CeMnAlH$_x$, a new metal hydride

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Abstract

In contrast to CeAl$_2$, which does not form hydrides, and Ce–Mn which does not form binary intermetallic compounds at all, CeMnAl absorbs considerable amounts of hydrogen. A stable hydride phase (β-phase) is formed at low pressures (<10 mbar) with a capacity of about 1.2 H/formula unit (f.u.). Hydrogen is absorbed up to 2.4 H/f.u. at pressures >10 mbar (at 300 K). In this work we show the absorption characteristics and structural properties of this new metal hydride. The intermetallic compound CeMnAl crystallizes in the cubic C15 Laves phase as observed by X-ray diffraction. Neutron scattering experiments on this intermetallic compound show that the Mn and Al atoms are distributed randomly on the B sites in this AB$_2$-type C15 Laves phase compound (A=Ce; B=Mn, Al). Upon hydride (deuteride) formation the C15 structure is preserved. The deuterium atoms occupy only the 2A-2B-tetrahedral interstitial sites (96g-positions) over the investigated concentration range $0.0 < x \leq 2.5$ in CeMnAlD$_x$. © 1997 Elsevier Science S.A.

Keywords: Metal hydride; Laves phase; Neutron scattering; X-ray diffraction; Pressure-concentration-isotherms

1. Introduction

Some AB$_2$ intermetallic compounds forming the Laves phases are known to absorb almost 6 H/(f. u.), e.g., ZrV$_2$H$_{5.6}$ [1,2]. CeAl$_2$ forms the cubic C15 Laves phase [3]. Unfortunately, attempts to activate CeAl$_2$ for hydrogen absorption (pressures up to 100 bar and temperatures up to 400 °C) did not lead to the formation of a hydride. No intermetallic compounds exist in the binary Ce–Mn system [3]. Ternary Al-Ce-Mn phase diagrams [4,5] show no indication of the existence of a Laves phase compound. However, Dwight [6] reported that some intermetallic compounds in the system RE(M$_{1-y}$Al$_y$)$_2$ (RE=Rare Earth metals, M=Fe, Mn), e.g. Ce(Mn$_{1-y}$Al$_y$)$_2$, form Laves phases with hexagonal C14 and cubic C15 structure.

Hydrogen absorbing RET$_2$ (T=transition metal) Laves phase compounds are well known, e.g., CeFe$_2$. Unfortunately, upon hydrogen uptake they amorphise (hydrogen-induced amorphisation) and decompose into very stable RE-hydride phases and intermetallic compounds or hydrides [7]. Consequently, reversible hydrogen storage properties cannot be achieved. The aim of our effort is to

find new low cost systems for hydrogen storage for technical applications. In this paper we report on the development of Laves phase alloys composed of rare earth metals, aluminum and manganese that absorb considerable amounts of hydrogen forming ternary hydrides without decomposition reaction.

2. Experiments

CeMnAl was prepared from high purity elemental metals: Ce (99.9%), Mn (99.99%) and Al (99.99%). To remove oxides on the surface of the pure metal pieces, Ce and Al were mechanically cleaned. The flake-like Mn pieces which are very brittle, were etched in diluted nitric acid followed by water flushing and drying. However, due to the high reactivity of Ce and Mn with oxygen during the melting process and the initial oxygen content of Ce, the melted samples are not completely free of oxides. The samples were alloyed in a water cooled copper crucible by r.f.-levitation heating under a reduced Ar atmosphere of 0.5 bar. To improve homogeneity, the samples were melted three times and each time the pellet was turned upside down. Because of the need for large sample quantities to perform hydrogen absorption measurements, X-ray diffraction and neutron diffraction, the results pre-

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sented in this article are obtained from three pellets (about 15 g each): samples A, B and C. Each sample has the same initial nominal stoichiometry 1:1:1 and they were produced under the same melting conditions. However, the final atomic composition of the individual samples can slightly differ from one another.

Hydrogenation and deuteration were done with a constant gas-flow system. For the diffraction measurements the alloys were ground to a powder in an Argon glove box to prevent oxide formation. X-ray diffraction was performed with a SIEMENS D500 MP Diffractometer using Cu Kα radiation. For the neutron scattering experiment, we used copper coated cylindrical vanadium sample holders with 10 and 15 mm diameter, length ≈50 mm and wall thickness of 0.25 mm (contains about 10 g sample materials). High capacity measurements were done with these sample holders up to a pressure of 20 bar.

