

Superconductivity in the chalcogens up to multimegabar pressures

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Highly sensitive magnetic-susceptibility techniques were used to measure the superconducting transition temperatures in S up to $231(\pm 5)$ GPa. S transforms to a superconductor with T_c of 10 K and has a discontinuity in T_c dependence at 160 GPa corresponding to the bco to β -Po phase transition. Above this pressure, T_c in S has a maximum reaching about $17.3(\pm 0.5)$ K at 200 GPa and then slowly decreases with pressure to 15 K at the highest pressures measured. This trend in the pressure dependence parallels the behavior of the heavier chalcogens Se and Te. Superconductivity in Se was observed from 15 to 25 GPa with T_c changing from 4 to 6 K and above 150 GPa with T_c of 8 K. Similarities in the T_c dependences for S, Se, and Te, and implications for oxygen are discussed.

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I. INTRODUCTION

Comparative study of the high-pressure behavior of groups of elements with identical valences provides detailed insight into the effects of compression on electronic structure and its control of physical properties. The chalcogen elements, or members of group VIA, exhibit a variety of phases as a function of pressure and temperature and exhibit a broad range of interesting physical properties.¹ The lighter members of the family form molecular crystals. The first is oxygen, which forms a diatomic molecular crystal and persists in a variety of molecular phases to at least 100 GPa.² It also has peculiar magnetic interactions, being the only magnetic insulator among the elements.¹ At very high pressures, however, oxygen not only becomes metallic³ but is also superconducting⁴ above 95 GPa. Theoretical calculations predict that the high-pressure ζ -O₂ phase (above 95 GPa) is a molecular metal,⁵ while unambiguous experimental evidence of its molecular character is still not available. Sulfur, the next member of the family, has one of the most complex diagrams of the elements.¹ Under ambient conditions, sulfur is molecular and consists of S₈ species that form rings in the crystalline state. Under pressure, sulfur undergoes a series of both stable and metastable phase transitions up to ~ 90 GPa, finally becoming metallic at higher pressures.⁶

Under pressure the VIA elements below oxygen undergo structural phase transitions involving nonmolecular or extended structures and become metallic (with the exception of Po that is a metal at room pressure). Sulfur, selenium, and tellurium follow similar trends in the sequence of observed crystal structures. At comparatively low pressures, they crystallize in base-centered orthorhombic (bco) structures and are metallic and superconducting. The situation is more complex at pressures below the stability range of the bco phase. The observed sequence of phase transitions in Se below 30 GPa depends on the starting phase of the material.⁷ An unidentified metallic phase was found in Se (starting from about 13 GPa) that was observed to be superconducting with $T_c = 5.2$ K at 17 GPa.⁷ Sulfur also has an unidentified phase below 90 GPa,⁸ which is, however, semiconducting.⁶ On fur-

ther compression in the bco phase, S, Se, and Te transform to the rhombohedral β -Po structure. If compressed to even higher pressures at room temperature, Te and Se transform to the body-centered cubic (bcc) structure at 27 GPa (Ref. 9) and 140 GPa (Ref. 10), respectively.

The high-pressure structural and electronic properties of these elements have been the subject of a variety of theoretical studies. Pseudopotential total-energy calculations¹¹ have been performed for three high-pressure phases of S. They suggested that S should transform from the β -Po to the bcc phase at 545 GPa that would have a strong electron-phonon coupling leading to a superconducting transition temperature of 15 K. More recent first-principles calculations¹² predict that compressed S favors the simple cubic (SC) structure over a wide range of pressures from 280 to 540 GPa before transforming to a bcc phase. The later work also showed that upon entering the simple cubic structure, the average phonon frequency $\langle \omega \rangle$ increases substantially, leading to a smaller λ and thus smaller T_c . It was predicted that T_c would drop below 10 K upon entering the proposed simple cubic phase.¹²

Recent experimental studies^{13,14} showed that sulfur becomes metallic and superconducting at 93 GPa (with $T_c = 10.1$ K) and when pressurized above 160 GPa in the β -Po phase it has one of the highest known transition temperatures among the elements (17 K). Here, we present a comparative study of pressure-induced superconductivity in the chalcogens up to multimegabar (>200 GPa) pressures. We extended the measurements of superconductivity in S by magnetic susceptibility up to $231(\pm 5)$ GPa, which appears to be a record pressure for such an experiment. We also present results for T_c in Se by direct resistance measurements from 15 to 25 GPa and by magnetic susceptibility up to $180(\pm 5)$ GPa in the bcc phase.

