Imma phase of germanium at ~80 GPa

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Ge has been studied to 81 GPa with angle-dispersive diffraction techniques, using an image-plate area detector and high-brilliance synchrotron radiation from the European Synchrotron Radiation Facility. A previously unknown phase of Ge, with orthorhombic symmetry *Imma*, is found to exist above ~75 GPa—between the well established β-tin and simple hexagonal phases. This phase is the same as that found recently between the β-tin and simple hexagonal phases of Si.

Until recently, silicon and germanium were both believed to transform from the ambient-pressure diamond phase first to a β-tin phase, and then to a simple hexagonal (SH) phase under increasing pressure.[1,2] These two transitions were reported at 10 GPa and 13–16 GPa in Si (Ref. 1) and 11 and 75 GPa in Ge.[2] However, it has now been discovered that there is an intermediate phase, with orthorhombic symmetry *Imma*, between the β-tin and SH phases in Si.[3] The *Imma* structure is shown in Fig. 1. It becomes the β-tin structure when $a=b$ and $\Delta=0.25$, and the SH structure when $b/c=\sqrt{3}$ and $\Delta=0.50$. A continuous structural change from β-tin-to-SH through *Imma* is thus possible. However, the β-tin-to-*Imma* transition at 13.2(3) GPa and the *Imma* to SH transition at 15.6(3) GPa were both found to be first order, with volume changes ($\Delta V/V_0$) of 0.2(1)% and 0.5(1)%, respectively.[4] There also appear to be discontinuous changes in Δ at the transitions; it was found to vary from ~0.3 to 0.4 over the stability range of the *Imma* phase.[4] The existence of an intermediate *Imma* phase from ~13 to ~16 GPa explains the quite wide variation of transition pressures previously reported for the supposed β-tin-to-SH transition.[1] And the apparently discontinuous nature of the two new transitions may account for previously unexplained changes in the superconducting transition temperature reported in the 12–16 GPa range.[5–8]

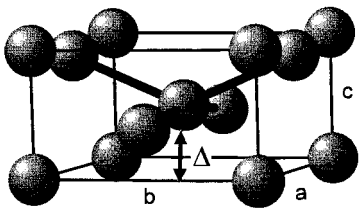

FIG. 1. The *Imma* structure of germanium, with atoms in the 4(e) positions at $(0,\frac{1}{4},\Delta/2)$, or $(0,\frac{1}{2},\Delta)$ relative to the origin chosen here. The origin has been moved from its standard position to facilitate comparison with the β-tin and simple hexagonal (SH) structures: when $a=b$ and $\Delta=0.25$, the *Imma* structure is equivalent to the β-tin structure, while if $b/c=\sqrt{3}$ and $\Delta=0.50$, the *Imma* structure is equivalent to the SH structure.

Ab initio calculations on the *Imma* phase have been performed by Lewis and Cohen.[9] They find that its energy is lower than, or equal to, that of the β-tin and SH phases over a wide range of V/V_0 from ~0.80 to 0.63, and they predict continuous β-tin-to-*Imma* and *Imma*-to-SH transitions. The observed range of existence is much smaller, from V/V_0~0.69 to 0.68, and the transitions appear to be discontinuous as said. However, there are several possible reasons for these discrepancies, one of which is the effect of finite temperature.[9] The calculations do agree well with the structural results in predicting only a small variation in Δ, from ~0.34 to ~0.37, over the observed range of stability of the phase.

In subsequent similar work on germanium, Lewis and Cohen[10] predict that it, too, should have an intermediate *Imma* phase between the β-tin and SH phases. The predicted behavior is very similar to that calculated for Si,[9] except that they find a much larger range over which the *Imma* phase is expected to be β-tin-like ($a\approx b$, $\Delta\approx 0.25$). Vohra *et al.* found a transition from β-tin direct to SH in Ge at 75(3) GPa.[2] We now report a reexamination of this transition, using angle-dispersive powder-diffraction techniques with an image-plate area detector. We find an *Imma* phase existing over the range from ~75 up to at least 81 GPa, the highest pressure reached in this study.

