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► **To cite this version:**

E. E McBride, A. Krygier, A. Ehnes, E. Galtier, M. Harmand, et al.. Phase transition lowering in dynamically compressed silicon. *Nature Physics*, 2019, 15 (1), pp.89-94. 10.1038/s41567-018-0290-x . insu-02270680

**HAL Id: insu-02270680**

**<https://insu.hal.science/insu-02270680>**

Submitted on 5 Jan 2021

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# Phase Transition Lowering in Dynamically-Compressed Silicon

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19 Silicon, being one of the most abundant elements in nature, attracts wide-ranging scientific and  
 20 technological interest. Specifically, in its elemental form, crystals of remarkable purity can be pro-  
 21 duced. One may assume that this would lead to Si being well understood, and indeed, this is the  
 22 case for many ambient properties, as well as for higher pressure behaviour under quasi-static loading.  
 23 However, despite many decades of study, a detailed understanding of the response of silicon to rapid  
 24 compression such as that experienced under shock impact – remains elusive. Here, we combine a  
 25 novel Free Electron Laser (FEL) based X-ray diffraction geometry with laser-driven compression to  
 26 elucidate the importance of shear generated during shock compression on the occurrence of phase tran-  
 27 sitions. We observe the lowering of the hydrostatic phase boundary in elemental silicon, an ideal model  
 28 system for investigating high-strength materials, analogous to planetary constituents. Moreover, we  
 29 unambiguously determine the onset of melting above 14 GPa, previously ascribed to a solid-solid phase  
 30 transition, undetectable in the now conventional shocked diffraction geometry; transitions to the liquid  
 31 state are expected to be ubiquitous in all systems at sufficiently high pressures and temperatures.

32 Since Bancroft[1] first reported shock-induced polymorphism over fifty years ago, solid-solid and solid-liquid phase  
 33 transitions have been the focus of innumerable shock-compression studies. Velocimetry techniques have been key  
 34 diagnostic tools in the inference of such phase transitions, with plateaus in density interpreted as plastic deformation  
 35 or phase transitions. However, such methods are not able to shed light on the crystallographic phase of material,  
 36 especially since effects, such as kinetics, have the potential to cause significant differences between statically and  
 37 dynamically determined sample response. In this work we focus on the behaviour of elemental silicon (Si), which  
 38 despite being well-understood under hydrostatic conditions, remains a subject of vigorous debate following dynamic  
 39 loading[2–6]. Under uniaxial compression conditions, significant shear is generated as the material resists compression,  
 40 a direct consequence of the material strength, yet the nature of the shear-relieving mechanism (plasticity or via a phase  
 41 transformation), and the structure(s) of the proposed high pressure phases remain largely unknown.

42 More generally, previous works suggest that phase boundaries in rapidly-compressed solids depend strongly on the  
 43 strain-rate of the compression, with a higher strain-rate drive (i.e. shock compression) leading to a higher transition  
 44 pressure[7, 8]. However, it is also suggested that the anisotropic nature of planar shock compression may lead to  
 45 significant shear stresses in samples, which can lead to lowering of phase transition boundaries from hydrostatically  
 46 determined values[9]. This points to the danger in the typical method of assigning phase transitions under shock  
 47 loading to those observed under hydrostatic conditions at similar pressure conditions. Moreover, it means that  
 48 phase transition pressures determined from dynamic compression experiments must be interpreted with care before  
 49 application to hydrostatic systems, such as planetary interiors.

50 As one of the most abundant elements in nature, Si attracts wide-ranging scientific and technological interest, and  
 51 hence many of its properties at ambient conditions, and at higher pressure under quasi-static loading, are well un-  
 52 derstood. Static compression experiments reveal a complex phase diagram, where thirteen different polymorphs have  
 53 been observed to date[10–17]. Of particular relevance to this work is the highly reconstructive phase transformation  
 54 from the ambient pressure semi-conducting cubic diamond (CD) structure to the metallic  $\beta$ -tin structure at  $\sim 12$  GPa,  
 55 with an associated 20% volume collapse[10]. On further increase of pressure, the closely related orthorhombic phase  
 56 *Imma* is formed, which in turn transforms to a simple hexagonal (SH) crystal structure at 16 GPa[11, 13].

57 However, among dynamic-loading experiments, a clear consensus in the data is yet to emerge. Such studies using  
 58 velocimetry measurements report the observation of three distinct waves traversing the sample[3–6]. For example,  
 59 early work by Gust & Royce find waves at 5.4 GPa, 10.1 GPa and 13.7 GPa for compression along the [111] crystal  
 60 direction. Such waves are often interpreted as occurring at the onset pressure of shear dissipation mechanisms, such  
 61 as plasticity i.e. by the generation and motion of defects, or via a phase transformation. These velocimetry data  
 62 are therefore often taken to suggest that the first phase transition occurs at 10 GPa, in broad agreement with the  
 63 hydrostatically determined value of 12 GPa. The second wave emerging at 5.4 GPa is then assigned to plasticity within  
 64 the compressed CD phase. However, positive identification of the mechanisms associated with these waves in silicon  
 65 is still outstanding.

66 Numerous laser-driven compression experiments coupled with traditional laser-plasma X-ray sources have failed to  
 67 find evidence for higher pressure phases in compressed single crystal samples. Molecular dynamics (MD) simulations  
 68 have suggested that this may be due to any new phases forming small (sub-micron), potentially misaligned grains,  
 69 which would lead to highly diffuse diffraction features, difficult to detect in experiments using these conventional  
 70 laser-plasma X-ray sources[18]. The structure of the high pressure phase(s) adopted by Si on the Hugoniot, and the  
 71 nature of the two waves which emerge following the elastic wave, remains unknown, leaving the dynamic behaviour  
 72 of Si a matter of ongoing debate.

73 Here, we present a systematic study of the behaviour of Si following laser-driven shock-compression. Specifically,  
 74 we employ polycrystalline Si samples, and exploit the high brightness X-rays offered by Free Electron Lasers to study  
 75 diffuse reciprocal space features. In doing so, we are able to identify the structural response of the sample from its  
 76 ambient CD phase, through to shock-induced melting at 14 GPa, coinciding with the emergence of the third wave.

