Superconductivity of solid solutions of hydrogen in Nb_3Me compounds (Me = Au, Pt, Ir, Os) with the A15 structure

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The composition and crystal structure were studied, and the superconducting transition temperatures T_c were determined for Nb_3Me–H phases prepared at 325 °C and molecular hydrogen pressures up to 70 kbar. These structures were based on the A15 structure compounds $Nb_{74}Au_{26}$, $Nb_{76}Pt_{24}$, $Nb_{75}Ir_{25}$, and $Nb_{75}Os_{25}$. The compounds were found to retain their crystal structure type and remain superconducting when saturated with hydrogen up to $H/M \approx 1$. The hydrogen content dependence of T_c for the Nb_3Me–H solid solutions obtained can be described qualitatively by the rigid band model.

One of the effective ways of studying the influence of alloying elements on the physical properties of materials is to investigate the composition dependences of these properties in solid solutions having a lattice type that is unaffected by alloying. For example, it has been shown[1] in this way that the main cause of change in the magnetic properties of 3d metals and their alloys having fcc and hcp lattices, under hydrogenation, is an increased occupation of the d band by electrons from hydrogen atoms, and that the fraction η of electrons coming into the d band is of the order of 0.5 per hydrogen atom.

A fairly reliable explanation of superconducting properties has so far been given for only one metal–hydrogen system, namely palladium–hydrogen, where the hydride formation is again unaccompanied by any change in the initial fcc palladium lattice type.[2] Most of the known superconducting hydrides, however, have a metal lattice that differs from that of the initial metals and alloys; see our earlier paper[3] and the references there given. Since a change in the crystal structure of the material can in itself cause a considerable alteration in the superconducting properties, the role of hydrogen in such cases is hard to elucidate.

Consequently, in order to progress further in understanding the superconducting properties of metal–hydrogen systems, it seems useful to search for and investigate new superconducting systems having broad ranges of continuous solutions of hydrogen in the initial lattice of the material undergoing hydrogenation.

Promising materials in this respect are compounds with A15 structure; for four of these, Ti_3Au (Ref. 4) Ti_3Sb (Ref. 5), Nb_3Sn (Ref. 6), and Nb_3Rh (Ref. 3), it has already been established that considerable amounts of hydrogen (up to a hydrogen/metal ratio by atoms $n \approx 0.1$-1) can be absorbed with no change in the lattice type. We chose for investigation the compounds of niobium with four 5d metals (osmium, iridium, platinum, gold) occupying successive places in the periodic stable, since this series of compounds shows a clear correlation between the superconducting properties and the electron density,[7] so that the effects due to the change in the latter under hydrogenation can be assessed.

1. SAMPLE PREPARATION AND EXPERIMENTAL METHOD

The compounds were prepared from gold 99.99% pure, platinum, iridium, and osmium 99.97% pure, and niobium purified by zone melting with resistance ratio $R_{300K}/R_{4.2K} \approx 500$. The alloy ingots were fused in an induction furnace, suspended in argon, and annealed under $\approx 10^{-6}$ Torr at 1100°C for 24 h, followed by cooling in the furnace. To obtain a single-phase state of $Nb_{75}Os_{25}$, the ingot was further annealed for 5 h at 1400°C (see Sec. 2). Samples were cut from the polycrystalline ingots with a WS-20A abrasive wire saw; a damaged surface layer ≈ 0.03 mm thick was then removed by electropolishing in sulfuric acid. The final dimensions of the samples were $\approx 3 \times 3 \times 0.3$ mm.

The alloys were hydrogenated by holding the samples in molecular hydrogen at 325°C under fixed pressures up to 70 kbar for 24 h, followed by rapid cooling under pressure to $\approx$–180°C; the method has been described previously,[1] and a check showed that the hydrogen content and phase composition of the samples become practically constant after 18 h. The errors in determining the hydrogen pressure and the temperature did not exceed 5% and ±7°C.

