

## Local Hydrogen Vibration in Crystalline and Amorphous Zirconium-Nickel Hydrides

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Local Hydrogen Vibration in Crystalline and Amorphous  
Zirconium-Nickel Hydrides\*

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Synopsis

The energy eigenvalues of the localized hydrogen vibration modes in both crystalline and amorphous zirconium-nickel hydrides are determined by means of the TOF neutron inelastic scattering experiment. A giant peak with maximum at 114 meV is observed for crystalline  $\text{ZrNiH}_{2.8}$ . The spectrum of amorphous  $\text{ZrNiH}_{1.8}$  shows a very broad peak with maximum at 113 meV; the FWHM is about 100 meV, which is almost double of that for the crystalline specimen. The broad peak for the amorphous hydride is found to split apparently rather than for the crystal.

I. Introduction

Hydrogen atoms tend to locate at interstitial sites in metallic materials. Interatomic bonds among hydrogen atoms and those between hydrogen and metal atoms are generally weaker than the metallic bonds. A hydrogen atom has only light mass comparing with the host metal atoms. Thermal vibration of hydrogen atoms can not be transmitted to the host lattice and the vibration is localized, because of the fact that interstitial hydrogen atoms introduce weak dynamical perturbation field around the hydrogen sites. The energy eigenvalues of such localized modes exist out of the density of vibration-state for the host lattice. The localized hydrogen vibration modes in binary metal-hydrogen systems have been studied by many investigators with neutron inelastic scattering measurements, but little work has been made on hydrides of intermetallic compounds<sup>1)</sup>.

Amorphous alloys have been recently received considerable

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attention as potential hydrogen storage materials<sup>2,3</sup>); a larger number of hydrogen sites in a unit volume may be involved in the amorphous state than in the crystalline state. On the other hand, the possibility to find a specific atomic configuration, in which a hydrogen atom can be located appropriately, decreases in the amorphous state because of the random atomic arrangement. Recently Rush, Row and Maeland<sup>4</sup>) have investigated the localized hydrogen vibration modes of copper-titanium hydrides in both crystalline and amorphous states. They have found a quite broad peak of neutron inelastic spectrum for amorphous  $\text{TiCuH}_{1.3}$  at roughly the same energy as a sharp peak for crystalline  $\text{TiCuH}_{0.93}$ . Their pioneer work has disclosed that the neutron inelastic spectra can provide an unusual probe of the local environments of hydrogen sites in amorphous alloys.

In the present work, we intend to determine energy eigenvalues of the localized vibration modes in crystalline and amorphous zirconium-nickel hydrides by means of the neutron inelastic scattering experiment. The purpose of the paper is to figure the difference in the local environments around hydrogen in the crystalline and amorphous states of zirconium-nickel hydrides.

## II. Structure of Zirconium-Nickel Hydride

In this paper, we study the hydrides of equiatomic zirconium-nickel alloy. The equilibrium phase diagram of binary zirconium-nickel system is shown in Fig. 1<sup>5</sup>). Aoki, Horata and Masumoto<sup>3</sup>) succeeded to obtain the amorphous alloys with the chemical compositions marked by filled circles in the figure.

Among many intermetallic compounds of the zirconium-nickel system, the crystal structure of  $\text{ZrNi}$  and the hydrogen location in it have

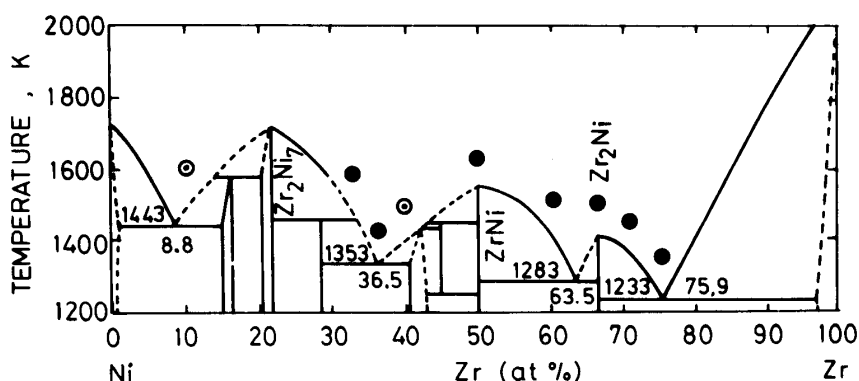


Fig. 1. Phase diagram of Zr-Ni alloy<sup>5</sup>). Double circles indicate the amorphous specimens containing a trace of crystals<sup>3</sup>).

