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► **To cite this version:**

Guillaume Fiquet, Chandrabhas Narayana, Christophe Bellin, Abhay Shukla, Imène Esteve, et al.. Structural phase transitions in aluminium above 320 GPa. *Comptes Rendus Géoscience*, 2018, 10.1016/j.crte.2018.08.006 . hal-01924782

HAL Id: hal-01924782

<https://hal.sorbonne-universite.fr/hal-01924782>

Submitted on 22 Oct 2021

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1 **Structural phase transitions in aluminium above 320 GPa**

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19 **Structural phase transitions in aluminium above 320 GPa**

20

21 With the application of pressure, a material decreases in volume as described in its
22 equation of state, which is governed by energy considerations. At extreme pressures,
23 common materials are thus expected to transform into new dense phases with extremely
24 compact atomic arrangements that may also have unusual physical properties. For
25 aluminium, first principle calculations have consistently predicted a phase transition
26 sequence fcc - hcp - bcc in a pressure range below 0.5 TPa (1-7). The hcp phase was
27 identified at 217 GPa in an experiment (13) and the bcc phase has been recently
28 confirmed in a dynamic ramp-compression experiment coupled with time-resolved X-
29 ray diffraction (16). Here we confirm this observation with a synchrotron-based X-ray
30 diffraction experiment carried out within a diamond-anvil cell and report indications of
31 the onset of the transition towards a bcc structure at pressures beyond 320 GPa. With
32 this work, we also demonstrate the possibility of routine static high-pressure
33 experiments with conventional bevelled diamond-anvil geometry in the 0.3-0.4 TPa
34 regime.

35 Keywords: aluminium, structural transition, x-ray diffraction, multi-megabar

36

37 **Introduction**

38 The extreme pressure phase diagram of materials is important not only for the
39 understanding of the interiors of planets or stars, but also for the fundamental
40 understanding of the relation between the crystal and electronic structures. Structural
41 transitions induced by extreme pressures are governed by the deformation of the charge

42 density of the valence electrons which bears the brunt of the increasing compression
43 while the relative volume occupied by the nearly incompressible ionic core electrons
44 increases. This fact is said to hold not only in the few hundred GPa range but also
45 beyond the terapascal regime where compression pushes ion cores together.
46 Experimental limitations will however keep the TPa regime in the realm of predictions,
47 at least as far as static pressure is concerned.

48 Early first principles calculations (1) for aluminium (Al) predicted an *fcc* \rightarrow *hcp* \rightarrow *bcc*
49 structural transition trend over a pressure range of roughly 0–500 GPa and these have
50 since been repeatedly confirmed (2-4) and refined (5-7). This non-intuitive generic
51 transition from a compact (*fcc* or *hcp*) to a more open (*bcc*) structure with increasing
52 pressure is said to be driven by the increasingly smaller and restricted volume available
53 for the valence electrons. This tends to reduce electronic bandwidth by the occupation
54 of an *s-d* band at a few hundred GPa (as opposed to the dispersive *s-p* band at low
55 pressures). Ultimately, theoretical calculations indicate that valence electrons can be
56 localized in “interstitial” spaces in an open-packed incommensurate host-guest structure
57 similar to that predicted at 3.2 TPa (8). That *d* electrons play a role in these transitions is
58 strongly suggested by the fact that the structure sequence with increasing pressure is
59 mirrored in transition metals as the number of *d* electrons increases (9) (the analogy has
60 obvious limitations since the underlying magnetism intervenes in transition metals
61 (10)). As the unit cell volume is reduced to fractions approaching half or less, the
62 initially unoccupied *d* bands in simple metals and in particular in aluminium approach,
63 narrow, and descend below the Fermi level triggering structural changes which can be
64 intuitively understood since the *bcc* structure is more compatible with a bonding
65 interaction between second nearest neighbour atoms than the *fcc* structure (1,2). Such a
66 transition has earlier been reported in Mg (11) and Pb (12) where it takes place at lower

67 pressures.

68 A simple system like Al is not only important as a benchmark for theory, but can also
69 be used as a standard for pressures in the TPa range and beyond, which are targeted at
70 dynamic compression facilities such as the National Ignition Facility (NIF) at the
71 Lawrence Livermore National Laboratory in the US or Laser Mégajoule (LMJ) in
72 Bordeaux in France. Confirming predictions of aluminium structure at extremely high
73 densities is thus paramount. According to a recent first principle calculation (7),
74 aluminium should undergo a phase transition from *fcc* to *hcp* structure around 200 GPa
75 and another transition from *hcp* to *bcc* with further compression beyond 300 GPa. The
76 *hcp* phase around 217 GPa was reported in an earlier room-temperature static high-
77 pressure experiment where a maximum pressure of 330 GPa was achieved (13). An
78 earlier classical shock-compression study found no evidence of the predicted *fcc* to *hcp*
79 transition (14) but it is expected that *fcc* aluminium melts at 125-150 GPa along
80 principal Hugoniot (see (16)). More recently, *bcc* aluminium has been synthesized in
81 the non-equilibrium conditions of an ultra-fast laser-induced micro-explosion confined
82 inside a sapphire (α -Al₂O₃) rod (15). This recent report of the *bcc* super-dense phase of
83 Al is interpreted as a complex route of synthesis via a spatial separation of Al and O
84 ions in short-lived hot non-equilibrium plasma of solid-state density. The micro-
85 explosion confined inside a sapphire capsule leads to this *bcc*-Al phase, which survives
86 in a compressed state after fast quenching. However, if confined micro-explosions
87 provide an interesting route to create and recover high-density polymorphs, such an
88 experiment does not allow the determination of a transition pressure nor does it show
89 any evidence of the presence of a quenched *hcp* phase. Very recently, an experiment
90 succeeded to combine nanosecond *in situ* x-ray diffraction and simultaneous
91 velocimetry measurements to determine the crystal structure and pressure of ramp-

92 compressed aluminium at stress states between 111 and 475 GPa (16). The solid-solid
93 Al phase transformations, fcc–hcp and hcp–bcc, are reported at 216 ± 9 and 321 ± 12
94 GPa, respectively. In this article, we confirm this observation with a synchrotron-based
95 X-ray diffraction experiment carried out within a diamond-anvil cell and report
96 indications of the onset of the transition towards a bcc structure at pressures beyond 320
97 GPa.

