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Incoherent inelastic neutron scattering from the C-15 Laves phase $ZrTi_2H_{3.6}$

J.F. Fernandez[1], M. Kemali, D.K. Ross*

Joule Laboratory, Dept. of Physics, University of Salford, Salford M5 4WT, UK

Abstract

Incoherent inelastic neutron scattering data were obtained for the C-15 Laves phase compound $ZrTi_2H_{3.6}$ using the time-focused crystal analyzer spectrometer at ISIS, Rutherford–Appleton Laboratory, UK. A doublet and a singlet were observed in the first harmonic region of the localized hydrogen vibrations. This result is compatible with hydrogen occupying the e-type (3Ti–1Zr) site. The measured spectra are discussed in terms of an interatomic potential of the Born–Mayer type.

Keywords: C-15 Laves phases; $ZrTi_2H_x$; Incoherent inelastic neutron scattering; Localized hydrogen vibrations; Hydrogen potential well

1. Introduction

In the recent past, considerable attention has been paid to the AB_2 compounds in which both A and B are transitional elements [1]. A great number of these AB_2 compounds crystallize in either the cubic, $MgCu_2$, C-15 or the hexagonal, $MgZn_2$, C-14 structure (Laves phases). The AB_2 Laves phase compounds have been shown to be very valuable for hydrogen storage purposes as well as for negative electrodes in nickel–metal hydride batteries. High hydrogen capacity and high hydrogen diffusivity as required in these applications are provided by some of the AB_2 Laves phase compounds although multicomponent alloys of the AB_2 form have to be used for real applications. Three different tetrahedral sites are available for hydrogen in the C-15 AB_2 compounds [2], g-type (A_2B_2), e-type (AB_3) and b-type (B_4).

Of all C-15 Laves phase compounds, $ZrTi_2$ is a special case in the sense that the C-15 phase is only formed when hydrogen is added to the compound. It is well known that Laves phases are only found when certain ratios of atomic radii and certain values of electronic density are reached. For the $ZrTi_2$ system the electronic density is not appropriate to form the C-15 phase and the stable phase is a disordered hexagonal structure. On adding hydrogen to the compound, however, the electronic density changes to a value where the C-15 phase is stable. Another special feature of the $ZrTi_2$, C-15 Laves phase is that the site occupied by hydrogen seems to be the e-site (1Zr–3Ti) [3]. In contrast, most of the C-15 Laves phase compounds in which a study of the hydrogen site occupancy has been done, show the g-site (2Zr–2Ti) as the preferred site for hydrogen, with a slight occupancy of the e-site when H-concentration is increased [2]. Both features made the study of the interaction of hydrogen with $ZrTi_2$ specially interesting.

Incoherent inelastic neutron scattering (IINS) is a very powerful technique to provide information on the optic and acoustic vibrational modes of hydrogen in the lattice. The optic modes are strongly dependent on the chemical and topological environment around the hydrogen atom. In the present work, IINS spectra for $ZrTi_2H_{3.6}$ are presented and information about the potential well and the site occupied by the light atom are extracted.

2. Experimental

The alloy was prepared by arc melting the appropriate constituents under an argon atmosphere. Purity of the metals was better than 99.95%. Several remeltings of the alloy were performed in order to improve the homogeneity of the sample. Before hydrogenation, the sample was annealed for 16 h at 973 K in vacuum (better than 10^{-3} Pa). The hydrogenation of the sample was done at 873 K in a volumetric apparatus (hydrogen purity 99.999%). The hydrogen content of the sample was then measured by observing the pressure drop in a calibrated volume. A

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*Corresponding author.

[1] On leave from Dpto. Fisica de materiales, Facultad de Ciencias, Universidad Autonoma de Madrid, 28049 Madrid, SPAIN.

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figure of $x=1.2\pm0.1$ hydrogen to metal ratio was obtained. According to X-ray and neutron diffraction data [3] the sample at this H-concentration should be C-15 Laves phase with a lattice parameter of 8.19 Å.

