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# A single-crystal high-pressure x-ray diffraction study of decagonal Al–Co–Cu up to 19.1 GPa

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**Abstract**

An *in situ* single-crystal high-pressure x-ray diffraction study of decagonal Al–Co–Cu up to 19.1 GPa has been performed using diamond anvil cells and synchrotron radiation. Quantitative reciprocal space reconstruction from image plate data was used for data analysis. No significant variations with pressure were observed in Bragg as well as diffuse scattering, indicating the high stability of the quasiperiodic structure in the investigated pressure range. The bulk modulus at zero pressure was determined from fitting a second-order Birch–Murnaghan equation of state as $K_0 = 131(8)$ GPa. The influence of different crystal orientations on the accessible amount of reciprocal space data is discussed.

## 1. Introduction

What governs the formation of quasicrystals? Are they entropy or energy stabilized? Entropy stabilization would mean quasicrystals are high-temperature phases, whereas energy stabilization would characterize the quasicrystalline state as a ground state of matter. After 20 years of research on quasicrystals, this question is still not answered. To answer it, the behaviour of quasicrystals at non-ambient conditions is of great interest. The stability of the quasiperiodic structure and knowledge of the mechanisms of phase transitions (if they occur) give valuable clues to answer the fundamental question of stabilization (for a review see [1]).

Phase transitions in quasicrystals are in some cases just observable as very subtle changes in the diffraction pattern. Decagonal Al–Co–Ni, for example, shows a phase transition at about 800 °C that goes along with the disappearance of weak superstructure reflections and a change in the shape of the diffuse scattering. Both features can only be observed with *in situ* high-temperature single-crystal diffraction [2].

Especially in the study of structural disorder and phase transitions in quasicrystals, reciprocal space imaging with area detectors has proven to be a powerful tool [3]. The use

  

of single crystals offers a much higher degree of observable diffraction features compared to powders and is essential for the study of weak diffraction phenomena such as diffuse scattering or superstructure reflections. A recent feasibility study has shown the possibility of reciprocal space reconstruction from data obtained using a diamond anvil cell [4].

Nearly all of the known *in situ* high-pressure studies on quasicrystals were based on powder samples and most of them focus on icosahedral quasicrystals (see for example [5] and references therein). The applied pressures range up to 70 GPa [6] and the investigated quasicrystals show a remarkable stability in the investigated pressure ranges. Icosahedral Al–Li–Cu is the only compound for which a transformation, from a quasiperiodic to an amorphous phase, was observed [7]. For icosahedral Cd–Yb [8], Al–Cu–Ru, and Al–Pd–Re [9], a Bragg peak broadening in the powder pattern was reported above 10 GPa. In the case of Al–Cu–Ru and Al–Pd–Re it was interpreted as a pressure-induced phason strain that stabilizes the icosahedral symmetry.

Icosahedral quasicrystals are quasiperiodic in all directions, whereas decagonal quasicrystals are periodic in one direction. They combine periodicity and quasiperiodicity in their crystal structure and are therefore of special interest for the study of structural transitions. Until now, only decagonal quasicrystals of the Al–Co–Ni [10, 6, 4] and Al–Co–Cu [5] (up to 10.9 GPa) systems have been investigated. Here we report on results concerning decagonal Al–Co–Cu up to 19.1 GPa. This compound shows a high degree of structural disorder, together with very well structured diffuse scattering. Furthermore, a transition to a B2 phase, induced by high-energy ball-milling at room temperature [11], and electron irradiation [12], respectively, was reported.

## 2. Experimental details

*In situ* high-pressure single-crystal x-ray diffraction studies were carried out using a standard [13] and a modified ETH diamond anvil cell (DAC):

(i) *Standard setup.* When the standard configuration of the cell was used, the beryllium plugs, which are normally used with the ETH DAC for fitting the beryllium backing-plates to simplify the absorption correction, were not used to minimize unwanted scattering. A stainless steel gasket with 200 $\mu$m hole diameter and diamond anvils with a culet diameter of 600 $\mu$m were used. Ruby chips placed beneath the crystal served as the pressure calibrant and a mixture of methanol and ethanol (ratio 4:1) was used as the pressure transmitting medium. The quasicrystal (approximately 40 $\mu$m in diameter, 40 $\mu$m in length) was oriented with its decagonal axis parallel to the x-ray beam (perpendicular to the culet of the diamond) to be able to image a high amount of the quasiperiodic reciprocal layer with $h_5 = 0$ (see figure 1(a)).

