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In situ study of icosahedral Zn–Mg–Dy and Co-rich decagonal Al–Co–Ni at high pressures and high temperatures

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Abstract

An *in situ* high-pressure high-temperature x-ray diffraction study on single-crystalline icosahedral Zn–Mg–Dy up to 12.5(4) GPa at 873 K and powdered Co-rich decagonal Al–Co–Ni up to 12.3(4) GPa at 973 K has been performed using a heatable diamond-anvil cell and synchrotron radiation. Quantitative reciprocal-space reconstruction from image plate data was used for evaluating the single-crystal data. The compressibility of the materials at ambient temperature was determined from x-ray powder diffraction up to 30.3(2) GPa for icosahedral Zn–Mg–Dy and 61.4(1) GPa for Co-rich decagonal Al–Co–Ni. The bulk modulus at zero pressure and its pressure derivative were determined from fitting third-order Birch–Murnaghan equations of state as $K_0 = 92(4)$ GPa, $K' = 3.1(3)$ for icosahedral Zn–Mg–Dy and $K_0 = 120(11)$ GPa, $K' = 7.1(7)$ for Co-rich decagonal Al–Co–Ni, respectively. The compressibilities of the quasicrystals are discussed with respect to their structure types and the available literature data. To a first approximation, a linear dependency of the squared electron density at the border of the Wigner–Seitz atomic cell from the ratio of the bulk modulus and the molar volume was found. This behaviour is comparable to that of periodic alloys.

1. Introduction

Quasicrystals show a remarkable stability at high pressures within the investigated pressure ranges up to 70 GPa (see, for example, Krauss *et al* [1] and references therein). Only for a single quasicrystalline compound, i-Al–Cu–Li, was a phase transformation via an amorphous to a periodic phase reported [2].

Structural disorder is often observed in quasicrystals (for a review of decagonal phases see Steurer [3]). This raises the question of stabilization of quasicrystals. Entropy stabilization would mean that quasicrystals are high-temperature phases, whereas a pure energy stabilization

would mean that the quasicrystalline state is a ground state of matter. Answering this question experimentally is difficult, but the behaviour of quasicrystals under non-ambient conditions may contribute to an answer.

Most of the high-pressure studies on quasicrystals known in the literature were done at ambient temperature based on powder samples. Reconstructive phase transitions, which would be expected for the transformation from a quasiperiodic to a periodic crystal, need activation energy and may therefore be kinetically hindered at ambient temperature. Phase transitions in quasicrystals are sometimes accompanied by only small changes in the diffraction images, as shown for example in a high-temperature study of d-Al–Co–Ni [4]. Therefore single-crystal investigations at high pressures and high temperatures are of special interest. It has been shown recently that diffraction patterns from single crystals of decagonal quasicrystals obtained at ambient temperature using a diamond-anvil cell (DAC) and reciprocal-space imaging techniques yield a comparable number of observable diffraction features as measurements without a DAC [5, 6]. A recent high-pressure study on single-crystalline icosahedral Al–Pd–Mn has demonstrated that it is possible to determine the bulk modulus of a quasicrystal with comparable accuracy to periodic crystals [7].

The subject of the present *in situ* high-pressure high-temperature study are icosahedral Zn–Mg–Dy and Co-rich decagonal Al–Co–Ni. Icosahedral Zn–Mg–Dy was chosen because of its low melting point, the small amount of structural disorder present in the crystal structure and also since a decagonal phase exists in the Zn–Mg–Dy ternary system [8]. The closely related compound i-Zn–Mg–Y was found to be stable up to 70 GPa based on powder measurements at ambient temperature [9]. For i-Zn–Mg–RE compounds (RE being rare earth element) with RE = Y, Sm a reversible transformation from a hexagonal low-temperature to an icosahedral high-temperature modification was observed between 773 and 873 K [10]. The Al–Co–Ni system is one of the best-studied decagonal quasicrystals systems [3]. The present study of the Co-rich decagonal quasicrystal completes the high-pressure studies in this system, as the Ni-rich quasicrystal as well as the so-called Edagawa-phase, a superstructure of the decagonal phase, have already been studied at high pressures [11, 12, 5].

