

## Structure of Deuterided NbVCo

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**Abstract**—A deuteride of composition NbVCoD<sub>2.5</sub> has been prepared at high deuterium pressures (up to  $p_{D_2} = 0.2$  GPa), and the positions of the metal and D atoms in its structure have been determined by x-ray and neutron diffraction techniques. The deuteride has the same structure as NbVCo (hexagonal Laves phase structure), with the V and Co atoms occupying positions  $2a$  and  $6h$  (B site in AB<sub>2</sub>) at random and the D atoms residing predominantly in positions  $24l$  and  $12k$ , typical of hydrogen in hexagonal Laves phases. This hydrogen distribution is due to the blocking of sites adjacent to those occupied by hydrogen.

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### INTRODUCTION

Many intermetallic compounds with the general formula AB<sub>2</sub> and Laves-phase structures are capable of reversibly absorbing significant amounts of hydrogen and are, therefore, of interest as hydrogen-storage materials [1]. According to experimental studies [2] and theoretical predictions [3], the hydrogen content of such intermetallics may attain 6.0–6.5 atoms per formula unit. The intermetallic compound ZrVCo with the hexagonal Laves phase structure *C14* readily absorbs hydrogen up to the composition AB<sub>2</sub>H<sub>3.3</sub> [4]. At the same time, the compound NbVCo, which has a similar structure and a slightly smaller (by 10%) unit-cell volume, can only be hydrided at high hydrogen pressures [5].

In this paper, we present x-ray and neutron diffraction studies of the structure of hydrided NbVCo synthesized at a high pressure.

### EXPERIMENTAL

The NbVCo alloy was prepared by arc-melting pure metals in an inert atmosphere and was then annealed at 1070 K for 240 h in an evacuated silica tube. The deuteride was synthesized at a deuterium pressure  $p_{D_2} = 0.2$  GPa in the high-pressure apparatus described earlier [6]. The resultant NbVCoD<sub>2.5</sub> sample was passivated by cooling and holding in liquid nitrogen. The amount of absorbed deuterium was determined by thermal desorption measurements. X-ray diffraction (XRD) patterns were collected on a ThermoARL diffractometer after heating the sample to room temperature. Neutron diffraction measurements were performed with a DISK diffractometer [7] at room tempe-

rature and 77 K in a purpose-designed cryostat.<sup>1</sup> Neutron diffraction and XRD results showed that the deuterium content of the deuteride dropped to the composition NbVCoD<sub>2.25</sub> as a result of heating and to NbVCoD<sub>2.05</sub> during subsequent long-term storage at room temperature. Structural data were analyzed by the Rietveld method using Fullprof and Rietan programs.

### RESULTS AND DISCUSSION

XRD examination showed that the NbVCo sample was phase-pure and had the *C14* structure. Its lattice parameters (Table 1) agree with those reported in the literature [8].

A noteworthy feature of NbVCo is that V and Co, elements close in atomic number, differ little in x-ray atomic scattering factor and that vanadium atoms are invisible to neutrons. Using both XRD and neutron diffraction (Tables 2, 3; Figs. 1, 2), we found that the Nb atoms in the as-prepared intermetallic compound occupied position  $4f$  (the A site in AB<sub>2</sub>), while the V and Co atoms occupied positions  $2a$  and  $6h$  (the B site in the hexagonal Laves phase structure) at random, according to the composition of the compound.

The deuterium in NbVCoD<sub>2.5</sub> was found to occupy all positions with A<sub>2</sub>B<sub>2</sub> coordination, characteristic of hexagonal Laves phases ( $l$ ,  $k$ ,  $h_1$ , and  $h_2$ ), but with different occupancies (Table 2). Most of the hydrogen atoms reside in positions  $l$  and  $k$  (in the ratio 4 : 1), while positions  $h$  contain 0.84 hydrogen atoms per unit cell. With decreasing hydrogen content, the number of hydrogens in positions  $h$  drops to 0.6 per unit cell.

<sup>1</sup> Neutron diffraction measurements were made at the Russian Research Centre Kurchatov Institute.

