

Structural Relations between Vanadium, Niobium, Tantalum Hydrides and Deuterides

BY J. HAUCK

Institut für Festkörperforschung der KFA Jülich D-5170 Jülich, Federal Republic of Germany

(Received 13 October 1977; accepted 26 November 1977)

The phase diagrams and crystal structures of V, Nb, Ta (=M) hydrides and deuterides show a close relationship, with some substantial differences at lower temperatures. At high temperatures (~500 K) H atoms form a disordered solid solution at tetrahedral interstices of a b.c.c. metal lattice in the composition range MH_x with $0 < x \lesssim 1$ (α -MH). At lower temperatures (~300 K) the composition is limited to a non-stoichiometric solid solution $MH_{0.5}$ -MH. The H ordering in ζ -NbH (β -TaH structure, composition $MH_{0.5}$, space group C222) and γ -NbH (MH , $I\bar{4}m2$) is closely related to β -NbH (MH , $Cccm$). The symmetry is lowered to $B2/m$ (β -VH structure, $MH_{0.5}$) for a similar distribution of H at octahedral interstices. The crystal structures can be characterized by the translation vectors T_1 ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) and T_2 ($0\frac{1}{2}\frac{1}{2}$) between nearest H atoms. α -MH exhibits a short-range order with a preference of T_1 and T_2 between neighbouring H atoms. In $MH_{0.5}$ - MH_{ss} the percentage $[T]$ of T_1 and T_2 translations changes with composition and temperature. The different low-temperature phases and the order-disorder transitions can be characterized by the ratio $[T_1]/([T_1] + [T_2])$.

Introduction

The transition metals of the fifth group V, Nb and Ta form hydrides with an interstitial solid solution of H in the b.c. metal lattice. At high temperatures (~500 K) the H atoms are distributed randomly on tetrahedral sites. At lower temperatures certain phases with an ordered H distribution are formed within the approximate composition range $MH_{0.5}$ -MH. From V and Nb, MH_2 hydrides could also be obtained. These have the f.c.c. fluorite lattice (Maeland, Gibb & Schumacher, 1961; Brauer & Müller, 1961). In this investigation only the crystal structures and phase relations of hydrides with a b.c. metal lattice will be considered.

The hydrides of V, Nb and Ta have been investigated extensively by different methods. The results concerning structural details are summarized in Table 1 (the code to the references is given in Table 2). There are some contradictions between different investigations, caused mainly by difficulties in the determination of H ordering. X-ray diffraction is insensitive to scattering by H atoms. The symmetry of the lattice, however, can be determined from polycrystalline samples if the distortion of the metal lattice (caused by the H atoms) is large enough to be resolved by accurate X-ray diffraction. Neutron diffraction on single crystals would be appropriate for determining the location of the H or D atoms. Unfortunately, single crystals of the metals charged with H show many differently orientated domains (Schober, Linke & Wenzl, 1974) which are too small for neutron diffraction on one domain only. For neutron powder diffraction the resolution is not high enough to resolve split reflections of the slightly

distorted lattices. The best method to determine the space group seems to be electron diffraction on single domains. In addition, quasielastic and inelastic neutron scattering, NMR, and channelling experiments give data about the location of H or D on octahedral or tetrahedral interstices. Based on all these data, structural models can be evaluated. Also, the calculation of Coulomb interactions was shown to be valuable for the interpretation of such models (Hauck & Schenk, 1977).

β -NbH structure

Nb and Ta form hydrides and deuterides with the β -NbH structure (Somenkov, Gurskaya, Zemlyanov, Kost, Chernoplekov & Chertkov, 1968). For V only the deuteride is known (δ -VD). H or D are at tetrahedral interstices as shown in Fig. 1. In δ -VD probably some minor fraction of D is on octahedral sites (Chervyakov, Entin, Somenkov, Shil'shtein & Chertkov, 1972) which are related to the tetrahedral sites by the translation T ($\frac{1}{4}00$) (Fig. 1).

An orthorhombic, trigonal or tetragonal distortion of the originally b.c.c. metal lattice was reported from X-ray diffraction data (Table 1). The correct symmetry of the lattice however is orthorhombic (Fig. 2).

So far it has been impossible to determine whether the slight deviation from 90° of the b.c. metal lattice is positive or negative. From calculations of the Coulomb interaction a positive deviation with the repulsion of nearest H atoms seems more favourable (Hauck, 1977a).

Table 1. Symmetry of hydride lattice and site preference of H or D as determined by X-ray (*x*), neutron (*n*) or electron diffraction (*e*), inelastic neutron scattering (*in*), nuclear magnetic resonance (NMR) or channelling experiments (*ch*)

The code for the references is given in Table 2.

Phase	Symmetry of hydride lattice	Reference	Site preference of H or D	Reference
<i>(a)</i> High-temperature phases with the α -NbH structure				
α -VH			in : tet.	5,6
α -VD	<i>n</i> : <i>Im</i> 3 <i>m</i>	1	<i>n</i> : 10% oct.	7
	<i>n,x</i> : b.c.c.	2	<i>n</i> : tet.	1,2
			NMR : tet.	8,9
α -NbH	<i>x</i> : b.c.c.	20	in : tet.	10
			in : not tet. or oct.	11
α -NbD	<i>n</i> : cubic	3	ch : tet.	12
			<i>n</i> : tet.	3,15
α -TaH	<i>x</i> : b.c.c.	20	in : tet.	13
α -TaD	<i>n</i> : cubic	4	ch : >90% tet.	14
			<i>n</i> : tet.	4
<i>(b)</i> Ordered MH phases with the β -NbH structure				
δ -VD	<i>n</i> : <i>Cccm/Ama</i> 2	7	<i>n</i> : tet. or oct.	2
	<i>n</i> : <i>C2/m</i> or <i>C222</i>	2	<i>n</i> : tet.	1
	<i>n</i> : <i>Pnnn</i>	1	<i>n</i> : 10% oct.	7
	<i>x</i> : orthorh.	16	NMR : tet.	31
	<i>x</i> : cubic	2		
β -NbH	<i>e</i> : orthorh.	17	in : tet.	6,32
	<i>n</i> : <i>Pnnn</i>	3	<i>n</i> : tet.	3
	<i>x</i> : tetr.	18		
	<i>x</i> : b.c. trigonal	19		
	<i>x</i> : orthorh.	6,20		
		21,22		
		23,24		
		25,26		
β -NbD	<i>n</i> : <i>Pnnn</i>	3	ch : tet.	12
	<i>x</i> : orthorh.	27	<i>n</i> : tet.	3
			NMR : tet.	31,33
TaH	<i>x</i> : tetr.	28		
	<i>x</i> : orthorh.	20,29		
		24		
TaD	<i>n</i> : <i>Pnnn</i>	4,30	<i>n</i> : tet.	4,30
	<i>x</i> : orthorh.	30		
<i>(c)</i> Ordered $MH_{0.5}$ phases with the β -TaH or β -VH structure				
β -VH	<i>x,e</i> : monocl.	34,35	<i>e</i> : tet.	39
	<i>x</i> : tetr.	5,6	<i>e</i> : oct.	50
		36,37	in : tet. + oct.	5
		38	NMR : oct.	9
	<i>e</i> : <i>B2, Bm</i>	39		
	NMR : tetr.	31		
β -VD	<i>n</i> : <i>Cm</i> or <i>I4₁/amd</i>	1	<i>n</i> : 95% oct.	40
	<i>n</i> : <i>Cm</i>	2	<i>n</i> : 85% oct.	1
	<i>n</i> : <i>Bm</i> or <i>B2/m</i>	40	<i>n</i> : oct.	2
	NMR : tetr.	31	NMR : oct.	31,51
	<i>x</i> : tetr.	16,27		
ζ -NbH	<i>e</i> : orthorh.	41		
β -TaH	<i>e</i> : monocl.	42	in : tet.	6,13
	NMR : tetr.	43	NMR : oct. + tet.	43
	<i>x</i> : tetr.	6,29		
		24		
	<i>x</i> : orthorh.	44,45		

Table 1 (cont.)