2. Experimental details

Icosahedral Zn–Mg–Dy single crystals were grown as described elsewhere [13]. Small pieces were cut from a large single crystal (dodecahedron, edge length about 3 mm) with nominal composition $\text{Zn}_{62.8}\text{Mg}_{30.2}\text{Dy}_{7.0}$. A single crystal with dimensions of about $0.1 \times 0.1 \times 0.04 \text{ mm}^3$ was used for the high-pressure/high-temperature (hp/hT) experiment. This crystal was first characterized in-house (Fixdif, Ag $K\alpha$ radiation, mar research mar345 image-plate scanner). Powder samples were obtained from several pieces of the large single crystal, which were ground in an agate mortar. Powder samples of Co-rich decagonal Al–Co–Ni were obtained from a single-phase sample with nominal composition $\text{Al}_{73}\text{Co}_{21}\text{Ni}_6$ [14].

A Diacell DXR-7H heatable DAC with an Inconel gasket was used for the hp/hT measurements. Ar served as the pressure-transmitting medium for the measurement of single-crystalline i-Zn–Mg–Dy. A small amount of NaCl powder was added as a pressure sensor. For the hp/hT measurement of powdered d-Al–Co–Ni NaCl was used as the pressure-transmitting medium and pressure sensor. In both cases, the pressures were determined by applying Birch's equation of state [15]. The experiments were carried out at the MS beamline, Swiss Light Source (SLS), Villigen, Switzerland. A mar research image-plate scanner was used at a wavelength of 0.6185 Å. For the single-crystal measurement, a step width of $\Delta\varphi = 0.75^\circ$ and an exposure time of 60 s per image was applied, covering a total rotation angle of 45° . The cell pressure was initially set to 11.9(4) GPa at ambient temperature and datasets were measured

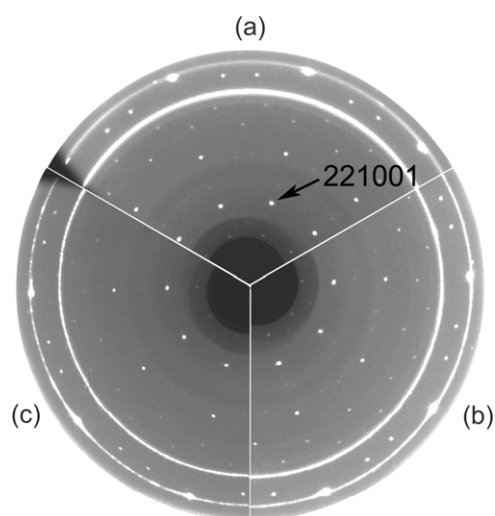


Figure 1. Reconstructed sections of reciprocal-space layers of *i*-Zn-Mg-Dy perpendicular to a fivefold axis and containing the origin as a function of pressure and temperature (diameter 0.95 \AA^{-1}): (a) at 373 K and 11.9(4) GPa; (b) at 573 K and 13.1(4) GPa; (c) at 873 K and 12.5(4) GPa (0.6185 \AA , MS-beamline, SLS). The powder rings result from the pressure medium Ar, the pressure sensor NaCl and the gasket.

at 373, 573 and 873 K. The applied heating rate was 10 K min^{-1} and the temperature was held constant for at least 15 min before the start of each measurement. The program *xcavate* [16] was used to quantitatively reconstruct undistorted images of reciprocal-space sections from a series of adjacent diffraction images collected by the rotation method (reciprocal-space imaging). For the *hp/hT* measurement of *d*-Al-Co-Ni powder a heating rate of 10 K min^{-1} was applied and measurements were done in steps of 100 K between 373 and 973 K. The cell pressure was initially set to about 22 GPa.

An ETH-type DAC was used for the determination of the bulk modulus of both compounds at ambient temperature. The ruby-fluorescence method was applied for pressure determination and a methanol ethanol mixture (4:1) served as the pressure-transmitting medium. A powdered sample of *d*-Al-Co-Ni was measured at SLS using the conditions described above. The measurement of a powdered sample of icosahedral Zn-Mg-Dy was performed at the Swiss-Norwegian Beam Lines (SNBL), ESRF, Grenoble, France using a *mar research mar345* image-plate scanner and a wavelength of 0.7000 \AA . One-dimensional powder patterns were obtained from the 2D data by using the program *fit2d* [17]. Equations of state were fitted using *EosFit5.2* [18].