98

99 **Experimental**

100 *Sample preparation*

101 Central to our experiment was the establishment of a protocol for reaching pressures
102 exceeding 350 GPa in a diamond-anvil cell with a pure aluminium sample (Fig. 1)
103 confined inside a conventional gasket (Fig. 2), which limits the deviatoric stress
104 component to moderate values. Very fine-grained aluminium powder is very difficult to
105 handle and is pyrophoric in nature. It can thus easily oxidize. We used instead an
106 aluminium foil (99.999 % purity, 15 μm thick, Goodfellow) as starting material.
107 Samples were pre-cut from this foil with a focused ion beam (FIB) so as to obtain
108 cylinders (Fig. 1) with dimensions fitting the holes prepared in pre-indented rhenium
109 gaskets.

110

111 *High-pressure cells preparation and sample loading*

112 Our experiments were conducted in symmetrical diamond anvil cells equipped with
113 single bevelled diamonds (8° bevel) mounted on X-ray transparent cubic boron nitride
114 seats. Two separate experimental runs were carried out at ambient temperature with
115 diamonds having centre flat culets of 35 and 20 μm diameters respectively. The first

116 experiment with the 35 μm culet anvil reached 257 GPa whereas the second one
117 reached pressures of about 370 GPa. In our experiments, no pressure-transmitting
118 medium was used. As noted by Akahama et al. (13), Al has a relatively low shear
119 modulus and is expected to keep low uniaxial stresses in the diamond-anvil cell.
120 Success of experiments in this pressure range are highly dependent on handling samples
121 inside a hole of less than 10 μm , which has to be perfectly centred on a culet of 20 μm
122 made on a gasket pre-indented to less than 10 μm . Manipulating a sample of such small
123 dimensions inside a highly contoured gasket terrain to place it perfectly into the hole is
124 yet another challenge. In the present experiment, we have used the focused ion beam for
125 drilling such tiny holes (see 17) in rhenium with a centring precision better than 1 μm
126 and causing very little defects to the gaskets. Rhenium gaskets were pre-indented to
127 reach an initial thickness of about 12 μm , and then drilled with the focused ion beam
128 (FIB). Preparation of gaskets and sample loading were carried out in the FIB chamber,
129 so as to have a perfect sample loading in the pressure chambers (see Fig. 2). Above 300
130 GPa, pressure was estimated according to the equation of state of rhenium (18). In the
131 *fcc* stability field, pressure was measured with available equations of state reported for
132 aluminium (13, 19). Both methods yield pressure measurements in very good agreement
133 (*i.e.* within error bars) up to 300 GPa. Alternatively, the equation of state for rhenium
134 proposed by Dubrovinsky et al. (20) could be used but the latter yields significant
135 pressure overestimate when compared to other measurements (as large as 70 GPa at 300
136 GPa).

137

138 *X-ray diffraction experiments*

139 In situ X-ray diffraction high-pressure experiments were conducted at the high-pressure
140 beamline ID27 of the European Synchrotron Radiation Facility (ESRF, Grenoble,

141 France). X-ray diffraction pattern were collected using an angle dispersive
142 monochromatic set-up with a wavelength of 0.3738 Å (iodine K-edge at 33.3 keV)
143 focused with KB mirrors down to a spot of 2.5 x 3 μm FWHM at sample location. Such
144 a spot size explains why rhenium diffraction lines are completely absent in the first run
145 conducted with bevelled diamonds with a central culet of 35 μm in diameter and a
146 sample chamber of 14 μm in diameter which reached a pressure of 240 GPa (see Fig. 3).
147 Rhenium lines are visible in the second run designed to reach a higher pressure (Fig. 5)
148 with a smaller sample having a diameter of about 8 μm mounted on 20 μm culets.
149 Exposure time varied from 60 s below 100 GPa to 240 s at pressures exceeding 370
150 GPa, thus compensating for the thickness reduction as pressure was increased. We used
151 a two-dimensional MAR CCD detector located at a distance of 207 mm from the
152 sample. Images were then integrated using the Fit2D software (21) in order to obtain a
153 conventional diffraction pattern. Data analysis was then carried out using the GSAS
154 package (22, 23). Cell parameters were refined using LeBail method for the extraction
155 of reflection intensity. Preferred orientations were not refined. Graphics were realized
156 with the Datlab software (courtesy K. Syassen, MPI Stuttgart). All X-ray diffraction
157 patterns are background subtracted.

158

159 **Results and discussion**

160 *X-ray pattern analysis*

161 The first run presented in Fig. 3 show a smooth evolution of the *fcc* structure at lower
162 pressures. The pattern at 213 GPa can be unambiguously assigned to a *fcc* lattice with a
163 lattice parameter $a = 3.246(1)$ Å and a unit cell volume of $34.190(31)$ Å³. With four
164 atoms per unit cell in the *fcc* structure, the atomic volume is 8.548 Å³. As pressure was

165 increased, new peaks appeared around 220 ± 5 GPa. At the pressure of 235 GPa, as
166 shown in Fig. 4, these new lines can be unambiguously assigned to a *hcp* structure with
167 lattice parameters $a = 2.266$ (1) Å and $c = 3.720$ (2) Å and a unit cell volume of 16.542
168 (23) Å³, coexisting with an *fcc* lattice with $a = 3.211$ (1) Å and a unit cell volume of
169 33.097 (30) Å³. We find, within error, a similar atomic volume, $V_A = 8.274$ (7) Å³ for
170 the *fcc* structure and $V_A = 8.269$ (11) Å³ for the *hcp* structure and a large coexistence
171 domain which can be explained by the small enthalpy difference between the two
172 phases (6, 7, 13). These observations are in perfect agreement with the transition
173 pressure of 215-222 GPa reported in the previous X-ray diffraction work cited above
174 (13) or in the dynamic compression experiment (16). Alternatively, a slightly lower
175 pressure of 210 GPa is obtained when using another room temperature high-pressure
176 equation of state for aluminium (19). This *fcc* to *hcp* transition takes place at a
177 compression of 0.5, in general agreement with theoretical predictions (*e.g.* ref 7) or
178 experimental measurements (13).

