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Instability in the Imma phase of Si

S. L. Qiu\(^{(a)}\) and P. M. Marcus\(^{2}\)

\(^{1}\)Department of Physics, Florida Atlantic University - Boca Raton, FL 33431-0991, USA
\(^{2}\)IBM Research Division, T. J. Watson Research Center - Yorktown Heights, NY 10598, USA

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Abstract – The Imma phase of Si is found by first-principles calculations to have unstable states at the two ends of its structural range. These instabilities force first-order transitions to both the \(\beta\)-Sn and the simple hexagonal phase. These transitions occur for the non-vibrating crystal at 96 and 110 kbar, respectively. Two special computational procedures are described that have been developed to find the instabilities.

The Imma phase of Si is the ground state between a state of \(\beta\)-Sn phase and a state of the simple hexagonal (sh) phase. The crystal structure consists of two interpenetrating body-centered-orthorhombic (bco) lattices, unit cell sides \(a\), \(b\), \(c\), with a separation distance \(\upsilon\), where \(\upsilon\) is an internal parameter that varies from 0.25 to 0.50. At \(\upsilon = 0.25\) the Imma structure is identical to the structure of the \(\beta\)-Sn phase of Si; at \(\upsilon = 0.50\) the Imma structure is identical to the sh phase of Si. However the stable range between the phase transitions to \(\beta\)-Sn and sh is shorter than the structural range, as is observed experimentally [1,2] and will be derived here theoretically.

The pressures at the \(\beta\)-Sn and sh phase transitions to Imma are measured experimentally to be 132 kbar and 156 kbar, respectively [1,2]. The theoretical values vary widely [3–12]. In a 2004 paper [7] the pressures are given as 103 and 189 kbar. In a 2006 paper [8] the pressures are 115 and 142 kbar. In 2008 papers [11,12] the pressures are 155 and 220 kbar. In this work we find the pressures 96 and 110 kbar for a non-vibrating crystal of Si, and give a plausible argument that lattice vibrations will increase the pressure. These transition pressures are forced by previously unreported instabilities of the Imma phase in structural ranges near the \(\beta\)-Sn and sh phases. The instabilities narrow the stable range of Imma and make the phase transitions first order, both features in agreement with experiment.

The two instabilities have different characters. They have been established by two different first-principles calculation procedures [13,14] both based on calculation of total energies \(E\) per atom of a given structure with the well-tested band-structure program WIEN2k [15]. The WIEN2k program is based on the density functional theory (DFT), and includes the generalized gradient approximation (GGA). The calculations use a plane-wave cutoff \(R_{\text{MT}} K_{\text{max}} = 7\), \(R_{\text{MT}} = 2.0\) au, \(G_{\text{max}} = 12\), mixer = 0.05 and 1000 \(k\)-points in the irreducible Brillouin zone. The convergence criterion on the energies is set at \(1 \times 10^{-3}\) mRyd \((10^{-6}\) Ryd) per unit cell. One procedure, which we call a sweep [13], follows the minima of \(E\) at constant volume \(V\) as we sweep through the three independent degrees of freedom \((b, a, \upsilon)\). The state of a minimum in the triply minimized energy \(E_{\text{mmm}}(V)\) is then a stable phase at constant \(V\). When this minimum fails to exist at \(\upsilon \leq 0.35\) the structure is unstable.

A second procedure, which we call the minimum path procedure (MNP) [14], starts with the phase structures found by the sweep procedure and the corresponding pressure \(p\) found from \(dE_{\text{mmm}}/dV = -p\) using adjacent volumes. Then the MNP finds a state at that \(p\) in which \(a, b, c\) have been adjusted to satisfy the boundary conditions for equilibrium \(\partial G/\partial a = \partial G/\partial b = \partial G/\partial c = 0\), where \(G = E + pV\) is the Gibbs free energy of the state. The value of \(\upsilon\) is not adjusted by the MNP, but by varying the initial value of \(\upsilon\) we can search for a \(\upsilon\) at which \(\partial G/\partial \upsilon = 0\). If no \(\upsilon\) is found for which \(\partial G/\partial \upsilon = 0\), then one of the conditions for equilibrium is not satisfied and the structure at the given \(p\) is unstable.

