A Born-Mayer approach to the hydrogen potential in C-15 Laves phase compounds

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Abstract

The potential wells seen by hydrogen in several interstitial sites in the C-15 Laves phase compounds $ZrTi_2$, $ZrCr_2$ and $TiCr_{1.85}$ have been investigated using incoherent inelastic neutron scattering (IINS) data. Parameters describing the harmonic terms in the H-potential well in the three compounds are obtained from the first localised hydrogen vibrations as measured by IINS. The H-potential well is created by the sum of the pairwise potentials between the hydrogen and the four metallic atoms forming the different types of tetrahedral sites which are labelled (A_2B_2), (AB_3) or (B_4) in the C-15 structure. A Born-Mayer potential has been used to model these pairwise interactions with parameters determined from the IINS data. It has been shown that the hydrogen potential well can be described by parameters characteristic of each metal. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Hydrogen potential well; C-15 Laves phase compounds; Born-Mayer interatomic potential

1. Introduction

The C-15 Laves phase compounds have been the subject of many investigations due to their ability to absorb large amounts of hydrogen. Depending on the hydrogen concentration and the metallic elements involved, different type of interstitial sites can be occupied by hydrogen. Three different tetrahedral interstitial sites are available for occupation by H in this phase, namely the g site (A_2B_2), the e site (AB_3) and the b site (B_4) [1]. Each unit cell contains 96 g sites, 32 e sites and 8 b sites. Simultaneous occupation of all these sites would give a maximum hydrogen–metal ratio, x, of around 6. In practice, significantly lower H concentrations are achieved. Predictions of the site occupied by the H and of the maximum H content in C-15 compounds have usually been made using the so-called Westlake criteria, based on purely geometrical considerations [1]. These criteria state that the radius of the interstitial 'hole'—calculated assuming touching hard-spheres—should be larger than 0.4 Å and that the distance between hydrogen atoms should be greater than 2.1 Å. Application of the Westlake criteria would, in general, lead to the conclusion that, at low H concentrations, the g site is preferentially occupied and that only when the H con-

centration increases would the e site be partially occupied. Maximum H/M ratio of around $x = 4.5$ is obtained when the above criteria are fulfilled.

To investigate the different sites in which hydrogen can be accommodated we have used the incoherent inelastic neutron scattering technique (IINS). We present here an IINS study of the hydrogenated C-15 Laves phase compounds $ZrCr_2$ and $TiCr_{1.85}$. Previous IINS data on $ZrTi_2H_{3.6}$ compound [2] together with data from other authors on the ZrV_2 alloy [3] are also included in the discussion.

The measurements were made at different temperatures in several compounds loaded with various hydrogen concentrations. The parameters describing the hydrogen potential well can then be obtained from the first localised hydrogen vibrations. The interatomic potential was assumed to be of the Born-Mayer type.

2. Experimental

The intermetallic alloys were prepared in argon atmosphere by arc melting of appropriate quantities of the elemental components (99.95% purity). Several remeltings of the alloys were performed in order to improve their homogeneity. The composition of the samples was checked by energy dispersive X-ray (EDX) analysis to be

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$ZrCr_2$, $TiCr_{1.85}$ and $ZrTi_2$. Before hydrogenation, the alloys were annealed at appropriate temperatures (973 K, 1273 K and 1525 K for the $ZrTi_2$, $TiCr_{1.85}$ and $ZrCr_2$ samples, respectively) in a vacuum better than 10^{-3} Pa. This is an important step, particularly for the $ZrCr_2$ and $TiCr_{1.85}$ samples, where both the C-14 and the C-15 phases can be present [4]. Hydrogenation was accomplished in a Sieverts-type apparatus, described elsewhere [5]. The H/M ratio, x, was determined from the hydrogen pressure drop in a calibrated volume to an accuracy of 0.01 in x. For the $TiCr_{1.85}$ sample, surface deactivation with air was needed to prevent loss of hydrogen because of its high equilibrium pressure under ambient conditions [6]. Table 1 shows the values of x for the $ZrTi_2$, $ZrCr_2$ and $TiCr_{1.85}$ samples. X-ray patterns were obtained for the hydrogenated samples. All of them show the C-15 structure as the main phase. They were refined with the Fullprof software [7] and the lattice parameters obtained from the refinement are shown in Table 1. The lattice parameters and x values agree well with the published data on these compounds [6,8,9]. A minority phase was observed for the $ZrCr_2$ compound that can be indexed as the C-14 phase, which is the stable structure at low temperatures. As mentioned above, the $ZrCr_2$ sample was annealed at 1525 K and then quenched to room temperature to prevent the formation of that phase. However, partial transformation to the low-temperature C-14 phase was difficult to avoid. On the other hand, the $TiCr_{1.85}$ and $ZrTi_2$ X-ray patterns show no sign of additional phases.

