Phonons in the $\beta$-tin, Imma, and sh phases of Silicon from ab initio calculations

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We present a new interpretation of measured Raman frequencies of a high-pressure structure of Silicon which was assigned previously to the $\beta$-tin phase. Our results show that the $\beta$-tin $\rightarrow$ Imma $\rightarrow$ sh phase transitions have been already indicated in this experiment which was performed before the discovery of the $\beta$-tin phase. We have calculated phonon-dispersion curves for the $\beta$-tin, Imma, and sh phases of silicon using the plane-wave pseudopotential approach to the density-functional theory and the density-functional perturbation theory within the local density approximation. With the new assignment, the calculated phonon frequencies display an excellent agreement with the experimental data, and can be also used to determine precisely the transition pressure for the Imma $\rightarrow$ $\beta$-tin phase transition. The sh $\rightarrow$ Imma transition is accompanied by soft modes.

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In 1993 a new high-pressure phase was found between the $\beta$-tin (SIH, body centered tetragonal structure) and the sh (SIV, simple hexagonal structure) phase of silicon [1]. This phase was called Imma phase after its space group and has a body-centered orthorhombic structure (SIXI). In the diffraction experiment, the phase transitions to and from the Imma phase appear as of first order with a discontinuity in the volume and the lattice parameters [2]. Previous ab initio calculations of the phase transitions $\beta$-tin $\rightarrow$ Imma $\rightarrow$ sh have indicated both phase transitions to be of second order [3] or both of first order [4]. A theoretical investigation of elastic stabilities has shown a second-order phase transition $\beta$-tin $\rightarrow$ Imma [5]. From group-theoretical arguments [6], the phase transition $\beta$-tin $\rightarrow$ Imma can be of second order, whereas the phase transition Imma $\rightarrow$ sh has to be of first order. This conclusion was strongly supported by an ab initio calculation in our previous work [7].

An intermediate phase similar to the Imma phase, with a structure more general than the $\beta$-tin and the sh phase was considered theoretically before [8] with a prediction that the phase transitions might be accompanied by soft phonon modes. Since the Imma structure results from a distortion and a relative sublattice shift of $\beta$-tin along the $c$-direction, which corresponds to a soft $\Gamma$ phonon displacement [9], it is worthwhile to investigate the pressure dependence of the phonon-dispersion curves. Especially, it was speculated that the superconductivity of these metallic high-pressure phases of silicon might be enhanced by these soft modes [10, 11]. Available experimental and theoretical data for superconducting properties [12] did not consider the Imma phase, because its existence was not known at that time. In the experiment, the superconducting temperature as a function of pressure shows a kink [11, 12] within the assumed stability range of the sh phase. In the corresponding theoretical work this kink was traced back to some soft modes from calculations of a few phonon modes under pressure for the sh structure with a frozen-phonon technique [12]. However, in our opinion this kink corresponds to the phase transition Imma $\rightarrow$ sh. A first step towards the determination of the superconducting transition temperature by calculating the electron-phonon coupling is an analysis of the phonon frequencies of all phases.

In this contribution we examine the phonons of the high-pressure phases $\beta$-tin, Imma, and sh and their behaviour near the phase transitions. In particular, we are interested in soft modes and the pressure-dependent phonon frequencies. An indication of a soft-mode behaviour has been already found experimentally: The low-energy optical phonon frequency of the $\beta$-tin phase at the $\Gamma$-point decreases with increasing external pressure [17]. Restricting ourselves to just the $\beta$-tin phase we did not find a vanishing frequency even beyond the stability range of this phase [18, 19], but we find a lowering of the lower optical phonon frequency, whereas the degenerate upper ones increase. In the following we want to include especially the Imma and the sh phases in our consideration.

This paper is organised as follows: First, we give a short overview of the methods on which our calculations are based. Second, we describe in brief the structures, the relaxation and the pressure dependence of the structural parameters of the three phases. Third, phonon-dispersion curves of the three phases are presented as well as an analysis of the phonon frequencies at the zone-center and at a zone-boundary point as a function of the external pressure. Finally, we draw a conclusion.

