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Study of compressed sulfur based on reliable first-principles calculations

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We investigated the high-pressure phases of sulfur using first-principles calculations with high precision. In a previous study, Rudin *et al.* [Phys. Rev. Lett. **83**, 3049 (1999)] predicted that the β-Po type rhombohedral structure is followed by a simple cubic (sc) structure. Strictly limiting the comparison to the work of Rudin *et al.* and four atoms per unit cell, our high-precision calculations that couple an originally developed structure search method demonstrate that the proposed sc structure is not the ground state at any pressure value, and that compressed S undergoes a first-order phase transition to a body-centered-cubic phase above 500 GPa. The potential energy surface constructed by the pseudopotential employed by Rudin *et al.* does not conform with that constructed by an all-electron calculation. Our findings extensively contribute to the ongoing effort in forming an accurate picture of the structural phase transitions of compressed S, and also brings to light the importance of careful treatments necessary when calculating high-pressure states using the pseudopotential method.

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I. INTRODUCTION

Chalcogens are a group of elemental solids that comprises sulfur (S), selenium (Se), and tellurium (Te), which are at the heart of high-pressure experimental and theoretical studies because of the rich variety of structures and electronic properties they exhibit. The element S is, especially, receiving increased attention due to its presence in the compressed carbonaceous sulfur hydride, which demonstrated room-temperature superconductivity recently [1]. Compressed elemental S was investigated by Luo *et al.*, and observed a β-Po type rhombohedral structure up to 262 GPa [2], but no further experiments have been reported since then. From first-principles calculations, Rudin *et al.* reported that the β-Po type structure transforms to a simple cubic (sc) structure at 260 GPa, and that it undergoes yet another transformation to a body-centered-cubic (bcc) structure at 540 GPa [3]. When the rhombohedral angle of the β-Po type phase is changed, it becomes face-centered cubic (fcc) at 60°, sc at 90°, and bcc at 109.47°. Based on this, they predicted the most stable structure by calculating the total energy as a function of the rhombohedral angle for constant unit-cell volumes. Recently, Gavryushkin *et al.* also reported similar results [4].

In recent years, the high-pressure phases of Te were experimentally investigated up to 330 GPa by Akahama *et al.* [5,6], and reported that the bcc phase transforms to a mixed phase at 100 GPa, in which the fcc structure coexists with the double hexagonal closed-packed (dhcp) structure. The dhcp structure coexists up to 160 GPa, and the fcc structure remains stable up to 330 GPa. Geshi and Funashima investigated this using an originally developed structure search method based on the first-principles calculations [7], and confirmed the coexistence of the dhcp structure from a computational perspective. In the study by Geshi and Funashima, the transition from the bcc to the fcc structure was also investigated from a microscopic point of view, and suggested that the bcc structure transforms to the fcc one via the tetragonal pathway, which is caused by a uniaxial distortion [7]. The rhombohedral pathway predicted by the changes in the rhombohedral angle is highly unlikely due to the high energy barrier involved. In the case of Se, the experimentally observed highest-pressure phase is the bcc structure at approximately 140 GPa reported by Akahama *et al.* [8], and this transition was computationally investigated by Geshi *et al.* [9] Rudin *et al.* reported structural transitions in the sequence β-Po → bcc → fcc from total energy calculations as a function of the rhombohedral angle for constant unit-cell volumes [10]. However, there are no reports of experimental observations of the fcc phase of Se thus far.

We revisited compressed S, and applied first-principles based structure searching to investigate the pressure-induced structural phase transition(s) that follow the β-Po type structure. The stable structures at different pressure values were investigated with high precision, and we obtained interesting results indicating that the sc structure proposed by earlier works is not the stable structure that follows the β-Po type phase. We report that the sc structure of compressed S is energetically unstable in contract to the works by Rudin *et al.* [3] and Gavryushkin *et al.* [4]. The sc structure does not have a lower enthalpy than the β-Po type structure in any pressure range as we show later. With these results at hand, we also make useful comparisons between S, Se, and Te. Through our study we bring attention to the importance of high computational precision required when predicting physical properties. In addition to selecting an appropriate cutoff energy and k-point sampling, it is important to ensure that the results produced by the pseudopotential method is consistent with the all-electron calculations.

