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A Study on Superconductivities of High-Pressure Phases  
in the Re-H, Ru-H, Rh-H, and Ni-H Systems

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A technique for compressing gaseous hydrogen to high pressures developed at the Institute of Solid State Physics of the Academy of Sciences of the USSR enabled the synthesis of solid Me-H solutions on the base of a number of VI to VIII group transition metals and their alloys with hydrogen concentrations exceeding those achieved earlier /1/. Many of the phases obtained are of interest as related to their superconducting properties.

Under atmospheric pressure, all these phases are stable relative to decomposition into the metal and molecular hydrogen at liquid nitrogen temperature, but are unstable at room temperature. So, when the samples are placed into a conventional apparatus for measuring superconducting properties, an essential loss of hydrogen is observed. Earlier we studied superconductivities of the high-pressure Me-H phases in a specially designed installation with pumping-out the He<sup>4</sup> vapour at  $T \cong 1.2$  to 2 K. At present we have built an installation with He<sup>3</sup> vapour pumping-out, which permits loading the samples without their heating above the liquid nitrogen temperature and which enables their examination at temperatures down to 0.3 K.

This note presents the results obtained on this installation on measuring the superconducting temperature in the Me-H phases on the base of Re, Ru, Rh, and Ni metals.

The samples were in the form of plates of about  $3 \times 3 \times 0.2$  mm<sup>3</sup> in size. Hydrogenation on the samples was conducted by a 24 h exposure in an atmosphere of molecular hydrogen at fixed magnitudes of temperature and pressure with subsequent "quenching" down to  $\approx -150$  °C by the method described in /1/. The pressure was determined to an accuracy of  $\pm 3\%$ , the temperature was kept constant to within  $\pm 10$  K. The conditions of hydrogenation provided saturation of the samples with hydrogen up to concen-

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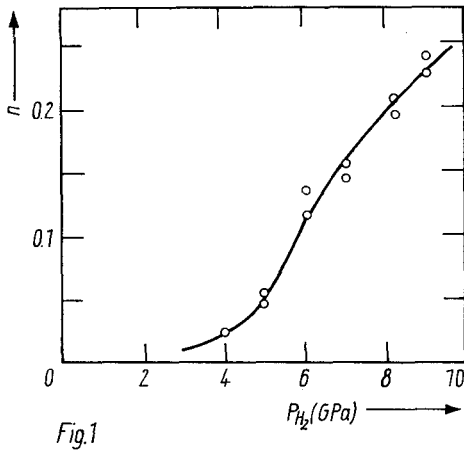


Fig.1

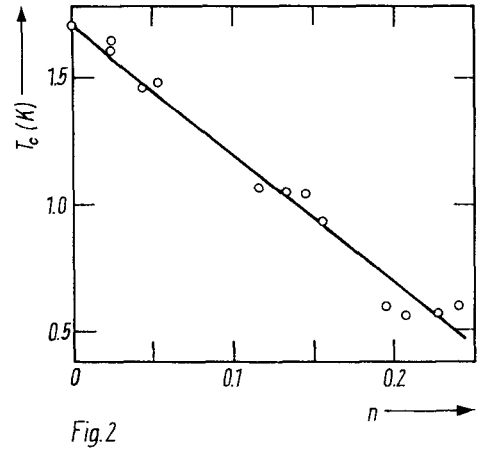


Fig.2

Fig. 1. Hydrogen content,  $n$ , of the Re-H samples versus pressure,  $P_{H_2}$ , of their synthesis at  $T = 350^\circ\text{C}$

Fig. 2. Dependence of the superconducting temperature,  $T_c$ , on the hydrogen concentration,  $n$ , for the Re-H solid solutions

trations close to thermodynamic equilibrium ones at chosen values of  $T$  and  $P_{H_2}$ , and the conditions of "quenching" ruled out possible losses of hydrogen by the samples when the pressure was decreased to the atmospheric one. The values of the superconducting temperature,  $T_c$ , in the samples obtained were estimated from the step midpoints on the temperature dependence of their magnetic susceptibility, determined by the inductance method. An X-ray study of the samples was carried out by a phototechnique at  $T = 100\text{ K}$  using a DRON-2,0 diffractometer with  $\text{CuK}\alpha$  radiation. The hydrogen content of the samples was determined from the amount of  $\text{H}_2$  liberated in their thermal decomposition in vacuum at temperatures up to  $500^\circ\text{C}$ , the method was described in /2/; the error was  $\delta n \approx 0.01$  at  $n \lesssim 0.1$  and increased to  $\delta n \approx 0.03$  at  $n \approx 1$ , where  $n$  is the H-to-metal atomic ratio.

