



High Pressure Structure of Lanthanum

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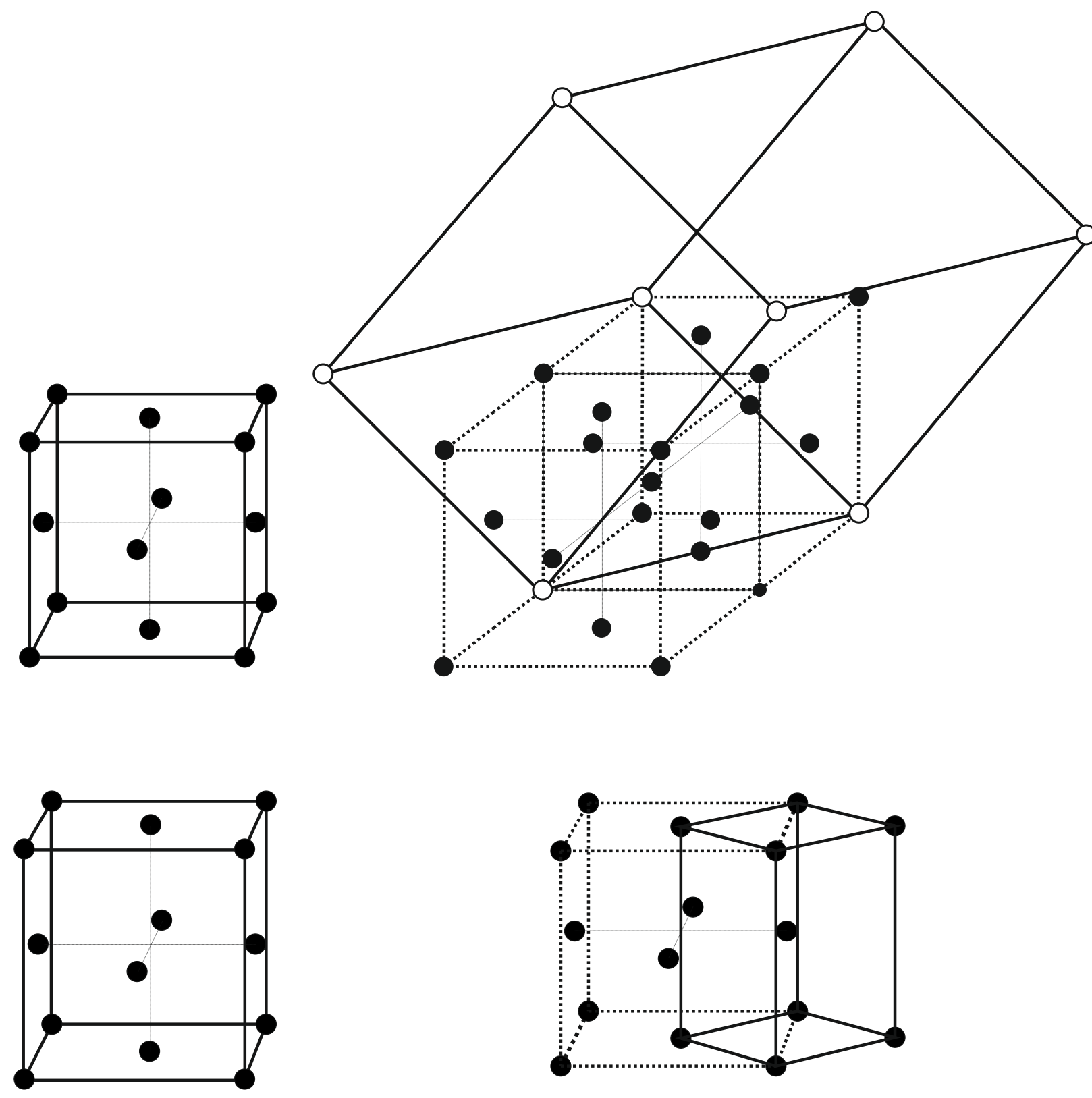
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Background/Motivation

Lanthanides, the group of elements characterised by 4f electrons, have similar behaviours and structures under high pressure as the actinides, characterised by 5f electrons. Studying the lanthanides can therefore provide insight into the actinides under similar conditions [1]. Although it has no 4f electrons, lanthanum (La) has a similar sequence of high pressure phases to other lanthanides. La is also of interest as lanthanum super-hydrides are superconducting at near room temperature under high pressure [2]. The structure and density of La is then crucial for identifying the hydrogen content in super-hydrides.