Quite recently, Whaley-Baldwin *et al.* reported about compressed S with more than four atoms per unit cell, which also indicated the absence of the sc phase at high pressure [11,12]. They revealed an incommensurate host-guest (HG) phase [12]. We have confirmed that their proposed *Fdd*2 structure consisting of 16 atoms per unit cell takes lower enthalpy than those of the β-Po type and sc structures. We note that we are primarily focusing on structures with four atoms per unit cell because we wish to make useful comparisons with the works of Rudin *et al.* and Gavryushkin *et al.* By doing so, we focus on the importance of the computational precision determined by the cutoff energy and k-point sampling, and the necessity for cross validation between the all-electron method and the pseudopotential method.

II. COMPUTATIONAL DETAILS

We developed an original method that generates an initial set of structures covering the space groups of important crystal structures, and combined it with an approach to look for lower symmetry structures in a random manner [7]. Initial structures from space group index 75 ($P4$) through 230 ($Ia\bar{3}d$) were generated for a unit cell consisting of four atoms. These cover the tetragonal, trigonal, hexagonal, and cubic structures as initial structures. As the subsequent structural relaxations are performed without fixing the symmetry, the aforementioned symmetries apply only to the initial structures. Although low symmetry structures are covered to some extent during the structural relaxation, it may not be adequate to cover all the potential structures with a lower symmetry. Therefore, we reinforced this by investigating the possibility of lower symmetry structures in a random manner at a given pressure [7]. It is noted that we did not perform the structural relaxation for all the randomly generated initial structures. Instead, we picked a set of low enthalpy structures obtained from a self-consistent field calculation, and performed a full optimization on those chosen ones only. We generated 200 initial structures and selected 20 low enthalpy structures. Consequently, no structures with lower symmetry and enthalpy other than the bcc, sc, or β-Po type rhombohedral ones were found.

As emphasized in our previous work also [7], the crucial point is the precision of first-principles calculations, which requires sufficient cutoff energy and k-point sampling to correctly reproduce (or predict) a structure. Our calculations were performed using the ultrasoft pseudopotential [13] in the QUANTUM ESPRESSO package [14]. The cutoff energy for the wave function was 80 or 120 Ry, and the cutoff energy for the charge density was 960 or 1440 Ry, respectively. The Brillouin zone for each structure was sampled using the Monkhorst-Pack [15] k-point meshes of $24 \times 24 \times 24$. To ensure precision, we also sampled the meshes of $16 \times 16 \times 16$ and $32 \times 32 \times 32$. In confirming the *Fdd*2 structure with 16 atoms in the unit cell proposed by Whaley-Baldwin *et al.* [12], the cutoff energy for the wave function was set at 80 Ry, and a k-point mesh of $16 \times 16 \times 16$ was used. The full-potential linearized augmented plane wave (FLAPW) method of WIEN2K [16] was used to further confirm the precision. The $R_{\mathrm{MT}}K_{\max}$ was set to 10, and the k-point sampling was set to 110 points in the irreducible Brillouin zone. The exchange-correlation potentials were both based on the generalized gradient approximation (GGA) [17]. The same muffin-tin sphere was used for each volume.

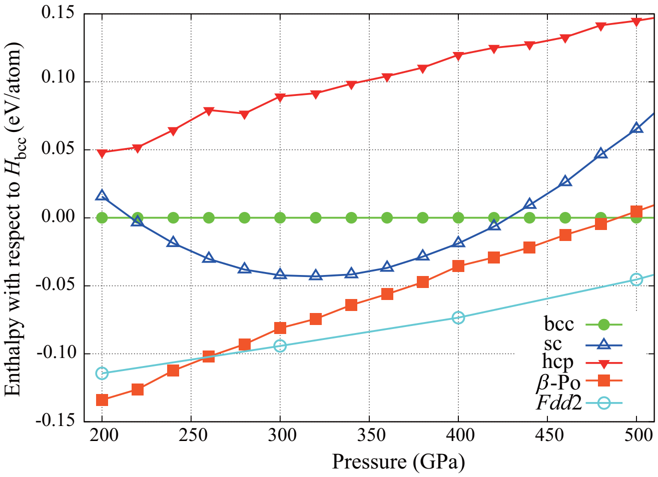

FIG. 1. The calculated enthalpy H for sc, hcp, β-Po, and *Fdd*2 structures of S relative to the bcc one as a function of pressure. The solid circle, open triangle, solid triangle, solid square, and open circle represent the enthalpies of the bcc, sc, hcp, β-Po, and *Fdd*2 structures, respectively. We note that the bcc, sc, hcp, and β-Po structures have four atoms per unit cell, whereas the *Fdd*2 one has 16 atoms per unit cell in reproducing the results of Whaley-Baldwin *et al.* [11]. The solid lines are guides to the eye.