Diffraction data were collected on beamline 3 at the European Synchrotron Radiation Facility (ESRF), Grenoble, using an image-plate area detector. A Si(111) Laue-Bragg monochromator was used to select a wavelength of $\lambda=0.4592$ Å from the white beam produced by a hybrid wiggler, and a Si mirror was used to focus the beam vertically and to remove higher order harmonics. Although the mirror is able to focus a 600 μm white beam to less than 20 μm, the optical combination of the Laue-Bragg monochromator with the mirror focuses such a beam only to approximately 120 μm full width at half maximum. Attenuators

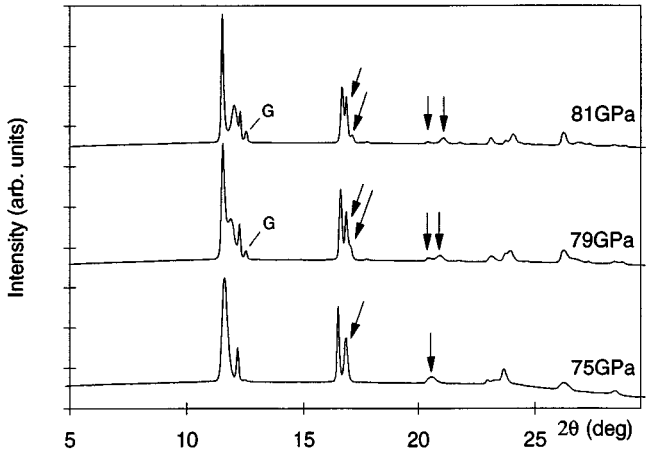

FIG. 2. Integrated profiles of powder-diffraction patterns recorded from germanium at 75, 79, and 81 GPa. The vertical and inclined arrows in the 75 GPa profile mark two single peaks of the β-tin phase which each split into two separate peaks in the 79 and 81 GPa profiles, as indicated. The peak marked "*G*" in the 79 and 81 GPa profiles is a weak tungsten gasket line.

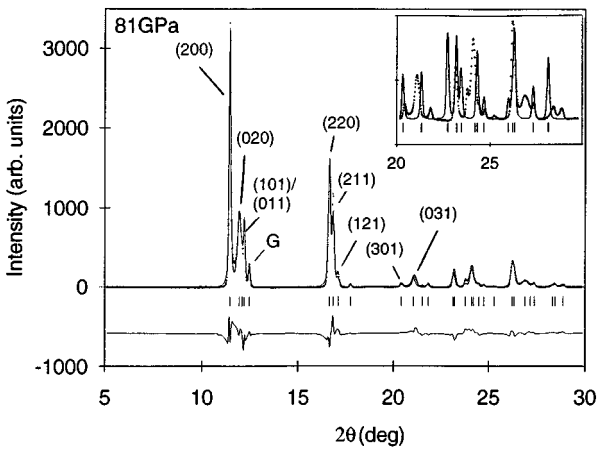

FIG. 3. Fit to the profile of Ge at 81 GPa with the *Imma* structure, and also a component of bcc tungsten to model the gasket lines. The tick marks show the positions of all the reflections allowed by symmetry. The difference between the observed and calculated profiles is displayed below the tick marks. Some principal reflections are indexed. The peak marked "*G*" is the strongest tungsten gasket line. The inset shows the higher angle part of the best fit obtained to the 81 GPa profile with a mixed-phase β-tin/SH model (plus, again, tungsten for the gasket lines): the calculated peak positions are shown by the tick marks.

were used to remove the unwanted long wavelength part of the wiggler spectrum in order to preserve the optical quality of the first monochromator crystal, and 20×20 μm^2 slits were used to define the beam for the very high pressure measurements. The sample to image-plate distance was ~370 mm, and was calibrated using a standard Si sample. Image plates were read on a Molecular Dynamics scanner using a pixel size of 176×176 μm^2, and were then integrated around the powder rings to produce 1-*d* profiles. Details of the experimental set up and pattern integration software are reported in Refs. 11 and 12.