**Table 1.** Lattice parameters of NbVCo and NbVCoD<sub>2.5</sub>

Composition	<i>a</i> , nm	<i>c</i> , nm	<i>V</i> , nm <sup>3</sup>	Δ <i>V/V</i> , %
XRD data				
NbVCo	0.4932(2)	0.803(1)	16.9	–
NbVCoD <sub>2.5</sub>	0.5129(2)	0.838(3)	19.1	13.0
Neutron diffraction data				
NbVCo	0.4916(2)	0.803(2)	16.8	–
NbVCoD <sub>2.5</sub>	0.5129(2)	0.836(2)	19.0	13.1

**Table 2.** Crystal data for NbVCo and NbVCoD<sub>2.5</sub>

Atom	Position	<i>Z</i>	<i>x</i>	<i>y</i>	<i>z</i>
XRD data					
NbVCo					
Nb	4 <i>f</i>	4.00(2)	0.333	0.666	0.064(2)
Co(1)	2 <i>a</i>	0.98(3)	0	0	0
V(1)	2 <i>a</i>	1.01(3)	0	0	0
Co(2)	6 <i>h</i>	3.00(2)	0.830(2)	0.660(2)	0.25
V(2)	6 <i>h</i>	2.88(2)	0.830(2)	0.660(2)	0.25
<i>R<sub>p</sub></i> = 9.7%, <i>R<sub>w</sub></i> = 7.5%					
NbVCoD <sub>2.5</sub>					
Nb	4 <i>f</i>	4.00(3)	0.333	0.666	0.067(3)
Co(1)	2 <i>a</i>	1.20(3)	0	0	0
V(1)	2 <i>a</i>	1.08(2)	0	0	0
Co(2)	6 <i>h</i>	2.82(1)	0.831(2)	0.662(2)	0.25
V(2)	6 <i>h</i>	2.94(2)	0.831(2)	0.662(2)	0.25
<i>R<sub>p</sub></i> = 9.4%, <i>R<sub>w</sub></i> = 8.6%					
Neutron diffraction data for deuterated NbVCo					
Nb	4 <i>f</i>	4.00(1)	0.333	0.666	0.087(3)
Co(1)	2 <i>a</i>	0.90(2)	0	0	0
V(1)	2 <i>a</i>	1.02(3)	0	0	0
Co(2)	6 <i>h</i>	3.30(1)	0.833(1)	0.666(1)	0.25
V(2)	6 <i>h</i>	2.94(1)	0.833(1)	0.666(1)	0.25
D(1)	24 <i>l</i>	6.48(2)	0.026(2)	0.338(3)	0.549(3)
D(2)	12 <i>k</i> <sub>2</sub>	1.68(1)	0.410(2)	0.820(2)	0.610(3)
D(3)	6 <i>h</i> <sub>1</sub>	0.48(3)	0.429(2)	0.858(2)	0.25
D(4)	6 <i>h</i> <sub>2</sub>	0.36(2)	0.201(2)	0.402(2)	0.25
<i>R<sub>p</sub></i> = 10.4%, <i>R<sub>w</sub></i> = 9.5%, Nb <sub>4.00</sub> V <sub>3.96</sub> Co <sub>4.20</sub> D <sub>9.00</sub>					

Note: *Z* is the number of atoms in the specified position per unit cell.

The present results indicate that the hydrogen occupancy on the A<sub>2</sub>B<sub>2</sub> tetrahedral sites decreases in the order 24*l* > 12*k*<sub>2</sub> > 6*h*<sub>1</sub> > 6*h*<sub>2</sub>. Similar results were reported earlier by Souberoux et al. [4] for hydrided ZrVCo. The 6*h* hydrogen content is rather low, on the

order of one hydrogen atom per unit cell, varies little with temperature, and is obviously determined by the deviation from the ideal stoichiometry (AB<sub>2</sub>D<sub>2</sub> for NbVCo and AB<sub>2</sub>D<sub>3</sub> for ZrVCo). The superstoichiometric hydrogen content (about one hydrogen atom per unit