III. RESULTS AND DISCUSSION

Figure 1 plots the enthalpies of the sc, hexagonal close-packed (hcp), β-Po type rhombohedral, and *Fdd*2 structures with respect to the bcc structure of compressed S. This is the result of plotting the lowest enthalpy structures produced by the structure search method at different pressure values. We note that these are not the results of calculations performed at different pressures assuming the four types of structures. Only the *Fdd*2 structure containing 16 atoms in the unit cell is assumed and fully relaxed in this work. The calculations were performed up to 2400 GPa. The fcc and dhcp structures found in the case of Te have higher enthalpies than the hcp structure, hence they do not appear near the most stable structure of compressed S, which is the β-Po type structure in the pressure range approximately below 500 GPa assuming four atoms per unit cell. The sc structure has an enthalpy close to the β-Po type one, but it is not the most stable structure at any pressure value. The sc structure is the third-lowest enthalpy structure from 220 to 420 GPa. This is the main difference between our results and those of previous studies by Rudin *et al.* and Gavryushkin *et al.* [3,4]. Our results are consistent with those of Whaley-Baldwin *et al.* with regard to the absence of the sc structure, and also the appearance of an *Fdd*2 structure when 16 atoms are considered in the unit cell.

Careful consideration of the calculation conditions used by Gavryushkin *et al.* indicates that the cutoff energy for the wave function was set at 350 eV(=25.7 Ry). We believe that this clearly results in less precision because the minimum

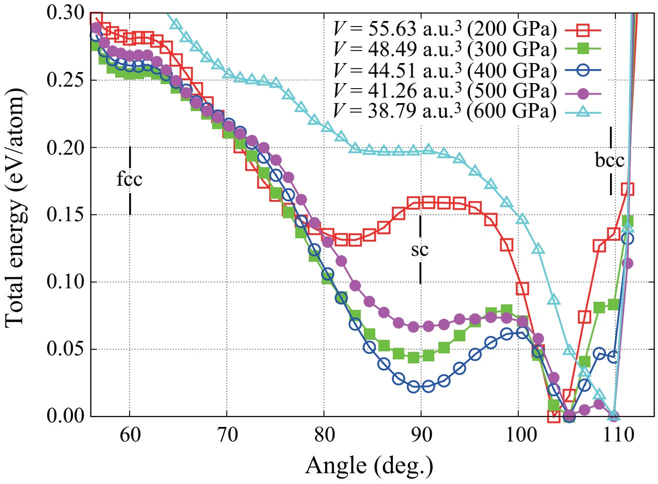

FIG. 2. The variation of the total energy as a function of the rhombohedral angle at constant unit cell volumes V of 55.63 a.u.^{3} (200 GPa) (open square), 48.48 a.u.^{3} (300 GPa) (solid square), 44.51 a.u.^{3} (400 GPa) (open circle), 41.26 a.u.^{3} (500 GPa) (solid circle), and 38.79 a.u.^{3} (600 GPa) (open triangle). The calculations are based on the ultrasoft pseudopotential method of QUANTUM ESPRESSO. The angle around 104° corresponds to the local β-Po minimum.

enthalpy difference in the pressure range 300–400 GPa is 0.0224 eV/atom. Our calculations show that the results obtained with a cutoff energy of 25 Ry entail an energy error of 0.1 eV/atom compared to a cutoff energy of 80 Ry used in our study, rendering 25 Ry not precise enough to discuss differences in the enthalpy of the structures under discussion. On the other hand, we note that the conditions of Rudin *et al.* with a cutoff energy of 70 Ry and k-point sampling of 20^3 are sufficient.

