

Inelastic neutron scattering in $\text{Zr}_2\text{NiH}_{1.9}$ and $\text{Zr}_2\text{NiH}_{4.6}$

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Abstract. In this paper we report the results obtained from inelastic neutron scattering measurements on $\text{Zr}_2\text{NiH}_{1.9}$ and $\text{Zr}_2\text{NiH}_{4.6}$ using triple-axis spectrometer at Dhruva reactor, Trombay. The spectrum up to 35 meV represents largely the lattice modes of Zr and Ni atoms. The vibrational frequencies of hydrogen atoms are expected predominantly at higher energies. The phonon spectra from 35–180 meV were recorded using a Be filter as analyser. In order to analyse the observed neutron spectra, we assume a set of Einstein modes due to the hydrogen atoms which are delta functions in energy. These delta functions are broadened by the resolution of the instrument. The vibrational frequencies obtained from the fitting of the observed phonon spectra have been assigned to various tetrahedral sites in both the compounds.

Keywords. Neutron inelastic scattering; intermetallic compounds; phonon; hydrogen in metals.

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1. Introduction

The C16 class of intermetallic compounds Zr_2M ($M = \text{Ni, Fe, Co, Rh}$) have been studied extensively [1–6] because of their superconducting properties. The superconducting transition temperature T_c for these compounds varies from a maximum of 11.2 K for Zr_2Rh to a minimum of 0.17 K for Zr_2Fe . These compounds can also absorb large amount of hydrogen in both their crystalline and amorphous phases. The crystal structure and the hydrogen sites have been extensively investigated [1,5,7] for Zr_2Ni intermetallics. X-ray studies of Zr_2NiH_x ($0 < x < 5.1$) show [5] that it retains tetragonal (space group I4/mcm) structure up to hydrogen concentrations of $x = 4.9$. The tetragonal unit cell parameters a and c increase with expansion of the lattice on absorption of hydrogen. Monoclinic distortion of the tetragonal unit cell is observed [5] for $\text{Zr}_2\text{NiH}_{5.1}$.

Inelastic neutron scattering measurements have been reported [8,9] on ZrNiH_x and ZrCoH(D)_x to determine the vibrational frequencies of hydrogen atoms. Similar studies have also been reported [10] on crystalline as well as amorphous

Zr₂NiH_{4.6}. The spectra of Zr₂NiH_{4.6} could not be analysed since hydrogen sites in Zr₂Ni were not known. Earlier we reported [11] inelastic neutron scattering measurements and lattice dynamical calculations for the C16 structured intermetallics Zr₂Ni. In this paper we give results obtained from our inelastic neutron scattering measurements on Zr₂NiH_{1.9} and Zr₂NiH_{4.6}. The spectra up to 35 meV represent largely the lattice modes of Zr and Ni atoms. The spectra in the range 35–180 meV have been fitted to a number of vibrational frequencies of H-atoms. These vibrational frequencies have been related to the H-atom sites determined by neutron diffraction.

2. Experimental

Crystalline Zr₂NiH_{1.9} and Zr₂NiH_{4.6} were prepared by the procedure described by Raj *et al* [12]. The samples were characterized by powder X-ray diffraction for its phase purity. The phonon spectra at 300 K were measured using a medium-resolution triple-axis spectrometer [13] at Dhruva reactor, Trombay. The polycrystalline samples were placed in a thin aluminum container for neutron measurements. The incident neutron energy was varied using a Cu (1 1 1) monochromator. The phonon spectra in the range 35–180 meV were measured using a Be filter as analyser. Several inelastic runs were recorded for both Zr₂NiH_{1.9} and Zr₂NiH_{4.6}. All the measurements were carried out in the energy loss mode.

3. Results and discussion

The modes up to 35 meV represent [11] the lattice modes of Zr and Ni atoms. The vibrational frequencies of hydrogen atoms are expected predominantly at higher energies. Figure 1 shows the observed neutron spectra $I(E)$ of both Zr₂NiH_{1.9} and Zr₂NiH_{4.6} in the 35–180 meV range. The spectra are centered at about 130 meV. The width of the spectrum for Zr₂NiH_{4.6} is broader than that for Zr₂NiH_{1.9}. The vibrational energies of hydrogens at octahedral sites [9] are typically 60 meV. Since there is no scattered intensity between 40 and 80 meV, it can be concluded that there are no octahedral sites occupied by hydrogen. This is consistent with the analysis of neutron diffraction pattern for Zr₂Ni, which shows that only tetrahedral sites [1] are significantly occupied by hydrogen atoms.