IINS measurements were performed on the time-focused crystal analyzer (TFXA) spectrometer at the spallation neutron source, ISIS, at the Rutherford Appleton Laboratory, UK. Around 6 g of sample was loaded in an aluminum foil in a flat geometry. A transmission of 70% can be calculated assuming a scattering cross section of 20 barns for hydrogen and the known scattering cross sections of the metals. Two spectra, 25 K and 200 K, were acquired. The lower temperature spectrum was run for more than 7 h showing very good statistics. On the other hand, poor statistics were obtained in the 200 K spectrum due to a lower counting time (~2 h). The spectrometer has a typical resolution of $\Delta E/E$~2% for energy transfers in the range 2–500 meV.

3. Results and discussion

Fig. 1 shows the IINS data in the energy range 0–500 meV for the two temperatures investigated: (a) 25 K and (b) 200 K. Two well defined peaks corresponding to the first harmonic localized hydrogen vibrations can be seen at energies between 100–200 meV. Second harmonics, above 200 meV, can also be seen in this figure but their structure cannot be resolved. The acoustic contribution to the scattering from the metal atoms enhanced by the hydrogen can be seen at low energy transfer, <45 meV. A neutron diffraction pattern was collected at the same time as the IINS data. As far as we know, no phase diagram of the $ZrTi_2H_x$ alloy has been published, so the possibility of a phase transformation when temperature is lowered, as has been shown in HfV_2H_x or ZrV_2H_x [4,5], cannot be ignored. Despite the high incoherent background due to hydrogen, the diffraction pattern can be indexed fairly well with a C-15 Laves phase with a lattice parameter of 8.16 Å, slightly smaller than 8.19 Å, the value found by Miron et al. [3] from their neutron and X-ray diffraction measurements at room temperature and hence we have concluded that no phase transformation occurs.

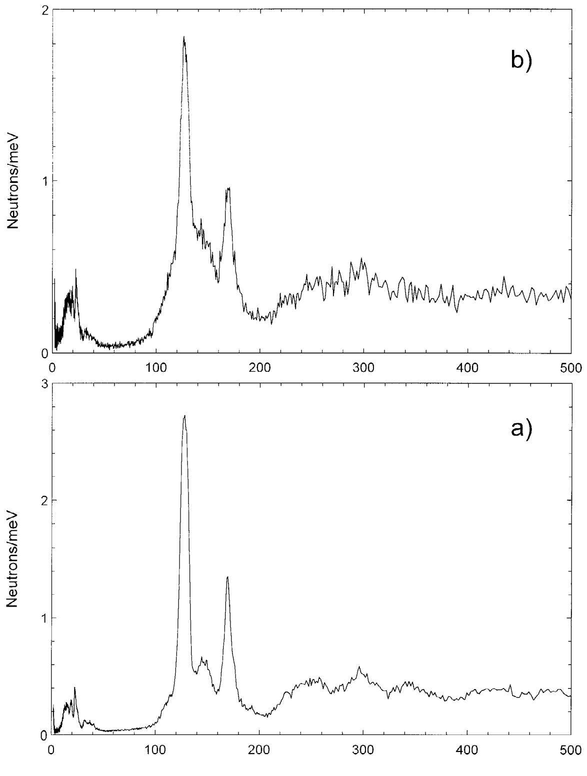

Fig. 1. IINS spectra obtained in $ZrTi_2H_{3.6}$ using the TFXA instrument: (a) $T=25$ K; (b) $T=200$ K.

Fig. 2 shows an enhanced view of the IINS spectrum at 25 K in the 80–200 meV energy range where the first harmonics of the localized hydrogen vibrations appear. The solid line represents a fit to the data with three gaussians (one for each localized vibration) plus their corresponding side bands coming from the optic–acoustic two phonon processes. A gaussian approximation for the side bands has been used. A sloping background has been subtracted from the data. The individual components can be seen as dashed lines in Fig. 2. Besides the components mentioned above, additional contributions (dot–dashed line in Fig. 2) have been included in order to obtain a proper fit to the bumps seen around 115 meV and between the main peaks. These bumps are also present in the 200 K spectra as can be seen in Fig. 1b. No clear explanation of the origin of these components is known at the moment. A possible explanation could arise if a fraction of the g-sites are also occupied by hydrogen. They could also be explained by the presence of minority phases. Additional