3. Results and discussion

3.1. Icosahedral Zn-Mg-Dy

3.1.1. Single-crystal *hp/hT* study. The diffraction pattern of *i*-Zn-Mg-Dy shows nearly no diffuse scattering. This indicates a high degree of structural order and therefore structural disorder can be ruled out as major entropic contribution to the stabilization of the structure. Figure 1 shows sections of reconstructed reciprocal-space layers measured at 373 K, 11.9(4) GPa (a), 573 K, 13.1(4) GPa (b) and 873 K, 12.5(4) GPa (c). The orientation of the layers is perpendicular to a fivefold axis and they contain the origin. As expected, the intensities

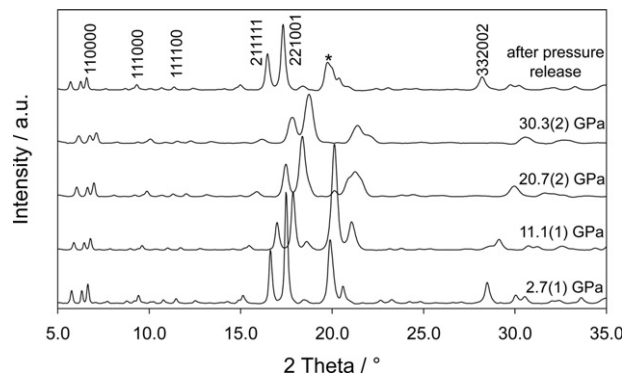


Figure 2. Typical x-ray diffraction patterns of i-Zn-Mg-Dy as a function of pressure at ambient temperature (0.7000 Å, SNBL, ESRF). Despite a peak broadening at higher pressures no drastic changes are observable. The indexed reflections were used for the determination of the bulk modulus. The reflection indicated with an asterisk belongs to the rhenium gasket.

of the Bragg reflections decrease with increasing temperature. The number of observable reflections and their intensity distribution is comparable at low and high temperatures. There are no indications for violations of the icosahedral symmetry, peak splitting or an occurrence of diffuse scattering. As the temperature reached is close to the melting point of i-Zn-Mg-Dy at ambient pressure (about 930 K), sluggish kinetics inhibiting a possible phase transition can be ruled out. Hence, it has to be concluded that icosahedral Zn-Mg-Dy is stable within the framework of the experiment.

3.1.2. Compressibility at ambient temperature. The compressibility of i-Zn-Mg-Dy was studied between ambient pressure and 30.3(2) GPa. Figure 2 shows typical x-ray diffraction patterns within the experimental pressure range. All the reflections can be assigned to the icosahedral quasicrystal (and the gasket). Due to non-hydrostatic conditions and internal strain, the peaks are broadened at high pressures.

The d -values of several isolated reflections (indexed in figure 2) as a function of pressure are listed in table 1. The d -values decrease monotonically with pressure. As a measure for symmetry distortions the ratio of the d -values of reflections located at a threefold and a twofold rotation axis can be chosen. The ratio d_{111000}/d_{221001} corresponds to a three- and twofold direction, respectively. Within the errors of the measurements this ratio remains constant over the entire investigated pressure range (table 1). There are no indications of a phase transition. Icosahedral Zn-Mg-Dy is stable within the investigated pressure range up to 30.3(2) GPa.

The bulk modulus was calculated based on the ratio $(d/d_0)^3$. This procedure was also used by Hasegawa *et al* [9] for i-Zn-Mg-Y. The ratio $(d/d_0)^3$ for all indexed reflections (table 1) was fitted as a function of pressure using a third-order Birch-Murnaghan equation of state (figure 3). The obtained values of the bulk modulus at zero pressure are $K_0 = 92(4)$ GPa and its pressure derivative $K' = 3.1(3)$. The bulk modulus is larger than the value reported for i-Zn-Mg-Y ($K_0 = 73(1)$ GPa, $K' = 3.6(1)$) [9]. Correlations between chemical composition and the bulk modulus will be discussed in section 3.3.

3.2. Co-rich decagonal Al-Co-Ni

3.2.1. H_p/hT powder study. Figure 4 shows powder patterns measured at different pressures and temperatures up to 12.3(4) GPa at 973 K. There are no indications for a phase transition

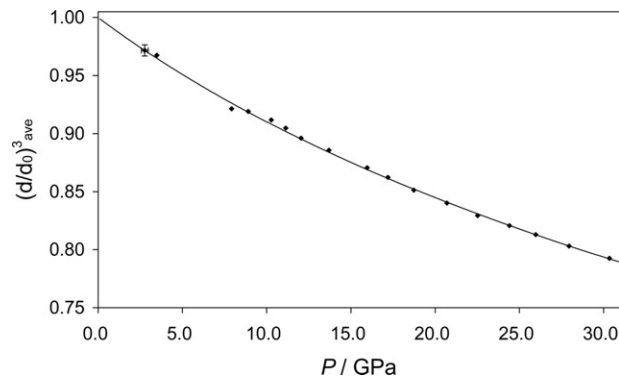


Figure 3. The ratio $(d/d_0)^3$ as a function of pressure (dots) and the fitted third-order Birch-Murnaghan equation of state with $K_0 = 92(4)$ GPa and $K' = 3.1(3)$ (line) for i-Zn-Mg-Dy.