II. EXPERIMENTAL DETAILS

We performed the measurements of T_c of S and Se using an improved extension of a highly sensitive diamond-anvil cell magnetic-susceptibility technique described previously.¹⁵ This technique is based on the quenching of superconductivity

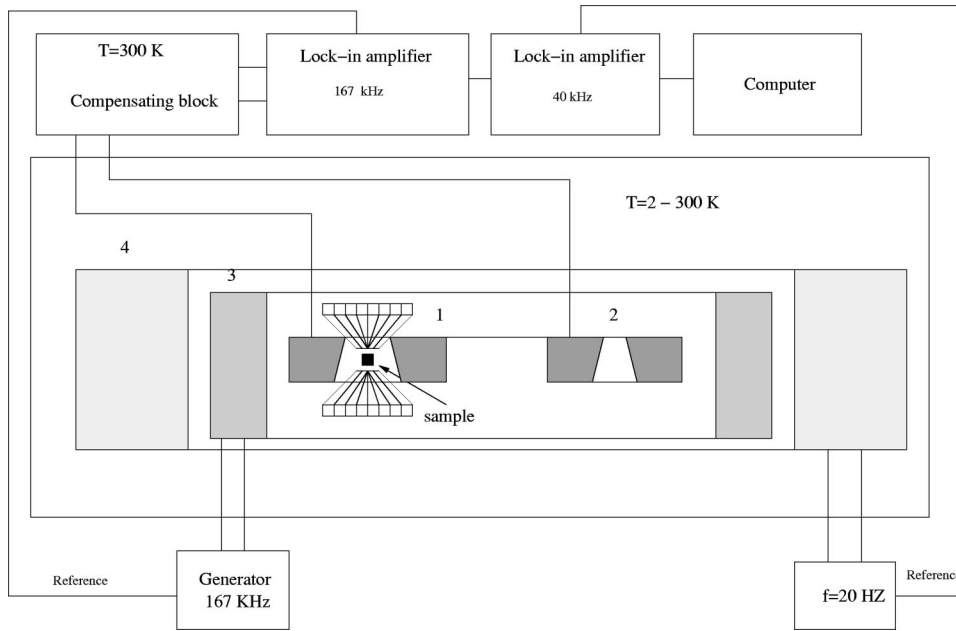


FIG. 1. Schematic diagram of the diamond-anvil cell magnetic-susceptibility technique used in these experiments.

ity and suppression of the Meisner effect in the sample by an external magnetic field. The susceptibility of the metallic diamagnetic parts of the diamond cell is essentially independent of the external field. Applying a magnetic field to the diamond cell (and sample) will therefore change the signal coming from the sample while the background arising from the surrounding diamagnetic parts will be nearly constant. The measurements are done with four coils (shown in Fig. 1). The two small coils consist of a signal coil, which is wound around the sample (1) and a compensating coil (2) connected in opposition. The excitation coil (3) encompasses both the signal and compensating coils. An alternating high-frequency magnetic field at the signal coil is created by the excitation coil fed from the high-frequency generator. The alternating magnetic field excites electromotive forces in the signal coil. The fourth coil (4) placed around the diamond cell is used to destroy the superconductivity in the sample near the superconducting transition by application of a low-frequency ($f=20$ Hz) magnetic field with an amplitude of several tens of Oersteds. This leads to a change in magnetic susceptibility of the sample from -1 to 0 twice in a given period and produces a modulation of the signal amplitude in the signal coil with a frequency $2f$. A lock-in technique is used to record this signal as a function of temperature. The technique sensitivity was improved recently by using a higher modulation frequency in the excitation-pickup coil set up.¹⁶