Previous Studies of La



Previous high-pressure studies of lanthanum have determined a sequence of phases from its ambient-pressure hcp structure (*hP4*) to cubic fcc (*cF4*), to a distorted-fcc phase, common among lanthanides, and a re-entry to cubic fcc, behaviour which is unique to lanthanum.

$hP4 \rightarrow cF4$ (face centred-cubic) $\rightarrow$ (distorted-fcc) $\rightarrow cP4$

Beyond 70 GPa, where La undergoes another phase transition, the structure has remained contested. Some groups reported the *hR24* distorted-fcc (d-fcc) structure remaining beyond 70 GPa [2, 3], while Chen reported a different d-fcc structure, *oF4* [4].

Munro [5] reported a body-centred tetragonal (bct), *tI2*, structure up to 280 GPa. This structure is another subtle distortion of the fcc structure, and is also seen in the lanthanides Ce and Pr. The same *tI2* structure has been recently predicted by DFT calculations [6].

Figure 1: Crystal structures of (a) cubic, (b) and (c) distorted cubic structures *hR24* and *oF4*, (d) *tI2* (bct), showing the relations to cubic (dotted line). From [7].

La Phase Diagram

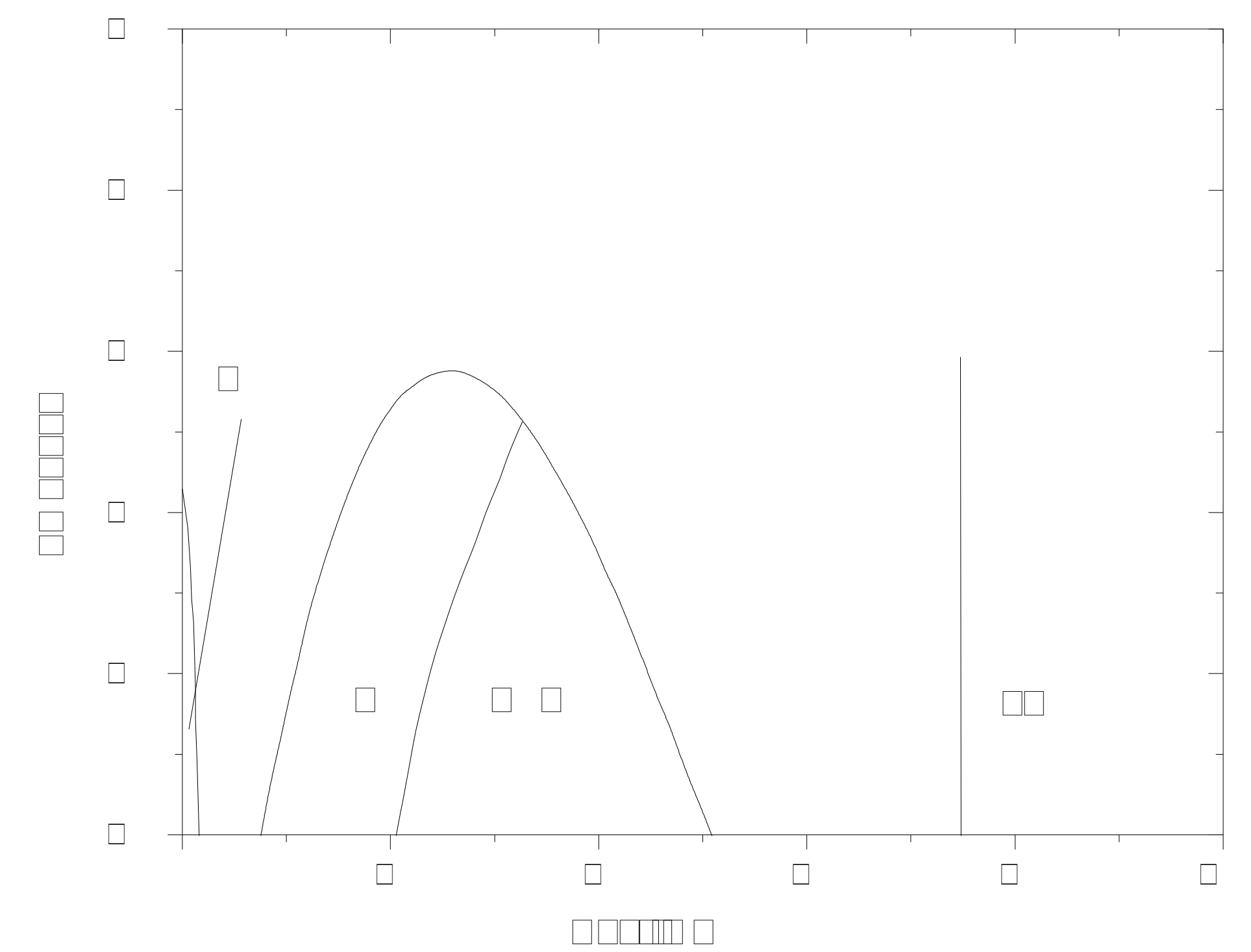


Figure 2: Phase diagram of La from previous studies up to 100 GPa and 800 K. The post-*cF4* structure has been reported as *oF4*, *hR24* or *tI2*. Adapted from [7]

Diamond Anvil Cell

Multi-megabar pressures can be reached in diamond anvil cells (DACs) on microscopic samples. DACs are hand-sized and the transparent diamonds allow for x-ray diffraction. The gasket, made of tungsten, supports the sample.

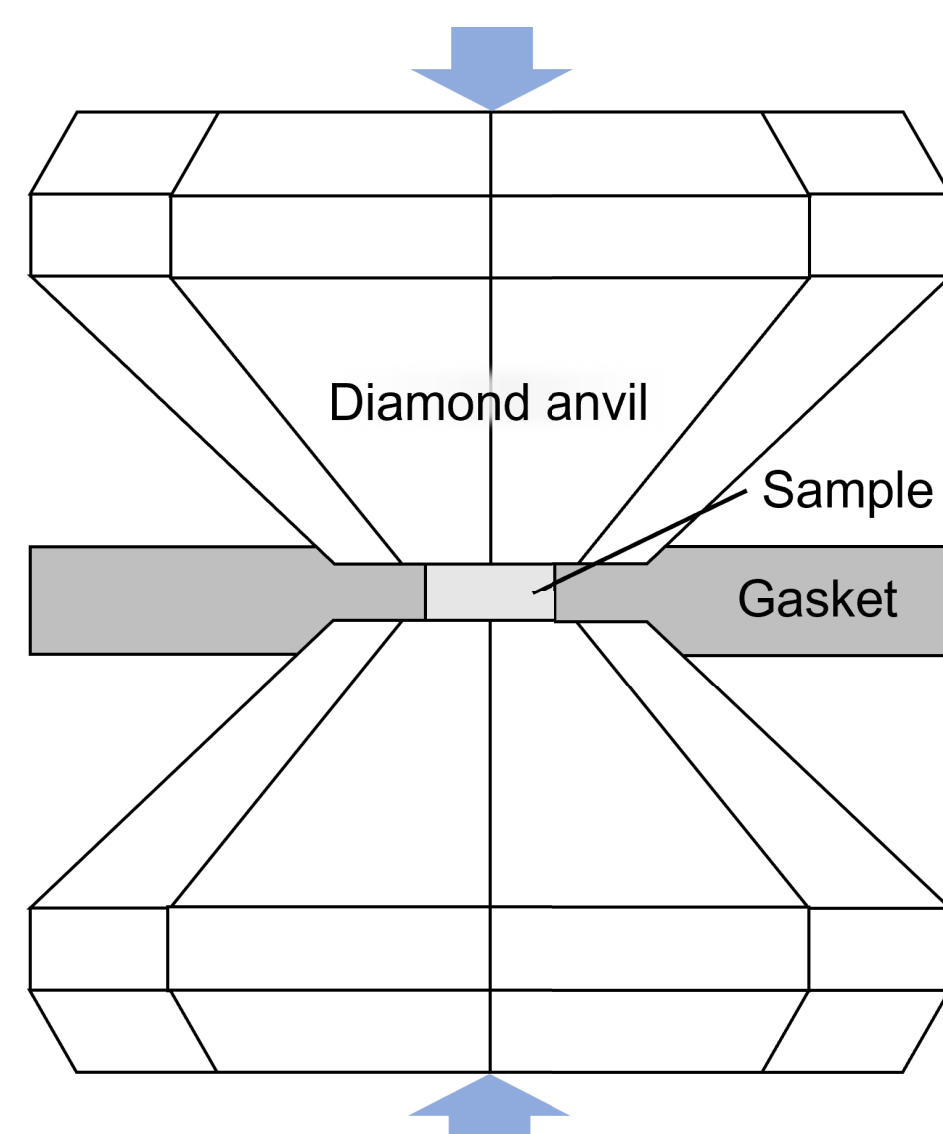


Figure 3: Diagram showing the principle of a DAC. Blue arrows indicate direction of force, applied by tightening screws, which increases pressure on the sample.