been investigated most extensively. The structure of ZrNi is base-centered orthorhombic as shown in Fig. 2 (space group Cmcm, No. 63)<sup>6)</sup>. Except for small changes in positional parameters and a lattice expansion, the metal sublattice remains unchanged with addition of hydrogen up to NiZrH<sub>3</sub><sup>7)</sup>. The lattice parameters at H/Zr = 2.7 are  $a = 3.53 \text{ \AA}$ ,  $b = 10.48 \text{ \AA}$  and  $c = 4.30 \text{ \AA}$ <sup>6)</sup>. The lattice parameters in the figure are the estimated values at the composition of ZrNiH<sub>3.0</sub> by Westlake<sup>8)</sup>. The positional parameters of metal and hydrogen atoms refined by X-ray and neutron diffraction work of Irodova et al.<sup>9)</sup> are listed in Fig. 2.

The hydrogen atoms in ZrNi locate at so called b-sites and c-sites<sup>7,8,9)</sup>. The b-site is a four-fold position (4c) with a  $y$  parameter, and has a five-atoms coordination with the point symmetry  $C_{2v}$  (mm). The c-site is a eight-fold position (8f) with  $y$  and  $z$  parameters, and has a four-atoms coordination with the symmetry  $C_s$  (m). Three zirconium atoms are coordinated at both sites. It is not clear whether the three-zirconium configurations at both sites are accidental coincidence or not, but it is worthwhile to be acknowledged.

### III. Neutron Spectroscopy and Specimen Preparation

A time-focused crystal analyzer<sup>10,11)</sup> with an invert geometry has been utilized for the present work. Schematic arrangement of the spectrometer installed at Tohoku Linac is shown in Fig. 3. A pulsed thermal neutron beam, of which the energy value is repeatedly and chronologically changing, irradiates a sample. An analyzer crystal of pyrolytic graphite and a cooled beryllium filter are placed in front of the He<sup>3</sup> counter bank for the purpose to filtrate only 4 meV neutrons. Scattered 4 meV neutrons are counted as a function of time.

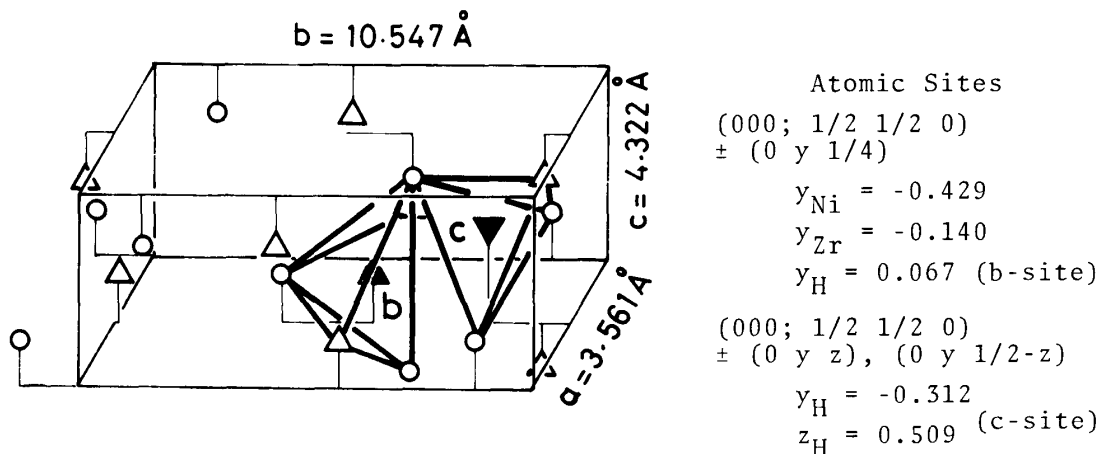


Fig. 2. Crystal structure of ZrNiH<sub>3</sub>.  $\Delta$  and  $\circ$  indicate nickel and zirconium atoms, and  $\blacktriangle$  and  $\blacktriangledown$  are hydrogen atoms at b- and c-sites, respectively.