For the neutron scattering experiment we had access at the high flux reactor of the ILL in Grenoble (France) to instrument D1A, a high resolution powder diffractometer [8]. Thermal neutrons with the wavelength $\lambda = 1.908$ Å were used. All measurements were performed at room temperature. For the neutron scattering experiment the

magnitude of the scattering lengths b of Al and Mn are approximately the same; however, they are essentially distinguished through the opposite sign (Al: $+3.45$ fm, Mn: -3.73 fm [9]).

For the profile refinement of the X-ray and the neutron diffraction patterns we used the Rietveld method by applying the Thompson-Cox-Hastings pseudo-Voigt function [10] for the peak shape fitting. It takes into account size and micro strain contributions to the peak shapes. The data set was treated with the "fullprof" program [11].

3. Results and discussion

Upon exposure to hydrogen gas, sample pieces previously crushed and filled into a stainless steel autoclave under an Ar-atmosphere immediately start to absorb hydrogen without any activation treatment. CeMnAl absorbs hydrogen up to a concentration of 2.4 H/f.u. at room temperature and 20 bar. The absorption pressure curve of sample A is shown in Fig. 1. The pressure-concentration curve is characterized through two different regions of evolution with hydrogen concentration. About 1.2 H/f.u. is
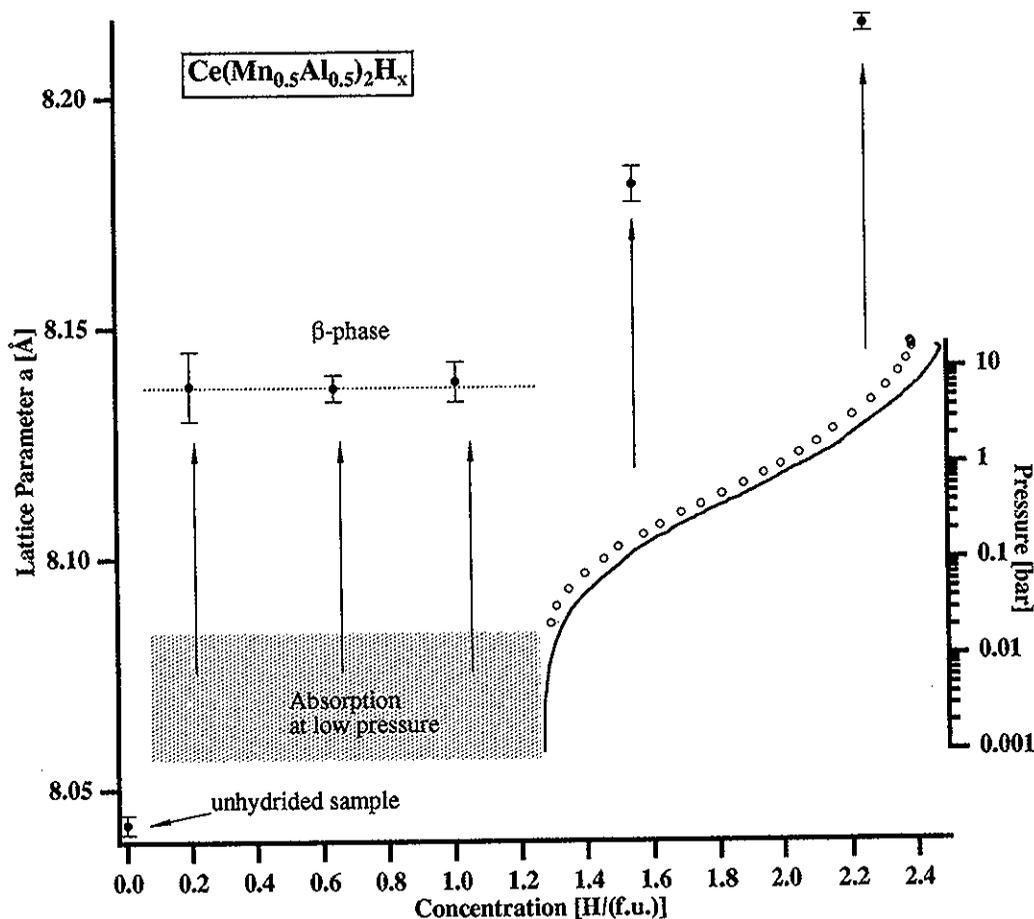

