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Predicted Simple-Cubic Phase and Superconducting Properties for Compressed Sulfur

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First-principles calculations predict that compressed sulfur favors the simple-cubic structure over a wide range of pressures (280 to 540 GPa), contrary to expectations based on the high-pressure phase diagrams of the heavier chalcogenides selenium and tellurium. The calculated phonon spectrum and electron-phonon coupling strength for the lower-pressure β-Po phase is consistent with the measured superconducting transition temperature of 17 K at 160 GPa. The transition temperature is calculated to drop below 10 K upon transformation to the predicted simple-cubic phase.

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The group-VIa elements exhibit a rich variety of structures both at ambient pressures and upon compression [1–5]. At low pressure, sulfur, selenium, and tellurium crystallize in different sequences of insulating molecular solids, but with enough compression they all adopt a metallic base-centered orthorhombic (bco) structure. At higher pressures, all three elements are observed to transform into a rhombohedral β-Po structure, which can be viewed as a simple cubic lattice compressed along the body diagonal. Se and Te are observed to transform into the body-centered-cubic (bcc) phase with even further compression; for S, the bcc phase is predicted theoretically to become stable at 550 GPa [6], but this pressure has not yet been attained in experimental studies of compressed S. Electrical [7,8] and magnetic [9] measurements find the bco phase of all three materials to be superconducting, with superconducting transition temperatures near the bco transition of $T_C \approx 10$, 5, and 3 K in S, Se, and Te, respectively. Recent experiments show that S differs from the heavier chalcogenides in that T_C increases rather than decreases with pressure, rising to 14 K just below the crystallographic transformation to the β-Po phase at 160 GPa [9]. At the transition, T_C jumps to 17 K, which is the highest known superconducting transition temperature among elemental solids. Earlier first-principles calculations had predicted the hypothetical bcc phase of S to be superconducting with a similar transition temperature of about 15 K near 550 GPa [6].

The observed high T_C and positive dT_C/dp in S near 160 GPa and the predicted high T_C at much higher pressures are intriguing and raise the question of what happens at intermediate pressures. Here we present first-principles studies of the structural phase transformations and electron-phonon coupling in S at pressures above 160 GPa. We predict that, contrary to expectations based on the behavior of Se and Te, S does not transform directly from the β-Po phase into the bcc structure with increasing pressure, but rather favors the simple cubic (sc) structure at intermediate pressures. This is surprising because the openness of the sc structure does not make it an immediately apparent candidate for a high-pressure phase [10]. Moreover, calculations for Se and Te show that the sc structure is not only energetically unfavorable, but also elastically unstable at positive pressures [11,12]. The stability of the sc structure in S can be understood in terms of the role played by $3d$ valence states that become increasingly occupied with pressure. For the electron-phonon coupling strength in compressed S, our results are consistent with the large observed value of T_C near the transformation to the β-Po phase, and we predict a drop in T_C upon the structural transformation to the sc phase. The drop is attributable to a hardening of the phonon spectrum.

The calculations are performed in the local density approximation (LDA) of density functional theory; the Kohn-Sham equations are solved self-consistently using the Perdew-Zunger parametrization of the correlation energy [13]. The core electrons are eliminated from the calculation by using a pseudopotential generated by the improved Troullier and Martins scheme [14]. A kinetic energy cutoff of 70 Ry is used for the plane-wave expansion of the Kohn-Sham orbitals. These are calculated on a mesh of 20^3 $\mathbf{k}$ points in the Brillouin zone [770 in the irreducible Brillouin zone (IBZ) for the β-Po structure]. A variable-cell-shaped molecular-dynamics approach is used to optimize structures at a given pressure [15]. To accelerate convergence for this metallic system, we use first-order Hermite-Gaussian smearing with a width of 0.01 Ry [16]. The vibrational properties and the electron-phonon coupling are determined using the linear-response approach for calculating the self-consistent first-order change in the electron density with respect to atomic displacements, again in the LDA [17]. This change is used to calculate the dynamical matrix for 32 and 35 irreducible phonon wave vectors $\mathbf{q}$ in the β-Po and sc Brillouin zones, respectively. Diagonalization of these dynamical matrices yields the phonon eigenvectors and frequencies.