179 In the second run, we explored pressures above 300 GPa. Patterns are cut at a maximum
180 angle of 20 degrees 2-theta because of the use of higher diamonds. With such a
181 configuration, diamond seats and cell mechanical opening prevented us to collect
182 diffraction at higher angles. In this second run (see Fig. 5), we also observe without
183 ambiguity the progressive growth of the *hcp* phase at the expense of the *fcc* phase, with
184 the complete disappearance of the *fcc* peaks at a pressure which can be estimated of
185 about 280 GPa according to the equation of state of aluminium (19) or that of rhenium
186 (18). In this run, the presence of rhenium reflections could not be avoided with a sample
187 chamber typically smaller than 8 µm as soon as pressure has been increased. At 235
188 GPa, lattice parameters $a = 2.266$ (1) Å and $c = 3.720$ (2) Å for the *hcp* structure yield a
189 c/a ratio of 1.642 (2). At 370 GPa, with $a = 2.182$ (2) Å and $c = 3.557$ (5), c/a ratio is

190 1.630 (4). It thus seems that the trend followed by c/a ratio is a decrease when pressure
191 is increased. Between 320 GPa and 350 GPa, the most interesting feature is the
192 observation of a splitting of the 002 reflection of the *hcp* structure (see Fig. 6). The
193 remaining peaks corresponding to the *hcp* structure (100 and 101) do not show any
194 significant broadening nor splitting. It is indeed shown in Fig. 6B and 6C that a new line
195 here interpreted as the 110 *bcc* grows as a shoulder of the *hcp* 002 line. Some diffracted
196 intensity detected around a 2θ value of 17° close to the aluminium 102 *hcp*
197 reflection (see Fig. 5) can tentatively be interpreted as the 200 *bcc* reflection.

198

199

200 **Discussion**

201 The *hcp* \leftrightarrow *bcc* transformations with pressure are martensitic transitions which result
202 from small relative movements of atoms. The *hcp* \rightarrow *bcc* transition has been studied in
203 some detail from the theoretical point of view for the case of Mg (24, 25). It is thought
204 to involve a distortion of the regular hexagonal atomic arrangement in the (001) *hcp*
205 plane as well as a shear between adjacent (001) planes (see Figure 7). The distortion
206 accounts for the transformation of the (001) *hcp* planes into the (110) *bcc* planes while
207 the shear transforms the ABAB stacking along the [001] *hcp* direction to one
208 compatible with the *bcc* structure. This mechanism principally involves the (001) *hcp*
209 planes and would thus manifest itself by changes in peaks with 001 *hcp* character. This
210 is exactly what we observe in our experiments as shown in Fig. 6 with a clear splitting
211 of the 002 *hcp* line when pressure exceeds 320 GPa. It is expected the 002 *hcp*
212 reflection should totally disappear with the appearance of a single 110 *bcc* peak when
213 the transition is completed. However, it is likely the martensitic nature of such a
214 transition makes the phase transition sluggish at ambient temperature where the

215 transformation is kinetically inhibited, as observed in other system at room temperature
216 (see 26). Both low-pressure and high-pressure structures coexist on a large pressure
217 domain and *hcp* reflections can still be observed at the pressure of 370 GPa as shown
218 shown in Fig. 5 and 6, although the *bcc* features are less marked at this maximum
219 pressure because of a diminution of the quality of our diffraction images. Though, our
220 observations are compatible with the observations reported in the ramp-compressed
221 aluminium experiment (16) where coexistence of the two high-pressure structures is no
222 longer observed above 380 GPa. It is however likely kinetic barriers can be more easily
223 overcome in shock experiments whereas it was impossible to heat up our sample kept
224 under such pressure conditions in our experiment. We propose therefore that the peak
225 splitting observed above 320 GPa correspond to the onset of the *hcp* to *bcc* structure
226 transition, with compression along the [001] axis. In a rigid atom model, the *bcc*->*hcp*
227 transition can be explained simply by using the relationships between atomic radius r
228 and lattice parameters a_0 and c_0 with $a_0=2r$, $c_0\approx 1.633a_0$ for a *hcp* structure and $a_0 =$
229 $4r/\sqrt{3}$ for a *bcc* structure, since the atomic packing fraction is higher in the *hcp* phase. In
230 addition, the relations $a_{hcp}=\sqrt{3}a_{bcc}/2$ and $c_{hcp}=\sqrt{2}a_{bcc}$ can also be written for such a
231 transition (see 27 for instance) and the cell parameters we could deduce from our
232 experiments satisfy these relations. In our experiment, the unit cell volume fitted for the
233 *hcp* structure at 320 GPa is $V_{hcp}=15.655 (41) \text{ \AA}^3$ while that calculated assuming that the
234 split peak corresponds to 002 *bcc* yields $V_{bcc}=15.719 (56)$, which are indiscernible
235 within error bars at the onset of the transition. Observed pattern and reflections are
236 shown for the two phases at 320 GPa in Fig.7. At this pressure, aluminium d-spacing for
237 *bcc* 110 reflection is 1.771, which is comparable to values reported at the same pressure
238 in (16).

