# The H-Nb (Hydrogen-Niobium) and

1.00794 92.9064

# D-Nb (Deuterium-Niobium) Systems

2.0141018 92.9064

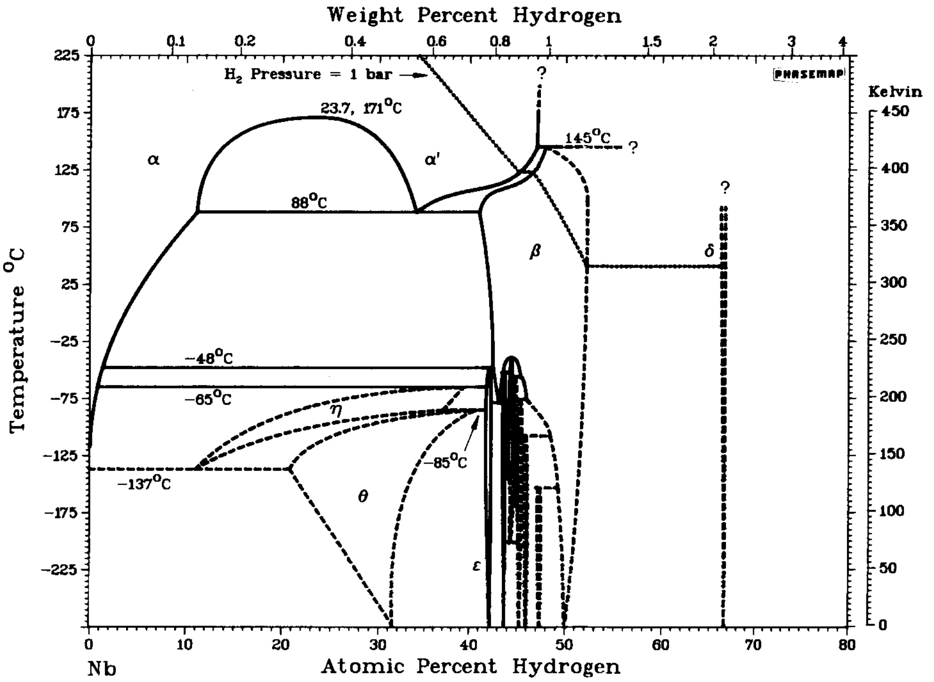
By J. F. Smith
Iowa State University

## Phase Relationships

**General Features.** A phase diagram for the Nb-H system is shown in Fig. 1; this diagram is based on a composite of available information, but with the low-temperature region below 250 K (−23 °C) at compositions less than 53 at.% H being taken essentially intact from Köbler and Welter [82Köb]. In contrast to the V-H and V-D systems (see [82Smi]), which exhibit significantly different phase relationships, available data indicate that phase equilibria in the Nb-D system are closely comparable to those of the Nb-H system, with only minor differences in the temperature-composition coordinates of the phase boundaries, and a separate phase diagram for the Nb-D system is not presented. For instance, in the Nb-rich region at temperatures below the temperature of the monotectoid reaction, three independent investigations [75Wes, 71Buc, 76Whi] of the *α* terminal solid solution each found that, within experimental precision, the D solubility in Nb is the same as the H solubility in Nb; however, there appear to be small differences between the partial molar enthalpies, $\Delta\bar{H}_H$ and $\Delta\bar{H}_D$, and the partial molar entropies, $\Delta\bar{S}_H$ and $\Delta\bar{S}_D$, for the *α* solid solution [75Ste, 79Fuj1, 79Fuj2]. Further, where structural information is available for comparable alloys, the D phases and the H phases were found to be isomorphous [68Som, 78Sch, 79Asa, 79Som, 79Bru], but indication that the temperature-composition coordinates of the phase boundaries are somewhat different comes from reports that showed transition temperatures for H phases to be lower than transition temperatures for D phases [68Som, 75Ent, 78Sch, 79Som, 79Fuj1, 79Fuj2]. An example of these reported temperature differences comes from the work of Fujita *et al.* [79Fuj1, 79Fuj2], in which resistometric measurements indicated a monotectoid temperature of 373 K (100 °C) for the Nb-H system and of 403 K (130 °C) for the Nb-D system. It seems quite unlikely that such a temperature difference could be attributable to a difference in coherency effects, because the same basic experimental procedure was used for both systems.

Coherency effects characteristically arise from the misfit stresses that are generated when phase separation occurs, with the two daughter phases having differing compositions and lattice parameters. The associated strain energy can produce inhomogeneities in the H concentration

**Fig. 1 Nb-H Phase Diagram**



J. F. Smith, 1983.

to prevail over thermodynamic equilibrium. In the specific instance of the spinodal decomposition of the α Nb-H phase to form α and α′, Zabel and Peisl [76Zab, 79Zab, 80Zab] showed that experimental determinations of the phase boundaries depend sensitively on sample shape, thermal history of the sample, and method and temperature of H charging. They concluded that coherency effects are the major cause of the differences among the reported equilibria for this decomposition reaction, and that long, thin wire specimens with length very much greater than diameter provide the best approximation for compositionally equilibrated incoherent material. In this context, incoherent material can be defined as material in which the misfit energy is assuaged by the formation of dislocations that minimize the misfit stresses. Zabel and Peisl's values of 444 K (171 °C) and 23.7 at.% H for the critical temperature and critical composition have been used for the diagram in Fig. 1. It should be further noted that, at temperatures below the monotectoid reaction, all Nb-H phases can be viewed as arising from differing types and degrees of H order in the same basic Nb lattice. On this basis, coherency effects associated with the reordering of H may be a complicating factor in experimental elucidation of low-temperature equilibria in this system.

