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Journal of Alloys and Compounds 224 (1995) 241–243

Journal of ALLOYS AND COMPOUNDS

Temperature-induced structural changes in $Be_2ZrD_{1.5}$ studied by powder neutron diffraction

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Received 3 December 1994

Abstract

Based on Rietveld analysis of powder neutron diffraction data, the deuterium atoms in $Be_2ZrD_{1.5}$ are found at 298 K to occupy trigonal bipyramidal sites. In the AlB_2 type structure, two tetrahedral and one trigonal bipyramidal sites are closely located and can only be occupied by one deuterium atom. The coordination found at 298 K may represent an average of deuterium atoms occupying all the three mentioned positions, which is indicated by a large displacement factor. At low temperatures, $T<250$ K, new reflections appear indicating a superstructure. The few additional reflections did not allow determination of the low temperature structure. However, the Rietveld refinements of the filled up AlB_2 type structure in space group *P6/mmm*, showed significant improvement for the model where deuterium solely occupies tetrahedral sites. The results indicate a continuous transition from a (partly) ordered structure at $T=12$ K with deuterium in tetrahedral sites, to a disordered structure with deuterium, in average, filling the trigonal bipyramidal sites at 298 K.

Keywords: Powder neutron diffraction; Rietveld analysis; Metal hydrides

1. Introduction

The crystal structure of Be_2Zr is capable of incorporating hydrogen atoms up to a composition of about $Be_2ZrH_{1.5}$ [1,2]. According to powder neutron diffraction data at room temperature, the basic structure is hexagonal of AlB_2 type, space group *P6/mmm*, with zirconium in (0,0,0), beryllium in (1/3,2/3,1/2) and deuterium in (1/3,2/3,0).

Westlake [3] applied a simple geometric model to predict preferred hydrogen sites in several Be-based intermetallic phases, including $Be_2ZrD_{1.5}$. Formation of stable hydrides is excluded for a hole radius less than 40 pm and/or H–H (or D–D) distances less than 210 pm. In Be_2Zr both the tetrahedral sites [Zr_3Be coordination polyhedron; 4h position, (1/3,2/3,z) with $z\approx0.02$] and the trigonal bipyramidal sites [Zr_3Be_2 coordination polyhedron; 2c position, (1/3,2/3,0)] satisfy these criteria.

The earlier powder neutron diffraction study showed that deuterium occupies the trigonal bipyramidal sites at 298 K [1,2]. This type of coordination is very unusual for hydrogen in metal hydrides. It was pointed out by Westlake [3] that since the 4h and 2c positions are very closely located it may be difficult to determine which of these is actually occupied. In the earlier study, a statistical distribution of deuterium over the 4h and 2c positions was tested out during the profile refinements, however, without improving the fit relative to the model with just 2c occupancy.

Hydrogen diffusion is substantial in several metal hydrides [4]. A recent study shows that in Be_2Zr the diffusion is actually two-dimensional in nature [4], probably owing to the closeness of hydrogen sites within the basal *ab*-plane of the structure and blocking of *c* axis diffusion owing to dense "Be layers". The earlier powder neutron diffraction (PND) study was restricted to 298 K [1,2]. However, in order to better judge whether hydrogen may be statically or dynamically distributed over more sites it was considered necessary to reinvestigate $Be_2ZrD_{1.5}$ with neutron diffraction techniques, in particular at low temperatures. During these investigations, clear indications for a different hydrogen occupancy were found, which called for careful studies of the temperature dependence of the phenomenon. The present paper provides independent indications for an order/disorder-like change in the occupancy, from tetrahedral at low temperature to trigonal bipyramidal (in average) at room temperature.

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0925-8388/95/$09.50
SSDI 0925-8388(95)01539-6

2. Experimental

The Be_2Zr sample was prepared by arc melting and deuterated at room temperature and atmospheric pressure (for details, see [1]). Since Be_2Zr forms via a peritectic reaction, it was difficult to achieve a completely pure and homogeneous sample. The powder neutron diffraction (PND) patterns showed weak additional peaks at all temperatures, without significant temperature dependence. The intensities of Bragg reflections from possible impurities were calculated by the LAZY PULVERIX program [5]. All additional peaks at 298 K could be attributed to $ZrBe_5$.

PND data were collected on the OPUS IV two-axis diffractometer [6] at the JEEP II reactor, Kjeller, using monochromatic neutrons of wavelength 182.5 pm. Intensity data were collected between $2\theta = 15$ and 105° in steps of $\Delta(2\theta) = 0.05°$ at 12 and 298 K. A closed-cycle helium DISPLEX cooling system with a Lake Shore temperature controller was used for obtaining intermediate temperatures. The Hewat version [7] of the Rietveld program [8] was used in the profile refinements. The neutron scattering lengths (in 10^{-12} cm) $b_{Be} = 0.78$, $b_{Zr} = 0.70$ and $b_D = 0.667$ were taken from [9].