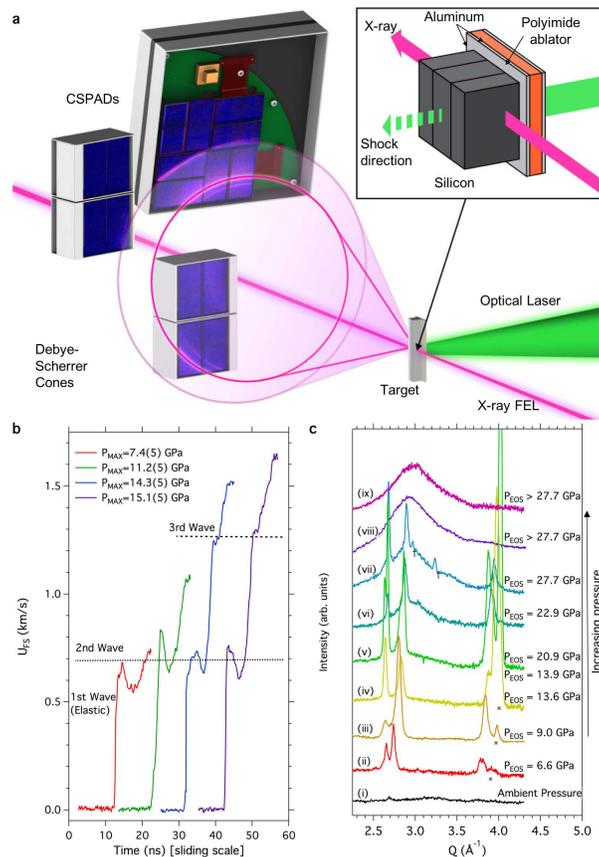


FIG. 1. **Experimental configuration and data examples:** **a** the transverse configuration whereby the compression laser was perpendicular to the X-ray beam. **b** Velocimetry data (VISAR) lineouts showing free surface velocity ( $U_{FS}$ ). Laser intensity increases to the right. Dashed lines indicate the onset of the 2nd and 3rd wave. **c** Azimuthally integrated 1D diffraction patterns as a function of increasing laser intensity and hence increasing pressure in both the transverse: (i), (ii), (iv), (v), (ix) and collinear (iii), (vi), (vii), (viii) configurations. Peaks marked with the \* symbol belong to the compressed cubic diamond phase. Peaks marked with the † symbol cannot be described by the cubic diamond,  $\beta$ -tin,  $Imma$ , or simple hexagonal phases.

77 Crucially, we observe a lowering of two solid-solid phase boundaries from their hydrostatically determined values,  
78 suggesting the significant role that shear stress plays in modifying the phase diagram of Si.

79 Experiments were conducted at the Matter in Extreme Conditions (MEC) endstation at the Linear Coherent  
80 Light Source (LCLS)[19]. Polycrystalline silicon samples, with  $50 \mu\text{m}$  polyimide ablators, were shock compressed  
81 via irradiation with the nanosecond pulsed Nd:glass laser system. During shock transit through the Si sample, the  
82 high brightness LCLS X-ray beam was used to determine the structure of the material via X-ray diffraction in a  
83 Debye-Scherrer geometry. Two distinct experimental geometries were employed in this work. The first is a ‘collinear’  
84 geometry, where the X-ray beam is incident at around  $11^\circ$  to the target normal, and thus to the direction of shock  
85 compression. This is a common geometry at LCLS[20–24], and other laser-plasma based experiments[25–28]. It is  
86 described in Supp. Info. Sec. I.

87 However, this configuration has the distinct disadvantage of providing a signal that integrates through all states  
88 within the sample. This greatly complicates both the detection and the analysis of low-symmetry complex phases on  
89 the Hugoniot, including melting, where multiple high-pressure phases may be present in successive compression waves.  
90 The second ‘transverse’ geometry aims to resolve this shortcoming by driving the shockwave *perpendicular* to the LCLS  
91 beam direction (Fig. 1 (a)). In this configuration, by taking advantage of the highly collimated and microfocused  
92 beam available at the LCLS we ensure that, predominantly, a single wave in the multi-wave compression response is  
93 probed, greatly aiding interpretation and phase identification. Further details of the experimental configurations and  
94 target designs employed are confined to the Methods section and Supp. Info. Secs. I-III. A detailed comparison of  
95 the collinear and transverse configurations is found in the Supp. Info. Sec. VI.

96 Utilising optical velocimetry (VISAR) combined with X-ray diffraction in the collinear configuration, the wave  
97 profile as a function of laser intensity was investigated, and the sample pressure was inferred from the free surface

98 velocity,  $U_{FS}$  (Supp. Info. Sec. IV). An example of typical velocimetry traces may be seen in Fig. 1 (b). The  
 99 wave profiles observed were in good agreement with previous laser and gas-gun based shock experiments[3, 6]. Here,  
 100 consistent with previous studies, we observe the significant elastic response, followed by a pullback and a second wave,  
 101 often ascribed to plastic deformation. Above 14 GPa ( $U_{FS} \sim 1.3$  km/s), we observe a plateau in the velocity-time data  
 102 indicating a change in sound speed in the sample. Following the plateau we observe the emergence of a third wave,  
 103 again consistent with previous studies. The plateau is described as the onset of a structural phase transition. As these  
 104 polycrystalline samples have large grains ( $\sim 100$   $\mu\text{m}$ ) with different orientations, we observe that the magnitude of the  
 105 elastic response differs from shot to shot depending on the starting orientation of the sample – varying from 6.6(5)  
 106 GPa to 7.9(5) GPa (Supp. Info. Fig. 6). This is consistent with the previously-reported orientational dependence  
 107 of the elastic response of single-crystal[4]. We also note that the plateau observed is *independent* of the starting  
 108 orientation, consistent with previous studies[6].

109 Figure 1 (c) shows azimuthally integrated 1D diffraction patterns as a function of increasing laser intensity, and  
 110 hence increasing pressure, in both geometries (see caption). As the initial grain size of the sample is large compared  
 111 to the X-ray beam diameter (10-40  $\mu\text{m}$ ), prior to the shock, we are unlikely to satisfy the Bragg condition due to  
 112 preferred orientation. Therefore the diffraction profile is flat (Fig. 1 (c i)). As laser intensity is increased we observe  
 113 the emergence of sharp peaks, consistent with the formation of a new phase (Fig. 1 (c ii)). Note, in some diffraction  
 114 patterns we also observe reflections belonging to the compressed CD phase (\* symbols), suggesting the generation  
 115 of smaller grains of CD material between domains of the newly formed high pressure phase. An example of the 2D  
 116 diffraction images may be seen in Fig. 1 (a), and in Supp. Info. Fig. 7. Here, the smooth Debye-Scherrer rings  
 117 belong to the high pressure phase, and indicate that the large grains of the initial CD phase have broken up into  
 118 nanometer-sized grains, inferred from the smooth powder rings observed in the 2D diffraction patterns.