IINS experiments were carried out on both the INIB beryllium filter detector instrument at the ILL (Grenoble, France) ($ZrCr_2$ and $TiCr_{1.85}$) and the TFXA instrument at the ISIS spallation neutron source (Rutherford Appleton Laboratory, Didcot, UK) ($ZrTi_2$, $ZrCr_2$ and $TiCr_{1.85}$). Spectra were acquired at 20 K and 200 K for the $ZrCr_2$ and $ZrTi_2$ samples and at 20 K, 100 K and 200 K for the $TiCr_{1.85}$ sample. The TFXA instrument allows a simultaneous determination of the neutron diffraction pattern at moderate resolution. The diffraction data are very useful in confirming that there is no phase transformation at the measurement temperatures, because this is known to happen below room temperature in other C-15 alloys, such as ZrV_2 and HfV_2 [3,10].
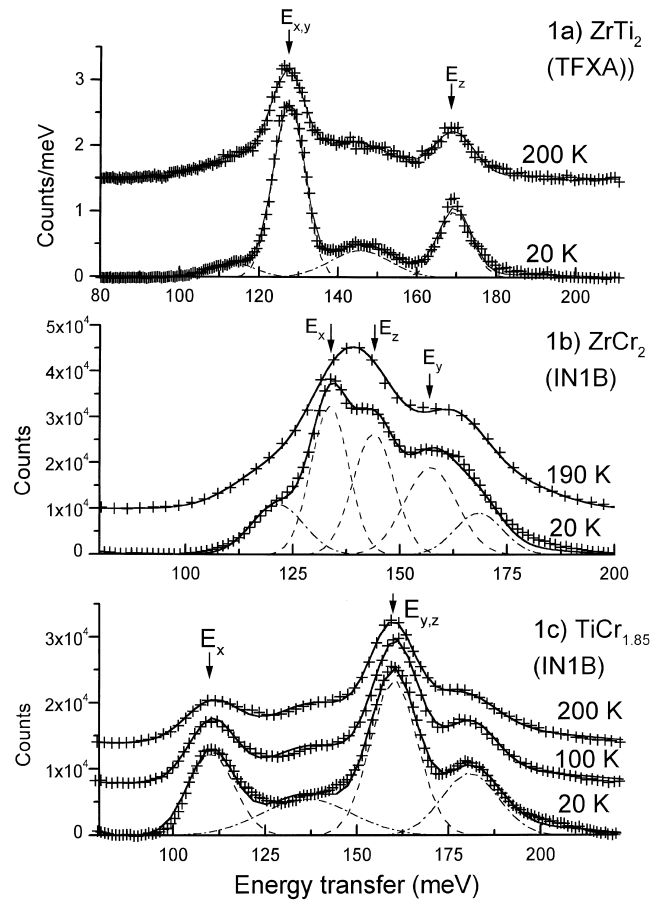

Fig. 1. IINS spectra from the three samples: (a) $ZrTi_2H_{3.6}$, TFXA; (b) $ZrCr_2H_{0.9}$, IN1B; and (c) $TiCr_{1.85}H_{0.4}$, IN1B. Spectra at several temperatures are displayed. Solid lines are the best fit to the data with three local modes plus sidebands and additional bands (see text). Local modes and additional bands are shown as dashed and dot-dashed curves, respectively. Sidebands are not shown. The mean positions of the local modes at 20 K are shown by arrows.

