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Phase Transition Lowering in Dynamically-Compressed Silicon

E. E. McBride^{1,*†}, A. Krygier², A. Ehnes¹, E. Galtier³, M. Harmand², Z. Konôpková¹, H. J. Lee³,
H.-P. Liermann¹, B. Nagler³, A. Pelka⁴, M. Rödel⁴, A. Schropp¹, R. F. Smith⁵, C. Spindloe⁶,
D. Swift⁵, F. Tavella³, S. Toleikis¹, T. Tschentscher⁷, J. S. Wark⁸, and A. Higginbotham⁹

¹*Photon Science, Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, D-22607, Hamburg, Germany*

²*IMPMC, UPMC, MNHN, IRD, Paris, France*

³*SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA*

⁴*Helmholtz-Zentrum Dresden-Rossendorf, P.O. Box 510119, D-01314 Dresden, Germany*

⁵*Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, California 94550, USA*

⁶*Central Laser Facility, STFC, Rutherford Appleton Laboratory,
Harwell Oxford, Didcot, OX11 0QX, United Kingdom*

⁷*European XFEL GmbH, Holzkoppel 4, D-22869 Schenefeld, Germany*

⁸*Department of Physics, Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, UK*

⁹*York Plasma Institute, Department of Physics, University of York, York, YO10 5DD, UK*

**emcbride@slac.stanford.edu*

*† Present address: SLAC National Accelerator Laboratory,
2575 Sand Hill Road, Menlo Park, California 94025, USA and*

‡ European XFEL GmbH, Albert-Einstein-Ring 19, D-22761 Hamburg, Germany

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 β -tin structure at ~ 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.

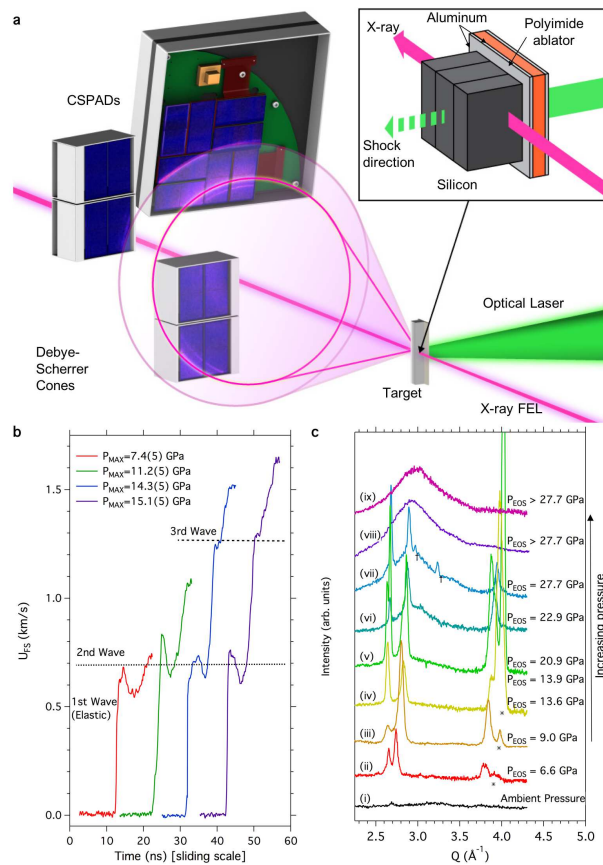


FIG. 1. **Experimental configuration and data examples:** **a** the transverse configuration whereby the compression laser was perpendicular to the X-ray beam. **b** Velocimetry data (VISAR) lineouts showing free surface velocity (U_{FS}). Laser intensity increases to the right. Dashed lines indicate 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, β -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 ablaters, 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° 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 (~ 100 μm) 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 μm), 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 $Q \sim 3.8$ \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 β -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 β -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 β -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 β -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 Moggi *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 β -
 136 tin phase, rather than *Imma* as they suggest. Moreover, we note a considerable lowering of the onset of the β -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 β -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 β -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