(ii) *Modified setup.* In the modified cell, the beryllium backing-plates were replaced by single-crystalline diamond backing-plates, as described in [14]. The modified cell has an opening angle of 60°. A rhenium gasket with 150 $\mu$m hole diameter and diamond anvils with 450 $\mu$m culet diameter were used. Some ruby chips were added as pressure calibrants and argon was used as the pressure transmitting medium. The quasicrystal (approximately 40 $\mu$m in diameter, 60 $\mu$m in length) was oriented with its decagonal axis perpendicular to the x-ray beam and parallel to the rotation axis (see figure 1(b)). This reduces the accessible amount of the quasiperiodic reciprocal layer with $h_5 = 0$, but increases the amount of accessible higher reciprocal layers, compared to (i).

Both samples were taken from one single crystal with nominal composition $Al_{65}Co_{15}Cu_{20}$. It was grown from a homogenized melt (1200 °C, 15 min) with a cooling rate of 0.5 K min$^{-1}$ down to 850 °C and after 4 h annealing time at 850 °C quenched to room temperature. A full dataset at ambient conditions was collected previously at the Swiss-Norwegian Beam Lines

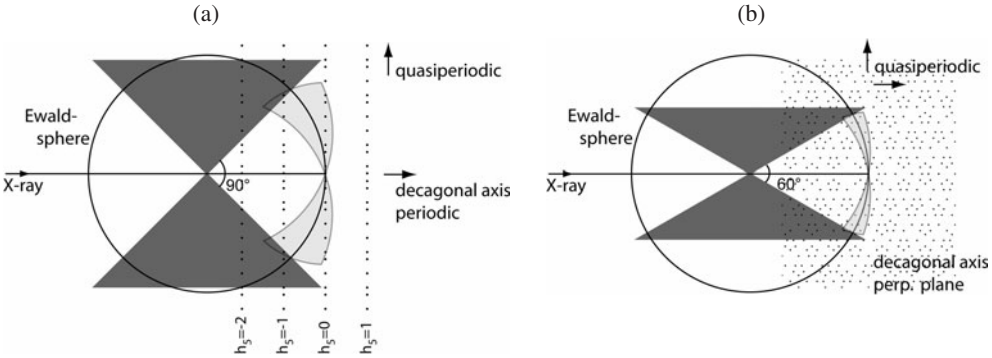


**Figure 1.** Schematic drawing of the accessible reciprocal space with the use of a standard ETH DAC with beryllium backing-plates and opening angle 90° (a), and a modified cell with single-crystalline diamond backing-plates and opening angle 60° (b). The light grey area gives the region of reciprocal space that can be imaged by the use of the rotation method when a decagonal quasicrystal is aligned with its decagonal axis parallel (a) and perpendicular (b) to the x-ray beam (viewed along the rotation axis).

(SNBL), European Synchrotron Radiation Facility (ESRF), Grenoble ($\lambda = 0.7110$ Å, step width $\Delta\varphi = 0.25°$, [15]). The experimental parameters for the high-pressure measurements at SNBL were: $\lambda = 0.7110$ Å (standard cell) and $\lambda = 0.7195$ Å (modified cell), Marresearch 345 image plate, distance between sample and detector 220 mm, step width $\Delta\varphi = 0.5°$, exposure time 60 s per image, beam size about $0.1 \times 0.1$ mm$^2$, total $\varphi$-range between 30° and 60°. Measurements with the standard setup were carried out at 2.075(2), 6.65(3), and 10.95(30) GPa. The modified setup was used for measurements at 2.91(2), 11.9(1), and 19.1(1) GPa. After pressure release, in-house equipment was used for measurements without a DAC (RAG, 50 kV, 80 mA, Johansson monochromator, Mo K$\alpha_1$ radiation, Marresearch 300 image plate). The layers of reciprocal space were quantitatively reconstructed by the use of the program xcavate [3].

