

## Electrical behavior of Te, Se, and S at very high pressures and low temperatures: Superconduction transitions

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At sufficiently high pressures Te, Se, and S transform to metallic or semimetallic forms. Earlier work showed the metallic forms of Te and Se to be superconductors, and very recent Soviet reports indicate that high-pressure metallic S becomes superconducting. The work reported in this article covers more refined measurements of the resistivities and temperature coefficients of these elements in metallic form as related to pressure, and the resistance behavior from room temperature down to 2.7 K. Metallic Te and Se prove to be good superconductors. In our experiments semimetallic S shows a minimum resistance in the 150–100-K zone, and a reproducible and consistent “jog” in the  $R(T)$  curve at about 10 K. This resistance behavior of sulfur over the range 12 to 300 K can be formulated as a series combination of a metal-like component and a semiconductinglike component, as might be expected in a partially converted specimen. In such a case a possible explanation of the downward jog in the 10-K region could be a superconduction transition in the metallic component. However the magnitude of the observed jog is actually far too small to be accounted for by such a model. It may be that the unusual resistance and temperature behavior is the result of complicated electronic properties of a high-density, complex, linear sulfur structure which involves electron hopping from one linear molecule to another. Some fits to a Mott  $T^{-1/4}$ -type model and an Anderson  $T^{-1}$  type are tried but appear to be only partially successful.

### I. INTRODUCTION

At high pressures the usual semiconducting forms of Te and Se are known to transform to metallic forms<sup>1–5</sup> which become superconducting at sufficiently low temperatures.<sup>4–6</sup> More recently, with apparatus capable of higher pressures, S has been shown to transform to a saturated semimetallic form.<sup>7–9</sup> Very recently there have been two reports<sup>10,11</sup> of observations of superconduction transitions in this semimetallic S.

At our laboratory we have adapted our sintered diamond-tipped opposed-piston apparatus<sup>12</sup> to cryogenic-type experiments by equipping it with a clamp press arrangement which can be lowered into a large Dewar and cooled to liquid-He temperatures.<sup>13</sup> This facility has been used to study the behavior of a number of high-pressure metals down to low temperatures while held at pressure. The purpose of this paper is to report our new observations on Te, Se, and S.

### II. APPARATUS

For the cryogenic high-pressure work the stressed binding rings of the diamond-tipped apparatus were made of stainless steel which is not subject to brittle fracture at very low temperatures. The clamp press which held the apparatus under pressure was a

squirrel-cage structure with thick top and bottom platens of A-286 stainless steel connected by eight 17-7PH stainless-steel tension rods capable of holding the apparatus under sustained loading of up to 40 tons. The pressure apparatus and clamp press assembly was brought up to the desired loading in a hydraulic press, the clamping nuts tightened, the hydraulic press load released, and the clamped and loaded assembly transferred to a large Dewar where it was cooled in steps in liquid N<sub>2</sub> and then by liquid He. By reducing the pressure above the liquid He, the temperature of the assembly could be lowered rather easily to 2.7 K. Temperatures were monitored under nearly thermal equilibrium conditions during very slow warm-up by calibrated copper and carbon resistors. The resistances of the monitoring sensors were measured by four-terminal systems with a weak dc exciting current applied to one set of terminals and the ir potential drop determined on the other set. In our apparatus it was not practicable to extend the four-terminal monitoring to the high-pressure specimen itself. Instead, the four-terminal net extended to the bases of the pistons of the pressure apparatus. The electrode resistance between those points and the specimen itself within the high-pressure zone was kept as low as possible, and was evaluated in control runs at various loadings and temperatures by replacing the specimen with a zero resistance link.

It is recognized that in measurements of the kind being reported here one must be on guard against su-

perposed effects of contact resistance, electrochemical effects, pressure gradient effects in the specimen, thermal emf's, etc. Such factors were eliminated, minimized, or evaluated by control experiments. Our considerable experience with the apparatus indicated that there was no significant pressure gradient within the specimen region. However, as shown in Ref. 3 and 7, the phase-transformation behavior for the elements reported on here could be slow, and sometimes capricious at the higher temperatures, because of nucleation conditions and competition of phases. We were satisfied that such behavior was not due to pressure gradients in the apparatus because other simpler specimen elements showed quite sharp and clean transitions under the same apparatus conditions.

### III. RESULTS

**Tellurium.** Because of the relatively high electrical conductivity of high-pressure metallic Te, the obtaining of meaningful quantitative measurements in our apparatus required the specimens to be of the order of  $1 \mu\text{m}$  thick and the cell electrode resistance to be quite small. The specimens consisted of a film of Te which had been evaporated on to thin sheets of mica under clean conditions. A small rectangular piece was cut out and laid into the cell with the Te film in contact with gold foil electrodes at each end. X-ray diffraction showed the film to be hexagonal Te. At room temperature the resistance of the gold foil (or Pt foil) and tungsten wire electrode system in the cell was measured to be about 0.15 ohm, while at liquid-He temperature it was a little over 0.02 ohm. These electrode resistances were subtracted from the measured total cell resistance to get the net specimen resistance. The resistivities reported here in Fig. 1 are based on the initial dimensions of the Te film between the electrodes, and they may be considered accurate in the absolute sense to only about a factor of 2 because of the lack of precise knowledge of the actual dimensions of the specimen while under pressure. However, the observed variations of resistance with pressure and temperature may be considered reliable because the specimens were taken from the same mica sheet with the same Te film thickness, and the pressure and temperature excursions were made with a given specimen in the cell.