Table 1. d -values of selected isolated reflections of i-Zn-Mg-Dy as a function of pressure at ambient temperature. The reflections 111000 and 221001 correspond to a threefold and a twofold direction, respectively. The ratio of the d -values of these two reflections as a function of pressure remains constant. This means that the icosahedral quasicrystal is structurally stable within the framework of the experiment. The ratio $(d/d_0)^3$ is used to calculate the bulk modulus of this icosahedral quasicrystal.

P (GPa)	d (Å)						$\frac{d_{111000}}{d_{221001}}$	$(\frac{d}{d_0})^3$
	110000	111000	111100	211111	221001	332002		
2.7(1)	6.041	4.268	3.504	2.422	2.304	1.423	1.853	0.972
3.4(1)	6.032	4.261	3.499	2.419	2.301	1.422	1.852	0.968
7.9(1)	5.936	4.194	3.442	2.379	2.264	1.398	1.852	0.921
8.9(1)	5.932	4.190	3.441	2.377	2.261	1.397	1.853	0.919
10.2(1)	5.917	4.178	3.433	2.370	2.255	1.393	1.853	0.912
11.1(1)	5.902	4.170	3.422	2.364	2.249	1.389	1.854	0.905
12.0(1)	5.882	4.158	3.412	2.356	2.241	1.384	1.855	0.896
13.6(1)	5.861	4.141	3.399	2.347	2.233	1.378	1.855	0.886
15.9(1)	5.827	4.120	3.381	2.334	2.220	1.370	1.856	0.871
17.1(2)	5.807	4.106	3.369	2.327	2.213	1.366	1.855	0.862
18.7(2)	5.781	4.090	3.353	2.317	2.204	1.361	1.856	0.851
20.6(2)	5.757	4.070	3.343	2.306	2.194	1.354	1.855	0.840
22.5(2)	5.734	4.052	3.327	2.296	2.184	1.349	1.856	0.829
24.3(2)	5.715	4.041	3.313	2.288	2.176	1.344	1.857	0.821
25.9(2)	5.695	4.025	3.307	2.280	2.169	1.340	1.856	0.813
27.9(2)	5.673	4.010	3.292	2.271	2.160	1.335	1.856	0.803
30.3(2)	5.649	3.994	3.276	2.260	2.152	1.328	1.856	0.793
0.2(2)	6.101	4.309	3.538	2.445	2.326	1.437	1.853	

up to the highest pressure and temperature reached. As in the previous experiment, sluggish kinetics which may hinder a phase transition to an approximant phase can be ruled out. Therefore, it has to be concluded that Co-rich decagonal Al-Co-Ni is stable within the framework of the experiment.

3.2.2. Compressibility at ambient temperature. The compressibility of Co-rich d-Al-Co-Ni was studied between ambient pressure and 61.4(1) GPa. Some representative powder patterns are shown in figure 5.

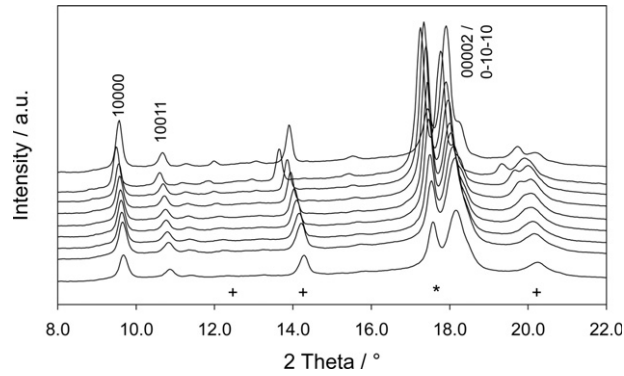


Figure 4. X-ray diffraction patterns of Co-rich d-Al-Co-Ni as a function of pressure and temperature (0.6185 Å, MS-beamline, SLS). The patterns were measured at P (GPa)/ T (K) (from bottom to top): 22.0/273, 20.7/373, 19.8/473, 18.8/573, 18.0/673, 16.6/773, 15.3/873, 12.3/973 and 14.5/298. Reflections from the NaCl pressure medium and the gasket are indicated by crosses and asterisks, respectively.