Samples of 99.9995% purity S were loaded in Mao-Bell cells¹⁷ made from Be-Cu and modified for measurements down to liquid helium temperatures. The gaskets made from nonmagnetic Ni-Cr alloy were used together with tungsten inserts to confine the sample, and no pressure transmitting medium was used. The gasket and insert may be responsible for the temperature dependent background seen in the raw temperature scans (e.g., Fig. 2). To reach pressures above 200 GPa we used beveled diamonds with 50- μm flats and 300 μm outer culets. The initial sample size was ~ 35 μm in

diameter and ~ 10 μm thickness. Pressures were measured by the ruby fluorescence technique (quasihydrostatic scale)¹⁸ using Ar^+ and Ti-sapphire laser excitation *in situ* at low temperatures.

For Se we performed direct conductivity measurements of sample resistance up to 35 GPa.¹⁹ Four electrical leads formed from platinum foil allowed four-electrode measurements of the resistance. To insulate the electrodes from the metallic gasket, an insulating layer made from a mixture of cubic boron nitride powder and epoxy was used. The superconducting transition was detected by direct resistance measurements and by using a modulating technique similar to that used in the susceptibility experiments. At higher pressures (up to 180 GPa), we used the magnetic susceptibility technique described above. The configurations of the cell,

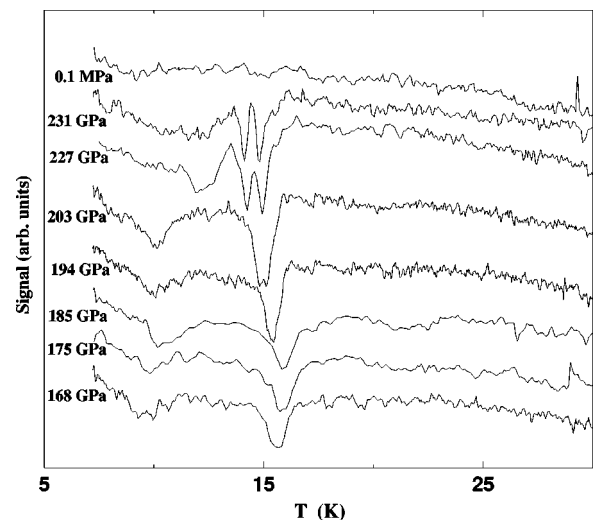


FIG. 2. Typical signal recorded for S during low-temperature scans. The top scan (background) was measured after the high-pressure run.

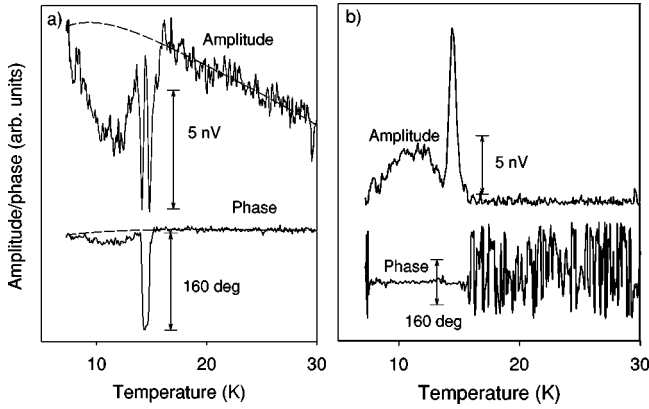


FIG. 3. Procedure for background subtraction. (a) Total signal can be represented as the complex variable $\mathbf{U} = A_{S+B}e^{i\phi_{S+B}}$ and the interpolated background is just $\mathbf{B} = A_B e^{i\phi_B}$. (b) The signal is equal to $\mathbf{S} = \mathbf{U} - \mathbf{B}$.

diamonds, gasket, and ruby fluorescence measurement technique were identical to that used in the S experiments.