The intermetallic compound Zr₂Ni is associated with [1] four types of tetrahedral interstitial sites for H-atom occupancy. The sites designated by *a* and *b* are surrounded by 4Zr atoms, while *c* and *d* are surrounded by (3Zr+Ni) and (2Zr+2Ni) atoms, respectively. Neutron diffraction measurements show that deuterium in Zr₂NiD₂ is mainly accommodated in *b* sites, while in Zr₂NiD_{4.8} [1] it is distributed over *b*, *c* and *d* sites with a large occupancy at *b* and *c* sites. The *b* and *c* sites occupy 2.7D and 1.5D per formula unit, respectively.

There is a strong difference in the electropositivity between Zr and Ni. The Zr would attract hydrogen more in comparison to Ni. Because of this, *d* sites formed by (2Zr + 2Ni) are almost empty. The *a* and *b* sites formed by 4Zr atoms are large enough (hole radius of more than 0.5 Å) to accommodate hydrogen. The absence of hydrogen in *a* sites could be due to repulsive interactions with hydrogen

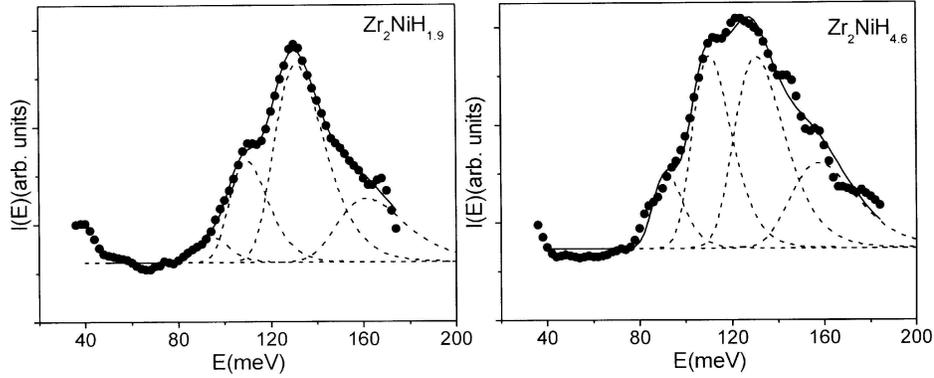


Figure 1. Inelastic neutron scattering spectra $I(E)$ of $Zr_2NiH_{1.9}$ and $Zr_2NiH_{4.6}$ in 35–180 meV range. Filled circles and full lines represent the experimental data and the fitted profiles to the experimental data. Dashed lines are the individual peaks fitted to the main profile. For $Zr_2NiH_{4.6}$, sharp features at about 140 and 155 meV are much narrower than the resolution of the instrument and are therefore not expected to be associated with the vibrational modes in the sample.

in the b sites (at a distance of about 1.4 Å) and c sites (distance of about 1.2 Å). This is consistent with the geometric models [14]. An interstitial site would be occupied by a H-atom if its hole radius is more than 0.4 Å. Two sites can be occupied simultaneously if they are separated by a distance of about 2.1 Å.

In order to analyse the observed neutron spectrum, we assume a set of Einstein modes due to the hydrogen atoms which are delta functions in energy. These delta functions are broadened by the resolution of the instrument. The observed spectrum has been described by the following distribution:

$$I(E) = \sum_i \frac{A_i e^{-(E-E_i)^2/2\sigma^2}}{\sqrt{2\pi}\sigma},$$

where $I(E)$ is the fitted intensity at energy transfer E from all the i peaks, A_i and E_i are the area and peak energy of the i th peak, respectively. In beryllium filter technique for our region of interest (energies 60–180 meV) the contributions to σ from beryllium analyser is not significant and is mainly from the monochromator crystal; $\sigma = (1/\sqrt{2\ln 2})E_n(\cot \theta)\alpha$ (E_n is the incident energy of neutron, θ is the Bragg angle for monochromator crystal). The value of effective collimation angle $\alpha (= 1.02^\circ)$ was obtained from fitting of the inelastic neutron scattering data [15] of a standard sample, namely, zirconium hydride, which has a vibrational frequency of hydrogen atom at 134 meV. The spectra for $Zr_2NiH_{1.9}$ and $Zr_2NiH_{4.6}$ are fitted to four peaks (figure 1) using a least square fitting program with the peak position E_i and area under the peak A_i as fitting parameters.