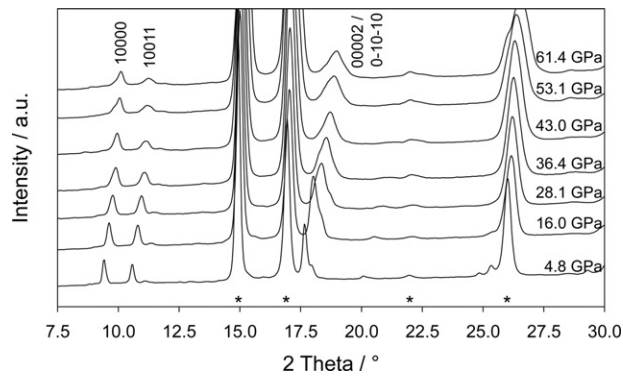


Figure 5. Typical x-ray diffraction patterns of Co-rich d-Al-Co-Ni as a function of pressure (0.6185 Å, MS-beamline, SLS). Despite a peak broadening at higher pressures, no drastic changes are observable. The bulk modulus was calculated based on the d -values of the two well-separated reflections 10000 and 10011. Reflections from the rhenium gasket are marked with an asterisk.

The lattice parameters were calculated from the d -values of the two well-separated reflections, 10000 and 10011, for each pattern (table 2). By fitting a third-order Birch–Murnaghan equation of state, and based on a monoclinic unit cell, the bulk modulus at zero pressure was calculated as $K_0 = 120(11)$ GPa and its pressure derivative $K' = 7.1(7)$. The pressure derivative is higher than expected for an ordinary metal ($K' \approx 4$) and for most other quasicrystals. For a comparison with published data, the compressibilities of the axes are given as the bulk modulus based on a_i^3 , the volume of a tentative cubic unit-cell based on the length of the periodic or quasiperiodic axes, respectively. Figure 6 shows the fitted Birch–Murnaghan equations of state for the periodic and the quasiperiodic direction. The values are slightly different (quasiperiodic direction, $K_0 = 127(15)$ GPa, $K' = 6.0(0.8)$; periodic direction, $K_0 = 118(9)$ GPa, $K' = 9.4(0.7)$), but the difference is within the experimental errors. A comparable observation was reported by Zhou *et al* [12] for d-Al₇₃Ni₁₇Co₁₀. In their case also the quasiperiodic direction ($K_0 = 144.3(10.3)$ GPa, $K' = 4.68(0.68)$) seemed to be less compressible than the periodic direction ($K_0 = 126.6(13.9)$ GPa, $K' = 5.95(1.02)$).

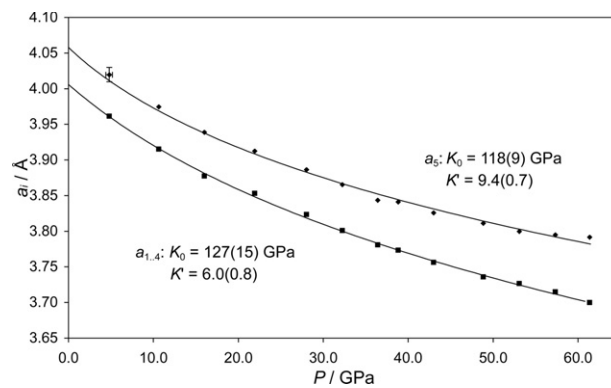


Figure 6. ‘Compressibility’ of the periodic a_5 and quasiperiodic $a_{1\dots4}$ axes of Co-rich d-Al–Co–Ni at ambient temperature.

Table 2. d -values of the two isolated reflections 10000 and 10011 and the derived quasiperiodic ($a_{1\dots4}$) and periodic (a_5) lattice parameter of Co-rich d-Al–Co–Ni as a function of pressure at ambient temperature.

P (GPa)	d_{10000} (Å)	d_{10011} (Å)	$a_{1\dots4}$ (Å)	a_5 (Å)
4.8(1)	3.768	3.356	3.962	4.019
10.6(1)	3.724	3.318	3.915	3.975
16.00(2)	3.688	3.287	3.878	3.939
21.9(1)	3.665	3.266	3.853	3.913
28.0(1)	3.636	3.243	3.823	3.886
32.2(1)	3.615	3.225	3.801	3.866
36.4(2)	3.596	3.207	3.781	3.844
38.8(2)	3.589	3.203	3.773	3.841
43.0(1)	3.572	3.190	3.756	3.826
48.4(4)	3.553	3.177	3.736	3.811
53.1(2)	3.544	3.168	3.727	3.800
57.3(4)	3.533	3.162	3.715	3.795
61.4(1)	3.519	3.156	3.700	3.792

