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Neutron diffraction study of the location of deuterium in the deuterium-stabilized $ZrTi_2D_{3.83}$ phase

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Abstract

The location of D atoms in the deuterium-stabilized $ZrTi_2D_{3.83}$ phase with C15-type host lattice has been studied by neutron diffraction in the temperature range 11–300 K. It is found that D atoms occupy two types of sites of the space group $Fd\bar{3}m$: 32*e* ($ZrTi_3$) and 96*g* (Zr_2Ti_2). Most of the deuterium atoms are located in 32*e* sites. The occupancy of these sites is found to increase from 0.81 at 300 K to 0.94 at 11 K. Thus, as the temperature decreases, the $ZrTi_2$–D system approaches the fully ordered state with the completely occupied sublattice of 32*e* sites. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The hydrogen-stabilized $ZrTi_2H_x(D_x)$ phase discovered by Miron et al. [1] is an interesting example of hydrogen-induced ordering in alloys. Zr and Ti form only disordered solid solutions with the hexagonal close-packed (h.c.p.) lattice. However, the absorption of hydrogen by the disordered h.c.p. alloy $Zr_{0.33}Ti_{0.67}$ results in the formation of the $ZrTi_2H_x(D_x)$ phase ($3 \leq x \leq 4$) with an ordered cubic C15-type host lattice [1,2]. Recently, a similar hydrogen-stabilized phase with a C15-type host lattice has been found in the $HfTi_2$–H(D) system [3,4].

Hydrogen atoms in C15-type hydrides $AB_2H_x(D_x)$ are known to occupy two types of tetrahedral interstitial sites: 32*e* (AB_3) and 96*g* (A_2B_2). In most of the studied C15 hydrides, H(D) atoms occupy only *g* sites at low hydrogen concentrations; *e* sites start to be filled above $x \approx 3$ [5,6]. On the basis of neutron diffraction measurements, H(D) atoms in C15-type $ZrTi_2H_x(D_x)$ have been reported [1] to occupy only *e* sites. However, a number of recent results make this conclusion questionable. (1) X-ray diffraction studies of the phase diagram of the $ZrTi_2$–H system over a wide range of hydrogen content [7] have shown that, for the C15-type $ZrTi_2H_x$ phase, a single-phase state at room temperature is retained up to $x = 4.7$. Since the complete filling of the *e*-site sublattice corresponds to $x = 4$, one may expect *g* sites to be partially occupied by hydrogen, at least for $x > 4$. (2) Quasielastic neutron scattering measurements [8] have revealed that a fraction of hydrogen atoms in $ZrTi_2H_{3.9}$ participate in the fast localized hopping within the hexagons formed by *g* sites. (3) The hydrogen vibrational spectrum of $ZrTi_2H_{3.6}$ measured by inelastic neutron scattering [9] contains additional weak peaks at 110 meV and 145 meV; these peaks may result [10] from a partial occupancy of *g* sites in this compound. (4) Neutron diffraction measurements on the closely related system $HfTi_2D_4$ [4] have shown that, at room temperature, about 3/4 of all D atoms occupy *e* sites, the rest of D atoms being in *g* sites. It should also be noted that, in the early diffraction work on $ZrTi_2D_x$ [1], the data treatment was semi-quantitative (the diffraction profile was not refined), and therefore the resulting site occupancies might not be quite reliable.

The aim of the present work is to study the location of deuterium in the deuterium-stabilized $ZrTi_2D_x$ phase and the changes in deuterium distribution with temperature. We have performed high-resolution neutron diffraction measurements on a powdered $ZrTi_2D_{3.83}$ sample in the temperature range 11–300 K. The results are analysed to

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determine the temperature dependence of the structural parameters, including the positions of D atoms and the occupancy of these positions. The structural parameters of $ZrTi_2D_{3.83}$ are compared to those of the related system $HfTi_2D_4$.

2. Experimental details

The $ZrTi_2$ alloy was prepared by arc melting and repeated remelting of appropriate amounts of high-purity Zr and Ti in a helium atmosphere. The ingot of $ZrTi_2$ was charged with deuterium using a Sieverts-type vacuum system. After annealing the ingot for 2 h in vacuum at 800°C, the calculated amount of D_2 gas was admitted to the system at this temperature. Consequently, the sample was slowly cooled to room temperature (for about 9 h) in a deuterium atmosphere. The deuterium content of the $ZrTi_2D_x$ sample, $x=3.83\pm0.08$, was determined from the pressure change in the calibrated volume of the system.