3. Results

Fig. 1 shows IINS spectra obtained for the three alloys: (a) $ZrTi_2$ (TFXA) [2]; (b) $ZrCr_2$ (IN1B); (c) $TiCr_{1.85}$ (IN1B) at several temperatures. The energy axis spans the range from 80 to 220 meV, within which the fundamental

Table 1
Hydrogen–metal ratio, x, lattice parameter, a, local modes energy, E_i, FWHM, Γ_i, and intensity ratio I_i/I_x for the three samples, $ZrTi_2$, $ZrCr_2$ and $TiCr_{1.85}$, at several temperatures

Sample	x (H/M)	a (Å)	Instrument	T (K)	E_x (meV)	E_y (meV)	E_z (meV)	Γ_x (meV)	Γ_y (meV)	Γ_z (meV)	I_y/I_x	I_z/I_x
$ZrTi_2$	1.2	8.183	TFXA	20	127.5	127.5	169.6	7.8	7.8	8.3	1.0	0.81
				200	127.0	127.0	169.2	8.4	8.4	9.9	1.0	1.17
$ZrCr_2$	0.3	7.338	IN1b	20	133.6	157.2	143.8	8.7	9.6	12.1	0.9	0.8
				190	135.0	161.8	144.4	14.0	14.2	1.8	0.95	0.90
$TiCr_{1.85}$	0.13	6.998	IN1b	20	110.2	160.1	160.1	12.5	12.6	12.6	0.96	0.96
				100	110.5	160.6	160.6	12.5	12.5	12.5	1.07	1.07
				200	110.6	159.7	159.7	14.5	12.2	12.2	1.08	1.08

modes of the localised hydrogen vibrations (optic modes) appear. Two ($ZrTi_2$), three ($ZrCr_2$) and two ($TiCr_{1.85}$) main peaks (dashed lines), corresponding to the first H excitations, are observed in the different IINS spectra. As can be seen from the figures, additional bands (dashed-dot lines) at 110 meV, 145 meV ($ZrTi_2$), 120 meV, 170 meV ($ZrCr_2$) and 130 meV, 180 meV ($TiCr_{1.85}$) appear in the experimental data. Solid lines represent the function fitted to the spectra with three or two bands representing the localised H vibrations plus the additional bands and the corresponding sidebands (not shown in Fig. 1) due to opto-acoustic processes (10−15% of the intensity of the local mode). A Gaussian profile is assumed for the bands. A sloping background has been subtracted from the data prior to fitting. To fit the data we have fixed the intensity ratio between the optic modes to be close to 1:1:1 (or 2:1) and have allowed for a small increase of the width of the bands with increasing energy transfer.

The data show that there is no important modification of the spectra with temperature except for the peak broadening due to reduced lifetimes in the excited states, presumably due to phonon–phonon coupling. Fitting of the higher temperature spectra were done starting from the values obtained for the lowest temperature fit, and allowing for an increase in the width of the peaks and a small change in the intensity ratio due to different Debye-Waller factors. No important change in the position of the peaks was observed with temperature, again indicating that there is no significant change in the crystalline structure of the samples.

Table 1 summarises the parameters obtained from these fits (fundamental mode energy, E_i, width of the peaks, Γ_i, and the intensity ratio, I_i/I_x, where x refers to the lowest energy mode). As discussed in [2], $ZrTi_2$ shows two optical modes, a doublet and a singlet, at 127 and 170 meV, respectively [Fig. 1(a)]. This is compatible with H being in an e site which has tetragonal symmetry, as is suggested for this compound by neutron diffraction [9]. Fig. 1(b) shows the spectra for the $ZrCr_2$ sample. They are described in terms of three main peaks at 134, 144 and 157 meV with intensity ratios close to 1. This is consistent with the absence of degeneracy as expected for H in a g site. H occupancy of a g site in $ZrCr_2$ is anticipated on the basis of the Westlake criteria and also from fits to the neutron diffraction data [11]. The IINS spectra obtained for the $ZrCr_2$ compound is quite similar to that reported for ZrV_2 [3] at similar H concentrations. The $TiCr_{1.85}$ sample shows a more complex spectrum [Fig. 1(c)]. Hydrogen occupation of a g site is also anticipated from Westlake criteria [1] in this compound. Taking into account our criteria of similar intensities for each optical mode, we assign one of these to the 110 meV peak and two overlapping modes to the 160 peak. The origin of the other peaks in the spectra will be discussed later on. In addition to the $ZrTi_2$, $ZrCr_2$ and $TiCr_{1.85}$, we have included in the discussion IINS data on a C-15 $ZrV_2H_{0.5}$ compound measured by other authors [3].