Phase	Symmetry of hydride lattice	Reference	Site preference of H or D	Reference
β -TaD	<i>n</i> : <i>A222</i>	46	<i>n</i> : tet.	46,47
	<i>n</i> : <i>I4</i>	47		30
	<i>n</i> : <i>I4</i>	48	NMR : tet.	31
	NMR : <i>A222</i>	49		
	<i>x</i> : orthorh.	27		
	<i>x,n</i> : <i>C222</i>	30		

(*d*) Low-temperature MH phases with the γ -NbH structure

γ -NbH	<i>x</i> : cubic	25
γ -TaH	<i>e</i> : pseudocubic	52

Table 2. Code for the references used in Tables 1, 4, 5 and 7

- ASANO, H. & HIRABAYASHI, M. (1973). *Phys. Status Solidi A*, **15**, 267–279.
- WESTLAKE, D. G., MUELLER, M. H. & KNOTT, H. W. (1973). *J. Appl. Cryst.* **6**, 206–216.
- SOMENKOV, V. A., GURSKAYA, A. V., ZEMLYANOV, M. G., KOST, M. E., CHERNOPEKOV, N. A. & CHERTKOV, A. A. (1968). *Sov. Phys. Solid State*, **10**, 1076–1082.
- SOMENKOV, V. A., GURSKAYA, A. V., ZEMLYANOV, M. G., KOST, M. E., CHERNOPEKOV, N. A. & CHERTKOV, A. A. (1969). *Sov. Phys. Solid State*, **10**, 2123–2127.
- RUSH, J. J. & FLOTOW, H. E. (1968). *J. Chem. Phys.* **48**, 3795–3804.
- SAKAMOTO, M. (1964). *J. Phys. Soc. Jpn*, **19**, 1862–1866.
- CHERVYAKOV, A. YU., ENTIN, I. R., SOMENKOV, V. A., SHIL'SHEIN, S. SH. & CHERTKOV, A. A. (1972). *Sov. Phys. Solid State*, **13**, 2172–2177.
- WESTLAKE, D. G. (1971). *J. Less-Common Met.* **23**, 89–91.
- ARONS, R. R., BOHN, H. G. & LÜTGEMEIER, H. (1974). 18th Ampère Congress, Nottingham, 1974, pp. 343–344.
- STUMP, N., GISSLER, W. & RUBIN, R. (1972). *Phys. Status Solidi*, **54**, 295–302.
- KISTNER, G., RUBIN, R. & SOSNOSWKA, I. (1971). *Phys. Rev. Lett.* **27**, 1576–1577.
- CARSTANJEN, H. D. & SIZMANN, R. (1972). *Ber. Bunsenges. Phys. Chem.* **76**, 1223–1229.
- RUSH, J. J., LIVINGSTON, R. C., DE GRAAF, L. A., FLOTOW, H. E. & ROWE, J. M. (1973). *J. Chem. Phys.* **59**, 6570–6576.
- ANTONINI, M. & CARSTANJEN, H. D. (1976). *Phys. Status Solidi A*, **34**, K153–157.
- BAUER, G. S., SCHMATZ, W. & JUST, W. (1977). Proc. 2nd Int. Conf. Hydrogen in Metals, Paris, 6–10 June 1977, Abstr. 2 C 15.
- HARDCASTLE, K. & GIBB, T. R. P. (1972). *J. Phys. Chem.* **76**, 927–930.
- SCHOBER, T., PICK, M. A. & WENZL, H. (1973). *Phys. Status Solidi A*, **18**, 175–182.
- ALBRECHT, W. M., MALLETT, M. W. & GOODE, W. D. (1958). *J. Electrochem. Soc.* **105**, 219–223.
- HARDIE, D. & MCINTYRE, P. (1972). *Met. Sci. J.* **6**, 40–46.
- BRAUER, G. & HERMANN, R. (1953). *Z. Anorg. Allg. Chem.* **274**, 11–23.
- WAINWRIGHT, C., COOK, A. J. & HOPKINS, B. E. (1964). *J. Less-Common Met.* **6**, 362–374.
- WALTER, R. J. & CHANDLER, W. T. (1965). *Trans. Metall. Soc. AIME*, **233**, 762–765.
- RAUCH, G. C., ROSE, R. M. & WULFF, J. (1965). *J. Less-Common Met.* **8**, 99–113.
- AMATO, I. & NEGRO, A. (1968). *J. Less-Common Met.* **16**, 468–471.
- PICK, M. A. (1973). Report JÜL-951-FF. Institut für Festkörperforschung der KFA Jülich.

Table 2 (cont.)