**α Phase.** The terminal solid solution of H in Nb in Fig. 1 has been designated the α phase. This phase has a random distribution of H (or D) atoms in the tetrahedral interstices of the elemental Nb structure [78Sch]. The solvus below 350 K (77 °C) may be described by the relationship:

$$\log_{10} c_H (\text{at.\%}) = [-558/T\ (\text{K})] + 2.60$$

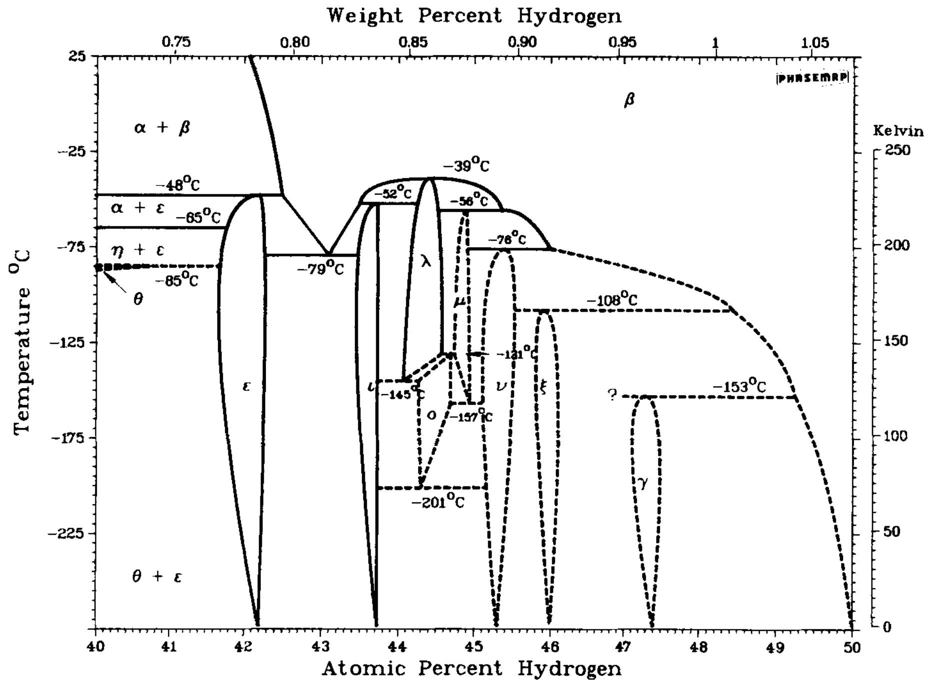
which accords reasonably with the composite of available data [75Wes, 71Buc, 76Whi]. The changes in slope of the solvus, which must be present near 225 K (−48 °C) and 208 K (−65 °C) if the phase diagram of Fig. 1 is correct, are not resolvable from the solubility data.

**β Phase.** The phase that has a range of homogeneity between 41 and 51 at.% H and which decomposes peritectically near 418 K (145 °C) has been designated the β phase. There is agreement that the formation of this phase from the α′ phase is a first-order transformation [79Som, 80Bec, 81Hir], even though the primary difference between the α′ and β phases is the difference between a disordered array and an ordered array of H or D atoms. The ordering of H atoms in the β phase appreciably affects the H mobility, resulting in a decrease of about two orders of magnitude for the mobility in the β phase as compared to the α′ phase [76Pic, 77Wel].

**ε, η, and θ Phases.** The diagram of Fig. 1 in the range 0 to 50 at.% H and below 250 K (−23 °C) is based on the magnetic susceptibility measurements that were made as functions of temperature at fixed composition by Köbler and Welter [82Köb]. This section of the diagram must be considered tentative because there is conflicting evidence to be found among the reports that pertain to this area of the phase diagram. In the region of the diagram that is labeled ε in Fig. 1, it seems probable that there is an identifiable crystallographic array with an ideal composition of $Nb_4H_3$ [68Som, 72Som, 75Schl, 78Sch]. There is, however, a disparity between the diagram proposed by Schober [78Sch] and the diagram of Fig. 1 [82Köb] with regard to the temperature associated with peritectoid dissociation of this phase. Schober [73Schl, 75Schl, 78Sch] reported peritectoid dissociation of the ε phase near 208 K (−65 °C) to form the α terminal solution plus a ζ phase, with the latter in turn decomposing near 225 K (−48 °C) to form the α terminal solution plus the β phase. The diagram of Fig. 1, on the other hand, shows no ζ phase; rather, the ε phase is indicated to be stable to 225 K. Close structural relationship between the β, ζ, and ε phases was shown by neutron diffraction [68Som] and by electron microscopy [75Schl]. Recently, Makenas and Birnbaum [82Mak] indicated that, on the basis of electron diffraction and electron microscopy, there are no morphological differences between the ε and β phases, but there are superlattice reflections associated with the ε phase that decrease in intensity and become diffuse through the temperature region earlier associated with the ζ phase. This indication of gradual transition between ε and β phases leaves open to question which, if either, temperature is the upper limit of stability of the ε phase or whether the ε → β transformation is one of higher order.

Pesch *et al.* [78Pes] reported the formation of an η phase at 207 K (−66 °C); their work indicated this phase to exist between the ε and ζ phases. Other than the temperature of formation, there is no evidence to confirm or refute that this is the same phase as the η phase of Fig. 1. Both the η and θ phases as drawn in Fig. 1 are based on anomalies in the magnetic susceptibility data of Köbler and Welter [82Köb]. These authors stated that studies of proton magnetic resonance [72Lüt] and of superconductivity [77Wel, 79Ohl, 80Isa] indicated persistence of the α phase on the H-rich side of the θ phase to very low temperatures. Such persistence, if in equilibrium, would be in violation of the phase rule if the θ phase were also an equilibrium phase. Köbler and Welter speculated that the contradictory results might be explicable on the basis of slow kinetics, with long times being required for complete formation of η and θ phases at low temperatures. In further rebuttal to the contradictory evidence, they also cited supporting evidence for the existence of the θ phase in unpublished DTA data of Welter, in nuclear magnetic resonance measurements at 77 K (−196 °C) [64Zam], and in an intensity change in the specific heat anomaly in the superconductivity study quoted above [79Ohl]. There are also some weak anomalies in the low-temperature heat capacity data of Heibel and Wollenberger [76Hei] for a 30 at.% H alloy that might be interpretable as being associated with θ and/or η phases. However, none of the subsidiary evidence, either pro or con, is strong. For instance, the proton magnetic resonance study [72Lüt], which Köbler and Welter [82Köb] saw as indicating the persistence of the α phase, might be interpreted as giving some support to the existence of the η phase. The published report of this resonance study shows a semilogarithmic plot of proton spin-lattice relaxation time vs reciprocal temperature of the β phase. In their plot, only points for a 23 at.% H alloy (H-deficient side of the θ phase) appear below ~225 K (−48 °C), and these points show a pronounced change in slope in the vicinity of 180 K (−93 °C). In Fig. 1, the upper phase boundary of the η phase occurs near 180 K (−93 °C) for a 23 at.% H alloy, so the resonance data correlate to this extent. However, there is no anomaly in the resonance data near 208 K (−65 °C) to be associated with the dissociation of the η phase, and the investigators themselves explained the change in slope as the onset of dominance of relaxation by the conduction electrons rather than by the lattice.