Fig. 1. Lattice parameter (left axis) (●) and equilibrium pressure for the first absorption (○) and after few absorption/desorption cycles (-) (right axis) vs. the hydrogen content H/f.u. in the cubic CeMnAlH$_x$ Laves phase. The shaded domain represents low pressure absorption, of about 1.2 H/f.u.

absorbed at pressures below 10 mbar and another 1.2 H/f.u. is absorbed over a wide pressure range up to 10 bar. Hydrogen desorption in the low pressure range occurs only during heating to 575 K and using a high vacuum pumping system ($\sim 10^{-6}$ mbar). Therefore, this part is attributed to the formation of a stable hydride phase. The second part of the pressure-concentration curve shows reversible absorption/desorption behaviour at room temperature. The slopy plateau in the equilibrium pressure curve is unusual and mostly apparent in disordered or amorphous hydride systems. However, the capacity and the equilibrium pressure for the absorption in the reversible part remains unchanged after few absorption/desorption cycles.

The X-ray patterns of all samples clearly show that the dominant phase of the CeMnAl intermetallic compound crystallizes as the cubic C15 Laves phase with $Fd\bar{3}m$ space group ($MgCu_2$-type structure) (Fig. 2). Unfortunately, single phase samples with high crystallinity were not yet producible. Consequently, the Bragg-reflections suffers from a strong line broadening and asymmetric peak-shapes, especially in the hydrided/deuterated samples. Minor phases were identified mostly as CeO impurity (≈ 2 wt.%) with NaCl-structure and the hexagonal Ce_2Mn_3Al C14 Laves phase (≈ 10 wt.%). Upon hydriding, no decomposition into binary Ce-hydride phases was observed. From the line shifts in the patterns of the main CeMnAl

phase of samples with different H-concentrations we determined the appropriate lattice expansions (Fig. 1). It was observed that the low pressure absorption is accompanied by a discrete lattice expansion of 3.6 vol.%. This is a further indication for the formation of a stable hydride phase (β-phase) with H/f.u.≈ 1.2. The additional absorbed hydrogen up to 2.4 H/f.u. shows that the unit cell lattice continuously expands up to 6.6 vol.% for the fully hydrided sample. We interpret this behaviour as the dissolution of further hydrogen in the stable hydride phase.