The stability of the hydrides produced, as regards decay into the metal and molecular hydrogen at atmospheric pressure, decreased with increasing n; for equal n, the niobium–gold–hydrogen hydrides were the most stable, and the niobium–osmium–hydrogen ones were the least. In particular, at room temperature no release of hydrogen from $Nb_{74}Au_{26}$–H

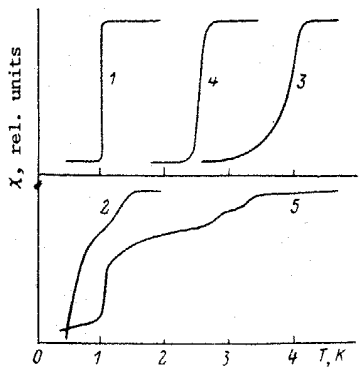

FIG. 1. Temperature dependences of the imbalance signal χ from an ac bridge in the ranges of transition to the superconducting state in Nb_3Me H (D) samples; 1-3) $Nb_{75}Os_{25}$–H, 4) $Nb_{76}Pt_{24}$–H, 5) $Nb_{76}Pt_{24}$–D; n: 1) 0, 2) 0.19, 3) 0.96, 4) 0.87, 5) 1.30.

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TABLE I. Pressure of production in hydrogen or deuterium at 325°C, composition, superconducting transition temperature, and metal sublattice parameters at atmospheric pressure and 100 K for solid solutions of hydrogen or deuterium in A15 structure niobium alloys

Samples	$P_{H_2(D_2)}$, kbar	n	T_c, K	a, Å	V_a Å³/atom	ΔV_a Å³/atom
$Nb_{74}Au_{26}$—H	—	0	10.1	5.198	17.56	—
	0.2	0.03	9.5	5.204	17.62	0.06
	5	0.7	3.8	5.410	19.79	2.23
	35	1.0	1.2	5.458	20.32	2.76
	70	1.08	<0.4	5.470	20.46	2.90
$Nb_{74}Au_{26}$—D	71.2	1.10	1.1	5.459	20.34	2.78
$Nb_{76}Pt_{24}$—H	—	0	9.2	5.161	17.18	—
	2	0.05	9.2	5.186	17.43	0.25
	32	1.0	2.3	5.407	19.76	2.58
	50—70	1.28	?	5.442	20.15	2.97
$Nb_{76}Pt_{24}$—D	70.6	1.30	?	5.438	20.10	2.92
$Nb_{75}Ir_{25}$—H	—	0	1.9	5.135	16.92	—
	20	0.02	2.4	5.139	16.96	0.04
	42	1.0	3.0	5.383	19.50	2.58
	60—70	1.18	2.7	5.412	19.81	2.89
$Nb_{75}Ir_{25}$—D	70.4	1.16	2.9	5.414	19.84	2.92
$Nb_{75}Os_{25}$—H	—	0	1.0	5.138	16.95	—
	52	0.9	4.3	5.376	19.42	2.47
	70	1.0	3.8	5.381	19.48	2.53
$Nb_{75}Os_{25}$—D	70.4	1.02	3.0	5.375	19.41	2.46

Note. $V_a = a^3/8$ is the volume per metal atom; $\Delta V_a = V_a(n) - V_a(0)$. For Nb_3Me—H solutions, the average values are given (continuous curves in the relevant diagrams).

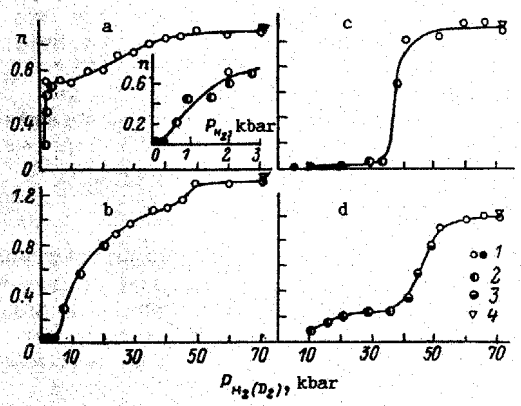

FIG. 2. Hydrogen and deuterium contents n for solid solutions of them in the alloys $Nb_{74}Au_{26}$ (a), $Nb_{26}Pt_{24}$ (b), $Nb_{75}Ir_{25}$ (c), and $Nb_{75}Os_{25}$ (d), made by holding the samples in molecular hydrogen or deuterium for 24 h at 325°C and the pressures shown as abscissas: 1) single-phase hydride samples, 2) two-phase, 3) three-phase, 4) single-phase deuteride samples.

with $n \approx 0.8$ was observed in the course of a week; from $Nb_{75}Os_{25}$—H with $n \geq 1$, most of the hydrogen was released in a few seconds even at $T \approx -60$°C. The design of the measuring equipment enabled the samples to be put into them without going above ≈100 K. To prevent hydrogen loss between measurements, the samples were kept in liquid nitrogen, which avoided any losses over at least a period of several months.

