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Local structure in hydrogenated Ti–Zr–Ni quasicrystals and approximants

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Abstract

We have investigated the influence of hydrogen on the local structure of Ti–Zr–Ni alloys, icosahedral quasicrystals or crystalline approximants, using extended X-ray absorption fine structure (EXAFS). With an increasing hydrogen-to-metal ratio from 0 to 1.7, a general increase of all the mean first distances was found except for the Zr–Ni (Ni–Zr) ones. The perturbation of the (quasi)lattice, induced by hydrogenation, is a maximum around the Ti and Zr atoms, which suggests that hydrogen atoms sit preferentially near titanium and zirconium atoms.

Keywords: Hydrogen storage materials; Liquid quenching; EXAFS; Synchrotron radiation; X-Ray spectroscopies

1. Introduction

The mechanism of hydrogen absorption has been intensively studied in amorphous and crystalline metal alloys. After the discovery of quasicrystals [1], a large body of theoretical and experimental work was devoted to the study of these intermetallic alloys with both long-range aperiodic order and crystallographically forbidden rotational symmetries. Among their physical properties, it has been found that some titanium/zirconium-based quasicrystals and their related alloys have a large capacity for hydrogen storage [2,3]. Quasicrystalline alloys or crystalline approximant phases contain a high number of tetrahedral sites, which are favourable to occupation by hydrogen. However, due to the lack of periodicity, the determination of the atomic structure is difficult in quasicrystals. Therefore, we have undertaken a study of the effect of hydrogenation on the local structure of Ti–Zr–Ni alloys, crystals or quasicrystals, by extended X-ray absorption fine structure (EXAFS) measurements using synchrotron radiation.

2. Experimental and data analysis

Samples of composition near $Ti_{45}Zr_{38}Ni_{17}$ for the icosahedral-phase quasicrystal and near $Ti_{50}Zr_{35}Ni_{15}$ for the 1/1 approximant (W-phase) were prepared and characterised at the Department of Physics of the Washington University (St. Louis, MO, USA) [3]. The samples were loaded with hydrogen from the gas phase [4]. Alloys hydrogenated to hydrogen to metal ratios (H/M) of 0.84, 1.2, 1.56 and 1.7 for the icosahedral phase and 1.2 and 1.4 for the crystalline phase were studied.

The EXAFS experiments, performed at the Ti, Ni and Zr K edges, were carried out at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE, Orsay, France) using the DCI synchrotron radiation facility on the experimental station EXAFS 13.

Standard procedures of normalization and background removal were followed to determine the EXAFS oscillations, χ, versus the photoelectron wave vector, k. The normalized EXAFS signals, $k^3\chi(k)$, are compared, for the different samples, in Figs. 1, 2 and 3, for, respectively the Ti, Zr and Ni edges. While the spectra look very similar for the icosahedral and 1/1 alloys with the same H/M (0 or 1.2), they show drastic differences between the non-hydrogenated samples and the hydrogenated ones (icosahedral or 1/1 phases), even for the less hydrogenated sample ($H/$

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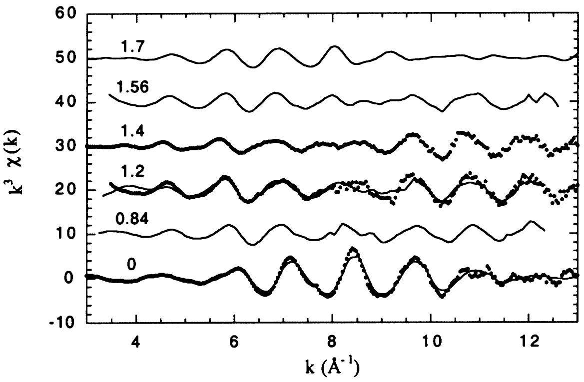

Fig. 1. The Ti K edge EXAFS spectra, $k^3\chi(k)$, of the icosahedral (solid line) and 1/1 (dots) Ti–Zr–Ni alloys.

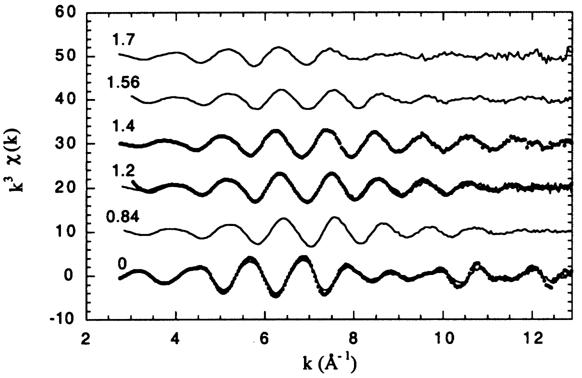

Fig. 2. The Zr K edge EXAFS spectra, $k^3\chi(k)$, of the icosahedral (solid line) and 1/1 (dots) Ti–Zr–Ni alloys.

$M=0.84$). There is a general tendency for the EXAFS oscillations to shift to lower k values when H/M increases, according to the simple idea that the interatomic distances increase together with the lattice parameter.