Re-H A single crystal of rhenium metal with the electric resistance ratio  $R_{300}/R_{4.2} \approx 100$  and  $T_c = 1.70\text{ K}$  was used as the starting material. The samples were hydrogenated at  $350^\circ\text{C}$  and hydrogen pressures up to 9 GPa. It has

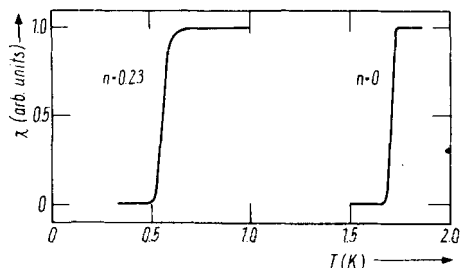


Fig. 3. Temperature dependences of the magnetic susceptibility,  $\chi$ , in the range of transition to the superconducting state for the initial Re samples ( $n = 0$ ) and a Re-H solid solution with  $n = 0.23$

been shown earlier /2/ that at  $T \approx 170$  to  $250^\circ\text{C}$  the hydrogen solubility in rhenium increases monotonically with pressure reaching  $n \approx 0.22$  at  $P_{\text{H}_2} = 9$  GPa, an increase in the hydrogen concentration of rhenium being accompanied by an approximately linear increase in the parameters of the initial h. c. p. metal lattice.

The pressure dependence of the hydrogen solubility in rhenium metal at  $T = 350^\circ\text{C}$  obtained in the present work is plotted in Fig. 1. The concentration of the Re-H solid solutions can be seen to increase monotonically with pressure up to nearly the same values,  $n \approx 0.23$ , at  $P_{\text{H}_2} = 9$  GPa. An X-ray examination has shown that under atmospheric pressure and  $T = 100$  K the concentration dependences of the rhenium sublattice parameters in the Re-H samples obtained are close to those found in /2/.

Incorporation of hydrogen into rhenium metal results in an approximately linear decrease in the  $T_c$ -values with the slope  $dT_c/dn = -(5.0 \pm 0.2)\text{K/H atom}$  (Fig. 2), the temperature interval of the superconducting transition remaining sufficiently narrow (Fig. 3), which points to a relatively homogeneous distribution of the hydrogen over the metal volume. After removal of the hydrogen from the Re-H samples by annealing in vacuum at  $500^\circ\text{C}$ , the magnitude of the superconducting temperature returns to the initial one,  $T_c = 1.70$  K. The absence of irreversible changes in the  $T_c$  value of rhenium after the hydrogenation-dehydrogenation cycle allows one to assume that the  $T_c$  values of the Re-H solutions under study are unambiguously related to their concentration.

Ru-H The samples were cut from a single crystal obtained by electron-beam melting of ruthenium powder (99.96 %) and had  $T_c = 0.495$  K. Ruthenium metal, as well as rhenium metal, has an h. c. p. crystal lattice. At  $250^\circ\text{C}$  the solubility of hydrogen in ruthenium increases monotonically with pressure reaching  $n \approx 0.03$  at  $P_{\text{H}_2} = 9$  GPa /1, 3/.

The Ru-H sample synthesized in the present work at  $T = 350^{\circ}\text{C}$  and  $P_{\text{H}_2} = 9 \text{ GPa}$  had the composition  $n = 0.035 \pm 0.01$  and  $T_c = 0.455 \text{ K}$ . The superconducting temperature of the sample annealed in vacuum at  $500^{\circ}\text{C}$  increased to its initial magnitude,  $0.495 \text{ K}$ . One may thus state that incorporation of hydrogen into the ruthenium metal leads to a decrease in its superconducting temperature with the initial slope  $dT_c/dn$  of the order of  $-1 \text{ K/H atom}$ .

Rh-H Polycrystalline rhodium (99.98%) was used. Hydrogenation of the sample was conducted at  $T = 350^{\circ}\text{C}$  and  $P_{\text{H}_2} = 7 \text{ GPa}$ . The hydride thus obtained had the composition  $n = 1.02 \pm 0.03$  and f. c. c. metal sublattice with  $a = (0.4024 \pm 0.0002) \text{ nm}$  under atmospheric pressure and  $T = 100 \text{ K}$ , which is in agreement with the data of /1, 3/.

Rhodium metal is a superconductor with  $T_c = 3.25 \times 10^{-4} \text{ K}$  /4/. Our measurements have shown the samples of the initial rhodium and its hydride to possess no superconductivity at  $T \geq 0.3 \text{ K}$ . The absence of superconductivity in the rhodium hydride is in line with the results of a quantum-mechanical calculation /5/.

Ni-H Polycrystalline nickel containing about  $10^{-3}\%$  Fe and less than  $10^{-4}\%$  of Cr, Mn, Co, Cu, Mg, and Al was used. A hydride with the composition  $n = 1.06 \pm 0.03$  was synthesized at  $T = 250^{\circ}\text{C}$  and  $P_{\text{H}_2} = 6.5 \text{ GPa}$ . The hydride had an f. c. c. metal sublattice with  $a = (0.3737 \pm 0.0002) \text{ nm}$  at atmospheric pressure and  $T = 100 \text{ K}$ , which is in agreement with the data of /1/ for a nickel hydride with  $n = 1.06$ .

It has been shown earlier that under atmospheric pressure nickel hydrides with  $0.7 \leq n \leq 1.18$  are paramagnetic at  $T \geq 4.2 \text{ K}$  and that the  $\text{NiH}_{1.18}$  hydride is not superconducting at  $T \geq 1.2 \text{ K}$  /1/. The  $\text{NiH}_{1.06}$  sample examined in the present work did not undergo a transition to a superconducting state at temperatures down to  $0.3 \text{ K}$ . The absence of superconductivity in the Ni hydride has been predicted theoretically /6/.

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