As a first structural investigation of this new material, CeMnAl and $CeMnAlD_x$ (samples B and C, respectively) with $1.5 \leq x \leq 2.5$ (the initial nominal value of x was determined from absorption/desorption measurements with the constant gas-flow system) were analyzed by means of neutron scattering (Fig. 3). The patterns of the deuterated samples contain weak contributions of α-phase of the cubic CeMnAl-deuteride. The most apparent impurity phase CeO and the minor Ce_2Mn_3Al C14 Laves phase were included into the profile refinement. We noticed that upon exposure of the samples to deuterium also the lattice parameters a and c of the minor Ce_2Mn_3Al C14 Laves phase increased indicating the absorption of deuterium. The analysis of the absorption properties and the structural properties with the related site occupancies in Ce_2Mn_3Al are under investigation [12]. Thus, we introduced
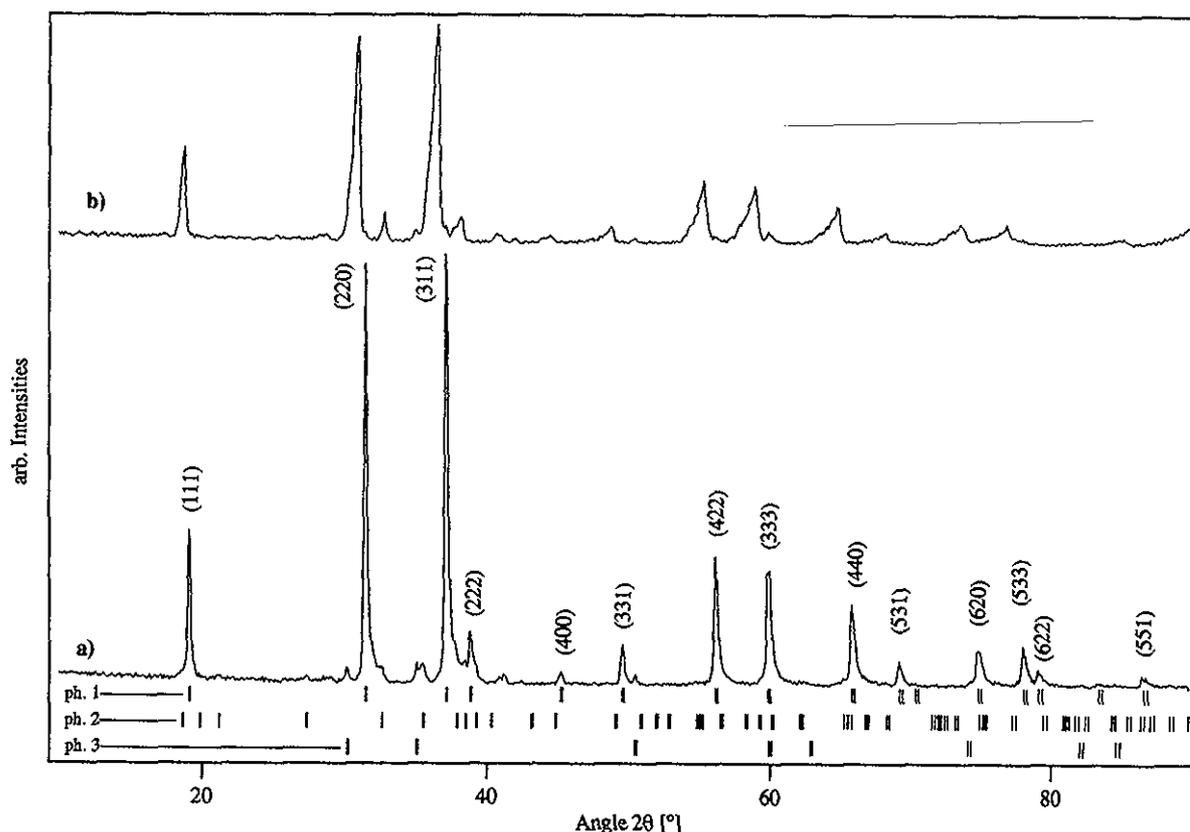

Fig. 2. X-ray diffraction patterns of (a) CeMnAl ((|) indicates the calculated positions of ph.1: CeMnAl and the impurity phases ph.2: Ce_2Mn_3Al and ph.3: CeO); (b) $CeMnAlH_{1.5}$ (sample A). The C15 Bragg-reflections are marked by the Miller-indices.
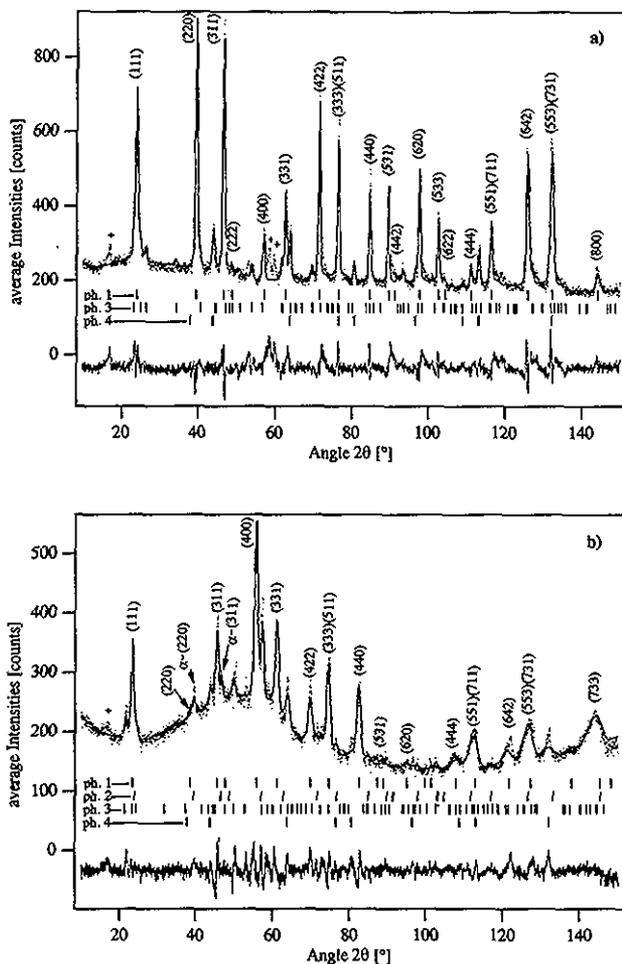
Fig. 3. Observed (dots), calculated (line) and difference (hair-line) neutron diffraction patterns of (a) CeMnAl (sample B) and of deuteride CeMnAlD$_x$ (sample C) with (b) x=1.74 and c) x=2.5. (|) indicates the calculated positions of ph.1: CeMnAl, ph.2: α-phase of CeMnAlD$_x$, ph.3: Ce$_2$Mn$_3$Al and ph.4: CeO. The cubic C15 Laves phase reflections are labeled with the Miller indices. Lines marked with (+) can be assigned to Ce$_7$O$_{12}$ (space group $R\bar{3}$).
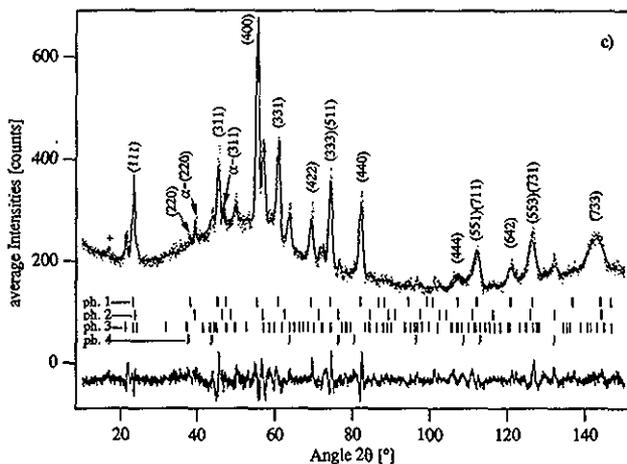

