

opposite extreme to the adiabatic approximation, as mentioned in Ref. 19, and was first used by Lee, Low, and Pines in the treatment of a lattice polaron in ionic crystals.<sup>18</sup> Their final result is not much different from that of the second-order perturbation method by Fröhlich, Pelzer, and Zienau,<sup>17</sup> but quite different from that of the SCF method by Pekar.<sup>22</sup> This may imply that the results of the second-order perturbation method for the polaron problem approach those of the dynamic approximation. We then conclude that it would be better to treat the large orbit of color centers using the dynamic approximation.

Finally, we would like to take the expression given by Eq. (30) as an example to discuss briefly the effective dielectric constant. When  $r \geq 4.7\lambda^{-1}$  the  $\epsilon_{\rho 0} \cong \epsilon_{\infty}$ , the high-frequency dielectric constant, and when  $r \leq 4.7\lambda^{-1}$  the  $\epsilon_{\rho 0}$  is smaller than the usual observed high-frequency

dielectric constant  $\epsilon_{\infty}$ . These conclusions agree qualitatively with those introduced by Haken<sup>24</sup> in his exciton theory based on the dynamic approximation, and are explained physically by Haken.

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<sup>24</sup> H. Haken, in Ref. 23, p. 312.

### Properties of the Group VI B Elements Under Pressure. III. Phase-Diagram Studies of Various Forms of Sulfur

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The phase diagram of sulfur has been investigated up to 60 kbar by differential thermal conductivity analysis in piston-cylinder and tetrahedral devices. The data indicate that the melting curve of orthorhombic sulfur rises to a triple point between orthorhombic, fibrous, and liquid sulfur at 37 kbar and 410°C. The solid-solid transformation appears to be irreversible, and the fibrous phase is identical to that produced at high pressure by Geller using annealing techniques. The apparent triple point can be changed to 29 kbar and 380°C by utilizing samples containing an initial nucleation of fibrous sulfur, indicating that the true equilibrium triple point is lower than that determined by ordinary "static" measurements. The pressure dependence of the melting points of fibrous and white (insoluble  $\omega$ ) sulfur produced metastably by annealing at high pressure and temperature was also determined. Since melting is found to be reversible above the triple point it is postulated that there exists a transition from the high-viscosity polymerized liquid present between 0.8 and 37 kbar to another liquid form. A possible mechanism for explaining the melting-curve maxima of Group VI B elements is discussed.

#### I. INTRODUCTION

A PREVIOUS paper in this series presented data on the high-pressure melting curves of the Group VI B elements S, Se, and Te.<sup>1</sup> The data were obtained using a differential thermal-conductivity analysis (DTCA) technique in a tetrahedral anvil high-pressure apparatus. The purpose of the present paper is to report a more detailed study of elemental sulfur since our previous experimental arrangement was not sensitive enough to allow the attainment of very reliable data for sulfur.

The present investigation employed primarily the DTCA technique in a piston-cylinder device, allowing accurate determination of the melting-point curve of

sulfur at elevated pressure and a solid-solid phase boundary above about 37 kbar. In addition, we report high-pressure melting curves and regions of formation for two of the metastable solid forms of sulfur which were produced under high-pressure conditions by Geller.<sup>2</sup>

Since the publication of our earlier work,<sup>1</sup> several investigations of the high-pressure phase diagram of sulfur have been made,<sup>2-4</sup> and there exists at present considerable disagreement among the various studies. It should be mentioned that our earlier data are somewhat inaccurate above about 20 kbar and our present results agree satisfactorily with those of Geller<sup>2</sup> and Susse *et al.*<sup>3</sup>

<sup>2</sup> S. Geller, *Science* **152**, 644 (1966).

<sup>3</sup> C. Susse, R. Epain, and B. Vodar, *Compt. Rend.* **258**, 4513 (1964).

<sup>4</sup> T. Baak, *Science* **148**, 1220 (1965).