119 In the collinear configuration, at a pressure of 7.4(5) GPa, just above the elastic limit, we observe an increase in  
 120 scattering intensity of diffraction features at  $Q \sim 2.7$  and  $Q \sim 3.8$   $\text{\AA}^{-1}$  (Fig. 2 (ii)), but here the structure cannot  
 121 be fully resolved. By using the same laser-drive conditions, in the transverse geometry we can clearly assign these  
 122 features to the  $\beta$ -tin structure, with a  $c/a$  ratio of 0.550, as shown by the diffraction pattern Fig. 2 (iii). A Le Bail fit  
 123 is shown by the dotted black line, and is in excellent agreement with the data [29]. A distinguishing feature used to  
 124 identify the high pressure phases is the evolution of the  $c/a$  ratio as a function of pressure. The  $\beta$ -tin structure has a  
 125  $c/a$  value of 0.550, and the SH a value of 0.533; the  $c/a$  ratio of the *Imma* structure evolves from 0.550 to 0.533 with  
 126 increasing pressure [12] (See Methods). As laser intensity, and hence pressure is increased to 9.0(5) GPa, we observe  
 127 what can be best described as a mixed phase (Fig. 1 (c iii)), consisting of both the  $\beta$ -tin and *Imma* structures. At  
 128 9.4(5) GPa, the high-pressure phase transforms completely to the *Imma* structure (Fig. 1 (c iv)), with no evidence of  
 129 co-existence with  $\beta$ -tin. The *Imma* structure also co-exists with the compressed CD phase. This phase co-existence  
 130 has previously been observed in quasi-hydrostatic diamond anvil cell studies [12, 13].

131 Hence, we observe that, for laser-driven compression, rather than through plastic deformation, the significant shear  
 132 stress at the Hugoniot elastic limit (HEL) is consistent with being relieved via a phase transformation to a mixed phase  
 133 of CD and a high-pressure structure i.e. the dominant shear dissipation mechanism as the material is compressed  
 134 beyond the HEL is a phase transformation. As suggested by Mogni *et al.*[18] in their MD simulations, we observe that  
 135 the second wave is concurrent with transformation to a body-centred tetragonal structure, yet we identify it as the  $\beta$ -  
 136 tin phase, rather than *Imma* as they suggest. Moreover, we note a considerable lowering of the onset of the  $\beta$ -tin phase  
 137 transformation as compared with hydrostatic diamond anvil cell experiments – from 12 GPa in ref. [12] down to as low  
 138 as 5.4(5) GPa in this work. Such an effect has been observed in *ab initio* simulations where it was suggested that the  
 139 transition pressure decreases from 11.4 GPa under hydrostatic conditions to 3.9 GPa under uniaxial compression[30].  
 140 Additionally, in experimental studies combining resistivity measurements with nanoindentation techniques, Gupta &  
 141 Ruoff[31] note that the onset of the metallic phase, interpreted as the onset of the  $\beta$ -tin phase, lowers from 12 GPa  
 142 in under static loading, to 8 GPa under a compression rate of 1 kbar/sec, for compression along the [100] axis. This  
 143 work, therefore, highlights the failure of the long-standing approach of understanding the nature of shock-induced  
 144 phase transformation through comparison with hydrostatic phase transformations occurring at similar pressures.

145 As the *Imma* structure is further compressed, we observe an evolution of the  $c/a$  ratio as a function of normalised  
 146 volume ( $V/V_0$ ), (Fig. 3 (a)) away from the ideal experimental and theoretical  $\beta$ -tin values (0.550 and 0.549) towards  
 147 the ideal SH values (0.535 and 0.533), with the same trend observed in both the collinear and transverse experimental  
 148 configurations[12, 32]. At a  $c/a$  ratio of 0.537, and a corresponding  $V/V_0$  of 0.681, we note a distinct change in the  
 149 gradient of the  $c/a$  ratio, indicating a change in compressibility of the structure. This change occurs at a pressure  
 150 inferred via VISAR of 13.8(5) GPa, coinciding with the emergence of the third wave discussed above. One should note  
 151 that in our data obtained in the collinear configuration, we do not observe any additional scattering in the diffraction  
 152 patterns, that would be indicative of the formation of a second new phase, and hence account for such a change in  
 153 compressibility (Fig. 3 (b)).

154 Owing to the unique ability that we are afforded by the transverse configuration, we are able to isolate each of the  
 155 different waves as they traverse the sample following shock compression. We are therefore able to determine that the

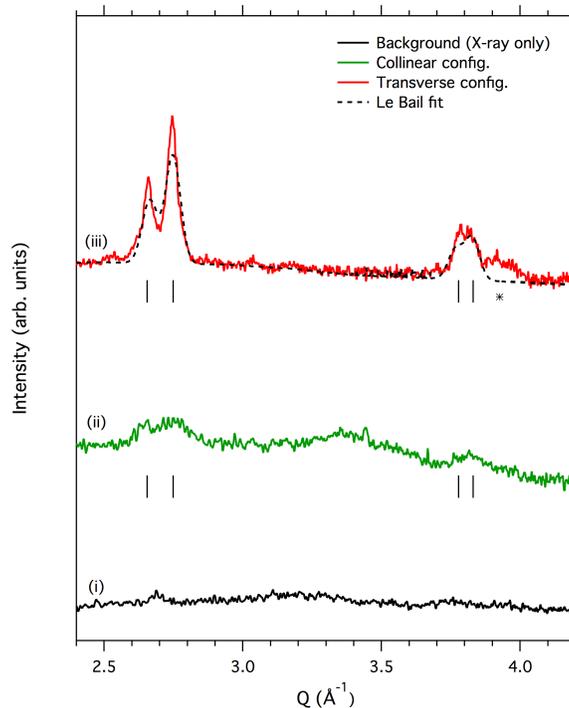


FIG. 2. **The greater sensitivity of the transverse configuration** 1D diffraction profiles in the collinear (ii) and transverse (iii) configurations. Profile (i) shows X-ray only pre-shot. The dotted black line under profile (iii) is a Le Bail fit to the  $\beta$ -tin structure. The tick marks underneath diffraction profiles (ii) and (iii) indicate the position of the first four  $\beta$ -tin reflections. The \* symbol indicates reflections belonging to the compressed cubic diamond phase.