The calculated pressure derivatives of the bulk modulus for the periodic and the quasiperiodic direction show a significant difference: with increasing pressure the quasiperiodic axis becomes stiffer than the periodic axis. Obviously this behaviour is also dominating the pressure derivative of the bulk modulus. Zhou *et al* reported the same trend, but less pronounced. A large value for the pressure derivative of the bulk modulus was found for metastable icosahedral Al–Cu–TM phases with TM = V, Cu, Mn [19]. The authors attributed anharmonic terms of the quasilattice potentials present in the metastable phases as a possible explanation.

3.3. Bulk modulus/composition/structure

According to Tsai [20] quasicrystals can be classified as Hume-Rothery compounds inasmuch the structure type is determined by the valence electron concentration [21]. Later, Tsai found a close relation between quasicrystal formation and the atomic size factor. The two most important rules given by Hume-Rothery and co-workers with respect to the present study are therefore:

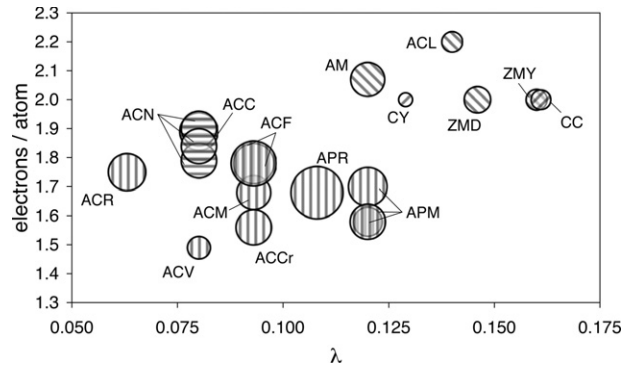


Figure 7. Structure map of the quasicrystals investigated *in situ* at high pressures as known from the literature. The diameter of the circles represents the bulk modulus of the quasicrystal. The different hatchings indicate the different structure types: horizontal, decagonal; vertical, i-Al-TM; bottom left to up right diagonal, i-Cd-Yb; bottom right to up left diagonal, Frank-Kasper type quasicrystals. The labels consist of the first letters of the constituting elements of the quasicrystals, e.g. ACC is i-Al-Cu-Co.

- (i) A certain structure type is determined by the valence-electron concentration e/a , i.e. the number of all valence electrons in the compound per number of atoms $e/a = \sum x_i Z_i$ with x_i the molar fraction and Z_i the number of valence electrons of the i th atom.
- (ii) The structure is unstable if the size mismatch λ of the constituting atoms is larger than 0.15. This atomic size factor is given for binary alloys as $\lambda = |(r_A - r_B)/r_A|$ with r_A and r_B the atomic radii of the matrix and solute atoms, respectively. It can be extended to ternary alloys as $\lambda = \frac{n_B}{n_B+n_C} |(r_A - r_B)/r_A| + \frac{n_C}{n_B+n_C} |(r_A - r_C)/r_A|$ with n_B and n_C the number of B and C atoms in the formula unit.

With respect to the high-pressure experiments it is most interesting to find out if there is a correlation of the bulk modulus, the atomic size factor λ and/or the valence electron concentration e/a of the quasicrystals.

Table 3 gives a summary of the calculated values of e/a and λ for all quasicrystals, for which *in situ* high pressure studies are known in the literature (to the best of our knowledge). The e/a values were calculated based on the valencies of the transition metals derived by Pauling [22]. For the calculation of the atomic size factor the atomic radii given by Slater [23] were used. The main constituent element was chosen as the matrix element A. A structure map including the experimentally determined values of the bulk modulus of the studied quasicrystals is shown in figure 7.

As proposed by Inoue *et al* [36] the investigated quasicrystals can be assigned to two different regions. For e/a -values between 2 and 2.2, Frank-Kasper phases and quasicrystals of the i-Cd-Yb type were found. Quasicrystals of the Al-TM type are located at $0.05 \leq \lambda \leq 0.12$ and $1.5 \leq e/a \leq 1.9$. The diameter of the circles in figure 7 represents the value of the bulk modulus. Obviously, there is no correlation of the values of the bulk modulus and the λ or e/a values. Hence, the influence of the crystal structure is only small and it can be concluded that the compressibility of the quasicrystals is dominated by their chemical composition.