Fig. 3. (continued)

Ce$_2$Mn$_3$Al into the present refinement of the deuterated samples only by applying the profile-matching-mode.

The line at $2\theta \approx 17°$ present in the neutron diffraction patterns of CeMnAl and CeMnAlD$_x$, which do not shift by deuteration of the sample, could not be definitely identified. A possible explanation for this reflection could be Ce$_7$O$_{12}$ (space group $R\bar{3}$).

The main results from the structure refinement of the neutron scattering patterns for the cubic Laves phase are summarized in Table 1. The Al and Mn atoms are randomly distributed on the B sites (16d-positions) in this AB$_2$-type phase. The ratio Al/Mn=1 causes almost annihilation of the intensities of the coherently scattered neutrons by these two metals: $\bar{b}=(x_{Al}\cdot b_{Al}+x_{Mn}\times b_{Mn})=$ 0.15 fm. Because of nearly cancellation of coherent Mn-Al contributions, the temperature factor B (isotropic displacement) was considered to be equal for the Ce, Mn and Al atomic positions. For the same reason, magnetic ordering due to Ce and Mn at room temperature is unlikely (CeAl$_2$ shows non-chiral spiral ordering of Ce below T_N=3.8 K [13]). For the deuterated samples CeMnAlD$_x$ with $1.5 \le x \le 2.5$ we found within the precision of the present data that the D atoms are located only on the 96g-sites (2A-2B interstitial sites). The atomic positions x/a and z/a are similar to those found in ZrV$_2$D$_x$ [14]. The consideration of 32e-site occupations leads to negative occupation numbers. The successive D-filling of the 96g-positions is mostly pronounced in a strong intensity reduction of the (220)-Bragg reflection as seen from theoretical pattern calculations (Fig. 4). The calculated occupancies of the 96g-positions are in good agreement with the capacities determined from the prior constant deuterium-gas-flow absorption/desorption measurements.