We also performed a structure search in a random manner [7] with a unit cell having four atoms at pressure values of 300, 400, and 1000 GPa. In our previous work, the aim of the structure search method was to reinforce areas of high symmetry in the search space by the structure search in a random manner. The approach here was basically equivalent, but the aim was to compensate for areas of lower symmetry in the search space by the structure search in the proposed random manner. This search method also confirmed that the β-Po type rhombohedral structure is the lowest enthalpy structure at 300 and 400 GPa given a unit cell of four atoms, as opposed to the previously proposed sc structure. At 1000 GPa, the lowest enthalpy structure is found to be a bcc one.

Figure 2 shows the change in the total energy when the rhombohedral angle is systematically changed at constant unit cell volumes of 55.63 a.u.^{3} (200 GPa), 48.48 a.u.^{3} (300 GPa), 44.51 a.u.^{3} (400 GPa), 41.26 a.u.^{3} (500 GPa), and 38.79 a.u.^{3} (600 GPa). These results also confirm that the proposed sc structure is not the lowest in energy in the specified pressure range (200–600 GPa). The sc structure does not become the most stable structure in the calculated pressure range according to our results and the recent work of Whaley-Baldwin *et al.* [12]. Even though the current results and those of Whaley-Baldwin *et al.* agree about the absence of the sc structure, converging upon agreeable results does not mean that we can overlook why there are considerable differences with the previous works. There is an important lesson to learn from these discrepancies with regard to calculating the high-pressure phases.

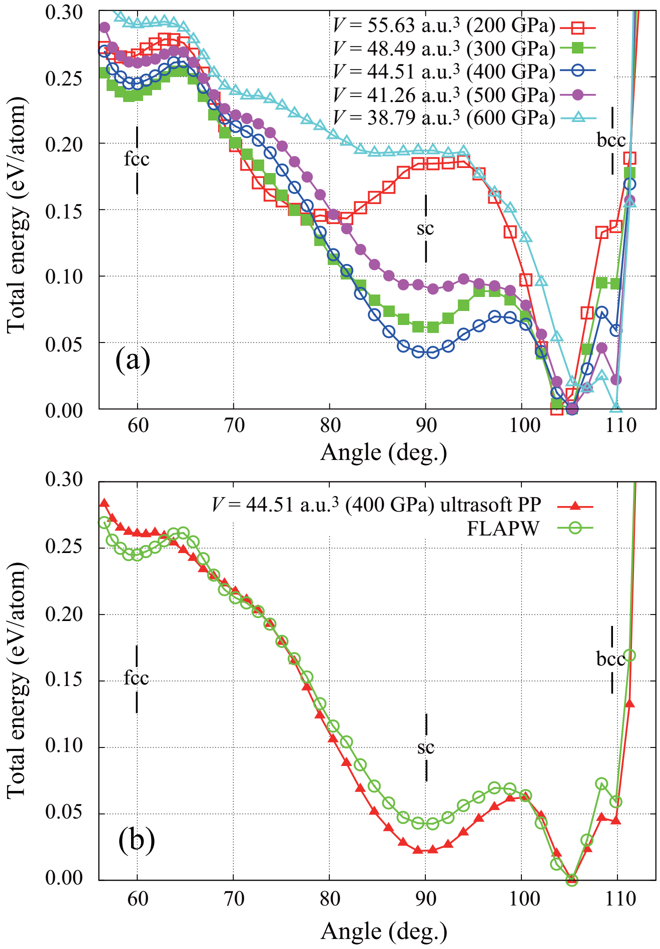

FIG. 3. The variation of the total energy as a function of the rhombohedral angle at constant unit cell volumes V. (a) The calculations based on the FLAPW method of WIEN2K at 55.63 a.u.^{3} (200 GPa) (open square), 48.48 a.u.^{3} (300 GPa) (solid square), 44.51 a.u.^{3} (400 GPa) (open circle), 41.26 a.u.^{3} (500 GPa) (solid circle), and 38.79 a.u.^{3} (600 GPa) (open triangle). (b) The comparison between the results obtained by the ultrasoft pseudopotential (PP) [9] method (solid triangle) and the FLAPW method (open circle) at the unit cell volume of 44.51 a.u.^{3} (400 GPa). The solid lines are guides to the eye. The angle around 104° corresponds to the local β-Po minimum.

