the length of an elementary diffusion step, ℓ, may be calculated from the relation between Γ and the diffusity, D, namely, $\Gamma = hDq^2$ and $D = vl^2/n$. This rate is equal to the Larmor precession rate at the temperature of the minimum in the nuclear magnetic relaxation time. We find ℓ lies between 2 and 2.5Å from the Arrhenius relation of Figure 2 and either our own measurements of the relaxation or those of ref. /3/. As it depends on simple formulae and extrapolation of the data this result should be treated with some caution. Nevertheless, the best evidence we have is that the jump length is about equal to the second neighbour distance rather than the first. The transition may not take place directly but through the near-neighbour site since this route involves the least movement of the metal atoms. The observed jump length may be interpreted as an indication that the site-blocking is maintained.

The very small pre-exponential factor implies that the motion is not tightly coupled to the hydrogen optic modes. The reason for this is not very apparent but explanation may be sought from the details of the hopping mode. In the double transitions the atom moves to an empty, but blocked, site before reaching the vacancy. In order for this to occur, some re-distribution of the atoms which are the source of the blocking must take place. It may be accomplished by a local expansion of the hydrogen atom distribution rather than movement between sites. Thus the diffusion depends on the acoustic rather than the optic modes. The observed value of Γ_0 supports this notion.

References

1 Didisheim J.-J, Yvon K, Fischer P and Tissot P. Solid State Commun. 38 637 (1981).

2 Irodova A.V, Glazkov V.P, Somenkov V.A and Shil´shtein S.Sh. Sov. Phys. Solid State. 22 45 (1980)

3 Shinar J, Davidov D and Shaltiel D. Phys. Rev. B 30 6331 (1984).

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Localized Vibrational Motions of Hydrogen in the Storage Compound $Ti_{0.8}Zr_{0.2}CrMnH_3$ Studied by Slow Neutron Inelastic Scattering *

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The localized hydrogen vibrations in $Ti_{0.8}Zr_{0.2}CrMnH_3$ have been studied by inelastic neutron scattering. It was observed that there are basically only three types of tetrahedral interstices in this compound which differs in composition of Ti and Zr atoms. The larger radius of the Zr atoms leads to the formation of larger interstitial hole sizes, making the absorption of hydrogen in this compound easier.

Introduction

The interstitial hole size strongly influences the hydrogen absorption and thermodynamic properties of the hydrides formed from intermetallic compounds. In general, the larger the holes the more stable are the corresponding hydrides/1/.
The intermetallic pseudo-binary compound $Ti_{0.8}Zr_{0.2}CrMnH_3$ was developed for hydrogen storage/2/ keeping in mind that the corresponding iso-structural compound $TiMn_2$ does not absorb hydrogen, while another isostructural, $ZrMn_2$ easily absorbs large amounts of hydrogen. By

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appropriate combination of Ti and Zr atoms it is possible to control the stability of the corresponding hydride for practical applications. The only parameters that changed are the atoms radii, therefore it is believed that it is essentially the mean interstitial hole sizes which controls the hydrogen absorption in the intermetallic compound.

Neutron scattering has been used to study several properties of the interstitial sites occupied by hydrogen. Properties related to the hydrogen potential energy/3/, occupancy of different crystallographic sites/4/ and structural analysis of compounds/5/ have been achieved by this technique.

In this work a neutron spectroscopic analysis of the localized vibrational motions of hydrogen atoms in $Ti_{0.8}Zr_{0.2}CrMnH_3$ is presented and correlated with different hole sizes due to the difference in the atomic radii of Ti and Zr.

Theory

The differential scattering cross-section for neutrons from localized hydrogen vibrations in the interstitial site of type j is written as:

$$\left(\frac{\partial^2\sigma}{\partial\Omega\partial\omega}\right)_j = c_j \frac{N\sigma_i}{4\pi} \sum_{\ell=1}^{3} \frac{k_f}{k_i} \{n(\omega)+1\} \exp\{-2W_j(Q)\} \frac{\hbar Q^2}{2M\omega_{\ell j}} G(\omega-\omega_{\ell j}) \qquad (1)$$

where $\hbar\omega=E_i-E_f$ represents the neutron energy transter on scattering; c_j is the relative concentration of interstices of type j; N is the total number of hydrogen atoms; σ_i is the incoherent microscopic scattering cross-section; k_f and k_i are the final and initial neutron wave numbers respectively, $\{n(\omega)+1\}$ is the thermal occupation number; $\exp\{-2W_j(Q)\}$ is the Debye-Waller factor; Q is the scattering vector; $\omega_{\ell j}$ is the localized frequency; M is the hydrogen mass and $G(\omega-\omega_{\ell j})$ is a gaussian function which represents a resolution function convoluted with any dispersion function, if present.

In an inelastic neutron scattering experiment on hydrides, the contribution only due to hydrogen is easily isolated and enables us to determine directly the relative concentration of interstices of type j and the respective vibrational frequencies.