Observed neutron inelastic spectra are due to the energy-loss of incident neutrons. The energy resolution of the spectrometer falls  $\Delta E/E \approx 0.04$  in the energy range from 50 to 200 meV. The good resolution of energy is provided on the sacrifice of the momentum resolution. The observed spectra are analyzed in terms of the product of incoherent cross-section, Debye-Waller factor and the density of state function with temperature factor, i.e., the Bose-Einstein statistics.

Crystalline ZrNi was prepared from pure metals (99.6 % Zr and 99.95 % Ni) by arc-melting in an argon atmosphere using zirconium oxygen-getter. Amorphous ZrNi ribbons were obtained by the rotating wheel method. Crystalline  $\text{ZrNiH}_{2.8}$  was prepared by heating up to 200°C in an atmosphere of purified hydrogen. Amorphous  $\text{ZrNiH}_{1.8}$  was prepared by heating the ribbons at 250°C in 50 atm. pressure of hydrogen. Though the amorphous ribbons contained a trace of crystals, crystallization did not proceed further during the hydrogen charge process. For the neutron spectroscopy, powdered crystalline hydrides are used. The amorphous hydride ribbons are about 0.02 mm thick and 2 mm wide, and the mass used for each measurement is about 50 g.

#### IV. Experimental Results

Figs. 4 and 5 show the neutron inelastic scattering spectra of crystalline  $\text{ZrNiH}_{2.8}$  and amorphous  $\text{ZrNiH}_{1.8}$ , respectively. Central large peaks near 110 meV in both figures are due to the primary

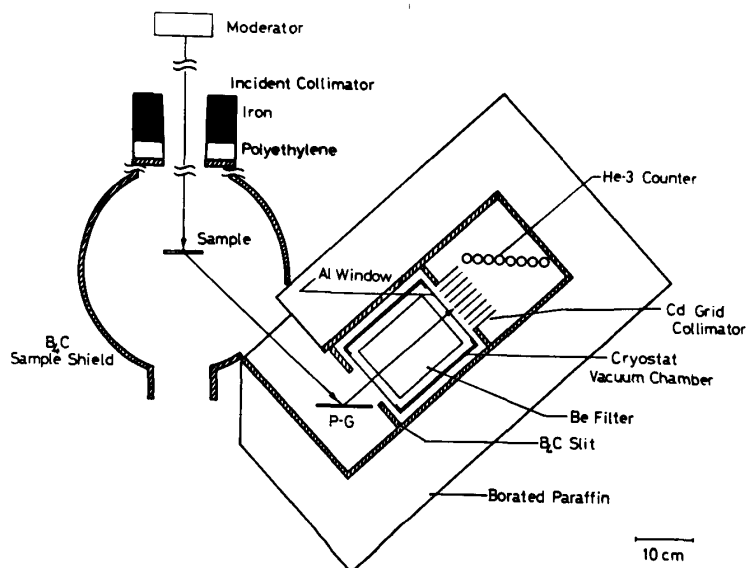


Fig. 3. Schematic illustration of neutron spectrometer<sup>10</sup>). Sample, pyrolytic graphite and counters are aligned in parallel.