The x-ray study of the samples at 100 K was made photographically with a DRON-20 diffractometer and Cu K_α radiation. The T_c values were found inductively from the middle of the step on the temperature dependence of the imbalance signal χ from an ac bridge. For $T \geq 1.5$ K the measurements were made with ^{4}He evacuation, for $T \geq 0.35$ K with ^{3}He evacuation. The hydrogen content of the samples was determined after completing all other measurements, and was estimated with relative accuracy ±3% from the amount of hydrogen evolved during thermal decomposition up to 500°C; the method has been described elsewhere.[3]

2. EXPERIMENTAL RESULTS

Initial samples

Studies after vacuum annealing at 1100°C gave the following results. The alloys $Nb_{74}Au_{26}$ and $Nb_{75}Os_{25}$ contained only the A15 structure phase; $Nb_{76}Pt_{24}$ and $Nb_{75}Ir_{25}$ had traces of a σ phase corresponding to a lower niobium content than in the A15 phases. Because the σ phase content was low, the $\chi(T)$ curves for $Nb_{76}Pt_{24}$ and $Nb_{75}Ir_{25}$ showed, as in the single-phase $Nb_{75}Au_{26}$, only one step, corresponding to the transition to the superconducting state. The T_c values and the A15 lattice parameters for these three alloys (rows with n = 0 in Table I) agreed with those published previously.[8]

The $\chi(T)$ curve for $Nb_{75}Os_{25}$ showed two steps, at $T \approx 0.8$ and 1.8 K; accordingly, this alloy had two different superconducting phases. Further annealing in vacuum at 1300°C for 5 h broadened the temperature ranges of the superconducting transitions in both phases; the x-ray picture showed lines of a new phase, again with the A15 structure but with a larger lattice parameter, $a \approx 5.14$ Å in comparison with the initial $a = 5.120$ Å. After annealing at 1400°C for 5 h, the alloy showed only one superconducting transition (curve 1 in Fig. 1) at 1.0 K, in agreement with published results[8] for the $Nb_{75}Os_{25}$ A15 phase; the diffraction pattern retained only the lines for the phase with $a \approx 5.138$ Å.

The measurements show that at $1100 \lesssim T \lesssim 1400$°C there is a structure change in $Nb_{75}Os_{25}$, tha A15 lattice parameter increasing. This is con-

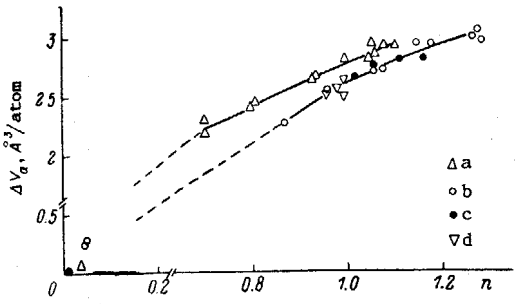

FIG. 3. Dependences of the volume increase ΔV_a per metal atom on the hydrogen content n in the solid solutions $Nb_{74}Au_{26}$–H (a), $Nb_{76}Pt_{24}$–H (b), $Nb_{75}Ir_{25}$–H (c), and $Nb_{75}Os_{25}$–H (d).

sistent with various authors' findings[8] that Nb_3Os has lattice parameters between 5.121 and 5.1359 Å.