Fig. 2 Enlargement of the Peritectoid Cascade Region of the Nb-H Phase Diagram



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**λ Phases and γ Phase.** The cascade of peritectoid reactions in Fig. 2 in the vicinity of 41.9 at.% H ($NbH_{0.72}$) and below 234 K (−39 °C) are reproduced from Köbler and Welter [82Köb]. There seems little doubt that such a series of crystallographically identifiable structures exists in the indicated temperature and composition region, but the exact number of phases and the details of the phase equilibria must be considered tentative. With regard to the number of these phases, Brun *et al.* [79Bru] observed superlattice reflections in the relevant temperature-composition region and reported "four λ phases in $NbD_x$ by neutron diffraction" and "three of these were observed in $NbH_x$ by electron diffraction". The diffraction results were interpreted in terms of long-range modulation of the H or D atom distributions analogous to the observations of Pesch [82Pes] for the low-temperature phases in the V-D system. Makenas and Birnbaum [82Mak], on the basis of electron microscopy and diffraction, agreed that at least three λ superlattices exist in the Nb-H system. The interpretation of the λ superlattices as long-range modulations of the H or D densities leaves open the possibility of dissipation of the modulation via higher-order phase transitions. It is now believed that many of the structures earlier identified as "λ phases" are, in fact, crystallographically separate species noted here as ι, μ, ν, o, and ξ.

The existence of a phase near 47.4 at.% H and below ~120 K (−153 °C) was reported by Pick [72Pic]; this is the γ phase of Fig. 1. Pick's neutron diffraction patterns showed the Nb sublattice to have pseudocubic symmetry, but the proposed H positions [77Hau1, 77Hau2] are significantly different from those of the β and λ phases and require tetragonal symmetry. These proposed H positions have not been confirmed experimentally [81Hir], and Makenas and Birnbaum [82Mak] reported finding no evidence for a pseudocubic structure in the temperature and composition range of the original report.

**δ Phase.** The δ phase of Fig. 1 is $NbH_2$ and was first reported by Brauer and Müller [58Bra]. The $H_2$ vapor pressure over this phase is of the order of 1 atm (~1 bar) near room temperature [70Rei, 70Aro], so, at ambient temperatures, phase stability requires a high partial pressure of $H_2$ in the phase environment. Even in a dessicator, samples that were produced by cathodic hydration were found to decompose very slowly [70Aro]. Schober [75Sch2] used electron microscopy to observe that the δ phase precipitates from the β phase at ambient temperature when H is charged into Nb to concentration levels exceeding ~50 at.% H. There is evidence [61Bra, 70Rei] that the phase has a concentration range of stability that may be as wide as 65.5 to 67.4 at.% H.

## Crystallography

**α, α′ Phase.** Above the critical point at H or D pressures of 1 atm (~1 bar) or less, α and α′ form a continuous solid solution with statistical distribution of H or D in the bcc structure of pure Nb [78Sch]. The lattice parameter of the phase increases linearly with increasing solute concentration [65Wal], and at room temperature the increase may be described as:

$$a(c) = 0.3303\ (1 + 4.7 \times 10^{-4}\ c)\ \text{nm}$$

with $c$ in at.% H. Carstanjen and Sizmann [72Car] found that D, and presumably therefore H, occupies tetrahedral interstices.

**β Phase.** Somenkov *et al.* [68Som] used neutron diffraction to examine powdered samples of the β phase at compositions close to $NbH_{0.84}$, $NbH_{0.95}$, $NbD_{0.85}$, and $NbD_{0.95}$. Superlattice reflections in the resulting diffraction patterns were interpretable as indicating an ordering of the solute species to produce a slight orthorhombic distortion of the original cubic Nb sublattice such that:

$$\begin{array}{ll} \vec{a}_\beta \simeq a_\alpha - \vec{b}_\alpha & |\vec{a}_\beta| \simeq \sqrt{2}\,|\vec{a}_\alpha| \\ \vec{b}_\beta \simeq \vec{a}_\alpha + \vec{b}_\alpha & |\vec{b}_\beta| \simeq \sqrt{2}\,|\vec{a}_\alpha| \\ \vec{c}_\beta \simeq \vec{c}_\alpha & |\vec{c}_\beta| \simeq |\vec{a}_\alpha| \end{array}$$

Experimental diffraction intensities from the $NbD_{0.95}$ material were found to agree closely with intensities calculated for an orthorhombic structure with Nb atoms at the positions: 000, $\frac{1}{2}\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$; and D atoms at the positions: $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{3}{4}\frac{3}{4}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$, $\frac{3}{4}\frac{1}{4}\frac{1}{4}$. This structure has been corroborated by electron diffraction [73Sch2] and is compatible with earlier X-ray diffraction data [53Bra, 64Sak]. The extensive range of homogeneity toward lower solute concentrations results from statistical absences of solute atoms [82Mak]. Lattice parameters change linearly with H concentrations [76Pic, 79Som].