239 We note that the transition to the *bcc* phase is predicted in the region between 290 and

240 310 GPa (6) or around 380 GPa (28) by first principles calculations, which respectively
241 account for zero-point thermal vibrations or neglect these. These pressures compare
242 well with the onset of the transition that we place at 320 GPa. We also have a perfect
243 agreement with the 321 ± 12 GPa measured by velocimetry in the dynamic compression
244 experiments (16). According to theoretical studies, the calculated enthalpy difference
245 between these phases is only a few mRy (6, 7, 11) and one would experimentally expect
246 these phases to co-exist over a large pressure range as in the case of the *fcc* to *hcp*
247 transition. We can thus anticipate a very sluggish *hcp* to *bcc* transition. Our observations
248 correspond to the first step of this transition, built here on a distortion of the *hcp* lattice.
249 Our experiment thus confirms the measured and predicted *fcc-hcp-bcc* phase transitions
250 for Al. It also supports the predicted mechanism for this martensitic transition via a
251 distortion and shear of the (001) *hcp* planes. Experiments permitting higher pressures
252 than those reached here will be needed to detect a pure *bcc* phase unequivocally.
253 Though a recent static pressure experiment has reached a pressure exceeding 1 TPa
254 (29), our experiment performed on a sample of physical interest in conventional static
255 pressure geometry, still opens new perspectives. It provides a large pressure window
256 (up to 4 Mbar) for the study of a wide variety of materials and phenomena in
257 conventional diamond-anvil cell geometry. These range from structural phase
258 transitions or the detection of novel physical properties (such as superconductivity) in
259 elemental or more complicated materials of physical or geophysical interest (30, 31).

260

261 **Acknowledgements**

262 The focused ion beam (FIB) and scanning electron microscopy (SEM) facility of the
263 Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie is supported by

264 Région Ile de France grant SESAME 2006 N°I-07-593/R, INSU-CNRS, INP-CNRS,
265 University Pierre et Marie Curie-Paris 6, and by the French National Research Agency
266 (ANR) grant ANR-07-BLAN-0124-01. G. Fiquet acknowledges the program MATISSE
267 that contributed to the visit of Pr. Narayana at IMPMC-Sorbonne Université. MATISSE
268 is a Cluster of Excellence led by Sorbonne Universités and managed by ANR within the
269 Investissements d’Avenir program under reference ANR-11-IDEX-0004-02.

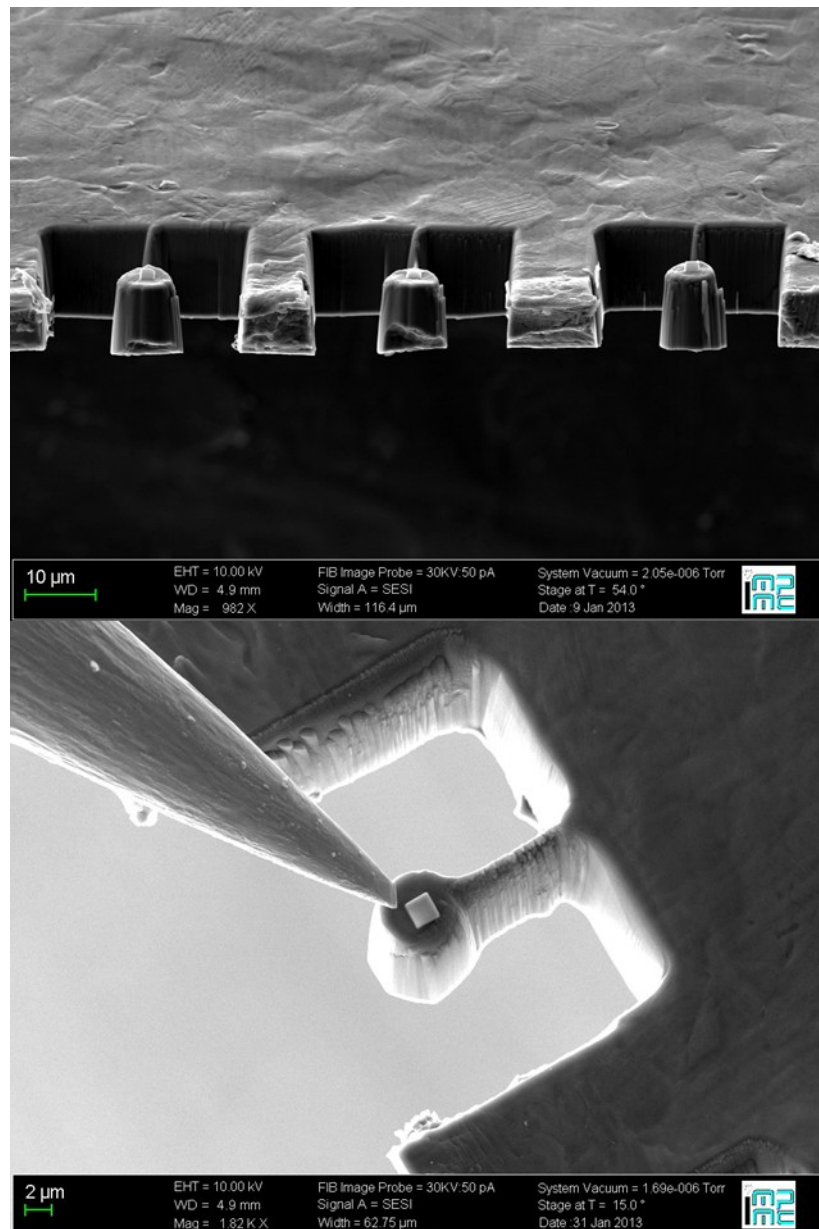
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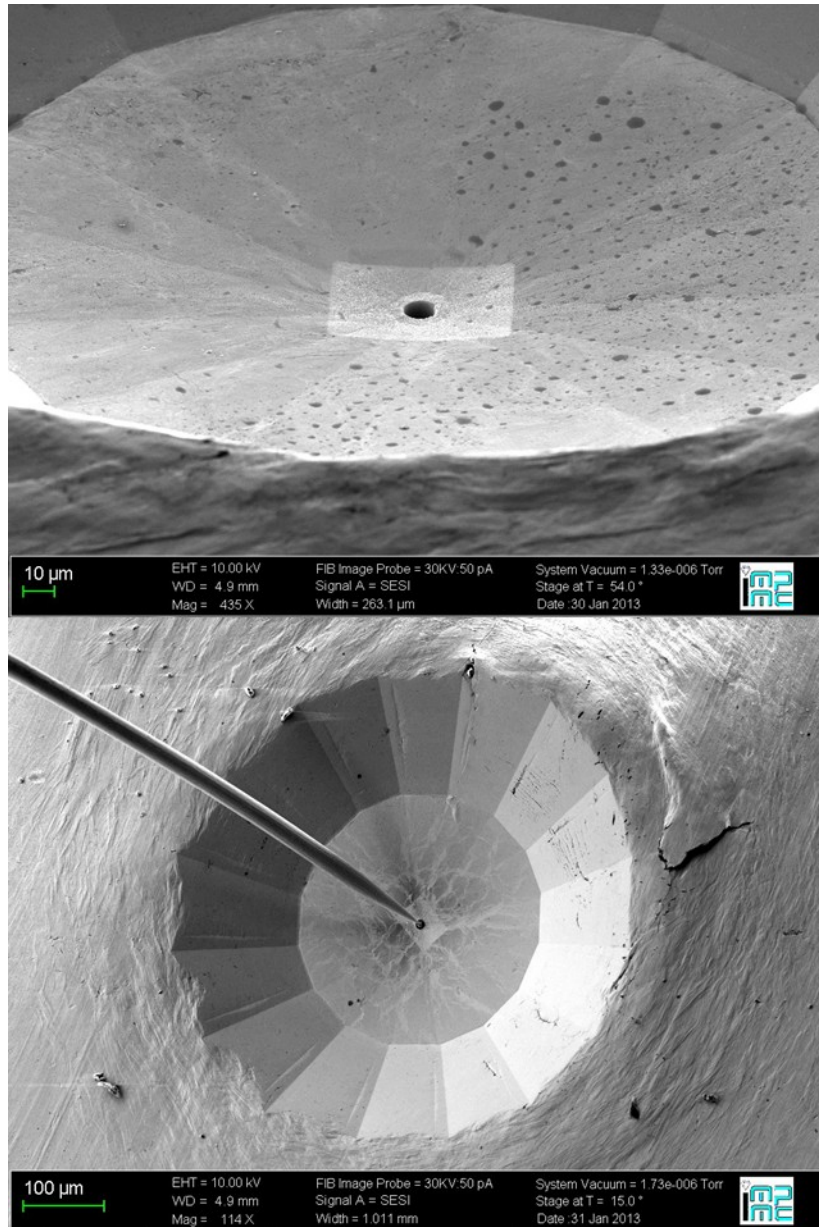


