

Superconductivity in Hydrides of Nb-Pd and Nb-Rh*

This study forms part of an effort to investigate hydriding characteristics of binary intermetallic systems, with an eye on creating superconductivity as a result of the introduction of hydrogen. We have chosen as one component Pd because of the interesting superconducting properties of PdH ($T_c = 9^\circ\text{K}$) (1-9).

This NaCl type compound, however, is not at equilibrium at room temperature, decomposes and has to be prepared via high pressure synthesis, ion implantation or electrolysis. It was, therefore, of interest to see whether compound formation with a more electro-positive metal such as Nb which is known to form higher hydrides would also induce Pd to bond with more hydrogen. When we found an increase in T_c on hydride formation in the *b.c.c.* structure we investigated materials on the basis of Re, Ru, and Rh (in place of Pd) in order to better understand the origins of this effect. We describe only Nb rich specimens because only those could be induced to take up hydrogen under the conditions of our experiments.

Alloys were prepared on water cooled Cu boats under Ar atmosphere by induction melting. Elements were of purity >99.9%. Materials were identified structurally by X-ray diffraction. Hydriding was attempted at constant temperatures in steel containers by exposing bulk materials to hydrogen at pressures around 100 atm. Prior to this procedure the samples were evacuated at about 400°C. The amount of hydrogen uptake was measured by pressure monitoring in a known volume system with a pressure transducer (Viatran Corp.) and, independently, by

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weighing. Superconducting transition temperatures were measured by standard inductive methods using a factory calibrated Ge resistance thermometer. Critical onset temperatures are determined as the temperature where 10% of the sample has become superconducting.

Quick quenching during preparation of specimens in Nb-Pd resulted in large homogeneous regions of mutual uptake, commensurate with earlier phase studies (10). However, hydriding is only observed in specimens relatively rich in Nb. $\text{Nb}_{0.8}\text{Pd}_{0.2}$ of body centered cubic structure ($a_0 = 3.253 \text{ \AA}$) when held under hydrogen pressure of 100 atm around 400°C for about a day takes up hydrogen to a limiting composition $\text{Nb}_{0.8}\text{Pd}_{0.2}\text{H}_{0.39}$.

The X-ray diagram of this material shows small amounts (~25%) of one body centered cubic structure ($a_0 = 3.269 \text{ \AA}$) as well as a new body centered structure ($a_0 = 3.387 \text{ \AA}$, 75%) among traces of unidentified diffraction lines. This material was transferred immediately after preparation to liquid N_2 and later to liquid He for measurement of its superconducting properties. This measurement yielded $T_c = 2.5^\circ\text{K}$ (midpoint) and $T_c = 2.7^\circ\text{K}$ (onset) while a measurement of the unhydrided $\text{Nb}_{0.8}\text{Pd}_{0.2}$ yielded $T_c = 1.87^\circ\text{K}$ (midpoint) and $T_c = 2.02^\circ\text{K}$ (onset). Part of the hydrided specimen was kept under air for several months and was then remeasured giving $T_c = 4.84^\circ\text{K}$ (midpoint) and 5.10°K (onset). An X-ray diffraction of the material showed an increase in the proportion of the smaller lattice parameter, body centered cubic crystal type ($a_0 = 3.252 \text{ \AA}$) as well as some unidentified reflections (~30%).

In order to elucidate the importance of Pd in the Nb base alloys, analog materials were

prepared on the basis of $T = \text{Rh}$, Ru , and Re at composition $\text{Nb}_{0.8}\text{T}_{0.2}$. Measurable amounts of hydrogen take up were only observed with $\text{Nb}_{0.8}\text{Rh}_{0.2}$ ($a_0 = 3.241 \text{ \AA}$) leading to $\text{Nb}_{0.8}\text{Rh}_{0.2}\text{H}_{0.10}$ of body centered cubic structure with a slightly expanded lattice constant ($a_0 = 3.254 \text{ \AA}$). No signs for the presence of other phases beyond the limit of detection ($\sim 5\%$) were observed. This material was transferred to the cryogenic equipment immediately after preparation. It exhibited $T_c = 5.64^\circ\text{K}$ (midpoint) and 5.96°K (onset) while the parent compound $\text{Nb}_{0.8}\text{Rh}_{0.2}$ showed $T_c = 2.65^\circ\text{K}$ (midpoint) and $T_c = 2.75^\circ\text{K}$ (onset).

The decreased amount of hydrogen takeup in $\text{Nb}_{0.8}\text{Pd}_{0.2}$, compared to Nb , as well as the absence of hydride formation at higher Pd concentrations appears to be a result of the strong interactions between Nb and Pd . The extraordinary stability of alloys and compounds, especially, towards the composition NbPd_3 (11, 12), precludes hydrogen uptake. A similar behavior has also been recently found in compounds between Th and Pd (13).

This study is the first to show that hydrogen take up under retention of the body centered cubic structure, characteristic of VB and VIB metals, can raise T_c . This is the case for both the original $\text{Nb}_{0.8}\text{Pd}_{0.2}\text{H}_{0.39}$ as well as $\text{Nb}_{0.8}\text{Rh}_{0.2}\text{H}_{0.10}$. The situation is less clear in the case of the aged hydride of $\text{Nb}_{0.8}\text{Pd}_{0.2}$. So far hydrogen take up either in Nb^{14} as well as compounds such as $\text{Nb}_3\text{Sn}^{15}$ has been proven to be deleterious to superconductivity.

Recently two papers appeared (16, 17) reporting increases of T_c upon hydriding around $\text{Nb}_{0.8}\text{Pd}_{0.2}$ and $\text{Nb}_{0.8}\text{Ru}_{0.2}$. In this study hydriding was achieved by electrolysis at relatively low temperatures. This method yielded somewhat larger amounts of hydrogen take up compared to the present study ($\text{Nb}_{0.8}\text{Pd}_{0.2}\text{H}_{0.74}$, maximum composition, $T_c = 4.17^\circ\text{K}$ onset). The relatively high values of T_c in the hydride phases has been ascribed to the presence of a new face centered cubic crystal structure comparable to the NaCl type in PdH . We have explicitly looked for this face centered cubic phase but so far not found signs of it in Nb-Pd-H , although our values of T_c are comparable with the ones reported.

The increases of T_c upon hydriding of Nb-Pd and Nb-Rh alloys can, among other factors, be explained in a straightforward fashion on the basis of lattice parameter. Alloying Nb with Rh decreases the lattice parameter of Nb as well as T_c . Hydriding increases the lattice parameters again. The concomitant increase in T_c should then not be surprising as it reestablishes the original spacial situation. A similar situation holds concerning straightforward electron rules. However, beyond simple spacial and electronic arguments there will certainly be some electronic rearrangements and modifications in bonding which will have a decisive influence on superconductivity. In fact a relation can be expected to the respectable superconducting transition temperatures found in a variety of metastable compounds between Nb and noble metals at relatively high Nb concentrations (18).

The present study opens the possibility of achieving high values of T_c by modifying lattice parameters and electronic structure via the introduction of hydrogen.

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