

SUPERCONDUCTIVITIES OF HIGH-PRESSURE PHASES IN THE METAL-HYDROGEN SYSTEMS

V. E. ANTONOV, T. E. ANTONOVA, I. T. BELASH and V. I. RASHUPKIN

Institute of Solid State Physics, USSR Academy of Sciences, Moscow, USSR

KEY WORDS: Superconductivity, high-pressure, hydrides, incorporation, crystal structure, lattice.

The superconducting properties of the d-metal hydrides rank among the most interesting and less studied of their characteristics. Correct and complete data have only been obtained for one superconducting hydride, the palladium hydride¹. The long studies on phases forming in the d-metal-hydrogen systems in the well-mastered pressure range up to tens of atmospheres have not exhibited any new superconductors, and the scope of systems which could be of interest from this viewpoint has been mainly exhausted¹.

At the same time, it has become clear that further elucidation of superconducting properties of the metal-hydrogen systems is impossible without experimental discovery and examination of new superconducting hydrides.

The development of the technique for compressing gaseous hydrogen to high (of the order of several GPa) pressures enlarged the number of objects accessible for hydrogenation. For instance, it has become possible to produce massive homogeneous samples of Mn, Fe, Co, Ni, Mo, Tc, Rh, Re hydrides and of their numerous alloys^{2,3}.

As for the high-pressure Me-H phases on the base of pure metals, the following has been found, see Ref. 2. The hydrides of Mn, Fe and Co possess a magnetic order and do not thus possess superconductivity. The molybdenum hydride (HCP(ϵ) metal lattice, H-to-metal atomic ratio $n=1.23 \pm 0.03$) exhibits no superconductivity at $T \geq 2$ K. The hydrides of Ni (FCC(γ) metal lattice, $n=1.06 \pm 0.03$) and Rh (γ , $n=1.02 \pm 0.03$) do not become superconducting at $T \geq 0.3$ K. An increase in the hydrogen concentration in ϵ -Re ($T_c=1.70$ K) up to $n \approx 0.23$ and in ϵ -Ru ($T_c=0.495$ K) up to $n \approx 0.03$ leads to a decrease in their T_c -values with the slopes $dT_c/dn = -5.0 \pm 0.2$ K/atom H and ≈ -1 K/atom H, respectively. For the primary hydrogen solid solutions in ϵ -Tc ($T_c \approx 7.85$ K) with $n \leq 0.04$ the value $dT_c/dn \approx -10$ K/atom H; and the ϵ -hydrides of Tc with $0.39 \leq n \leq 0.78$ possess no superconductivity at $T \geq 2$ K.

Therefore, the study of pure-metal hydrides did not reveal any new superconductors, and only hydrides of the alloys remained to count on. But then the question was what rules one might follow while choosing the alloys for hydrogenation.

In the case of d-metal alloys (without hydrogen) the concentration dependences of T_c can at least be qualitatively described by the rigid band model⁴. In order to evaluate what role the changes in the degree of occupation of the host-metal conduction band by electrons may play in varying the T_c -values on hydrogenation, we examined the effect of hydrogen on T_c 's suitable for this purpose BCC(α) Nb-Ti alloys with 20, 35 and 50 at.% Ti and for all the three alloys found out a sharp (~ -15 K/atom H) decrease in T_c ⁵. The effect cannot be accounted for by the changes in the electron concentration of the alloys and should necessarily be attributed to the variation in their phonon spectrum. So, in the case of hydrogen solutions it is hardly possible to rely on the predictions made on the basis of the rigid band model, and for the search for new superconducting hydrides to be purposeful other guides should be taken.

And we made use of the literature data that incorporation of hydrogen into the Nb-Ru⁶, Nb-Rh⁷ and Nb-Pd^{7,8} alloys may increase the T_c -values of the samples. The Nb-Me-H samples being inhomogeneous and multi-phase, no reliable data on the hydrogen content and crystal structure of superconducting phases were obtained in Refs. 6 to 8. We have studied the phases forming under high (up to 7 to 9 GPa) hydrogen pressures and $T=300$ or 325°C in the Nb-Ru-H⁹, V-Ru-H¹⁰ and Ta-Ru-H¹¹ systems; the basic results are listed in the table.

As one can see from the table, superconducting hydrides were found for the alloys of Ru with all the d-metals of V group (V, Nb, Ta), that is, these alloys being chemically analogous turned out to be analogous as for possessing superconducting hydrides too. Since the alloys of Nb with all the 4d-metals of VIII group (Ru, Rh, Pd) seem also to have superconducting hydrides, then proceeding from the chemical similarity of the alloys, one may expect that the alloys of all the d-metals of V group with 4d-metals of VIII group form superconducting hydrides as well. We tried to extend the scope of alloys forming superconducting hydrides by substituting Ru for its nearest analogue, Os, in the alloys with V and Ta, but no success has been achieved so far, see the table.