The quasiperiodic lattice parameters $a_1, \ldots, a_4$ were determined from the positions of all observable symmetrically equivalent 1 0 0 0 0 reflections in the reconstructed images (by use of the program view.pl [16]). This reduces the influence of distortions in the reconstructed images, caused by uncertainties in the experimental parameters (e.g. centre of the image plate or crystal orientation). The periodic lattice parameter $a_5$ was determined from the observable cuts of the quasiperiodic layers in reconstructed images perpendicular to the fivefold layers. Due to the limited accessible reciprocal space data, the periodic lattice parameter $a_5$ was only determined from measurements using the modified setup. For calculating the equations of state, the program EosFit5.2 [17] was used.

## 3. Results and discussion

### *3.1. Crystal orientation and experimental setup*

In figure 2 reconstructed reciprocal-space layers perpendicular and parallel to the tenfold axis, measured at ambient pressure without a DAC, at 2.075(2) GPa using the standard ETH DAC, and at 2.91(2) GPa using the modified ETH DAC, are shown.

The results of the measurements without a DAC [15] indicate that the investigated crystal was a quasicrystal and not a microcrystalline phase, as described for a phase in the system Al–Co–Cu–Si [18].

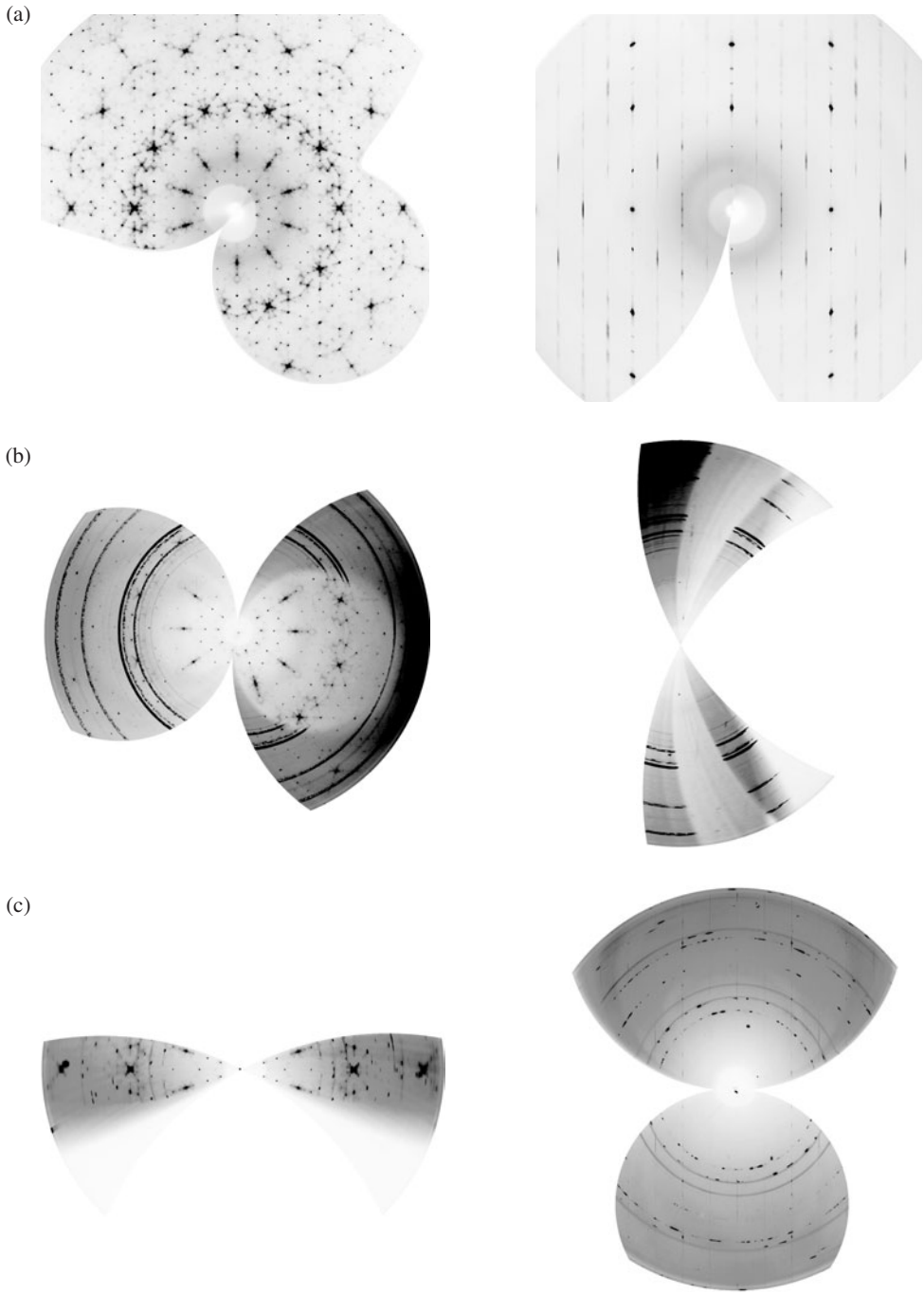


**Figure 2.** Reconstructed reciprocal-space layers of decagonal Al–Co–Cu perpendicular (left, $h_5 = 0$) and parallel (right, containing 0 0 0 0 0) to the tenfold axis at ambient pressure without a DAC (a), at 2.075(2) GPa using the standard ETH DAC (b), and at 2.91(2) GPa, using the modified setup with single-crystalline diamond backing-plates (c), as described in the text. The use of single-crystalline diamond backing-plates significantly reduces the unwanted scattering (c). (The powder rings result from the beryllium backing-plates, the gasket, and the pressure-transmitting medium (argon). The additional strong spots are diamond reflections.)

