

paramètres physiques. Dès que l'épaisseur de l'échantillon dépasse un certain seuil, la diffraction électronique ne peut plus être décrite par des approximations simples et la théorie à faisceaux multiples doit être utilisée. Malheureusement, les épaisseurs qui donnent un contraste optimum se situent au-dessus de ce seuil qui est d'ailleurs très bas (quelques dizaines d'ångströms au maximum).

Par ailleurs, si l'on veut faire une analyse suffisamment fine des résultats expérimentaux, des phénomènes aussi importants que la diffusion inélastique ne peuvent plus être négligés comme c'était le cas jusqu'à ce jour. Nous nous sommes surtout attardés sur l'éclairage axial à trois faisceaux qui possède la propriété très importante de fournir une image sans déplacement latéral des franges.

Mais d'autres modes opératoires sont aussi à étudier qui peuvent prendre une importance accrue dans un proche avenir. Nous pensons en particulier aux champs sombres dont l'efficacité a été prouvée pour la visibilité des atomes lourds et peut être aussi à des techniques de faisceaux faibles.

Enfin, rappelons que le seul but de ce travail était de préciser les conditions d'obtention d'images de plans atomiques avec un contraste optimum. Un problème sans doute plus important encore est celui qui consiste à obtenir des renseignements (autres que la périodicité) sur le cristal diffractant à partir de telles images. En effet, il est clair aujourd'hui que l'intensité

image ne représente par une projection 'directe' de la répartition de potentiel dans l'atome. Si l'on est bien capable de calculer correctement le contraste obtenu à partir d'une répartition de potentiel donnée, le chemin inverse s'avère plus délicat.

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Ordering of Hydrogen in Niobium Hydride Phases

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The ordering of H in α , β , γ and δ -niobium hydride phases can be classified on the basis of electrostatic forces. In α and α' -NbH the H atoms should not be distributed statistically on all tetrahedral sites of the b.c.c. Nb lattice, but should prefer short-range ordering. In agreement with the structure determination, the Madelung energy of orthorhombic β -NbH increases at a positive deviation from the 90° Nb lattice, whereas in γ -NbH the maximum energy is at 90° . NbH₂ has a higher Madelung energy in the fluorite structure than in structural models based on the b.c.c. Nb lattice.

Introduction

The hydrides of the transition metals are usually classified as mainly metallic or mainly ionic in character (Gibb, 1962; Libowitz, 1965). The structures are derived from those of the pure metals with non-stoichiometric amounts of H in tetrahedral or octahedral interstices. The ionic hydrides form structures which are different from those of the pure metals, but which are often found in typically ionic compounds.

The niobium hydrides can be considered as metallic

or ionic depending on the composition. At a composition $H/Nb \leq 1.1$ (Reilly & Wiswall, 1970) NbH forms solid solutions with H in tetrahedral interstices (Somenkov, Gurskaya, Zemlyanov, Kost, Chernoplekov & Chertkov, 1968; Carstanjen & Sizmann, 1972; Stump, Gissler & Rubin, 1972) of the b.c.c. lattice of Nb. In α and α' -NbH, which are stable at high temperatures, H is distributed randomly on tetrahedral sites. At low temperatures H is localized on certain positions of the β , γ , ε and ζ -NbH structures (Schober, Pick & Wenzl, 1973; Schober, 1975). With

increasing H content the metal lattice is only slightly expanded (Pick, 1973). Because of the difference in the electronegativity of Nb and H, the electrons of the metals should become partially localized. At the composition NbH_2 the b.c.c. sublattice of the Nb atoms

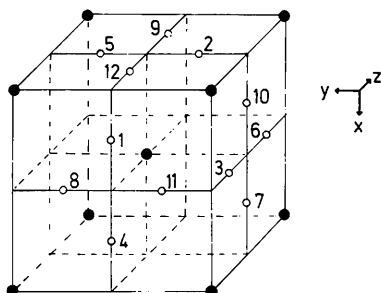


Fig. 1. Tetrahedral interstices in b.c.c. Nb lattice.