Hydrogen solubility in alloys and the crystal structure of solutions

Figure 2 shows the hydrogen solubility isotherms for the Nb_3Me compounds studied. A general feature is the slight increase in the solubility as the pressure increases initially, followed by a rapid increase at the phase transition and a further gradual rise at higher pressures. The phase transition pressure is least for $Nb_{74}Au_{26}$–H, and increases steadily with decreasing atomic number of the second component, reaching a maximum for $Nb_{75}Os_{25}$–H. The phase transition is isomorphous in every system; the concentrated solutions (hydrides) Nb_2Me–H have metal lattices of the same A15 type as the initial compounds Nb_3Me but with larger parameter values.

Figure 3 shows $\Delta V_a(n) = V_a(n) - V_a(0)$, the volume increase per metal atom in the Nb_3Me–H solid solution samples shown by x ray to be single-phase. The $\Delta V_a(n)$ values for $Nb_{74}Au_{26}$–H are somewhat higher than for the other three solutions, but on the whole the $\Delta V_a(n)$ curves are close to one another and to the curves for all the metal–hydrogen solid solutions previously studied, which have various crystal structures.[1,9] Another typical feature of these curves is the decrease in the slope $\partial \Delta V_a/\partial n$ with increasing n; to show this decrease more clearly, the dashed lines in Fig. 3 are drawn to pass through the origin.

Only the $Nb_{75}Os_{25}$–H system showed a somewhat unusual behavior (Fig. 2d). Samples made at 325°C with $P_{H_2} \lesssim 35$ kbar contained two A15 phases with different lattice parameters, and their $\chi(T)$ curves had two blurred steps (curve 2 in Fig. 1) corresponding to superconducting transitions. After removal of hydrogen from the samples by annealing in vacuum at 500°C for 30 min, they remained two-phase, with the phase lattice parameters a ≈ 5.12 and 5.138 Å; the $\chi(T)$ curves were almost unchanged. Almost the same phase composition and $\chi(T)$ curve near the superconducting transition occurred for the initial alloy $Nb_{75}Os_{25}$ after annealing in vacuum at 1300°C. It is reasonable to suppose that, when $Nb_{75}Os_{25}$ is saturated with hydrogen at 325°C and $P_{H_2} \lesssim 35$ kbar, a phase change occurs in it which is the opposite of that observed in vacuum annealing at T > 1100°C.

Saturation of $Nb_{75}Os_{25}$ with hydrogen at 325°C and $35 \lesssim P_{H_2} \lesssim 50$ kbar formed a new A15 hydride phase, the only one present in samples made at $P_{H_2} > 50$ kbar (Fig. 2d). The $\chi(T)$ dependences in these samples, single-phase according to x ray, is evidence that they have only one superconducting transition, though spread over a considerable temperature range (curve 3 in Fig. 1). Removal of hydrogen from these samples by annealing in vacuum at 500°C restored the $Nb_{75}Os_{25}$ lattice parameter and T_c to their initial values, a = 5.138 Å and T_c = 1 K.

Superconductivity of Nb_3Me–H solid solutions

Figure 4 shows the T_c values for samples single-phase according to x ray, for various hydrogen contents.

A general feature of all four Nb_3Me–H systems studied is that T_c decreases with increasing n in solutions where the hydrogen concentration is high. In other respects, the $T_c(n)$ dependences are very different.

In $Nb_{74}Au_{26}$–H solutions, the T_c values fall almost linearly with increasing n over the whole range of hydrogen contents studied, with $dT_c/dn \approx -8.9$ K/hydrogen atom. In the primary $Nb_{76}Pt_{24}$–H solutions with $n \lesssim 0.05$, the temperature of the superconducting transition is independent of n; hydrides with $n \gtrsim 0.87$ have T_c values much less than in the initial alloy $Nb_{76}Pt_{24}$. Dissolving hydrogen as far as $n \approx 0.02$ in $Nb_{75}Ir_{25}$ makes T_c noticeably higher, and even higher T_c values occur for the hydrides of this alloy. There is also a rise in T_c when hydrides of $Nb_{75}Os_{25}$ are formed.

All the Nb_3Me–H samples single-phase by x ray, except $Nb_{76}Pt_{24}$–H with $n \gtrsim 1.14$, have superconducting transitions over relatively narrow temperature ranges. Removal of hydrogen from the samples by vacuum annealing at 500°C restores the lattice parameter and T_c to their initial values. The absence of irreversible changes in the hydrogenation–dehydrogenation cycle gives reason to suppose that these properties of the Nb_3Me–H samples are determined only by the content of dissolved hydrogen.