The sc, bcc, and β-Po structures can all be described using a single-atom rhombohedral unit cell with rhombohedral angles α of 90°, 109.47°, and about 104°, respectively. Figure 1 shows the calculated total energy as a function of the rhombohedral angle for constant unit-cell volumes. For a volume of 56 a.u., which corresponds to

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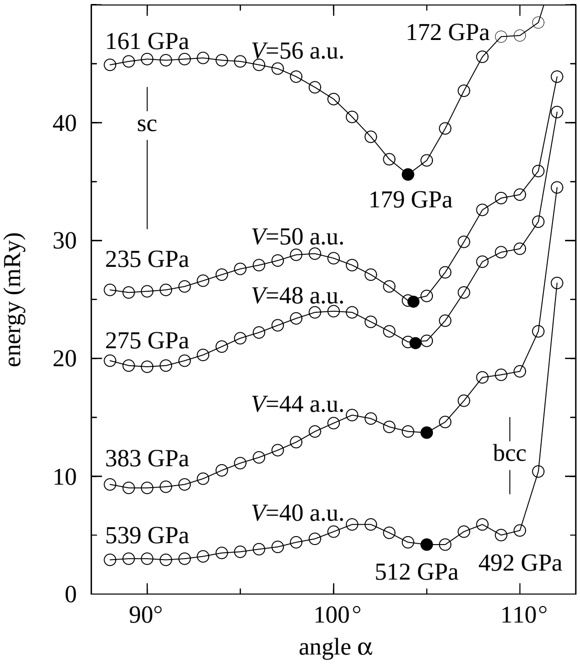

FIG. 1. Total energy of constant-volume rhombohedral structures as a function of the rhombohedral angle α. The curves have been shifted in energy by arbitrary amounts to facilitate comparison of the results for different volumes. The pressure is given at $\alpha = 90°$ for each volume and for the local β-Po minimum and bcc structure at the largest and smallest volumes. Solid circles mark the angle corresponding to the local β-Po minimum.

a pressure slightly larger than the experimental β-Po transition pressure, the β-Po structure with $\alpha = 104°$ is the only stable rhombohedral structure with $\alpha \geq 90°$. With decreasing volume, local minima appear both at $\alpha = 90°$ (sc) and $\alpha = 109.47°$ (bcc). The sc structure is lowest in energy at volumes between about 49 and 39 a.u., and the bcc structure is favored at smaller volumes. The β-Po structure remains a local minimum throughout this range of volumes, with α increasing to about 105° at 39 a.u. For any given volume, only a few values of α correspond to structures under hydrostatic pressure, i.e., structures with diagonal stress tensors whose elements are equal to the external pressure. The values $\alpha = 90°$, $\alpha \approx 104°$, and $\alpha \approx 109.47°$ are always among these.

We have investigated several additional structures, but none was found to be competitive in energy with the sc, bcc, and β-Po phases in the pressure range of interest. These include the α-Hg structures with a rhombohedral angle $60° \leq \alpha \leq 90°$ (where $\alpha = 60°$ is the face-centered-cubic structure), the simple hexagonal, the Cs-IV, and the related β-Sn structures.

The transition pressures for the β-Po → sc and sc → bcc transformations can be determined by comparing the enthalpies as a function of pressure, as shown in Fig. 2. The sc structure lies lowest in enthalpy in the pressure range 260–540 GPa. Since we find that the phonon spectra of the β-Po and sc structures differ significantly near the transition to the sc phase, zero point contributions should be considered in estimates of the transition pressure. As is discussed in more detail below, at a pressure of 280 GPa the average phonon frequencies $\langle \omega \rangle$ are 13.9 and 17.4 THz for the β-Po and sc structures, respectively. This difference shifts the enthalpy curve for the β-Po structure down relative to the sc enthalpy by approximately 1.6 mRy near the transition, thereby increasing the $T = 0$ transition pressure to approximately 280 GPa.

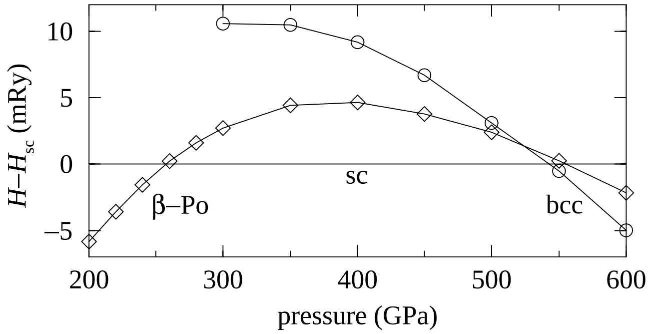

FIG. 2. Calculated enthalpy H for β-Po and bcc S, relative to the sc structure, as a function of pressure. The sc structure is lowest in enthalpy in the pressure range 260–540 GPa (at $T = 0$).

