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# INTERSTITIAL SITE OCCUPATION IN ZrNiH*

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## ABSTRACT

In-situ x-ray diffraction measurements during step-wise hydrogenation of the intermetallic compound ZrNi have confirmed the existence of a stable compound ZrNiH. Neutron diffraction measurements on ZrNiD have allowed a determination of the site occupied by D. This site is tetrahedrally coordinated by four Zr atoms as predicted earlier from a model based solely on geometric considerations. Occupation of this site causes the lattice to distort from an orthorhombic to a triclinic structure. The trihydride is formed when two completely different types of sites are filled, to the exclusion of the sites occupied originally, causing reversion of the lattice to an orthorhombic structure. Other confirmed predictions of the geometric model are discussed.

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## Introduction

A model, based on hole sizes and H-H distances, was recently proposed by Westlake (1) to rationalize the observed (2-5) stoichiometry and H-site occupation in $ZrNiH_3$. Further, he predicted that a stable compound ZrNiH should exist and that, in the monohydride, H would most probably be found in those sites tetrahedrally coordinated by four Zr atoms. Pressure-composition isotherms of the ZrNi-H system (2) gave some indication of the existence of a monohydride. The present collaborative investigation was undertaken to confirm or deny its existence by the use of "in-situ" x-ray diffraction and to test the H-site prediction (1) by the use of neutron diffraction.

## Experimental

Westinghouse crystal bar Zr was rolled to 6mm diameter and given a zone refining treatment of four passes. The resulting rod contained 200 at. ppm Hf and only 8 at. ppm Fe. A Ni rod (Marz grade) of the same diameter

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was obtained from Materials Research Corporation. The intermetallic compound ZrNi was prepared by arc-melting with care to achieve homogeneity. Combining analyses of the two metals, we conclude that the interstitial impurity content of the intermetallic compound could not exceed 2000 at. ppm.

ZrNiD was prepared at ANL by reaction of the ZrNi with a measured quantity of $D_2$ gas while cooling from 1075 K to 375 K. Purified $D_2$, obtained by thermal decomposition of $UD_3$, was used in this reaction. We determined gravimetrically that the desired stoichiometry had been achieved to within less than 1%. This sample was powdered under an argon atmosphere and sealed in a vanadium capsule for neutron diffraction experiments, which were performed with the pulsed neutron source ZING P' (6) at ANL.

At NRIM, another sample of ZrNi, from the same arc-melted button, was reacted with gaseous $H_2$ at 533 K and cooled to room temperature. The specimen was pulverized under an argon atmosphere. The resulting powder (under 250 mesh) was dehydrogenated and residual stress was relieved by heating at 1025 K in a vacuum of $1.3 \times 10^{-4}$ Pa. An anneal at 575 K had failed to remove all of the hydrogen, and even an anneal at 775 K did not completely relieve the residual strain. The powdered and stress-relieved sample of ZrNi was mounted on a specially designed sample holder in an argon atmosphere. The "in-situ" x-ray diffraction measurements, with $\lambda = 1.54178$ Å, were made under various $H_2$ pressures at 533 K. Measurements at room temperature were not possible because the equilibrium $H_2$ pressure for ZrNiH is too low; pressures lower than 6.6 kPa could not be controlled properly in the autoclave, which has been described elsewhere (7).

## Results and Crystallography

### A. Lattices of the Hydrides of ZrNi

The pulverized specimen of ZrNi was studied with x-rays at several steps

of its hydrogenation. The spectra corresponding to ZrNi, ZrNiH and $ZrNiH_3$ are shown in Fig. 1, and the respective $H_2$ pressures are given. At a pressure of 0.152 MPa, the patterns of both ZrNiH and $ZrNiH_3$ were apparent, but between 0.223 and 5.0 MPa only the pattern of $ZrNiH_3$ could be detected. For both ZrNiH and $ZrNiH_3$, changing the pressure caused virtually no changes in positions of the lines. The spectra of ZrNi and of $ZrNiH_3$ were indexed according to orthorhombic lattices (Table I) in agreement with previously published results (3,4,8). The ZrNiH spectrum, on the other hand, exhibited splitting of the orthorhombic lines, which indicates that it has a triclinic lattice.

The specimen of ZrNiD was studied by neutron scattering. Part of the observed time-of-flight spectrum is shown in Fig. 2. The neutron spectrum of ZrNiD and the X-ray spectrum of ZrNiH were indexed according to a triclinic lattice (Table I). In both spectra, reflections of residual ZrNi(H) or ZrNi(D) (i.e., solid solution of H or D in α ZrNi) were observed and indexed according to the orthorhombic lattice (Table I). The resolution of the x-ray spectrum was insufficient to allow any conclusion regarding an isotope effect on the volume expansion of the lattice due to solute H(D).