Quasi-elastic scattering data were collected with the time of flight instrument, TOF, installed at the liquid hydrogen cold source at the JEEP II reactor. The energy of the monochromatic incoming neutrons was 4.62 meV, and the measurements were carried out at a scattering angle of 80°. The DISPLEX system was used to achieve temperatures between 12 and 298 K.

Low- and high-temperature powder X-ray diffraction data were collected between 120 and 1200 K using a Guinier Simon camera (Enraf Nonius) with Cu $K\alpha_1$ radiation. The sample was kept inside sealed, evacuated quartz capillaries. Differential scanning calorimetric measurements were performed between 100 and 400 K using a Mettler TA 3000 system.

3. Results and discussion

Powder X-ray diffraction (PXD) data at room temperature gave sharp reflections in full conformity with a hexagonal unit cell. The unit cell upon deuteriding expands anisotropically, from $a = 381.9(1)$ pm, $c = 323.4(1)$ pm and $V = 40.85 \times 10^6$ pm^3 for Be_2Zr to $a = 371.6(1)$ pm, $c = 347.5(1)$ pm and $V = 41.56 \times 10^6$ pm^3 for $Be_2ZrD_{1.5}$. According to low- and high-temperature PXD data, neither line splittings nor additional reflections occur in the temperature range 120–600 K for Be_2Zr and $Be_2ZrD_{1.5}$.

The PND room-temperature data complied well with the earlier structure description for $Be_2ZrD_{1.5}$ [1,2]. The results are given in Table 1. Some very weak additional peaks were attributed to a $ZrBe_5$ impurity. The refined isotropic displacement factor for deuterium positioned in trigonal bipyramidal sites is rather large at 298 K, $B(D) = 2.06 \times 10^4$ pm^2 (Table 1). However, no improvements in the R-factor could be obtained on distributing the D atoms between tetrahedral sites, which is in full agreement with the findings in [2].

Table 1

Refined parameters for $Be_2ZrD_{1.5}$ from powder neutron diffraction data. Calculated standard deviations in parentheses. Space group *P6/mmm*. Be in 2d, Zr in 1a and deuterium in 2c (at 298 K) or 4h (at 12 K). Isotropic displacement factors given in 10^4 pm^2

	12 K	298 K
a/pm	371.79(2)	371.97(2)
c/pm	347.73(1)	347.57(2)
z(D)	0.044(3)	0
B(Be)	0.64(11)	1.48(10)
B(Zr)	0.00(10)	0.14(10)
B(D)	1.17(14)	2.06(9)
$R(F^2)$	3.07	2.34
R_{prof}	6.36	7.27

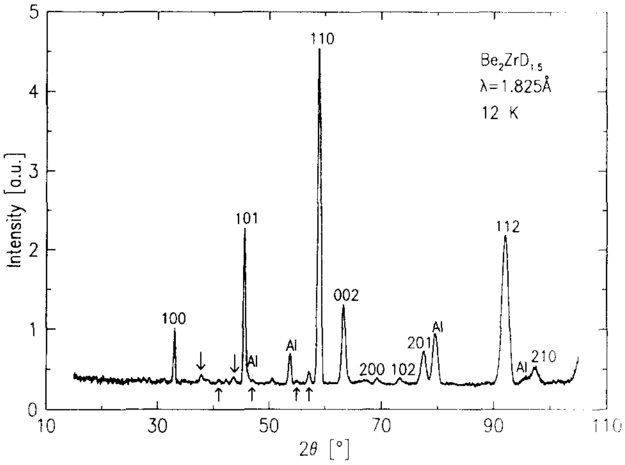

Fig. 1. Powder neutron diffraction diagram of $Be_2ZrD_{1.5}$ at 12 K, λ = 182.5 pm. Indexing of reflections given on the illustration. Reflections ascribed to $ZrBe_5$ impurity are marked ↑, additional reflections appearing on cooling indicating superstructure formation are marked ↓.