The first localized hydrogen vibrations in this compound appear at energies 140.4 meV, 146.6 meV and 158.2 meV as measured by IINS at 200 K.

4. Discussion

The Hamiltonian for the proton in the alloy can be written as

$$\left[-\frac{\hbar^2}{2m} \left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right\} + V(\vec{r}) \right] \varphi(\vec{r}) = E\varphi(\vec{r}) \qquad (1)$$

where $V(r)$ is the potential energy of the H, $\varphi(r)$ its wave function and m is the proton mass. As a first approximation, $V(r)$ can be considered to be a linear superposition of the potential energies for the interaction of the H with each nearest-neighbour metal atom. As mentioned in Section 1, H in C-15 compounds occupies only tetrahedral sites, i.e. sites formed by four metal atoms. We have chosen Born-Mayer potentials to describe these interactions. On this assumption, the total potential energy, $V(r)$ is given by

$$V(\vec{r}) = \sum_i C_i \exp\left(-\frac{|\vec{r} - \vec{R_i}|}{\rho_i} \right) \qquad (2)$$

C_i and ρ_i are parameters characteristic of each metal atom forming the site, $|R_i|$ the metal–hydrogen distance and the sum is extended to the four nearest neighbour atoms. The eigenvalue problem is solved in the harmonic approximation by expanding the potential to second order around its minimum. The frequencies, ω_x, ω_y and ω_z are dependent on the C_i and ρ_i parameters and on the $|R_i|$ distances and are given by

$$\omega_j^2 = \frac{1}{m} \left. \frac{\partial^2 V(\vec{r})}{\partial x_j^2} \right|_{\vec{r}=\vec{r}_0} \qquad (3)$$

where the second derivatives are evaluated at the minimum of the potential, r_o. An extra equation is obtained from the condition of hydrogen being at the minimum of the potential.

The experimental values of the first hydrogen excitations (Table 1) are used as inputs to calculate, through ω_x, ω_y and ω_z, the potential parameters C_A, ρ_A, C_B and ρ_B where A and B stand for the A type atom and the B type atom in the C-15 AB_2 structure. In order to reduce the number of degrees of freedom we have fixed the metal–hydrogen distances. This can be done in a touching hard-spheres approach by using the values of the hydrogen hole size calculated by Westlake [1] (0.44 Å ($ZrTi_2$), 0.48 Å ($ZrCr_2$), 0.37 Å ($TiCr_{1.85}$) and 0.40 Å (ZrV_2) at the H concentrations used in this work) and the well known atomic radii of the metallic elements [1] (1.602 Å, 1.462 Å, 1.282 Å, and 1.346 Å for Zr, Ti, Cr and V, respectively). The calculated values for the metal–hydrogen dis-

Table 2
The parameters describing the H potential well in the three alloys, C_A, C_B, ρ_A and ρ_B [a]

Sample	Site	C_A (eV)	ρ_A (Å)	C_B (eV)	ρ_B (Å)	E_x (meV)	E_y (meV)	E_z (meV)	R_A (Å)	R_B (Å)
ZrTi$_2$	e	12898 ◊	0.180 ◊	60202 ●	0.1412 ●	127.0	127.0	170.1	2.040	1.904
ZrCr$_2$	g	10102 ◊	0.180 ◊	1507 *	0.1815 *	134.8	159.1	143.3	1.990	1.668
ZrV$_2$	g	10041 ◊	0.180 ◊	10843 +	0.1517 +	137.9	161.6	143.4	2.000	1.739
TiCr$_{1.85}$	g	51429 ●	0.140 ●	1349 *	0.1784 *	109.7	155.2	164.6	1.830	1.666

[a] The energy of the local modes, E_i, and the metal–hydrogen distances, R_i, obtained from our calculations. The C and ρ values corresponding to the same metal have been marked with the same symbols: ◊, Zr; ●, Ti; *, Cr; and +, V. The subscripts A and B stand for the A type atom and B type atom in the C-15 AB$_2$ compounds.

tances using this approach are summarised in Table 2. Neutron diffraction experiments on these compounds have been done recently by the authors. From the obtained results, we expect to improve the accuracy on the evaluation of metal–hydrogen distances.