The sweep procedure and the MNP procedure agree on the instability at and below \(\upsilon = 0.35\); they disagree for \(\upsilon\).
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Fig. 1: (a) \(a/c\) vs. \(\upsilon\) and (b) \(b/c\) vs. \(\upsilon\) for the Imma phase of Si, where \(a, b, c\) are the equilibrium lattice parameters of the bco cell, \(\upsilon\) is the equilibrium internal parameter giving the spacing of bco sublattices (in terms of \(c\)). The open circles and \(\times\)'s denote, respectively, the theoretical stable and unstable states of the Imma phase. The solid circles are the experimental data deduced from figs. 3, 4 and 5 of [2].

between 0.46 and 0.50. The sweep procedure shows that Imma is stable at constant volume up to \(\upsilon = 0.50\), whereas MNP finds Imma is unstable at constant \(p\) in that range of \(\upsilon\). Since the experiment is at constant \(p\), Imma is not observed for \(\upsilon = 0.46\) to 0.50.

The results of these two procedures are shown in fig. 1 which plots \(a/c\) and \(b/c\) vs. \(\upsilon\) for the stable Imma states (open circles) with \(\upsilon\) between 0.35 and 0.46. The observed structures of Imma (solid circles) [1,2] are also plotted and show a reasonable correspondence.

Figure 2 plots \(G(p)\) for the \(\beta\)-Sn, Imma and sh phases of Si. The Imma phase is stable for \(p\) between 96 and 110 kbar at which first-order transitions occur. For \(p < 96\) kbar the Imma phase does not exist, there are no equilibrium states and the plot of \(G(p)\) along the equilibrium line terminates at 96 kbar. For \(p > 96\) kbar the equilibrium line at constant \(p\) (the experimental condition) terminates at 110 kbar but exists at constant \(V\) and goes up in pressure to merge with the sh structure at 113 kbar.

Three kinds of instability are illustrated in fig. 2. The termination of the equilibrium line at \(p = 96\) kbar shows a complete instability and a loss of the Imma phase below 96 kbar. The existence of the equilibrium line of Imma for \(p\) between 110 and 113 kbar when \(V\) is held constant, but unstable at constant \(p\), shows a delicate instability at constant \(p\) produced by the failure to satisfy just one of the conditions of equilibrium, i.e., the condition \(\partial G/\partial \upsilon = 0\). The \(\times\)'s along the \(\beta\)-Sn and sh \(G(p)\) curves show that the equilibrium line exists in those ranges of \(p\), but the state is unstable for a third reason, i.e., because \(G\) on the equilibrium line is a saddle point rather than a minimum with respect to structure variations. An equilibrium state has a definite structure at a particular value of \(p\) and \(V\). It also satisfies the condition that the first derivative of \(G\) with respect to the structural parameters vanish. However,
to be stable, the second derivatives of $G$ with respect to the structural parameters must all be positive (in the principal directions), i.e., $G$ is a minimum for all variations of the structural parameters. A saddle point means there is a change of parameter for which $G$ decreases, hence instability.

The existence range of the Imma phase at constant $p$ is thus shown to be between 96 and 110 kbar, whereas the experiment observes the phase between 132 and 156 kbar [1,2]. However, the calculation is for a non-vibrating crystal. If lattice vibrations are considered, an internal pressure will be generated by the vibrations which must be matched by the applied pressure to achieve equilibrium. This vibration pressure will be added to the pressure that corresponds to the structure. Our calculation finds only the pressure fixing the structure. In fact we find the vibration pressure will be added to the pressure at the $p$ found from $\frac{dE_{mmm}(V)}{dV}$ – the structure is the same.

More significantly the range of $p$ for stable Imma is found to be small (110 – 96 – 14 kbar), to be compared with the observed range of 156 – 132 = 24 kbar; thus our calculated range shows a closer correspondence with experiment than previous papers (e.g. [7,8]). However, a detailed study of the effects of vibrations is called for. This calculation should be for a crystal at constant $V$ for a given stable state in two independent calculations – from $\frac{dE_{mmm}(V)}{dV}$ of stable structures at constant $V$, and from minimizing $G$ with respect to the structure at the $p$ found from $\frac{dE_{mmm}(V)}{dV}$ – the structure is the same.

Finally, we note that our results are significantly different from the work of Gaal-Nagy (GN) et al. [7,8], who also applied first-principles theory to the non-vibrating Si crystal. We note GN did not find the instabilities and favored a second-order transition to the $\beta$-Sn phase. The transition pressure to the sh phase is given as 189 kbar in [7] and as 143 kbar in [8]. We find the value of 110 kbar in two ways which agree as noted above. Also we rely just on the accuracy of $E$ calculations for a given structure, which has second-order (variational) accuracy in the ASW formulation; GN rely on the stress matrix, which depends on the wave functions, and has only first-order accuracy. We note also that we do not find the hysteresis in structural values for increasing and decreasing $p$, found by GN, and that our Imma structure points for the curves $a/c (\nu)$ and $b/c (\nu)$ show very little scatter compared to the structure curves for the Imma phase found by GN.

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