In general, it is worth noting that the search for new superconductors in the Me-H systems based on the alloys for d-metals turned out to be a hard experimental problem. Typical results of studying such systems are presented in Figures 1–3. It is seen, in particular, that the pressure intervals, within which phases are formed, can be rather narrow (e.g., the γ -phase in the $\text{V}_{90}\text{Ru}_{10}$ -H system, Figure 1a), and the hydrogen content of the phase can be pressure-dependent (e.g., the ε -phase in the $\text{V}_{81.5}\text{Ru}_{18.5}$ -H system, Figure 2a). While concentration of the alloys under hydrogenation is varied, the phase equilibria sometimes change drastically and not in an obvious way (compare the data for the $\text{V}_{90}\text{Ru}_{10}$ -H and $\text{V}_{81.5}\text{Ru}_{18.5}$ -H systems, Figures 1a and 2a). The T - P_{H_2} diagrams of the systems-“analogues” may differ qualitatively (for example see Figure 3), an addition of 11.5 at.% Os into Ta diminishes solubility of hydrogen down to $n \approx 0.43$ even at $P_{\text{H}_2} = 9$ GPa, whereas the Ta-Ru alloy with 22.6 at.% Ru forms a hydride with $n \approx 1.1$ already at $P_{\text{H}_2} \geq 3$ GPa).

Fortunately, at the present initial stage of investigation the sphere of quest for superconducting hydrides might be noticeably reduced. As is seen from the table,

Table 1 Composition, superconducting temperature, pressure of synthesis, structure and parameters of the metal sublattice at atmospheric pressure and $T=83$ K for the Me-Ru-H and Me-Os-H solid solutions.

<i>Alloy</i>	<i>n</i>	<i>T_c</i> , K	<i>P_{H₂}</i> , GPa	<i>Structure</i>	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å
*V ₉₀ Ru ₁₀	0	<2	—	α	3.011	—	—
	0.5	<2	0.8	β	2.996	—	3.302
	1.04	3.0	1.1 ... 3.6	γ_1	3.971	—	—
	2.0	<2	>3.8	γ_2	4.265	—	—
*V _{81.5} Ru _{18.5}	0	<2	—	α	3.005	—	—
	1.12	<2	1.3	ϵ	2.787	—	4.688
	1.36	<2	7	ϵ	2.858	—	4.696
*V ₆₆ Ru ₃₄	0	<2	—	α^{or}	2.995	—	—
	1.24	<2	2.4	ϵ	2.810	—	4.577
	1.34	<2	7	ϵ	2.822	—	4.572
Nb ₈₃ Ru ₁₇	0	<2	—	α	3.242	—	—
	1.92	<2	>4	ϵ'	5.391	5.113	3.170
Nb _{74.5} Ru _{25.5}	0	<2	—	α	3.217	—	—
	1.04	5.08	1.2	γ'	4.244	—	4.180
	1.72	<2	7	ϵ	3.082	—	5.033
Nb ₆₉ Ru ₃₁	0	<2	—	α	3.199	—	—
	1.04	4.3	2	γ'	4.23	—	4.16
	≥ 1.5	?	7	ϵ	3.05	—	4.98
Nb ₅₀ Ru ₅₀	0	<2	—	γ^*	4.371	4.225	3.396
	0.24	<2	1.0 ... 1.4	γ_2^*	4.379	4.327	3.459
	1.13	<2	2.2 ... 7	ϵ'	5.098	4.727	2.914
	1.25						
*Ta _{77.4} Ru _{22.6}	0	<2	—	α	3.316	—	—
	1.10	3.1	>3.2	ϵ'	5.188	4.951	2.966
*Ta ₆₉ Ru ₃₁	0	<2	—	α^{or}	3.194	—	—
	0.95	2.8	>4.2	ϵ'	5.163	4.881	2.937
V ₉₁ Os ₉	0	<2	—	α	3.012	—	—
	0.6	<2	2	α	3.110	—	—
	>1.7	<2	>3	γ_2	4.250	—	—
V _{79.5} Os _{20.5}	0	<2	—	α	3.004	—	—
	0.2	<2	3.5	α	3.037	—	—
	1.03	<2	>4	ϵ	2.848	—	4.665
Ta _{88.5} Os _{11.5}	0	<2	—	α	3.256	—	—
	0.43	<2	9	α	3.324	—	—

Stars indicate the alloys hydrogenated at 300°C, the rest of the alloys were hydrogenated at 325°C. α , BCC; α^{or} , of CsCl type; β , of β -V₂H type (values of a_0 and c_0 for the tetragonal pseudocell are given); γ , FCC; γ' , FC tetragonal; γ^* , the structure on the base of FC orthorhombic pseudocell; ϵ , HCP; ϵ' , rhombically distorted HCP.

