Lattice Instability during Solid-Solid Structural Transformations under a General Applied Stress Tensor: Example of Si I → Si II with Metallization

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The density functional theory was employed to study the stress-strain behavior and elastic instabilities during the solid-solid phase transformation (PT) when subjected to a general stress tensor, as exemplified for semiconducting Si I and metallic Si II, where metallization precedes the PT, so stressed Si I can be a metal. The hydrostatic PT occurs at 76 GPa, while under uniaxial loading it is 11 GPa (3.7 GPa mean pressure), 21 times lower. The Si I → Si II PT is described by a critical value of the phase-field’s modified transformation work, and the PT criterion has only two parameters given six independent stress elements. Our findings reveal novel, more practical synthesis routes for new or known high-pressure phases under predictable nonhydrostatic loading, where competition of instabilities can serve for phase selection rather than free energy minima used for equilibrium processing.

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Phase transformations (PTs) in solids are mostly characterized by equilibrium phase diagrams [1], whereas general nonhydrostatic stresses offer novel synthetic routes for new or known high-pressure phases. Here we augment temperature-pressure (T − P) equilibrium diagrams by a stress (σ) tensor that affects structural (and electronic) instabilities, providing guidance for creating more accessible processing routes of such phases under predictable nonhydrostatic deformation at significantly lower mean pressures. Indeed, observed PTs occur under a significant deviation from equilibrium [2–5], with large hysteresis. For carbon, the graphite-diamond PT at room temperature occurs at 2.45 GPa; however, due to hysteresis, the PT is observed at 70 GPa [3]. The actual PT pressure deviates from that of equilibrium due to an enthalpy barrier. When thermal fluctuations can be neglected, the PT criterion is related to disappearance of the enthalpy barrier, i.e., to the lattice instability. Hence, lattice instability conditions are necessarily studied under hydrostatic, uniaxial, and multiaxial loadings [6–12].

In experiments, a significant reduction in PT pressure occurs due to deviatoric (nonhydrostatic) stresses and plastic strains [5,13–16]. For example, plastic shear reduces the PT from hexagonal to superhard wurtzitic BN from 52.8 to 6.7 GPa [5]—an order of magnitude. This phenomenon is extremely important from fundamental and applied points of view, as it may reduce the PT pressure to a practical level for high-pressure phases that exhibit unique properties.

The suggested physical mechanism responsible for this reduction is related to dislocation pileups associated with a plastic strain [13]. As stresses at the tip of a pileup are proportional to the number of dislocations in a pileup (typically 10–100), local stresses exceed the lattice instability limit and cause the nucleation of a high-pressure phase even at a relatively small external pressure. This was rationalized based on an analytical model [13] and using a phase-field approach [17,18]. However, the phase-field inputs for the PT instability criteria for an ideal crystal under a general stress tensor were assumed hypothetically, as such criteria are not known for any material [19].

Because of the technological importance of Si and its PTs, a huge literature exists. Relevant are the PTs in Si I under hydrostatic and two-parametric nonhydrostatic loadings, studied with the density functional theory (DFT) [20,21], and the lattice instability under two-parametric loadings (unrelated to a PT) [10,22–24].

So, we perform a DFT study of the deformation process under an applied general stress and determine the lattice instabilities responsible for the cubic-to-tetragonal Si I → Si II PT, along with metallization that can occur prior to the Si II phase. While finding the instability criteria under all six stress components seems daunting, due to the large number of combinations, unexpected guidance came from the crystal lattice instability criterion formulated within the phase-field method [11,12,25,26]. The key result is that Si I → Si II PT can be described by the critical value of the modified transformation work. With normal stresses (σ₁, σ₂, σ₃) acting along (110), (110), and (001), respectively, the PT criterion is linear in normal stresses, depends on σ₁ + σ₂, is independent of σ₁ − σ₂ and shear stress τ₁₂, acting alone or with one more shear stress, and depends on...
all shear stresses via theoretically predicted geometric nonlinearity. The PT criterion has only two material parameters for a general applied stress, which can be determined by two DFT simulations under different normal stresses.