III. RESULTS AND DISCUSSION

A. Superconductivity in S to 230 GPa

Several runs were made with decreasing sample sizes and diamond culet dimensions to successively higher pressures. Measurements are made as a function of temperature. Representative results are shown in Figs. 2–4. No superconductivity was detected up to approximately 90 GPa. At 93 GPa however, a peak characteristic of the superconducting transition to the superconducting state was observed.¹⁵ T_c is identified as the temperature where the signal goes to zero on the high-temperature side (e.g., Fig. 4), which is the point at which magnetic flux completely enters the sample.¹⁵ Two peaks are clearly seen at ~ 10 – 12 K and ~ 17 K. The second broad peak at lower temperatures arises from the sample outside of the flat culet, where pressure is considerably lower than in the middle of the culet. At pressures over 190 GPa

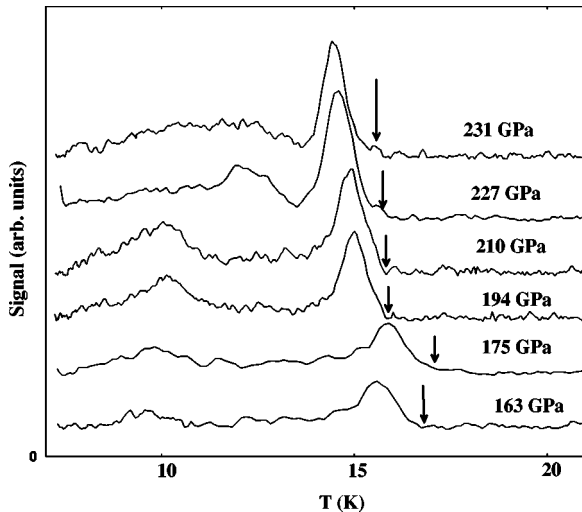


FIG. 4. Processed signal at a series of pressures for sulfur. The wide peak at lower temperatures is from the sample outside of the culet.

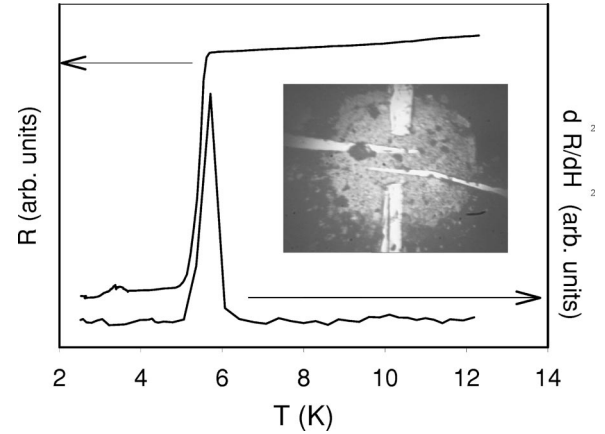


FIG. 5. Temperature dependence of resistance and resistance modulated by the magnetic field for Se. Inset: micrograph of the four-probe electrode arrangement used in these measurements.

the peak at 17 K becomes visibly split. This splitting is artificial and only reflects the fact that the signal amplitude has increased substantially with respect to the background.²⁰

The background signal in our measurements appeared to be ferromagnetic, as its phase is approximately opposite that of the signal from the sample (diamagnetic) (see Fig. 2). Because the background signal changes smoothly with temperature, we can separate the signal from the background by the simple procedure illustrated in Fig. 3. We measure the amplitude and phase of a sum of signal and background with the lock-in technique. The signal changes very abruptly in the vicinity of the superconducting transition, allowing us to see these changes both in amplitude and phase (Fig. 3). It is straightforward to interpolate the background in the range of the superconducting transition with a smooth polynomial function. The total signal can be represented as the complex variable $\mathbf{U} = A_{S+B}e^{i\phi_{S+B}}$, and the interpolated background as $\mathbf{B} = A_B e^{i\phi_B}$; our signal is then $\mathbf{S} = A_{S+B}e^{i\phi_{S+B}} - \mathbf{B}$ (the difference of two complex variables).

The signal with background subtracted is shown in Fig. 4. As in previous work,¹⁴ we observed the appearance of a T_c signal at ~ 93 GPa at 10 K. T_c gradually increases and upon entering the β -Po phase at 165 GPa it jumps to $17.0(\pm 0.5)$ K. For the next 35 GPa, it still slowly increases, reaching a weak maximum of $17.3(\pm 0.5)$ K at 180–200 GPa; it then decreases on further compression, dropping to 15 K at 231 GPa.