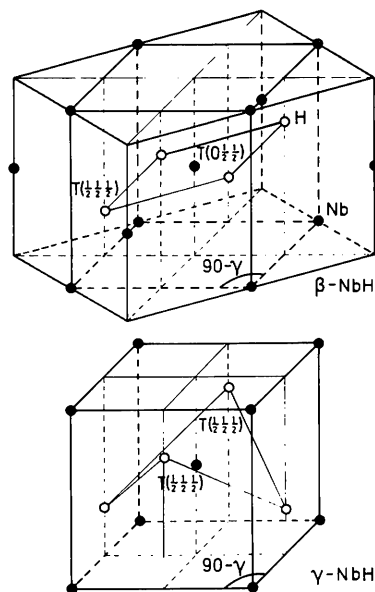


Fig. 2. Ordering of H atoms in β and γ -NbH.

changes to the f.c.c. lattice of the fluorite structure (Brauer & Müller, 1961) which is common in ionic compounds with large cations and small anions.

In this investigation it will be shown that some structural features of the metallic hydrides can be explained by considering partial ionic bonding. In compounds with similar compositions but different ordering of the H atoms on tetrahedral sites the band structure energy of the valence electrons, the energy of covalent bonding to the nearest neighbours, the Born repulsion energy, the van der Waals energy, the zero-point energy and the crystal-field energy should not change significantly. The Madelung energy of the partially ionic compounds, however, should be important for the ordering of the H atoms. In this investigation it is shown to be fruitful to consider the Madelung part of the lattice energy (MAPLE) as the sum of partial Madelung constants (PMC) (Hoppe, 1970) of the atoms as derived by Ewald (1921) and modified with respect to the Evjen (1932) method by van Gool & Piken (1969):

$$\begin{aligned} \text{MAPLE} &= \Sigma \text{PMC} \text{ (kcal mol}^{-1}\text{)} \\ \text{PMC} &= c q \varphi \text{ (kcal mol}^{-1}\text{)} \\ c &= e^2 N_L 10^8 = 331.81. \end{aligned}$$

The partial Madelung constants are related to the lattice self-potentials, φ , and indicate whether an atom is in a favourable position within the lattice. For a comparison of the Madelung energies all PMC values are for one Nb or H atom and all MAPLE values for one formula unit NbH_x . The charge q will be arbitrarily taken as $q(\text{Nb}) = +1$ and $q(\text{H}) = -1$ for all compounds of the composition $\text{NbH}_{1.0}$ and $q(\text{Nb}) = +2$, $q(\text{H}) = -1$ for NbH_2 , unless stated otherwise. The PMC values should be multiplied by q^2 when the charges of Nb and H are altered to q . In this way qualitative comparison of different hydrides is possible, although the actual electron distribution in Nb hydrides is unknown (Gibb, 1962; Aronsen, Reilly & Wiswall, 1970). Qualitatively the same result should be obtained with the Ewald-Fuchs potential, by which the Coulomb interaction in pure metals was calculated (Fuchs, 1935) or by some other kind of screened potential (Harrison, 1966; Heine & Weaire, 1970).

Table 1. Madelung part of the lattice energy (MAPLE) and partial Madelung constants (PMC) of Nb and H for seven structural models of short-range ordering of H within the b.c.c. Nb lattice [$a(\text{NbH}) = 3.4587 \text{ \AA}$]

Nearest H neighbours (Fig. 1)	Linkage of neighbouring HNb_4 tetrahedra	Translations between nearest H atoms	PMC (Nb^+) (kcal mol $^{-1}$)	PMC (H^-) (kcal mol $^{-1}$)	MAPLE (kcal mol $^{-1}$)
1, 7	Apices	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	140-706	140-706	281-412
1, 4*, 7*, 10	Apices and vertices	$0\frac{1}{2}\frac{1}{2}, \frac{1}{2}\frac{1}{2}\frac{1}{2}$	140-680	136-828	277-509
1, 10	Apices and vertices	$0\frac{1}{2}\frac{1}{2}$	140-706	130-164	270-871
1, 3	Apices and vertices	$\frac{1}{2}\frac{1}{2}$	140-706	127-679	268-385
1, 3, 4*, 6*	Apices and vertices	$\frac{1}{2}\frac{1}{2}, \frac{1}{2}\frac{1}{2}\frac{1}{2}$	182-647 at (011) 140-687 at ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) 98-727 at (001)	129-085 (1, 4*) 97-412 (3, 6*)	253-935
1, 4	Apices and vertices	$\frac{1}{2}00$	140-706	106-813	247-519
1, 11	Apices and faces	$\frac{1}{2}\frac{1}{2}0$	140-706	90-721	231-427

* Tetrahedral sites which are at the back side of the cell shown in Fig. 1, if it is different from the front side.

