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IPEN - PUB - 194

SÃO PAULO

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DEPARTAMENTO DE FÍSICA E QUÍMICA NUCLEARES

INIS Categories and Descriptors

A13.10

HYDROGEN
INELASTIC SCATTERING
INTERSTITIALS
MOTION
SLOW NEUTRONS
TITANIUM COMPOUNDS

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ABSTRACT

The vibrational localized motions of hydrogen in the storage compound $Ti_{0.8}Zr_{0.2}CrMnH_3$ have been studied by slow neutron scattering, utilizing a berilium-filter-time-of-flight spectrometer.

An energy distribution, consisting of three peaks 50 meV wide(FWHM), corresponding to the energy transfer of 85, 115 and 141 meV has been observed and was attributed to hydrogen localized vibrations in three types of interstices which differs in composition of Ti and Zr atoms.

From the analysis of the observed peaks intensities, it was concluded that the lowest measured hydrogen vibrational frequency is correlated with interstices that are rich in zirconium atoms whereas the highest frequency is due to interstices rich in titanium atoms. Therefore the larger radius of the Zr atoms leads to the formation of interstices with larger intersticial hole sizes, which, in turn, makes possible the absorption of hydrogen in this compound, in contrast to an isostructural compound which contains only atoms with smaller radii, like Ti, in place of the atomic group $Ti_{0.8}Zr_{0.2}$.

MOVIMENTOS VIBRACIONAIS LOCALIZADOS DO HIDROGÊNIO NO COMPOSTO ARMAZENADOR $Ti_{0.8}Zr_{0.2}CrMnH_3$: ESTUDO POR ESPALHAMENTO INELÁSTICO DE NÊUTRONS LENTOS

RESUMO

Os movimentos localizados de hidrogênio no composto armazenador $Ti_{0.8}Zr_{0.2}CrMnH_3$ foram estudados através da técnica de espalhamento inelástico de nêutrons lentos, utilizando um expectrômetro de filtro de berí lio-tempo de vôo.

Uma distribuição em energia, consistindo de três picos com 50 meV de largura total à meia altura, correspondentes às transferências de ener gia de 85, 115 e 141 meV, foi observada e atribuida a vibrações localiza das do hidrogênio em três tipos de interstícios que diferem em composição de átomos de Ti e Zr.

Da análise das intensidades dos picos, observou-se que a frequência de vibração mais baixa está correlacionada com interstícios ricos em áto mos de zircônio, enquanto que a frequência mais alta é devida a interstí cios ricos em átomos de titânio. Portanto, átomos com raios maiores, como

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no caso do Zr, levam à formação de interstícios com cavidades maiores,pos sibilitando a absorção de hidrogênio nesse composto, ao contrário dos com postos isoestruturais que contém somente átomos com raios menores, como Ti, ao invés do grupo atômico $Ti_{0,8}Zr_{0,2}$.

INTRODUCTION

Many intermetallic compound which were developed for hydrogen storage purposes, had been studied from a fundamental point of view. It was verified that they present interesting peculiar behavior on the mo bility of hydrogen. It is observed that owing to the high hydrogen concen tration in these compounds a blocking effect occurs in the long range diffusional motion of hydrogen[1]. Due to the same reason, a correlation between consecutive jumps (back-jumps) appears, and may give rise to a relatively high local jump frequency[2]. Moreover, as in general the existing interstices in these compounds are only partialy occupied, one frequently observes a rapid localized motion of hydrogen like a rotational diffusion[3,4]. Finally the existence of different energetically non--equivalent hydrogen sites lead to more than one time scale for diffusional motion[2] or even to an inverse hydrogen concentration dependence of the diffusion coefficient[5].

These energetically non-equivalent hydrogen sites may uniquely be observed by neutron inelastic scattering as the frequencies of the hydrogen vibrations are strongly dependent on the metal-hydrogen distances and the degeneracy of the three vibrational modes depend on the point symetry of the corresponding interstitial hydrogen site. The neutron inelastic scattering technique has been thorougly utilized for determining the properties of the interstitial sites occupied by hydrogen. Properties related to the hydrogen potential energy[6], occupancy of different crys- tallographic sites as the hydrogen concentration increases[7] and even structural analysis of compounds[8] has been achieved by this technique.

The interstitial hole size strongly influences the hydrogen ab- sorption and thermodynamic properties of the hydrides formed from inter- metallic compounds. In general, larger the holes more stable the corre- sponding hydride[9].

The intermetallic pseudo-binary compound $Ti_{0,8}Zr_{0,2}CrMn$ was de- veloped for hydrogen storage[10] keeping in mind that the corresponding

isostructural compound $TiMn_2$ does not absorbs hydrogen while another iso-structural $ZrMn_2$ easily absorbs large amount of hydrogen. By appropriate combination of Ti and Zr atoms in a unique material it is possible to control the stability of the corresponding hydride for practical applications. In this way, since the only parameters that change are the atomic radii, it is believed that what is essentially controlled is the mean interstitial hole sizes in the intermetallic compound.