X-ray Powder Diffraction

X-rays diffract from the sample according to Bragg's law at different angles resulting in a diffraction image of Bragg rings since the crystals are randomly oriented. Integrating the intensity around the rings gives a diffraction profile.

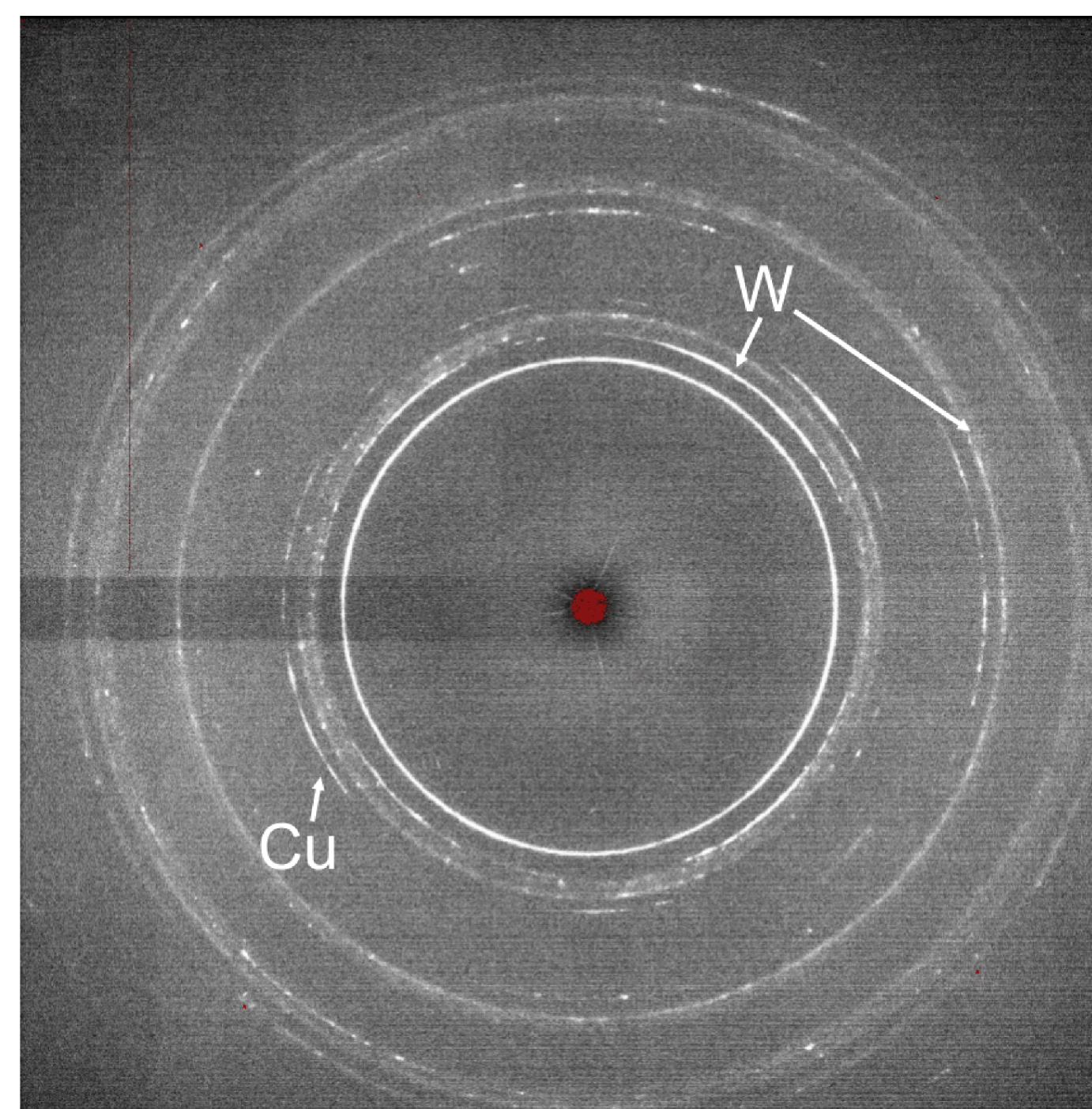


Figure 4: Diffraction image at 227 GPa. Arrows show rings from Cu pressure calibrant and tungsten gasket.