Compared to the image obtained at ambient conditions without a DAC, the usable area is much smaller employing the standard ETH DAC. Limited by the opening angle of the beryllium backing-plates, an oscillation of about 22° can be performed without hitting the backing-plates by the x-ray beam. When the beam hits the backing-plates, broad rings occur in the diffraction image (see figure 2(b)). The lines caused by the gasket can be avoided by the use of a small beam diameter and letting the beam penetrate the cell almost perpendicularly, as in this case with an angle of about 80°–100°. With a small oscillation angle, a large amount of the quasiperiodic reciprocal space layer perpendicular to the tenfold axis ($h_5 = 0$) can be imaged and the maximal diffraction angle is primarily determined by the oscillation angle. The accessible amount of the reciprocal layer perpendicular to this layer, which contains the tenfold axis, is limited by the rotation angle and the opening angle of the DAC.

In the modified setup, the crystal is oriented with its decagonal axis perpendicular to the x-ray beam (and parallel to the rotation axis), i.e. inverted to the standard setup (see figures 1, 2(c)). The accessible amount of the reciprocal layer with $h_5 = 0$ is more limited than with the standard setup. In this case, the section of the quasiperiodic reciprocal layer equals a segment of a circle with an opening angle equal to the oscillation. The maximal diffraction angle is limited by the opening angle of the DAC. In the layer perpendicular to the quasiperiodic layer, cuts of higher quasiperiodic reciprocal layers are visible. With increasing diffraction angle, the broadening of the reflections increases, caused by the geometry of the rotation method and the oscillation angle used per frame (0.5°). The images obtained with the modified ETH DAC show additional reflections from the gasket, due to the smaller hole, which is hit by the x-ray beam, and of the solidified pressure-transmitting medium (argon). The single-crystalline diamond backing-plates reduce the background significantly, as only very few strong diamond reflections but no further powder rings occur in the diffraction image. Because of the tenfold symmetry of the decagonal quasicrystals, an oscillation of at least 36° is sufficient to image the asymmetric unit and to obtain meaningful results.