Empirically, Miedema *et al* [37] have shown that for metallic elements a rather simple approximation can be given correlating the bulk modulus K_0 , the molar volume V_m and the electron density at the boundary of the Wigner-Seitz atomic cell, n_{WS} :

$$n_{WS}^2 = \frac{K_0}{V_m}. \quad (1)$$

Table 3. *In situ* high-pressure studies on quasicrystals known from the literature. The given values are explained in the text.

Compound	S ^a	K_0 (GPa)	K'	e/a	λ	\bar{V}_m (cm ³ mol ⁻¹)	\bar{n}_{WS} (au)	Ref.
i-Al ₆ CuLi ₃	an	71		2.2	0.140	10.612	2.22	[24]
i-Al ₆₂ Cu _{25.5} V _{12.5}	ms	79(6)	10.7(1.6)	1.49	0.080	9.061	3.04	[19]
i-Al ₆₂ Cu _{25.5} Cr _{12.5}	ms	122(2)	12(1)	1.56	0.093	8.919	3.13	[19]
i-Al ₆₂ Cu _{25.5} Mn _{12.5}	ms	116(7)	9.5(2)	1.68	0.093	8.934	3.01	[19]
i-Al ₆₂ Cu _{25.5} Fe _{12.5}	an	136(6)	2.7	1.78	0.093	8.902	3.18	[25]
i-Al ₆₂ Cu _{25.5} Fe _{12.5}		139	2.7	1.78	0.093	8.902	3.18	[26]
i-Al ₆₂ Cu _{25.5} Fe _{12.5}	an	155(10)	2	1.78	0.093	8.902	3.18	[27]
d-Al ₆₅ Cu ₂₀ Co ₁₅	aq	131(8)	4	1.89	0.080	8.903	3.20	[6]
i-Al ₆₅ Cu ₂₀ Ru ₁₅	aq	128(10)	5(1)	1.75	0.063	9.057	3.31	[28]
d-Al ₇₂ Co ₈ Ni ₂₀		120	5	1.90	0.080	9.056	3.44	[11]
d-Al ₇₃ Co ₁₀ Ni ₁₇ ^b				1.92	0.080	9.092	3.42	[12]
d-Al ₇₀ Co ₁₂ Ni ₁₈	aq	121(8)	3.5(1.4)	1.79	0.080	8.992	3.50	[5]
d-Al ₇₃ Co ₂₁ Ni ₆	aq	120(11)	7.1(7)	1.84	0.080	9.103	3.42	This work
i-Al ₈₆ Mn ₁₄		117.6(16.8)	6(2.4)	2.07	0.049	9.629	2.91	[29]
i-Al _{68.7} Pd _{21.7} Mn _{9.6}		100(12)	5.3(9)	1.58	0.120	9.507	3.27	[30]
i-Al ₇₂ Pd _{18.5} Mn _{9.5}	fz	133(5)	5(1)	1.70	0.120	9.545	3.20	[31]
i-Al _{68.2} Pd _{22.8} Mn ₉		122(1)	4.23(5)	1.58	0.120	9.511	3.28	[7]
i-Al _{70.5} Pd ₂₁ Re _{8.5}	an	180(10)	5(1)	1.68	0.108	9.670	3.42	[28]
i-Zn ₅₅ Mg ₃₅ Y ₁₀	an	73(1)	3.6(0.1)	2.0	0.160	11.934	2.00	[9]
i-Zn _{62.8} Mg _{30.2} Dy _{7.0}	B	92(4)	3.1(3)	2.0	0.146	11.317	2.06	This work
i-Cd ₈₄ Ca ₁₆	ag	68(2)	4.3(2)	2.0	0.161	15.112	1.72	[32]
i-Cd ₈₄ Yb ₁₆		49	4	2.0	0.129	14.899	1.73	[33]
i-Ti _{52.8} Zr _{26.2} Ni ₂₁	ms	173(5)	2.3(5)			10.640	3.71	[34]
i-Ti ₅₃ Zr ₂₇ Ni ₂₀	ms	130(10)	5.5(1.0)			10.707	3.69	[35]

^a Synthesis as given in the literature: an, annealed; ms, melt spinning; aq, annealed and quenched; fz, floating-zone; B, Bridgman; ag, as-grown.

^b Bulk modulus not given.