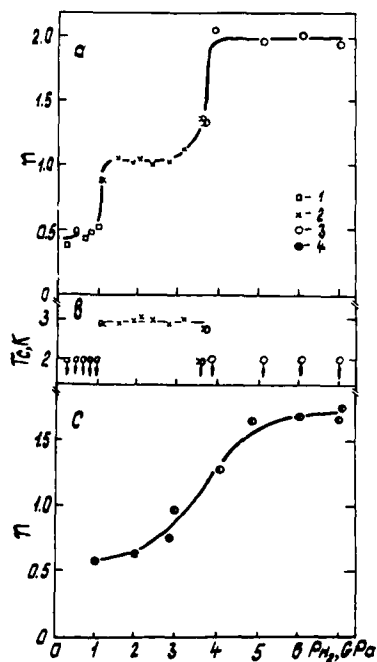


Figure 1 Hydrogen content, n , (a) and superconducting temperature, T_c , (b) for the $V_{90}Ru_{10}$ -H solid solutions produced by exposure for 24 h at 300°C and under the hydrogen pressures indicated on the abscissa; (c) values of n for the V_9Os_9 -H solutions (24 h at 325°C). 1, data for the β -solutions; 2, γ_1 ; 3, γ_2 ; 4, α . Combinations of halves of the different symbols refer to the two-phase samples. Symbols with arrows in Figure 1b show that the samples are not superconducting at $T \geq 2$ K.

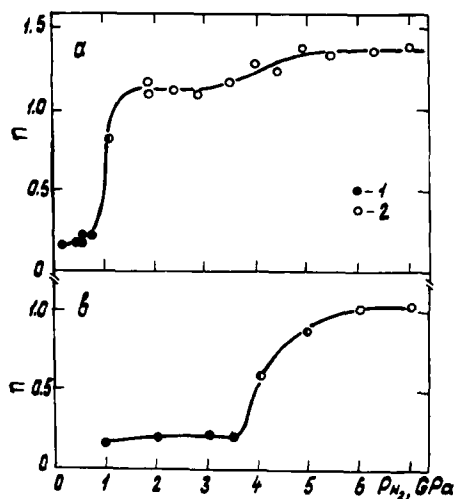


Figure 2 Hydrogen content, n , for the $V_{81.5}Ru_{18.5}$ -H (a) and $V_{79.5}Os_{20.5}$ -H (b) solid solutions produced by exposure for 24 h under the hydrogen pressures indicated on the abscissa and at temperatures 300 and 325°C, respectively. 1, data for the α -solutions; 2, ϵ . Half-blackened symbols stand for the two-phase ($\alpha + \epsilon$) samples.

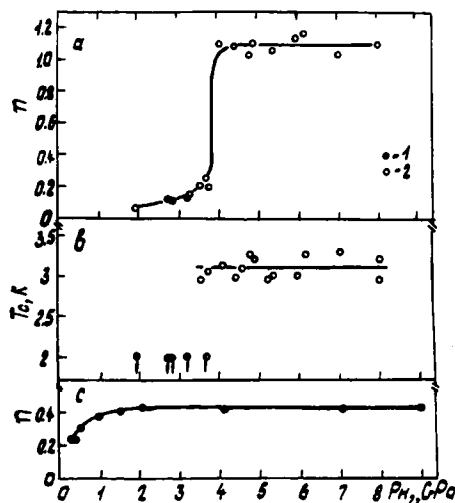


Figure 3 Values of n (a) and T_c (b) for the $\text{Ta}_{77.4}\text{Ru}_{22.6}\text{-H}$ solid solutions (24 h at 300°C) and values of n (c) for the $\text{Ta}_{88.5}\text{Os}_{11.5}\text{-H}$ solutions (24 h at 325°C) given as functions of pressure of the samples synthesis. 1, data for the α -solutions; 2, ϵ' . Half-blackened symbols refer to the two-phase samples. Symbols with arrows in Figure 3b show that the samples are not superconducting at $T \geq 2$ K.

only the phases with $n \approx 1$ based on the closest packings of metal atoms happened to be superconducting among the set of the synthesized phases. Note that the Pd hydride is also formed on the base of the closest (FCC) packing of the metal atoms, and its T_c reaches the maximum value at $n \approx 1$. All the foregoing is unlikely to be of a random nature, and it would be sensible in the first place to search for superconductors in yet uninvestigated Me-H systems, namely among the phases of such type.

The data available on the composition and crystal structure of the hydrides allow one also to speculate why some phases with $n \approx 1$ are superconducting. There are two kinds of interstitials in the close-packed lattices, the octa- and tetrahedral ones, the oscillation frequencies of hydrogens in the octapores being essentially lower¹², and the composition $n = 1$ corresponds to the complete filling of all the octapores with hydrogens. Superconductivity of the palladium hydride is considerably conditioned by the interaction of electrons just with the optical oscillations of hydrogens in the octapores¹. It seems quite probable that a similar situation takes place with the Me-Ru-H superconducting hydrides as well.

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