- (26) RASHID, M. S. & SCOTT, T. E. (1973). *J. Less-Common Met.* **30**, 399–403.
- (27) PEDERSEN, B. & SLOTFELDT-ELLINGSEN, D. (1971). *J. Less-Common Met.* **23**, 223–227.
- (28) MATSUYAMA, T. & DOHI, S. (1972). *Proc. Jpn. Congr. Mater. Res.* **16**, 22–26.
- (29) WAITE, T. R., WALLACE, W. E. & CRAIG, R. S. (1956). *J. Chem. Phys.* **24**, 634.
- (30) ASANO, H., ISHINO, Y., YAMADA, R. & HIRABAYASHI, M. (1975). *J. Solid State Chem.* **15**, 45–53.
- (31) ARONS, R. R., BOHN, H. G. & LÜTGEMEIER, H. (1974). *J. Phys. Chem. Solids*, **35**, 207–214.
- (32) PAN, S. S., YEATER, M. L. & MOORE, W. E. (1967). *Nat. Bur. Stand. (US) Spec. Publ.* **301**, 315–318.
- (33) NAKAMURA, K. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2028–2034.
- (34) CAMBINI, M., SERNEELS, R. & GEVERS, R. (1974). *Phys. Status Solidi A*, **21**, K51–59.
- (35) TAKANO, S. & SUZUKI, T. (1974). *Acta Metall.* **22**, 265–274.
- (36) ZANOWICK, R. L. & WALLACE, W. E. (1962). *J. Chem. Phys.* **36**, 2059–2062.
- (37) MAELAND, A. J. (1964). *J. Phys. Chem.* **68**, 2197–2200.
- (38) REILLY, J. J. & WISWALL, R. H. JR (1970). *Inorg. Chem.* **9**, 1678–1682.
- (39) WANAGEL, J., SASS, S. L. & BATTERMAN, B. W. (1972). *Phys. Status Solidi A*, **10**, 49–57.
- (40) SOMENKOV, V. A., ENTIN, I. R., CHERVYAKOV, A. YU., SHIL'SHTEIN, S. SH. & CHERTKOV, A. A. (1972). *Sov. Phys. Solid State*, **13**, 2178–2182.
- (41) SCHOBER, T. (1975). *Phys. Status Solidi A*, **30**, 107–116.
- (42) WANAGEL, J., SASS, S. L. & BATTERMAN, B. W. (1972). *Phys. Status Solidi A*, **11**, K97–100.
- (43) STALINSKI, B. & ZOGAL, O. T. (1966). *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **14**, 143–147.
- (44) DUCASTELLE, F., CANDRON, R. & COSTA, P. (1970). *J. Phys. Chem. Solids*, **31**, 1247–1256.
- (45) STALINSKI, B. (1954). *Bull. Acad. Polon. Sci. Cl. 3*, **2**, 245–247.
- (46) PETRUNIN, V. F., SOMENKOV, V. A., SHIL'SHTEIN, S. SH. & CHERTKOV, A. A. (1970). *Sov. Phys. Crystallogr.* **15**, 137–139.
- (47) WALLACE, W. E. (1961). *J. Chem. Phys.* **35**, 2156–2164.
- (48) PALENIK, G. J. (1964). *J. Chem. Phys.* **41**, 3260–3261.
- (49) NAKAMURA, K. (1972). *Bull. Chem. Soc. Jpn*, **45**, 3356–3362.
- (50) SERNEELS, R., DAVID, M. & GEVERS, R. (1975). *Phys. Status Solidi B*, **72**, 123–133.
- (51) NAKAMURA, K. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2588–2589.
- (52) SCHOBER, T. & HAUCK, J. (1976). Frühjahrstagung der DPG, Freudenstadt 1976; *IFF-Bulletin* 9/1, 24.
- (53) ASANO, H., ABE, Y. & HIRABAYASHI, M. (1976). *Acta Metall.* **24**, 95–99.
- (54) ALBRECHT, W. M., GOODE, W. D. & MALLETT, M. W. (1959). *J. Electrochem. Soc.* **106**, 981–986.
- (55) VELECKIS, E. (1960). PhD Thesis, Illinois Inst. of Techn. ASTIA AD 282.
- (56) TRETROWSKI, J. (1969). Report JÜL-626-FN. Institut für Festkörperforschung der KFA Jülich.
- (57) GISSLER, W., ALEFELD, G. & SPRINGER, T. (1970). *J. Phys. Chem. Solids*, **31**, 2361–2369.
- (58) WIPF, H. (1976). *J. Less-Common Met.* **49**, 291–307.
- (59) ZABEL, H. & PEISL, H. (1976). *Phys. Status Solidi A*, **37**, K67–70.
- (60) ZIERATH, J. (1969). PhD Thesis: *Die thermodynamischen Eigenschaften des Systems Tantal-Wasserstoff*, Münster.
- (61) PRYDE, J. A. & TSONG, I. S. T. (1971). *Trans. Faraday Soc.* **67**, 297–304.
- (62) SLOTFELDT-ELLINGSEN, D. & PEDERSEN, B. (1974). *Phys. Status Solidi A*, **25**, 115–124.
- (63) WESTLAKE, D. G., OCKERS, S. T. & GRAY, W. R. (1970). *Metall. Trans.* **1**, 1361–1364.
- (64) SCHOBER, T. & WENZL, H. (1977). In *Hydrogen in Metals*, edited by G. ALEFELD & J. VÖLKL. Berlin: Springer.
- (65) LÜTGEMEIER, H., ARONS, R. R. & BOHN, H. G. (1972). *J. Magn. Reson.* **8**, 74–79.
- (66) LÜTGEMEIER, H., BOHN, H. G. & ARONS, R. R. (1972). *J. Magn. Reson.* **8**, 80–86.
- (67) SABA, W. G., WALLACE, W. E., SANDMO, H. & CRAIG, R. S. (1961). *J. Chem. Phys.* **35**, 2148–2155.
- (68) KOFSTAD, P. & BUTERA, R. A. (1963). *J. Appl. Phys.* **34**, 1517–1520.
- (69) PEDERSEN, B., KROGDAHL, T. & STOKKELAND, O. (1965). *J. Chem. Phys.* **42**, 72–79.
- (70) BERLINCOURT, T. G. & BICKEL, P. W. (1970). *Phys. Rev. B*, **2**, 4838–4843.
- (71) WESTLAKE, D. G. & OCKERS, S. T. (1975). *J. Less-Common Met.* **42**, 255–260.
- (72) SCHOBER, T. (1977). Proc. 2nd Int. Conf. Hydrogen in Metals, Paris 6–10 June 1977, Abstr. 1 D 2.
- (73) BRAUER, G. & MÜLLER, H. (1961). *J. Inorg. Nucl. Chem.* **17**, 102–107.
- (74) SCHOBER, T. & WENZL, H. (1976). *Phys. Status Solidi A*, **33**, 673–681.
- (75) SOMENKOV, V. A., ZEMLYANOV, M. G., KOST, M. E., CHERNOPEKOV, N. A. & CHERTKOV, A. A. (1969). *Sov. Phys. Dokl.* **13**, 669–671.
- (76) ROBERTS, B. W. (1955). *Phys. Rev.* **100**, 1257.
- (77) ZAMIR, D. & COTTS, R. M. (1964). *Phys. Rev.* **134**, A666–A675.
- (78) AMANO, M., MATSUMOTO, T. C. & SASAKI, Y. (1973). *Scripta Metall.* **7**, 371–375.
- (79) SOMENKOV, V. A., PETRUNIN, V. F., SHIL'SHTEIN, S. SH. & CHERTKOV, A. A. (1970). *Sov. Phys. Crystallogr.* **14**, 522–530.
- (80) WANAGEL, J., SASS, S. L. & BATTERMAN, B. W. (1972). *Phys. Status Solidi A*, **11**, 767–770.
- (81) WESTLAKE, D. G., OCKERS, S. T., MUELLER, M. H. & ANDERSON, K. D. (1972). *Metall. Trans.* **3**, 1709–1710.
- (82) HIRABAYASHI, M., YAMAGUCHI, S., ASANO, H. & HIRAGA, K. (1974). *Proceedings of the International Symposium on Order-Disorder Transformations in Alloys, Tübingen*, 1973, pp. 266–302. Berlin: Springer.
- (83) SOMENKOV, V. A., CHERVYAKOV, A. YU., SHIL'SHTEIN, S. SH. & CHERTKOV, A. A. (1972). *Sov. Phys. Crystallogr.* **17**, 274–277.
- (84) WELTER, J.-M., PICK, M. A., SCHOBER, T., HAUCK, J., FENZL, H. J. & WENZL, H. (1977). Proc. 2nd Int. Conf. Hydrogen in Metals, Paris 6–10 June 1977, Abstr. 1 D 3.

γ -NbH structure

Orthorhombic β -NbH with the approximate composition NbH_{0.9} transforms to a cubic lattice below 180 K, as determined by X-ray diffraction (Pick, 1973), or at some lower temperature as determined

metallographically (Schober, Linke & Wenzl, 1974). The neutron powder pattern of γ -NbH shows only two weak reflections, which were indexed on the basis of an orthorhombic cell with twice the cell constants of β -NbH (Pick, 1973). By comparison with the neutron powder pattern of Nb₄H₃ or Nb₄D₃ (Somenkov,

Petrinin, Shil'shtein & Chertkov, 1970), one can see that these reflections can be attributed to some Nb_4H_3 within the sample. Thus pure $\gamma\text{-NbH}$ would show no superstructure reflections. The only possible ordering with H on tetrahedral sites which shows no superstructure reflections is that of Fig. 1 where the H atoms have the same translational vector $\mathbf{T}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ as the Nb atoms (Hauck, 1976). This structure contains the fourfold axis but no threefold axis as does b.c.c. $\alpha\text{-NbH}$ (Fig. 2). Therefore the symmetry is lowered to tetragonal. The distortion of the Nb lattice was found to be

similar for the three axes, thus indicating a pseudo-cubic lattice by X-ray diffraction (Pick, 1973).

Recently, this structure-type phase was also detected in the TaH system by electron diffraction below 123 K at about 89% H (Schober & Hauck, 1976).

In the VH system a similar structure-type phase with the same translational vector between H atoms but with H at octahedral interstices ($\gamma\text{-NbH}_{\text{oct}}$ structure, Table 3, Fig. 1) was proposed from neutron diffraction and calorimetric studies of $\beta_2\text{-VH}$ (Asano, Abe & Hirabayashi (1976a,b).