**Energy landscape.**—The DFT potential energy (versus lattice constants $a_i = b_i$ and $c_i$) is given in Fig. 1; the data are in Supplemental Material [27]. We find two local energy minima, corresponding to the fully relaxed (stress-free) Si I and Si II, and a saddle point (SP)—the unstable state corresponding to the enthalpy barrier (Fig. 1). The tetragonal cell of Si I is bounded by (110), (110), and (001) planes. The DFT energies and lattice constants (stress-free) Si I and Si II, and a saddle point (SP) for Si I ↔ Si II PTs are in Supplemental Material [27]. We find two local energy minima, corresponding to the fully relaxed (stress-free) Si I and Si II, and a saddle point (SP)—the unstable state corresponding to the enthalpy barrier (Fig. 1).

The tetragonal cell of Si I is bounded by (110), (110), and (001) planes. The DFT energies and lattice constants relative to the stress-free Si I ($a_1 = 3.8653$ Å, $c_1 = \sqrt{2}a_1 = 5.4665$ Å) are 0.2949 eV/atom for Si II ($a_2 = 4.8030$ Å, $c_2 = 2.6592$ Å) and 0.4192 eV/atom for the SP state ($a = 4.4847$ Å, $c = 3.4763$ Å). The calculated $c_1$ is +0.7% of the experiment (5.43 Å) [40].

We designate tensors with boldface; e.g., $I$ is the unit tensor. Contractions of tensors $A = \{A_{ij}\}$ and $B = \{B_{jk}\}$ over one and two indices in Einstein notations are $A:B = \{A_{ij}B_{jk}\}$ and $A:B = A_{ij}B_{ji}$, respectively. The inverse and transpose of $A$ are $A^{-1}$ and $A^T$, respectively.

**Deformation gradient.**—$F = F_e \cdot U_t$, mapping an undeformed state of a crystal into a deformed state, is decomposed into elastic $F_e$ and transformational $U_t$ parts. Deformation gradient $U_t$ changes the Si I stress-free cell to the Si II stress-free cell; its diagonal components are $U_{11} = U_{12} = a_2/a_1 = 1.243$ and $U_{13} = c_2/c_1 = 0.486$. For a Tersoff potential [11,12], it is quite different: $U_{11} = U_{12} = 1.175$ and $U_{13} = 0.553$. We label tetragonal directions $a = b$ and $c$ by indices 1, 2, and 3. We use true Cauchy stress $\sigma$ (force per unit deformed area) and Lagrangian strain $E = \frac{1}{2}(F^T \cdot F - I)$.

**Stress strain.**—$\sigma c_3 - E_3$ curves for fixed lateral stresses $\sigma_1 = \sigma_2$ are in Fig. 2, along with corresponding transformation paths in the $(F_1 = F_2, F_3)$ plane. The elastic instability occurs when the determinant of the elastic moduli tensor, modified by some geometrically nonlinear terms, reduces to zero [6–10]. This results in a condition that some elastic moduli (or combination thereof) reduce to zero. We will use an alternative (more strict) condition: Elastic lattice instability at true stress $\sigma$ occurs at stresses above (or below for the reverse PT) which the crystal cannot be at equilibrium. Instability points correspond to the stress maximum for forward (reverse) PT. The dashed line shows hydrostatic loading.

A tetragonal stressed lattice of Si I transforms into a tetragonal stressed lattice of Si II (Figs. 1 and 2), and the lattice instability does not change this tetragonal symmetry. The slope of the stress-strain curve is continuous and is zero at instability points. Under hydrostatic loading (dashed line in Fig. 2), a cubic lattice loses its stability under tetragonal
perturbations; i.e., there is a bifurcation from a primary isotropic deformation to a secondary tetragonal deformation; hence, the derivative at the hydrostatic instability point is discontinuous. Under both hydrostatic \( (\sigma_1 = \sigma_2 = \sigma_3) \) and uniaxial \( (\sigma_1 = \sigma_2 = 0) \) compression, there are three stress-free states (Fig. 1): Si I, Si II (stable or metastable enthalpy minima), and an intermediate unstable state at the SP (enthalpy barrier). Interestingly, a stress-free Si II is metastable with stable phonons \([21,41,42]\). Thus, one could search for a pressure-plastic shear path for arresting the metastable Si II, as suggested in Ref. [13] for any metastable phase. In experiments, a stress-free Si II was not observed.

**Elastic lattice instability.**—Conditions under two-parametric loading at \( \sigma_1 = \sigma_2 \) for forward (direct) (\( \sigma_{3y} \)) and reverse (\( \sigma_{3r} \)) PTs are approximated by linear relationships in Fig. 3. Tersoff-potential (TP) results from Refs. [11,12] for Si I \( \rightarrow \) Si II PT are generally in good agreement with the present DFT results; however, there is a difference for tensile and small compressive \( \sigma_1 \), where TP results are slightly higher and nonlinear. Under hydrostatic loading, the PT pressure from DFT and TP is 75.81 and 79.58 GPa, respectively.