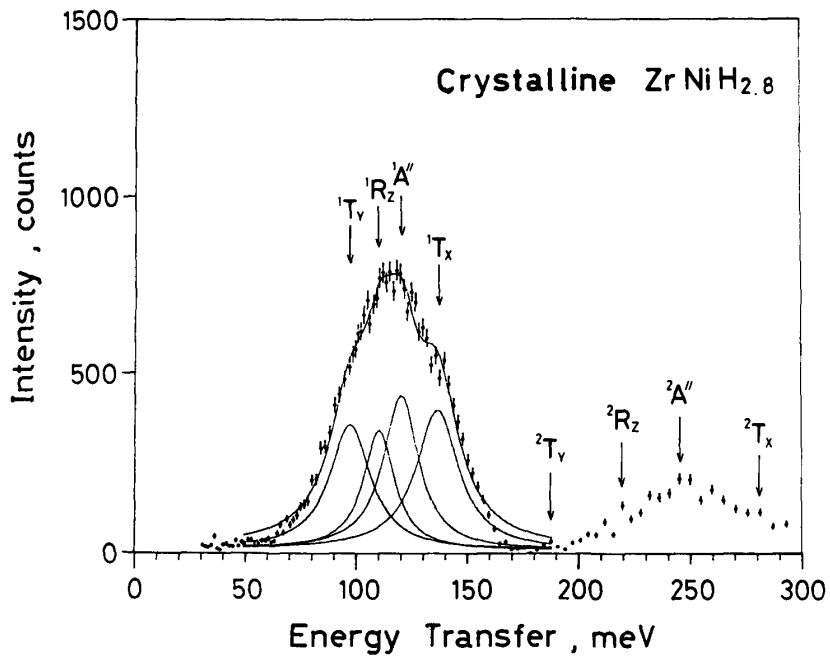


Fig. 4. Inelastic scattering spectrum of crystalline  $\text{ZrNiH}_{2.8}$ . Four Lorentzian peaks are deduced out of the central peak by the iterative deconvolution.

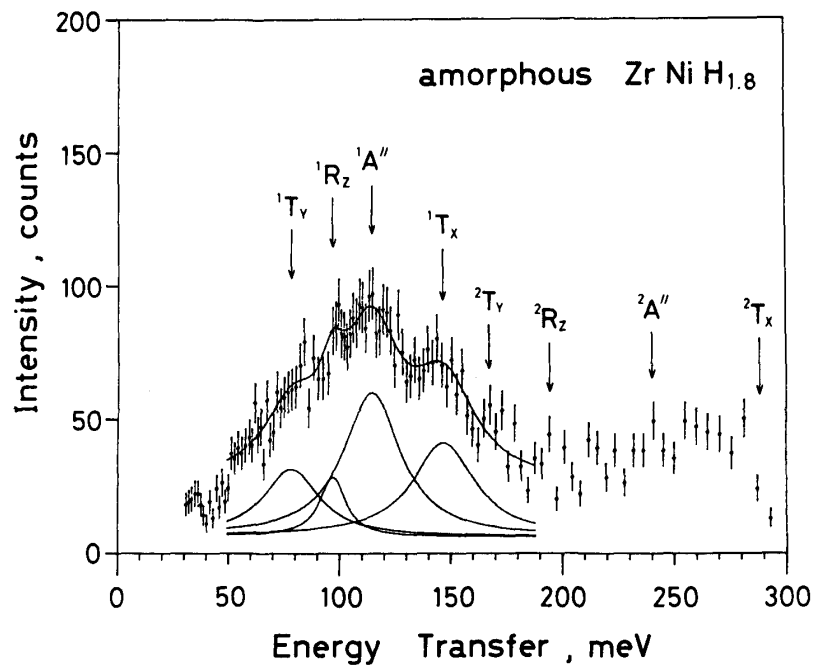


Fig. 5. Inelastic scattering spectrum of amorphous  $\text{ZrNiH}_{1.8}$ . Four broad Lorentzian peaks are deduced by the same calculation as in Fig. 4.

vibration modes. Low but broad peaks in the energy range from 180 to 300 meV are due to the secondary vibration modes which have the energy eigenvalues of almost twice as much as the primary ones. We note a strike difference in the width of the peaks of the two spectra. For the amorphous hydride, the peak width expands broader than for the crystal in the order of twice as much. However, the location of both peaks is almost identical on the energy scale.

On account of the local symmetry at the hydrogen sites in crystalline  $\text{ZrNiH}_{2.8}$ , it is concluded that three separate modes may be excited at the b-site and just one mode at the c-site. Consequently four primary vibration modes are considered to overlap in the central giant peak in Fig. 4.