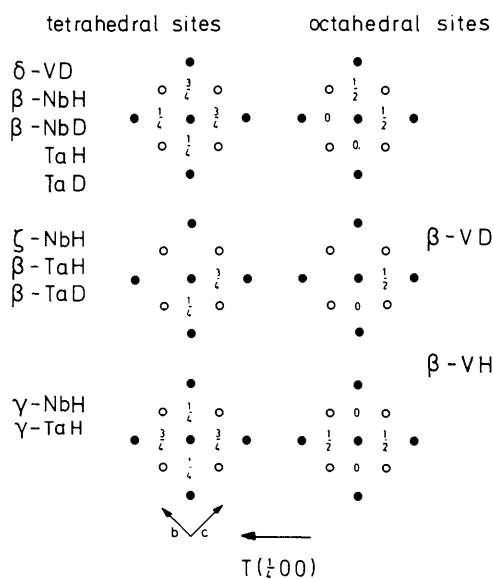


Fig. 1. Ordering of H on octahedral or tetrahedral sites in closely related crystal structures of V, Nb and Ta hydrides (open circles represent metal atoms at $x = 0$, full circles at $x = 0.5$; the numbers indicate the height of the H atoms projected on the bc plane).

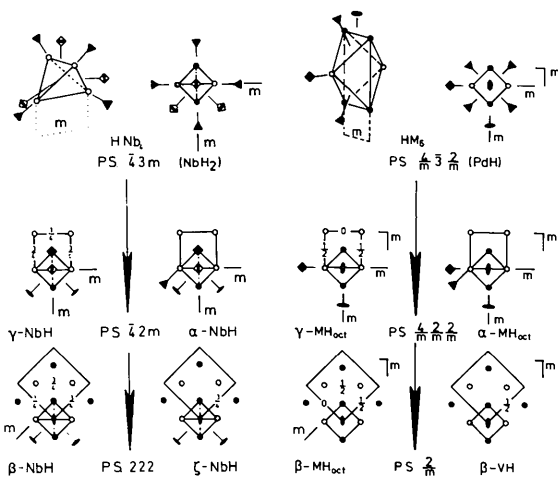


Fig. 2. Point symmetry of H atoms at tetrahedral or octahedral sites of hydride structures.

$\beta\text{-TaH}$ and $\beta\text{-VH}$ structure

$\beta\text{-VH}$, $\beta\text{-VD}$, $\beta\text{-TaH}$ and $\beta\text{-TaD}$ have the same reciprocal lattice as confirmed by neutron or electron diffraction (Table 1). Schober (1975) reported a new phase, $\zeta\text{-NbH}$, which was detected by electron diffraction within the temperature range 208–228 K. The reciprocal lattice is identical with that of $\beta\text{-TaH}$ (Hauck, 1976). Unfortunately the composition of the small domains, where electron diffraction was performed, could not be analysed. According to the NbH phase diagram it might be assumed that $\zeta\text{-NbH}$ has the approximate composition $\text{NbH}_{0.75}$ with a transformation to the $\beta\text{-NbH}$ structure at about 228 K. In the NbD system an ordered distribution of interstitials probably exists at even higher D content. Somenkov *et al.* (1968) reported neutron diffraction data for $\text{NbD}_{0.95}$ with a very weak reflection at low θ which does not belong to $\beta\text{-NbD}$.

It was confirmed by neutron diffraction and NMR measurements (Table 1) that H or D mainly occupies octahedral sites in $\beta\text{-VH}$, $\beta\text{-VD}$ and tetrahedral sites in $\beta\text{-TaH}$, $\beta\text{-TaD}$. One can assume that tetrahedral sites are also occupied in $\zeta\text{-NbH}$. Both structures are closely related by a translation $\mathbf{T}(\frac{1}{4}00)$ of the H atoms from octahedral to tetrahedral sites (Fig. 1). The symmetry however changes from monoclinic to orthorhombic (Table 3).

For $\beta\text{-TaD}$ a slight deviation of the metal atoms from the ideal position $z = \frac{1}{4}$ resulted from a least-squares refinement of the neutron powder diffraction data with $z = 0.262$ at 298 K and $z = 0.267$ at 77 K (Petrinin, Somenkov, Shil'shtein & Chertkov, 1970; Asano, Ishino, Yamada & Hirabayashi, 1975).

The lattice distortion is partly due to the repulsion of nearest H atoms, as indicated by calculations of the Coulomb interaction (Hauck & Schenk, 1976) and electron diffraction measurements on $\beta\text{-TaH}$ (Schober & Wenzl, 1976). For $\beta\text{-VD}$ only the monoclinic angle (about 95°) was determined, not the difference of the monoclinic axes (Westlake, Mueller & Knott, 1973; Somenkov, Entin, Chervyakov, Shil'shtein & Chertkov, 1972). A monoclinic angle of about 91° has been reported for $\beta\text{-VH}$ (Takano & Suzuki, 1974; Cambini, Serneels & Gevers, 1974).

Table 3. Space group, lattice parameters and positional parameters for α , β , γ -NbH, β -TaH, β -VH and related structure models with octahedral site preference of H

α -NbH, α -NbH_{oct}
Lattice constant a_0
Space group: $Im\bar{3}m$ (O_h^2) (229)

Atom	Position	Coordinates
Nb	2(a)	000; b.c.
H _{tet}	12(d)	$\frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0, 0\frac{1}{2}\frac{1}{2}$; b.c.
H _{oct}	6(b)	$0\frac{1}{2}, \frac{1}{2}0, \frac{1}{2}0$; b.c.

β , γ and ζ -NbH (β -TaH)

Lattice constants: $a \approx a_0$, $b \approx c \approx a_0\sqrt{2}$
Space group: $C222$ (D_2^2) (21)

Atom	Position	Coordinates
Nb	4(k)	$\frac{1}{2}z, \frac{1}{2}\bar{z}, \frac{3}{4}z, \frac{3}{4}\bar{z}$ with $z \approx \frac{1}{4}$
H	2(c)	$\frac{1}{2}0, 0\frac{1}{2}$
H	2(a)	000, $\frac{1}{2}0$ ζ -NbH
H	2(d)	$00\frac{1}{2}, \frac{1}{2}0$

} γ -NbH_{ss}
} β -NbH_{ss}

β -VH, β -NbH_{oct} and γ -NbH_{oct}

Lattice constants: $a \approx b \approx a_0\sqrt{2}$, $c \approx a_0$, $\alpha = \beta = 90^\circ$
Space group: $B2/m$ (C_{2h}^2) (12)

Atom	Position	Coordinates
V, Nb	4(i)	$xy0; \bar{x}\bar{y}0; x + \frac{1}{2}, y, \frac{1}{2}; \frac{1}{2} - x, \bar{y}, \frac{1}{2}$ with $x \approx \frac{1}{4}, y \approx \frac{1}{4}$
H	2(d)	$0\frac{1}{2}, \frac{1}{2}0$
H	2(a)	000, $\frac{1}{2}0$ β -VH
H	2(c)	$0\frac{1}{2}0, \frac{1}{2}0$

} γ -NbH_{oct ss}
} β -NbH_{oct ss}

γ -NbH

Lattice constants: $a = b \approx c \approx a_0$
Space group: $I4m2$ (D_{2d}^2) (119)

Atom	Position	Coordinates
Nb	2(a)	000, $\frac{1}{2}\frac{1}{2}$
H	2(c)	$0\frac{1}{2}, \frac{1}{2}0$

γ -NbH_{oct}

Lattice constants: $a = b \approx c \approx a_0$
Space group: $I4/mmm$ (D_{4h}^{17}) (139)

Atom	Position	Coordinates
Nb	2(a)	000, $\frac{1}{2}\frac{1}{2}$
H	2(b)	$00\frac{1}{2}, \frac{1}{2}0$

β -NbH

Lattice constants: $a \approx a_0$, $b \approx c \approx a_0\sqrt{2}$
Space group: $Cccm$ (D_{2h}^2) (66)

Atom	Position	Coordinates
Nb	4(e)	$\frac{1}{4}0, \frac{3}{4}\frac{1}{2}, \frac{3}{4}0, \frac{3}{4}\frac{1}{2}$
H	4(a)	$00\frac{1}{2}, 00\frac{1}{2}, \frac{1}{2}\frac{1}{2}, \frac{1}{2}\frac{1}{2}$