The PT stress for uniaxial compression is \(-11.03 \text{ GPa} \) (\( \sigma_{3y} \)) at \( E_3 = -0.154 \). Then the pressure for uniaxial loading is \(-\sigma_{3y}/3 = 3.68 \text{ GPa} \), which is 75.81/3.68 = 20.6 times lower than the hydrostatic case. This characterizes the very strong effect of nonhydrostatic stresses on PT, which can partially explain a scatter in experimental data under quasi-hydrostatic conditions and a significantly lower experimental PT pressure than the predicted hydrostatic instability pressure. The instability lines are described by \( \sigma_{3y} = -10.9 + 1.20\sigma_1 \) for \( \sigma_1 \subset [-75.81; 17] \) and \( \sigma_{3y} = 7.175 + 0.4209\sigma_1 \) for \( \sigma_1 \subset [-70; 17] \). The theoretical strength is approximately \( \sigma_{3y} = -10.6 + 0.77\sigma_1 \) for \( \sigma_1 \subset [-15; 12] \). As it is close to our result, the instability in Ref. [23] is related to Si I \( \rightarrow \) Si II PT.

While the instability line for forward PT, calculated in Refs. [11,12] using TP, is quite close to our DFT results, for reverse PT the TP results are completely different from DFT. Thus, none of the classical potentials in Refs. [11,12] (Tersoff, modified Tersoff, and Stillinger-Weber) are able to describe the reverse PT.

**Metallization.**—This electronic transition from a semiconducting to a metallic phase (band gap \( \rightarrow \) zero) is caused by deformation of Si I under combinations of \( \sigma_1 \) and fixed \( \sigma_2 = \sigma_3 \) (Fig. 3). The band gap versus compressive or tensile strain is given in Fig. S2 [27]. The electronic transition is found to precede the structural PT for all combinations of stresses; i.e., a sufficiently deformed Si I under stress is metallic (Fig. 3). This transition does not change the continuity of the stress-strain curves and their first derivatives (Fig. 2); this differs from the stress discontinuity in magnetostructural phase transitions [43]. The metallization curve is closed in the \((\sigma_{3y}, \sigma_1)\) plane and surrounds the stress-free Si I; it can be approximated by two straight lines \( \sigma_{3y} = -5.605 + 0.8417\sigma_1 \) and \( \sigma_{3y} = 13.04 + 1.396\sigma_1 \) and a parabolic section \( \sigma_{3y} = 11.95 + 2.378\sigma_1 + 0.16\sigma_1^2 \). While one of the metallization lines is relatively close and approximately parallel to the Si I \( \rightarrow \) Si II PT line, two other lines are deeply in the region of stability of Si I (Fig. 3). Metallization occurs at compressive \(-36.82 \text{ GPa}\) and tensile \(+13.91 \text{ GPa}\) under hydrostatic pressure, \(-5.4 \) and \(+12.78 \text{ GPa}\) under uniaxial loading at \( \sigma_1 = \sigma_2 = 0 \) and \(-6.69 \) and \(+8.79 \text{ GPa}\) under biaxial loading at \( \sigma_3 = 0 \). Hence, the effect of nonhydrostatic stresses is extremely strong.

**Elastic lattice instability under triaxial loading.**—Evidently, DFT results for \( \sigma_1 \neq \sigma_2 \) case (Fig. 4) suggest that the criterion for forward Si I \( \rightarrow \) Si II PT is described accurately in 3D space of normal stresses by a plane:

\[
\sigma_3 = -9.911 + 0.4145(\sigma_1 + \sigma_2).
\]
It is very surprising that the elastic instability for a material with strong physical and geometric nonlinearities can be approximated by a linear criterion.