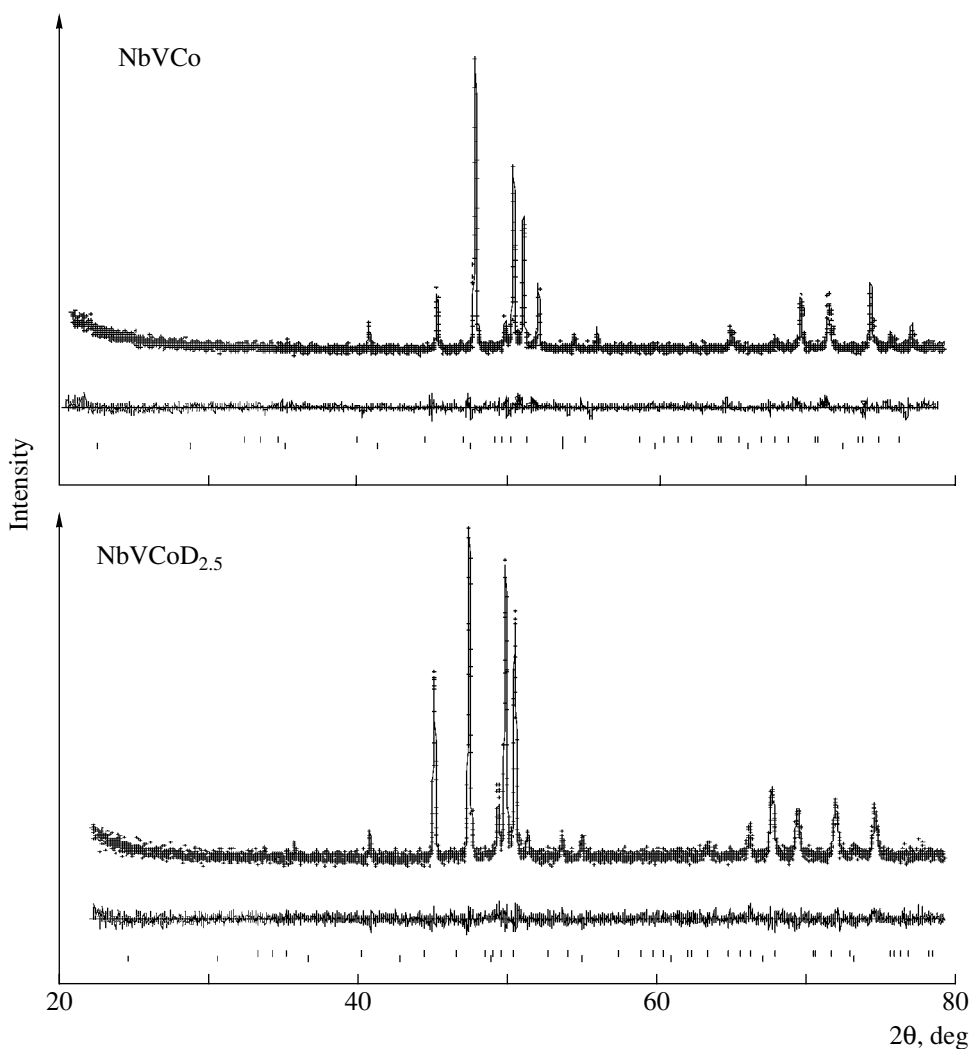


Fig. 1. XRD patterns of NbVCo and NbVCoD<sub>2.5</sub>.

cell) corresponds approximately to the hydrogen occupancy on the  $6h$  sites. Thus, it is reasonable to expect that, in the stoichiometric hydride, only positions  $24l$  and  $12k_2$  will be occupied.