On cooling and at low temperatures, several independent pieces of indications for changes in the D-site preferences were obtained:

(1) A couple of new reflections appear in the PND pattern on cooling below 250 K, which may indicate an ordering of deuterium atoms. The strongest new reflections at $2\theta = 37.8$ and 43.6° are indicated in the PND pattern collected at 12 K shown in Fig. 1. The temperature dependence of the integrated intensity of the reflection at $2\theta = 43.6°$ is shown in Fig. 2. The additional reflections could not be indexed on the hexagonal unit cell. They could, however, be indexed on enlarged orthorhombic cells but the limited data

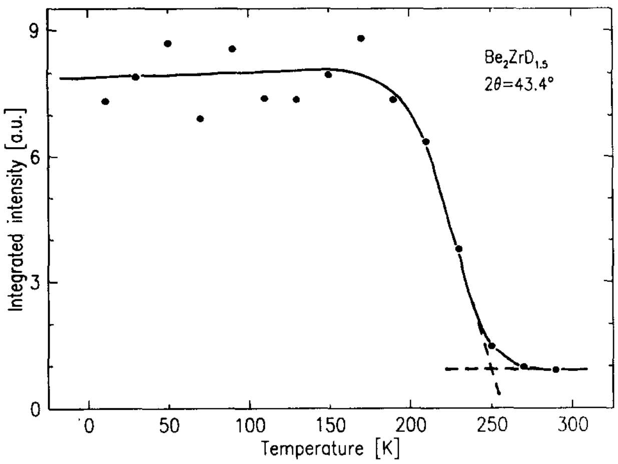

Fig. 2. Temperature dependence of the integrated intensity of the reflection at $2\theta = 43.4°$.

do not allow further speculations. Since the reflections only appear on cooling, it is not probable that they represent impurity phases.

(2) The observed reversibility of the transition and lack of hysteresis indicate furthermore that the reflections are not connected with any phase decomposition of $Be_2ZrD_{1.5}$ during the cooling. The variation of the integrated intensity in Fig. 2 indicates a transition of second order.

(3) Different models were tested out in the Rietveld refinements of the PND data collected at 12 K. Model I (the same as at 298 K) with deuterium in 2*c* positions (trigonal bipyramidal sites) gave $R_{\text{prof}} = 7.00$. Model II, with deuterium randomly distributed over 4*h* sites (tetrahedral sites), gave $R_{\text{prof}} = 6.36$. For model I, the refined displacement factor for deuterium is $B_{\text{iso, D}} = 1.87(13) \times 10^4$ pm^2, whereas for model II, $B_{\text{iso, D}} = 1.17(14) \times 10^4$ pm^2. At 12 K, the thermal motion of deuterium is considered small, and the large $B_{\text{iso, D}}$ for model I is believed to indicate that a significant amount of deuterium occupies the neighbouring tetrahedral holes.

(4) Of the four tetrahedral holes per unit cell, only 1.5 are on average simultaneously occupied by deuterium. Obviously, the two tetrahedra sharing a common face are only singly occupied. The deuterium atoms may undertake two types of jump: off-plane jumps between the neighbouring tetrahedral sites (separation 30.6 pm) and in-plane jumps to three neighbouring sets of tetrahedral/trigonal bipyramidal sites (separation 214.7 pm) leading to two-dimensional diffusion [4]. The time scale for both types of jump are outside the observation window of the TOF instrument at the JEEP II reactor. Nevertheless, TOF data were collected on $Be_2ZrH_{1.5}$ in order to check whether changes in the quasi-elastic scattering were observed between 12 and 298 K. A small, yet significant reduction in the line width of the base of the elastic peak was observed in the temperature interval 298–220 K, and it is tempting to associate this with changes in the thermal motion of hydrogen. Unfortunately, no NMR data are available for the low-temperature regime.

It is believed that the four indications described above in sum give clear support to the picture of temperature-induced changes in the site preference for deuterium in $Be_2ZrD_{1.5}$. In conclusion, the deuterium atoms are considered to mainly occupy tetrahedral sites at 12 K (in a superstructure), undergoing a continuous disordering at 250 K with deuterium on average occupying trigonal bipyramidal sites at 298 K.

References

[1] A.F. Andresen, K. Otnes and A.J. Maeland, *J. Less-Common Met., 89* (1983) 201.
[2] A.F. Andresen, H. Fjellvåg and A.J. Maeland, *J. Less-Common Met., 103* (1984) 27.
[3] D.G. Westlake, *Mater. Res. Bull., 18* (1983) 1409.
[4] A.F. McDowell, C.F. Mendelsohn, M.S. Conradi, R.C. Bowman Jr. and A.J. Maeland, *Phys. Rev. B, 51* (1995) 6336.
[5] K. Yvon, W. Jeitschko and E. Parthe, *J. Appl. Crystallogr., 10* (1977) 73.
[6] B.C. Hauback, O. Steinsvoll, H. Fjellvåg and H. Strand, Report IFE/I-92 005 (1992).
[7] A.W. Hewat, Harwell Report RRL 73/239, 1973.
[8] H.M. Rietveld, *J. Appl. Crystallogr., 2* (1969) 65.
[9] L. Koester and Y.B. Yelon, in Y.B. Yelon (ed.), *Neutron Diffraction Newsletter,* Missouri (1983).