β -NbH_{oct}

Lattice constants: $a \approx b \approx a_0\sqrt{2}$, $c \approx a_0$
Space group: $Ama2$ (C_{2v}^2) (40)

Atom	Position	Coordinates
Nb	4(b)	$\frac{1}{2}yz; \frac{1}{2}\bar{y}\bar{z}; \frac{1}{4}, y + \frac{1}{2}, z + \frac{1}{2}; \frac{3}{4}, \frac{1}{2} - y, \frac{1}{2} + z$ with $y \approx \frac{1}{4}, z \approx 0$
H	4(a)	$00z; \frac{1}{2}0z; 0, \frac{1}{2}, z + \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, z + \frac{1}{2}$ with $z = 0$

α -NbH structure

At high temperatures V, Nb and Ta form solid solutions with H randomly distributed on tetrahedral sites (Table 1). In α -VD probably octahedral sites of the metal lattice are also partly occupied (Chervyakov *et al.*, 1972). Neutron diffraction data on α -VD (Asano & Hirabayashi, 1973), α -NbD (Somenkov *et al.*, 1968), and α -TaD (Somenkov *et al.*, 1969) show a small but distinct superstructure reflection, which so far has been either ignored or interpreted as belonging to non-equilibrated δ -VD, β -NbD or TaD. Indeed, this reflection also occurs in the ordered β -NbH structure as 110 with the lattice constants of Table 3. However, there should be no non-equilibrated phase at the high temperatures. Also, the other superstructure reflections of the β -NbH structure phase are missing. The 110 reflection is strongest just above the transition from the ordered phase and its intensity decreases with increasing temperature (Somenkov *et al.*, 1968). This indicates a special short-range order of H just above the temperature of the phase transition.

Calculations of the Coulomb interaction (Hauck, 1977a) had shown that the ordering of H within the β and γ -NbH structures is most favoured. In β -NbH neighbouring H atoms are transferred by the translations T_1 ($\frac{1}{2}\frac{1}{2}$) and T_2 ($0\frac{1}{2}$), in γ -NbH only by T_1 ($\frac{1}{2}\frac{1}{2}$). A short-range order with a preference of T_1 ($\frac{1}{2}\frac{1}{2}$) will only slightly change the intensities of the metal-lattice reflections. A favoured translation T_2 ($0\frac{1}{2}$) between neighbouring H atoms however will create (HKL) reflections of orthorhombic indexing (Table 3) with $H + K = 2n$ and $L = 2n$, mainly at low Bragg angles. 110 is the reflection at the lowest θ value with this condition. The decreasing intensity of this reflection might be explained by the decreasing short-range order at increasing temperatures. In the hydrides of the α -phase this reflection might be too small to be detected by neutron diffraction.

The short-range order should also decrease at low H content. At H concentrations lower than $\sim MH_{0.4}$ most of the H atoms do not have nearest H atoms with T_1 and T_2 translations (Hauck, Mihelcic & Schröck-Pauli, 1977). This might also be one reason that ordered hydrides with an H content lower than $\sim MH_{0.4}$ are not formed from α -phases.

NMR is sensitive to short-range ordering. The appearance of the quadrupole splitting at temperatures near the phase transition, where the central line of the α phase occurs, was observed by Arons, Bohn & Lütgemeier (1974) for the VD and by Nakamura (1972) for the TaD system. This probably can also be explained by partial order in the α -NbH phase and partial disorder in β -NbH near the phase transition, if the samples are single phase.

The configurational entropy of the α phase is considerably smaller than that expected from a statisti-

cal distribution (Asano *et al.*, 1975; Nakamura, 1972; Saba, Wallace, Sandmo & Craig, 1961; Oates, Lambert & Gallagher, 1969). From quasielastic neutron scattering data (Rowe, Sköld, Flotow & Rush, 1971; Gissler, 1972) it was concluded that H mainly jumps to second-nearest neighbours by the diffusion process. It can be assumed that T_1 and T_2 are favoured H translations of the diffusion process at lower temperatures. The jump rate of H or D is very high, especially at temperatures where a complete solid solution of the α -phase is formed. At 500 K, for example, the mean residence time at the interstices varies between 10^{-12} to 10^{-13} s (Gissler, 1972). At these temperatures there is a considerable period where the H atoms are not localized at the interstices (Kehr, 1975). This point must be considered for structure factor calculations.

Stoichiometry and phase relations of V, Nb, Ta hydrides and deuterides

The phase relations of V, Nb, Ta hydride and deuteride systems are reported in many publications. Unfortunately there are contradictions depending mainly on the different sensitivity of the various methods for finding phase transitions; *e.g.* differential thermoanalysis, X-ray, electron and neutron diffraction, resistivity and susceptibility measurements, optical and electron microscopy, nuclear magnetic resonance and internal friction measurements. For a comparison of the results obtained by different methods, schematic diagrams were set up, showing only some characteristic features of the phase relations (Fig. 3).

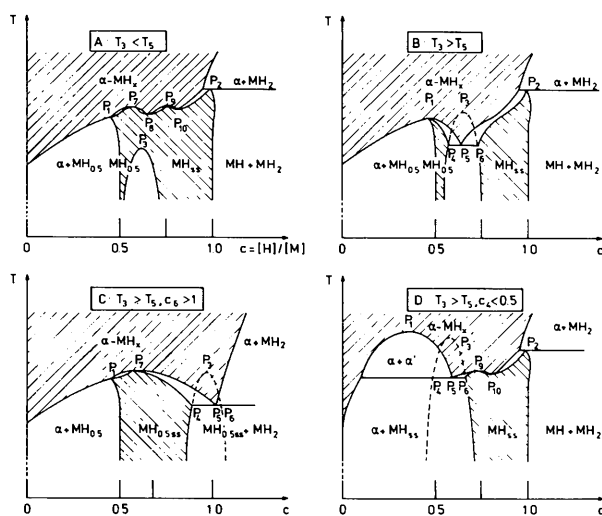


Fig. 3. Schematic phase diagrams for MH ($M = V, Nb, Ta$) hydrides and deuterides.

Substantial differences between the systems arise with decreasing temperatures where H and D show a different interaction with the V, Nb and Ta metal lattice. At high temperatures (~ 500 K) H is dissolved in the disordered α - MH_x phase within the range $0 < x \lesssim 1$ in all systems. At temperatures of ~ 300 K the phase field is restricted to a partially ordered non-stoichiometric solid solution of $MH_{0.5}$ - MH . With decreasing temperature several ordered phases appear out of $MH_{0.5}$ - MH_{ss} . At very low temperatures the composition of these phases must be restricted to a certain stoichiometry as indicated in Fig. 3.

Little is known about the phase relations between the ordered low-temperature phases and the partially ordered $MH_{0.5}$ - MH_{ss} . Some recent results can be found in the review article of Schober & Wenzl (1977).

The phase relations between α - MH_x and $MH_{0.5}$ - MH_{ss} can be characterized by six points with temperature T and composition $c = [H]/[M]$. In all diagrams the α phase has a miscibility gap below P_1 , where it decomposes to $\alpha + MH_{0.5}$ (phase diagrams A, B, C, Fig. 3) or to $\alpha + \alpha'$ and $\alpha + MH_{ss}$ at lower temperatures (phase diagram D, Fig. 3). The non-stoichiometric solid solution $MH_{0.5}$ - MH is formed between P_1 and P_2 . With decreasing temperatures several other miscibility gaps should restrict also this solid solution to certain stoichiometric compounds. One of these miscibility gaps with a location below P_3 might be characteristic for the different phase diagrams of V, Nb, Ta hydrides and deuterides (Fig. 3). If P_3 is not within the $MH_{0.5}$ - MH_{ss} phase field (phase diagram B, C, D, Fig. 3) $MH_{0.5ss}$ and MH_{ss} are limited by P_4 and P_6 , respectively. In that case the hydrogen-rich α -phase decomposes in a eutectoid reaction below P_5 .

