to the transformation is virtually completely due to the boron nitride gasket material and other leaks in parallel with the sample. The resistivity of the sulfur at the transition has dropped from about 10^{15} Ω cm to about 10 Ω cm. Upon increasing the force further the B_4C pistons fractured. It is conceivable that the final resistance of this phase is at higher pressures still lower than found here. The lowest resistance found in any of our experiments was 500 Ω.

Altogether, 6 ZnS and S comparison pairs and 6 S and GaP pairs were studied. The sulfur transition occurred at a force midway between ZnS and GaP. Interpolation of the forces in a linear fashion leads to the conclusion that the transition pressure of sulfur is about 175 kbars (based on 145 kbars for ZnS and 205 kbars for GaP, the latter being the average of the values given in Refs. 6 and 8). (While we have some reservations about using linear interpolation, they are mild compared to our reservations about using linear extrapolation although the latter has been routinely used in high pressure work and has led to drastically wrong conclusions.)

The sulfur transition in our cell configuration showed considerable time dependence (unlike zinc sulfide); for example, a specimen left at constant loads above the transition begins pressure dropped in resistance from 10^4 to 10^3 Ω when held at constant load for 10 hrs. It is entirely possible that the kinetic processes in this transition are highly shear dependent.

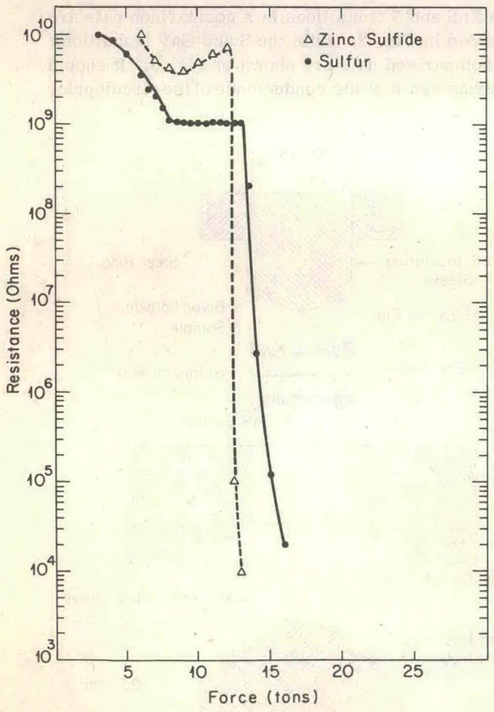

FIG. 2. Resistance versus force curves obtained simultaneously for ZnS and S. The resistance of the sulfur sample circuit prior to the transformation is primiaily due to the gasket and other factors rather than due to the sulfur sample itself. After the transition the resistance value for the sulfur circuit is essentially entirely due to the sulfur.

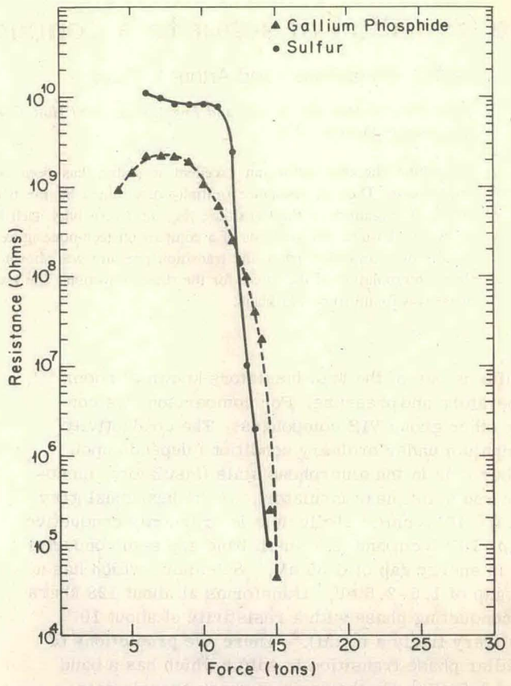

FIG. 3. Resistance versus force curves obtained simultaneously for S and GaP. The resistance of the sulfur sample circuit prior to the transformation is primarily due to the gasket and other factors rather than due to the sulfur sample itself. After the transition the resistance value for the sulfur circuit is essentially entirely due to the sulfur.