**Lattice instability under general stress tensor—The phase-field approach.**—As shown in Refs. [11,12,25,26], a PT condition linear in normal stress can be derived by the phase-field approach to martensitic PTs. Using several assumptions, the instability $\text{Si I} \rightarrow \text{Si II}$ PT criterion is

$$2W = \sigma : F_{I}^{T} \cdot \frac{d^2 U}{d n^2} \bigg|_{\eta=0} \cdot F_{I}^{T} \geq 2A,$$  

where deformation gradient $U_{I}(\eta) \equiv I + \epsilon_{I}(\eta)$, and other material parameters [e.g., elastic moduli and transformation strain $\epsilon_{I}(\eta)$] depend on the order parameter $\eta$, which changes during the transformation process from $\eta = 0$ for Si I [\(\epsilon_{I}(0) = 0\)] to $\eta = 1$ for Si II [\(\epsilon_{I}(1) = \epsilon_{I} = \text{diag}(\epsilon_{I11}, \epsilon_{I12}, \epsilon_{I13})\)]. $W$ is called the modified transformation work [11, and $A$ is the magnitude of the double-well barrier. For a cubic-to-tetragonal transformation, $[d^2 U]/(d n^2)_{\eta=0} = 2\text{diag}(b_1 \epsilon_{I1}, b_1 \epsilon_{I2}, b_1 \epsilon_{I3})$, where $b_1$ are the coefficients in the interpolation of $\epsilon_{I}(\eta)$. For the loading by three stresses to the chosen above faces, all tensors in Eq. (2) are coaxial, tensors $F_{I}^{T-1}$ and $F_{I}^{T}$ eliminate each other, and Eq. (2) reduces to the linear modified transformation work criterion:

$$W = b_3 \sigma_3 \epsilon_{I3} + b_1 (\sigma_1 + \sigma_2) \epsilon_{I1} = A.$$  

The equality is used to describe the combination of stresses at the limit of stability and calibrate material parameters. $W$ reduces to the transformation work for $b_1 = b_3 = 1$. The consequence of Eq. (3) for cubic-to-tetragonal PT is that, with $\epsilon_{I1} = \epsilon_{I2}$, the stresses $\sigma_1$ and $\sigma_2$ contribute to the instability criterion via $\sigma_1 + \sigma_2$, as in Eq. (1). Comparing Eqs. (3) and (1) with $\epsilon_{I1} = U_{I1} - 1 = 0.243$ and $\epsilon_{I3} = U_{I3} - 1 = -0.514$ leads to $A(\theta)/b_3 = 5.094$ GPa and $b_3/b_1 = 1.141$.

When shear stresses $\tau_{ij}$ are applied, causing nonzero deformation gradients $F_{21}, F_{31}$, and $F_{32}$, with rigid-body rotations excluded by imposing a constraint $F_{12} = F_{13} = F_{23} = 0$, Eq. (2) reduces to

$$W = b_3 \sigma_3 \epsilon_{I3} + b_1 (\sigma_1 + \sigma_2) \epsilon_{I1} + \frac{b_1 \epsilon_{I1} - b_3 \epsilon_{I3}}{F_{11} F_{22}} \left[ \tau_{32} F_{32}^{c} F_{11}^{c} + \tau_{31} (F_{31}^{c} F_{22}^{c} - F_{32}^{c} F_{21}^{c}) \right] = A,$$  

where $(b_1 \epsilon_{I1} - b_3 \epsilon_{I3})/A = 0.143$ and the terms proportional to $\epsilon_{I2} - \epsilon_{I1}$ are eliminated. With transformation shears absent in a cubic-to-tetragonal PT, the shear transformation work is absent. The terms proportional to the shear stresses are due to geometric nonlinearity (finite strains); they do not contain any additional material parameters. Shear stresses change the geometry of the crystal, and this affects transformation work along the normal components of transformation strain.

For the obtained parameters, and because $F_{32}^{c} > 0$ and $\tau_{32} > 0$, when $\tau_{32}$ and $F_{32}^{c}$ or $\tau_{31}$ and $F_{31}^{c}$ are applied alone, the contribution of shear stresses to $W$ is positive; i.e., they promote tetragonal instabilities. Shear stress $\tau_{31}$ (more exactly, elastic shear strain $F_{31}^{c}$) alone or with $\tau_{32}$ does not contribute to the instability condition; but $\tau_{32}$ contributes when two other stresses, $\tau_{31}$ and $\tau_{32}$, are applied simultaneously, and, depending on signs of all shear stresses, $\tau_{31}$ may promote or suppress tetragonal instability.

**Shear stress-strain curves and shear lattice instability.**—typical shear-stress–deformation-gradient ($\tau_{31} - F_{31}^{c}$) curves (Fig. S3[27]), shear instability starts at the maximum shear stress. This instability does not lead to Si II but rather to possible amorphization or hexagonal diamond Si IV (which is beyond our present focus).