1. Hydrogen ordering in α and α' -NbH

In α and α' -NbH, which are stable at high temperatures, and in α -NbH, which is also stable at very low H concentrations and lower temperatures (Walter & Chandler, 1965; Reilly & Wiswall, 1970), the H atoms are distributed randomly on tetrahedral sites of the b.c.c. Nb lattice. There are 12 different tetrahedral interstices within the unit cell of Nb (Fig. 1). At a composition $\text{NbH}_{1.0}$ only two sites will be occupied by H. Each Nb atom should have four nearest H atoms if the charge is compensated by the nearest neighbours. Seven possibilities of short-range ordering for H atoms are listed in Table 1. The Madelung energies of the different distributions are quite different. The two configurations with the highest value are realized in two NbH phases. The highest value occurs for the ordered γ -phase (Hauck, 1977) (Fig. 2), which is stable below 185 K at a composition of about $\text{NbH}_{0.9}$ and a larger composition range at lower temperatures (Pick, 1973). β -NbH, stable up to about 414 K (Walter & Chandler, 1965), has an orthorhombic lattice corresponding to the second model of H ordering (Somenkov *et al.*, 1968) (Fig. 2). At higher temperatures the H atoms are not localized but distributed randomly on tetrahedral interstices. Considering however the different Madelung values, the H atoms may not be distributed statistically but should prefer short-range ordering with the translations $1\frac{1}{2}0$, 100 , $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}0$ to the neighbouring H atoms. Because of these preferred translations the superstructure reflexion observed in α - $\text{NbD}_{0.95}$ by neutron diffraction (Somenkov *et al.*, 1968) can also be explained (Hauck, 1977). The short-range ordering decreases with increasing temperature.

2. The crystal structure of β and γ -NbH

β - NbH_x has an orthorhombic lattice. The cell constants vary slightly with the stoichiometry and possibly also with temperature. At room temperature the angle $90 - \gamma$ (Fig. 2) deviates from 90° by about 0.4° at $x = 0.7$ and by about 0.9° at $x = 1.0$ (Brauer & Hermann, 1953; Pick, 1973; Rashid & Scott, 1973). The distortion was measured by X-ray diffraction. However, it could not be determined whether γ is positive or negative. In neutron powder diffraction the resolution is not high enough to resolve the satellite reflexions. For the calculated Coulomb interactions (Fig. 3) γ was varied but the cell volume was left constant ($a \times b = 23.8274 \text{ \AA}^2$, $c = 3.473 \text{ \AA}$). The Madelung energy reaches a maximum at 93° with a positive deviation from 90° . The partial Madelung energies clearly show that the distortion is caused by the H atoms, whereas the PMC values of the Nb atoms are still at a maximum at 90° . The orthorhombic distortion by the H atoms will be smaller if a smaller charge on the H atoms is considered. Fig. 4 shows that the measured value of $\gamma \approx 0.9^\circ$ is reached if the negative charge at the H compensates only 75% of the charge at the Nb atom. In this model the re-

maining electrons should behave as a free electron gas in the hydride lattice (see also Gibb, 1962, p. 375). If the stoichiometry of β -NbH changes to a lower H

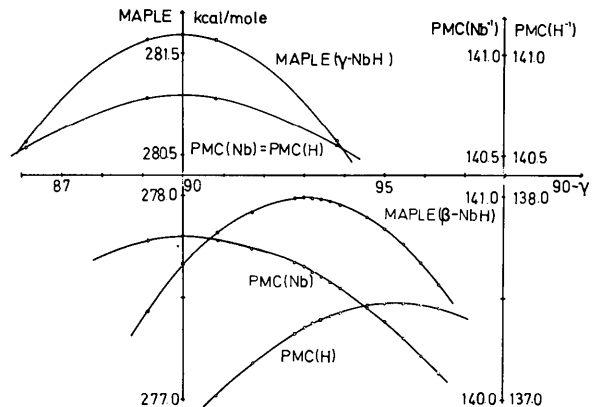


Fig. 3. Madelung part of the lattice energy (MAPLE) and partial Madelung constants (PMC) of Nb^{1+} and H^{1-} in β and γ -NbH as a function of an orthorhombic distortion.