At high pressures, where empty space in the lattice is energetically expensive, the stability of S in the sc structure, which is very open compared to both the bcc and β-Po structures, is surprising. In fact, calculations find the sc structure to be unstable for both Se and Te at high pressures [11,12], and indeed it has not been observed in experiments. While S, Se, and Te are chemically similar, the fact that S has no d states in the core means the valence electrons experience a much stronger d potential in S. At low pressures, the $3d$ states lie just above the Fermi level in S, and the transfer of electrons to these d states upon compression is the key to stabilizing the sc structure. The repulsive Hartree and ion-ion $1/r$ interactions favor closely packed structures with more uniform distributions of charge, whereas the attractive electron-ion Coulomb interaction favors open structures which tend to have very nonuniform charge distributions. Because electrons occupying d states in compressed S see a deep ionic potential, there is a range of pressures in which the open sc structure is energetically favored, in contrast to Se and Te which have much weaker d potentials. Eventually, with enough compression, the repulsive Ewald term dominates, and the more closely packed bcc structure becomes favored in all three materials.

This raises the question of why compressed solid S first appears in the β-Po structure before entering the sc phase. Figure 3 shows the electronic density of states (DOS) for the sc and the β-Po structures at a volume of 56 a.u., where the β-Po structure is stable. For both structures a valley appears near the top of the occupied states. The

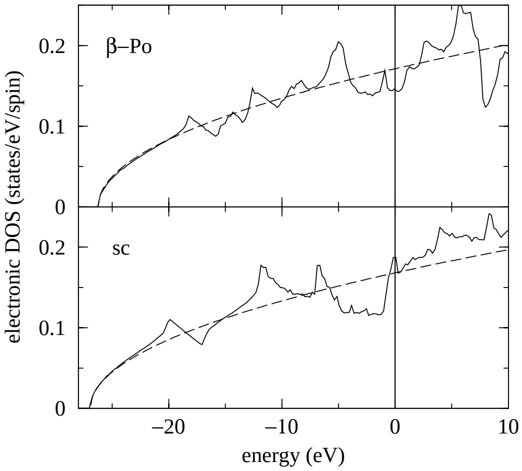

FIG. 3. Electronic density of states for β-Po and sc S at unit cell volume 56 a.u. The Fermi level is at 0 eV. Relaxing the sc structure into the β-Po structure by compressing it along the body diagonal brings the Fermi level into a valley in the DOS.

Fermi level lies just above the valley for the sc structure, whereas for the β-Po structure the Fermi level sits in the valley. The one-electron energy thus favors a distortion of the sc lattice into the β-Po structure at this volume. There is no energy barrier to this distortion (see Fig. 1). With increasing pressure the peaks and valleys in the DOS are washed out and the sc phase stabilizes, separated from the β-Po structure by an energy barrier.

Table I compares the β-Po structure at three pressures and the sc structure at the transition pressure in terms of parameters that characterize the phonon spectra and the electron-phonon coupling. At 160 GPa, where β-Po S is experimentally observed to be superconducting with $T_C = 17$ K [9], we find the electron-phonon mass renormalization parameter λ to be only moderately large at 0.76. This is significantly smaller than experimental and theoretical estimates for λ in Nb, for example, which has a smaller T_C of 9.2 K [18]. It is also smaller than estimates of λ for In, which superconducts at 3.4 K [19]. Our result for β-Po S, however, is consistent with the large measured transition temperature because the scale of phonon energies in compressed S is very high, e.g., approximately a factor 4 (8) that of Nb (In). The approximate formula of Allen and Dynes [20] relates T_C to λ, $\langle\omega_{ln}\rangle$ (an average of the phonon frequencies weighted to reflect the strength of the electron-phonon coupling), and the Morel-Anderson pseudopotential μ^*, which is an effective Coulomb repulsion parameter that is not easily calculated from first-principles. To reproduce the measured value of T_C at 160 GPa using the calculated values for λ and $\langle\omega_{ln}\rangle$, we need to assume $\mu^* = 0.11$, which is well within the range of typical values for this parameter.

TABLE I. Calculated values of phonon and electron-phonon coupling parameters for the β-Po and sc structures at various pressures. The q-points used for the β-Po structure are from a $6 \times 6 \times 6$ mesh (32 q-points in the IBZ), while those used for the sc structure are based on a $8 \times 8 \times 8$ mesh (35 q-points in the IBZ). The transition temperatures are estimated with the Allen-Dynes formula, in which the Morel-Anderson pseudopotential μ^* is fixed at 0.11, which gives the measured $T_C = 17$ K in the β-Po structure at 160 GPa.