Under an initial (before shear) hydrostatic compression, the shear instability at an infinitesimal shear starts at 72 GPa, i.e., below the tetragonal mode of lattice instability. This may explain amorphization in nanocrystalline Si I under increasing pressure when Si II PT is kinetically suppressed [44]. Amorphization may be caused by virtual melting [45] after crossing the metastable continuation of the melting line, as the melting temperature for Si reduces with pressure.

**Effect of shear stresses on tetragonal instability.**—$\sigma_1 - E_{3}$ curves were obtained for different fixed shears, along the path in the $(F_{1} = F_{2}, F_{3})$ plane corresponding to $\sigma_1 = \sigma_2$ before shear. The instability stress (Fig. S4) is determined as the local maximum of $|\sigma_3|$ (Fig. 2). While during shear $\sigma_1 \neq \sigma_2$, but their sum $\sigma_1 + \sigma_2$ practically does not change. That is why curves in Fig. S4 are given for the fixed values of $(\sigma_1 + \sigma_2)/2$.

Absolute and relative deviations between the actual instability stress $\sigma_1$ and $\sigma_{3}^{\text{a}}$ based on the analytical prediction (4) are small (Figs. S5 and S6) and can be neglected. Thus, the tetragonal lattice instability under the action of all six components of the stress tensor is described by the critical value of the modified transformation work [Eq. (4)], which (a) is linear in normal stresses, depends on $\sigma_1 + \sigma_2$, and has only two adjustable coefficients ($b_1$ and $b_3$), (b) is independent of $\sigma_1 - \sigma_2$ and shear stress $\tau_{31}$ acting alone or with one more shear stress, and (c) contains a geometric nonlinear term describing the contribution of all shear stresses without any additional adjustable parameters.

In summary, we augmented standard $T - P$ diagrams with criteria for structural and electronic instabilities (PTs) under a general applied stress tensor, providing guidance for more accessible processing routes for new or known high-pressure phases with novel properties. Our comprehensive DFT study of the PT between semiconducting Si I and metallic Si II under general applied stresses investigated stress-strain curves, elastic lattice instabilities, and regions of metallization. Metallization occurs deeply in the region of stability of Si I and is not caused by Si I $\rightarrow$ Si II PT. Deformed Si I becomes metallic, and the effect of
nonhydrostatic stresses is very strong. The hydrostatic PT pressure is ~21 times larger than for uniaxial loading. Such a strong nonhydrostatic stress effect at least partially explains the significant difference between the observed PT pressure (9–12 GPa) and the instability pressure of 75.81 GPa and the scatter in measured data under quasi-hydrostatic conditions. Our key result is that Si I → Si II PT is given by a critical value of the modified transformation work [Eq. (4)]. For a general stress tensor (six independent variables), the PT criterion has just two parameters. Hence, PT criterion can be determined by just two DFT calculations versus applied stress.

These results are significant for creating new, more practical, and economical processing routes for discovery and stabilizing materials with novel properties. While comparison of the Gibbs free energy minima defines thermodynamic equilibrium (possibly unachievable in practice), we suggest the competition of instabilities to serve for phase selection. Critically, this approach enables ways to reduce PT pressure due to nonhydrostatic stresses by an order of magnitude or more [5,13−15]. They can also be used for quantitative studies of the influence of crystal defects on phase transitions [17,18] and quantitatively rationalize connections between PT conditions for ideal and real (defective) crystals.

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[27] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.121.165701 for simulation methods, a comparison of results with DFT and Tersoff potentials, the electronic band gap under loading, shear lattice instability, the effect of shear on tetragonal instability, and Refs. [28–38], as well as the data sets for all figures [39].


SUPPLEMENTAL MATERIAL

Lattice instability during solid-solid structural transformations under general applied stress tensor: example of Si I $\rightarrow$ Si II with metallization

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SIMULATION METHODS

We used DFT as implemented in VASP [1–3] with the projector augmented waves (PAW) basis [4, 5] and PBE exchange-correlation functional [6]. The PAW-PBE pseudopotential of Si had 4 valence electrons ($s^2p^2$) and 1.9 Å cutoff radius. The plane-wave energy cutoff (ENCUT) was 306.7 eV, while an augmentation charge (ENAUG) was 322.1 eV. We used a Davidson block iteration scheme (IALGO=38) for the electronic energy minimization. Electronic structure was calculated with a fixed number of bands (NBANDS=16) in a tetragonal 4-atom unit cell (a supercell of a 2-atom primitive cell). Brillouin zone integrations were done in $\Gamma$-centered Monkhorst-Pack mesh [7] containing 55 to 110 $k$-points per Å$^{-1}$ (fewer during atomic relaxation, more for the final energy calculation). Accelerated convergence of the self-consistent charge calculations was achieved using a modified Broyden’s method [8].