**$\varepsilon$ Phase.** Cooling of the $\beta$ phase at stoichiometries near $NbH_{\sim 0.7}$ results in an ordering of the H atoms [82Mak]. When the cooling is carried to sufficiently low temperatures, diffraction patterns have been observed to contain additional superlattice reflections that are characteristic of an $\varepsilon$ structure [70Som, 72Som, 81Asa]. The ordered arrangement remains orthorhombic, but the ordering results in a doubling of the $\vec{a}$ and $\vec{b}$ lattice parameters of the $\beta$ phase:

$$\begin{array}{ll} \vec{a}_\varepsilon \simeq 2(\vec{a}_\alpha - \vec{b}_\alpha) & |\vec{a}_\varepsilon| \simeq 2\sqrt{2}\,|\vec{a}_\alpha| \\ \vec{b}_\varepsilon \simeq 2(\vec{a}_\alpha + \vec{b}_\alpha) & |\vec{b}_\varepsilon| \simeq 2\sqrt{2}\,|\vec{a}_\alpha| \\ \vec{c}_\varepsilon \simeq \vec{c}_\alpha & |\vec{c}_\varepsilon| \simeq |\vec{a}_\alpha| \end{array}$$

The ideal stoichiometry of the $\varepsilon$ phase is $Nb_4D_3$ or $Nb_4H_3$, and the orthorhombic positional parameters are:

16 Nb at 000, $\frac{1}{2}00$, $0\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{4}\frac{1}{4}0$, $\frac{1}{4}\frac{3}{4}0$, $\frac{3}{4}\frac{1}{4}0$, $\frac{3}{4}\frac{3}{4}0$, $\frac{1}{4}0\frac{1}{2}$, $0\frac{1}{4}\frac{1}{2}$,
$\frac{3}{4}0\frac{1}{2}$, $0\frac{3}{4}\frac{1}{2}$, $\frac{1}{2}\frac{1}{4}\frac{1}{2}$, $\frac{1}{4}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}\frac{3}{4}\frac{1}{2}$, $\frac{3}{4}\frac{1}{2}\frac{1}{2}$;

and 12 D or H at $\frac{3}{8}\frac{1}{8}0$, $\frac{5}{8}\frac{1}{8}0$, $\frac{7}{8}\frac{1}{8}0$, $\frac{3}{8}\frac{3}{8}\frac{1}{2}$, $\frac{5}{8}\frac{3}{8}\frac{1}{2}$, $\frac{7}{8}\frac{3}{8}\frac{1}{2}$,
$\frac{1}{8}\frac{5}{8}0$, $\frac{3}{8}\frac{5}{8}0$, $\frac{7}{8}\frac{5}{8}0$, $\frac{1}{8}\frac{7}{8}\frac{1}{2}$, $\frac{3}{8}\frac{7}{8}\frac{1}{2}$, $\frac{7}{8}\frac{7}{8}\frac{1}{2}$.

The positions $\frac{1}{8}\frac{1}{8}0$, $\frac{1}{8}\frac{3}{8}\frac{1}{2}$, $\frac{5}{8}\frac{5}{8}0$, and $\frac{5}{8}\frac{7}{8}\frac{1}{2}$ are vacant and would, if filled, alter the structure and symmetry to that of H-saturated $\beta$ NbH. What has been called a $\zeta$ phase is a partially ordered intermediate between the $\beta$ and $\varepsilon$ structures [82Mak].

**$\lambda$ Phases.** The low-temperature phases between 43 and 47 at.% H, formerly grouped together as "$\lambda$ phases", are now thought to be separate phases noted here as $\iota$, $\mu$, $\nu$, $o$, and $\xi$. Like the $\varepsilon$ phase, they can be viewed as an ordering of H atoms in a H-deficient $\beta$ structure. Structural details for all of the $\lambda$ phases have not been clarified, but superlattice reflections have been interpreted as indicating modulations of the H density to produce long-range periodicities ($|\vec{c}_\lambda|$ ~5 to 14 times $|\vec{a}_\alpha|$) along the $\vec{c}$ direction while retaining the $\vec{a}$ and $\vec{b}$ parameters of the $\beta$ phase [79Bru, 81Hir, 82Mak].

**$\gamma$ Phase.** An ordering for the H distribution in the $\gamma$ phase was proposed by Hauck [77Hau2]. This arrangement is face-centered tetragonal (fct) with $|\vec{a}_\gamma| = |\vec{b}_\gamma| \simeq \sqrt{2}\,|\vec{a}_\alpha|$ and $|\vec{c}_\gamma| \simeq |\vec{a}_\alpha|$. The proposed fct arrangement of H is significantly different from the arrangements in the $\beta$, $\varepsilon$, and $\lambda$ phases and has not been confirmed experimentally. On the contrary, Makenas and Birnbaum [82Mak] stated specifically that they found no evidence for the "pseudocubic" fct structure in any sample in the composition range 42 to 49 at.% H. Thus, if a $\gamma$ phase exists, as indicated by Köbler and Welter [82Köb], the postulated structure is likely to need revision.

**$\delta$ Phase.** X-ray and electron diffraction patterns of the $\delta$ phase exhibit fcc symmetry [61Bra, 70Rei, 75Sch2]. Determination of the H or D positions by neutron diffraction has not been reported, but, because of the stoichiometry, symmetry, and lattice parameter, it is generally presumed that the phase is isostructural with $CaF_2$. The fact that H compositions were reported in excess of $NbH_2$ [61Bra] implies that the phase is capable of accepting some H on octahedral sites.

A synopsis of crystal structure data is given in Table 1.

## Thermodynamics

**Heat of Solution.** The equation for the terminal solubility of H or D in Nb that is given for temperatures below 350 K (77 °C) in the section on phase relationships indicates a heat of solution of 10.7 kJ/mol H or D. The scatter in this value among three independent investigations [71Buc, 75Wes, 76Whi] is less than ±1 kJ/mol.