The powdered sample was sealed under helium gas in a cylindrical vanadium container with a diameter of 8 mm. Neutron diffraction measurements were performed on the high-resolution powder diffractometer BT1 at the NIST Center for Neutron Research (National Institute of Standards and Technology, Gaithersburg, MD) using the Cu(311) monochromator. The neutron wavelength λ was 1.5402 Å. Horizontal collimations of 15′, 20′, and 7′ of arc were used before and after the monochromator and after the sample, respectively. Neutron diffraction patterns were recorded in the scattering angle range $3° \leq 2\theta \leq 160°$ with a step of 0.05° at temperatures $T=11$, 100, 200 and 300 K. A closed-cycle helium refrigerator was used for sample cooling. Profile refinements of the diffraction patterns were made with the GSAS program [11]. Neutron scattering amplitudes used in the refinements were 7.16 fm for Zr, −3.44 fm for Ti, and 6.67 fm for D [12].

3. Results and discussion

The neutron diffraction patterns and the agreement between the observed and calculated intensities for $ZrTiD_{3.83}$ at 300 and 11 K are shown in Fig. 1. Over the entire temperature range studied the experimental diffraction patterns can be attributed to the cubic C15-type structure (space group $Fd\bar{3}m$) with Zr atoms in 8*a* (1/8, 1/8, 1/8), Ti atoms in 16*d* (1/2, 1/2, 1/2) and D atoms partially occupying 32*e* (x_1, x_1, x_1) and 96*g* (x_2, x_2, z_2) sites. The initial unconstrained structure refinements have led to the total deuterium content slightly exceeding 4 atoms per formula unit and to a negative value of the isotropic temperature factor *B* for Zr at 11 K. In the final refinement the occupancies of 32*e* and 96*g* sites have been constrained to yield the total D content of 3.9 atoms per formula unit. This value is close (being within the experimental uncertainty) to the value $x=3.83\pm0.08$ determined from deuterium absorption. We have also assumed that the isotropic temperature factors for D in 32*e* and 96*g* sites are equal. The occupancy of 96*g* sites at low temperatures is found to be very small; therefore, the positional parameters of D atoms in 96*g* sites at $T \leq 200$ K have been fixed to the values of these parameters at 300 K. The structural parameters and the agreement factors resulting from the fits to the data at different temperatures are listed in Table 1.

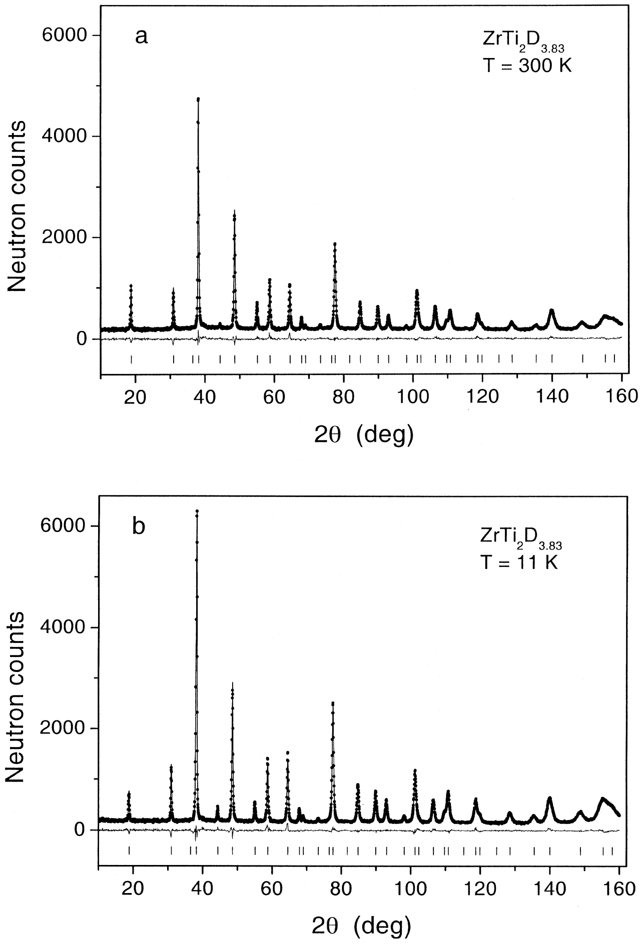

Fig. 1. Observed (circles) and calculated (solid line) neutron diffraction patterns for $ZrTi_2D_{3.83}$ at 300 K (a) and 11 K (b). The solid line below the data shows the difference between the observed and calculated diffraction patterns. Vertical bars indicate the calculated positions of Bragg peaks.