B. Superconductivity in Se to 180 GPa

Two sets of experiments were performed on Se. In the first experiment, we used 99.999% pure amorphous Se as the starting material with NaCl as pressure transmitting medium. Raman spectra showed that Se crystallized at around 11 GPa.²¹ A measurable T_c signal appeared at ~ 25 GPa at 5.8 K, in agreement with previous studies.²² Figure 5 shows the dependence of resistance and its modulations by the magnetic field as a function of temperature. In both cases, the onset of the superconducting transition in the sample is clearly seen. After reaching 35 GPa, the pressure was released. The T_c signal was observable down to 18 GPa and decreased with releasing pressure.

In the second set of experiments amorphous Se was pressurized up to 180 GPa and T_c was measured by susceptibility technique. Currently, it is difficult to measure T_c signals of $\sim 30 \mu\text{m}$ in diameter samples with this technique if the temperature of the superconducting transition is below 4 K due to a developing background signal that is probably related to paramagnetic signal from the gasket (tungsten inset and Ni-Cr-Al alloy gasket material). We were able to detect the superconducting signal in the bcc phase from 140 to 180 GPa. On decompression below 130 GPa, the measurable signal disappeared.

C. Comparison of T_c among the chalcogens

The pressure dependences of T_c in the group VIA elements are shown in Fig. 6, together with the observed transition pressures between the phases. It should be noted that the phase boundaries were determined by x-ray diffraction at room temperature while the observations of superconductivity were done at temperatures ranging from 2 to 18 K. It may be assumed that the phase boundaries at low temperatures (if any) would be shifted in pressure. The observed structures are illustrated in Fig. 7.

Tellurium becomes superconducting in the monoclinic phase at ~ 4 GPa. As shown in Fig. 6(c), T_c rises linearly with pressure in this phase upon transforming to the bcc structure, it levels off and starts to decrease, passing through the field of stability of the β -Po phase. T_c then jumps by almost a factor of three and starts to come down again. This jump in T_c happens at 35 GPa while room-temperature phase transition to bcc phase happens at 27 GPa.

Under ambient conditions, Se can be found in trigonal, monoclinic, or amorphous forms. Akahama, Kobayashi, and Kawamura⁷ showed that monoclinic and trigonal Se become metallic at 12 and 23 GPa, respectively. Under pressure amorphous Se crystallizes in a trigonal structure and becomes metallic at 12 GPa. It was shown⁷ that if α -monoclinic Se used as the starting material, it transforms at 12 GPa to an unidentified metallic phase that is superconducting at 17 GPa but no pressure dependence of T_c was given. Figure 6(b) shows our results for Se combined with the results of Ref. 22. The trend in the T_c dependence for Se is remarkably similar to that of Te, although unlike the latter, Se becomes metallic and superconducting in an unidentified phase from 14 to 23 GPa. The structural sequence is identical to that of Te starting from 23 GPa where Se enters the monoclinic phase. Unlike the situation for Te, T_c within this phase changes little with pressure. When Se is compressed further, the abrupt decrease in T_c starts at 33 GPa which can be attributed to the transition to the bco phase; this happens at 27 GPa at room temperature. There are no experimental measurements of T_c for Se from 60 to 150 GPa, but theoretical calculations²⁴ predict a decrease of T_c in the β -Po phase, followed by an increase to much higher values around 140 GPa where Se transforms to the bcc structure (at 300 K). The values of T_c in Se at 150–170 GPa measured here are very close to those calculated in Ref. 24.