**Thermodynamic Functions for the $\alpha$ Phase.** There have been several independent investigations of $H_2$ vapor pressures over $\alpha$-phase Nb-H alloys. Most of these have

**Table 1 Nb-H Crystal Structure Data**

| Phase | Approximate composition(a), at.% H | Pearson symbol | Prototype | Lattice parameters, nm a | b | c | Composition(b), at.% H | References |
|---|---|---|---|---|---|---|---|---|
| $\alpha$, $\alpha'$ ...................... | 0-47 | *cI*2 | W | 0.3303 | ··· | ··· | 0 | [65Wal] |
| | | | | 0.3310 | ··· | ··· | 4.9 | [65Wal] |
| $\beta$ ........................ | 42-51 | *oP*8 | ··· | 0.4827 | 0.4869 | 0.3425 | 42.2 | [Pearson2] |
| | | | | 0.4837 | 0.4896 | 0.3449 | 45.7 | [Pearson2] |
| | | | | 0.483 | 0.489 | 0.344 | 47 | [53Bra] |
| | | | | 0.4849 | 0.4854 | 0.3382 | ··· | [64Sak] |
| $\varepsilon$ ........................ | ~42 | *oP*28 | ··· | ~0.93 | ~0.93 | ~0.33 | ··· | [70Som] |
| $\delta$ ........................ | ~67 | *cF*12 | $CaF_2$ | 0.453 | ··· | ··· | ··· | [70Rei] |
| | | | | 0.4563 | ··· | ··· | ··· | [61Bra] |
| | | | | 0.4556 | ··· | ··· | ··· | [75Sch2] |

(a) From the phase diagram. (b) Composition at which the lattice parameters were measured.

## Table 2 Comparison of the Partial Molar Enthalpies and Entropies from Eight Independent Investigations of the $\alpha$ Phase Region of the Nb-H System

| Mole fraction, $N_H$ | [58Alb], [59Alb] | [60Kom](a) | [61Kat] | [69Vel] | [74Kle] | [75Ste] | [79Sub] | [79Fuj2] | Average |
|---|---|---|---|---|---|---|---|---|---|
| $-\Delta\overline{H}_H$ (kJ/mol H) | | | | | | | | | |
| 0.01 | 33.5 | 34.8 | ... | 35.9 | ... | ... | 31.9 | 40.8 | ... |
| 0.02 | 33.8 | 38.6 | ... | 36.2 | ... | ... | 30.5 | 39.9 | ... |
| 0.03 | 34.1 | 41.5 | ... | 36.4 | ... | ... | ... | 39.4 | ... |
| 0.04 | 34.3 | 43.6 | ... | 36.5 | ... | 35.9 | ... | 39.2 | ... |
| 0.05 | 34.5 | 45.0 | 34.6 | 36.7 | 37.8 | 36.8 | 30.8 | 39.3 | 35.8 ± 1.1 |
| 0.10 | 35.6 | 48.0 | 39.4 | 38.3 | 39.3 | 38.8 | 35.1 | 41.1 | 38.2 ± 0.8 |
| 0.15 | 37.0 | 49.6 | 40.3 | 39.7 | 40.8 | 40.4 | 37.0 | 42.3 | 39.6 ± 0.8 |
| 0.20 | 38.7 | 52.2 | 41.5 | 41.0 | 42.3 | 41.4 | 40.0 | 42.9 | 41.1 ± 0.5 |
| 0.25 | 40.1 | 54.9 | 43.0 | 42.6 | 43.9 | ... | 44.2 | 44.3 | 43.0 ± 0.7 |
| 0.30 | 41.1 | 57.2 | 44.6 | 44.0 | 45.6 | ... | ... | 46.7 | 44.4 ± 0.9 |
| 0.35 | 42.1 | 59.8 | 45.6 | 45.5 | ... | ... | ... | 48.4 | 45.4 ± 1.3 |
| 0.39 | 43.4 | 64.0 | 45.1 | 45.9 | ... | ... | ... | 46.9 | 45.3 ± 0.7 |
| $-\Delta\overline{S}_H$ (J/mol·K H) | | | | | | | | | |
| 0.01 | 16.3 | 24.9 | ... | 20.5 | ... | ... | 16.8 | 27.0 | ... |
| 0.02 | 21.5 | 30.7 | ... | 26.6 | ... | ... | 20.5 | 29.8 | ... |
| 0.03 | 25.7 | 35.4 | ... | 30.0 | ... | ... | ... | 32.4 | ... |
| 0.04 | 29.0 | 39.2 | ... | 32.5 | ... | 34.0 | ... | 34.8 | ... |
| 0.05 | 31.7 | 42.3 | 30.8 | 34.4 | 33.5 | 35.6 | 27.7 | 36.9 | 32.9 ± 1.2 |
| 0.10 | 39.1 | 51.7 | 42.7 | 41.5 | 42.6 | 41.7 | 38.0 | 44.3 | 41.4 ± 0.8 |
| 0.15 | 43.1 | 57.3 | 46.8 | 46.0 | 47.4 | 46.3 | 42.7 | 48.4 | 45.8 ± 0.8 |
| 0.20 | 47.1 | 62.3 | 50.6 | 49.5 | 51.3 | 49.4 | 48.5 | 51.3 | 49.7 ± 0.6 |
| 0.25 | 51.3 | 67.1 | 53.5 | 53.1 | 54.7 | ... | 56.0 | 54.8 | 53.9 ± 0.7 |
| 0.30 | 54.8 | 73.6 | 57.4 | 56.5 | 58.5 | ... | ... | 59.3 | 57.3 ± 0.8 |
| 0.35 | 57.2 | 83.0 | 61.3 | 60.9 | ... | ... | ... | 64.0 | 60.9 ± 1.4 |
| 0.39 | 58.8 | 95.2 | 64.5 | 68.2 | ... | ... | ... | 66.8 | 64.6 ± 2.1 |

(a) Not included in the averaged values.

been done with some form of Sieverts' technique and refer to the following temperature and composition ranges:

| Composition range, at.% H | Temperature range K | Temperature range °C | Reference |
|---|---|---|---|
| 0-25 | 657-1217 | 384- 944 | [79Sub] |
| 0-39 | 625- 944 | 352- 671 | [69Vel] |
| 0-41 | 498- 786 | 225- 513 | [61Kat] |
| 0-46 | 573-1773 | 300-1500 | [60Kom] |
| 1-40 | 353- 773 | 80- 500 | [79Fuj2] |
| 1-46 | 373-1173 | 100- 900 | [58Alb, 59Alb] |
| 2-20 | 535- 773 | 262- 500 | [75Ste] |