As can be seen from this table, most of the D atoms are located in *e* sites. However, at 300 K a significant fraction of D atoms (~17%) is found to occupy *g* sites. This is consistent with the results of recent quasielastic neutron scattering measurements [8] showing that a fraction of H atoms in $ZrTi_2H_{3.9}$ participates in the fast localized motion on the *g*-site sublattice.

As the temperature decreases, *g* sites are progressively depopulated, so that at 100 K and 11 K the occupancy of *g* sites is negligible. It should be noted that the unconstrained

Table 1
Temperature dependence of the structural parameters of $ZrTi_2D_{3.83}$ resulting from the profile refinements for the space group $Fd\bar{3}m$[a]

Atom	Position	Parameter	300 K	200 K	100 K	11 K
		a (Å)	8.1551(2)	8.1538(2)	8.1541(2)	8.1542(2)
Zr	8*a* (1/8, 1/8, 1/8)	n	1	1	1	1
		B (Å^2)	0.52(3)	0.34(3)	0.16(2)	0.08(2)
Ti	16*d* (1/2, 1/2, 1/2)	n	1	1	1	1
		B (Å^2)	0.99(3)	0.75(3)	0.65(3)	0.62(3)
D1	32*e* (x_1, x_1, x_1)	x_1	0.26883(6)	0.26870(5)	0.26849(4)	0.26838(4)
		n_1	0.809(2)	0.889(2)	0.939(2)	0.940(2)
		w_1	3.236(8)	3.556(8)	3.756(8)	3.760(8)
		B_1 (Å^2)	1.46(2)	1.27(2)	1.12(2)	1.03(2)
D2	96*g* (x_2, x_2, z_2)	x_2	0.0565(7)	0.0565	0.0565	0.0565
		z_2	0.8864(8)	0.8864	0.8864	0.8864
		n_2	0.055(1)	0.029(1)	0.012(1)	0.012(1)
		w_2	0.66(1)	0.35(1)	0.14(1)	0.14(1)
		$B_2 = B_1$ (Å^2)	1.46(2)	1.27(2)	1.12(2)	1.03(2)
		R_{wp} (%)	5.15	5.13	5.43	5.26
		R_p (%)	4.33	4.30	4.57	4.38
		χ^2	1.186	1.195	1.301	1.310

[a] a is the lattice parameter; n is the site occupancy factor and B is the isotropic temperature factor. The subscripts 1 and 2 refer to D atoms in 32*e* and 96*g* sites, respectively. w_i are the numbers of D atoms per formula unit located in the corresponding sites. R_{wp}, R_p and χ^2 are the standard agreement factors [11]. Calculated standard deviations for parameters are given in parentheses.

refinements of the structural parameters lead to a similar behaviour of site occupancies, including a significant degree of *g*-site filling at 300 K and a negligible *g*-site occupancy at low temperatures. The changes in the occupancies of *e* and *g* sites with temperature lead to considerable changes in the Bragg peak intensities (compare the relative intensities of the low-angle peaks at 300 K and 11 K in Fig. 1). Such a redistribution of D atoms between *e* and *g* sites indicates that the ground state energy of deuterium in *e* sites is lower than that in *g* sites. The redistribution of D atoms with temperature in $ZrTi_2D_{3.83}$ is similar to that observed in the related deuterium-stabilized $HfTi_2D_4$ phase [4]. For the latter system the occupancy of *g* sites n_2 is found to decrease from 0.086 at 293 K to 0.050 at 1.5 K [4]. Comparison with the corresponding data in Table 1 shows that in the temperature range studied, the *g*-site occupancy in $ZrTi_2$–D is lower than in $HfTi_2$–D. The numbers of interstitial atoms occupying two types of sites, w_i ($i = 1$, 2), are usually described by the standard expression [13]

$$\frac{(M_1 - w_1)w_2}{(M_2 - w_2)w_1} = \exp\left(\frac{E_1 - E_2}{k_B T}\right), \qquad (1)$$

where M_i are the multiplicities of sites (in our case, $M_1 = 4$ and $M_2 = 12$ per formula unit) and E_i are the corresponding site energies. However, we have found that the observed temperature dependence of w_i in $ZrTi_2D_{3.83}$ cannot be described in terms of Eq. (1) with the constant energy gap $\Delta E = E_2 - E_1$. Similar conclusions have been made on the basis of the inelastic neutron scattering results for C15-type ZrV_2H_x [14] and the neutron diffraction data for $HfTi_2D_4$ [4]. Kinetic restrictions on deuterium redistribution at low temperatures may be responsible for the failure of Eq. (1).