We have studied the solutions of Eqs. (3) by a trial and error method and the results can be seen in Figs. 2(a–c). The x axis spans the ρ range in which it is possible to found solutions to Eqs. (3) at the imposed metal–hydrogen distances. The variation of C with ρ for Zr (a), Ti (b) and Cr and V (c) in the four compounds, ZrTi$_2$, ZrCr$_2$, TiCr$_{1.85}$ and ZrV$_2$, are shown. To obtain these curves we allow for a small variation of the metal–hydrogen distances, 0.001 Å, from the value calculated with the touching hard-spheres method and also we have taken into account the error involved on the determination of the experimental frequencies, 1 meV for isolated peaks and 2–5 meV in the case of overlapping peaks. The C–ρ curves for Zr (a) in the different compounds are quite similar. It means that if we assume similar ρ_{Zr} values ZrTi$_2$, ZrCr$_2$ and ZrV$_2$ compounds then the C_{Zr} values are also similar and then the interatomic potential created by zirconium in the three compounds is similar. This conclusion can also be extended to the titanium atom in ZrTi$_2$ and TiCr$_{1.85}$ compounds [Fig. 2(b)] and to the chromium atom in ZrCr$_2$ and TiCr$_{1.85}$ compounds [Fig. 2(c)].

However, the assumption that the same ρ_{Zr} value holds for Zr in ZrTi$_2$, ZrCr$_2$ and ZrV$_2$ compounds, the same ρ_{Ti} holds for Ti in ZrTi$_2$ and TiCr$_{1.85}$ compounds and the same ρ_{Cr} holds for Cr in ZrCr$_2$ and TiCr$_{1.85}$ compounds put some restrictions to the possible ρ values. This can be seen in Figs. 3(a–c). Fig. 3(a) shows the dependence of ρ_B with ρ_A in the four alloys. An almost linear dependence is obtained. If we chose a certain value for ρ_{Zr} in the ZrTi$_2$ alloy, let say 0.15 Å, the value for ρ_{Ti} should be around 0.12 Å. Then ρ_{Ti} in the TiCr$_{1.85}$ alloy should be also around 0.12 Å which fix the possible ρ_{Cr} values in the TiCr$_{1.85}$ and ZrCr$_2$ alloys. The interdependence between the parameters is more clearly shown in Figs. 3(b–c) where ρ_{Cr} (b) and C_{Cr} (c) as a function of ρ_{Ti} are displayed. It should be pointed out that the dependence of ρ_{Cr} and C_{Cr} with ρ_{Ti} in the ZrCr$_2$ alloy has been obtained through the dependence of ρ_{Ti} with ρ_{Zr} in the ZrTi$_2$ alloy, assuming same values of ρ_{Zr} in ZrCr$_2$ and ZrTi$_2$ alloys. As can be seen, values of ρ_{Ti} in the range 0.10–0.15 Å are needed in order to have similar ρ_{Cr} and C_{Cr} values in the ZrCr$_2$ and TiCr$_{1.85}$ compounds. This range of ρ_{Ti} corresponds to values in the range 0.12–0.20 Å for ρ_{Zr} as can be seen from the curve for the ZrTi$_2$ alloy in Fig. 3(a).