B. The Positions of D Atoms in ZrNiD

In a previous publication (1), five inequivalent interstitial sites in ZrNi were considered on the basis of hole size and H-H distance for possible occupancy by hydrogen (Fig. 3). In the present work, the structure factors for neutron scattering by ZrNiD were calculated for the five alternative sites of the D atoms (Table II). Cmcm symmetry (9) was assumed for ZrNiD in these calculations. This assumption is justified as an approximation, because the triclinic distortion is not large and the split lines (e.g., 130, $1\bar{3}0$) are of approximately equal intensities. The $jF^2$ were calculated (from the structure

factors of Table II) for the five alternative sites and compared with the corresponding observed $jF^2$ (Table III). Obviously, there is good agreement with the calculated $jF^2$ for the first alternative and extremely poor agreement for the other four alternatives. Variations of the position parameter within a physically meaningful range cannot make any of these four alternatives agree with the observed data. The conclusion of the present study is, therefore, that the D atoms occupy the first alternative site (Table II), as predicted (1).

## Discussion

By obtaining x-ray diffraction spectra at 533 K under various $H_2$ pressures, we have unequivocally established the existence of a stable phase, ZrNiH, that can coexist either with the solid solution of H in ZrNi or with $ZrNiH_3$. Three other observations of the present study are also in accord with the predictions made earlier (1):

First, there were no shifts in positions of x-ray peaks as a function of pressure for either ZrNiH or $ZrNiH_3$, which seems to indicate very low (or no) solubility for H in both these phases. The reported (8) observation of $ZrNiH_{3.4}$ at T = 298 K with $P_{H_2}$ = 0.4 MPa cannot be attributed, therefore, to a hyperstoichiometric trihydride. Furthermore, one of the present experiments contradicts this report of $ZrNiH_{3.4}$. With T = 296 K and $P_{H_2}$ = 5 MPa, our observed lattice parameters did not exceed those expected for $ZrNiH_3$. It seems no longer necessary, therefore, to postulate (1) a substoichiometric $ZrNiH_4$ to explain the reported (8), but unsubstantiated, $ZrNiH_{3.4}$.

Second, the dihydride, $ZrNiH_2$, does not exist.

Finally, D was found by neutron diffraction to occupy all the interstitial sites in the lattice of ZrNiD that are tetrahedrally coordinated by four Zr atoms.

The lattice of NiZr is shown schematically in Fig. 3. It is known, now, that all sites of the type shown as diamonds are occupied by D in ZrNiD. This set of sites has the largest hole radius, 0.6Å, and the greatest H-H distance, 2.76 Å. Analysis of the combined x-ray and neutron results has revealed that occupation of this site by H(D) causes a distortion of the lattice to a triclinic structure.

During transformation of the monohydride to the trihydride, both kinds of sites represented by triangles (both base-up and base-down) in Fig. 3 become filled (4,5). This cannot be accomplished without emptying all the "diamond" sites, because, otherwise, the H-H distances would be far too short (1). The present results confirm that when the "diamond" sites are emptied and both sets of sites represented by triangles are filled the lattice reverts to an orthorhombic structure.

## Conclusion

X-ray and neutron diffraction experiments confirm the predictions of a model (1) based on geometric considerations regarding both stoichiometries and sites occupied by H in hydrides of the intermetallic compound ZrNi. Application of this simple model to other compounds with different structures and subsequent experimental testing of the results would seem to be warranted.

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FIGURE CAPTIONS

Fig. 1. X-ray (CuKα) spectra taken at 533 K. a) in vacuum, b) hydrogen pressure = 0.113 MPa, c) hydrogen pressure = 0.223 MPa. The reflections marked * belong to the sample holder. The reflections marked α belong to residual solid solution of H in ZrNi, ZrNi(H).

Fig. 2. Part of the time of flight spectrum of neutrons scattered by ZrNiD. Scattering angle is 160° and the counts were accumulated over 1.64 x $10^6$ pulses.

Fig. 3. Orthorhombic lattice of ZrNi. Zr, ○ ; Ni, □ . Examples of the interstitial sites corresponding to the numbers 1 through 5 in Table II are shown as ◆ , ▲ , ▼ , ● and ★ , respectively. Pentagonal symbols denote face centers.