The quality of the reconstructed images allows in both cases a detailed comparison of weak Bragg peaks and diffuse scattering as a function of pressure. Large areas of higher reciprocal space layers may be accessible by the use of crystals with different orientations.

### *3.2. High-pressure studies*

As mentioned before, decagonal Al–Co–Cu was studied up to 19.1 GPa, using two different setups. The standard setup was used up to 10.9 GPa, and decagonal Al–Co–Cu was found to be stable in this range [5]. Therefore, this section will focus on the pressure range above 10.9 GPa using the modified setup. In figure 3 reconstructed reciprocal space layers ($h_5 = 0$) are shown, obtained at ambient pressure, 2.91(2), 11.9(1), and 19.1 GPa.

The most obvious change in the reconstructed images is a broadening of the diffraction features at 19.1(1) GPa. The Bragg peaks are broadened and the diffuse scattering is smeared out. The broadening increases with increasing diffraction angle. This may result from shear stresses due to the increasing non-hydostaticity of the pressure medium. Figures 4(a) and (b) show a comparison of reciprocal space layers before and after the high-pressure studies. The radial splitting of the strong reflections after pressure release indicates a fracture of the single crystal, as proven by scanning electron microscopy (see figure 4(c)). The fractured crystal explains the radial broadening of the reflections. As the crystal was not squeezed between the diamond anvils, the cracking of the crystal may be explained by the deformation behaviour of decagonal Al–Co–Cu [19]. Decagonal Al–Co–Cu remains brittle up to elevated temperatures. Even at 550 °C, the samples cracked at a deformation of about 7–9%. At ambient temperature under non-hydrostatic pressure conditions, an even smaller deformation may therefore lead to a cracking of the single crystal.

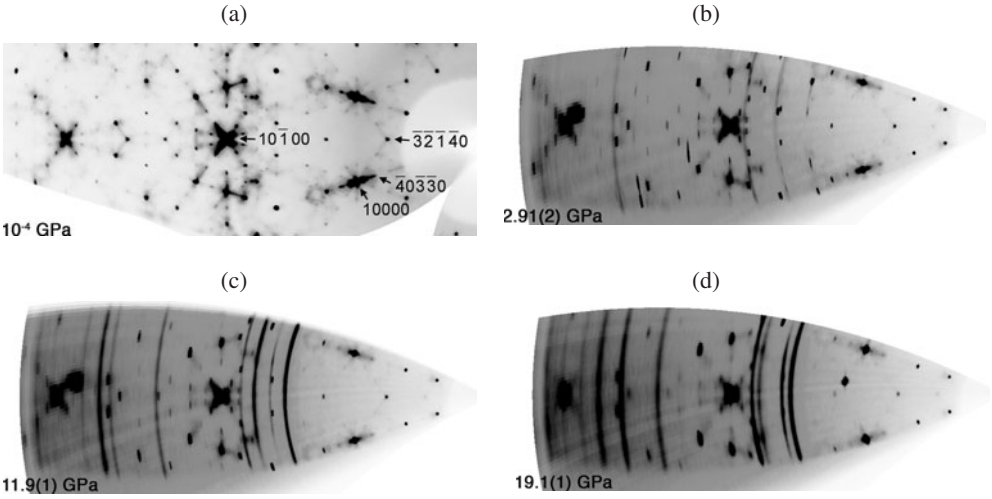


**Figure 3.** Reconstructed reciprocal space layers ($h_5 = 0$) of decagonal Al–Co–Cu perpendicular to the tenfold axis obtained at ambient pressure (a), 2.91(2) GPa (b), 11.9(1) GPa (c), and 19.1(1) GPa (d). Above 11.9(1) GPa, the peaks are broadened and the diffuse scattering is smeared out, caused by non-hydrostatic conditions and cracking of the crystal. (The powder rings result from the gasket and the pressure-transmitting medium (argon). The additional strong spots are diamond reflections.)