In $Nb_{76}Pt_{24}$–H samples, the temperature range of the superconducting transition remains relatively narrow at hydrogen concentrations as far as n =

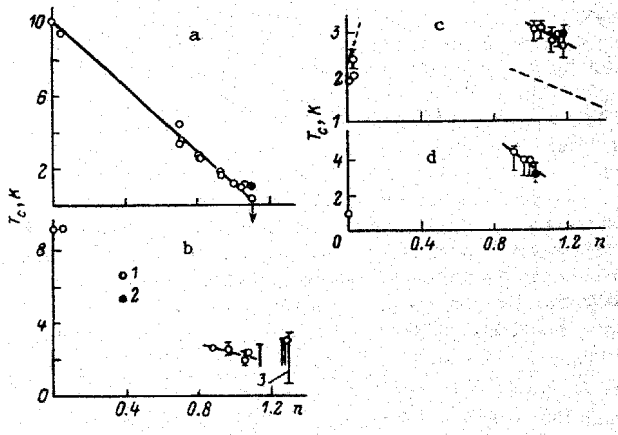

FIG. 4. Dependences of the superconducting transition temperature T_c on the hydrogen or deuterium content n in solid solutions (single-phase according to x ray) of hydrogen (1) and deuterium (2) in the alloys $Nb_{74}Au_{26}$ (a), $Nb_{76}Pt_{24}$ (b), $Nb_{75}Ir_{25}$ (c), and $Nb_{75}Os_{25}$ (d); in a, the arrow marks the absence of superconductivity for $T_c \gtrsim 0.35$ K; in b, 3 denotes the superconducting transition range in an $Nb_{76}Pt_{24}$–D sample; in c, the dashed curve shows $T_c(n)$ as found[3] for $Nb_{75}Rh_{25}$–H solutions.

1.08 (curve 4 in Fig. 1); for $n \gtrsim 1.14$, it becomes much wider, and $\chi(T)$ for such samples is typically as shown by curve 5 in Fig. 1. After removal of hydrogen from samples with $n \gtrsim 1.14$ by vacuum annealing at 500°C, the lattice parameter was restored to its initial value for $Nb_{76}Pt_{24}$, but the superconducting properties of the alloy were not restored: instead of a narrow step at 9.2 K, the $\chi(T)$ curves show a more or less smooth drop as the temperature falls from ≈7 to ≈3 K.

The absence of reversibility in the variation of the $Nb_{76}Pt_{24}$ superconducting properties during the hydrogenation–dehydrogenation cycle is evidence that the formation of $Nb_{76}Pt_{24}$–H solutions with $n \gtrsim 1.14$ is accompanied by irreversible changes in the metal sublattice also. These changes may have the nature of a phase transition. Certainly, the $n(P_{H_2})$ isotherm of the $Nb_{76}Pt_{24}$–H system at 325°C (Fig. 2b) shows a quite noticeable anomaly at $40 \lesssim P_{H_2} \lesssim 50$ kbar, the solution contents increasing from $n \approx 1.08$ to $n \approx 1.28$. The changes in the metal sublattice for solutions with $n \gtrsim 1.14$ seem to us to be most probably in the degree of atomic ordering; a strong dependence of T_c on the degree of order has been noted in Nb_3Pt, for example.[10]

In order to help readers to compare the properties of the Nb_3Me–H solutions studied here with the results of other work on metal hydrides, Table I gives numerical values for solutions that are single-phase by x ray, with several different hydrogen contents.

Nb_3Me–D solutions

As well as the hydrides, one sample of the deuteride of each Nb_3Me alloy was made at $P_{D_2} \approx$ 70 kbar and 325°C. Figures 2 and 4 and Table I show that the properties studied are the same for the deuterides as for the hydrides, within the experimental error.