An iterative method was adopted to deconvolute the observed spectrum into four peaks by fitting three parameters, i.e., maximum energy, full width at half maximum (FWHM) and peak height, for each Lorentzian peak. The four peaks are drawn by thin full lines in Fig. 4. The same method was also adopted for the spectrum of amorphous  $\text{ZrNiH}_{1.8}$ . Indices  $T_Y$ ,  $R_Z$ ,  $A''$  and  $T_X$  indicate the irreversible representations for each vibration mode in the crystalline  $\text{ZrNiH}_{2.8}$ . Prefixes 1 and 2 indicate the primary and the secondary vibration modes, respectively.  $T_Y$ ,  $R_Z$  and  $T_X$  modes are due to the hydrogen atoms located at the b-site, which are essentially linear motions along the a, b and c axes, respectively (see Fig. 6).  $A''$  mode is the motion at the c-site along the a axis which is perpendicular to the mirror plane. The indices for each peak are identified considering the population of hydrogen atoms at the b- and c-sites and the configuration of metal

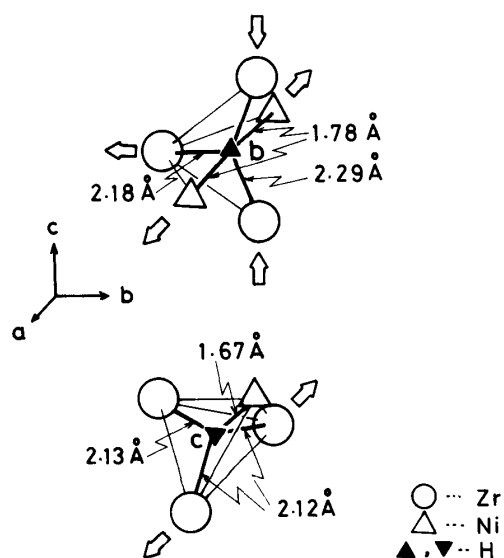


Fig. 6. Suggested displacement modes at the nearest neighbor metal atoms around the b- and c-sites in amorphous  $\text{ZrNiH}_{1.8}$ .

atoms surrounding the hydrogen atoms.

In the spectrum of the amorphous hydride, the deconvoluted peaks are obviously broad, but their locations are found to be similar in the crystal. The indices  $T_Y$ ,  $R_Z$ ,  $A''$  and  $T_X$  are provided in this context, even though the a, b and c axes can not be defined in the amorphous state. Table 1 summarizes the peak energy, FWHM and peak heights of the primary modes for the crystalline and amorphous zirconium-nickel hydrides. Except for the energy gain of  ${}^1T_X$  mode, the  ${}^1T_Y$ ,  ${}^1R_Z$  and  ${}^1A''$  modes loose the energy in the amorphous hydride.

### V. Discussion and Conclusion

The above results clearly show that the local environments around hydrogen sites in both the crystalline and amorphous zirconium-nickel hydrides are quite similar. However, the observed differences in energy of the modes imply that the arrangements of zirconium and nickel atoms in the amorphous hydride become more isotropic than in the crystal; the nearest neighbor metal atoms of hydrogen are pushed outward along the a and b axes but moved inward along the c axis. The expected displacement of the metal atoms at the b- and c-sites are illustrated in Fig. 6. Numerical values in the figure indicate the interatomic distances between hydrogen and metal atoms in the crystalline  $ZrNiH_3$ . Since the two-body potential between hydrogen and zirconium or nickel is not yet determined, the displacement of metal atoms can not be provided quantitatively. The broadening of the inelastic peaks for the amorphous hydride may be explained in terms of

Table 1. Energy eigenvalue, full width at half maximum and peak height of the deconvoluted peaks for the primary modes of crystalline and amorphous zirconium-nickel hydrides.

Mode	Crystalline $ZrNiH_{2.8}$			Amorphous $ZrNiH_{1.8}$		
	Energy meV	FWHM meV	Height	Energy meV	FWHM meV	Height
${}^1T_Y$	97	22	347	78	30	25
${}^1R_Z$	110	17	331	97	14 ?	22
${}^1A''$	120	19	428	114	31	54
${}^1T_X$	136	23	388	147	34	35



shorter life-time of each vibration mode due to the statistical fluctuation of configuration of metal atoms.

The energy eigenvalues of the secondary modes for the crystalline  $\text{ZrNiH}_{2.8}$  seem to deviate slightly from the twiced values of the primary modes. For instance, the eigenvalue of  $^2A''$  mode is about 10 meV higher than the twiced value of the primary mode, 240 meV. However, detailed discussion is tentatively avoided because of worse statistical errors of the experimental data in the higher energy range above 180 meV.

Calculation of the density of state curves of the localized hydrogen vibration by the self-consistent method is now under way. Detailed results will be published elsewhere.

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