In this work we present a neutron spectroscopic analysis of the localized vibrational motions of hydrogen atoms in the storage compound $Ti_{0.8}Zr_{0.2}CrMnH_3$ and correlate them with the different interstitial hole sizes introduced by the distinct atomic radii of Ti and Zr atoms.

THEORY

In neutron spectroscopy, a beam of monoenergetic neutrons is made incident on a sample and the energy of scattered neutrons at a fixed scattering angle is determined. In hydrogenated materials, the scattering contribution due to hydrogen is isolated, since the scattering cross section due to hydrogen is an order of magnitude higher than for other elements.

In dealing with localized hydrogen vibrations it is assumed that these vibrations consists of isolated Einstein oscillators, which is a good approximation when the hydrogen oscillations present only small or no dispersion, which is frequently the case for tetrahedral interstitial sites. In this case the differential scattering cross-section for localized hydrogen vibration in the interstitial site of type j is written as:

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

where $\hbar\omega = E_i - E_f$ represents the neutron energy transfer 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 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 for a isotropic oscillator; Q is scattering vector; $\omega_{\ell j}$ is the localized frequency; M is the hydorgen mass and $G(\omega - \omega_{\ell j})$ is a

gaussian function which represents a resolutiun function convoluted with any dispersion function, if present.

Thus the measurement of differential neutron scattering from hydrogen vibrations enables us to determine directly the relative concentration of interstices of type j, and the respective vibrational frequencies.

THE INTERSTICES IN $Ti_{0.8}Zr_{0.2}CrMnH_3$

Our starting point in finding the energetically different interstices in $Ti_{0.8}Zr_{0.2}CrMnH_3$ was the results reported by Didisheim et al[11] on the isostructural compound $ZrMn_2D_3$. Their results assert that in $ZrMn_2D_3$ the deuterium atoms only occupy tetrahedral sites formed by two manganese and two zirconium atoms. There are four distinct crystallographic types of these interstices, named D1 through D4.

As both compounds $Ti_{0.8}Zr_{0.2}CrMnH_3$ and $ZrMn_2D_3$ have the same Laves-phase C-14 type structure[10], we determined the spatial configuration of the metallic atoms for each of these types of interstices in $Ti_{0.8}Zr_{0.2}CrMnH_3$, based on crystallographic data presented by Didisheim et al but using the unit cell dimensions of our compound (a=5.311Å and c=8.660Å). In doing this, it is firstly assumed that Ti and Zr atoms have the same radii and similarly for the Cr and Mn atoms. We labeled the atomic group $Ti_{0.8}Zr_{0.2}$ as type Z atoms and the group CrMn as M type atoms. So, our interstices are composed of two Z type and two M type atoms.

These calculations demonstrated that for all the four cristallographically distinct interstices (D1 to D4),the corresponding metal-to--hydrogen and corresponding metal-to-metal distances are the same within less than 1%. In other words, all the four interstices present the same environment for hydrogen. The hydrogen-to-metal distances are 2.01Å for H to type Z atoms and 1.73Å for H to type M atoms. So, from the point of view of hydrogen vibrations the four interstices are all equivalent and belong to C_{2v} type point simetry group. From this one expects three non degenerate hydrogen vibrational frequencies.

When one takes into account the different sizes of Ti and Zr atoms one has the splitting of the equivalent interstices in three types of non equivalent interstices, formed by TiTiMM, TiZrMM and ZrZrMM atoms(M=Cr or Mn), with respective fractions given by 0.64, 0.32 and 0.04, and obtained directly from the composition formula of the compound. A total of

nine vibrational frequencies are then expected. No distinction was made between Cr and Mn atoms as their radii are nearly the same when compared with Ti and Zr. The chemical interaction of Cr and Mn with hydrogen is nearly of the same strenght, as viewed from thermodynamical data[12].

In sumary, we have basically only three types of interstices which can be observed by neutron inelastic scattering on hydrogen vibrations,in the relatively complex intermetallic compound $Ti_{0.8}Zr_{0.2}CrMnH_3$.

EXPERIMENTAL DETAILS AND RESULTS

The $Ti_{0.8}Zr_{0.2}CrMn$ intermetallic compound was produced by Gesell-schaft fur Electrometallurgie, Nurnberq, West Germany, and the method of preparation is described elsewere[13]. Hydrogenation was performed in our laboratory by a direct reaction of the metallic alloy with hydrogen gas (99.99% purity), utilizing a spectially developed stainless-steel reactor. Three cycles of charging-discharging were sufficient to give a uniform hydride sample, which was then sealed with a thin oxide layer by a slow reaction with oxigen at 77K[13]. The amount of absorbed hydrogen was determined by a controlled extraction of hydrogen at 870K in a fraction of previously prepared sample. An X-Ray diffraction pattern was obtained in order to confirm the existence of only one hydride phase. No unreacted material was detected[14].