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322

323 **Figure 1.** Secondary electron SEM images: series of sample cylinders shaped with
 324 focused ion beam (FIB) on the edge of the pure aluminium sample foil (top). Individual
 325 bulk aluminium sample piece during lift-out procedure. The small bridge holding the
 326 sample can easily be cut once micro-manipulator is attached. A platinum deposition (2 x
 327 2 µm light square shape on the top) is visible (bottom). This pressure marker was
 328 unfortunately not detected during X-ray diffraction experiments.

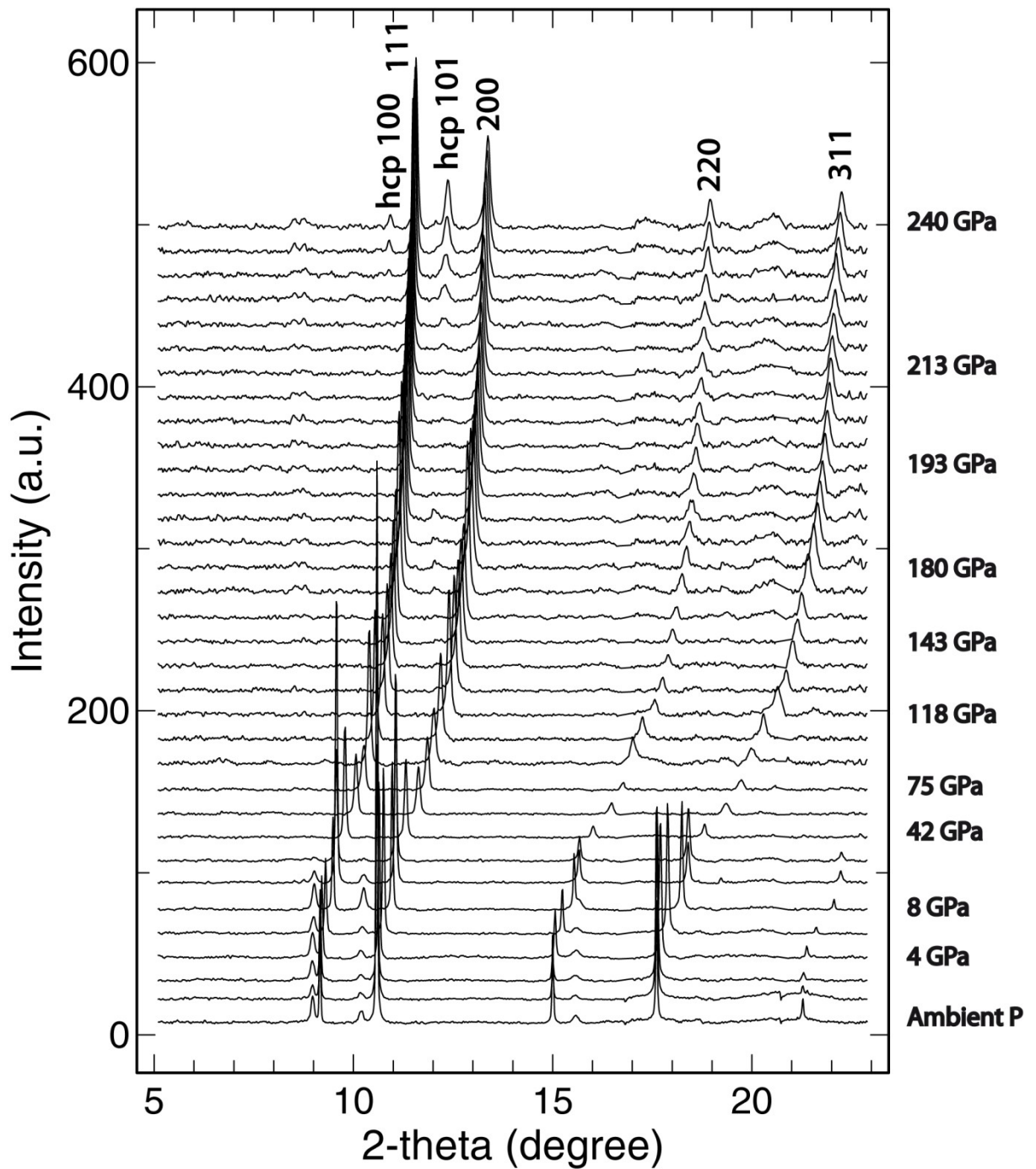
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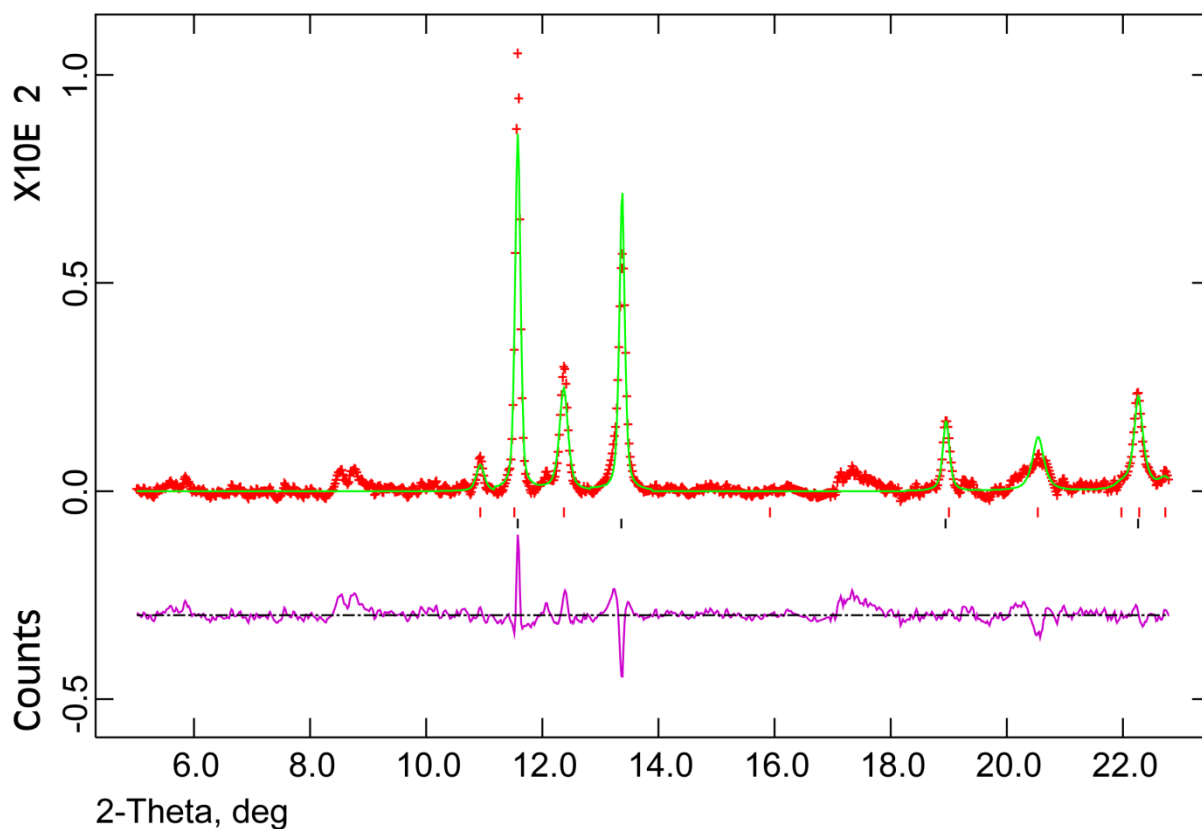
332 **Figure 2.** Secondary electron SEM images: 10 µm hole drilled with FIB at the center of
333 the 20 µm inner culet print on the rhenium gasket. Outer culet is 300 µm in diameter
334 (top). Sample cylinder loaded with micro-manipulator in sample chamber (bottom).



335

336

337 **Figure 3.** Diffraction pattern of an *fcc* aluminium sample compressed in a rhenium
 338 gasket at room temperature to 256 GPa in a diamond-anvil cell. Reflections
 339 corresponding to the hcp structure are detected at 213 GPa and pressures above.