Partial molar enthalpies and partial molar entropies from these investigations are summarized in Table 2, and integral enthalpies and entropies of alloy formation are summarized in Table 3. Also included in these two tables are data from Kleppa *et al.* [74Kle], and these data are based on a combination of calorimetric and vapor pressure measurements. Because of the direct calorimetric measurements, the values of Kleppa *et al.* for $\Delta\overline{H}_H$ are preferred, and it may be noted that these values are within experimental uncertainty of the overall average values. Values from Komjathy [60Kom] may be noted to be systematically higher than other values, particularly at higher H concentrations; the deviations exceed the normal statistical expectations, so the Komjathy data were not weighted in the derivation of any of the average values. Further, McQuillan and Wallbank [70Mcq] reported vapor pressure data for the temperature range 476 to 1111 K (203 to 838 °C), and, for compositions below 10 at.% H, these data yield values for $\Delta\overline{H}_H$ that are strongly temperature and composition dependent. Although there is some indication in the values of $\Delta\overline{H}_H$ from two other sets of data [79Sub, 79Fuj2] that there may be a mild extremum in compositional dependence below 5 at.% H, this extremum is very much weaker than the extrema in the compositional dependences reported by McQuillan and Wallbank, and there has been no corroboration in any other investigation of significant temperature dependence in values of $\Delta\overline{H}_H$. Therefore, the McQuillan-Wallbank data have not been included in Tables 2 and 3.

Two independent investigations [75Ste, 79Fuj1] of $D_2$ vapor pressures over portions of the Nb-D system were made, and values for the partial and integral enthalpies and entropies of alloy formation from these two investigations are summarized in Table 4. In each of these investigations, data were taken for the Nb-H system as well as the Nb-D system. In both instances, values of $\Delta\overline{H}_D$ were found to be systematically more negative by about 2 kJ/mol solute than corresponding values of $\Delta\overline{H}_H$. Similarly, values of $\Delta\overline{S}_D$ were found to be more negative than corresponding values for $\Delta\overline{S}_H$ by around 2 J/mol·K solute. Because the Steward data [75Ste] for the Nb-H system are in good accord with the average values from eight independent investigations, whereas the Fujita data [79Fuj2] tend to be high, and because in both investigations the Nb-H and Nb-D systems were investigated in the same way with the same equipment, the Steward data for the Nb-D system are preferred.

**Thermodynamic Functions for the $\beta$ Phase.** Values for $\Delta\overline{G}_H$ for the $\alpha$ + $\beta$ two-phase field can be evaluated by combining solvus values from the equation for the terminal solubility of H in Nb as given in the section on phase relationships, with $\Delta\overline{H}_H$ and $\Delta\overline{S}_H$ values from Table 2. This results in the relationship:

$$\Delta\overline{G}_H = -38.48 + 0.0422\,T \qquad \text{kJ/mol H}$$

for the two-phase field in the temperature range 225 to 361 K (−48 to 88 °C). Direct measurements of $H_2$ vapor pressures over the $\alpha + \beta$ two-phase field by Pryde and Titcomb [69Pry] are within 3% of the predictions of this relationship, and Lewis and Obermann [76Lew] reported that their emf measurements for alloys in this two-phase field yield values in accord with the Pryde and Titcomb data, though no quantitative comparison is given. Combination of solvus compositions for the $\alpha$ phase, the foregoing relationship for $\Delta\overline{G}_H$, and enthalpies and entropies of $\alpha$ phase formation from Table 3 allows the development of the relationship:

$$\Delta\overline{G}_{Nb} = 4.10 - 0.0153\,T \qquad \text{kJ/mol Nb}$$

for the $\alpha + \beta$ region. This relationship for $\Delta\overline{G}_{Nb}$ and the preceding relationship for $\Delta\overline{G}_H$ may be applied to compositions along the Nb-rich boundary of the $\beta$ phase to yield:

$$\Delta G_f = -14.7 + 0.014\,T - 6 \times 10^{-6}\,T^2 \qquad \text{kJ/mol}$$

for the formation of $\beta$ $Nb_xH_{1-x}$ in the Nb-rich region. The values for the Gibbs energies of formation along the $(\alpha + \beta)/\beta$ boundary from this expression range from −9.8 kJ/mol $\beta$ $Nb_xH_{1-x}$ at 350 K (77 °C) and the mole fraction of hydrogen $(X_H) = 0.41$ to −11.6 kJ/mol $\beta$ $Nb_xH_{1-x}$ at 250 K (−23 °C) and $X_H = 0.425$, whereas corresponding values of −9.7 kJ/mol $\alpha'$ $Nb_xH_{1-x}$ and −11.8 kJ/mol $\alpha'$ $Nb_xH_{1-x}$ may be computed by extrapolation of data from Table 3. The uncertainty in these numbers is at least ±1 kJ/mol, so the correspondence is much closer than might be expected and lends confidence to the order of magnitude of the $\Delta G_f$ values. Because of the uncertainty, the implied reversal in stability of $\alpha'$ with respect to $\beta$ at lower temperatures is meaningless.

Reilly and Wiswall [70Rei] measured $H_2$ vapor pressures over the $\beta + \delta$ two-phase field. Their data may be used to generate the relationship:

$$\Delta\overline{G}_H = -20.01 + 0.0657\,T \qquad \text{kJ/mol H}$$

for the two-phase region, and it may be noted that $\Delta\overline{G}_H$ from this expression passes through zero at 305 K (32 °C). Comparison of this expression for $\Delta\overline{G}_H$ along the Nb-poor boundary of the $\beta$ phase field with the foregoing expression for $\Delta\overline{G}_H$ along the Nb-rich boundary of the $\beta$ phase field indicates that, at room temperature, $\Delta\overline{G}_H$ in the $\beta$ phase becomes more positive with increasing H content by the order of 2.5 kJ/at.% H. Data are insufficient to generate a complete set of thermodynamic functions for the $\beta$ phase.