156 change in  $c/a$  ratio coincides with the emergence of a broad diffuse feature, characteristic of a liquid or amorphous  
 157 sample, in coexistence with the solid (Fig 3 (b) and Fig. 1 (c v)). Moreover, we note that both the shape and position  
 158 of the broad diffuse peak are in good agreement with that of liquid silicon at 14 GPa (Fig. 3 (c)), as determined  
 159 through static compression techniques combined with synchrotron X-ray diffraction[33]. Notably, we do not observe  
 160 the second strong broad diffraction peak at  $Q \sim 3.6 \text{ \AA}^{-1}$  characteristic of the high-density amorphous polymorph at  
 161  $P \sim 13 \text{ GPa}$ , and therefore conclude that the diffuse scattering is most consistent with the liquid state (Supp. Info.  
 162 Fig. 9).[34] The third wave, rather than being due to a solid-solid phase transition as previously reported, is therefore  
 163 attributed to shock-induced melting along the Hugoniot.

164 In comparing diffraction from both configurations, we note that in the collinear configuration we are overwhelmed  
 165 by the solid Bragg diffraction and insensitive to the presence of liquid diffraction until we have incubated a significant  
 166 fraction of the liquid phase (Supp. Info. Fig. 13). Moreover, in the collinear configuration, the amount of volumetric  
 167 compression as determined from the diffraction patterns is directly related to the timing of the X-rays with respect  
 168 to the supported shock (Supp. Info Fig. 12). It is clear from Fig. 3 (b) that, in the collinear geometry, depending on  
 169 the timing of the X-rays, we are sensitive to different parts of the wave profile, i.e. to different volumes (and hence  
 170 pressures), and insensitive to the onset of melting on the Hugoniot.

171 As pressure is increased, the solid  $Imma$  phase transforms to the SH phase, and the diffuse feature grows more  
 172 intense, as a larger volume fraction of the sample is now in the liquid state (Fig. 1 (c vi)). Due to the significant latent  
 173 heat of fusion of Si, the second highest of the elements, we observe that the Hugoniot follows the melting curve over  
 174 a considerable pressure range, as indicated by solid-liquid co-existence up to at least a  $V/V_0$  of 0.632 ( $P \sim 27 \text{ GPa}$ )  
 175 as shown in Fig. 1 (c vii). Above 27 GPa, the sample is able to overcome the latent heat of fusion and melts entirely  
 176 (Fig. 1 (c viii & ix)). Such a plateau of the Hugoniot along the melting line, and two-phase coexistence, has been  
 177 previously reported in laser-driven shock compression studies of diamond[35]. In contrast to recent shock-recovery  
 178 and MD studies on Si, at similar maximum pressures of 30 GPa, which suggest the formation of localised amorphous  
 179 banding[36, 37], we observe the occurrence of bulk, or complete, melting of the sample. Hence, we conclude that the  
 180 formation of bands of amorphous and CD Si is formed on release to ambient pressure following shock compression,  
 181 demonstrating the importance of *in situ* measurements.

182 In their recent work combining a gas-gun pressure driver and synchrotron X-ray diffraction, Turneaure *et al.* [38]  
 183 report that at  $P \sim 19 \text{ GPa}$ , above the onset of the third wave, Si adopts the SH structure. However, unlike our work,

184 they find no evidence of melting in their diffraction data. In their study, the sample was initially shock-compressed  
 185 to a peak pressure of 26 GPa, and only conclusively identified transforming to the SH structure after at least one  
 186 reflection of the phase transformation wave had passed back through the silicon, releasing pressure. Hence they were  
 187 probing an off-Hugoniot, and rather complex, hydrodynamic state.

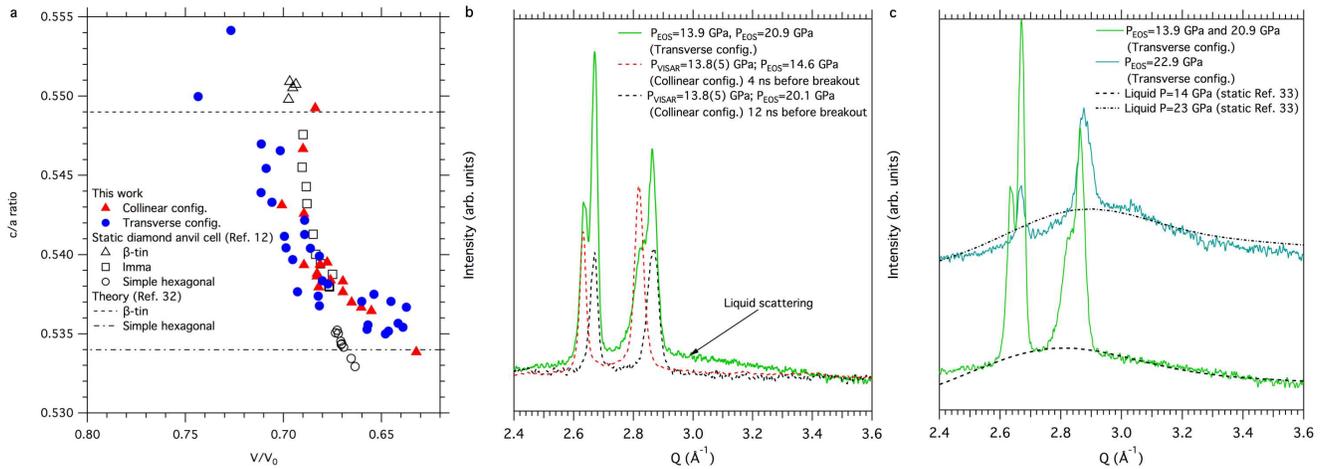


FIG. 3. **Evidence of the onset of melting:** **a** Evolution of the  $c/a$  ratio as a function of volumetric change ( $V/V_0$ ) in the collinear (blue circles) and transverse (red triangles) configurations. Open symbols are from a hydrostatic diamond anvil cell study Ref. 12:  $\beta$ -tin (triangles),  $Imma$  (squares), simple hexagonal (circles). Theoretical ideal  $c/a$  ratios from Ref. 32 are shown for  $\beta$ -tin (dashed line) and the simple hexagonal (dot-dashed line). **b** Comparison of azimuthally integrated 1D diffraction patterns in the collinear and transverse configurations. In the transverse configuration we are more sensitive to the onset of melting, as indicated by the emergence of a broad diffuse peak characteristic of a liquid phase. **c** 1D diffraction patterns in the transverse configuration showing a significant region of solid-liquid co-existence on the Hugoniot. The emergence of the broad diffuse peak at  $\sim 14$  GPa is in good agreement with both the position and shape of the liquid peak as determined by static compression experiments, Ref. 33.