In the hexagonal structure  $C14$ , there are slightly distorted hexagons made up of hydrogens in positions  $k$ ,  $l$ ,  $h_1$ , and  $h_2$  around each A atom, which we will call hydrogen complexes by analogy with coordination

Table 3. Interatomic distances in NbVCoD<sub>2.5</sub>

Atoms	$\delta$ , nm	Atoms	$\delta$ , nm	Atoms	$\delta$ , nm
Nb–Nb	0.312	Nb–D(3)	1.91	Co, V–D(4)	0.164
Nb–Co, V	0.300	Nb–D(4)	1.97	D(1)–D(1)	0.281
Co, V–Co, V	0.257	Co, V–D(1)	0.170	D(2)–D(2)	0.267
Nb–D(1)	0.194	Co, V–D(2)	0.165	D(3)–D(3)	0.230
Nb–D(2)	0.191	Co, V–D(3)	0.170	D(4)–D(4)	0.226
Nb–Nb*	0.298	Co–Co*	0.265	V–V*	0.275
Nb–D*	0.160	Co–D*	0.186	V–D*	0.140–0.158

\* Interatomic distances in NbD<sub>0.8</sub>, CoD<sub>0.8</sub>, and VD<sub>0.8</sub> [9].

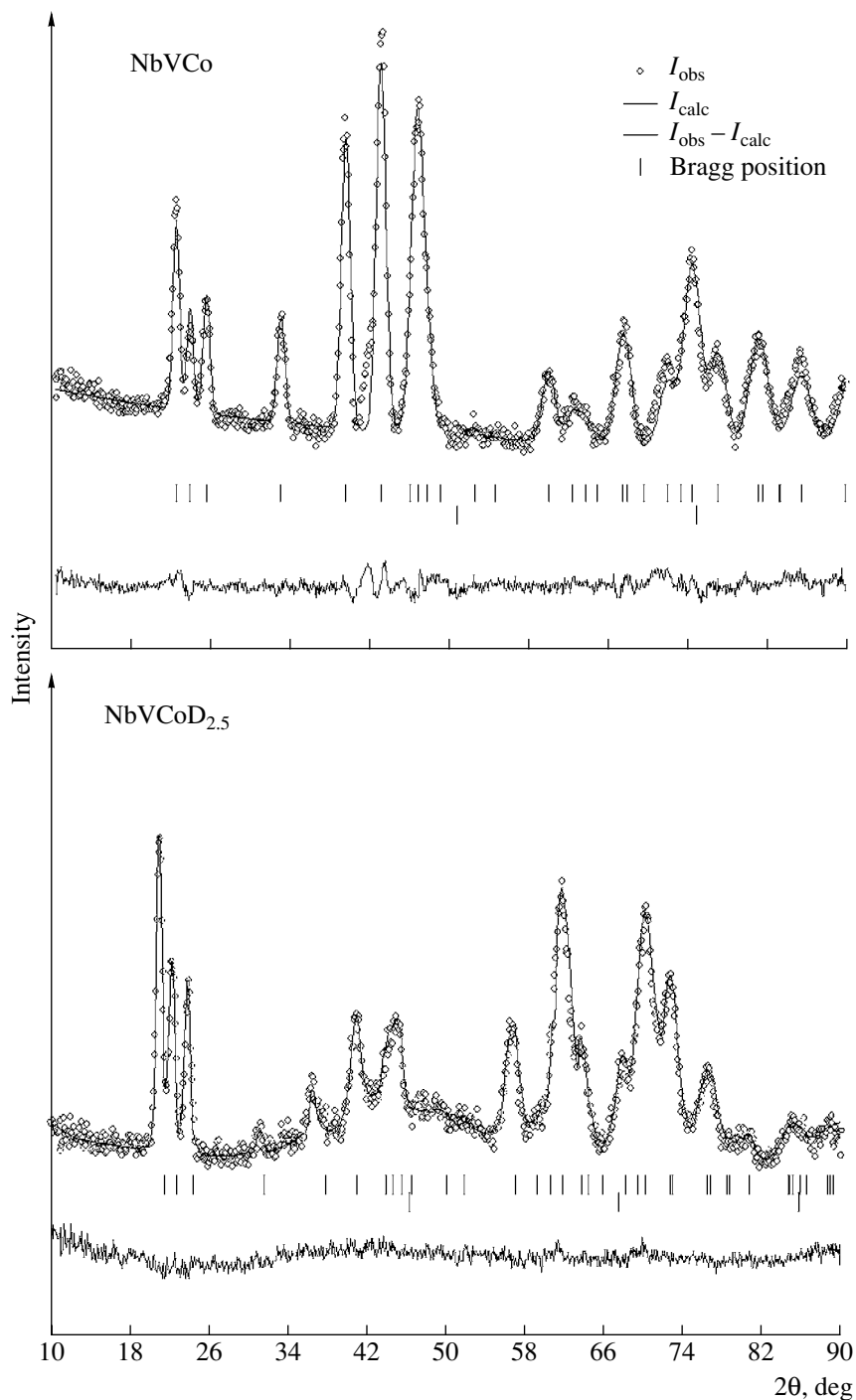


Fig. 2. Neutron diffraction patterns of NbVCo and NbVCoD<sub>2.5</sub>.

compounds (Fig. 3). Each A atom plays the role of the central metal atom in the  $[AH_x]^n$  complex. Consider the possible hydrogen distributions over the sites in question in terms of the interstice blocking model, formulated for both binary metal hydrides [9, 10] and intermetallic hydrides [2, 11]. This model takes into account the short-range order in the arrangement of interstitial atoms: the probability that a hydrogen atom will reside

in a site adjacent to an occupied site is low or zero. According to experimental data, the blocking radius  $R_0$  in various hydrides ranges from 0.18 to 0.22 nm, with an average of 0.2 nm.  $R_0$  should be compared to the intersite distances in the  $k-l$  and  $h-h$  hexagonal complexes (Tables 4, 5; Fig. 3), which depend on the lattice parameters of the intermetallic compound, the positional parameters of hydrogen in the structure of the