**Thermodynamic Functions for the $\delta$ Phase.** The $\Delta\overline{G}_H$ relationship, from the Reilly and Wiswall [70Rei] data that are given in the preceding paragraph, is also applicable to the Nb-rich boundary of the $\delta$ phase. Additional data are needed before a complete set of thermodynamic functions for the $\delta$ phase can be generated.

**Low-Temperature Heat Capacities.** Heat capacities for Nb-H alloys were measured [79Ohl] through the temperature range 1.5 to 16 K at compositions between 0 and 66 at.% H. Only the $\alpha$ phase has a superconducting contribution in this temperature range, with a $T_c$ of 9.3 K, and persistence of the $\alpha$ phase was detected in alloys between 0 and 39 at.% H, with the superconducting contribution decreasing with increasing H content. The heat capacities for all alloys, including the normal state behav-

**Table 3 Integral Enthalpies and Entropies of Formation of the $\alpha$ Phase $Nb_xH_{1-x}$**

| Mole fraction, $N_H = 1-x$ | [58Alb], [59Alb] | [60Kom](a) | [61Kat] | [69Vel] | [74Kle] | [75Ste] | [79Sub] | [79Fuj2] | Average |
|---|---|---|---|---|---|---|---|---|---|
| **$-\Delta H_f$ (kJ/mol $Nb_xH_{1-x}$)** | | | | | | | | | |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.01 | 0.33 | 0.32 | ··· | 0.36 | ··· | ··· | 0.32 | 0.42 | 0.36 ± 0.02 |
| 0.02 | 0.67 | 0.69 | ··· | 0.72 | ··· | ··· | 0.62 | 0.82 | 0.71 ± 0.04 |
| 0.03 | 1.01 | 1.10 | ··· | 1.08 | ··· | 0.97 | ··· | 1.21 | 1.07 ± 0.05 |
| 0.05 | 1.69 | 1.97 | 1.29 | 1.81 | 1.90 | 1.34 | 1.55 | 2.00 | 1.65 ± 0.10 |
| 0.10 | 3.45 | 4.34 | 3.32 | 3.68 | 3.87 | 3.26 | 3.27 | 4.01 | 3.55 ± 0.11 |
| 0.15 | 5.27 | 6.80 | 5.28 | 5.65 | 5.84 | 5.29 | 5.06 | 6.10 | 5.50 ± 0.15 |
| 0.20 | 7.19 | 9.39 | 7.38 | 7.70 | 8.00 | 7.38 | 7.03 | 8.25 | 7.56 ± 0.17 |
| 0.25 | 9.21 | 12.15 | 9.41 | 9.83 | 9.95 | ··· | 9.16 | 10.46 | 9.67 ± 0.21 |
| 0.30 | 11.30 | 15.09 | 11.74 | 12.05 | 12.64 | ··· | ··· | 12.79 | 12.10 ± 0.28 |
| 0.35 | 13.47 | 18.18 | 14.03 | 14.39 | 15.02 | ··· | ··· | 15.29 | 14.40 ± 0.33 |
| 0.39 | 15.27 | 20.85 | 16.24 | 16.32 | ··· | ··· | ··· | 17.30 | 16.28 ± 0.42 |
| **$-\Delta S_f$ (J/mol·K $Nb_xH_{1-x}$)** | | | | | | | | | |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.01 | 0.13 | 0.21 | ··· | 0.13 | ··· | ··· | 0.13 | 0.25 | 0.16 ± 0.03 |
| 0.02 | 0.32 | 0.49 | ··· | 0.36 | ··· | ··· | 0.31 | 0.54 | 0.38 ± 0.03 |
| 0.03 | 0.56 | 0.83 | ··· | 0.64 | ··· | 0.68 | ··· | 0.85 | 0.68 ± 0.06 |
| 0.05 | 1.15 | 1.61 | 0.96 | 1.30 | 1.09 | 1.36 | 1.09 | 1.55 | 1.21 ± 0.08 |
| 0.10 | 2.99 | 4.04 | 2.94 | 3.24 | 3.08 | 3.32 | 2.86 | 3.62 | 3.15 ± 0.10 |
| 0.15 | 5.11 | 6.85 | 5.27 | 5.48 | 5.42 | 5.61 | 4.94 | 6.01 | 5.41 ± 0.13 |
| 0.20 | 7.46 | 9.96 | 7.73 | 7.99 | 8.01 | 8.08 | 7.28 | 8.59 | 7.88 ± 0.16 |
| 0.25 | 10.08 | 13.40 | 10.39 | 10.71 | 10.82 | ··· | 10.08 | 11.37 | 10.58 ± 0.20 |
| 0.30 | 12.95 | 17.21 | 13.13 | 13.64 | 13.87 | ··· | ··· | 14.42 | 13.60 ± 0.26 |
| 0.35 | 16.03 | 21.55 | 16.55 | 16.86 | ··· | ··· | ··· | 17.80 | 16.81 ± 0.37 |
| 0.39 | 18.61 | 25.69 | 19.76 | 19.71 | ··· | ··· | ··· | 20.73 | 19.70 ± 0.43 |

(a) Not included in the averaged values.