<sup>1</sup> B. C. Deaton and F. A. Blum, Jr., *Phys. Rev.* **137**, A1131 (1965).

## II. EXPERIMENTAL

The experiments were performed utilizing the previously described DTCA method<sup>5</sup> in a piston-cylinder apparatus similar to that of Kennedy and Newton.<sup>6</sup> Pressures ranging to 45 kbar were obtained using a  $\frac{1}{2}$  in. single-stage piston cylinder and pressures to 60 kbar were attained by double staging. The DTCA sample cell is shown in cross section in Fig. 1 and is very similar to that used in our previous work except that a considerably larger sample size is possible. Pressures were determined by placing a Bi or Tl resistance wire in the DTCA sample cell and correlating the ram pressure with the accepted pressures necessary to induce phase transitions at 25.4 kbar in Bi and 36.7 kbar in Tl.<sup>7</sup> Pressures are believed accurate to  $\pm 0.5$  kbar. Temperatures were measured with chromel-alumel thermocouples and no correction was made for the effect of pressure on their output. Temperatures of phase-boundary points using the DTCA technique are thought to be accurate to  $\pm 4^\circ\text{C}$ . Auxiliary experiments for corroboration at the higher pressures were made in a tetrahedral anvil device utilizing essentially the same experimental techniques described previously.<sup>1</sup>

Powder samples of 99.9999% pure crystalline orthorhombic sulfur obtained from Electronic Space Products, Inc., Los Angeles, California were used in the experiments. The sulfur was compacted around the center thermocouple in the boron nitride holder. The experimental data were automatically recorded on an X-Y recorder; measurements consisted of monitoring the difference in temperature between the center and outside thermocouples  $\Delta T$  as the center temperature or the pressure varied. If the thermal conductivity of the sample differs in magnitude on each side of a phase

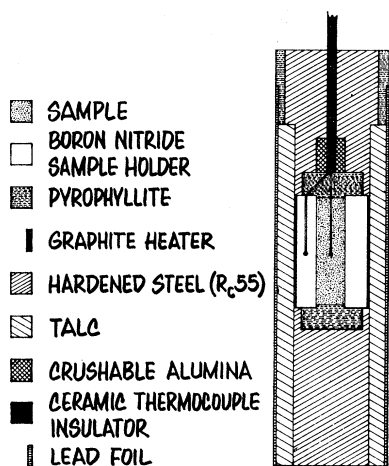


FIG. 1. Cross section of the DTCA sample cell used in the piston-cylinder apparatus.

boundary, the transition between phases is reflected by a discontinuity in  $\Delta T$ . The experimentally determined signals indicative of phase transitions were not discontinuous in the mathematical sense, so the midpoint of the spread was taken as the transition point.

The samples of sulfur designated as phases I and II by Geller were prepared using the normal DTCA cell. Orthorhombic sulfur was first melted at high pressure and then annealed at the same pressure at a temperature slightly below the melting point for 15 to 90 minutes. By monitoring  $\Delta T$  as a function of anneal time, it was possible to determine when the sample had completely transformed into either phase I or II. The new forms were then subjected to other various temperature and pressure conditions which will be described later.

## III. RESULTS

### A. Orthorhombic Sulfur

The present data on the melting of orthorhombic sulfur at high pressures are shown in Fig. 2, which depicts our results on melting and the solid-solid phase boundary to 60 kbar. As reported previously,<sup>1</sup> rhombic sulfur is found to transform irreversibly to plastic sulfur upon melting at pressures greater than 0.8 kbar. However, in contrast with our earlier results, no DTCA signals corresponding to freezing or melting of plastic sulfur could be found. These much more reliable data therefore indicate that plastic sulfur is amorphous in the most strict sense and invalidate our previous conjecture that plastic sulfur might have a melting curve. The misinterpretation of data which caused this speculation also is responsible for the fact that our previous results above 20 kbar are inaccurately high. Typical recorder tracings of  $\Delta T$  as a function of sample temperature for orthorhombic and plastic sulfur are shown in Fig. 3(a) for increasing temperature.