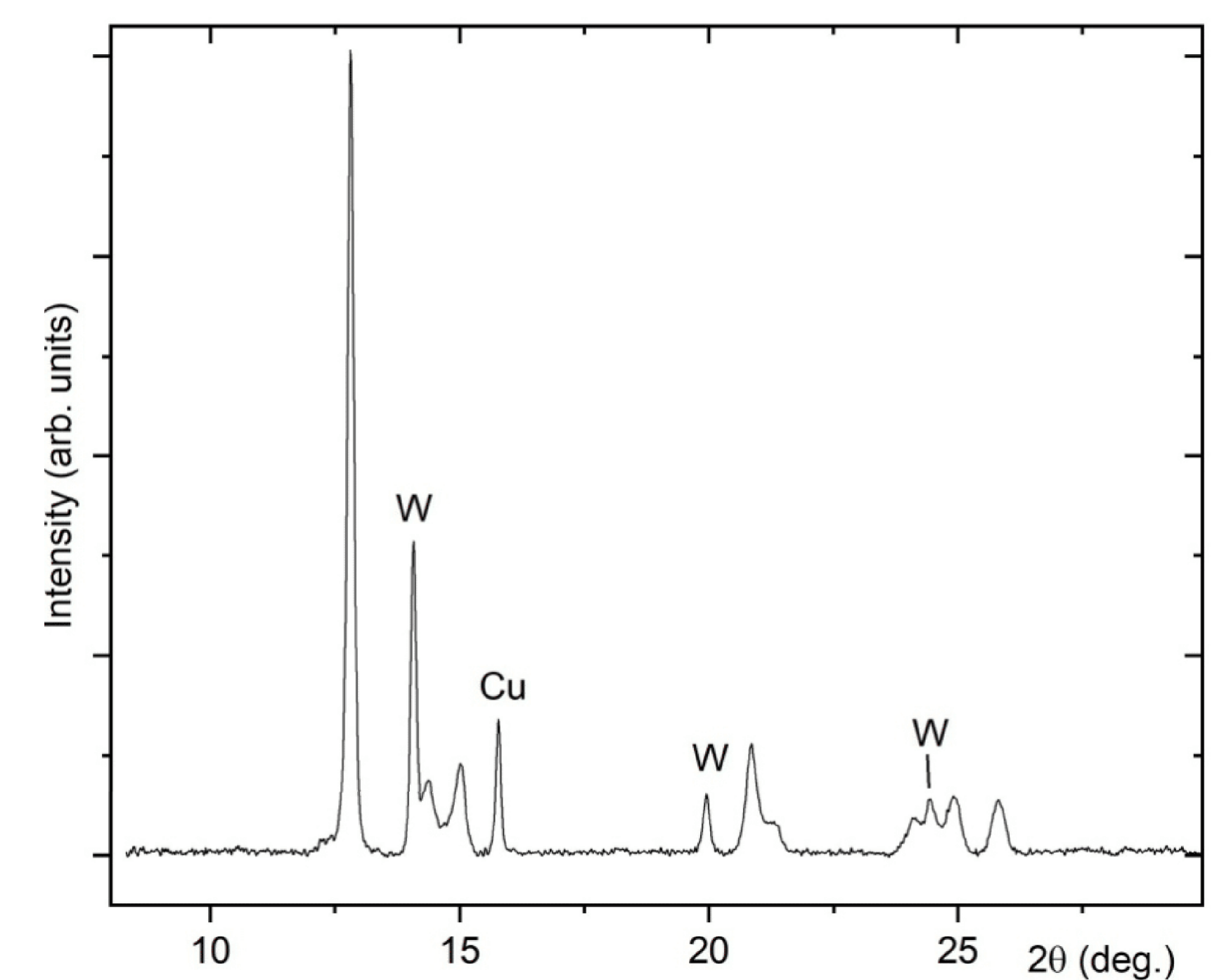


Figure 5: Resulting diffraction profile at 227 GPa with W and Cu peaks labelled. All other peaks are La.