The neutron diffraction patterns of the deuterated samples show diffuse background contribution in the angle range $40° \le 2\theta \le 60°$. The same behaviour is also observed

Table 1
Main results from the profile refinement of the neutron diffraction patterns of CeMnAl and its deuterides for room temperature (space group $Fd\bar{3}m$). Numbers in brackets represent the estimated standard deviations (e.s.d.). x are capacities determined from the absorption/desorption measurement with the constant gas-flow system. N$_D$ are capacities calculated from the occupation numbers of the 96g-sites

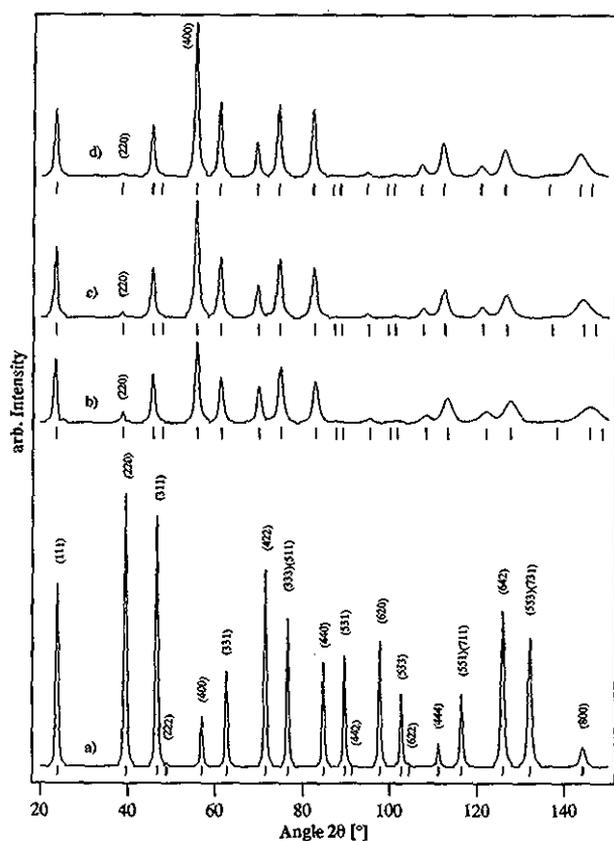|	Sample B	Sample C	
x [D/f.u.]	0.0	1.94	2.22
p [bar]	1 (He-atm)	0.4 (D$_2$)	10 (D$_2$)
a [Å]	8.024(1)	8.180(2)	8.210(2)
$B_{(8b)}$ [Å^2]	1.5(1)	2.1(1)	2.0(1)
$B_{(16d)}$ [Å^2]	1.5(1)	2.1(1)	2.0(1)
$B_{(96g)}$ [Å^2]	–	2.3(2)	4.7(9)
x_D	–	0.085(1)	0.084(1)
z_D	–	0.857(1)	0.856(1)
N_D [D/f.u.]	–	1.74(2)	2.50(5)
R_{wp} [%]	6.68	4.64	4.39
R_{exp} [%]	2.89	2.91	2.87
R_{Bragg} [%]	8.42	6.78	5.52
χ^2	5.33	2.53	2.33

Fig. 4. Calculated neutron diffraction patterns of the cubic CeMnAlD$_x$ Laves Phase with exclusive occupation of the 96g-sites: (a) x=0.0, (b) x=1.5, (c) x=2.0 and (d) x=2.5.

in neutron diffraction patterns of other deuterated Laves phase compounds [15]. It was attributed to mobile deuterium atoms in the lattice and indicates a certain degree of disorder (short-range correlations) in the deuteride. The patterns of the deuterides show strong line broadening and, at higher angles, strong asymmetry in the peak shape. This is often observed in hydrides and deuterides and may be explained by lattice defects, residual stress associated with volume expansions or anisotropy in the crystallites.

Recent experiments in our laboratory have shown that annealing at 1100°C improves the sample quality markedly and nearly single phase alloys are obtained (Fig. 5). The results from the refinement of the X-ray diffraction pattern of an annealed CeMnAl samples confirm that the Al and Mn atoms are randomly distributed on the 16d-sites. Further neutron scattering experiments on theses samples are planned, in particular at low temperatures.