### B. Solid-Solid Transition

Our data indicate the presence of a solid-solid-liquid triple point at 37 kbar and  $410^\circ\text{C}$ . Melting above this triple point is found to be a reversible process so that it is possible to obtain several melting points during a single run. After several temperature cycles, however, the melting points tended to fall low, probably because of contamination of the sample by impurities. It also appeared to require a higher temperature to nucleate the new solid form on the first temperature cycle than on later cycles where a nucleus of the new form seems to have been established. Each of these facts introduces considerable scatter in the data above the triple point. A typical recorder tracing of  $\Delta T$  as a function of sample temperature showing the solid-solid transition and melting is shown in Fig. 3(b). The solid-solid transition phase boundary is perhaps the same as that observed by Baak<sup>4</sup> in quenching-type experiments, although the reported triple point differs considerably from the

<sup>5</sup> F. A. Blum, Jr., and B. C. Deaton, *Phys. Rev. Letters* **12**, 697 (1964).

<sup>6</sup> G. C. Kennedy and R. C. Newton, *Solids Under Pressure* (McGraw-Hill Book Company, Inc., New York, 1963).

<sup>7</sup> G. C. Kennedy and P. N. LaMori, *J. Geophys. Res.* **67**, 851 (1962).

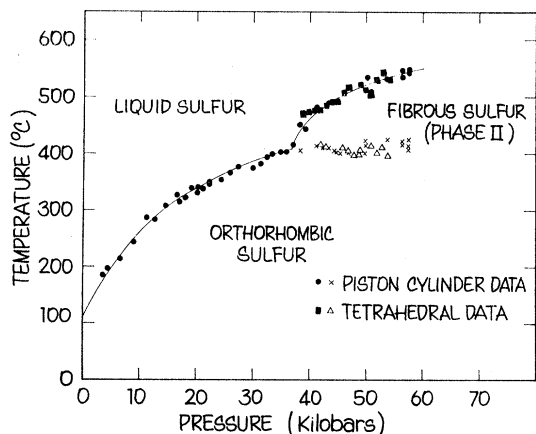


Fig. 2. Experimental data on the phase boundaries of orthorhombic and fibrous (phase-II) sulfur.

present value. It should be noted also that the magnitude of the slope of the solid-solid boundary in the present experiments is considerably less than that given by Baak.

In order to investigate further the high-pressure polymorph, several samples at 40 kbar were heated from room temperature until the solid-solid transition was completed at 405°C, and then annealed for an hour at this temperature. Upon cooling to room temperature and reheating, no solid-solid transition was indicated but the melting occurred at the expected 40 kbar solid-liquid temperature. When the melt was cooled and then heated again the solid-solid transition occurred as usual. These experiments therefore indicate that when sulfur is annealed in the new solid phase, this phase persists even when the temperature is lowered. An x-ray diffraction analysis after such an annealing process revealed that this solid polymorph is identical with phase-II fibrous sulfur studied by Geller and

described later in this paper. It is to be noted that the melting process is not necessary for the irreversible formation of this form of sulfur above the triple point. Further investigations indicated that the solid-solid transition seems to be completely irreversible, so that merely crossing this phase boundary (without melting or annealing) will allow formation of phase II.

### C. Properties of Phase-I (White) and Phase-II (Fibrous) Sulfur

As mentioned earlier, the pressure-induced forms of sulfur were produced in a manner similar to that described by Geller.<sup>2</sup> Phase I was obtained within the range 20–29 kbar, and phase II at pressures above 29 kbar. X-ray diffraction patterns of these two forms agree well with those reported by Geller<sup>2</sup> and indicate that phase I appears to be the same as white sulfur (often called insoluble  $\omega$  sulfur), while phase II is fibrous sulfur.