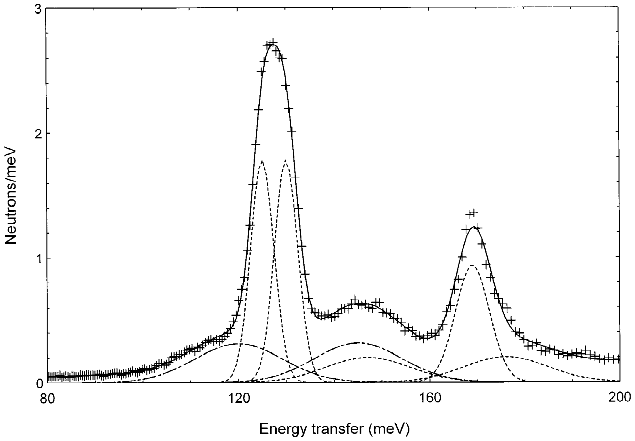

Fig. 2. Enlarged plot of the IINS spectra ($T=25$ K) in the region of the first excited levels of the hydrogen vibrations. Crosses represent the experimental points. Solid lines represent the full fit. Dashed lines represent the three localized vibrations as well as their sidebands. Dash–dot lines stand for the additional components needed to obtain a good fit to the experimental data (see text).

research will be carried out in our laboratory in order to understand the nature of these components in the IINS spectra.

Table 1 shows the parameters obtained from the fit: namely energy, full width–half maximum and intensity. The three localized hydrogen vibrations appear at 125, 130 and 169 meV. A small splitting of 5 meV is extracted for the lower energy peak (where the resolution of the instrument is 2.6 meV approximately) although this splitting is not clearly resolved. The value of the splitting is, however, very dependent on how the side bands and the additional components are taken into account and, therefore, this may be only an artifact of the fitting procedure. The difference in width between the higher and lower energy peak is also very dependent on the fitting procedure. In fact, as the splitting of the doublet diminishes so does the difference in width, these being almost identical if no splitting is considered. A 2:1 intensity ratio for the doublet and a singlet would be expected for an harmonic potential. Although, apparently the intensity ratio is higher than this value, once the E and Q dependence of the double differential scattering cross section are taken into account, values close to the 2:1 ratio are obtained.

Our assignment of the localized frequencies is thus as follows. The lower energy excitations at ~127 meV correspond to motions in the X–Y plane, this being the plane parallel to the basal plane of a tetrahedral, at the corners of which the titanium atoms are situated. The higher energy excitation, at 169 meV, corresponds to the motion along the Z axis in the direction of the zirconium atom situated at the top of the tetrahedral. In Table 1, we have also included the mean energies of the second harmonic structures. It will be noted that these are quite close to the values expected for an anisotropic harmonic oscillator which would imply energies of, 255, 297.5 and 340 meV. These data suggest that the hydrogen potential must be harmonic although the lack of resolution for these peaks precludes a precise conclusion on this point.

A doublet and a singlet producing two peaks in the IINS spectrum can be expected from a tetrahedral site like the e-site in $ZrTi_2H_x$. On the other hand, a g-site should produce three singlets, i.e., three different peaks in the IINS spectrum. A clear distinction between the e-site and the g-site by means of IINS can be complicated by several factors. Anharmonic terms and hydrogen–hydrogen interactions can break the degeneracy of the doublet. Also, for the g-site, the energy difference between two of the singlets could be small, so as to be indistinguishable from a doublet. As mentioned above, diffraction data suggests that the e-site is the preferred one for hydrogen in C-15 $ZrTi_2H_{3.6}$ [3]. Our IINS data are also consistent with e-site hydrogen occupation, subject to the possible complications mentioned above.

