Compressibility of Al$_{64}$Pd$_{30.4}$Fe$_{5.6}$

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Abstract. The stability of C2-Al$_{64}$Pd$_{30.4}$Fe$_{5.6}$, an approximant phase to the icosahdral Al−Fe−Pd quasicrystal, has been investigated by high-pressure X-ray diffraction using a diamond-anvil cell and synchrotron radiation up to 24.30(1) GPa. The material is structurally stable within the framework of the experiment. The unit cell volume as a function of pressure follows a second-order Birch-Murnaghan equation of state with $K_0 = 169.5(2.5)$ GPa. This value is comparable to that of other quasicrystals and approximant phases containing Al and heavy transition metals.

Introduction

The knowledge of a materials' behaviour at non-ambient conditions may give important hints for the understanding of the stabilisation mechanisms of the materials. Complex metallic alloys (CMAs) and quasicrystals are of special interest due to the presence of different length scales in their structures, as *e.g.* the lattice periodicity and intra-cluster distances (clusters in the meaning of small structural entities). Several quasicrystalline phases have been studied *in situ* at high pressures, some also at high temperatures (see *e.g.* Krauss, Gu, Katrych and Steurer 2007 and references therein). The quasicrystalline phases turned out to be impressively stable within the framework of the experiments. With the only exception *i*-Al−Cu−Li, no phase transitions were observed for these phases. Our recent investigations on approximant phases and CMAs also showed that these relatively close-packed structures show no transitions at higher pressures, as *e.g.* the W-Al−Co−Ni phase (Krauss, Gu, Katrych, Deloudi and Steurer, 2007), Rh$_3$Bi$_{14}$ (Gu, Krauss, Grin and Steurer, 2007) or Mg$_2$Co$_3$Sn$_{10+x}$ (Krauss and Gu, 2008). It turned out, as could be expected, that the bulk modulus is more related to the constituting elements than to the crystal structure.

The subject of the present study, the so-called C2-phase Al$_{64.0}$Pd$_{30.4}$Fe$_{5.6}$ is characterized by a large amount of structural substitutional disorder and a number of va-

cancies present in the structure (Edler, Gramlich and Steurer, 1998). Further on, it can be regarded as an approximant to the metastable icosahedral Al−Fe−Pd. This was the motivation for the present high-pressure study on this compound. The question to be answered is about the stability of this phase at higher pressures, *i.e.* the influence of the structural disorder and the compressibility.

Experimental

Nearly single-phase (ca. 0.5 vol% of β-phase), polycrystalline material of the C2 phase of the Al−Pd−Fe system was annealed at 900 °C for 138 h (sample ID C2APFKT1a). The composition of the single-phase material is Al$_{64.0}$Pd$_{30.4}$Fe$_{5.6}$ as determined by an energy dispersive X-ray (EDX) analysis. Small single-crystalline pieces (ca. $100 \times 100 \times 100$ μm^3) of this sample were measured on an Oxford-Diffraction XCalibur XP diffractometer equipped with an Onyx CCD-detector using MoK_α radiation (Oxford enhance). Numerical absorption correction of measured intensities was performed by use of the CrysAlis program package (Oxford Diffraction Ltd., 2007). The crystal structure was solved by direct methods using ShelXS and refined against F^2 using the ShelXL97 program (Sheldrick, 1997).

High-pressure studies were done on powdered samples. A marresearch mar345 image plate detector was used at the Materials Science (MS) beamline, Swiss Light Source (SLS), Villigen, Switzerland, at a wavelength of 0.564 Å. The size of the X-ray beam was reduced to about 50×60 μm^2 by the use of slits. High pressures up to 24.30(7) GPa were generated by use of a diamond-anvil cell (ETH-DAC). A mixture of methanol and ethanol in ratio 4:1 served as pressure transmitting medium. The sample chamber in the rhenium gasket was filled to about 70% with the sample material to reduce deviatoric stress and keep enough amount of sample material to achieve adequate exposure times. The gasket was preindented to a thickness of about 50 μm with diamond anvils having a culet diameter of 300 μm. The diameter of the sample chamber was 125 μm. A small ruby chip was added as a pressure marker and the pressures determined by the ruby fluorescence technique. The integration of the 2D diffraction patterns was performed with the program fit2d (Ham-

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mersley, Svensson, Hanfland, Fitch and Häusermann, 1996). Lattice parameters were refined by the use of the program GSAS (Larson and Von Dreele, 2004) and equations-of-state calculations were done with EosFit5.2 (Angel, 2000).