Despite the peak broadening, the intensity distribution of strong and weak reflections, as well as the shape of the diffuse scattering, are comparable at low and high pressures. Observable reflections with large internal component like for example $\bar{4}0\bar{3}\bar{3}0$ or $\bar{3}\bar{2}\bar{1}\bar{4}0$ do not differ significantly in relative position or intensity as a function of pressure. The local symmetry is still maintained, indicating the quasiperiodicity, and also the shape of the diffuse scattering does not change significantly. Therefore, it can be assumed that decagonal Al–Co–Cu is stable up to 19.1 GPa, within the framework of the experiment.

This result is in good agreement with the results of all known high-pressure studies on quasicrystals, where no structural transition below 10 GPa at ambient temperature and in some cases a peak broadening above 10 GPa was reported (see [5] and references therein).

The transformation of decagonal Al–Co–Cu to a B2 phase, which was observed during high-energy ball milling [11], may therefore not only be a result of the applied pressures. At ambient temperature, atomic diffusion is very slow and therefore the structure may remain metastable at elevated pressures. By introducing a high amount of defects in the crystal structure, for example during high-energy ball milling, atomic diffusion may be activated and the decagonal quasicrystal transforms into a B2 phase. It has to be noted that the transformation into a B2 phase can also be induced by electron irradiation [12].

### *3.3. Bulk modulus*

The quasiperiodic lattice parameters $a_1, \ldots, a_4$ were determined from all observable symmetry equivalent $1\,0\,0\,0\,0$ reflections. Significant differences of the lattice parameters within the quasiperiodic layers were not observed, indicating the presence of the tenfold symmetry even at 19.1 GPa. The periodic lattice parameter $a_5$ was determined from cuts of higher quasiperiodic layers in the reconstructed images parallel to the tenfold axis. The statistical error of the determined lattice parameters is below 0.004 Å, which is obviously an underestimate of the