hydride, and hydrogen content. If the hydrogen distribution in such complexes were uniform (no blocking), the fraction of occupied  $k$  sites in the  $k$ - $l$  complex would be determined by the site multiplicity and would be  $1/2$ . If the blocking radius  $R_0$  of hydrogen atoms in position  $l$  is greater than the nearest neighbor distance but smaller than the second neighbor distance (Fig. 3), the fraction of occupied  $k$  sites must be  $1/3$ . Finally, if  $R_0$  is greater than the second neighbor distance, the fraction of occupied  $k$  sites must be zero. A similar situation holds for the  $h$ - $h$  complexes. Thus, the presence of hydrogen in a single position is only likely for large blocking radii, dense lattices, and low hydrogen contents. Otherwise, hydrogen would be expected to occupy several positions.

In the intermetallic hydride studied here, the occupied  $k$  and  $l$  sites are approximately in the ratio 1 : 4, like in hydrided ZrVCo. This implies that the blocking radius is on the order of 0.19 nm, so that the sites adjacent to a hydrogen atom in position  $l$  are fully blocked (unoccupied), while the second neighbor sites are blocked only partially. These conclusions are supported by interstitial hydrogen diffusion data [12], which indicate that the jump distance in hexagonal ZrCr<sub>2</sub>H<sub>0.5</sub> (C14 structure), as determined using quasi-elastic neutron scattering, is  $\langle \bar{r} \rangle = 0.116$  nm. This is equal to the weighted average of the distances to the unoccupied (blocked) nearest neighbor sites. Thus, the hierarchy in the hydrogen occupancy on different sites in hexagonal Laves phases reflects the short-range order (blocking) in the arrangement of hydrogen atoms (given that all of the A<sub>2</sub>B<sub>2</sub>-coordinated interstitial sites are close in

