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ORDERED AND DISORDERED HYDROGEN INTERSTITIALS IN NIOBIUM,
TANTALUM AND VANADIUM CRYSTALS :
STRUCTURES AND PHASE DIAGRAMS

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Abstract. — Structures and phase diagrams of the interstitial alloys Nb-H, Ta-H and V-H are summarized. These systems are unique for several reasons:

a) Large concentrations of H are possible.
b) Thermodynamic equilibrium is reached fast even at liquid nitrogen temperatures due to the extremely high mobility of H in interstitial space.
c) Disordered and ordered structures exist which can be considered as realizations of a lattice gas with phase transitions.

1. Introduction. — Lacher [1], G. Alefeld [2] and others [3] have demonstrated the usefulness of lattice gas models for understanding phase transitions in V-H, Nb-H and Ta-H systems. The application of these models is based on several properties:

a) Neglecting some of the V-H (D) phases hydrogen occupies tetrahedral interstitial sites. Six tetrahedral sites are available per matrix atom. These sites can be filled by exothermic transfer of hydrogen from the molecular gas phase, although blocking of more than one site by one interstitial atom has prevented so far the theoretical possibility to surpass the maximum concentration of 2 interstitials per metal atom reached experimentally in V and Nb.
b) Migration of hydrogen through the lattice is characterized by a large diffusion coefficient of about $10^{-5}$ cm$^2$/s which has only a weak temperature dependence [4]. In spite of this high mobility, the occupation of tetrahedral sites is normally well defined. Thermodynamic equilibrium can be reached down to temperatures of liquid nitrogen.

Structures, phase diagrams, phase morphologies and methods of preparation are discussed in detail in two review publications [5, 6]. In this article the main results of the investigations on structures and phase diagrams are summarized.

2. Structures. — Figure 1 shows the main structures occurring in these systems. In the upper row the tetrahedral sites are indicated as dots on the faces of the bcc cell, H interstitials as discs, atoms as circles. Distortions of the unit cells due to ordering of H are not taken into account in this row to facilitate a comparison of different structures. The second and third row show projections of three successive layers of tetrahedral sites in two different directions as indicated. Only a few of the metal atoms are drawn as open circles to demonstrate the character of the unit cells.

Fig. 1. — Three main structures of H based on disordered and ordered occupation of tetrahedral sites in an initially bcc lattice.
Three different arrangements of H on the lattice of tetrahedral sites are indicated:

a) Figure 1, left: structure of the disordered α and α' phases (lattice gas or lattice liquid). The tetragonal elastic distortions induced by each H interstitial due to H-metal interactions average out: The structure remains bcc. The volume increases linearly with concentration as shown in figure 2.

b) Figure 1, middle: structure of the ordered β-phase in Nb with composition NbH. The bcc symmetry is broken due to the formation of H-superlattice planes (see projection along [010]) and the corresponding structural transition of the metal to fcc. The distortion of the bcc cell is rather small, less than 1%. The H-H interactions along the H-chains in [011] direction are repulsive (W. Pesch, Diploma-work RWTH Aachen and KFA Jülich, to be published). Therefore, the bcc cell is elongated along the [011] direction, which changes the angles between the [010] and [001], unit cell vectors from 90° to about 89° at the stoichiometric composition of NbH.

The elastic H-metal repulsion is superimposed and gives rise to an increase in atomic volume (figure 2).

The ε and ζ phases in Ta and most low temperature phases in Nb are derived from this structure.

Large concentrations of vacancies are possible in these ordered phases. The vacancies are disordered at about room temperature. They order at low temperatures according to certain branching schemes [7].

c) Figure 1, right: structure of the ordered δ-phase NbH₂ and γ-phase VH₂. The metal has a fcc cell; NbH₂ and VH₂ have the CaF₂ structure.

3. Phase diagrams. — Figure 3 outlines the phase diagrams as determined by many investigations using a variety of physical properties.

![Fig. 2. Volume per Nb atom \( v_0 \) at about 300 K as a function of hydrogen concentration as determined by X-ray diffraction (\( \Delta v/v_0 \approx 0.15 \)). A similar linear relation holds for the V-H system in the range \( 0 \leq c \leq 2 \) (\( \Delta v/v_0 \approx 0.17 \)) and for the Ta-H system known in the range \( c \leq 0.8 \) (\( \Delta v/v_0 \approx 0.16 \)). The linearity of the relation between average atomic volume and hydrogen concentration \( c \) (ratio of H and M atoms) for all systems over the whole range of phases and compositions is striking. This seems to indicate that the forces between H and surrounding metal atoms have a small range, not exceeding the distance between nearest H-atoms in the ordered structures with composition MH or MH₂.

![Fig. 3. Phase diagrams in the temperature (T)-concentration projection as determined experimentally. The concentration is measured by the ratio of hydrogen atoms and metal atoms in the sample. Most of the observed phase transitions are non-continuous, of 1st order. Tentative phase boundaries are indicated by dashed lines.](image-url)
The NbH system has the character of a model system. It contains explicitly the lattice gas phase $\alpha$, the lattice liquid phase $\alpha'$, and the main lattice crystal phase $\beta$. The $(\alpha + \alpha')$ phase separation is governed by longrange elastic H-H interactions [8, 9]. Various ordered low-temperature phases are formed from substoichiometric NbH ($\beta$). In Ta and V the critical point of the $(\alpha + \alpha')$ phase separation would occur below room temperature and, therefore, is hidden below the disorder-order phase transitions.

The nomenclature is not yet consistent. Similar structures may have different names, e.g. NbH ($\beta$) and TaH ($\delta$), or NbH$_2$ ($\delta$) and VH$_2$ ($\gamma$).

Large isotope effects have been observed in V.

References