In addition to the 12 two-sample comparison experiments, seven experiments were carried out with single sample cells containing sulfur. In these cases the force at the transition could be compared with the forces required for the ZnS transition or the GaP transitions obtained earlier using the single sample cell. In all of these tests the force for the sulfur transition was less than the force required for the gallium phosphide transition but more than the force required for the zinc sulfide transition. Again, force comparison suggests a transition pressure of 175 kbars.

Several blank tests, in which solid BN pellets were used with no sample present, were made. In all cases the resistance remained high (10^9 Ω), so that any potential complicating factors which could be introduced by the gasket are eliminated.

In conclusion there is convincing evidence, from 19 tests, that sulfur transforms to a conductive phase at a pressure of 175 kbars.

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The transition of sulfur to a conducting phase

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Crystalline rhombic sulfur, an excellent insulator, has been converted to a conducting phase in 19 experiments. The cell resistance (initially determined by the boron nitride gasket) drops by at least six orders of magnitude at the transition; the sulfur resistivity itself has changed by a factor of 10^{-15} compared to its initial value. On the basis of a comparison technique utilizing a two sample cell with either ZnS and S pairs or S and GaP pairs, the transition pressure was shown to be between that for ZnS and for GaP. From interpolation of the forces for the three transitions, the transition pressure of sulfur to a conducting phase was found to be 175 kbars.

Sulfur is one of the best insulators known at room temperature and pressure. For comparison, we consider other group VIB compounds. The conductivity of selenium under ordinary conditions depends upon whether it is in the amorphous state (insulator), monoclinic red state (near insulator), or the hexagonal grey state ($\rho \approx 10^5\ \Omega$ cm).[1] Tellurium is ordinarily conductive with $\rho \approx 10^{-1}\ \Omega$ cm and is a small band gap semiconductor with an energy gap of 0.35 eV.[1] Selenium, which has a band gap of 1.5–2.5 eV,[1] transforms at about 128 kbars to a conducting phase with a resistivity of about $10^{-4}\ \Omega$ cm (very likely a metal).[2] There are predictions of a similar phase transition in sulfur which has a band gap of 2.5 eV.[1] On the basis of shock experiments along with simultaneous resistance measurements, David and Hamman[3] concluded that sulfur probably had a metallic transition at or below 230 kbars. Slykhouse and Drickamer,[4] on the basis of optical studies below 100 kbars and by comparison with selenium (on a fractional volume basis), estimated (admittedly a rough prediction) that sulfur would transform to a metal at 400 kbars; however, the pressure scale has since been modified extensively, and approximate corrections applied to their optical data based on a modern pressure scale lead to the conclusion that the energy band gap would extrapolate to zero at a pressure in the neighborhood of 180–240 kbars (on the same assumption as used before).

The present experiments utilized a method developed earlier by Wanagel, Arnold and Ruoff[5] in which samples of two different materials were simultaneously placed in separate but symmetrical positions in an opposed anvil device; the resistance of each sample was then monitored independently vs the applied force. The anvil tips in the present experiments were 0.0625 cm in diameter, considerably smaller than those used earlier. The comparison cell is shown in Fig. 1. The initial experiments used ZnS and S pairs. Zinc sulfide was chosen because the transition is sharp and because the transition pressure can be placed with reasonable confidence in the 140–150 kbar range.[6,7]

After observing the initial transformation and repeating the experiment three times, it was apparent that the transformation was lower than the 230 kbars which David and Hamman[3] had set as an upper bound based on their shock experiments. We therefore used the two sample comparison technique with GaP and S pairs and in repeated experiments the sulfur transition always preceded the gallium phosphide transition as the force was increased. The transition pressure for gallium phosphide is not as well characterized as that for zinc sulfide since at the present time the range of transition pressures varies from 190–240 kbars.[8–11] The value of 220 kbars that Piermarini and Block[6] have for GaP cannot be accepted as readily as their ZnS value at the lower pressure of about 150 kbars because of the larger possible negative quadratic contribution in the pressure vs ruby wavelength shift relation at the higher pressure of the GaP transition.

The ZnS and S transitions in a comparison pair are illustrated in Fig. 2, while the S and GaP transitions for a comparison pair are shown in Fig. 3. It should be emphasized that the conductance of the circuit prior

FIG. 1. Supported opposed-anvil decive used for simultaneous resistance measurements of two samples. The boron carbide anvils which are silver coated (by vapor deposition) are used as individual leads and the center foil is used as a common ground.