188 Moreover, the lack of liquid signal in their diffraction data is likely due to the transmission (collinear configuration)  
 189 geometry employed in their experiment. As we have demonstrated, in the oft used collinear geometry one is unable  
 190 to resolve the various components of a complex, multi-wave shock structure, and specifically one is insensitive to the  
 191 incubation of melting along the Hugoniot, particularly where there are regions of solid-liquid coexistence. By using the  
 192 novel transverse approach, collecting diffraction patterns perpendicular to the shock propagation direction, we have  
 193 much greater sensitivity to the onset of low-symmetry phase transitions and melting along the Hugoniot, expected in  
 194 all systems at sufficiently high pressures and temperatures.

195 The stress-volume plot shown in Fig. 4 compares the relative volume ( $V/V_0$ ) of the high-pressure phases from this  
 196 work with recent density functional theory calculations[39], and with static diamond anvil cell work.[12] We clearly  
 197 observe the occurrence of a shear-relieving solid-solid transition concurrent with the HEL, and the observation of the  
 198 high-pressure phases at considerably lower pressures than previously reported, below the stability field of the static  
 199 phases. It should also be noted that the additional reflections marked with the  $\dagger$  symbol in diffraction profiles Fig. 1  
 200 (c vii) cannot be accounted for by any of the candidate structures observed statically up to 30 GPa – the CD,  $\beta$ -tin,  
 201  $Imma$  or SH structure described in this manuscript. These diffraction peaks suggest that prior to melting entirely, we  
 202 may reach a mixed phase region between the liquid, the SH phase, and an additional solid phase. A likely candidate  
 203 is the  $Cmca$  structure, which has been reported to co-exist with the SH phase at room temperature at close to 30  
 204 GPa[15]. However, with the observation of only a few weak reflections it is impossible to provide a full structural  
 205 solution to conclusively determine from which structure these additional peaks arise.

206 In conclusion, we have determined the nature of the multiple waves that traverse silicon samples following shock  
 207 compression. We show that the second wave is concurrent with a phase transition to a  $\beta$ -tin structure, rather than  
 208 due to plasticity. We further determine that the third wave observed above  $P \sim 14$  GPa is due to the onset of melting  
 209 along the Hugoniot, rather than due to a solid-solid transition as was previously reported. We observe that the solid  
 210 and liquid co-exist over a significant pressure range of  $\Delta P \sim 10$  GPa, before enough energy is supplied to overcome  
 211 the significant latent heat of fusion of silicon where the sample melts entirely, as indicated by the observation of only  
 212 the broad diffuse scattering at the highest pressure achieved, 30 GPa. We demonstrate that the now conventional  
 213 X-ray diffraction geometry for probing shock-compressed matter is insensitive to the onset of melting, expected in all  
 214 systems at extreme conditions.

215 Crucially, we demonstrate a shock-induced lowering of the onset of phase transitions, and thus modification of the

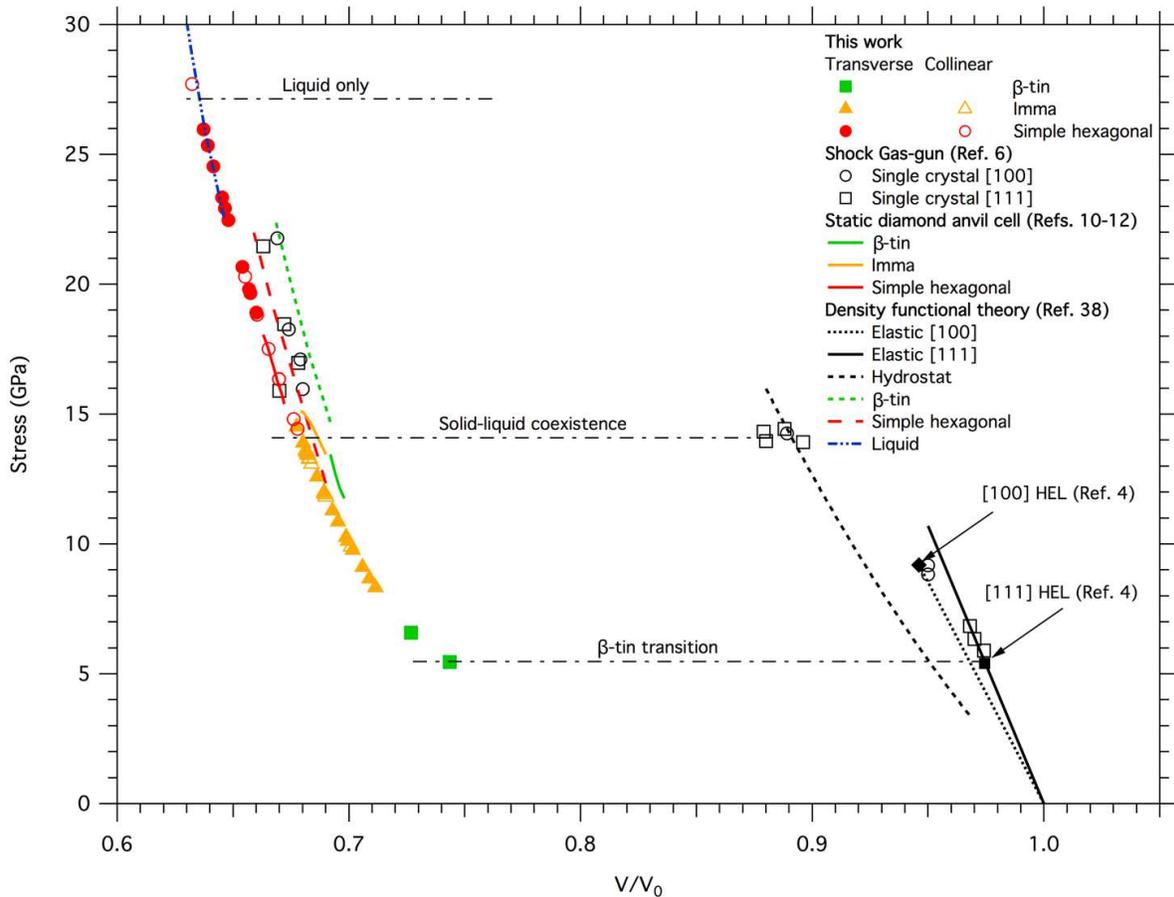


FIG. 4. **Dynamic shear-lowering of phase transition boundaries:** Stress-Volume plot of data obtained in this study, compared with density functional theory calculations (Ref. 39) and static diamond anvil cell experiments (Refs. 10-12). Hugoniot Elastic Limits for the [100] and [111] directions are from Ref. 4. Horizontal dot-dashed lines indicate phase transition boundaries from this study.