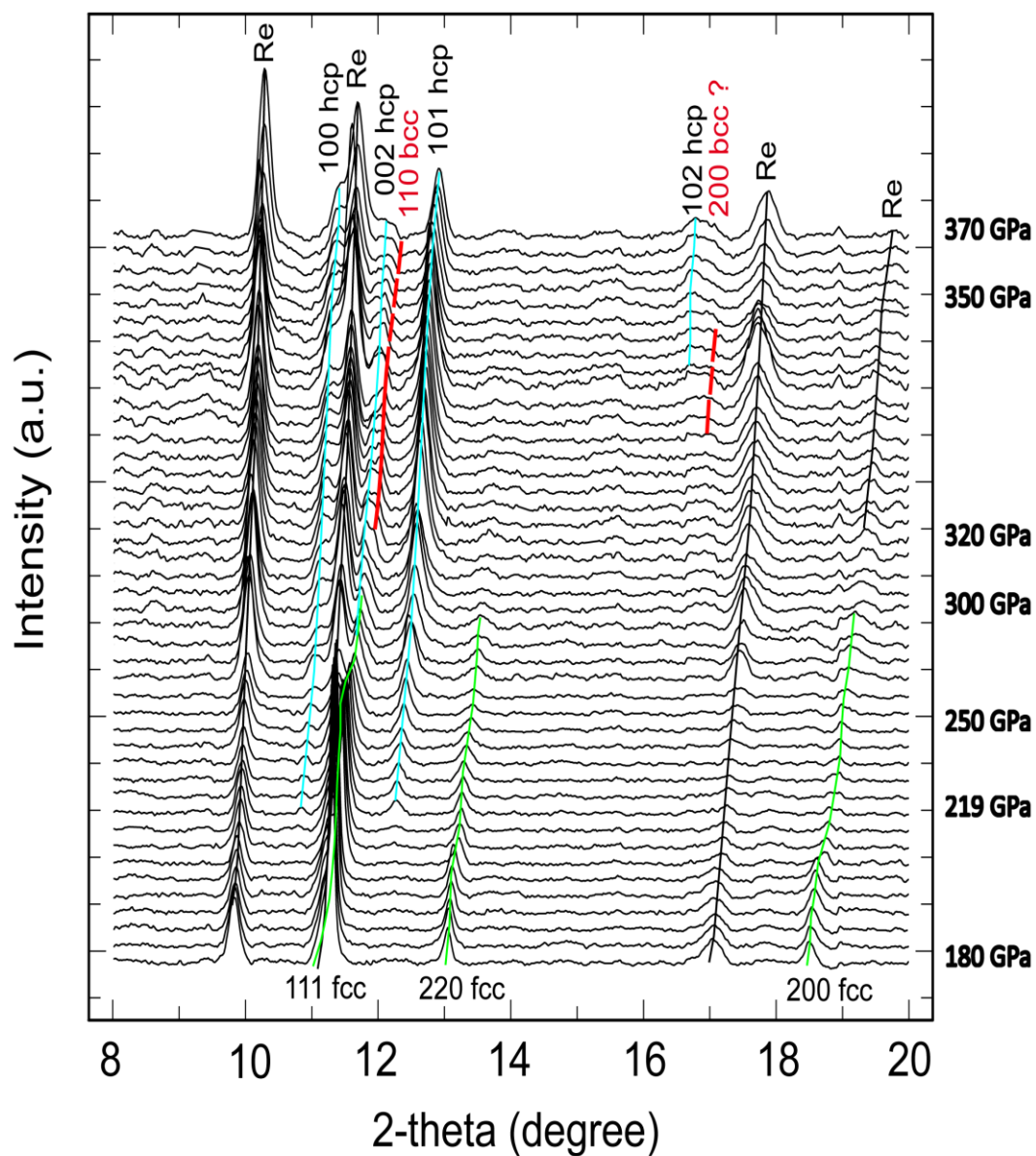
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341

342 **Figure 4.** Analysis of X-ray diffraction pattern of aluminium collected at a pressure of
 343 235 GPa, showing coexisting *fcc* and *hcp* structures. Cell parameters are $a= 3.211 (1) \text{ \AA}$
 344 and volume is $V=33.097 (30) \text{ \AA}^3$ for the *fcc* phase. Cell parameters are $a=2.266 (1) \text{ \AA}$
 345 and $c=3.720 (2) \text{ \AA}$ with volume $V=16.539 (23) \text{ \AA}^3$ for the *hcp* phase.

346

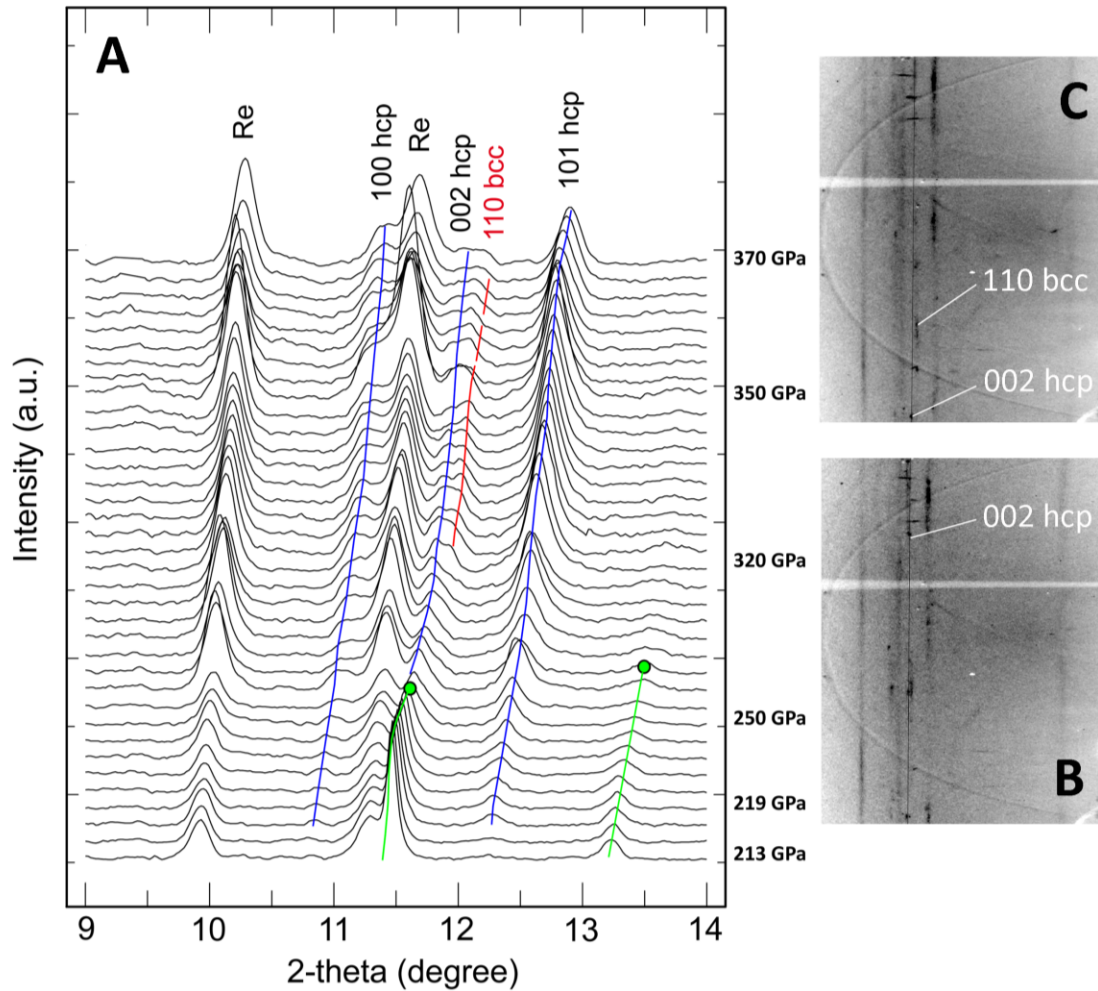
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348
 349 **Figure 5.** Series of full diffraction pattern collected between 180 to 370 GPa from
 350 bottom to top of the figure. Green lines (*fcc*), blue lines (*hcp*) and red lines (*bcc*) are
 351 guide to the eye for the different aluminium phases. The *fcc* phase is no longer observed
 352 at pressures exceeding 280 GPa. With the reduced size of the rhenium gasket pressure
 353 chamber, rhenium diffraction lines cannot be avoided at these pressures.