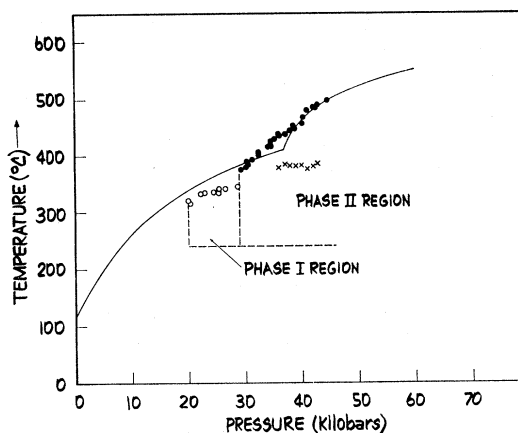


Fig. 4. Melting curves and regions in which the pressure-induced forms of sulfur can be produced by annealing.

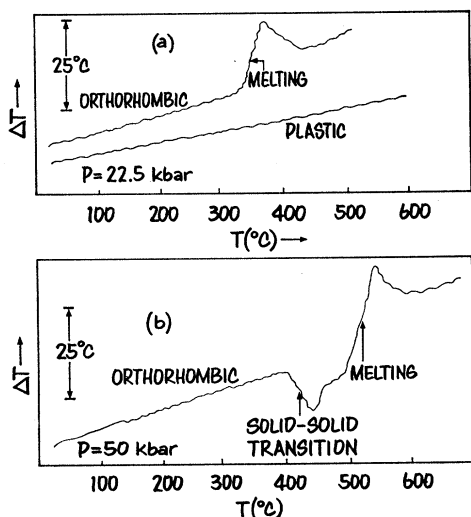


Fig. 3. Typical recorder tracings of DTCA output signals for sulfur at various pressures.

A determination of the 27 kbar melting point of white sulfur prepared in the normal manner<sup>8</sup> corroborated this conclusion since it reconciled with the phase I melting curve.

After formation of these pressure-induced polymorphs by annealing samples in the DTCA sample cell, their specific properties were then investigated in detail. It was found that once phase II was produced by annealing there was no need to re-anneal it even after it had been melted. Phase I, on the other hand, had to be annealed after each melting, since it converted back to plastic sulfur upon melting. The melting curves obtained for phases I and II are shown in Fig. 4, along with a solid line depicting the melting data from Fig. 2. The solid-solid transition, which is also found to appear in runs after phase II has been melted, is also shown and indicates an apparent triple point now at 29 kbar and

<sup>8</sup> J. Donohue and B. Meyer, in *Elemental Sulfur*, edited by Beat Meyer (Interscience Publishers, Inc., New York, 1965), p. 7.

385°C. Despite repeated attempts, after the annealed phase II had been initially melted, in no case (except upon re-annealing) was the sample melted without first observing the solid-solid transition. From these data it must therefore be concluded that when phase II is melted and cooled, the sample initially crystallizes into orthorhombic sulfur. This implies that there is a drastic change in liquid sulfur when the fibrous phase is melted as compared to when orthorhombic sulfur melts.

The dashed lines in Fig. 4 roughly define the pressure and temperature boundaries of the regions in which the pressure-induced forms of sulfur can be produced by annealing. It is interesting to note that when phase I is melted in the phase-II region, the melting point falls on the phase-II curve; conversely, when a sample annealed in the high-pressure region is melted at lower pressures, the melting point falls on the phase-I curve. Both forms were found to melt on the orthorhombic curve below approximately 20 kbar. Isobaric and isothermal entrances of phase I into the phase-II region revealed no definite DTA or DTCA discontinuities corresponding to a phase boundary. It is probable that the kinetics of the system are such that these transitions cannot be observed in the times utilized in typical experimental heating and pressurizing investigations.