Table 2 shows the parameters obtained from the analysis above to describe the potential well of H in the ZrTi$_2$, ZrCr$_2$, TiCr$_{1.85}$ and ZrV$_2$ compounds. As shown above, the condition of $C - \rho$ values characteristic of each metal is
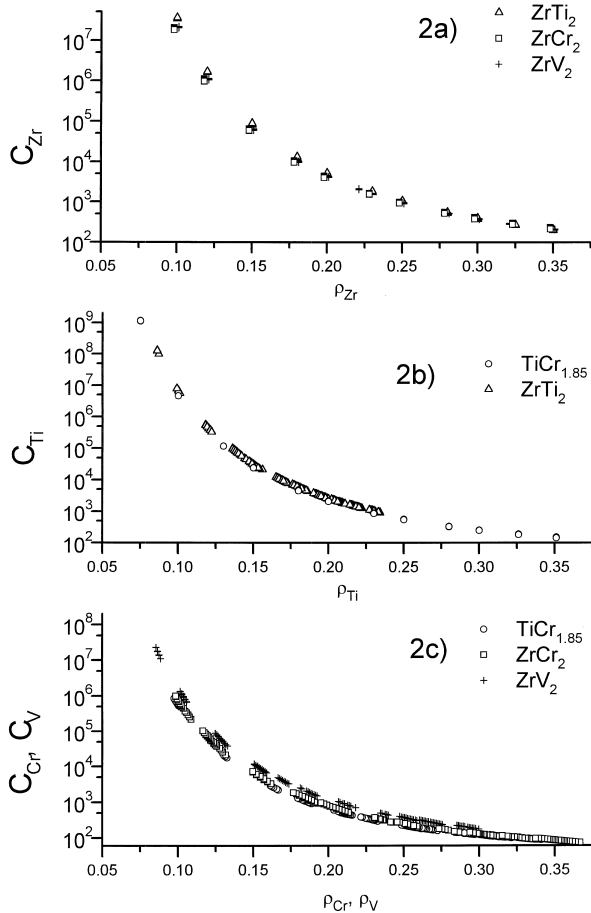

Fig. 2. Relationship between ρ (Å) and C (eV) parameters for zirconium in ZrTi$_2$, ZrCr$_2$, ZrV$_2$ alloys (a), titanium in TiCr$_{1.85}$, ZrTi$_2$ alloys (b), and chromium and vanadium in ZrCr$_2$, TiCr$_{1.85}$ and ZrV$_2$ alloys (c).
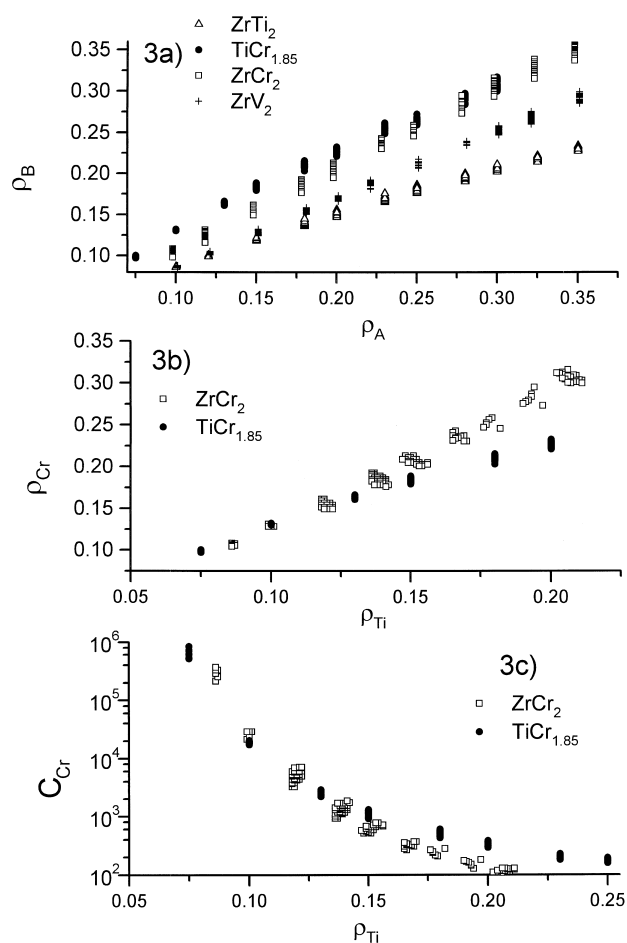
Fig. 3. (a) Relationship between ρ_A and ρ_B in the four alloys. Dependence of ρ_{Cr} (b) and C_{Cr} (c) with ρ_{Ti} in the $ZrCr_2$ and $TiCr_{1.85}$ compounds. ρ is given in Å and C in eV.

fulfilled inside a small range of $C - \rho$ values. The values quoted in Table 2 are those showing the smallest differences for the same metal in the different alloys. As can be seen, the potential well can be described by C and ρ parameters characteristic of each metal, with small variations between them.

