.
- 3 V.E. Antonov, T.E. Antonova, I.T. Belash and V.I. Rashupkin, High Press. Res., 1 (1989) 315.
- 4 V.E. Antonov, T.E. Antonova, I.T. Belash, O.V. Zharikov, A.I. Latynin, A.V. Pal'nichenko and V.I. Rashchupkin, *Fiz. Tverd. Tela (Leningrad), 31* (1989) 12 (Engl. translation Sov. *Phys. – Solid State, 31* (1989) 1659).
- 5 E.M. Savitskii, Yu.V. Efimov, Ch. Raub and H.R. Khan, Superconductivity of Noble Metal Alloys, Metallurgiya, Moscow, 1985 (in Russian).
- 6 D. Taupin, J. Appl. Crystallogr., 22 (1989) 455.
- 7 P.M. de Wolf, J. Appl. Crystallogr., 1 (1968) 108.
- 8 G.S. Smith and R.L. Snyder, J. Appl. Crystallogr., 12 (1979) 60.
- 9 R.M. van Essen and K.H.J. Buschow, J. Less-Common Met., 64 (1979) 277.

- 10 S.W. Peterson, V.N. Sadana and W.L. Korst, J. Phys. (Paris), 25 (1964) 451.
- 11 K. Yvon, W. Jeitschko and E. Parthe, J. Appl. Crystallogr., 10 (1977) 73.
- 12 R.A. Young and D.B. Wiles, J. Appl. Crystallogr., 15 (1982) 430.
- 13 C. Greaves, A.J. Jacobson, B.C. Tofield and B.E. Fender, Acta Crystallogr. B, 31 (1975) 641.
- 14 V.A. Somenkov and S.Sh. Shil'stien, Z. Phys. Chem. N.F., 117 (1979) 125.
- 15 A.C. Switendick, Solid State Commun., 8 (1970) 1463; Ber. Bunsenges. Phys. Chem., 76 (1972) 535.
- 16 S.V. Vonsovsky, Yu.A. Izyumov and E.Z. Kurmaev, Superconductivity of Transition Metals, Springer, Berlin, 1982.
- 17 B.W. Roberts, J. Phys. Chem. Ref. Data, 5 (1976) 581.
- 18 B. Stritzker and H. Whül, in G. Alefeld and J. Völkl (eds.), Topics in Applied Physics, Vol. 29, Hydrogen in Metals II, Springer, Berlin, 1978, p. 243.
- 19 V.E. Antonov, I.T. Belash, K.G. Bukov, O.V. Zharikov, A.V. Pal'nichenko and V.M. Teplinsky, *Fiz. Met. Metall.*, 68 (1989) 1198 (in Russian).
- V.E. Antonov, I.T. Belash, O.V. Zharikov, A.I. Latynin and A.V. Pal'nichenko, *Fiz. Tverd. Tela (Leningrad)*, 30 (1988) 598 (Engl. translation Sov. Phys. - Solid State, 30 (1988) 344).
- 21 V.E. Antonov, T.E. Antonova, I.T. Belash, O.V. Zharikov, A.V. Pal'nichenko, E.G. Ponyatovskii and V.I. Rashchupkin, *Fiz. Tverd. Tela (Leningrad), 30* (1988) 2152 (Engl. translation *Sov. Phys. – Solid State, 30* (1988) 1240).
- 22 P.V. Gel'd, R.A. Ryabov and L.P. Mokhracheva, *Hydrogen* and *Physical Properties of Metals and Alloys*, Nauka, Moscow, 1985 (in Russian).
- 23 A.I. Kolesnikov, I. Natcaniec, V.E. Antonov, I.T. Belash, V.K. Fedotov, J. Krawczyk, J. Mayer and E.G. Ponyatovsky, *Physica B*, 174 (1991) 257.
- 24 V.N. Kuznetsov and G.P. Zhmurko, J. Less-Common Met., 163 (1990) 1.
- 25 H.L. Skriver, Phys. Rev. B, 31 (1985) 1909.
- 26 V.E. Antonov, I.T. Belash, V.F. Degtyareva, D.N. Mogilyansky, B.K. Ponomarev and V.Sh. Shekhtman, *Int. J. Hydrogen Energy*, 14 (1989) 371.
- 27 B.I. Nikolin, *Multilayer Structures and Polytypes in Metal Alloys*, Naukova Dumka, Kiev, 1984 (in Russian).
- 28 R. Andrievskii and Ya. Umanskii, *Interstitial Phases*, Nauka, Moscow, 1977 (in Russian).