The observed neutron intensity $I(E)$ is related to $S(Q, E)$. In beryllium filter technique, $S(Q, E)$ is close to the phonon density of states for modes of energy $E \gg KT$, because the factor $1/E$ and Q^2 in the neutron scattering cross-section largely cancel each other. For our region of interest (60–180 meV) at room temperature this

Table 1. The results of peak fits to the phonon spectra of $\text{Zr}_2\text{NiH}_{1.9}$ and $\text{Zr}_2\text{NiH}_{4.6}$. Peak areas (A_i) have been normalized to the number of degrees of freedom associated with the hydrogen atoms ($3N$) per formula unit in each sample.

| | Peak 1 | | Peak 2 | | Peak 3 | | Peak 4 | |
|-------------------------------|-----------|-------|-----------|-------|-----------|-------|-----------|-------|
| | E (meV) | A_1 | E (meV) | A_2 | E (meV) | A_3 | E (meV) | A_4 |
| $\text{Zr}_2\text{NiH}_{1.9}$ | 163 | 1.3 | 132 | 3.0 | 110 | 1.2 | 95 | 0.2 |
| $\text{Zr}_2\text{NiH}_{4.6}$ | 160 | 3.1 | 132 | 5.3 | 112 | 4.2 | 92 | 1.2 |

approximation is valid. The areas of the peaks A_i are proportional to the number of hydrogen atoms at the corresponding site times the degeneracy of the mode. Therefore, peak areas have been normalized to the number of degrees of freedom associated with the hydrogen atoms ($3N$) per formula unit in each sample. The parameters obtained from the fitting of the phonon spectra of both the compounds are given in table 1. The vibrational frequencies lie in the expected range for the tetrahedral sites.

For $\text{Zr}_2\text{NiH}_{1.9}$, H-atoms are expected [1] to occupy only b sites. Our measurements indicate (table 1) essentially three vibrational frequencies for these H-atoms. Further, it can be seen (table 1) that for $\text{Zr}_2\text{NiH}_{4.6}$ the three frequencies (112, 132 and 160 meV) of H-atoms are almost the same as that in the case of $\text{Zr}_2\text{NiH}_{1.9}$. However, the weights of H-atoms associated with different peaks have increased in $\text{Zr}_2\text{NiH}_{4.6}$, which reveals the vibrational modes of additional H-atoms. The increase in weights of different peaks may be due to roughly the same vibrational frequencies of H-atoms in both the b and c sites in $\text{Zr}_2\text{NiH}_{4.6}$. The occupancy for hydrogen atoms in b and c sites in $\text{Zr}_2\text{NiH}_{4.6}$ is found to be about 3.2 and 1, which is roughly the same as determined for $\text{Zr}_2\text{NiD}_{4.8}$ from the diffraction experiments [1].

The deuterium atoms mainly occupy the b and c sites in $\text{Zr}_2\text{NiD}_{4.8}$ [1]. However, about 0.2 deuterium per formula unit also occupy the d site formed by $(2\text{Zr}+2\text{Ni})$. The deuterium/hydrogen in this site would be loosely bound in comparison with those at b and c sites, which would result in a smaller frequency. The peak at 95 meV (table 1) may be associated to d site occupancy of hydrogen atom in $\text{Zr}_2\text{NiH}_{4.6}$.

4. Conclusions

The inelastic neutron scattering measurements have been reported for both $\text{Zr}_2\text{NiH}_{1.9}$ and $\text{Zr}_2\text{NiH}_{4.6}$. The observed vibrational frequencies in the range of 35–180 meV are assigned to the vibration of hydrogen atoms in tetrahedral sites in both the compounds.

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