#### IV. CONCLUSIONS

The results of this investigation emphasize the complexity of the high-pressure-high-temperature phase diagram of sulfur. The presence of regions of formation of metastable phases which can be obtained in various ways gives partial insight into the disparity of the results reported recently concerning the melting of sulfur at elevated pressures. In addition, evidence has been found in our study supporting the conclusions of Bates, Dachille, and Roy<sup>9</sup> that "static" phase diagrams in certain materials may well be taken under what are not equilibrium conditions. The difficulty in inducing nucleation of phase II on initial isobaric temperature cycles, along with the indicated existence of the orthorhombic-fibrous-liquid triple point at a lower pressure than our static data denote, seems to corroborate this hypothesis. The data on phase-II sulfur indicate that the true equilibrium triple point is probably near 29 kbar, and not at 37 kbar, as found statically on orthorhombic runs containing no phase-II nuclei.

Our data suggest that the melting point curve of orthorhombic sulfur rises from 113°C at atmospheric pressure to the previously mentioned triple point. The new solid phase has been identified as fibrous sulfur, and the slope of the orthorhombic-fibrous phase boundary is so small that orthorhombic sulfur should be stable up to very high pressures. This would explain the absence of transitions at room temperature, for example,

in optical-absorption studies by Balchan and Drickamer<sup>10</sup> to over 100 kbar. The present measurements, in conjunction with those of Geller, now seem to establish quite firmly the melting curve of orthorhombic sulfur. These data also agree fairly well with Susse *et al.*<sup>3</sup> except for the absence of the triple point in their data; it should be noted that the solid-solid boundary could have been easily overlooked by Susse *et al.* because the DTA signals for this phase change are quite small. The fact that the scatter in our data is most pronounced around 20 kbar is difficult to explain, and might possibly be caused by another triple point in this vicinity, although repeated efforts have revealed no DTCA signals corresponding to a transition in this region. It was noted by Susse *et al.*<sup>3</sup> that a triple point might exist below 20 kbar, since their data did not seem to extrapolate to the atmospheric-pressure melting point, a difficulty not found in our experiments. It therefore appears that at least qualitative agreement exists among several independent investigations of the sulfur phase diagram to 60 kbar. We are unable, however, to explain satisfactorily the large discrepancies between these investigations and the pressure-temperature coordinates found by Baak.<sup>4</sup>

As discussed previously,<sup>1</sup> it has been established that above 0.8 kbar orthorhombic sulfur melts into a high-viscosity polymerized liquid which converts into plastic sulfur upon cooling. It is from this plastic modification that the metastable phases I and II are obtained by annealing within their particular regions of formation. As noted earlier, however, above the triple point when fibrous sulfur is melted and then cooled, the sample seems to convert to the orthorhombic modification. It must thus be concluded that the high-viscosity sulfur is not the only phase in the melt above the triple point. Because of the statistical nature of liquid structure changes, the transition from the polymeric liquid to a different liquid form is probably not well defined, so that part of a sample cooled from the melt above the triple point will consist of plastic sulfur. This has been observed in our experiments as well as those of Geller.

A maximum has recently been observed in the melting curve of sulfur at 16 kbar by Tonkov.<sup>11</sup> All three of the Group VIB elements investigated have thus been shown to exhibit melting-curve maxima.<sup>1,11,12</sup> In accordance with the investigation by von Hippel<sup>13</sup> of the progressive crystal structure of the Group VIB elements, it seems possible that pressure will serve to bring these elements to the metallic polonium structure, but the melting-curve maxima appear to be associated with the tellurium and selenium hexagonal, chain-type structure. Pressure is found to inhibit the preservation of the chain structure upon melting, thereby causing the liquid

<sup>10</sup> A. S. Balchan and H. G. Drickamer, *Rev. Sci. Instr.* **31**, 511 (1960).

<sup>11</sup> E. Yu. Tonkov (private communication).

<sup>12</sup> C. Susse and R. Epain, *Compt. Rend.* **259**, 3756 (1964).

<sup>13</sup> A. von Hippel, *J. Chem. Phys.* **16**, 372 (1948).