Atomic relaxation in a fixed unit cell (ISIF=2) was performed using the conjugate gradient algorithm (IBRION=2), allowing symmetry breaking (ISYM=0). The transformation path was confirmed by nudged-elastic band (NEB) calculations, performed using the C2NEB code [9]. We used DFT forces in ab initio molecular dynamics (MD) to verify stability of the relaxed atomic structures. Si atoms were assumed to have mass POMASS=28.085 atomic mass units (amu). The time step for the atomic motion was set to POTIM=0.5 fs. Additionally, our classical MD simulations used a Tersoff potential (TP), as described in [10].

CONVERGENCE OF STRESS-STRAIN CURVES OBTAINED WITH DFT AND TERSOFF POTENTIALS

Stress-strain $\sigma_3$–$E_3$ curves for a uniaxial compression at $\sigma_1 = \sigma_2 = 0$, obtained with DFT and Tersoff potential, are compared in Fig. S2. While the maximal stresses for Si I corresponding to the elastic lattice instability (see below) are comparable in both approaches, other features differ significantly, including elastic rule for Si I, strain for the lattice instability of Si I, and the transformation strain. The TP-based stress-strain curve does not intersect zero-stress axis, i.e., stress-free Si II is unstable in a classical force field. The same is true for the Stillinger-Weber and modified-Tersoff potentials [12].

DFT codes, including VASP, typically return energy with a fairly high precision, but have larger errors in stress components calculated using the Hellmann-Feynman theorem [11] within a less precise linear-response method. We avoided this issue by calculating the energy versus deformation on a grid and used exclusively finite differences to find derivatives of energy with respect to deformation and stress components.

As an example of convergence versus plane-wave energy cutoff (ENCUT) for the structure with $a = b = 4.1279$ Å and $c = 4.4638$ Å, identified as the stress barrier under uniaxial loading at $\sigma_1 = \sigma_2 = 0$, we fixed $a = b$, varied $c$ by ±1%, obtained the finite-difference derivative of energy $dE/dc \approx [E(c + \delta) - E(c - \delta)]/2\delta$, and plotted $\sigma_3$ versus ENCUT ($E_{\text{cut}}$) in Fig. S1. The chosen plane-wave energy cutoff of 306.7 eV is sufficient to achieve convergence within ±0.1 GPa (1 kBar) for the finite-difference method, which we use.

FIG. S1. Convergence of stress component $\sigma_3$ obtained from energy derivatives calculated using finite-difference and Hellmann-Feynman linear-response methods. We use exclusively the finite differences. The chosen energy cutoff of 306.7 eV (vertical dashed green line) is sufficient to achieve convergence within ±0.1 GPa (horizontal dashed lines) within the finite-difference calculations.
BAND GAP UNDER TWO-PARAMETRIC LOADING

The electronic structure in Si I had been studied under different combinations of \( \sigma_3 \) and fixed \( \sigma_1 = \sigma_2 \). Examples of the electronic band gap vs. compressive or tensile strain are given in Fig. S3. For each \( \sigma_1 = \sigma_2 \), there is a strain \( E_3 \), for which the band gap reaches its maximum, while a substantial deformation in any direction reduces the band gap to zero producing the metallization curve, shown in Fig. 3 in the main text. The band gap is maximal near \( \sigma_1 = \sigma_2 = \sigma_3 \approx -10 \text{ GPa} \), see Fig. S3.

SHEAR STRESS-STRAIN CURVES AND SHEAR LATTICE INSTABILITY

Increasing simple shears \( F_{31}, F_{31}, F_{32} \) and their combinations were applied at various fixed \( F_{11} = F_{22} \) (2 – 3% before and after tetragonal instability points) and \( F_{33} \), for which stresses \( \sigma_1 = \sigma_2 \) were equal to values given in Fig. S4 before shear loading. Typical shear stress \( \tau_{31} \) deformation gradient \( F_{31} \) curves are shown in Fig. S4. Shear instability starts at the maximum shear stress. This instability does not lead to Si II but rather to possible amorphization or hexagonal diamond Si IV (which is beyond our present focus). Here we study the effect of shear stresses on the tetragonal instability mode, responsible for the PT to Si II, which typically happens before the shear instability is reached.