α	P (GPa)	V (a.u.)	$N(E_f)$[a]	$\langle\omega\rangle$ (THz)	$\langle\omega_{ln}\rangle$ (THz)	λ	T_C (K)
104.00°	160	57.87	0.148	11.27	9.15	0.76	17[b]
104.11°	200	54.22	0.156	12.28	9.77	0.78	19.2
104.35°	280	48.77	0.152	13.89	10.28	0.66	13.5
90.00°	280	47.80	0.162	17.43	11.67	0.53	7.4

[a] States per eV per spin.

[b] Measured experimentally, Ref. [9].

The electron-phonon coupling parameter λ for β-Po S changes very little in going from 160 to 200 GPa, but it decreases as the transition to the sc phase near 280 GPa is approached. The contribution to λ from a given phonon wave vector $\mathbf{q}$ and branch ν can be written as $\lambda_{\mathbf{q}\nu} = \gamma_{\mathbf{q}\nu}/[N(E_F)\hbar\pi\omega_{\mathbf{q}\nu}^2]$, where $N(E_F)$ is the electronic density of states at the Fermi level, $\omega_{\mathbf{q}\nu}$ is the phonon frequency, and $\gamma_{\mathbf{q}\nu}$ is the phonon linewidth. The linewidth is proportional to $[N(E_F)]^2$ but does not depend explicitly on $\omega_{\mathbf{q}\nu}$. Between 160 and 200 GPa, the effect of an overall increase in frequencies is offset by increases in the linewidths, due in part to an increase in $N(E_F)$. At higher compressions, $N(E_F)$ decreases while the frequencies continue to rise, thereby driving the average coupling strength down. Assuming that μ^* remains constant [21], we estimate that over the range of stability of the β-Po phase, T_C first follows the increase in $\langle\omega_{ln}\rangle$, which sets the scale in the expression for T_C, then decreases as the coupling weakens at higher pressures.

We find that λ decreases further upon transformation to the sc structure, with $\lambda = 0.53$ in sc S at 280 GPa. The structure dependence of λ results primarily from differences in the phonon spectra of the two phases. Figure 4 shows the phonon density of states for the β-Po and sc structures at 280 GPa. The dramatic shift to higher frequencies in the sc phase arises in part because of a roughly 5% shortening of nearest-neighbor distances in going from the β-Po phase to the sc phase at this pressure, but more importantly because of the openness of the sc lattice. Since very little charge occupies the large interstitial regions in the sc lattice, the charge density along the bonds connecting neighboring atoms is large, resulting in a very stiff lattice. The smaller λ for the sc phase is attributable to the overall increase in phonon frequencies. The change in $\langle\omega_{ln}\rangle$ is significantly smaller than the jump in the average phonon frequency $\langle\omega\rangle$ because the former is most strongly influenced by low-frequency modes of which there are fewer in the sc phase. The net result is that the superconducting transition temperature is expected to decrease significantly upon transformation to the sc structure.

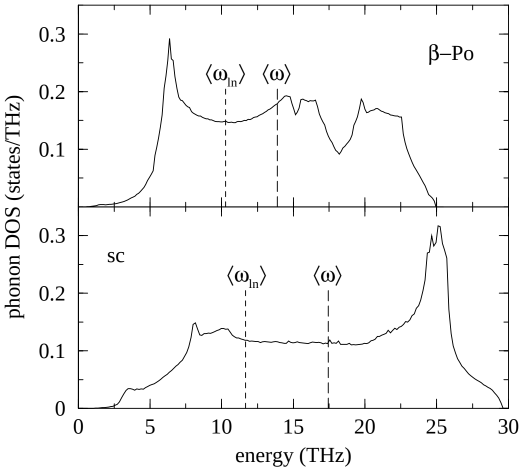

FIG. 4. Phonon density of states for β-Po and sc S at pressure 280 GPa. The strong shift to higher frequencies in the sc phase is brought on by a higher concentration of electrons in the sc bonds, which are also roughly 5% shorter.

In summary, first-principles calculations predict that compressed sulfur deviates from the bco → β-Po → bcc sequence of pressure-induced structural phase transitions observed in the isovalent elements, Se and Te. For S the sequence includes a sc phase: bco → β-Po → sc → bcc. We predict the sc structure will be stable at pressures near 280 GPa, which is within the range accessible in diamond anvil cell experiments. The calculated phonon spectra and electron-phonon coupling parameters are consistent with the large superconducting transition temperature that has been measured for β-Po S at 160 GPa, and they suggest a drop in the transition temperature to roughly 7 K in the sc phase.

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