To compare the first coordination shell around Ti, Zr, and Ni atoms in the different samples, Fourier transforms of these EXAFS signals were obtained and the peaks of first neighbours were isolated and backtransformed to k space. These Fourier-filtered spectra were simulated using Gaussian distributions of neighbours. A structural model of the W phase, based on X-ray and neutron diffraction measurements and ab initio calculations [5], was used to analyse the EXAFS spectra of the approximant. Then, the local structure of the non-hydrogenated quasicrystalline phase and of the hydrogenated alloys was derived from that of the W phase. The number, N, of nearest neighbours was fixed to the values found in the model of the 1/1 phase, while the distances, R, and the disorder parameter (Debye–Waller factor), σ, were adjusted to fit the calculated spectra to the experimental data. The distances and disorder parameters used to reconstruct the EXAFS spectra are given in Table 1.

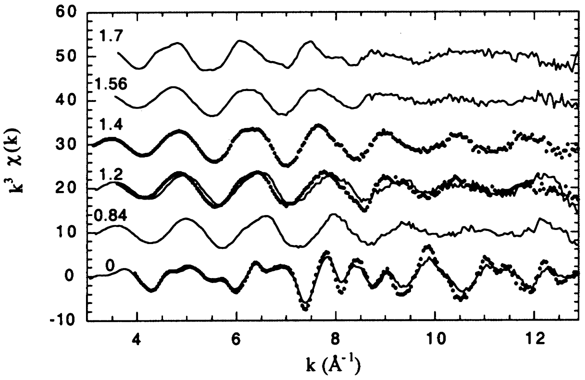

Fig. 3. The Ni K edge EXAFS spectra, $k^3\chi(k)$, of the icosahedral (solid line) and 1/1 (dots) Ti–Zr–Ni alloys.

3. Results and discussion

The basic cluster for W Ti–Zr–Ni is the Bergman-type cluster, the center being occupied by a nickel atom. A first icosahedral shell around nickel atoms is occupied by 12 titanium atoms at 2.78 Å. A larger, second-shell, icosahedron is filled with 12 titanium/zirconium atoms. A large number of available, more or less distorted, tetrahedral sites can be found in the structure.

The average distances determined by EXAFS in the 1/1 phase are in good agreement with the diffraction results. There is also a good correlation of the distances and disorder parameters obtained for the heterogeneous pairs from the different edges. The distributions of distances are very broad in the model of the 1/1 phase, which does not allow a precise determination of the mean distances by EXAFS. Most average interatomic distances have values near the sum of the atomic radii (Ti: 1.47 Å, Zr: 1.60 Å, Ni: 1.24 Å). However, the first Ti–Ni correlation, 2.46 Å, is clearly shorter than the sum of the atomic radii of Ti and Ni (2.71 Å). Also, the Zr–Ni (Ni–Zr) mean distance, 3.21 Å, is greater than the sum of the atomic radii of Zr and Ni (2.84 Å).

For the icosahedral phase, the R values are close to those found for the 1/1 phase (Table 1), which agrees with the similarity observed in the EXAFS spectra of the icosahedral and 1/1 phases. Therefore, similar clusters should be found in both types of alloys. Somewhat greater σ values were found, which could mean either that the icosahedral phase is more disordered than the 1/1 phase, or that it has a broader distribution of distances.

The spectra of the hydrogenated alloys could be correctly simulated considering that the mean coordination numbers remain unchanged. The distances and disorder parameters, used to fit the spectra are given in Table 1. There is a rather good correlation of the distances obtained for the heterogeneous pairs from the different edges. With hydrogenation, some larger values of the σ parameter were generally obtained.

The evolution of the distances as a function of H/M is

Table 1
First environments in Ti–Zr–Ni and Ti–Zr–Ni:H icosahedral alloys or 1/1 approximants

Central atom			1/1		i		$i+0.84$		$i+1.2$		1/1+1.2		1/1+1.4		$i+1.56$		$i+1.7$	
			R (Å)	σ (Å)	R (Å)	σ (Å)	R (Å)	σ (Å)	R (Å)	σ (Å)	R (Å)	σ (Å)	R (Å)	σ (Å)	R (Å)	σ (Å)	R (Å)	σ (Å)
Ti	1	Ni	2.45	0.105	2.46	0.115	2.60	0.18	2.60	0.19	2.49	0.15	2.62	0.12	2.58	0.12	2.58	0.13
	1	Ni	2.82	0.08	2.80	0.06	2.82	0.06	2.83	0.06	2.82	0.04	2.84	0.06	2.84	0.07	2.71	0.15
	4.9	Ti	2.85	0.18	2.85	0.19	2.95	0.24	2.99	0.20	2.88	0.21	3.04	0.19	2.93	0.20	2.95	0.14
	5.1	Zr	3.02	0.12	3.02	0.13	3.21	0.13	3.22	0.12	3.24	0.13	3.27	0.13	3.25	0.125	3.20	0.14
Zr	8	Ti	3.05	0.12	3.06	0.135	3.20	0.16	3.24	0.16	3.24	0.17	3.28	0.19	3.20	0.19	3.30	0.16
	2.75	Ni	3.25	0.09	3.28	0.11	3.22	0.20	3.21	0.18	3.23	0.12	3.25	0.10	3.16	0.14	3.11	0.12
	4.5	Zr	3.33	0.10	3.34	0.11	3.39	0.12	3.42	0.12	3.43	0.13	3.45	0.14	3.39	0.14	3.50	0.12
Ni	2.8	Ti	2.48	0.08	2.50	0.10	2.54	0.09	2.56	0.10	2.59	0.09	2.58	0.09	2.62	0.11	2.62	0.11
	2.8	Ti	2.71	0.09	2.72	0.11	2.70	0.15	2.71	0.14	2.73	0.15	2.75	0.11	2.76	0.16	2.74	0.14
	5.6	Zr	3.18	0.12	3.18	0.13	3.15	0.18	3.21	0.17	3.18	0.17	3.26	0.17	3.26	0.18	3.10	0.21