Under an initial (before shear) hydrostatic compression, shear stresses for any \( F_{31} \) in the cubic phase reduce with increasing volumetric strain and pressure (see curves for four lower combinations of \( F_3 \) and \( F_1 \) in Fig. S4 (a)), which is qualitatively consistent with the limited results in [16] for the \([1\bar{1}2](111)\) slip system. After reaching the instability pressure for Si I \( \rightarrow \) Si II PT and following the tetragonal branch of deformation gradient (see curves for three upper combinations of \( F_3 \) and \( F_1 \) in Fig. S4 (a)), a crossover is observed and a shear stress for any \( F_{31} \) increases with further growth of \( F_3 \) and volumetric strain, while the pressure reduces along the unstable branch of pressure – \( E_3 \) (or volumetric strain) curve. The shear instability at an infinitesimal shear starts at 72 GPa, i.e., below the tetragonal mode of lattice instability. This may explain amorphization in nanocrystalline Si I under increasing pressure when PT to Si II is kinetically suppressed [17]. Amorphization may be caused by virtual melting [18] after crossing metastable continuation of the melting line, since melting temperature for Si reduces with pressure.

The effect of pressure on the \( \tau_{31} - F_{21} \) curves is qualitatively similar to that for the \( \tau_{31} - F_{31} \) curves. However, a shear instability for any \( F_{21} \leq 0.25 \) starts after the tetragonal instability.

At a non-hydrostatic initial loading, the physics is essentially different. At the initial stress \( \sigma_1 = \sigma_2 = -69.61 \text{ GPa} \), shear instability for an infinitesimal \( F_{31} \) starts practically simultaneously with the tetragonal instability (see green curve for the middle values of \( F_3 \) and \( F_1 \) in Fig. S4 (b)). Before tetragonal instability, the shear instability shifts to larger

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FIG. S2. Comparison of the Cauchy stress vs. Lagrangian strain \((\sigma_3-E_3 \text{ curves})\) for a uniaxial compression along \( c \) at fixed lateral stresses \( \sigma_1 = \sigma_2 = 0 \) for Si I↔Si II PTs, obtained from DFT and Tersoff-based simulations.

FIG. S3. Band gap width in deformed Si I vs. strain \( E_3 \) at various fixed \( \sigma_1 = \sigma_2 \), ranging from –14 to +20 GPa.
Shear stress $\tau_{31}$ decreases with increasing $|E_3|$ monotonously, in contrast to hydrostatic loading. At the same time, shear instability occurs for $F_{21} > 0.2$ after tetragonal instability. Both $\tau_{31}$ and $\tau_{21}$ decrease with increasing $|E_3|$; for all $|E_3|$ and equal shears one has $\tau_{31} < \tau_{21}$. This tendency in stress-strain curves is kept to $\sigma_1 = \sigma_2 = -39.63$ GPa with increasing shear instability strain $F_{31}$ and without essential change in the instability strain $F_{21}$. Amplitude of both shear stresses increases with reducing $|\sigma_1| = |\sigma_2|$. Effect of lateral $F_1$ and corresponding axial $F_3$ compressions on both shear stress-strain curves reduces with decreasing $|\sigma_1| = |\sigma_2|$. At $|\sigma_1| = |\sigma_2| = 29.68$ GPa a crossover occurs, i.e., shear stresses slightly increase with $|E_3|$.

**EFFECT OF SHEAR STRESSES ON TETRAGONAL INSTABILITY**

The $\sigma_3 - E_3$ curves [along the path in the $(F_1 = F_2, F_3)$ plane corresponding to $\sigma_1 = \sigma_2$ before shear] have been obtained for different fixed shears. The instability stress in Fig. S5 is determined as the local maximum of $|\sigma_3|$, see Fig. S2. While during shear $\sigma_1 \neq \sigma_2$ but their sum $\sigma_1 + \sigma_2$ practically does not change. That is why curves in Fig. S5 are given for the approximately fixed values of $(\sigma_1 + \sigma_2)/2$.