## Table 4 Comparison of Partial Molar Enthalpies and Entropies and Integral Enthalpies and Entropies from Two Independent Investigations of the Nb-D System

| Mole fraction, D $N_D = 1-x$ | $-\Delta\overline{H}_D$ (kJ/mol D) |  | $-\Delta\overline{S}_D$ (J/mol·K D) |  | $-\Delta H_f$ (kJ/mol $Nb_xD_{1-x}$) |  | $-\Delta S_f$ (J/mol·K $Nb_xD_{1-x}$) |  |
|---|---|---|---|---|---|---|---|---|
|  | [75Ste] | [79Fuj1] | [75Ste] | [79Fuj1] | [75Ste] | [79Fuj1] | [75Ste] | [79Fuj1] |
| 0 | ··· | ··· | ··· | ··· | 0 | 0 | 0 | 0 |
| 0.01 | ··· | 41.6 | ··· | 33.9 | ··· | 0.42 | ··· | 0.33 |
| 0.02 | ··· | 41.5 | ··· | 36.2 | ··· | 0.83 | ··· | 0.68 |
| 0.03 | ··· | 41.4 | ··· | 38.5 | ··· | 1.25 | ··· | 1.05 |
| 0.04 | 38.9 | 41.5 | 36.1 | 40.6 | 1.38 | 1.66 | 0.97 | 1.45 |
| 0.05 | 39.0 | 41.7 | 37.8 | 42.5 | 1.77 | 2.07 | 1.35 | 1.87 |
| 0.10 | 40.3 | 42.9 | 44.5 | 49.4 | 3.76 | 4.19 | 3.46 | 4.21 |
| 0.15 | 42.3 | 43.9 | 49.8 | 52.6 | 5.85 | 6.37 | 5.91 | 6.83 |
| 0.20 | 43.0 | 44.9 | 52.4 | 54.9 | 8.02 | 8.60 | 8.56 | 9.59 |
| 0.25 | ··· | 46.6 | ··· | 58.6 | ··· | 10.92 | ··· | 12.53 |
| 0.30 | ··· | 49.1 | ··· | 63.8 | ··· | 13.38 | ··· | 15.77 |
| 0.35 | ··· | 51.8 | ··· | 67.6 | ··· | 16.03 | ··· | 19.36 |
| 0.39 | ··· | 53.4 | ··· | 66.8 | ··· | 18.28 | ··· | 22.33 |

ior of the $\alpha$ phase, were describable for this temperature range by relations of the form:

$$C_p = aT + bT^3 + cT^5 \qquad \text{J/mol Nb}$$

and values for $a$, $b$, and $c$ are given together with values of the Debye temperature, $\theta_D$, in Table 5. These heat capacities are per mol Nb (not per mol alloy).

Heibel and Wollenberger [76Hei] measured the heat capacities of two alloys, $Nb_{0.7}H_{0.3}$ and $Nb_{0.69}H_{0.31}$, in the temperature range 160 to 240 K (−113 to −33 °C). They found a heat of transition near 208 K (−65 °C) amounting to ~90 J/mol of alloy. Immediately above this transition, the heat capacity was found to be near 20 J/K·mol $Nb_{0.7}H_{0.3}$. No heat anomaly was found near 225 K (−48 °C).

## Table 5 Coefficients for the Heat Capacity Relation $C_p = aT + bT^3 + cT^5$ J/mol Nb and Debye Temperatures ($\theta_D$) for Various Compositions in the Nb-H System [79Ohl]

| Composition at.% H | $a \times 10^3$ | Coefficients $b \times 10^5$ | $c \times 10^8$ | Debye temperature, ($\theta_D$), K |
|---|---|---|---|---|
| 0 | 8.22 | 13.19 | −8.48 | 245 |
| 19 | 6.53 | 9.97 | −3.99 | 269 |
| 30 | 4.66 | 7.83 | −3.20 | 292 |
| 39 | 2.86 | 4.82 | 0.421 | 343 |
| 41 | 1.96 | 4.47 | ··· | 352 |
| 44 | 1.75 | 4.19 | ··· | 359 |
| 45 | 2.36 | 4.18 | ··· | 360 |
| 48 | 1.52 | 4.28 | ··· | 357 |
| 49 | 1.58 | 4.47 | ··· | 352 |
| 66 | 3.60 | 3.60 | 4.52 | 378 |

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*Indicates key paper.

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# The Nb-V (Niobium-Vanadium) System

92.9064 50.9415

**By J. F. Smith and O. N. Carlson**
**Iowa State University**

## Phase Relationships

Nb and V form a continuous series of solid solutions with a minimum melting point near the V-rich end of the system. This may be seen in Fig. 1, which is the diagram proposed by Rudy [69Rud], with the minimum at 1860 °C and 22 at.% Nb. Other investigations also have reported the existence of a minimum melting point, with Wilhelm *et al.* [54Wil] placing it at 1810 °C and 23 at.% Nb and Baron *et al.* [60Bar] placing it at 1720 °C and 26.8 at.% Nb. The agreement between the composition for the minimum reported by Wilhelm *et al.* and that reported by Rudy is quite good in view of the flatness of the solidus in the region of the minimum. The differences among the values from the three investigations are quite probably attributable to variations in purities of the V and/or Nb that were used. Wilhelm *et al.* indicated the purity of their V as approximately 99.7%, with a melting point of 1860 °C, whereas Baron *et al.* indicated a purity of 99.4% for their V, with a melting point of 1890 °C. For Nb, Wilhelm *et al.* reported a purity of 99.9%, with a melting point of 2420 °C, whereas Baron *et al.* reported a purity of 99.9%, with a melting point of 2415 °C. Although Rudy gave no purity specifications for his base metals, his observed melting points for V (1926 ± 6 °C) and Nb (2468 ± 10 °C) are close to currently accepted values for these metals [81BAP], which indicates that his metals were relatively pure. On this basis, Rudy's diagram is preferred.

Recent work at the Ames Laboratory [82Sch] provides additional corroboration for the existence of the melting minimum. A large single crystal was grown of a 22 at.% Nb-78 at.% V alloy by electron-beam melting. Growth of single crystals by this technique is generally successful only with congruently melting alloys and is usually unsuccessful for alloys with a melting range. Thus, the fact that a single crystal was obtained implies that 22 at.% Nb is at or near the composition of congruent melting.

The general features of the phase diagram in Fig. 1 are additionally supported by the thermodynamic calculations of Molokanov *et al.* [77Mol] and of Balakrishna and Mallik [79Bal]. In both instances, the calculated liquidus and solidus curves meet to form an azeotropic melting minimum near the composition of the melting minimum of Fig. 1. The calculations of Molokanov *et al.* [77Mol] were, however, carried a step further to predict the existence of a miscibility gap in the solid bcc phase field with a critical point of 380 °C and 50 at.% Nb. The significance of this prediction is questionable because a regular solution model was employed which, with a positive interaction