Table I. Lattice parameters for the hydrides of ZrNi

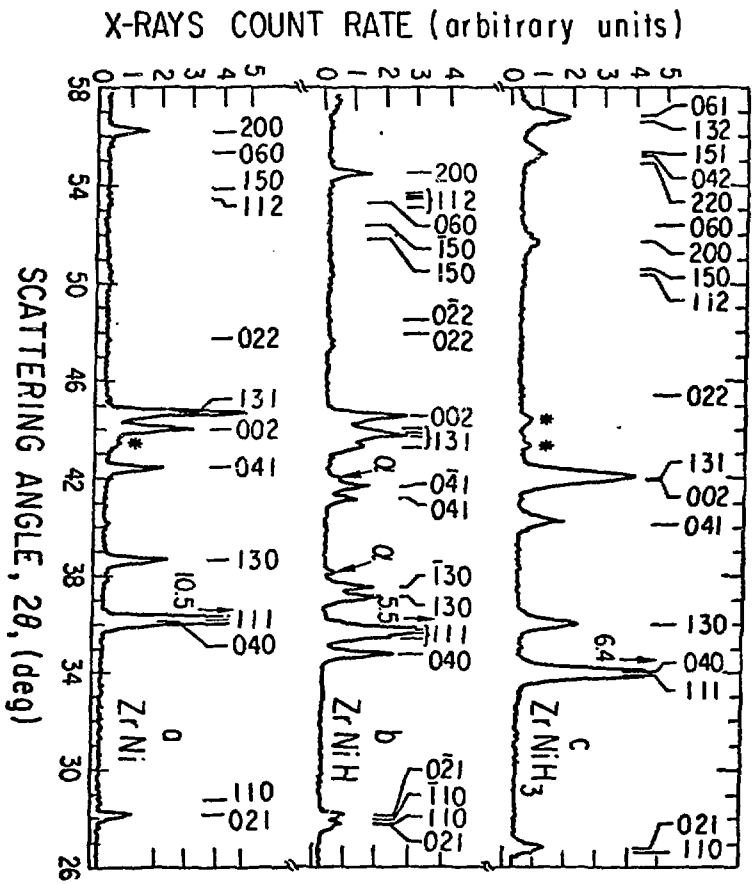
| COMPOUND | $a_o$(Å) [α(°)] | $b_o$(Å) [β(°)] | $c_o$(Å) [γ(°)] | VOLUME (Å$^3$) |
|---|---|---|---|---|
| ZrNi | 3.272±0.005 | 9.965±0.005 | 4.115± 0.005 | 134.2±0.4 |
| ZrNi(H)<br>ZrNi(D) | 3.28 ± 0.01 | 10.12 ± 0.01 | 4.05 ± 0.01 | 134.6±0.7 |
| ZrNiH<br>ZrNiD | 3.367± 0.002<br>[89.18 ± 0.03] | 10.313±0.004<br>[89.60 ±0.05] | 4.063± 0.002<br>[89.43 ± 0.03] | 141.1±0.2 |
| $ZrNiH_3$ | 3.53 ± 0.01 | 10.48 ± 0.02 | 4.30 ± 0.02 | 159.1±1.5 |

Table II. Input for the calculation of the structure factor of ZrNiD for the five alternative sites of D

| ELEMENT | b | ALTERN | SITE | x | y | z | F |
|---|---|---|---|---|---|---|---|
| Zr | 0.70 | - | 4c | 0 | -0.140 | 0.25 | $4b\cos 2\pi(ky + \frac{\ell}{4})$ |
| Ni | 1.03 | - | 4c | 0 | -0.429 | 0.25 | |
| | | 1 | 4c | 0 | 0.2152 | 0.25 | |
| | | 2 | 4c | 0 | 0.067 | 0.25 | |
| D | 0.67 | 3 | 8f | 0 | -0.312 | 0.509 | $4b\cos 2\pi(ky+\frac{\ell}{4})\cos 2\pi\ell(z-\frac{1}{4})$ |
| | | 4 | 8f | 0 | 0.4283 | 0.3833 | |
| | | 5 | 8e | 0.2275 | 0 | 0 | $4b\cos\pi\frac{\ell}{2}\cos 2\pi hx$ |

Table III. Calculated and observed structure factors of ZrNiD for the five alternative sites of D. A is a scale factor such that $AjF^2_{131} = 1000$.