The sample material was a finely ground powder prepared from 99.9999% pure Ge purchased from the Aldrich Chemical Company. Samples were loaded into Diacell DXR-5 and DXR-GMW diamond-anvil pressure cells,[13] with a 4:1 methanol:ethanol mixture as a pressure-transmitting medium. Flat 200-μm-culet diamonds were used, with tungsten gaskets. In these pressure cells, the diamond anvils are supported on Be discs, and so complete 2-*d* powder patterns are obtained. The pressure was measured using the ruby fluorescence technique.[14] The structural results were obtained from full Rietveld refinement of the integrated profiles using the program MPROF.[15]

As the sample pressure was increased, the transition to the β-tin phase was observed and then no further changes other than compression occurred until ~70 GPa. At this pressure, the first strong line in the powder pattern started to become discernibly broadened and asymmetric. Figure 2 shows three profiles then collected at 75, 79, and 81 GPa. The broadening and asymmetry of the first line is evident in the 75 GPa profile. At 79 GPa, it has clearly split into two peaks and the separation increases at 81 GPa. This is very similar to the sequence of changes shown in Fig. 2 of Ref. 4 for the *Imma* phase of Si. As in Si, the first reflection can be seen to move to *lower* 2θ as the pressure increases. Other key features are the splitting of the single peaks marked by an inclined and a vertical arrow in the 75 GPa profile, into two separate peaks in the 79 GPa profile, and (further apart still) in the 81 GPa profile.

Figure 3 shows the fit obtained in a Rietveld refinement of the *Imma* structure for the 81 GPa profile. The refined unit-cell dimensions at this pressure are $a=4.572(1)$ Å, $b=4.386(1)$ Å, and $c=2.461(1)$ Å, and Δ refines to 0.390(4). As for Si, we also tested a mixed β-tin/SH model. This can fit the low-angle group of reflections quite well, but the very poor fit at higher angles—illustrated in the inset to Fig. 3—clearly allows this interpretation to be rejected. Ge evidently has the same *Imma* phase as Si, as predicted by the recent calculations.[10] The fact that this phase was not detected in the previous study (Ref. 2) can be attributed to the lower resolution of energy-dispersive data. Figure 1 of Ref. 2 shows a diffraction pattern of the β-tin phase at 72 GPa. The first two β-tin reflections (200 and 101) are only just resolved, and the second doublet (220 and 211) is not resolved at all. Clearly, the reflections shown in our Fig. 2 appearing between 200 and 101 of β-tin (at $2\theta\sim12°$), and as a shoulder on the high-angle side of 211 of β-tin (at $2\theta\sim17°$), would not have been detectable. However, Vohra *et al.*[2] do indicate that their diffraction pattern at 77.7 GPa could not be completely indexed as SH.

The distortion of the *Imma* unit cell from the tetragonal symmetry of β-tin can be characterized by $(a-b)/(a+b)\neq0$ and $\Delta\neq0.25$; and the distortion from SH by $b/c\neq\sqrt{3}$ and $\Delta\neq0.5$. At 81 GPa, $(a-b)/(a+b)=0.0208(2)$ and $b/c=1.782(6)$. These values are the same as in Si at 14.4(2) GPa,[4] while the value of Δ appears to correspond to that in Si at a slightly higher pressure of ~15 GPa. However, this (small) difference may not be significant as there was quite a large variation in the Δ values obtained for Si on pressure increase and pressure decrease.[4]

As discussed above, the evidence from this study indicates that the transition from the β-tin phase to *Imma* occurs at approximately 75 GPa. However, the maximum pressure we were able to reach (81 GPa) was not sufficient to locate the transition from *Imma* to the SH phase. If the transition has a small discontinuity as in Si,[4] an estimate of ~85 GPa can be obtained for the transition pressure from the rate of change between 79 GPa and 81 GPa in Fig. 2. This would accord with the report of a single-phase SH diffraction pattern at 90 GPa by Vohra *et al.*[2] Hence the best present estimate of the stability range of the *Imma* phase is ~75 to ~85 GPa.

We conclude that Ge behaves the same way as Si in transforming from its β-tin phase to an intermediate orthorhombic *Imma* phase on increasing pressure. The two systems exhibit very similar orthorhombic distortions in terms of the unit-cell dimensions and also the variable atomic coordinate, Δ. Further work is now planned to determine the β-tin-to-*Imma* and *Imma*-to-SH transition pressures, and to follow the structural pressure dependence of this phase in Ge—where the greater range of stability will allow the relationship between the cell dimensions and Δ to be explored in more detail. It is of particular interest to relate the distortion of the pseudohexagonal *bc* layers to the range of structural stability, with reference both to the calculations of Lewis and Cohen,[10] and our recent study of an *Imma* phase stable over at least 40 GPa in (site-disordered) GaSb.[16]

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