The calculations have been carried out using a plane-wave pseudopotential scheme [20] within the density-functional theory [21, 22] and the density-functional perturbation theory [23, 24] implemented in the PWscf package [26]. The ion core of silicon has been described by a norm-conserving pseudopotential [27, 28] created following a scheme by v. Barth and Car [29], which is described in [30]. The exchange-correlation energy is calculated with the use of the local-density approximation.
The pressure corresponding to a given structure is obtained by evaluating the stress tensor \[ \Delta = 0 \]. We have used a kinetic-energy cutoff \( E_{\text{cut}} \) of 40 Ry and 1165 special Monkhorst-Pack points \[ 32 \] in the irreducible part of the Brillouin zone with a Methfessel-Paxton \[ 30 \] smearing of 0.03 Ry, because of the metallic character of the system. With these parameters the convergence is better than 0.01 mRy for energy differences, and the pressure related to the Pulay stress \[ 31, 32 \] is smaller than 1 kbar. The phonon frequencies have been calculated on a discrete mesh of 18 points in the irreducible Brillouin zone, and the phonon-dispersion curves have been calculated by Fourier interpolation.

All these three structures have been determined using the same body-centered orthorhombic (bco) cell with lattice constants \( a \neq b \neq c \) and two atoms at \( (0,0,0) \) and \( (0,0.5b,0c) \) to which we refer as BCO. In this cell the \( \beta \)-tin phase can be reproduced by choosing \( a = b \) and \( \Delta = 0.25 \) and the structure of the sh phase by \( b = \sqrt{3}c \) and \( \Delta = 0.5 \). The relaxation of the lattice parameters has been carried out by evaluating the total energy as a function of the lattice constants. The equilibrium lattice parameters for a fixed volume have been determined by the condition \( p_x = p_y = p_z \) where \( p_x \), \( p_y \), and \( p_z \) are the negative diagonal components of the stress tensor. Therefore, the external pressure can be taken from the stress tensor since it is diagonal with equal components for a relaxed structure. For the BCO structure, the internal parameter \( \Delta \) has been relaxed in addition to the lattice constants, while for the \( \beta \)-tin and the sh phases \( \Delta \) was fixed at the corresponding value. In the latter case the ideal relation \( a = b \) has been reached for the \( \beta \)-tin phase but not exactly for the sh one. On the other hand, the deviations from \( b = \sqrt{3}c \) are negligible and do not affect the calculation of the phonon frequencies. The results corresponding to these structures are denoted as BCT and SH.

In fact, for a free relaxation of the BCO cell we obtain the lattice parameters of the \( \beta \)-tin phase for large volumes (small pressures), the ones of the sh phase for small volumes (large pressures) and between these phases the \( \text{Imma} \) phase with \( 0.25 < \Delta < 0.5 \) as apparent in Fig. 1. Here, with \( \Delta \) being discontinuous the phase transition \( \beta \)-tin\( \text{Imma} \) seems to be of first order, while the \( \text{Imma} \rightarrow \text{sh} \) transition seems to be of second order because of a missing discontinuity of \( \Delta \). The enthalpy barrier between the \( \text{Imma} \) and the sh phase is only a few meV \[ 31 \], which is less than the precision of our calculations. Therefore, the determination of the order of the phase transitions from the behaviour of the lattice parameters as a function of the pressure or total energy is unreliable. Nevertheless, we can estimate the transition pressures from Fig. 1 and we find that the \( \beta \)-tin\( \text{Imma} \) transition occurs between 115 and 118 kbar and the \( \text{Imma} \rightarrow \text{sh} \) one between 142 and 143 kbar, which is in good agreement with the experimental values \[ 2 \] if those data are evaluated in the same way (for further details and a review of available experimental and theoretical results see \[ 7 \]). In the following we will inspect the phonon spectra as a possible source for clearer conclusions.

Phonon-dispersion curves have been calculated for the three phases at various pressures. For each structure at a given volume within the stability range of the corresponding phase the phonon frequencies along selected high-symmetry wave-vector directions are shown in Fig. 2. Compared to the curves of the \( \beta \)-tin phase some degeneracies of frequencies phase at high-symmetry points are lifted in the \( \text{Imma} \) because of the symmetry of the this phase being lower than that of \( \beta \)-tin, see, e.g., at the \( \Gamma \)- and the X-point. For the sh phase new degeneracies ap-
pear because of the higher symmetry of this phase with respect to the *Imma* phase. Surprisingly, while for the \( \beta \)-tin and the *Imma* phase the polarisations of the modes are very similar (even a simultaneous exchange of the polarisation of two modes along some directions), some major changes appear between the *Imma* and the sh phase. For example, around the middle of the XUI-direction the third mode (counted from high to low frequency at \( U \)) has a longitudinal acoustic polarisation whereas it has a transverse optic polarisation in the case of *Imma* and \( \beta \)-tin.