The phase diagrams determined for the TaH and TaD systems resemble that of type A. There is still some uncertainty about the phase relations at high H content, in particular whether TaH₂ could not be obtained because of the excessively high hydrogen pressure needed or a general instability of this phase. The phase relations of the VD system are best characterized by diagram B. The VH phase diagram is remarkably different and resembles C. Some explanation for the different behaviour of H and D in V was given by Hauck (1977b). The NbH and NbD systems are similar to D. The concentration and temperature values of the characteristic points were obtained from literature data (code to references in Table 2) and are summarized in Table 4.

The ϵ or β_2 high-temperature phases which were proposed from DTA measurements near P_1 are not included in these phase diagrams. Their probable structural relations to ordered $MH_{0.5}$ and disordered α - MH_x as intermediate partially ordered phases and also the points P_7 - P_{10} of Fig. 3 will be discussed below. The VH system might resemble more closely phase diagram

from orthorhombic to tetragonal distortion, (c) for the formation of a disordered structure with partial occupation of 2(c) and 2(d) the β -TaH superstructure reflections would decrease at higher H content; the orthorhombic distortion should change only slightly.

The room-temperature dependence of the lattice constants on H concentration as determined by X-ray diffraction (Table 1) leads to the conclusion that β -NbH and β -NbD_{ss} mainly belong to (a) whereas TaH, TaD and probably δ -VD have an H ordering intermediate between (a) and (c). The small orthorhombic distortion, especially of the latter cases, could often not be distinguished from tetragonal distortion by X-ray diffraction. The neutron diffraction results of Somenkov, Gurskaya, Zemlyanov, Kost, Chernoplekov & Chertkov (1969) show that the superstructure reflections of TaD are relatively weaker than those of β -NbD. This observation can also be explained by the assumption of partial disorder.

β -VH is reported with a tetragonal distorted metal lattice. It extends to the composition VH_{0.90} or VH_{0.95} (Table 4). For the occupation of octahedral interstices the symmetry of the lattice is monoclinic for MH_{0.5} and orthorhombic for MH with the β -NbH_{oct} structure. A tetragonal distortion would be expected for MH with the γ -NbH_{oct} structure (Fig. 2 and Table 3). A disordered structure (c) can be assumed for VH with high H content. This can also be confirmed by electron diffraction where the intensities of the superstructure reflections are lower at high H content (Wanagel, Sass & Batterman, 1972),

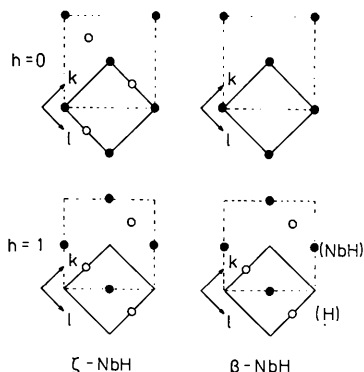


Fig. 4. Relation between superstructure reflections (open circles) of the ζ -NbH (β -TaH) and β -NbH structures.

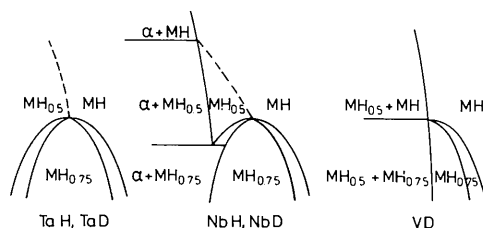


Fig. 5. Probable phase relation of low-temperature M_4H_3 phases.

In addition to the concentration-dependent disorder of H atoms in non-stoichiometric solid solution, a temperature-dependent disorder can also be assumed. The neutron diffraction intensities of the superstructure reflections decrease with increasing temperature near the transition to the α -phase as was reported for the VH system (Asano, Abe & Hirabayashi, 1976a), for VD (Chervyakov *et al.*, 1972; Westlake, Mueller & Knott, 1973; Asano & Hirabayashi, 1973), for NbD (Somenkov *et al.*, 1968) and for TaD (Somenkov *et al.*, 1969; Asano *et al.*, 1975). This indicates an increasing disorder for the temperature range where the phase is still single phase. The orthorhombic distortion also changes with temperature (Zanowick & Wallace, 1962; Walter & Chandler, 1965; Asano & Hirabayashi, 1973; Takano & Suzuki, 1974). The asymmetry parameter of NMR measurements on β -NbD (Lütgemeier, Bohn & Arons, 1972) and β -TaD (Nakamura, 1972) changes slightly with temperature.

The β -TaH structure probably changes to the β -NbH structure in $MH_{0.5}$ - MH_{ss} by a second-order phase transition.* In the β -TaH structure additional hkl superstructure reflections occur at $l = 2n + 1$, $k = 2n$ for the $\{hkl\}$ planes at $h = 2n$ (Fig. 4). At this phase transition the additional H atoms of $MH_{0.5ss}$ and the empty interstices of MH_{ss} are distributed randomly with equal probability. Possible phase relations are outlined in Fig. 5. For the NbH and TaH phase diagrams this second-order-transformation line ends at the boundary of the low-temperature M_4H_3 phases which will be discussed in the next section. In the VD system $MH_{0.5}$ and MH are separated by a two-phase field (Asano & Hirabayashi, 1973).

Low-temperature phases

At low temperatures an ordering of $MH_{0.5}$ - MH_{ss} is reported for the $MH_{0.75}$ composition, in the VH system probably at some lower H content (Table 5). The structures reported for the $MH_{0.75}$ compounds ($M = V, Nb$ and Ta) can be related to $MH_{0.5}$ - MH_{ss} (β -TaH/ β -NbH structure) with an ordered arrangement of additional H atoms of $MH_{0.5ss}$ and empty interstices of MH_{ss} (Fig. 6). The non-stoichiometric region of these phases with a higher degree of order is very limited.

Every second row of H atoms with T_1 translations is occupied just as in the β -TaH structure. At the composition $MH_{0.75}$ the intermediate rows are only 50% occupied and show different distributions for V_4D_3 , Nb_4D_3 and Ta_4D_3 . The V_4D_3 structure as determined by Westlake, Mueller & Knott (1973) (considering tetrahedral sites) can be considered as composed of layers of the β -TaH ($MH_{0.5}$) and β -NbH

* The author is indebted to Professor Horner, Heidelberg, for a discussion of this point.

Table 5. Composition and temperature of phase transformation, and structural data of low-temperature phases, chronological listing of the data

The list of references may be found in Table 2.

Composition	Stable below (K)	Site preference of H	Structure	Reference
VH _x	200			80
VH _{0.75}	224			81
VH _{0.57}	200			31
VH _{0.67}		oct.		82
VD _{0.5}	248			16
VD _{0.75}	>77			76
VD _{0.75}	148	tet.	Pcc2	1
VD _{0.75}	160	tet. or oct.	P2 or P1	2
VD _{0.75}	153	tet.		51
NbH _x	203			78
NbH _{0.75}	208		Nb ₄ D ₃	41
NbD _{0.75}	170	tet.	P2 ₁ 2 ₁ 2 ₁	79
TaH _{0.75}	208			52
TaD _{0.75}	250	tet.	I222	83
TaD _{0.72}	203			30

(MH) structure. Nb₄D₃ and Ta₄D₃ contain one 'layer' with D alternating with empty interstices I by the sequence *DIDI* (Ta₄D₃) or *DDIIDDII* (Nb₄D₃). In the V₄D₃ structure (Asano & Hirabayashi, 1973) the rows of the β-TaH structure would be partially occupied and would have a higher percentage of T₂ translations than the β-TaH/β-NbH structure solid solution. The V₃H₂ structure can be considered as β-VH/γ-NbH_{oct ss} with every third row of the γ-NbH_{oct} structure not occupied by H.