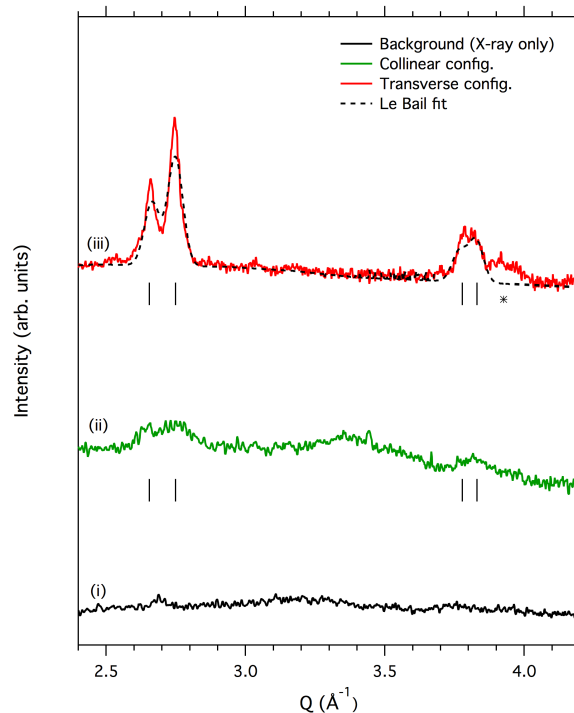


FIG. 2. **The greater sensitivity of the transverse configuration** 1D diffraction profiles in the collinear (ii) and transverse (iii) configurations. Profile (i) shows X-ray only pre-shot. The dotted black line under profile (iii) is a Le Bail fit to the β -tin structure. The tick marks underneath diffraction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

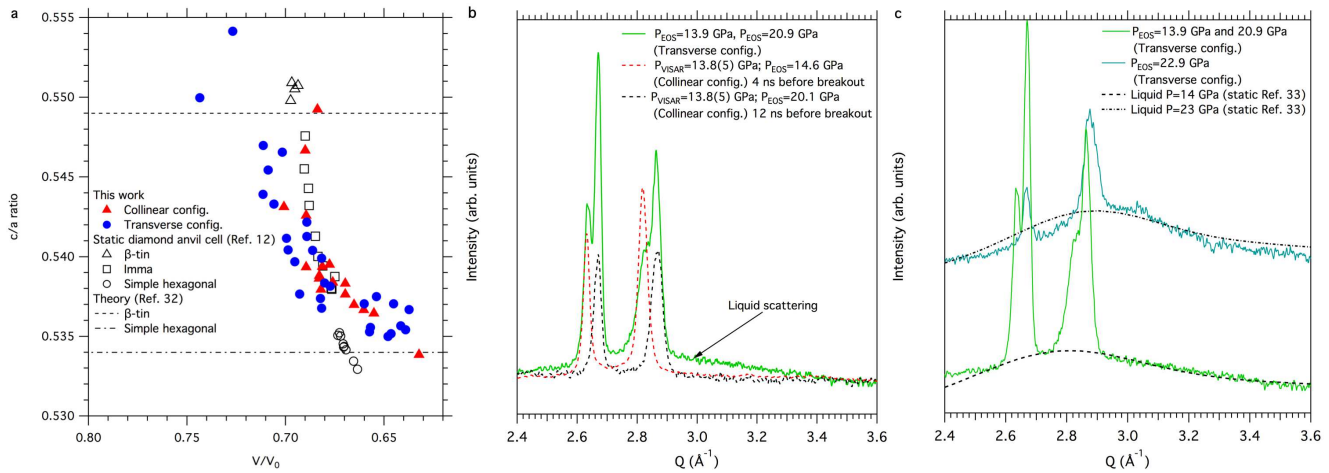


FIG. 3. **Evidence of the onset of melting:** **a** Evolution of the c/a ratio as a function of volumetric change (V/V_0) in the collinear (blue circles) and transverse (red triangles) configurations. Open symbols are from a hydrostatic diamond anvil cell study Ref. 12: β -tin (triangles), *Imma* (squares), simple hexagonal (circles). Theoretical ideal c/a ratios from Ref. 32 are shown for β -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 ~ 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 † 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, β -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 β -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