216 phase diagram away from that which would be determined utilising a diamond anvil cell-based (quasi-hydrostatic)  
 217 approach. Here, we find the lowering of two subsequent solid-solid phase transitions:  $CD \rightarrow \beta\text{-tin} \rightarrow Imma$ , illustrating  
 218 that shock-compression experiments can have a profound impact on hydrostatic phase boundaries. Previous shock-  
 219 compression studies suggest that high strain-rates may cause phase transition boundaries to be shifted upwards in  
 220 pressure, relative to their static boundaries[7, 8]. Clearly, the influence of shock-induced shear and strain-rate on the  
 221 occurrence of phase transitions is non-trivial, and will have a significant impact when employing dynamic compression  
 222 techniques to explore high pressure phases of materials found in planetary interiors, where conditions are largely  
 223 hydrostatic and strain-rates are very low. In particular, careful attention will need to be paid when investigating  
 224 non-metallic systems, the dominant constituents of planetary interiors, which typically exhibit higher strength, and  
 225 may thus be more susceptible to the effects of shear-induced phase boundary modification.

226

## I. ACKNOWLEDGEMENTS

227 E.E.M and A.S. acknowledge funding from the Volkswagen Foundation. J.S.W. is grateful for support from EPSRC  
 228 under grant EP/J017256/1. This work is supported by the French Agence Nationale de la Recherche (ANR) with  
 229 the ANR IRONFEL 12-PDOC-0011 Use of the Linac Coherent Light Source (LCLS), SLAC National Accelerator  
 230 Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under  
 231 Contract No. DE-AC02-76SF00515. The MEC instrument is supported by the U.S. Department of Energy, Office of  
 232 Science, Office of Fusion Energy Sciences under contract No. SF00515. The authors thank J. B. Hastings and L. B.  
 233 Fletcher for a critical review of the manuscript.

## II. AUTHOR CONTRIBUTIONS

235 E.E.M., A.H., and A.N. designed the experiment, and E.E.M., A.H., D.S. and C.S. designed the targets, and C.S.  
 236 manufactured the targets. E.E.M., A.K., M.H., E.G., Z.K., H.-J.L., B.N., A.P., M.R., A.S., C.S., F.T., S.T., T.T. and  
 237 A.H. contributed to the setup of the experiment and data collection. E.E.M. analysed the data, with assistance from  
 238 A.K., M.H., R.F.S. and A.H.. E.E.M. and A.H. interpreted the data. E.E.M., A.H. and J.S.W. wrote the manuscript.  
 239 All authors commented critically on the manuscript.

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- 240 [1] Bancroft, D., Peterson, E. L. & Minshall, S., Polymorphism of iron at high pressure. *J. Appl. Phys.* **27**, 291-298 (1956)  
 241 [2] Colburn N. L., Forbes, J. W. & Jones, H. D., Electrical measurements in silicon under shock-wave compression. *J. Appl.*  
 242 *Phys.* **43**, 5007-5012 (1972)  
 243 [3] Smith, R. F., Minich, R. W., Rudd, R. E., Eggert, J. H., Bolme, C. A., *et al.*, Orientation and rate dependence in high  
 244 strain-rate compression of single-crystal silicon. *Phys. Rev. B*, **86**, 245204 (2012)  
 245 [4] Gust W. H. & Royce, E. B., Axial yield strengths and two successive phase transition stresses for crystalline silicon. *J.*  
 246 *Appl. Phys.* **42**, 1897-1905 (1971)  
 247 [5] Goto, T., Sato, T. & Syono, Y., Reduction of shear strength and phase-transition in shock-loaded silicon. *Jpn. J. Appl.*  
 248 *Phys.* **21**, L369-L371 (1982)  
 249 [6] Turneaure, S. J., & Gupta, Y. M., Inelastic deformation and phase transformation of shock compressed silicon single  
 250 crystals. *Appl. Phys. Lett.* **91**, 201913 (2007)  
 251 [7] Smith, R. F., Eggert, J. H., Saculla, M. D., Jankowski, A. F., Bastea, M., *et al.*, Ultrafast dynamic compression technique  
 252 to study the kinetics of phase transformations in bismuth. *Phys. Rev. Lett.* **101**, 065701 (2008)  
 253 [8] Smith, R. F., Eggert, J. H., Swift, D. C., Wang, J., Duffy, T. S., *et al.*, Time-dependence of the alpha to epsilon phase  
 254 transformation in iron. *J. Appl. Phys.* **114**, 223507 (2013)  
 255 [9] Higginbotham, A., Stubley, P. G., Comley, A. J., Eggert, J. H., Foster, J. M., *et al.*, Inelastic response of silicon to shock  
 256 compression. *Sci. Rep.* **6**, 24211 (2016)  
 257 [10] Jamieson, J. C., Crystal structures at high pressures of metallic modifications of silicon and germanium, *Science* **139**,  
 258 762-764 (1963)  
 259 [11] McMahan, M. I. & Nelmes R. J., New high-pressure phase of Si. *Phys. Rev. B* **47**, 8337-8340 (1993)  
 260 [12] McMahan, M. I., Nelmes, R. J., Wright, N. G. & Allan, D. R., Pressure dependence of the Imma phase of silicon. *Phys.*  
 261 *Rev. B* **50**, 739-743 (1994)  
 262 [13] Olijnyk, H., Sikka, S. K. & Holzapfel, W. B., Structural phase transitions in Si and Ge under pressures up to 50 GPa.  
 263 *Phys. Lett. A* **103**, 137-140 (1984)  
 264 [14] Duclos, S. J., Vohra, Y. K. & Ruoff, A. L., hcp-to-fcc transition in silicon at 78 GPa and studies to 100 GPa. *Phys. Rev.*  
 265 *Lett.* **58**, 775-777 (1987)  
 266 [15] Hanfland, M., Schwarz, U., Syassen, K. & Takemura, K., Crystal Structure of the High-Pressure Phase Silicon VI. *Phys.*  
 267 *Rev. Lett.* **82**, 1197-1200 (1999)  
 268 [16] Wentorf, R. H., & Kasper, J. S., Two new forms of silicon. *Science* **139**, 338-339 (1963)  
 269 [17] Piltz, R. O., Maclean, J. R., Clark, S. J., Ackland, G. J., Hatton, P. D., *et al.*, Structure and properties of silicon XII: A  
 270 complex tetrahedrally bonded phase. *Phys. Rev. B* **52**, 4072-4085 (1995)  
 271 [18] Mogni, G., Higginbotham, A., Gaál-Nagy, K., Park, N. & Wark, J. S., Molecular dynamics simulations of shock-compressed  
 272 single-crystal silicon, *Phys. Rev. B* **89**, 064104 (2014)  
 273 [19] Nagler, B., Arnold, B., Bouchard, G., Boyce, R. F., Boyce, R. M., Callen, *et al.*, The Matter in Extreme Conditions  
 274 instrument at the Linac Coherent Light Source. *J. Synchrotron Radiat.* **22**, 520-525 (2015)  
 275 [20] Fletcher, L. B., Lee, H. J., Döppner, T., Galtier, E., Nagler, B., *et al.*, Ultrabright X-ray laser scattering for dynamic warm  
 276 dense matter physics. *Nature Photon.* **9**, 274-279 (2015)  
 277 [21] Gorman, M. G., Briggs, R., McBride, E. E., Higginbotham, A., Arnold, B., *et al.*, Direct observation of melting in  
 278 shock-compressed bismuth with femtosecond X-ray diffraction. *Phys. Rev. Lett.* **115**, 095701 (2015)  
 279 [22] Gleason, A. E., Bolme, C. A., Lee, H. J., Nagler, B., Galtier, E., *et al.*, Ultrafast visualization of crystallization and grain  
 280 growth in shock-compressed SiO<sub>2</sub>. *Nature Comms.* **6**, 8191 (2015)  
 281 [23] Harmand, M., Ravasio, A., Mazevet, S., Bouchet, J., Denoëud, A., *et al.*, X-ray absorption spectroscopy of iron at  
 282 multimegabar pressures in laser shock experiments. *Phys. Rev. B* **92**, 024108 (2015)  
 283 [24] Kraus, D., Ravasio, A., Gauthier, M., Gericke, D. O., Vorberger, J., *et al.*, Nanosecond formation of diamond and ionsdaleite  
 284 by shock compression of graphite. *Nature Comms.* **7**, 10970 (2016)  
 285 [25] Rygg, J. R., Eggert, J. H., Lazicki, A. E., Coppari, F., Hawreliak, J. A., *et al.*, Powder diffraction from solids in the  
 286 terapascal regime. *Rev. Sci. Inst.* **83**, 113904 (2012)  
 287 [26] Coppari, F., Smith, R. F., Eggert, J. H., Wang, J., Rygg, J. R., *et al.*, Experimental evidence for a phase transition in  
 288 magnesium oxide at exoplanet pressures. *Nature Geo.* **6** 926-929 (2013)  
 289 [27] Lazicki, A., Rygg, J. R., Coppari, F., Smith, R., Fratanduono, D., *et al.*, X-ray diffraction of solid tin to 1.2 TPa. *Phys.*  
 290 *Rev. Lett.* **115**, 075502 (2015)