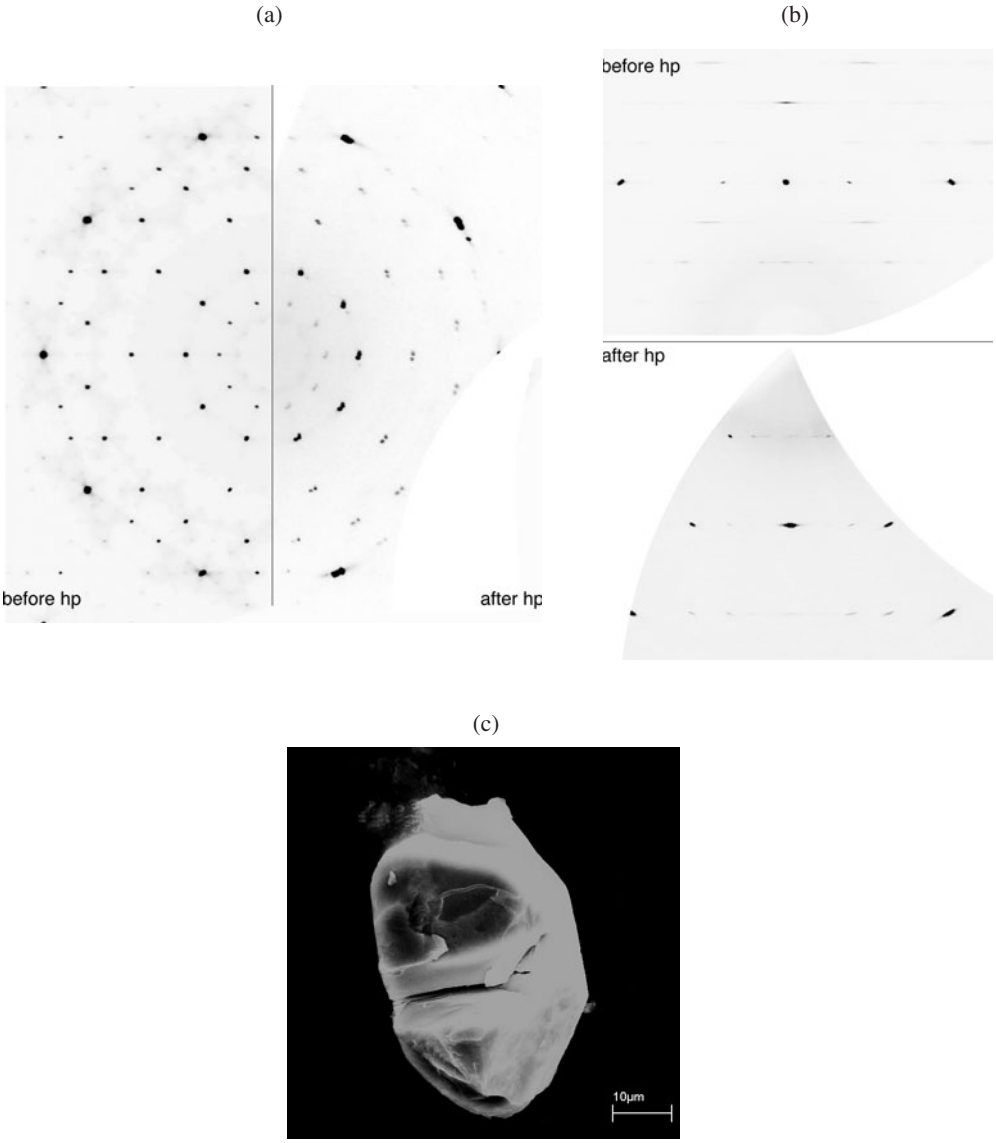


**Figure 4.** (a) Quasiperiodic reciprocal space layer with $h_5 = 1$ before (left) and after (right) the high-pressure studies. A radial peak splitting can be observed, which is also present in layers perpendicular to the quasiperiodic layers ((b), top before, bottom after high-pressure studies; note that layers with different orientation, but including the tenfold axis, are shown). This indicates the cracking of the crystal, as shown on an SEM image of the crystal after the high-pressure studies (c).

total error, as the lattice parameters were determined from only very few reflections. The parameters mainly contributing to the overall uncertainty in the lattice parameters are sample-to-detector distance, wavelength, and centre of the image-plate (beam centre). The sample-to-detector distance is the dominating uncertainty of the experimental setup, mainly caused by difficulties in centring the crystal along the beam direction. An estimate of the uncertainty in the sample-to-detector distance of 0.5 mm is adequate and results in an absolute error in the lattice parameter of $\pm 0.01$ Å. Table 1 shows the variation of lattice parameters with pressure.

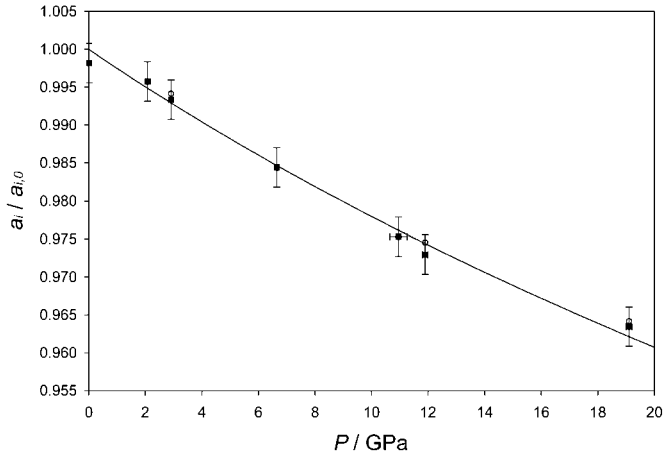


**Figure 5.** Relative lattice parameters $a_i/a_{i,0}$ of decagonal Al–Co–Cu as a function of pressure. The solid line represents the second-order Birch–Murnaghan equation of state with $K_0 = 131(8)$ GPa, $a_{i,0} = 3.797(10)$ Å (solid squares: $a_i/a_{i,0}$ $(i = 1, \ldots, 4)$; hollow circles: $a_5/a_{5,\mathrm{obs}}$; if not otherwise given, the error in pressure is less than the width of the symbol).