The powder sample was introduced in an aluminium container with dimensions 9.5x4.5x0.025 cm^3 and with 0.1 cm wall thickness. The sample transmission was 85% for 4.8Å neutrons.

The neutron spectrometer utilized in this work is a traditional Be--filter-time-of-flight spectrometer instaled in a beam port of a material testing swimming-pool reactor at IPEN-SP[15]. 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).

Several spectra were recorded with the sample in the temperature range of 299K to 398K and scattering angle in the range 25 to 90 degrees[16]. Here we present one spectrum of scattered neutrons in the region of localized hydrogen vibrations, taken for scattering angle of 45 degrees and temperature of 299K after corrections for unwanted counting, detector efficiency and chopper transmission[14].

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The result is shown in figure 1 in which a distribution consisting of three wide peaks is observed indicating that there are three distinct localized frequencies with considerable dispersion. All other recorded spectra present the same shape. The full curve in figure 1 is the result of a fit of three gaussian functions with a common width to reduce the number of adjustable parameters.

In going from a time-of-flight distribution, presented in figure 1, to a frequency distribution, a strong distrortion of the spectrum is observed due to the thermal occupation factor. Due to this, a small shift toward higher frequencies is acceptable as the widths of the gaussian functions are larger than the resolution width. The Debye temperature employed was 311K[14].

The overall results of this analysis is that the three distinct localized modes have following frequencies centered at (energy scale): 141 $\pm$ 5 meV, 115 $\pm$ 5 meV and 85 $\pm$ 5 meV with respective relative intensities given by: 75 $\pm$ 7%, 18 $\pm$ 7% and 6.5 $\pm$ 4%. The resolution corrected widths of the peaks are 51 $\pm$ 9 meV(FWHM).

DISCUSSION

It is readily observed that the relative intensities of the three localized modes, experimentally determined in this work, resemble that of the relative occurence of the three types of non equivalent intertices existing in the compound $Ti_{0.8}Zr_{0.2}CrMnH_3$ (64%, 32% and 4% occurences respectively for TiTiMM, TiZrMM and ZrZrMM sites). This indicates a tendency for each experimental peak to be composed of the three non degenerate modes of hydrogen vibration in each non equivalent site. This is not an unexpected result for, in spite of the fact that the sites are of C_{2v} type point simetry group (orthorhombic), they are not strongly departed from the isotropic one (cubic).

We made a calculation of the frequencies which would be observed if the force constants were hydrogen-to-metal distance dependent as $k \sim R^{-3}$[17]. The result was that the difference between the two extreme frequencies was less than 30 meV which is less than the experimentally observed widths and therefore confirms the assertion above.

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 fairly 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 115 meV peak is due to only two modes of TiZrMM site and the 85 meV peak correspond to 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 . Further more, the TiZrMM site is the most assymetric one of all the three sites leading us to expect that their three modes will be more split in frequency than the modes of other two sites. This explains only quali- tatively why one of the modes of TiZrMM sites would be shifted toward other peak. An experiment with more resolution is needed for more clear assertion.

A very stricking feature of our results is that the lower observed frequencies are correlated with sites rich in zirconium atoms while the higher frequencies are due to sites which are rich in titanium atoms . Therefore 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[17] 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 $0.40\overset{\circ}{A}$ and that, according to Westlake[18], no hydrogen is absorbed in compounds which present interstitial holes with sizes lower than that value, it is readily seen why isostructures with larger atoms like Zr absorbs hydrogen easily than those with smaller atoms like Ti.

Finally it should be mentioned that this type of experiments are frequently carried out in a neutron energy-loss configuration that avoids the thermal occupation correction. In our case, in the neutron energy- -gain mode we have observed a well defined peak at 85 meV which can hardly be detected by the energy-loss experiment, due to its small intensi ty in a density-of-states plot.

CONCLUSION

The observed density-of-states of the localized motions of hydrogen in the storage compound $Ti_{0.8}Zr_{0.2}CrMnH_3$ is well explained by the ex- istence of three non equivalent intertices which differ in composition of

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Ti and Zr atoms. It is concluded that larger atoms induces the appearence
of larger interstitial holes and makes easy the absorption of hydrogen in
this or other similar compounds.

ACKNOWLEDGMENTS

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CAPTIONS FIGURES

Figure 1   -   Time-of-flight Distribution of Neutron   Scattered by
Hydrogen in $Ti_{0.8}Zr_{0.2}CrMnH_3$

Time per channel   = 16 us
Flight path   = 3.15 m