As a first approximation, the potential well in which the H-atom is located can be considered to be generated by the four metal atoms forming the tetrahedral site. The frequencies of the localized vibrations of the H-atoms can be obtained by solving the eigenvalue problem.

$$|\partial^2 V_t / \partial x_i \partial x_j - \delta_{ij} M \omega^2| = 0$$

where V_t is the potential seen by the hydrogen and is made up of the sum of the potentials generated by each metal atom, where x_i and x_j are the cartesian coordinates, M is the hydrogen mass and ω the frequency of the optic modes. A possible candidate for the interatomic potential is the Born–Mayer form

$$V(|r - R|) = A \exp(-|r - R|/b)$$

where A and b are adjustable parameters and $|r - R|$ is the distance between the hydrogen and the metal. Fukai and Sugimoto [6] have used a Born–Mayer potential to explain the smooth decrease of the fundamental frequency of the H vibrations with increasing lattice parameter in metal hydrides with the fluorite structure previously noted [7]. The experimental data in these compounds can be explained assuming that the ratio R/b (R metal–hydrogen distance) is constant. Also, Born–Mayer potentials have been used before to explain the localized vibrations of hydrogen in TaV_2 [8]. In that work, the b parameter was assumed to be the same for the four atoms and equal to 0.2 Å and the A parameters were taken as the values needed to fit the experimentally determined localized frequencies of hydrogen in the fluorite hydride phases. This approach does not fit the measured optic frequencies observed in the present case. In order to achieve consistency between our experimental data and the model, a slightly different approach has been used. The A parameters have been extracted as in [8] from the optic modes of 143 and 147 meV for titanium and zirconium respectively [7,9,10], and the well known metal–hydrogen distances in the pure metal, 1.93 Å and 2.08 Å respectively for titanium and

Table 1
Mean excitation energies, E, full width–half maximum, (FWHM), and intensity of the localized vibrations of hydrogen in $ZrTi_2H_{3.6}$ at 25 K

	Peak number	E (meV)	FWHM (meV)	Intensity (a.u.)
First harmonics	1	125	5.8	11.0
	2	130	5.8	11.0
	3	169	8.1	8.1
Second harmonics	1	254	-	-
	2	295	-	-
	3	343	-	-

zirconium hydride [11]. The metal–hydrogen distance in the C-15 phase $ZrTi_2H_x$ sample has been obtained by finding the minimum of the potential well. It has been found that this minimum is slightly away from the middle of the site, being closer to the basal plane of the titanium atoms. Values of 1.87 Å and 1.96 Å were obtained for the Ti–H and Zr–H distances, respectively. These values are slightly different from those obtained in Ref. [3], the same distance, 1.92 Å, for the four atoms. The *b* parameters were simultaneously allowed to vary for both metals. This model reproduces the experimental data with a small decrease of the 0.2 Å *b* value by 5% and 6% respectively for titanium and zirconium atoms. It is worth mentioning that the frequencies are very dependent on the choice of the *b* parameter. Small changes in *b* produce drastic changes in the resultant frequencies.

The *b* parameter can be considered roughly as a screening parameter. Taking into account the fact that the metal–hydrogen distances in the pure metal and the alloy are quite similar (see above), we can conclude that the differences in the *b* value arise from different electronic structures of each atom. In fact, from this point of view assuming small variations in the *b* value for different components of the alloy rather than equal values, seems to be a more sensible choice in intermetallic compounds. The C-15 Laves phases offer us an opportunity to establish whether there is a unique set of values of *A* and *b* (or at least a small range of variation) that will represent the metal–hydrogen interactions in these systems in a way that also works for the case of the pure metal hydrides with the fluorite structure [6]. Extension of this work to other C-15 Laves phase systems is in progress.

4. Conclusions

The IINS spectra were measured for the C-15 Laves phase compound $ZrTi_2H_{3.6}$. An unresolved doublet (~127 meV) and a singlet (169 meV) have been assigned to the first harmonics of the local hydrogen vibrational modes. This result is compatible with hydrogen occupying the e-site (3Ti–1Zr). Broad "second harmonics" peaks were observed at energies in the range of those expected for an harmonic potential, but are difficult to interpret quantitatively. The interatomic potential seen by hydrogen was calculated by using a Born–Mayer potential using reasonable parameters. In order to achieve consistency between experimental data and the model, different *b* values for titanium and zirconium were allowed.

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