**Table 1.** Observed lattice parameters at various pressures. The lattice parameters were determined from the positions of Friedel pairs of symmetry equivalent reflections in reconstructed reciprocal space layers. The error in the lattice parameters was estimated to ±0.01 Å as described in the text (the quasiperiodic lattice parameters are as given in [20]). In the last two columns, the ratios $r_i = a_i/a_i(P = 10^{-4}$ GPa) are given to illustrate the relative change as a function of pressure.

| $P$ (GPa) | $a_{1,\ldots,4}$ (Å) | $a_5$ (Å) | $r_{1,\ldots,4}$ | $r_5$ |
|---|---|---|---|---|
| $10^{-4}$ | 3.790 | 4.116 | 1 | 1 |
| 2.075(2) | 3.781 | | 0.9976 | |
| 2.91(2) | 3.772 | 4.092 | 0.9952 | 0.9942 |
| 6.65(3) | 3.738 | | 0.9862 | |
| 10.95(30) | 3.703 | | 0.9771 | |
| 11.9(1) | 3.694 | 4.012 | 0.9747 | 0.9747 |
| 19.1(1) | 3.658 | 3.969 | 0.9652 | 0.9643 |

The zero-pressure bulk modulus $K_0$ was calculated by fitting a second-order Birch–Murnaghan equation of state, based on the quasiperiodic lattice parameters $a_1, \ldots, a_4$ ($K_0$ is related to the compressibilities along the axes, $\beta_0$, by $K_0 = -1/(3\beta_0)$). The equation of state with $K_0 = 131(8)$ GPa, $a_{i,0} = 3.797(10)$ Å, and the change of the relative lattice parameters $a_i/a_{i,0}$ $(i = 1, \ldots, 4)$ as a function of pressure, are plotted in figure 5.

The refined value for the quasiperiodic lattice parameter at zero pressure, $a_{i,0} = 3.797(10)$ Å, is within the error limits equal to the observed value of $a_i = 3.790(10)$ Å at ambient pressure. As it was only possible to extract $a_5$ from the images obtained with the modified setup, the amount of data was too small to get reasonable results from the fitting procedure. Nevertheless, the relative change of the quasiperiodic and periodic lattice parameters with pressure does not differ significantly (see table 1). Using the observed value of $a_{5,\mathrm{obs}} = 4.116(10)$ Å at ambient pressure as $a_{5,0}$ lets the $a_5$ lattice parameter follow the same equation of state as the quasiperiodic lattice parameters. Therefore, it can be assumed that the compressibilities along the periodic and quasiperiodic axes are the same and the compression behaviour of decagonal Al–Co–Cu in the investigated pressure range is almost isotropic.

The lattice parameters known to the literature, $a_{1,\ldots,4} = 3.765(3)$ Å and $a_5 = 4.1481(3)$ Å [20], differ from the observed values in this work. This may be caused by deviations in chemical composition or thermal treatment, which is not described in [20].

The value of the bulk modulus, $K_0 = 131(8)$ GPa, is in between the values reported for decagonal Al–Co–Ni (126.6(13.9) GPa [6] and 121(8) GPa [4]) and the related icosahedral Al–Cu–Ru (128(10) GPa [9]) and Al–Cu–Fe (139(6) GPa [21]) quasicrystals. This may have been expected due to the chemical affinity of iron, cobalt and nickel. It may be stated, that the compression behaviour is dominated by the chemical composition of the quasicrystals and the influence of the different quasiperiodic structures is only small.

## 4. Conclusions

An *in situ* single-crystal high-pressure study of decagonal Al–Co–Cu has shown that this quasicrystal is stable at least up to 19.1 GPa at ambient temperature. The value of the bulk modulus is comparable to the values of other quasicrystals with related compositions. The influence of crystal orientation on the accessible reciprocal space data was shown. More information on higher reciprocal space layers may be obtained by using single crystals in different orientations. *In situ* high-temperature high-pressure experiments may yield further information on the stability range of this quasicrystal. The reported phase transition during electron irradiation or high-energy ball milling was not observed at high pressure and ambient temperature, which might be caused by hindered kinetics.

## Acknowledgments

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