$\Delta R = \pm 0.05$ Å and $\Delta\sigma = \pm 0.04$ Å.

shown in Fig. 4. No distinction has been made between the two types of phases, crystalline or quasicrystalline, since very similar environments were obtained for both of them. The lines are guides for the eye. In agreement with the increase in the quasilattice constant measured by X-ray diffraction, there is a general increase of all the distances, except for the Zr–Ni (Ni–Zr) ones. The increase of the Zr–Ti correlation together with the decrease of the Zr–Ni distance results in a remarkable inversion of these distances around $H/M = 1$. Consequently, there is an inversion of the titanium and nickel atomic subshells in the environment of Zr atoms. The increase of distances is a maximum for the Ti–Zr correlation. Therefore, it can be concluded that the perturbation of the lattice due to hydrogenation is also a maximum around the Ti and Zr atoms and, consequently, that hydrogen atoms sit preferentially near Ti and Zr atoms, in agreement with previous EXAFS results [6].

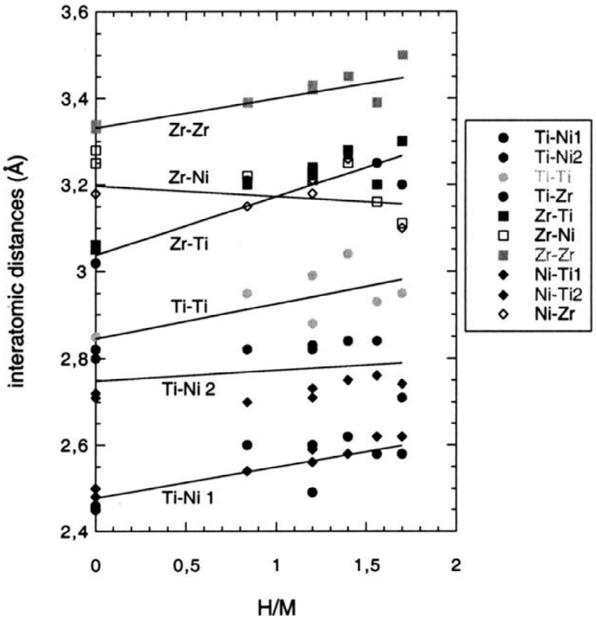

Fig. 4. Evolution of the first interatomic distances as a function of H/M in Ti–Zr–Ni alloys. The lines are guides for the eye.

In the model of the 1/1 phase, all Zr–Ni distances are larger than the sum of the atomic radii of Zr and Ni. As a consequence, these correlations could be more easily reduced upon hydrogenation, the corresponding Zr and Ni atoms being displaced from their ideal positions. The introduction of hydrogen in the (quasi)lattice induces, therefore, not only an expansion of the lattice, but can also bring some atoms closer together. As the changes in the distances are not the same for all types of atoms, although the lattice parameter increases linearly, the structure of the hydrogenated alloys is not a simple dilatation of that of the non-hydrogenated one. Moreover, the different changes in the distances could result, in the local structure, in large distortions, reflected by the larger values generally obtained for the disorder parameter.

4. Conclusions

EXAFS measurements are reported in Ti–Zr–Ni alloys, quasicrystals and approximants. The local structure was near identical in the crystalline and quasicrystalline alloys with the same H/M ratio (0 or 1.2). All the mean interatomic distances were found to increase with increasing hydrogen content, except for the Ni–Zr (Zr–Ni) ones, which show an anomalous behaviour, decreasing with increasing H/M. As the increase of distances is a maximum for the Ti–Zr correlation, the perturbation of the lattice due to hydrogenation is also a maximum around Ti and Zr neighbours. Therefore, it can be concluded that hydrogen atoms sit preferentially near Ti and Zr neighbours, confirming previous results. The increase of the Zr–Ti correlation together with the decrease of the Zr–Ni one results in a remarkable inversion of the atomic subshells of titanium and nickel around zirconium for a H/M ratio around 1. During the desorption process, the lattice is shrinking and the exchange of Ti and Ni atoms could be less easy, which could explain some difficulties to desorb completely the samples. The hydrogenation process appears of very complex nature, leading to a reorganization of the local structure, but leaving unchanged the long range structure.

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