<sup>9</sup> C. H. Bates, F. Dachille, and R. Roy, *Science* **147**, 860 (1965).

to increase in coordination with pressure to such a point that the liquid has a density greater than that of the corresponding solid.<sup>14</sup> This phenomenon in sulfure, however, is evidently associated with rhombic sulfur and is probably not caused by the same physical mechanism as the maxima observed in Te and Se. The fact that fibrous sulfur consists of close-packed helical chains of sulfur atoms suggests that yet another maximum in the melting curve of sulfur might be expected at pressures above 50 kbar.

The melting-point data in Fig. 2 were fitted to the Simon equation utilizing a computer program similar to that of Babb.<sup>15</sup> A reasonably good fit was obtained for the parameters  $a=3.0$  kbar and  $c=4.6$  below the triple point, and  $a=1.7$  kbar and  $c=1.4$  for melting of fibrous sulfur. The initial slope of the melting curve is found to be  $30^\circ\text{K}/\text{kbar}$ , in good agreement with the values of  $30^\circ\text{K}/\text{kbar}$  found by Tammann<sup>16</sup> and  $32^\circ\text{K}/\text{kbar}$  found from the Clapeyron equation.<sup>1</sup>

The present studies have revealed the relationship between the static phase diagram of sulfur and the pressure-induced metastable phase II, but we are unable to make definite statements as to how phase I fits into the equilibrium phase diagram. If phase I has a direct correlation with the static phase diagram, it might possibly be associated with the scatter of our data near 20 kbar. We have not attempted studies of yet another metastable form, called phase III by Geller, since it is possible that this modification is not an equilibrium phase. Our x-ray data on the metastable phases I and II are in excellent agreement with those of Geller, who has given a thorough description of their respective structures. It should merely be noted that phase I has been

identified as white or insoluble  $\omega$  sulfur, while phase II is fibrous sulfur, these polymorphs having been fabricated years ago by various methods at ambient pressure.<sup>8</sup> We found no evidence to support the x-ray data of Baak<sup>4</sup> during the investigation of any of the forms of sulfur which we produced at high pressures.

*Note added in proof.* Very recent investigations of the properties of sulfur at high pressures are quite relevant to the present studies.<sup>17,18</sup> Paukov *et al.* have observed a triple point at a pressure of 19 kbar which explains the scatter of our data in this region; our technique is apparently not sensitive enough to resolve this structure in the melting curve. The observed triple point apparently establishes the relationship between phase I and the static phase diagram of sulfur. The data on melting given in Fig. 2 agree within 2% with those of Paukov *et al.* except in the immediate vicinity of the triple point at 19 kbar, so that the sulfur melting curve below 40 kbar now seems to be well established. The studies of Shlar *et al.* on the preparation and investigation of the properties of a new phase of sulfur, which we believe to be fibrous sulfur, were carried out independently and earlier than Geller's work. Their data, obtained from quenching-type experiments in a belt apparatus, tend to agree with the present phase studies in most respects, but there are several discrepancies which are possibly due to the differences in the two types of experiments.

#### ACKNOWLEDGMENTS

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<sup>14</sup> It should be pointed out that this explanation is based on an interpretation of phase studies in tellurium (Ref. 1), and that there may not be an exact analogy with sulfur and selenium.

<sup>15</sup> S. E. Babb, Jr., *Rev. Mod. Phys.* **35**, 400 (1963).

<sup>16</sup> G. Tammann, *The States of Aggregation* (D. Van Nostrand Co., Inc., New York, 1925).

<sup>17</sup> I. E. Paukov, E. Yu. Tonkov, and D. S. Mirinskiy, *Dokl. Akad. Nauk. SSSR* **164**, 588 (1965).

<sup>18</sup> C. B. Schlar, L. C. Carrison, W. B. Gager, and O. M. Stewart, *J. Phys. Chem. Solids* **27**, 1339 (1966).