3. DISCUSSION

For transition metal alloys, there is a correlation, known as the Matthias rule, between T_c and the electron density N^e (the mean number of outer d + s electrons per alloy atom). Among the A15 structure compounds, this correlation can be most clearly traced in niobium and molybdenum (the latter being adjacent to niobium in the periodic table) alloyed with 5d metals (the dashed curve in Fig. 5); for niobium alloys, there is also a correlation with the density of electronic states at the Fermi level.[7] These results suggest[7] that, at least in niobium alloys, the behavior of the superconducting properties is satisfactorily represented by the rigid band model, i.e., over a wide range of electron density the alloy T_c values are governed mainly by the electron occupation of an almost undeformed conduction band.

In Nb_3Me, the density of d states at the Fermi level is much higher than that of s states,[7] and so the correlation between the T_c values and the density of states at the Fermi level in the rigid band model actually signifies the presence of a correlation between T_c and the position of the Fermi level relative to the d band, i.e., the electron occupation of the d band. Calculations[11] and experiments[1] show that for $n \lesssim 1$ the hydrogen coming into fcc and hcp transition metals causes only a slight deformation of the d bands near the Fermi

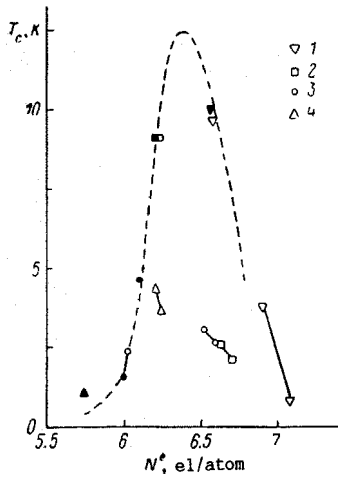

FIG. 5. Superconducting transition temperature T_c as a function of the electron density N^e for the initial samples Nb_3Me (black symbols) and the effective electron density $N^e + \eta n$ with η = 0.5 electron per hydrogen atom in Nb_3Me–H solid solutions single-phase according to x ray: 1) $Nb_{74}Au_{26}$–H, 2) $Nb_{76}Pt_{24}$–H for $n \lesssim 1.08$, 3) $Nb_{75}IR_{25}$–H, 4) $Nb_{75}Os_{25}$–H. The dashed curve shows $T_c(N^e)$ for A15 structure compounds of niobium and molybdenum with 5d metals.[15]

level, and increases the electron occupation by an amount η that is of the order of 0.5 electron per hydrogen atom (varying from ≈0.3 to ≈1 for different metals and alloys).

If this is assumed to be valid also for hydrogen in Nb_3Me and the main cause of the variation of T_c with n in Nb_3Me–H solutions is the increased electron occupation of the d band in the hydrogenated compounds, then the dependences $T_c(n)$ should follow curves $T_c(n) = T_c(N^e + \eta n)$, where $T_c(N^e)$ is the dashed curve in Fig. 5.

Figure 5 gives the observed T_c values for the single-phase Nb_3Me–H solutions studied here, plotted against $N^e + \eta n$ with η = 0.5 electron per hydrogen atom; in order not to complicate the diagram, T_c values are shown only at the limits of the composition dependences of T_c investigated. It is seen that the results for Nb_3Me–H solutions agree qualitatively with the dashed curve. In particular, the presence of hydrogen increases T_c in the primary $Nb_{75}Ir_{25}$–H solutions with $n \lesssim 0.02$; for $Nb_{75}Os_{25}$–H and $Nb_{75}Ir_{25}$–H, T_c is higher, and for $Nb_{76}Pt_{24}$–H and $Nb_{74}Au_{26}$–H it is lower, than in the original compounds.

There are also two pieces of indirect evidence in favor of the validity of the rigid band model for representing the variations of T_c in Mb_3Me compounds under hydrogenation: a) the dependence $T_c(n)$ for hydrogen solutions in Nb_3Rh, an isoelectronic analog of Nb_3Ir, is similar to that for Nb_3Ir solutions (Fig. 4c); b) for hydrogen solutions in $Nb_{75}Os_{25}$ and $Nb_{75}Ir_{25}$ alloys (as in $Nb_{76}Pt_{24}$ and $Nb_{74}Au_{26}$; see Fig. 4 and Table I), there is no increase in T_c (inverse isotope effect) when protium is replaced by deuterium, and this is to be expected by analogy with palladium–hydrogen solutions,[12] if the interaction of electrons with optical vibrations of hydrogen atoms is important as regards the increase of T_c in these alloys under hydrogenation.