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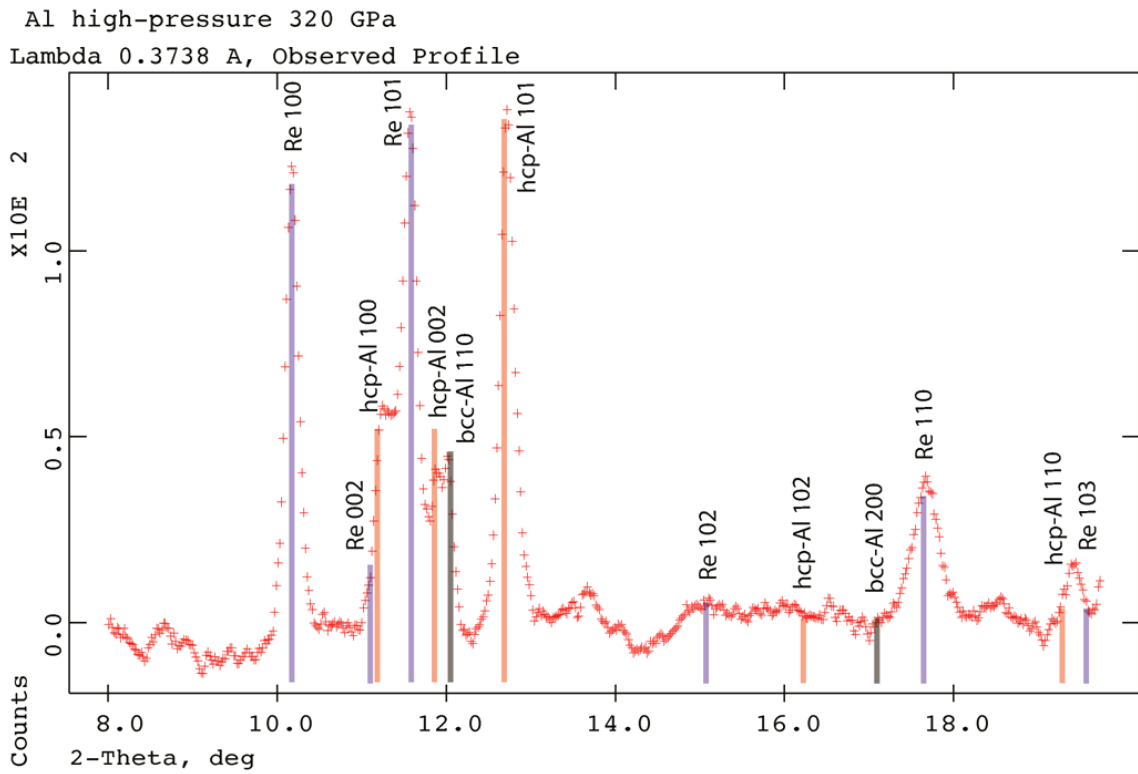
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358 **Figure 6.** (A) Detailed view of the peak splitting observed at pressures above 320 GPa.
 359 Pattern collected between 280 to 370 GPa from bottom to top of the figure. Blue lines
 360 (*hcp*) and red lines (*bcc*) are guide to the eye for the different aluminium phases. (B)
 361 Cake image of the pattern recorded at 310 GPa, showing *hcp* 002 spotty reflections (C)
 362 Cake image of the pattern recorded at 330 GPa, showing the splitting of *hcp* 002 and
 363 *bcc* 110 reflections. A thin black line serves as a reference guide for the 002 *hcp*
 364 reflection.

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367

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Figure 7. Observed diffraction at 320 GPa at the onset of the *hcp* – *bcc* transition. Fitted

369

cell parameters are $a = 2.230(2) \text{ \AA}$ and $c = 3.635(3) \text{ \AA}$ for a unit cell volume of 15.655

370

$(41) \text{ \AA}^3$ for the *hcp* structure, coexisting with a *bcc* lattice with $a = 2.505(3) \text{ \AA}$ and a unit

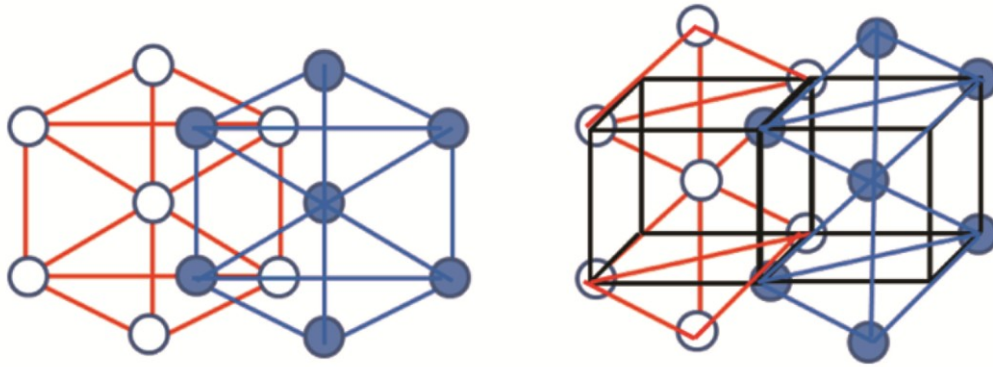
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cell volume of $15.719(56) \text{ \AA}^3$.

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376 **Figure 8.** Left panel: View of adjacent (001) planes with ABAB stacking in the *hcp*
377 structure, seen along the [001] axis. Right panel: View of adjacent (110) planes in the
378 *bcc* structure derived from the (001) *hcp* planes by distortion and shear, with underlying
379 *bcc* unit cells.

380