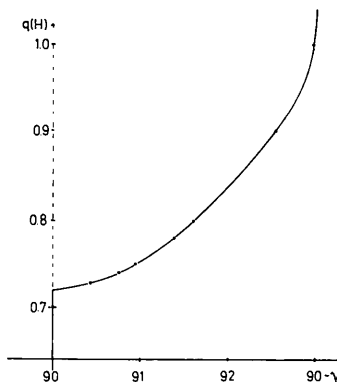


Fig. 4. Maximum of the Madelung energy of β -NbH at different charges q of the H atoms.

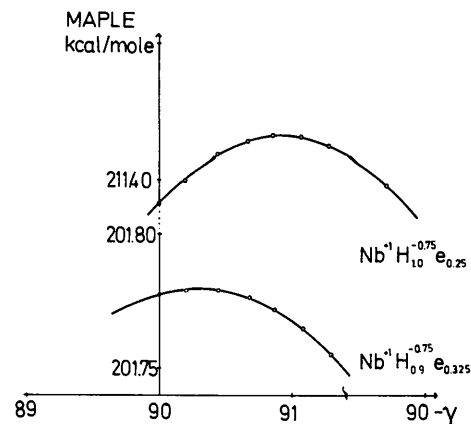


Fig. 5. Madelung part of the lattice energy of $\beta\text{-Nb}^{1+}\text{H}_{1.0}^{0.75-}e_{0.25}$ and $\beta\text{-Nb}^{1+}\text{H}_{0.9}^{0.75-}e_{0.325}$.

Table 2. Madelung part of the lattice energy (MAPLE) and partial Madelung constants (PMC) of NbH₂ for the fluorite structure and eight structural models with b.c.c. Nb latticesAll values are given in kcal mol⁻¹.

NbH ₂ structural model	PMC (Nb ²⁺)	PMC (H ¹⁻) _a	PMC (H ¹⁻) _b	PMC (H ¹⁻) _c	PMC (H ¹⁻) _d	MAPLE (Nb ²⁺ H ₂ ⁻)
CaF ₂ structure, <i>a</i> = 4.556 Å b.c.c. Nb (Fig. 1) <i>a</i> = 3.6161 Å	551.277	148.302				847.880
H at <i>a, b, c, d</i>						
1, 4, 7, 10	538.332	133.235	133.235	133.235	133.235	804.801
1, 2, 3, 5	538.332	138.357	118.398	138.357	118.398	795.086
1, 3, 4, 6	538.332	118.398	118.398	118.398	118.398	775.128
1, 3, 4, 10	538.332	120.775	103.007	130.859	117.844	774.574
1, 2, 3, 7	538.332	150.817	103.007	103.007	80.118	756.806
1, 2, 3, 10	538.332	140.734	103.007	103.007	70.034	746.722
1, 4, 5, 12	538.332	83.048	83.048	103.007	32.308	689.038
1, 4, 9, 12	538.332	47.699	47.699	47.699	47.699	633.730

content, the distortion should be smaller which is qualitatively in agreement with the measured values (Fig. 5).

Similar calculations for γ -NbH give a maximum of the Madelung energy at 90°. PMC and MAPLE values decrease with increasing distortion of the lattice (Fig. 3). For both structures (β and γ -NbH) the Madelung energy increases with increasing *c* at constant volume.

3. The crystal structure of NbH₂

In NbH₂ the structure of the Nb atoms changes from b.c.c. to f.c.c., although there would be enough tetrahedral interstices in the b.c.c. lattice for the composition NbH₂. Eight possible arrangements of the four H atoms on 12 different sites of the b.c.c. Nb lattice are listed in Table 2. If one assumes the same volume for all models ($V = 4.556^3/4 \text{ \AA}^3$ per NbH₂ formula unit, $a = 4.556 \text{ \AA}$ is the measured lattice constant of NbH₂) the calculations show that the models with a b.c.c. Nb lattice are less stable than the fluorite structure. However, no quantitative data are available for the change of metallic bonding, covalent bonding and Born repulsion when the Nb lattice transforms from b.c.c. to f.c.c.

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