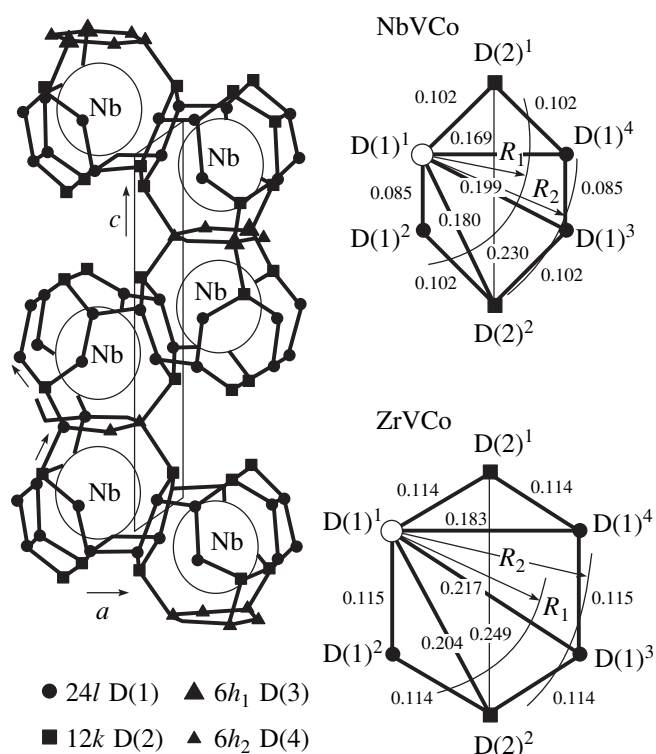


Fig. 3. Hydrogen sites in the structure of NbVCoD<sub>2.5</sub>.

energy). It is worth noting in this context that the concept of stoichiometry is more complex for mixed-metal hydrides compared to simple interstitial metallic solid solutions: in contrast to binary hydrides, the stoichiom-

Table 4. Intersite distances in NbVCoD<sub>2.5</sub>

Atoms	$\delta$ , nm	Atoms	$\delta$ , nm	Atoms	$\delta$ , nm
Nb-Nb	0.312	Co-V	0.256	D(1) <sup>1</sup> -D(1) <sup>4</sup>	0.169*
Nb-Co	0.300	V-V	0.257	D(1) <sup>1</sup> -D(2) <sup>2</sup>	0.180*
Nb-V	0.301	D(1) <sup>1</sup> -D(1) <sup>2</sup>	0.085*	D(1) <sup>1</sup> -D(1) <sup>3</sup>	0.199**
Co-Co	0.257	D(1) <sup>1</sup> -D(2) <sup>1</sup>	0.102*	D(2) <sup>1</sup> -D(2) <sup>2</sup>	0.230

\* Fully blocked sites.

\*\* Partially blocked sites.

Table 5. Intersite distances in ZrVCoD<sub>3.3</sub> [4]

Atoms	$\delta$ , nm	Atoms	$\delta$ , nm	Atoms	$\delta$ , nm
Zr-Zr	0.331	Co-V	0.273	D(1) <sup>1</sup> -D(1) <sup>4</sup>	0.183*
Zr-Co	0.316	V-V	0.273	D(1) <sup>1</sup> -D(2) <sup>2</sup>	0.204**
Zr-V	0.317	D(1) <sup>1</sup> -D(2) <sup>1</sup>	0.114*	D(1) <sup>1</sup> -D(1) <sup>3</sup>	0.217
Co-Co	0.261	D(1) <sup>1</sup> -D(1) <sup>2</sup>	0.115*	D(2) <sup>1</sup> -D(2) <sup>2</sup>	0.249

\* Fully blocked sites.

\*\* Partially blocked sites.

etry of intermetallic hydrides is determined not by the ratio of the number of interstices to that of metal atoms but by the ratio of the number of metal complexes to that of hydrogen complexes with allowance made for the number of inequivalent sites and the average hydrogen concentration in the complex (e.g.,  $AB_2(D^l(1)D^k(3)x)$ ).

### CONCLUSIONS

A deuteride with the limiting composition  $NbVCoD_{2.5}$  was prepared at high deuterium pressures, and its structure was determined by XRD and neutron diffraction. The results indicate that the deuterium atoms in this intermetallic deuteride reside predominantly in positions  $l$  and  $k$ , and that only the hyperstoichiometric deuterium occupies positions  $h$ . The observed hierarchy in the hydrogen occupancy on different sites in hexagonal Laves phases can be understood in terms of fully and partially blocked sites adjacent to a site occupied by hydrogen in a hexagonal complex.

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