The structures of the semiconducting phases of S below the 90 GPa transition are not known. The material becomes

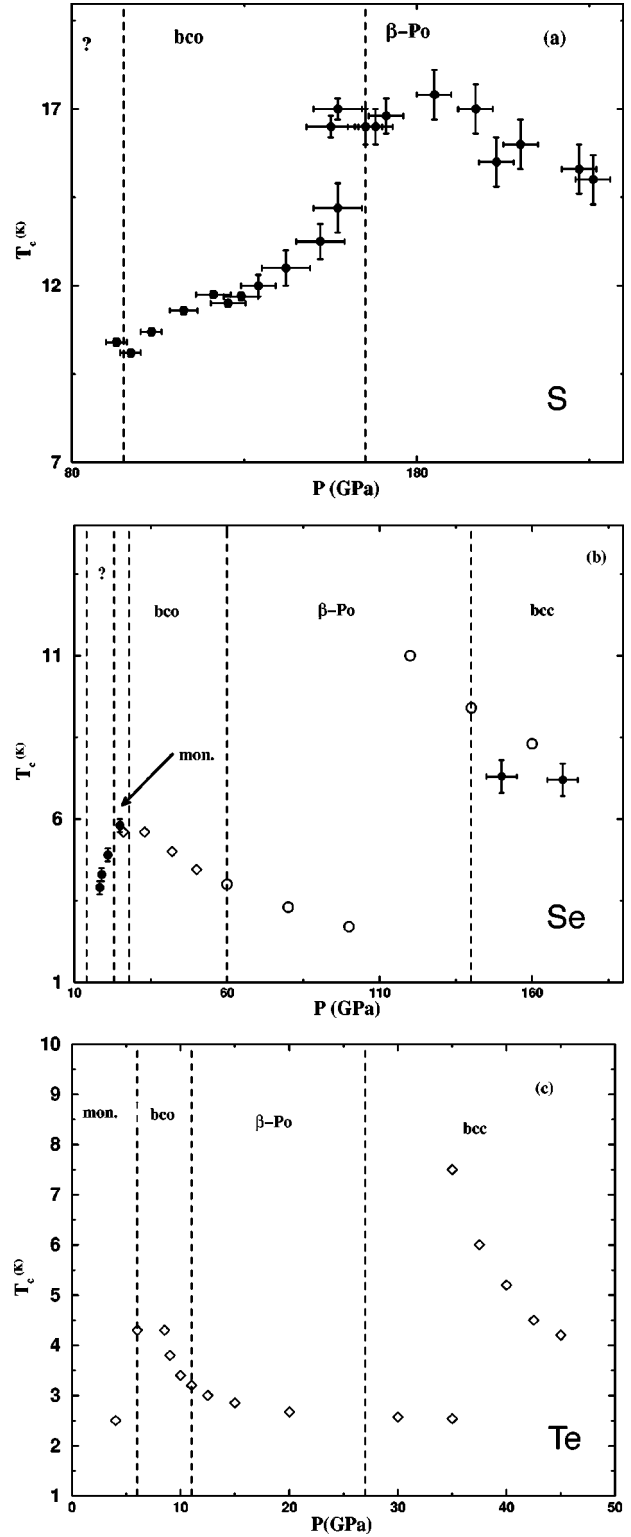


FIG. 6. Temperature dependences of $T_c(P)$ in (a) S, (b) Se, and (c) Te. The experimental points for Se and Te shown as open diamonds are from Refs. 22, 23. Theoretical results for Se are shown in (b) with open circles (Ref. 24). The dashed lines are the phase boundaries measured at room temperature by x-ray diffraction.

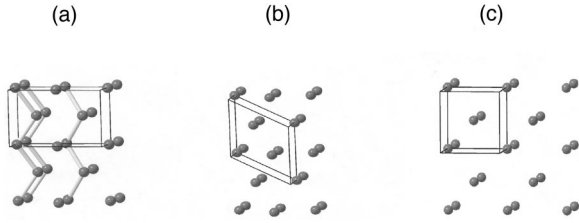


FIG. 7. Comparison between the (a) bco, (b) β -Po, and (c) bcc structures.

metallic and superconducting in the bco phase. Unlike the behavior of Se and Te, T_c in this phase of S increases with pressure and jumps abruptly upon entering the β -Po-type phase [Fig. 6(a)]. In the β -Po phase, T_c slowly decreases with further compression. This decrease is consistent with the theoretical calculations of Rudin and Liu,¹² which predicted a decrease in the electron-phonon coupling parameter λ as the sc phase is approached.¹²

It can be clearly seen from the behavior of T_c for the three elements that the transition temperatures cannot be simply explained by the existence of phase transitions and similar values for electron-phonon coupling alone. On the other hand, the similar trends are broadly consistent with changes towards higher-symmetry structures (transformation of layered phases to the close-packed structures at the highest pressures) with weakening of the directional covalent bonding, as we now discuss.