Results and discussion

The crystal structure of the C2-phase was published already ten years ago by Edler, Gramlich and Steurer (1998) with a composition of $Al_{39}Pd_{21}Fe_2$ (*i.e.* $Al_{62.9}Pd_{33.9}Fe_{3.2}$) from single-crystal structure analysis and slightly different, *i.e.* $Al_{63.5}Pd_{31.4}Fe_{5.1}$ from electron microprobe analysis. Both compositions are close to the composition of the sample used in this study, which was determined as $Al_{64.0}Pd_{30.4}Fe_{5.6}$ by an EDX analysis. The structure of the present sample was checked by single crystal diffraction and structure analysis. Within the experimental errors it proved to be similar to the crystal structure reported in the literature. $Al_{64.0}Pd_{30.4}Fe_{5.6}$ crystallises with space group $Fm\bar{3}$ and $a = 15.5044(1)$ Å. Table 1 summarizes the atomic parameters from Edler, Gramlich and Steurer (1998) to facilitate the understanding of the following discussion. The packing scheme of the crystal structure is shown in Fig. 1.

The crystal structure can be understood as a packing of three different types of icosahedra, occupying the positions of an fcc-lattice (type A), those of the octahedral (type B) and the tetrahedral voids (type C). Only the type B icosahedra contain structural disorder. In type A all positions are fully occupied. It is built around the mixed Fe/Al-position M5 by a cube of eight TM3-atoms overcapped by six Al6 atoms. The Pd2-icosahedron builds the outer shell of this cluster (Fig. 1b). This icosahedron shares common edges with the icosahdron type B. Pd2 is also the outermost shell of this cluster, which is centred around the mixed transition metal position TM4. Al8 and Al9 coordinate TM4 as a distorted cube. These two Al positions are occupied only by $^2/_5$ Al. The occupation of $^2/_5$ Al allows the idealized distorted cube-like coordination of TM4. A full occupation of this position would result in a too high

Table 1. Atomic coordinates and site occupancies for the C2-Al−Fe−Pd phase from Edler, Gramlich and Steurer (1998).

Atom		x	y	z	Occ.
Pd1	8c	$^1/_4$	$^1/_4$	$^1/_4$	1
Pd2	48h	0.7410(2)	0.3518(2)	1/2	1
TM3	32f	0.0972(1)	0.0972(1)	0.0972(1)	0.86(2)Pd & 0.14(2)Fe
TM4	4b	$^1/_4$	$^1/_2$	$^1/_2$	0.19(6)Pd & 0.81(6)Fe
M5	4a	0	0	0	0.22(8)Fe & 0.78(8)Al
Al6	24e	0.8095(9)	$^1/_2$	$^1/_2$	1
Al7	96i	0.6590(3)	0.2500(4)	0.5995(3)	1
Al8	32f	0.410(1)	0.410(1)	0.410(1)	$^2/_5$
Al9	48h	0.436(2)	0.643(2)	$^1/_2$	$^2/_5$

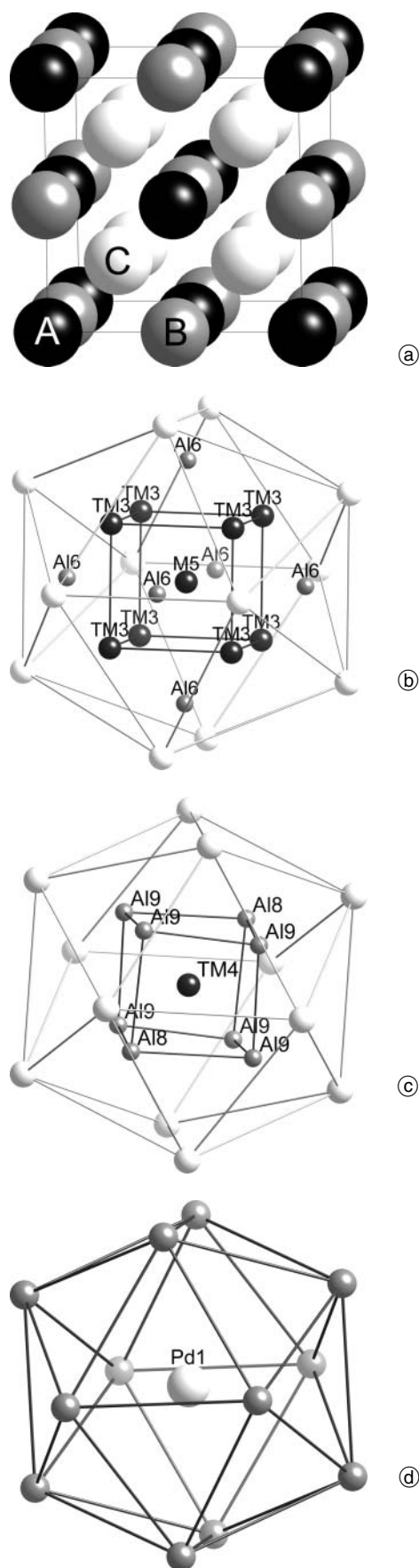**Fig. 1.** The packing-scheme of the crystal structure of $Al_{64}Pd_{30.4}Fe_{5.6}$. (**a**) The structure can be interpreted as an fcc packing of three different types of icosahedra, with occupied octahedral and tetrahedral voids. (**b**) Cluster type A: Pd2 icosahedron around M5; (**c**) cluster type B: Pd2 icosahedron around TM4; (**d**) cluster type C: Al7 icosahedron around Pd1.