We now turn back to the absorption characteristics. To explain the two different absorption behaviours (Fig. 1) we have to distinguish between 2A-2B-tetrahedra formed by 2Ce-2Al, 2Ce-2Mn and 2Ce-1Al-1Mn. For the cubic C15 Laves phase CeMnAl with a random distribution of Mn and Al on B-sites the probabilities of these tetrahedra are given by 1/4, 1/4 and 1/2, respectively. In the cubic C15 Laves phase a maximum of 5 2A-2B interstitial sites per AB$_2$ can be occupied by a deuterium (or hydrogen) atom [16]. Each of these tetrahedra results in the following capacities (by maximum occupation of each tetrahedron-type): 5/4 H/f.u. for 2Ce-2Al, 5/4 H/f.u. for 2Ce-2Mn
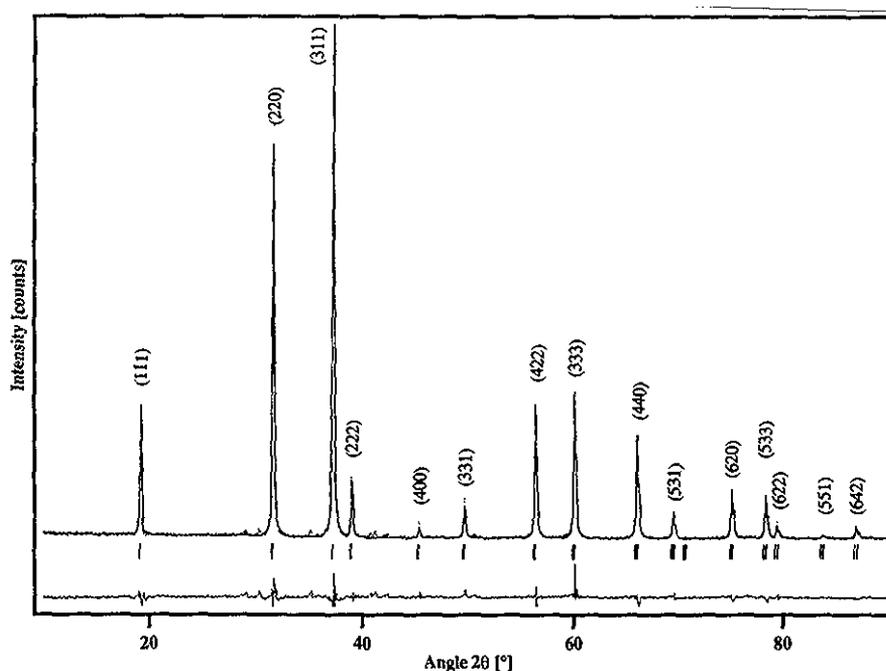

Fig. 5. Observed (dots), calculated (line) and difference (hair-line) X-ray diffraction pattern of an annealed CeMnAl sample. (|) indicates the calculated Bragg positions of the cubic C15 Laves phase. The main results form the profile refinement: a=7.999(1) Å, R_{wp}=11.0%, R_{exp}=9.80%, R_{Bragg}=4.73%, χ^2=2.64.

and $5/2$ H/f.u. for 2Ce-1Al-1Mn. Capacity measurements on samples with different Al/Mn-ratios have shown [17] that the absorbed quantity H/f.u. in the low pressure range corresponds to the number of available 2Ce-2Mn tetrahedra. There was also no indication that 2Ce-2Al interstitials are occupied (decreasing of capacity with increasing the Al-content). Consequently, the remaining absorbed hydrogen is assumed to partially occupy the 2Ce-1Al-1Mn tetrahedra. With the same procedure described by Shaltiel [1] and applied for ZrV_2 and $ZrMn_2$ by Didisheim [18], we calculated the imaginary enthalpies $\Delta H'^{(sol)}$ for diluted hydrogen in each tetrahedron type. These calculations show that hydrogen has the highest chemical affinity for 2Ce-2Mn sites (-165 kJ $mol^{-1}H_2$), followed by 2Ce-1Al-1Mn (-148 kJ $mol^{-1}H_2$) and the lowest for 2Ce-2Al (-131 kJ $mol^{-1}H_2$). This is a further indication for the subsequent filling of 2Ce-2Mn and 2Ce-1Mn-1Al tetrahedra.

4. Conclusions

In this work we have shown that the intermetallic compound CeMnAl forms a cubic C15 Laves phase with random Al-Mn distribution. In contrast to $CeAl_2$, CeMnAl absorbs considerable amounts of hydrogen (deuterium). According to the measured neutron diffraction data only the 96g-positions are occupied. The two different absorption characteristics can be explained through the subsequent occupation of the 2Ce-2Mn and 2Ce-1Mn-1Al-tetrahedra. 2Ce-2Al-tetrahedra and 32e-sites (1A-3B tetrahedra) remain empty. $CeMnAlH_x$ with $x \leq 2.5$ represents a new metal hydride of potential interest for applications around room temperature at hydrogen pressures <10 bar.

Acknowledgments

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