There is therefore reason to suppose that the qualitative agreement between $T_c(N^e + \eta n)$ and $T_c(N^e)$ in Fig. 5 is not accidental, and the rigid band model gives a correct account of the main features of $T_c(n)$ for Nb_3Me–H solutions.

In principle, the agreement of the experimental results with the $T_c(N^e)$ curve in Fig. 5 can be considerably improved by taking a different value of η for each Nb_3Me–H system: $\eta \approx 0.35$ electron per hydrogen atom for $Nb_{75}Os_{25}$–H, $\eta \approx 0.7$ for $Nb_{75}Ir_{25}$–H and $Nb_{76}Pt_{24}$–H; it is difficult to estimate η for the hydrides $Nb_{74}Au_{26}$–H, because of the lack of information about $T_c(N^e)$ in the relevant range of argument values. However, this additional fitting is unlikely to have any physical significance: it is seen from Fig. 5 that, on the assumption that the increased electron occupation of the d band is the only cause of the change in T_c for Nb_3Me compounds under hydrogenation, it is impossible to explain why, as n increases, T_c for the primary $Nb_{76}Pt_{24}$–H solutions does not increase, and for the $Nb_{75}Os_{25}$–H hydrides actually decreases.

It is therefore very likely that, alongside the increased occupation of the d band in Nb_3Me compounds under hydrogenation, another mechanism is at work to change the superconducting transition temperature and lower T_c as n increases. A considerable transition temperature and lower T_c as n increases. A considerable and almost linear decrease in T_c when hydrogen comes in ($dT_c/dn \approx -15$ K/hydrogen atom) has already been encountered[13] in our study of solid solutions of hydrogen in bcc niobium–titanium alloys. In these, the superconducting transition temperature depends slightly on N^e, and the decrease in T_c under hydrogenation is almost entirely governed by causes not directly related to the change in occupation of the d band.

For the Nb_3Me–H systems, in order to bring the $T_c(N^e + \eta n)$ values for the hydrides of $Nb_{75}Os_{25}$, $Nb_{75}Ir_{25}$, and $Nb_{76}Pt_{24}$ up to the $T_c(N^e)$ curve, we need to assume that, as the hydrogen content increases, as well as the change in T_c due to the occupation of the d band by electrons with $\eta \approx 0.5$ electron per hydrogen atom, there is also a steady decrease in T_c at a mean rate of about –5 to –10 K/hydrogen atom, of the same order of magnitude as in niobium–titanium–hydrogen solutions.[13] It may be that the causes of the decrease in T_c in Nb_3Me–H and Nb–Ti–H solutions are also the same. For example, changes in the phonon spectrum accompanied by an increased mean frequency of acoustic vibrations, as has been observed when hydrogen is dissolved in niobium and tantalum.[2] Other possibilities exist, of course, for instance a broadening of the alloy d bands and therefore a lowering of the density of states at the Fermi level because of hybridization of d states with s states of dissolved hydrogen atoms; in Nb_3Me alloys, there is a distinct correlation between T_c and the density of electron states at the Fermi level, the two increasing together.[7]

We should conclude, however, by emphasizing once more that, although the behavior of T_c for the Nb_3Me–H solutions studied is governed to a considerable extent by factors that cannot yet be definitely established, the main trends of T_c variation with the hydrogen content in these solutions are represented by the rigid band model, as seen from Fig. 5. The Nb_3Me–H solutions are so far the only ones where it has been possible to distinguish more or less reliably the contribution to the behavior of T_c from the changes in electron occupation of the conduction band, but we may expect that a similar contribution is important for several other metal–hydrogen solutions, such as the hydrides of niobium–ruthenium and tantalum–ruthenium alloys,[14] for which $\eta \approx 0.5$ electron per hydrogen atom and the $N^e + \eta n$ values are in the range 6.1-6.5 electron per atom near the $T_c(N^e)$ peak for transition metal alloys.

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