Al-content and too short Al—Al distances. There are several orientations of the cube possible, one of those is shown in Fig. 1c. The number of possible orientations is reflected in the low site occupation factor of only $^2/_5$ for both sites. Therefore, this number should not be interpreted as vacancies and the structure can still be interpreted as densely packed. Type C clusters are built of Al7-icosahedra centred by Pd1. These clusters fill the cubic voids built by four type A and four type B clusters.

High-pressure study

Figure 2 shows selected XRD patterns of Al$_{64.0}$Pd$_{30.4}$Fe$_{5.6}$ as a function of pressure. Due to a gasket failure at around 17 GPa, a second loading was used to obtain the data above this pressure. Obviously, the second loading was different from the first loading, what is reflected in the larger half widths of the peaks. Probably, the particle size was also smaller than for the first loading.

The lattice parameters as a function of pressure were obtained from Rietveld-refinements using the LeBail-method.

The obtained lattice parameters as a function of pressure are given in Table 2. All powder patterns up to the highest pressure of 24.30(1) GPa can be indexed based on the cubic unit cell of the C2-phase. Therefore, the compound is structurally stable within the framework of the experiment. Unfortunately, due to an unstable beam position and possible shielding of cell parts, the obtained intensities were not adequate for structural refinements using the Rietveld-method (Fig. 2).

The bulk modulus was calculated based on the best fit of a second-order Birch-Murnaghan (BM) equation of state (EOS) to the pressure-volume data (Table 2). The value of the bulk modulus was obtained as $K_0 = 169.5(2.5)$ GPa and $K' = 4$ (Fig. 3). Using a third-order BM EOS yields a comparable value for the bulk modulus ($K_0 = 174(13)$ GPa) and for its pressure derivative a value close to 4 ($K' = 3.6(1.1)$). Therefore, we assume that the description as a second-order BM EOS is adequate.
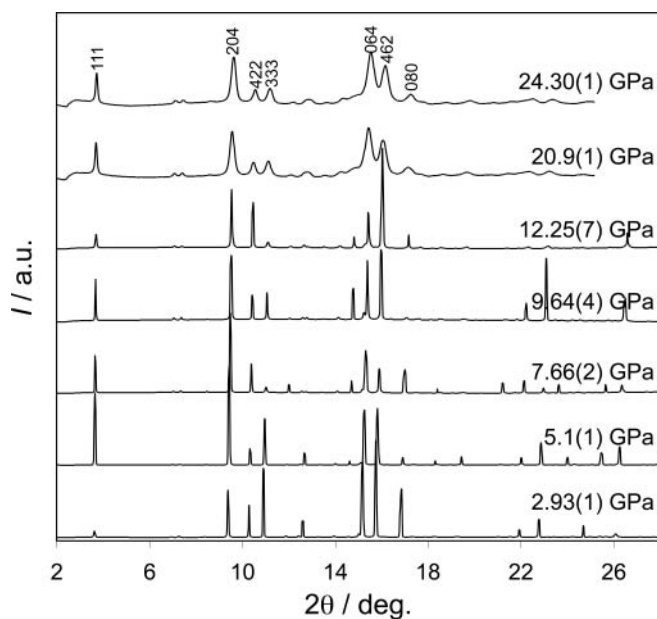

Fig. 2. Selected XRD powder patterns as a function of pressure (MS beamline, SLS, $\lambda = 0.564$ Å).