This empirical approximation implicitly contains information on the chemical bonding and therefore allows us to correlate the bulk modulus with the chemical composition. Li *et al* [38, 39] applied Miedema's model to predict the bulk modulus of binary and ternary alloys. In order to predict the bulk modulus of an alloy, its crystal structure has to be known. If the structure is not known, the above relation can be used to approximately correlate the value of the bulk modulus of an alloy with its chemical composition. This will be done for the quasicrystalline alloys in the following. As the density or the molar volume for most of the studied quasicrystals is not known, an average molar volume $\bar{V}_m = \sum x_i V_{m,i}$, with x_i the molar fraction and $V_{m,i}$ the molar volume of the constituents, was used. It was assumed that the calculated average molar volumes are within $\pm 10\%$ of the real molar volume (this holds, for example, for some periodic Al-based alloys and approximant phases like Al₁₀Mn₃ or Al₁₃Co₄). The calculated values of the average molar volumes are listed in table 3. The average electron density was estimated as $\bar{n}_{WS} = \sum x_i n_{WS,i}$ with $n_{WS,i}$ the electron density at the boundary of the Wigner–Seitz atomic cell of the i th element from [37]. Note, that Li *et al* scale this value in their calculation with the molar volumes of the elements and the alloy. Figure 8 shows $(K_0/\bar{V}_m)^{1/2}$ as a function of the average electron density \bar{n}_{WS} .¹ Within the mentioned approximations, the values of the bulk modulus show a trend of following equation (1). This

¹ The errors in $(K_0/\bar{V}_m)^{1/2}$ are calculated based on the experimental errors in K_0 and the assumed error of $\pm 10\%$ in \bar{V}_m as $\Delta(K_0/\bar{V}_m)^{1/2} = \left| \frac{\partial}{\partial K_0} (K_0/\bar{V}_m)^{1/2} \right| \Delta K_0 + \left| \frac{\partial}{\partial \bar{V}_m} (K_0/\bar{V}_m)^{1/2} \right| \Delta \bar{V}_m$.

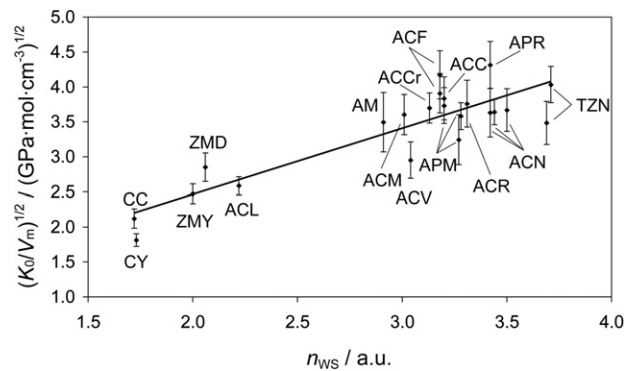


Figure 8. Correlation of bulk modulus, molar volume and the electron density at the border of the Wigner–Seitz atomic cell. The labels consist of the first letters of the constituting elements of the quasicrystals, e.g. ACC is i–Al–Cu–Co. More details are described in the text.

indicates that the bulk modulus is mainly dominated by the chemical elements forming the alloy and the influence of the different quasiperiodic structures is only small.

To derive more meaningful results, the molar volumes of the quasicrystals should be known and the big uncertainties in the bulk modulus values should be reduced. As the bulk modulus values given in table 3 show, there are big uncertainties in the determined values and also between the different reported results, as for example for i–Al–Cu–Fe or i–Al–Pd–Mn. Reasons for this can be found in the different synthesis conditions: some quasicrystalline phases are metastable and are therefore prepared by melt spinning, for example, while others have been annealed and are therefore in thermal equilibrium. Ponkratz *et al* [19] claimed the non-equilibrium to be a reason for the high value of K' . Another reason for the discrepancies of the reported values can be found in the diffraction pattern of the quasicrystals. The diffraction pattern consists of only a very few strong reflections but a huge number of very weak reflections. In the case of a powder diffraction study only a small number of non-overlapping strong reflections can be used for lattice parameter determination and therefore the accuracy is limited. Single-crystal studies would offer a much higher number of accessible reflections and improved data quality, as has been shown recently [7].

4. Conclusion

The stability of i–Zn–Mg–Dy and Co-rich d–Al–Co–Ni at high pressures and high temperatures has been shown by *in situ* experiments. The bulk modulus for both compounds was determined. The values are comparable with chemically related quasicrystalline phases. The values of the bulk modulus for the quasicrystals found in the literature approximately follow an empirical rule. Unfortunately, due to the scattering of the published data, it is difficult to correlate these values with other parameters. Synthesis conditions and the methodology of measurement and data evaluation strongly influence the resulting values.

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