The percentage [T₁] and [T₂] of T₁ and T₂ translations changes independently with temperature and H concentration as outlined before. The ratio $r =$

Table 6. Percentage [T] of T₁ ($\frac{111}{222}$) and T₂ ($\frac{011}{22}$) translational vectors between neighbouring H atoms in V₄D₃, V₃H₂, Nb₄D₃ and Ta₄D₃ (Fig. 6) compared with MH_{0.5}-MH_{ss}

	T ₁ ($\frac{111}{222}$) [%]	T ₂ ($\frac{011}{22}$) [%]	$r = \frac{[T_1]}{[T_1] + [T_2]}$
β-TaH/β-VH	25	0	1.00
β-TaH/β-VH-β-NbH _{ss} (1:1)	31.25	12.5	0.71
β-TaH/β-VH-γ-NbH _{ss} (1:1)	56.25	0	1.00
V ₃ H ₂	33.33	0	1.00
V ₄ D ₃ (a)	25	18.75	0.57
V ₄ D ₃ (b)	31.25	12.5	0.71
Nb ₄ D ₃	31.25	12.5	0.71
Ta ₄ D ₃	25	12.5	0.67
β-NbH	50	25	0.67
γ-NbH	100	0	1.00

* 8 T/b.c. cell \cong 100%.

$[T_1]/([T_1] + [T_2])$, however, can vary only within certain limits, which characterizes the non-stoichiometric phases and the relation between ordered and disordered structures. A large change of r at phase transitions can be related to a relatively large change of the configurational entropy. A phase with a relatively high degree of order will have a maximum stability for the smallest possible value of $|\Delta r|$ at the order-disorder transition. Thereby, the disordered phase can gain only a minimum of configurational entropy. The vibrational and electronic contributions to the entropy should change simultaneously with the nearest-neighbour configuration. The partial entropy which arises from the volume expansion should change continuously if the volume changes continuously. At very low temperatures r is restricted to certain values, some of which are listed in Table 6. The dependence of r on H

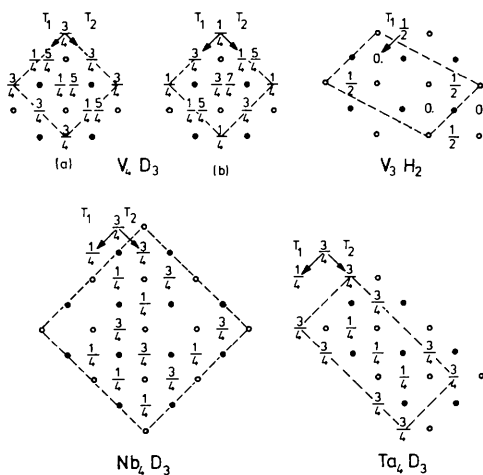


Fig. 6. Relation between the crystal structures of V₄D₃ (a) (Asano & Hirabayashi, 1973), V₄D₃ (b) (Westlake, Mueller & Knott, 1973), V₃H₂ (Hirabayashi, Yamaguchi, Asano & Hiraga, 1974), Nb₄D₃ (Somenkov, Petrunin, Shil'shtein & Chertkov, 1970) and Ta₄D₃ (Somenkov, Chervyakov, Shil'shtein & Chertkov, 1972).

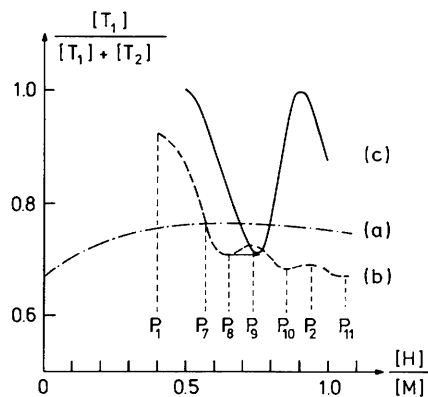


Fig. 7. Sketch for the variation of $r = [T_1]/([T_1] + [T_2])$ with H concentration (a) in the disordered α phase, (b) in MH_{0.5}-MH_{ss} below the order-disorder phase transition, and (c) at lower temperatures, where the γ-NbH structure type phase is stable. The arrow indicates the shift of r with decreasing temperature.

Table 7. Maxima P_7 , P_9 and minima P_8 , P_{10} for the order-disorder transition $MH_{0.5}-MH_{ss} \rightarrow \alpha-MH$ (Fig. 3)The list of references may be found in Table 2. c is in % $[H]/[M]$; T is in degrees K.

System	P_7		P_8		P_9		P_{10}		Reference
	c_7	T_7	c_8	T_8	c_9	T_9	c_{10}	T_{10}	
VH	~50	493 448	~61	~473					53
NbH	—	—	—	—	75	384	82	382	84
TaH	52	334	67	318					72

concentration within the non-stoichiometric regions is sketched in Fig. 7(a) for the disordered α phase, (b) for $MH_{0.5}-MH_{ss}$ below the order-disorder phase transition and (c) at lower temperatures, where the γ -NbH structure type phase is stable. The phase transition between the β -TaH and β -NbH structures occurs at $r = 0.71$. The V_4D_3 (b) and Nb_4D_3 structures have this ratio, whereas completely ordered and stoichiometric Ta_4D_3 possesses a slightly different value, $r = 0.67$. In Ta_4D_3 , therefore, a non-stoichiometric compound with $r = 0.71$ has the higher stability and transforms at a slightly higher temperature. A stepwise or continuous order-disorder phase transition of Ta_4D_3 was proposed from neutron powder diffraction data (Somenkov, Chervyakov, Shil'shtein & Chertkov, 1972; Asano *et al.*, 1975). Recent electron diffraction experiments on Ta_4H_3 single domains (Hauck, Schober & Schröck-Pauli, 1977), however, suggest that Ta_4H_3 transforms first to a second modification with the Nb_4H_3 structure, which becomes stable ~30 K below the phase transition to β -TaH at ~208 K. Both phase transitions are strongly dependent on composition. By similar considerations as for M_4H_3 phase transitions it can be explained that γ -NbH transforms to β -NbH at $[H]/[Nb] < 1$, where r should have a maximum in β - NbH_{ss} .

The phase transition of ordered $MH_{0.5}-MH_{ss}$ to completely disordered α -MH can also be accomplished by two steps with an intermediate partially ordered ε phase as indicated by previous investigations (Saba, Wallace, Sandmo & Craig, 1961; Pedersen, Krogdahl & Stokkeland, 1965; Ducastelle, Candron & Costa, 1970; Fukai & Kazama, 1975). This was confirmed by DTA measurements of the VH and TaH phase diagram (Asano, Abe & Hirabayashi, 1976b; Schober, 1977). From structural considerations it can be concluded that the single or two-step phase-transition boundary to the disordered α phase has at least one maximum of stability (P_7) for the β -TaH ($MH_{0.5ss}$) and one (P_9 or P_2) for the β -NbH (MH_{ss}) structure phase. At the lowest and highest H content of $MH_{0.5}-MH_{ss}$ the phases transform at lower temperatures (P_1 and P_{11}). Some values from phase diagrams recently determined are listed in Table 7. The line for the β -TaH/ β -NbH structure phase transition with $r = 0.71$ presumably

represents the minimum r value of $MH_{0.5}-MH_{ss}$ and therefore should end at P_8 , where $[\Delta r]$ is a maximum and the order-disorder transition has a minimum transition temperature. At higher temperatures the line is shifted to lower H content because of the increased disorder in $MH_{0.5}-MH_{ss}$.

A change of r with concentration and temperature should also be related to a change of the degree of lattice distortion. In the NbH system the orthorhombic phases β , ε and ζ -NbH show no change of domain structure at the phase transition (Schober, Linke & Wenzl, 1974) because of the close structural relation with about equal r values. The lattice constants of $MH_{0.5}-MH_{ss}$ should show some deviation from Vergard's rule, which, however, it has not as yet been possible to measure.