Refining the Post-*cF4* Structure

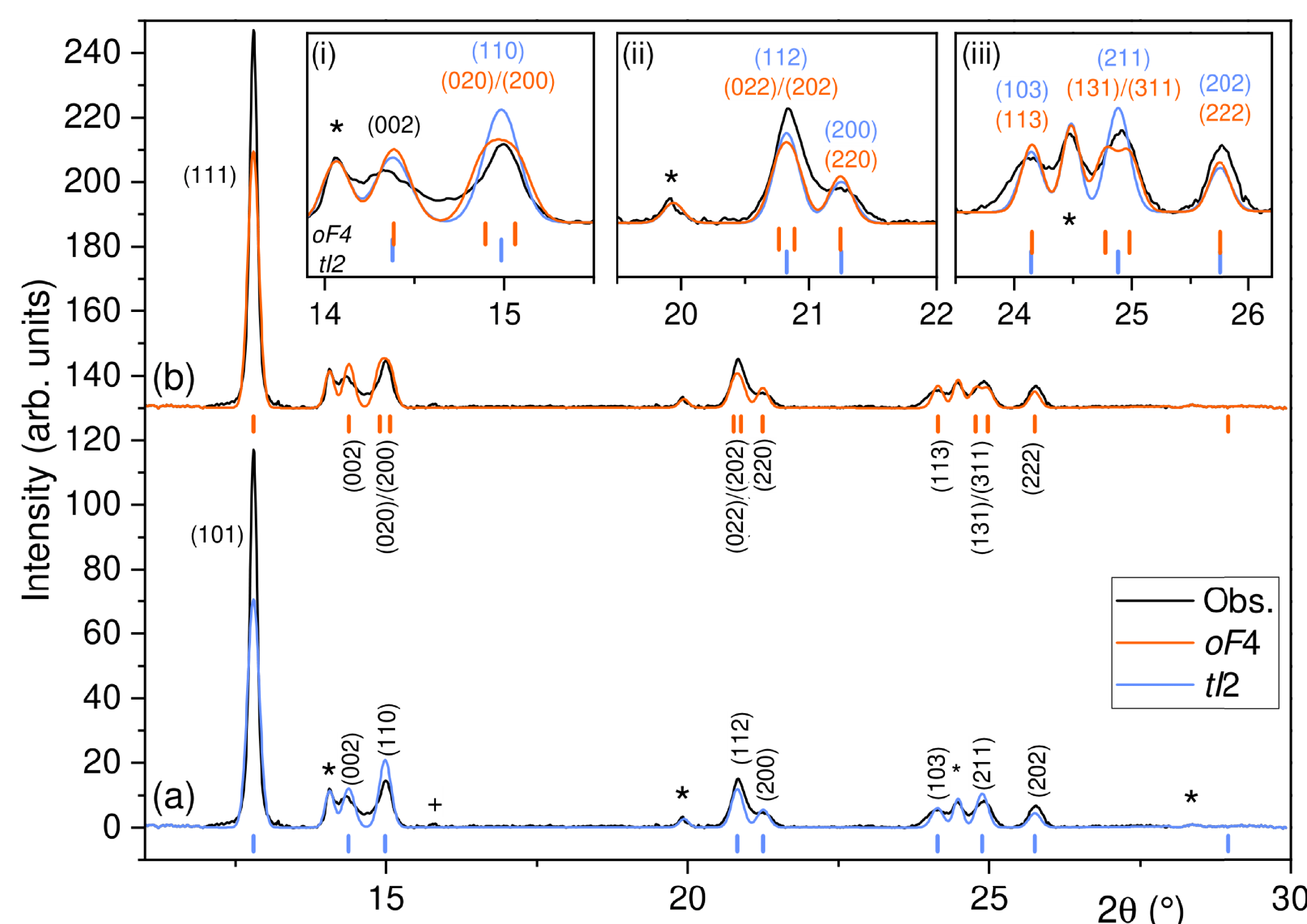
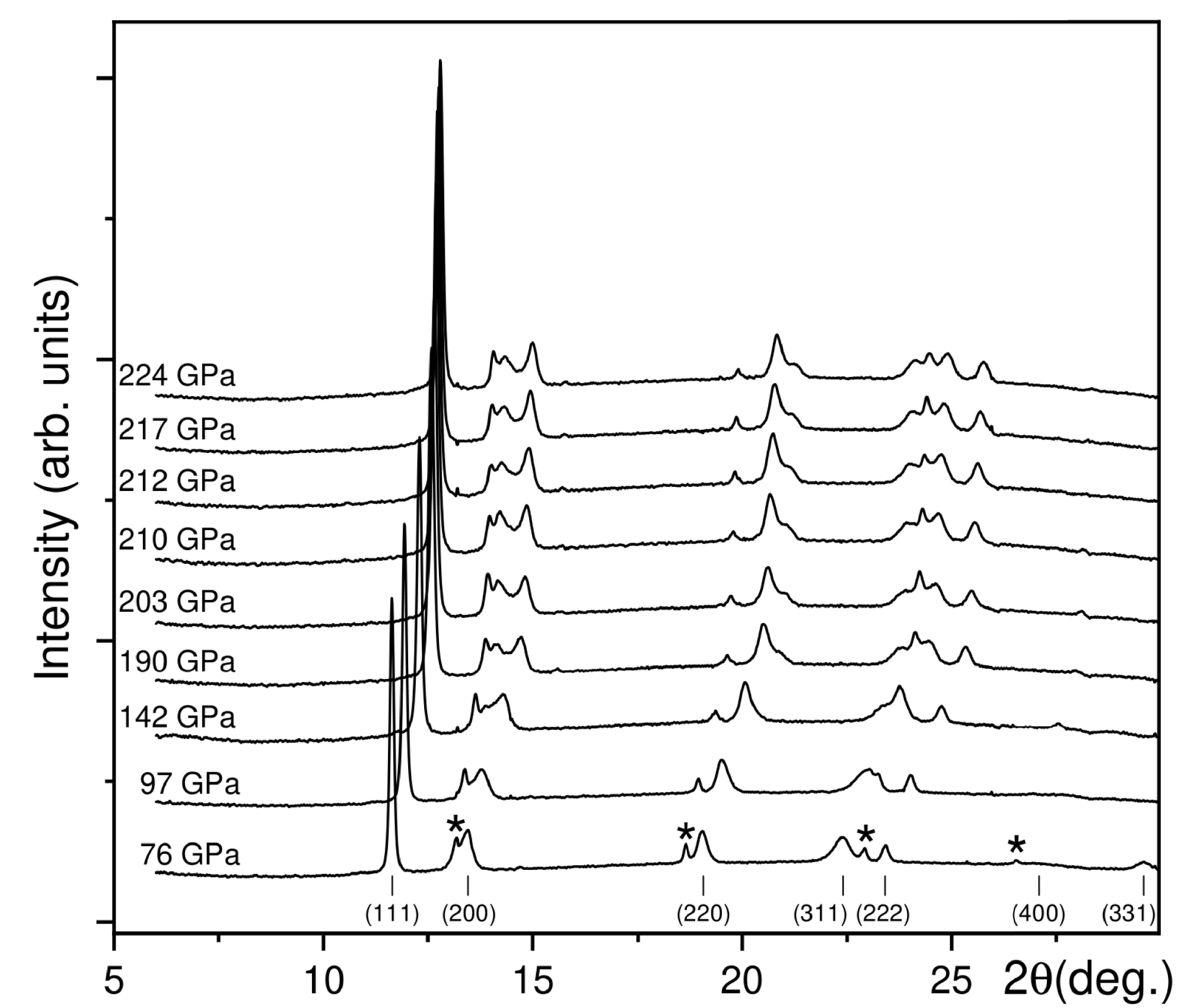


Figure 6: (Left) Diffraction profiles at 224 GPa with Rietveld refinements for *tI2* (blue) and *oF4* (orange) structures. Asterisks indicate peaks from gasket and Cu. Insets show selected peaks from the profile at 80 GPa when the phase transition to *tI2* occurs.

Figure 7: (Right) Diffraction profiles for pressures between 70 and 224 GPa showing the splitting of peaks throughout the phase transition.

Rietveld refinement is an algorithm used to optimise a particular structure to produce a predicted profile matching the observed profile.

Rietveld refinements show that the *tI2* structure explains the diffraction profile better: the peaks at around 15, 21 and 25 degrees are single peaks and not doublets, as they would be for an *oF4* structure.



References

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