| hkℓ | j | $AjF^2$ CALCULATED 1 | 2 | 3 | 4 | 5 | OBSERVED |
|---|---|---|---|---|---|---|---|
| 110 | 4 | 16 | 17 | 148 | 727 | 42 | 45 ± 8 |
| 021 | 4 | 27 | 384 | 2 | 35 | 4 | |
| 040 | 2 | 14 | 454 | 101 | 326 | 6 | 20 ± 5 |
| 111 | 8 | 31 | 1026 | 491 | 765 | 539 | 35 ± 5 |
| 130 | 4 | 227 | 427 | 15 | 608 | 159 | 285 ± 20 |
| 041 | 4 | 80 | 3790 | 462 | 423 | 437 | 135 ± 15 |
| 131 | 8 | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 ± 30 |
| 002 | 2 | 412 | 2839 | 154 | 853 | 803 | 440 ± 20 |
| 022 | 4 | 1 | 941 | 267 | 139 | 392 | 0 ± 10 |
| 112 | 8 | 33 | 34 | 29 | 220 | 84 | 50 ± 20 |
| 200 | 2 | 412 | 2930 | 785 | 1777 | 165 | 360 ± 20 |
| A | | 2.233 | 15.90 | 4.259 | 9.643 | 4.354 | 0.3189 |

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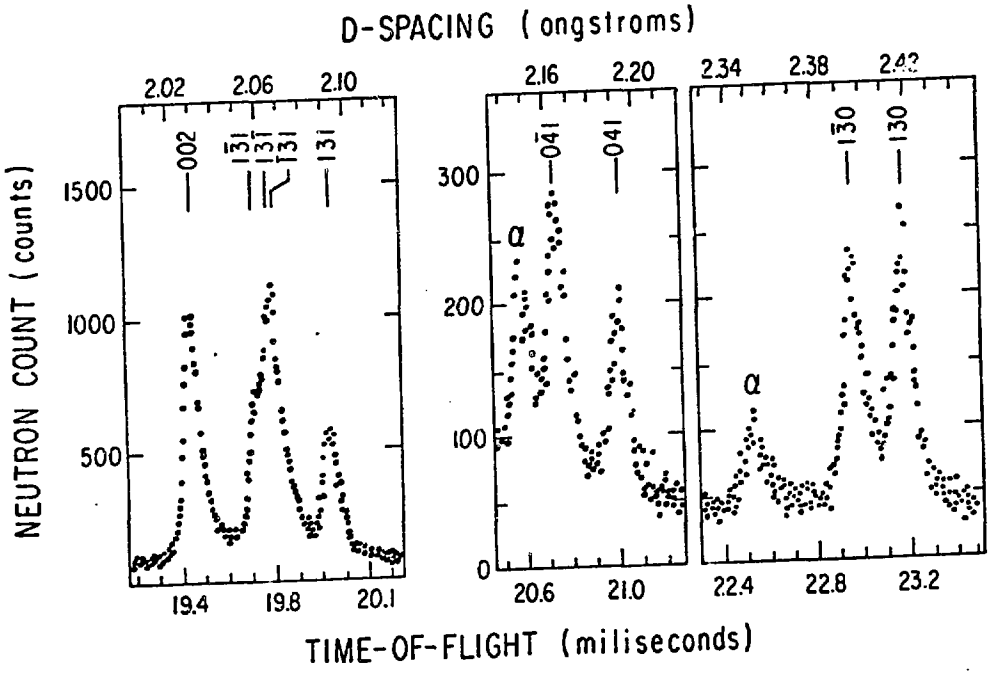


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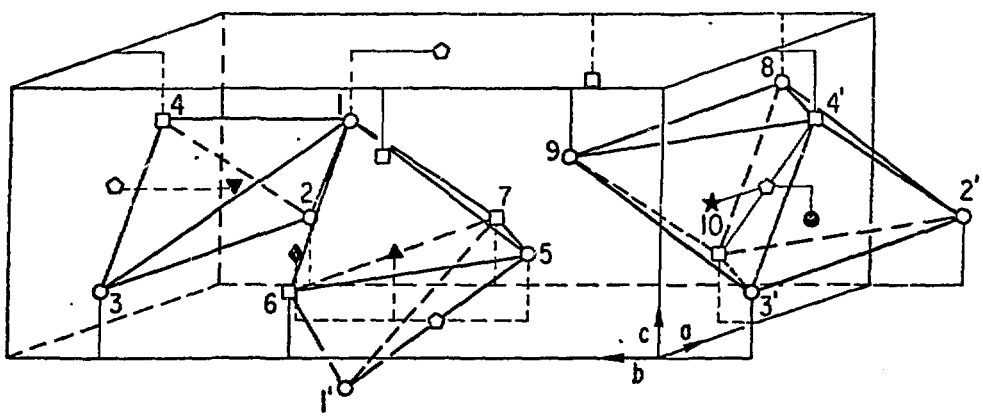


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