As the results of Rudin *et al.* and ours are based on the pseudopotential method, it is difficult to draw any final conclusions as to which may provide a more accurate picture of the structural phase transitions of compressed S. In addressing this, we performed further calculations using the FLAPW method. The variation of the total energy as a function of the rhombohedral angle at constant unit cell volumes is shown in Fig. 3(a). The results of the ultrasoft pseudopotential and FLAPW methods at the unit cell volume of 44.51 a.u.^{3} (400 GPa) is shown in Fig. 3(b). It is evident that the β-Po type rhombohedral structure is the most stable, given that there are four atoms in the unit cell. In Fig. 3(b), the error in the region

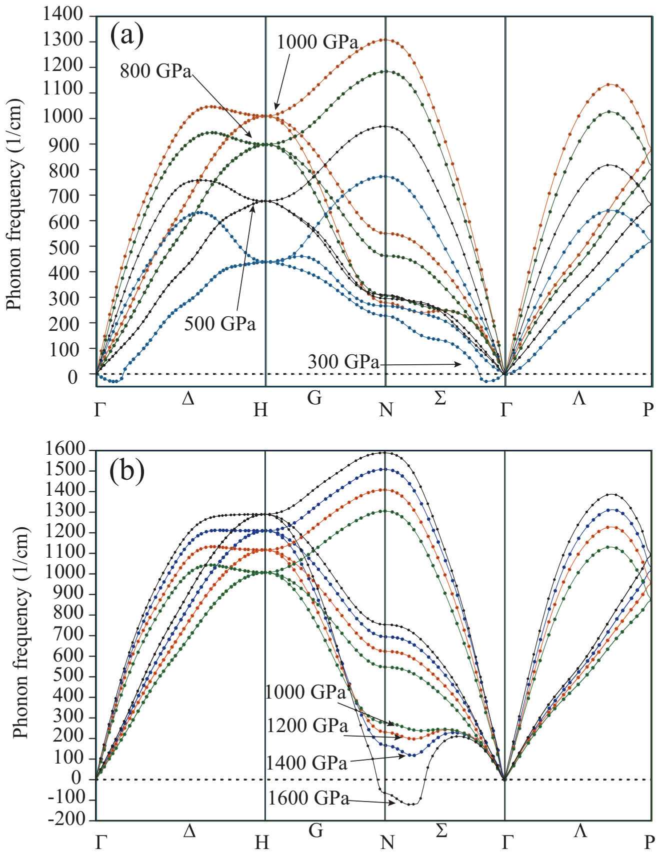

FIG. 4. The phonon dispersion curves of bcc S (a) at 300, 500, 800, and 1000 GPa, and (b) at 1000, 1200, 1400, and 1600 GPa. The solid lines are guides to the eyes.

around 90° is larger than the other regions, yet the results do not suggest that the sc structure is more stable than the β-Po type rhombohedral one.

We also investigated the stability of the bcc structure using phonon calculations with q-point meshes up to $8 \times 8 \times 8$ within the harmonic approximation. Furthermore, the elastic constant corresponding to the long wavelength approximation that cannot be covered by it was also investigated. In the absence of experimental results, it is important to consider both approaches even within the harmonic approximation. As can be seen from Fig. 1, the transition to the bcc structure from the β-Po type rhombohedral one occurs at approximately 500 GPa. We again note that we are comparing structures with four atoms per unit cell. However, the elastic constants of compressed S with the bcc structure are unstable at this pressure. The elastic constant C_{44} is negative although the phonon band dispersion with an $8 \times 8 \times 8$ q-point mesh is stable. The elastic constant C_{44} becomes positive at approximately 510 GPa. We note that this degree of calculation error is, however, acceptable. In Fig. 1, the interpolated intersection point is around 490 GPa, but we note that this pressure value is not accurate enough to strongly assert the difference between 500 and 490 GPa, especially, if and when the experimental value is observed.