We have not found any signs of phase transformations in $ZrTi_2D_{3.83}$. Most of the Laves-phase hydrides with considerable H(D) concentrations show hydrogen order–disorder transitions accompanied by host lattice distortions [5]. However, the $ZrTi_2D_{3.83}$ system appears to be close to the fully ordered state with a completely filled sublattice of *e* sites. Therefore, as the temperature decreases, this system approaches the fully ordered state by increasing the occupancy of *e* sites, i.e. without phase transitions.

The positional parameters, x_2 and z_2, of deuterium in *g* sites of $ZrTi_2D_{3.83}$ (Table 1) differ considerably from the corresponding 'ideal' values, $x_{id} = 0.063$ and $z_{id} = 0.875$, derived for the case of the closest packing of hard spheres. It has been suggested [15] that such displacements of H(D) atoms from the 'ideal' positions in *g* sites of the cubic Laves phase AB_2 are related to deviations of the actual ratio of the metallic radii R_A/R_B from its 'ideal' value, $(R_A/R_B)_{id} = 1.225$. In fact, for the deuterium-stabilized $ZrTi_2$–D phase the value of R_A/R_B is 1.096, being anomalously low for Laves-phase compounds [16]. It is interesting to note that for the C15-type system TaV_2 with nearly the same value of R_A/R_B ($= 1.090$), the positional parameters of D atoms in *g* sites ($x_2 = 0.055$, $z_2 = 0.888$ [17]) are very close to the corresponding values for $ZrTi_2D_{3.83}$. Thus, our results for $ZrTi_2$–D are consistent with the idea that for the cubic Laves phases, the ratio R_A/R_B is related to the positional parameters of H(D) atoms in g sites. For comparison, for C15-type $ZrCr_2$–D with $R_A/R_B = 1.250$, $x_2 = 0.064$ and $z_2 = 0.870$ [18], i.e. both the ratio R_A/R_B and the positional parameters x_2 and z_2 are close to the corresponding 'ideal' values.

The sublattice of g sites in cubic Laves phases consists of hexagons [6,15]; it can be characterized by the distance r_{g1} between the nearest sites within a hexagon and the distance r_{g2} between the nearest sites on different hexagons. Using our structural data for $ZrTi_2D_{3.83}$ at 300 K, we find that $r_{g1} = 1.13$ Å and $r_{g2} = 1.58$ Å. Note that the significant difference between the values of r_{g1} and r_{g2} is favourable for an observation of the fast localized motion of hydrogen within g-site hexagons [15]. Such a localized H motion has been recently revealed in $ZrTi_2H_{3.9}$ by means of quasielastic neutron scattering [8].

The value of the positional parameter x_1 for deuterium in e sites of $ZrTi_2D_{3.83}$ (0.2688 at 300 K) is close to the corresponding value found for $HfTi_2D_4$ (0.2668 at 293 K [4]). The distance r_{eg} between the nearest e and g sites in $ZrTi_2D_{3.83}$ is 1.34 Å. Since each g site has one nearest-neighbour e site and r_{eg} is shorter than the 'blocking' radius of 2.1 Å [6], the partial occupation of the sublattice of g sites by deuterium prevents the sublattice of e sites from being fully occupied. On the other hand, the distance between the nearest e sites, $r_{e1} = 2.45$ Å, is considerably longer than the 'blocking' radius; this means that there is no blocking within the sublattice of e sites. The distances between D atoms in e sites and the nearest-neighbour metal atoms at 300 K are $r_{\mathrm{Zr-D1}} = 2.03$ Å, $r_{\mathrm{Ti-D1}} = 1.90$ Å. As is typical for many intermetallic deuterides [5,6], these distances are close to the corresponding distances in the binary deuterides ZrD_2 (~2.07 Å) and TiD_2 (~1.92 Å).

4. Conclusions

The analysis of our neutron diffraction data for the deuterium-stabilized $ZrTi_2D_{3.83}$ phase with C15-type host lattice has shown that D atoms occupy two types of interstitial sites: 32e ($ZrTi_3$) and 96g (Zr_2Ti_2). In contrast to the results of the previous study of the structure of $ZrTi_2$–D [1], the occupancy of g sites is found to be significant at 300 K. The partial occupation of g sites is consistent with the results of recent quasielastic neutron scattering measurements on $ZrTi_2H_{3.9}$ [8]. As the temperature decreases, g sites are progressively depopulated, and the system gradually approaches the fully ordered state with the completely occupied sublattice of e sites.

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