- 291 [28] Wang, J., Coppari, F., Smith, R. F., Eggert, J. H., Lazicki, A. E., *et al.*, X-ray diffraction of molybdenum under shock  
292 compression to 450 GPa. *Phys. Rev. B* **92**, 174114 (2015)
- 293 [29] Le Bail, A. L., Whole powder pattern decomposition methods and applications: A retrospection. *Powder Diffraction* **20**,  
294 316-326 (2005)
- 295 [30] Cheng, C., Huang, W. H. & Li, H. J., Thermodynamics of uniaxial phase transition: Ab initio study of the diamond-to- $\beta$ -tin  
296 transition in Si and Ge. *Phys. Rev. B* **63**, 153202 (2001)
- 297 [31] Gupta, M. C. & Ruoff, A. L., Static compression of silicon in the [100] and in the [111] directions. *J. Appl. Phys.* **51**,  
298 1072-1075 (1980)
- 299 [32] Lewis, S. P. & Cohen, M. L., Theoretical study of high-pressure orthorhombic silicon. *Phys. Rev. B* **48**, 16144-16147 (1993)
- 300 [33] Funamori, N. & Tsuji, K., Pressure-induced structural changes of liquid silicon. *Phys. Rev. Lett.* **88**, 255508 (2002)
- 301 [34] Daisenberger, D., Wilson, M., McMillan, P. F., Quesada Cabrera, R., Wilding, M. C., *et al.*, High-pressure x-ray scattering  
302 and computer simulation studies of density-induced polyamorphism in silicon. *Phys. Rev. B* **75**, 224118 (2007)
- 303 [35] Eggert, J. H., Hicks, D. G., Celliers, P. M., Bradley, D. K., McWilliams, R. S., *et al.*, Melting temperature of diamond at  
304 ultrahigh pressure. *Nature. Phys.* **6**, 40-43 (2010)
- 305 [36] Hahn, E. N., Zhao, S., Bringa, E. M. & Meyers, M. A., Supersonic dislocation bursts in silicon. *Scientific Reports* **6**, 26977  
306 (2016)
- 307 [37] Zhao, S., Kad, B., Hahn, E. N., Remington, B. A., Wehrenberg, C. E., *et al.*, Pressure and shear-induced amorphization  
308 of silicon. *Extreme Mechanics Letters* **5**, 74 (2015)
- 309 [38] Turneaure, S. J., Sinclair, N. & Gupta, Y. M., Real-time examination of atomistic mechanisms during shock-induced  
310 structural transformation in silicon. *Phys. Rev. Lett.* **117**, 045502 (2016)
- 311 [39] Strickson, O. & Artacho, E., Ab initio calculation of the shock Hugoniot of bulk silicon. *Phys. Rev. B* **93**, 094107 (2016)
- 312 [40] Dixit, S. N., Lawson, J. K., Manes, K. R. & Powell, H. T., Kinoform phase plates for focal plane irradiance profile control.  
313 *Optics Letters* **19**, 417-419 (1994)

### 314 III. METHODS

#### 315 Experimental Configuration

316 Experiments were conducted at the Matter in Extreme Conditions (MEC) end station at the Linear Coherent Light  
317 Source (LCLS) at SLAC National Accelerator Laboratory. Polycrystalline silicon samples were shock compressed via  
318 irradiation with both arms of the nanosecond pulsed Nd:glass laser system. The incident laser light was frequency  
319 doubled to 527 nm, and a 20 ns temporally square pulse was combined with phase plate optics producing a spatially-  
320 smoothed 250  $\mu\text{m}$  spot size on target,[40] to achieve laser intensities on target in the range  $2 \times 10^{10}$ - $2 \times 10^{11}$  W/cm<sup>2</sup>.  
321 Two experimental geometries were employed in this work: (1) A ‘collinear’ geometry (Supp. Info. Sec I), where the  
322 X-ray beam is incident at 11° to the target normal, and thus along the direction of shock compression, and, (2) A  
323 transverse geometry, whereby the laser beam, and hence direction of shock compression was perpendicular to the  
324 X-ray direction (Fig. 1 (a)). In both configurations, the X-ray pulse length was approximately 80 fs, and the jitter  
325 between the optical drive laser and the X-ray beam was no more than 20 ps[19].