Figure 4 shows the phonon dispersion curves of the bcc structure at 300, 500, 800, 1000, 1200, 1400, and 1600 GPa. The bcc structure is unstable at comparatively lower pressure, for instance at 300 GPa. It becomes stable around 500 GPa and again becomes unstable at around 1600 GPa. From the results of Whaley-Baldwin *et al.* the enthalpy of the bcc structure is lowest above 679 GPa following the structural transformation from their proposed HG structure [12]. It is not clear up to what pressure the bcc structure will remain stable. We performed the structure searching up to 2400 GPa using four atoms in the unit cell. The bcc structure is stable up to about 1600 GPa in enthalpy. However, the phonon dispersions show imaginary frequencies in the Σ axis at 1600 GPa. Unlike the others, the phonon dispersions in the Σ axis soften starting at approximately 800 GPa. These are signs that the bcc structure is becoming unstable. It is not possible to discuss the possibility of a true structure without investigating the possibility of structures composed of more atoms also. We have found a candidate structure, but it is not definitive. We need to examine it more carefully in terms of calculation precision.

The experiments [5,6] and first-principles calculations [7] of Te showed that the bcc structure is followed by the fcc one. The prediction for Se from first-principles calculations is quite similar [10]. But compressed S does not follow a similar trend. We do not observe a transition to the fcc structure at least up to 2400 GPa. However, since the results strongly depend on the precision of the calculations as we have shown here, it is necessary to examine carefully whether the calculation parameters are appropriate for thousands of gigapascal pressures.

Our results emphasize that the first-principles calculations under high pressure must be performed very carefully (see Figs. 2 and 3). Most pseudopotentials are precise only near 0 GPa, and their precisions have not been fully verified up to very high pressure. Only a very few have compared and verified their results based on the pseudopotential method with those obtained by the FLAPW one. When employing the pseudopotential method, one would do well to make sure that the results are consistent with the all-electron calculations. But in practice, such comparisons are scarcely performed. One should at least investigate how much deviation there is. The results based on the pseudopotential we used conform with the results from the FLAPW method as shown in Fig. 3(b). But we note that there are still considerable deviations. If such discrepancies affect the phonon calculations, it may have a bearing on the precision of the superconducting transition temperature, which we do not discuss here.

Whaley-Baldwin *et al.* performed very high-precision calculations as shown in their Supplemental Material [12]. They created a pseudopotential for sulfur specially aimed at high-pressure studies, and carefully checked the convergence of the calculation as a function of k-point sampling and cutoff energy. However, we found no comparison with the all-electron method. We believe that comparing the results of the pseudopotential and all-electron methods is very important, in particular when calculating the high-pressure states, even if one does not necessarily create a new pseudopotential.

In recent years, computational structure searching has become a very active and fruitful field. However, there are many cases where the precision determined by the cutoff energy and k-point sampling of the first-principles calculations is not sufficient. In particular, the cutoff energy is often important, however, increasing it increases the computational load. Calculations with increased k-point sampling are relatively easy to realize with parallel computing, however, on the other hand, calculations with increased cutoff energy are computationally limited. Just as a microscope with poor resolution cannot reveal fine structures, it is impossible to predict correct structures using calculations with insufficient precision. We believe that it leads to serious prediction failures like in the case of compressed S, unless careful attention is paid to parameter values, and the validity of the results is confirmed from multiple methods. In particular, these points become quite crucial when accurately predicting other related physical properties.

IV. CONCLUSIONS

In conclusion, we investigated compressed S with four atoms per unit cell using the structure-search method developed by us and showed that the β-Po type rhombohedral structure undergoes the transition to the bcc structure with increasing pressure at approximately 500 GPa, rather than the sc structure predicted by some of the earlier works. The bcc phase of S remains stable even up to at least around 1600 GPa in contrast to Te. Whaley-Baldwin *et al.* reported that at 679 GPa their proposed HG structure transforms to the bcc structure by using the PBE exchange-correlation potential [12]. After the transition to the bcc structure, they have not found any additional transitions either.

We note that very high precision and careful calculation considerations are required to produce these results. Whaley-Baldwin *et al.* also paid careful attention to such points. We highlight the importance of ensuring the precision of the first-principles calculations determined by the cutoff energy and the number of k-point sampling, and confirming the consistency of the results from the pseudopotential method with the all-electron calculation when searching for structures under high pressure. Our work renders an important example of this. Such considerations are of utmost importance given that they have serious implications not only on the accuracy of the crystal structure, but also the related physical properties of elemental solids and compounds.

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