References*

- ARONS, R. R., BOHN, H. G. & LÜTGEMEIER, H. (1974). *J. Phys. Chem. Solids*, **35**, 207–214.
- ASANO, H., ABE, Y. & HIRABAYASHI, M. (1976a). *J. Phys. Soc. Jpn*, **41**, 974–976.
- ASANO, H., ABE, Y. & HIRABAYASHI, M. (1976b). *Acta Metall.* **24**, 95–99.
- ASANO, H. & HIRABAYASHI, M. (1973). *Phys. Status Solidi A*, **15**, 267–279.
- ASANO, H., ISHINO, Y., YAMADA, R. & HIRABAYASHI, M. (1975). *J. Solid State Chem.* **15**, 45–53.
- BRAUER, G. & MÜLLER, H. (1961). *J. Inorg. Nucl. Chem.* **17**, 102–107.
- CAMBINI, M., SERNEELS, R. & GEVERS, R. (1974). *Phys. Status Solidi A*, **21**, K51–59.
- CHERVYAKOV, A. YU., ENTIN, I. R., SOMENKOV, V. A., SHIL'SHTEIN, S. SH. & CHERTKOV, A. A. (1972). *Sov. Phys. Solid State*, **13**, 2172–2177.
- DUCASTELLE, F., CANDRON, R. & COSTA, P. (1970). *J. Phys. Chem. Solids*, **31**, 1247–1256.
- FUKAI, Y. & KAZAMA, S. (1975). *Scripta Metall.* **9**, 1073–1076.
- GISSLER, W. (1972). *Ber. Bunsenges. Phys. Chem.* **76**, 770–780.
- HAUCK, J. (1976). Frühjahrstagung der DPG, Freudenstadt 1976 and Europhysics Conference A-76, Amsterdam, 30 August–1 September.
- HAUCK, J. (1977a). *Acta Cryst.* **A33**, 720–723.

* See also Table 2.

- HAUCK, J. (1977b). Proc. 2nd Int. Conf. Hydrogen in Metals, Paris 6–10 June 1977, Abstr. 1 D 1.
- HAUCK, J., MIHELIC, M. & SCHRÖCK-PAULI, C. (1977). Unpublished.
- HAUCK, J. & SCHENK, H. J. (1976). *Proceedings of the Second International Conference on Crystal Field Effects in Metals and Alloys*, pp. 239–242. New York: Plenum.
- HAUCK, J. & SCHENK, H. J. (1977). *J. Less-Common Met.* **51**, 251–258.
- HAUCK, J., SCHOBER, T. & SCHRÖCK-PAULI, C. (1977). Unpublished.
- HIRABAYASHI, M., YAMAGUCHI, S., ASANO, H. & HIRAGA, K. (1974). *Proceedings of the International Symposium on Order-Disorder Transformations in Alloys, Tübingen, 1973*, pp. 266–302. Berlin: Springer.
- KEHR, K. W. (1975). Report JÜL-1211-FF. Institut für Festkörperforschung der KFA Jülich.
- LÜTGEMEIER, H., BONN, H. G. & ARONS, R. R. (1972). *J. Magn. Reson.* **8**, 80–86.
- MAELAND, A. J., GIBB, T. R. P. & SCHUMACHER, D. P. (1961). *J. Am. Chem. Soc.* **83**, 3728–3729.
- NAKAMURA, K. (1972). *Bull. Chem. Soc. Jpn*, **45**, 3356–3362.
- OATES, W. A., LAMBERT, J. A. & GALLAGHER, P. T. (1969). *Trans. Metall. Soc. AIME*, **245**, 47–54.
- PEDERSEN, B., KROGDAHL, T. & STOKKELAND, O. (1965). *J. Chem. Phys.* **42**, 72–79.
- PETRUNIN, V. F., SOMENKOV, V. A., SHIL'SHEIN, S. SH. & CHERTKOV, A. A. (1970). *Sov. Phys. Crystallogr.* **15**, 137–139.
- PICK, M. A. (1973). Report JÜL-951-FF. Institut für Festkörperforschung der KFA Jülich.
- ROWE, J. M., SKÖLD, K., FLOTOW, H. E. & RUSH, J. J. (1971). *J. Phys. Chem. Solids*, **32**, 41–54.
- SABA, W. G., WALLACE, W. E., SANDMO, H. & CRAIG, R. S. (1961). *J. Chem. Phys.* **35**, 2148–2155.
- SCHOBER, T. (1975). *Phys. Status Solidi A*, **30**, 107–116.
- SCHOBER, T. (1977). Proc. 2nd Int. Conf. Hydrogen in Metals, Paris 6–10 June 1977, Abstr. 1 D 2.
- SCHOBER, T. & HAUCK, J. (1976). Frühjahrstagung der DPG, Freudenstadt 1976; *IFF-Bulletin* **9/1**, 24.
- SCHOBER, T., LINKE, U. & WENZL, H. (1974). *Scripta Metall.* **8**, 805–811.
- SCHOBER, T. & WENZL, H. (1976). *Scripta Metall.* **10**, 819–822.
- SCHOBER, T. & WENZL, H. (1977). In *Hydrogen in Metals*, edited by G. ALEFELD & J. VÖLKL. Berlin: Springer.
- SOMENKOV, V. A., CHERVYAKOV, A. YU., SHIL'SHEIN, S. SH. & CHERTKOV, A. A. (1972). *Sov. Phys. Crystallogr.* **17**, 274–277.
- SOMENKOV, V. A., ENTIN, I. R., CHERVYAKOV, A. YU., SHIL'SHEIN, S. SH. & CHERTKOV, A. A. (1972). *Sov. Phys. Solid State*, **13**, 2178–2182.
- SOMENKOV, V. A., GURSKAYA, A. V., ZEMLYANOV, M. G., KOST, M. E., CHERNOPEKOV, N. A. & CHERTKOV, A. A. (1968). *Sov. Phys. Solid State*, **10**, 1076–1082.
- SOMENKOV, V. A., GURSKAYA, A. V., ZEMLYANOV, M. G., KOST, M. E., CHERNOPEKOV, N. A. & CHERTKOV, A. A. (1969). *Sov. Phys. Solid State*, **10**, 2123–2127.
- SOMENKOV, V. A., PETRUNIN, V. F., SHIL'SHEIN, S. SH. & CHERTKOV, A. A. (1970). *Sov. Phys. Crystallogr.* **14**, 522–530.
- TAKANO, S. & SUZUKI, T. (1974). *Acta Metall.* **22**, 265–274.
- WALTER, R. J. & CHANDLER, W. T. (1965). *Trans. Metall. Soc. AIME*, **233**, 762–765.
- WANAGEL, J., SASS, S. L. & BATTERMAN, B. W. (1972). *Phys. Status Solidi A*, **10**, 49–57.
- WESTLAKE, D. G., MUELLER, M. H. & KNOTT, H. W. (1973). *J. Appl. Cryst.* **6**, 206–216.
- ZANOWICK, R. L. & WALLACE, W. E. (1962). *J. Chem. Phys.* **36**, 2059–2062.

Acta Cryst. (1978). **A34**, 399–404

Crystal Perfection in a Non-Centrosymmetric Alloy. Refinement and Test of Twinning of the γ -Cu₃Al₄ Structure

BY LARS ARNBERG AND SVEN WESTMAN

Departments of Inorganic and Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-10691, Stockholm, Sweden

(Received 25 October 1977; accepted 15 November 1977)

The crystal structure of Cu₃Al₄ has been refined on the basis of 114 independent structure factors, averaged from a set of 2416 intensity measurements with a diffractometer on a spherical crystal of 0.05 mm diameter. Graphite-monochromatized Cu K α radiation was used. The final *R* value was 2.4% when corrections for absorption and extinction had been applied. Anisotropic thermal parameters were introduced and shown to be significant. The occurrence of coherently scattering antiphase domains was found to be less than 1%. All equivalent reflections and Friedel pairs were recorded with graphite-monochromatized Mo K α radiation for ten selected index combinations. Observed and calculated anomalous dispersion effects were found to match closely, indicating that incoherent twinning was also practically non-existent.