In addition, absolute and relative deviations between the actual instability stress $\sigma_3$ and $\sigma_3^{\text{th}}$ based on the analytical prediction (see Eq. (4) in the main text)

$$W = b_3 \sigma_3 \varepsilon_{15} + b_1 (\sigma_1 + \sigma_2) \varepsilon_{11} + \frac{b_1 \varepsilon_{11} - b_3 \varepsilon_{15}}{F_{31}^c F_{22}^c} [\tau_{32} F_{32}^c F_{11}^c + \tau_{31} (F_{31}^c F_{22}^c - F_{32}^c F_{21}^c)] = A, \quad (S1)$$

are presented in Figs. S6 and S7. As we already discussed in the main text, shear stress $\tau_{31}$ alone does not contribute to the analytical instability condition (S1) and practically (within the relative error of 6%) does not affect the instability stress $\sigma_3$ in a broad range of shear stresses $\tau_{21}$ below the shear instability, which is approximately described by $\tau_{21}^{\text{th}} = 11.09 + 0.1470 \sigma_1$. Shear instability stress $\tau_{21}^{\text{th}}$ varies from 11.09 GPa at $\sigma_1 = 0$ to 0 at $\sigma_1 \approx -75.44$ GPa.

An increasing shear stress $\tau_{31}$ causes some reduction in the instability stress $\sigma_3$ (Fig. S5). The relative error of the instabil-
FIG. S5. The effect of various combinations of shear stresses on the tetragonal instability stress $\sigma_3$ for different $\sigma_1 = \sigma_2$. Points with the largest shear stress approximately correspond to shear instability. Straight inclined lines are linear approximations of the relationship between $\sigma_3$ and shear stresses for shear instability.

ity stress with respect to the analytical prediction (S1) for most combinations of $\tau_{31}$ and $(\sigma_1 + \sigma_2)/2$ is between $+4\%$ and $-6\%$. However, there are three outliers at a large shear stress $\tau_{31} > 8.5$ GPa. At these points, stresses $-(\sigma_1 + \sigma_2)/2$ are small (from $-2$ to $10$ GPa) and the corresponding instability stress $-\sigma_3$ is also small (10–18 GPa); a ratio of smaller numbers with finite absolute errors has a larger relative error. The absolute error $\sigma_3 - \sigma_3^{\text{an}}$ for these points is just within $\pm 1$ GPa, see Fig. S7. A larger error of $\pm 2$ GPa appears for small shear stresses but large $-\sigma_1$ and consequently $-\sigma_3$ (from 50 to 75 GPa), i.e., close to the shear instability. A relative error there remains within $\pm 4\%$.

Thus, the main effect of a shear stress $\tau_{31}$ on the instability stress $\sigma_3$ is due to the theoretically predicted geometric non-linearity with zero linear term. The combined effect of two and three shear stresses on the instability stress $\sigma_3$ is smaller than the effect of $\tau_{31}$ alone (a) because of a smaller averaged shear stress that causes shear instability and (b) because of a small contribution of $\tau_{21}$ for two shear stresses and opposite contribution of $\tau_{21}$ for three stresses, according to Eq. (S1) for all positive shear stresses. Deviation from the prediction (S1) does not exceed $\pm 4\%$.

Thus, the tetragonal lattice instability under action of all six components of the stress tensor can be described by the critical value of the modified transformation work, namely, by Eq. (S1), which (a) is linear in normal stresses, depends on $\sigma_1 + \sigma_2$, and has only two adjustable coefficients ($b_1$ and $b_3$); (b) is independent of $\sigma_1 - \sigma_2$ and shear stress $\tau_{21}$ acting alone or with one more shear stress; (c) contains a geometric nonlinear term describing contribution of all shear stresses without any additional adjustable parameters.

For a neglected effect of shear stresses, an absolute deviation of $\sigma_3$ from the linear expression (3) in the main text is within 2 GPa for $\tau_{31} < 5$ GPa and within 3 GPa for $\tau_{31} < 8$ GPa, while its relative deviation is within $10\%$ for $\tau_{31} < 8$ GPa.
FIG. S6. Relative difference between the actual instability stress $\sigma_3$ and the instability stress $\sigma_{3}^{\text{an}}$ based on analytical prediction Eq.(S1) and corresponding values of $-\frac{(\sigma_1 + \sigma_2)}{2}$ versus shear stress $\tau_{21}$.

FIG. S7. Absolute and relative difference between the actual instability stress $\sigma_3$ and the instability stress $\sigma_{3}^{\text{an}}$ based on analytical prediction Eq.(S1) and corresponding values of $-\frac{(\sigma_1 + \sigma_2)}{2}$ versus shear stress $\tau_{31}$. 