The interstices in $Ti_{0.8}Zr_{0.2}CrMnH_3$

Energetically different interstices in $Ti_{0.8}Zr_{0.2}CrMnH_3$ were derived from the results reported by Didisheim et al./6/ on the isostructural compound $ZrMn_2D_3$, having an hexagonal Laves-phase C-14 type structure. From their results the deuterium atoms in $ZrMn_2D_3$ occupy tetrahedral sites formed by two manganese and two zirconium atoms. There are four such interstices, named D1 through D4, which differ in sizes and point symmetry group. Nevertheless these differences are small and the interstices can be considered as equivalent, presenting the same environment to hydrogen atoms. As the interstices belong to C_{2V} point symmetry group, no degenerate hydrogen vibrational frequencies are expected.

In $Ti_{0.8}Zr_{0.2}CrMnH_3$ we have a splitting of the equivalent interstices into three types formed by TiTiMM, TiZrMM and ZrZrMM atoms (M=Cr or Mn), with respective fractions given by 0.64, 0.32 and 0.04, obtained from the composition of the compound. A total of nine vibrational frequencies are then expected. No distiction was made between Cr and Mn atoms since their radii are nearly the same. Also the chemical interaction of Cr and Mn with hydrogen is nearly the same, as indicated by thermodynamical data/7/.

Experimental details and results

The $Ti_{0.8}Zr_{0.2}CrMn$ intermetallic compound was produced by Gesellschaft fur Electrometallurgie, Nuernberg, West Germany; the preparation is described elsewhere/8/. The hydrogenation was performed in our laboratory by a direct reaction of the metallic alloy with hydrogen gas(99.99% purity), and sealed with a thin oxide layer by a slow reaction with oxygen at 77K/8/. The amount of hydrogen absorbed was determined by a controlled extraction of hydrogen at 870K in a fraction of previously prepared sample/9/.

The neutron spectrometer utilized in this work is a traditional Be-filter-time-of-flight (TOF) spectrometer installed at the material testing reactor IEA-R1 at IPEN-SP/10/. The incident neutron spectrum is centered at 3.5 meV and is 2 meV wide (FWHM). The overall resolution for 100 meV neutrons is 16 meV (FWHM).

The result of the scattering experiment taken at 45 degrees scattering angle at 299K is shown in figure 1. Three peaks can be observed indicating three distinct localized frequencies with considerable dispersion. Other recorded spectra at different scattering angles and temperatures present the same shape/9/.

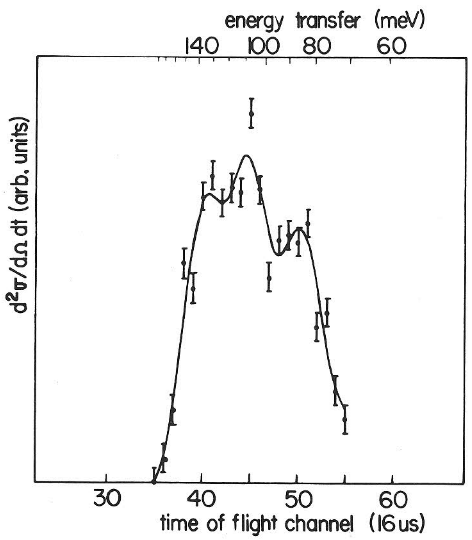

Figure 1. Time-of-flight distribution of neutrons scattered from localized motions of hydrogen in $Ti_{0.8}Zr_{0.2}CrMnH_3$ at 45º scattering angle and 299K temperature. Time per channel=16 μs. Flight path= 3.15 m.

Going from a TOF distribution, presented in figure 1, to a frequency distribution, a strong distortion of the spectrum occurs due to the thermal occupation factor and the visible structure observed in TOF spectrum disappears. Due to this, instead of the frequency data, the TOF data was fitted with three gaussian functions with common width, and is shown by the full curve in figure 1.

The energies of the modes were determined from the maxima of the gaussians after correction due to the thermal occupation number. The relative intensities of the three localized modes were derived from the areas of the three fitted gaussians according to equation (1) with the Debye temperature θ_D=311K/9/.

The overall results of this analysis is that the three distinct localized modes have the following frequencies centered at (energy scale): 141±5 meV, 109±5 meV and 83±5 meV and with the relative intensities 75±7%, 18±7% and 6.5±4% respectively. The resolution corrected mean

width of the peaks is 15±3 meV.

It should be mentioned that in this experiment, in a neutron energy-gain configuration, a well defined peak at 83 meV was observed, which can only hardly be detected in a neutron energy-loss configuration due to its small intensity in the frequency spectrum.