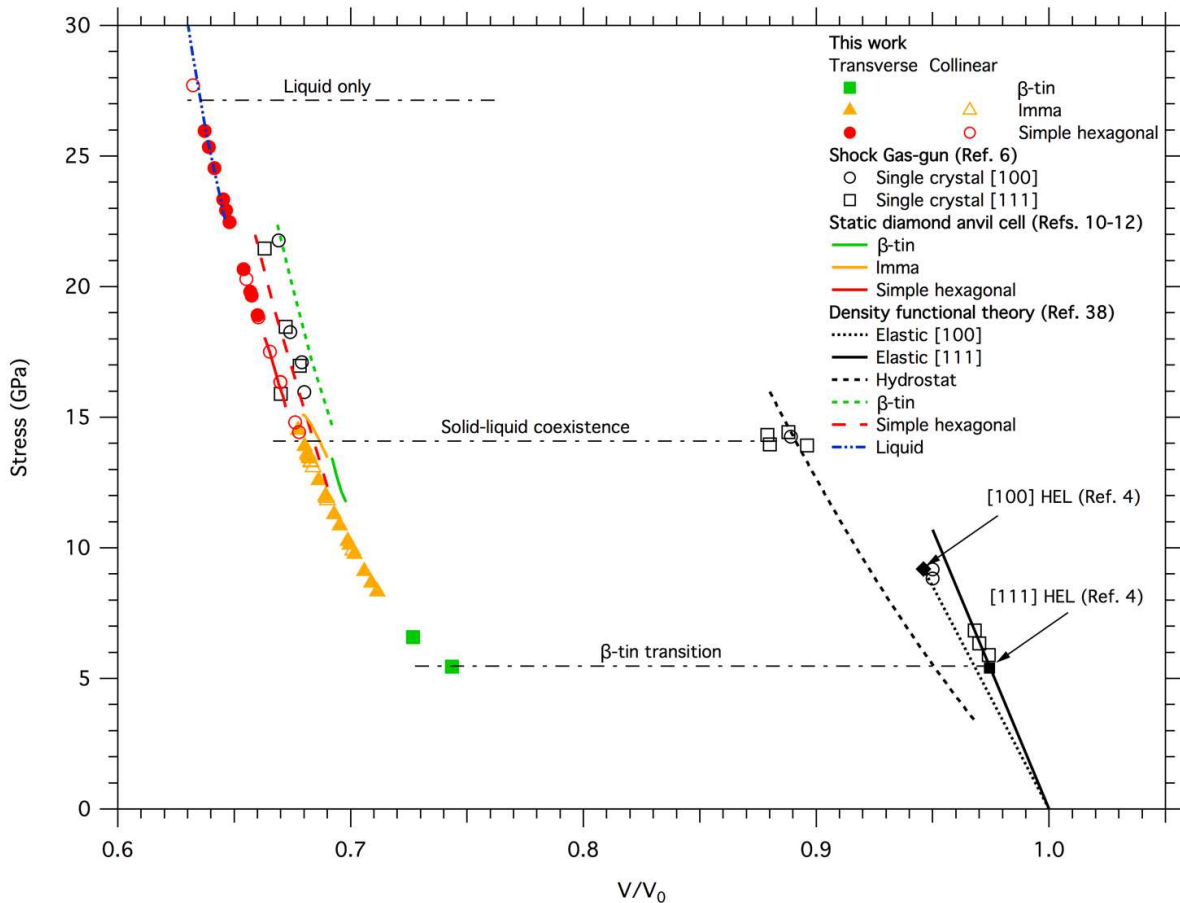


FIG. 4. **Dynamic shear-lowering of phase transition boundaries:** Stress-Volume plot of data obtained in this study, compared with density functional theory calculations (Ref. 39) and static diamond anvil cell experiments (Refs. 10-12). Hugoniot Elastic Limits for the [100] and [111] directions are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

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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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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 μm spot size on target,[40] to achieve laser intensities on target in the range 2×10^{10} - 2×10^{11} W/cm².
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

327 (1) Collinear Configuration

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

334

335 (2) Transverse Configuration

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

346

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 μm .
 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 μm
 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 μm of polycrystalline silicon was sandwiched between two 100 μm 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 μm , 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 μm 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 β -tin, *Imma*, and simple hexagonal
 368 phases may all be described through a common orthorhombic cell, in which the β -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 β -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 Δ has a value
 373 intermediate between 0.25 and 0.50. The *Imma* phase becomes the β -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