The first excited state energy level differences calculated from the fitted C and ρ values are also given in Table 2 for the preferred sites in each compound. These values can be compared with the experimental values recorded in Table 1. This model also allows to predict the expected energy level differences for H in the possible alternative tetrahedral sites in the C-15 structure. These energies have been calculated for the e sites in the $ZrCr_2$ and $TiCr_{1.85}$ compounds and for the g site in the $ZrTi_2$ compound. The energies for the e sites in the $ZrCr_2$ and $TiCr_{1.85}$ samples are higher (138 meV (doublet), 180 meV (singlet) for $ZrCr_2$ and 129 meV (doublet), 211 meV (singlet) for $TiCr_{1.85}$) than those obtained for the g site, reflecting the smaller size of the e site in these compounds. In the case of H in the g site of the $ZrTi_2$ compound, however, we predict

energies of 104 meV, 117 meV and 127 meV for the three modes of vibration. The additional weak peak at 110 meV observed in the IINS spectrum of the $ZrTi_2$ sample [Fig. 1(a)], could be an indication of partial occupancy of the g site in this compound.

The additional peaks observed in the $TiCr_{1.85}$ spectra [Fig. 1(c)] could be due to vibrations of H in g sites where a Cr atom has been replaced by Ti atom. It should be pointed out that the non-stoichiometric $TiCr_{1.85}$ alloy is obtained by partial substitution of Cr atoms by Ti atoms. We have calculated local mode energies of 102 meV, 177 meV and 201 meV for this type of site, ignoring any atomic displacements. This would explain the observed peak at 182 meV whereas a peak at 102 meV would be obscured by the regular g site peak at 111 meV. On the other hand the peak at 201 does not appear on the spectra of Fig. 1(c) indicating that the calculated mode energies are only approximated as we have not taken into account the expected atomic displacements on replacing a Cr atom by a Ti atom.

The application of the calculated potentials to the description of the occupancy of the different sites and the diffusion behaviour of H in this compound will be the matter of a future publication [12].

5. Conclusions

IINS spectra of the C-15 Laves phase compounds $ZrTi_2H_{3.6}$, $ZrCr_2H_{0.9}$ and $TiCr_{1.85}H_{0.4}$ have been acquired at temperatures between 20 K and 200 K and the local modes of hydrogen in these alloys have been measured. This information has been used to derive the potential well seen by H atoms in these alloys. It has been built up using an interatomic potential of the Born-Mayer type for each one of the metal atoms forming the tetrahedral sites, g (A_2B_2), e (AB_3) or b (B_4). It has been shown that the hydrogen potential well can be described by parameters characteristic of each metal, with small variations in the different alloys.

References

[1] D.G. Westlake, J. Alloys Comp. 90 (1983) 251.
[2] J.F. Fernández, M. Kemali, D.K. Ross, J. Alloys Comp. 253–254 (1997) 248.

[3] R. Hempelmann, D. Richter, O. Hartmann, E. Karlsson, R. Wappling, J. Chem. Phys. 90 (3) (1989) 1935.

[4] M. Hansen, in: Constitution of Binary Alloys, McGraw-Hill, New York, 1958, pp. 565–573.

[5] J.F. Fernández, F. Cuevas, M. Alguero, C. Sánchez, J. Alloys Comp. 231 (1995) 78.

[6] J.R. Johnson, J.J. Reilly, Inorganic Chemistry 17 (1978) 3103.

[7] J. Rodríguez-Carvajal, Physica B 192 (1993) 55.

[8] A.V. Skripov, M.Yu Belyaev, J. Phys.: Condens. Matter 5 (1993) 4767.

[9] N.F. Miron, V.I. Shcherbak, V.N. Bykov, V.A. Levdik, Soviet Physics, Crystallography 16 (1971) 266.

[10] A.C. Lawson, W.H. Zachariasen, Physics Lett. 38A (1) (1972) 1.

[11] D. Fruchart, A. Rouault, C.B. Shoemaker, D.P. Shoemaker, J. Less-Common Met. 73 (1980) 363.

[12] J.F. Fernández, M. Kemali, D.K. Ross, C. Sánchez, in press.