Like in the cd phase of Si [18] the high-energy optic frequencies increase and the low-energy acoustic ones decrease with increasing pressure. In the present case, an exceptionally strong decrease is found at the \( \Gamma \)- and the \( S \)-points. In order to find some critical phonon softening we have investigated the frequencies as a function of external pressure at these points. For this reason we were not only taking into account the fully relaxed BCO structure but also the BCT and SH structures. The results are presented in Fig. 3. Here the three phases are visible again, meaning that at small pressures the frequencies of BCO are identical with the ones from the BCT structure corresponding to the stability of the \( \beta \)-tin phase. At high pressures the same correspondence can be stated for sh. The shift of the frequencies between \( \beta \)-tin and *Imma* is much smaller than between *Imma* and sh which points to a second-order phase transition for \( \beta \)-tin\( \rightarrow \)*Imma* and a first-order phase transition *Imma*\( \rightarrow \)sh. We assume that the change will become more abrupt between *Imma* and sh for more accurate ground-state calculations which describe the energy barrier between these phases with more precision. Thus, we expect a discontinuity of the frequency at this pressure from a more accurate calculation.

In principle, the softening of a phonon mode indicates an instability against a displacive phase transition. We find a softening with decreasing pressure in the SH structure for the sh phase at the zone-enter \( \Gamma \)-point and at the zone-boundary \( S \)-point around the sh\( \rightarrow \)*Imma* phase transition. The instabilities at both points are related to an instability at the \( L \)-point of the Brillouin zone of a simple-hexagonal cell using the corresponding monatomic structure. A softening at a point on the zone boundary corresponds to a doubling of the unit cell. In fact, in the ideal SH symmetry the BCO unit cell contains two sh unit cells. We can estimate the transition pressure for the sh\( \rightarrow \)*Imma* transition from these soft modes and find the values 143.9 and 146.3 kbar from the softening at the \( \Gamma \)- and the \( S \)-point, respectively. These transition pressures are in good agreement with the ones obtained from the relaxed lattice parameters.

We find an excellent agreement also with the available experimental data of Olijnyk [17] who measured the pressure-dependent phonon frequencies for the \( \beta \)-tin structure at a time when the *Imma* phase was yet unknown. Wrongly assuming the \( \beta \)-tin phase, theoretical work has not been able to reproduce these data [18, 39, 40]. Our results agree completely with those of Ref. [17] in the low-pressure (\( \beta \)-tin) and the high-pressure (sh) range and describe the slope in between (*Imma*).

Therefore, Olijnyk was actually observing the phonon frequencies of all these three phases.

In the *Imma* phase the TO modes are split into two

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**FIG. 3:** Pressure dependence of the phonon frequencies at the \( \Gamma \)- and the \( S \)-point for the BCT-, BCO-, and SH structure. Imaginary frequencies are drawn along the negative frequency-axis. The dots represent calculated values. Lines are guides to the eye in the case of BCO, and in the case of BCT and SH are derived from the linear function \( \omega^2(p) \). Reference values from other calculations (TH) stem from [8] (square), [39] (diamonds), and [40] (triangles). Experimental data from [17] are denoted as crosses. The pictures of the Brillouin zones (bco upper panel, sh lower panel) are used as an illustration.
branches which are both Raman active. Since the peak in the experimental Raman spectrum is very broad and the frequency of the maximum is just a little bit lower than our calculated value we speculate that the second peak has a lower intensity and is unresolved from the high-frequency one. Besides, there might be a second-order background in the spectra: If the overtone spectra are dominant in the β-tin, Imma, and sh phases as they are in the diamond phase, then the spectra correlate with the DOS of Fig. 2 if the frequency axis is stretched by a factor of 2. In fact, the experimental intensity near 500 cm$^{-1}$ has a strong positive slope and is larger in the β-tin than in the Imma or sh phases.

In conclusion, we have investigated the phonon dispersion curves for the β-tin, Imma, and sh phases of Silicon. While the order of a phase transition often is derived from the behaviour of the structural parameters or of the volume, the order of the pressure-induced β-tin→Imma→sh phase transitions can also be obtained from the pressure dependence of the phonon frequencies. Here we find a small shift of the frequencies between the β-tin and the Imma phase and a large one between Imma and sh pointing to a second-order and first-order phase transition, respectively. Our calculations are able to reproduce the experimental data of Olijnyk 17 perfectly. This results in the insight that in the Raman spectra the Imma and the sh phases are visible rather than the assumed β-tin phase. There is a splitting of the Raman mode at the β-tin→Imma transition as well as a critical softening of the LO mode at Γ and S at the sh→Imma transition which has escaped experimental observation so far. Since the pressure-dependent behavior of these phases is known now, it should be a challenge to find the lower TO mode of the Imma and the sh phases and also the softening of the LO mode in the sh structure experimentally.

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