#### 326 (1) Collinear Configuration

327 In this configuration, velocimetry from the sample rear surface was recorded via optical velocimetry (VISAR)  
328 simultaneous with X-ray diffraction. The X-ray wavelength was 1.3051(2) Å. The beam was focussed to 40  $\mu\text{m}$ , and  
329 centred on the 250  $\mu\text{m}$  laser drive spot. In this configuration, X-rays were timed at 18 ns, 2 ns before the 20 ns laser  
330 pulse was turned off. This was to probe the maximum amount of material during a pressure-supported shock wave,  
331 before the falling edge of the laser pulse caused pressure to reduce. The rising edge of the pulse was measured to be 0.9  
332 ns, and the falling edge was measured to be 2.1 ns. The same laser pulse shape was used in the transverse configuration.  
333

#### 334 (2) Transverse Configuration

335 The X-ray wavelength was 1.3007(5) Å and X-ray beam was focussed to 10  $\mu\text{m}$ , and placed a distance of 50  $\mu\text{m}$  into  
336 the silicon sample i.e. 50  $\mu\text{m}$  from the ablator-silicon interface. This ensured that that the waves within the sample  
337 had separated out sufficiently to discriminate each individual wave, yet was close enough to the origin of the shock  
338 wave to ensure that wave reverberations and release from the target edges did not play a significant role. For the  
339 lowest pressures reported here, the Si targets were ablated directly. The X-ray beam was then placed 50  $\mu\text{m}$  from the  
340 drive surface. The phase plates were defocussed by 2 mm to a spot size of 380  $\mu\text{m}$  so that the entire target package is  
341 shock-compressed, maximising the amount of material in the shocked state. However, to reach the highest pressures,  
342 the 250  $\mu\text{m}$  spot at best focus was used. Images of the laser spot, and VISAR planarity shots are found in the Supp.  
343 Info. Here, the position of the X-ray beam was placed at the same position – 50  $\mu\text{m}$  – and the timing of the X-rays rel-  
344 ative to the drive laser was varied between 14 ns and 18 ns to capture the different multiple waves traversing the target.  
345

## 347 Target Design

348 Where specified, the polyimide ablaters had a 100 nm coating of aluminium on both the drive surface to prevent  
 349 tamped ablation. The polycrystalline silicon was quasi-single crystal in nature with grain sizes of order 100  $\mu\text{m}$ .  
 351 Hence, it was significantly larger than the X-ray beam in both configurations.

352 In the collinear configuration, targets consisted of the polyimide ablator, bonded to polycrystalline silicon, 125  $\mu\text{m}$   
 353 thick in the X-ray and shock direction. Perpendicular to the shock/X-ray direction, the samples were 3 $\times$ 3 mm squares,  
 354 significantly larger than the laser drive spot, hence limiting edge rarefaction effects at the silicon-vacuum interface.  
 355 In the transverse configuration, 125  $\mu\text{m}$  of polycrystalline silicon was sandwiched between two 100  $\mu\text{m}$  thick silicon  
 356 single crystals ([001] orientation), to provide good impedance matching and hence reduce complex wave interactions  
 357 between the silicon-vacuum interface at the target edge (perpendicular to the shock direction). The polyimide ablator  
 358 was bonded across all three layers of the target. Additional target information may be found in Supp. Info. Sec. II.

359 The transverse targets were characterised during laser-only beamtime with the VISAR diagnostic. Supp. Info. Fig.  
 360 10 a shows VISAR traces from the collinear and transverse configuration targets under identical laser conditions.  
 361 For a thickness of 100  $\mu\text{m}$ , there is no evidence of complex wave reverberations, and similar pressure conditions were  
 362 achieved with both targets, demonstrating that at a thickness of 50  $\mu\text{m}$  where we probed with the X-ray beam, one  
 363 would not expect reverberations to be significant. Similarly, Supp. Info. Fig. 10 b compares diffraction from the  
 364 collinear and transverse configurations, with no evidence of peak broadening, and hence pressure gradients, in the  
 365 sample.

## 366 Diffraction Analysis and Interpretation

367 In our assignment of the high-pressure phases observed we consider that the  $\beta$ -tin, *Imma*, and simple hexagonal  
 368 phases may all be described through a common orthorhombic cell, in which the  $\beta$ -tin and simple hexagonal phases  
 369 are special cases of the *Imma* structure, where  $a \neq b \neq c$ . Here, we consider space group 74, with atoms occupying  
 370 the 4(*e*) Wykoff positions. Using the non-standard setting where the origin is shifted to (0, -1/4, - $\Delta/2$ ), one may  
 371 consider the  $\beta$ -tin structure when  $a = b \neq c$ , and  $\Delta=0.25$ . When  $a \neq b \neq c$ ,  $b/c = \sqrt{3}$ , and  $\Delta = 0.50$ , one obtains the  
 372 simple hexagonal structure. For the intermediate *Imma* phase,  $a \neq b \neq c$ , and the atomic co-ordinate  $\Delta$  has a value  
 373 intermediate between 0.25 and 0.50. The *Imma* phase becomes the  $\beta$ -tin structure when  $a = b \neq c$ . When  $a \neq b \neq c$ ,  
 374  $b/c = \sqrt{3}$ , one obtains the simple hexagonal structure. For the intermediate *Imma* phase,  $a \neq b \neq c$ . All diffraction  
 375 patterns discussed here were analysed both using the Le Bail method,[29] and through least-squares fitting to the  
 376 observed *d*-spacings.

377 **Data Availability** The data that support the plots within this paper and other findings of this study are available  
 378 from the corresponding author upon reasonable request  
 379