The value of the bulk modulus of this approximant phase can be compared to the related quasicrystals. It has been found that for quasicrystals, the chemical composition is more relevant for the value of this mechanical property than the crystal structure (Krauss, et al. 2007). Therefore, the value can best be compared to compounds containing similar elements. The value of the bulk modulus is larger than for the i-Al—Cu—Fe ($K_0 = 136(6)\ldots155(10)$GPa) and i-Al—Pd—Mn ($K_0 = 100(12)\ldots133(5)$ GPa) quasicrystals (see Krauss, et al. 2007 and references therein). It is comparable to the value for the i-Al—Pd—Re quasicrystal ($K_0 = 180(10)$ GPa, Sadoc, Itié, Polian, Berger and Poon, 1998) and the Al$_{70}$Pd$_{19}$Os$_{11}$ approximant phase ($K_0 = 173(1)$ GPa, Hasegawa, Tamura, Asao, Yagi, Takeuchi and Inoue, 2002).

Table 2. Unit-cell volume of Al$_{64}$Pd$_{30.4}$Fe$_{5.6}$ as a function of pressure. The column labelled 'loading' indicates from which loading the values were obtained.

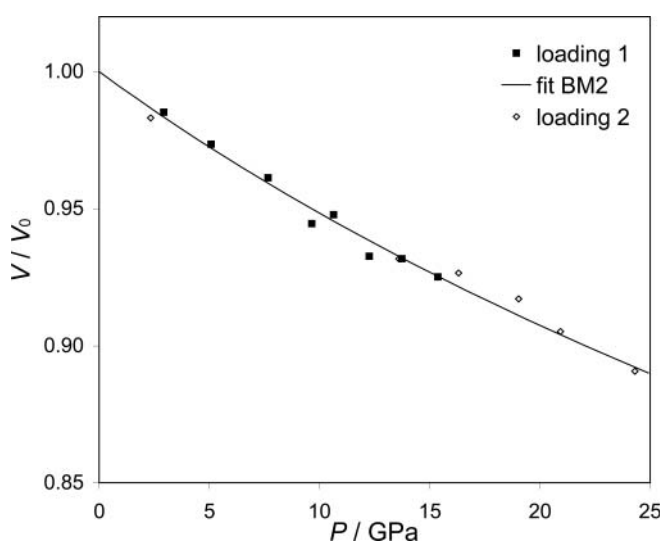| P/GPa	V/Å^3	loading
2.33(1)	3639.1(1)	2
2.93(1)	3640.4(4)	1
5.1(1)	3597.1(1)	1
7.66(2)	3552.1(1)	1
9.64(4)	3490.2(2)	1
10.64(2)	3502.1(1)	1
12.25(7)	3446.0(1)	1
13.6(1)	3448.9(2)	2
13.73(3)	3442.8(2)	1
15.37(2)	3418.2(7)	1
16.3(2)	3429.8(2)	2
19.0(1)	3394.6(2)	2
20.9(1)	3350.9(2)	2
24.30(1)	3297.1(3)	2

Fig. 3. Second-order Birch-Murnaghan equation of state fit to the pressure-volume data of Al$_{64}$Pd$_{30.4}$Fe$_{5.6}$. The errors are in the size of the symbols.

This can be expected, as the amount of the lighter transition metal iron in the structure is only small and as a first approximation from its composition, it can be compared to the heavy transition metal containing quasicrystal and approximant phase. The influence of structural disorder seems not to be very important, as no phase transition accompanied with symmetry change was observed, what would be expected from an ordering of the disordered polyhedra. Keeping in mind the fact that there are no real vacancies, as already mentioned in the description of the structure, but different possible orientations of the Al-cubes inside cluster type B, the structure can be seen as dense packing of atoms and therefore a structural phase transition at intermediate pressures may not be expected. This may also be substantiated by the presence of the rigid framework of type A and C clusters building up the structure.

Conclusion

The C2-phase of the system Al−Pd−Fe is structurally stable within the framework of the experiment up to at least 24.30(1) GPa. The compressibility of this material is comparable to quasicrystals and CMAs of chemically comparable systems, although they have different crystal structures.

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