Discussion

It is readily seen that the observed relative intensities of the three localized modes resemble the relative occurence of the three types of nonequivalent interstices in $Ti_{0.8}Zr_{0.2}CrMnH_3$ (64%, 32% and 4% occurrences respectively for TiTiMM, TiZrMM and ZrZrMM sites). This indicates a tendency for each experimental peak to be composed of the three nondegenerate modes of hydrogen vibrations in each nonequivalent site. This is not an unexpected result for, in spite of the fact that the sites are of C_{2V} type point symmetry group (orthorhombic), they are not very much different from the cubic one.

If one of the three modes of the TiZrMM site (32% occurence) is shifted toward the peak corresponding to the TiTiMM site (64% occurence), the following intensities would be expected: 74.67%, 21.33% and 4%, which are in good agreement with the experimental intensities. In this way the 141 meV peak contains the three vibrational modes of TiTiMM site plus one of TiZrMM site. The 109 meV peak is due to only two modes of TiZrMM site and the 83 meV peak corresponds to the three modes of ZrZrMM site. This is the only way in which the various modes can be distributed in the three observed peaks that can explain the observed intensities. The TiZrMM site is the most asymmetric one of the three sites and it may gives rise to a different distribution of its three vibrational modes when compared with the distribution of the modes of the other two sites.

A striking feature of our results is that the lower frequencies are correlated with sites rich in Zr atoms while the higher frequencies are due to sites rich in Ti atoms. The presence of the Zr atoms distorts the lattice in a way to form interstices with larger holes. Applying the $\omega \sim R^{-3/2}$ relation/11/ to our results it is estimated that sites with two Zr atoms are 40% larger than sites with two Ti atoms. Keeping in mind that the mean interstitial hole size in the compound $Ti_{0.8}Zr_{0.2}CrMnH_3$ is 0.40Å and that, according to Westlake/12/, no hydrogen is absorbed in compounds which present interstitial holes with sizes lower than this value, it is readily seen why isostructural compounds with larger atoms, like Zr, form more stable hydrides than those with smaller atoms like Ti.

It seems that in $Ti_{0.8}Zr_{0.2}CrMnH_3$, the absorption of hydrogen takes place first in interstices of type ZrZrMM and, as the lattice expands locally, the hydrogen atom can jump to a neighboring site of TiZrMM or TiTiMM type.

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References

1. Lundin C.E., Lynch F.E.,MaGee C.B., J.Less-Common Met.56,19(1977)
2. Topler J., Bernauer O., Buchner H., Saufferer H., J.Less-Common Met.898,519(1982)
3. Ikeda S., Watanabe N., J.Phys.Soc.Jap.56(2),565(1987)
4. Benham M.J., Browne J.D., Ross D.K., J.Less-Common Met.103,71(1984)
5. Hempelmann R.,Richter D., Eckold G.,Rush J.J., Rowe J.M., Montoya M., J.Less-Common Met.104,1(1984)
6. Didisheim J.J., Ivon K., Shaltiel D.,Solid State Comm.31,47(1979)
7. van Mal H.H., Stability of Thernary Hydrides and some Applications. Holland, Phyllips, 1976.
8. Hempelmann R., Richter D., Pugliesi R., Vinhas L.A., J.Phys.F: Met.Phys.(London)13,59(1983)
9. Mestnik Filho J., Thesis, São Paulo, 1987
10. Mestnik Filho J., Vinhas L.A., Fulfaro R., Nucl.Instrum.Meth.Phys. Res.A.224,149(1984) and references therein
11. Irvine S.J.C., Ross D.K., Harris I.R., Browne J.D., J.Phys.F:Met. Phys.(London)14,2881(1984)
12. Westlake D.G., J.Less-Common Met.75,177(1980)

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Dynamics of Hydrogen Atoms Dissolved in Intermetallic ZrV_2*

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Vibrational spectra of ZrV_2H_x have been measured by neutron inelastic scattering at various concentrations of hydrogen ($x = 1.78$; 3.37; 4.23) and different temperatures. The vibrational energies of the hydrogen atoms have been established for both g- and e-types of the sites. For $ZrV_2H_{1.78}$ it has been shown that at $T > 296$ K the lifetime of optical vibrations is limited by third-order anharmonicity processes. At $T < 240$ K a splitting of the hydrogen atoms vibrational spectrum has been found.

Introduction

It is known from structure investigation /1,2/ that in the ZrV_2H_x system the sites of one type are available for interstitial atoms at $x < 2$, and those of two types at $x > 4$. Both types of sites have a tetrahedral symmetry but differ in the nature of the nearest neighbour atoms (2 Zr + 2 V for g-sites and Zr + 3 V for e-sites). One should expect that the presence of two available interstitial sites and redistribution of the hydrogen atoms on these sites would be displayed in the vibrational spectrum of the interstitial atoms. In this connection, the neutron inelastic scattering method was used to study the temperature and concentration dependence of the spectral distribution of the hydrogen vibrations in the ZrV_2H_x system ($x = 1.78$; 3.37; 4.23).

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