Mössbauer studies of Te showed a decrease in the quadrupole splitting with pressure that was ascribed to strengthened interactions between neighboring chains and weakening of the covalent bonds within the chain.²⁷ The splitting disappeared when Te was pressurized into the bcc phase where no covalent bonding is present. Thus we assume that the continuous weakening of the covalent bonds with increasing pressure arises from increasing screening by free carriers due to increasing density of states at the Fermi level.

To analyze the possible T_c increase in the lower-pressure phases of the chalcogens due to changes in phonon spectra, we estimated T_c in the lower symmetry “layered” structures (i.e., monoclinic, bcc) using the Allen-Dynes formula²⁵ with literature values of λ (electron-phonon coupling constant) and μ^* (effective Coulomb repulsion potential). We assumed $\mu^* = 0.1$ and varied λ . The values of $\langle\omega_{\log}\rangle$ and $\langle\omega^2\rangle$, the averages of the phonon frequencies weighted to represent the strength of the electron-phonon coupling, were estimated with a phonon density of states that was assumed to have two cutoff Debye frequencies with values typical for Se and Te corresponding to intralayer bond-stretching and interlayer vibrations. In our estimates of T_c vs pressure, the lower-energy peak attributed to interlayer vibrations was allowed to move towards higher energies with pressure while the higher-energy peak representing intralayer bond-stretching modes was assumed to be pressure independent. The values of T_c

obtained in these calculations are within the range of the experimentally observed T_c for Se and Te in their monoclinic and bco structures. However, T_c is virtually independent of phonon spectra but instead depends on λ . From experimental data, λ increases with pressure, meaning that $N(E_F)\langle I^2\rangle$ increases faster than $M\langle\omega^2\rangle$ (which does not change substantially in our simplified model), where $\lambda = N(E_F)\langle I^2\rangle/M\langle\omega^2\rangle$, according to McMillan.²⁶ Here $N(E_F)\langle I^2\rangle$ is the Hopfield parameter, which is generally assumed to be inversely proportional to volume in simple s - p metals.²⁶ Thus, the increase in T_c observed in the monoclinic phase of Te and the unidentified phase of Se where covalent bonding is still significant is most probably governed by the increase in Hopfield parameter with pressure. Sulfur has increasing T_c in its bco phase where covalent bonding is still present.

The bco \rightarrow β -Po \rightarrow bcc structural sequence may also be possible for oxygen, although the stability of its diatomic state appears to extend to very high pressures (> 100 GPa²⁸). It remains to be determined at what pressures the oxygen molecules dissociate (at low temperature), and what crystal structures would form. The additional complication with oxygen is its magnetic properties, which could play an important role in determining T_c . If oxygen follows a similar structural trend in its nonmolecular state, a similar T_c dependence might be expected. Recent calculations²⁹ suggest that could be in 1 TPa range.

IV. CONCLUSIONS

We have measured T_c of S up to 231 GPa, a record pressure for both superconductivity and magnetic susceptibility techniques. The value of T_c at the highest pressures (15 K above 200 GPa, decreasing from 17 K at 160 GPa) in accord with the original theoretical predictions for the hypothetical bcc phase and more recent calculations for the β -Po structure. The superconducting behavior of Se was observed in an unidentified phase from 14 to 20 GPa. The T_c for Se is also in very good agreement with recent first-principles calculations²⁴ (assuming β -Po, bcc, and fcc structures). The data obtained in the present work, previously published experimental data, and recent theoretical calculations for the chalcogens allow us to conclude that at lower pressures T_c is controlled at least in part by changes in covalent bonding. In higher pressures the bcc phases of these materials, the behavior of T_c resembles normal p metals and decreases with pressure.

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