Our cryogenic test of Te at about 220 kbars over the temperature range 300–2.7 K yielded the results shown in Fig. 2 in which one curve shows the detailed  $R(T)$  behavior in the 2.7–28-K interval, and the other curve covers the span up to 300 K. Note that there is a well-defined superconduction transition in the temperature interval 5.5–6.8 K. This result is to be compared to earlier Soviet results,<sup>6</sup> shown here in Fig. 3, which indicate a  $T_c$  of about 2.8 K at 220

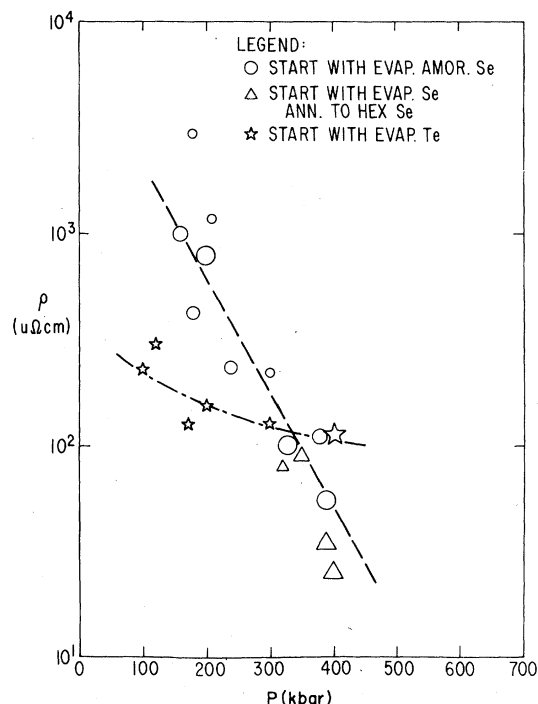


FIG. 1. Resistivities of the high-pressure forms of Te and Se as a function of pressure. The size of the symbol marking a datum point indicates the reliability of the point. The larger the symbol the more reliable the datum point. Although instrument performance was involved, there were factors related to the stability and character of the specimen which depended on the pressure, temperature, and time approach to the experimental point.

kbars (according to the pressure scale in use in 1972). When the pressure numbers shown in Fig. 3 are translated to the accepted modern (1975) pressure scale<sup>12,14</sup> the highest-pressure data points correspond to about 150 kbars. After the manuscript of this article was first submitted for publication additional work at our laboratory has shown that between 150 and 200 kbars, Te undergoes another transformation, without resistance jump, and the  $T_c$  of the higher pressure form does indeed go up to the high value shown in Fig. 2.<sup>15</sup>

Applying a graphical analysis based on a relation proposed by Grüneisen<sup>16</sup> and Borelius,<sup>17</sup>

$$\frac{R_T}{R_\Theta} = 1.17 \left( \frac{T}{\Theta} - 0.1453 \right),$$

to the 10 to 300 K curve of Fig. 2 one gets a Grüneisen characteristic temperature  $\Theta$  of about 179 K for this metallic Te.

**Selenium.** Our results with thin-film (i.e., approximately  $2 \mu\text{m}$ ) specimens of amorphous and hexagonal forms of Se at pressures below about 160 kbars essentially agreed with those reported earlier by other

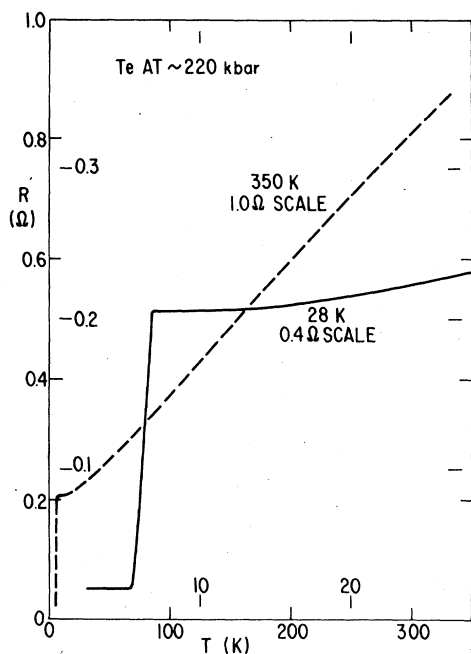


FIG. 2. Resistance vs temperature of Te at about 220 kbars in our cryogenic high-pressure cell. Note the superconducting transition between 5.5 and 6.8 K.

observers. In going to higher pressures we obtained the new result that the hexagonal form transforms to a metallic state at about 250 kbars.<sup>3</sup> This metallic state appears to be the same, as judged by its electrical characteristics, as the metallic form derived from amorphous Se at about 130 kbars. The resistivity of metallic Se as a function of pressure is shown in Fig. 1, in which the round data points apply to specimens derived from amorphous Se and the triangular ones to specimens derived from hexagonal Se. Comparison of these resistivity data for Se metal to those for Te metal shows that the Se material is much more pressure sensitive. Se at 400 kbars appears to be a good metal with resistivity in the order of  $40 \mu\Omega \text{ cm}$ . Also, the measured temperature coefficient of resistivity at this pressure is about  $0.004 \text{ K}^{-1}$ , which is normal for good metals. As shown in Ref. 3 the character and behavior of Se in the 130–250-kbars pressure range depends upon the allotropic form of the starting material and the pressure-temperature time path to the state at the time of the measurement.

We carried out three cryogenic experiments with metallic Se, two with specimens derived from amorphous Se (at about 170 and 190 kbars), and one from hexagonal Se (at about 330 kbars). As pointed out by Wittig,<sup>4</sup> in doing this type of experiment starting with amorphous Se, the specimen has to be cooled without delay after it drops into the metallic state at 130–140 kbars. Otherwise, if it stands in this condi-

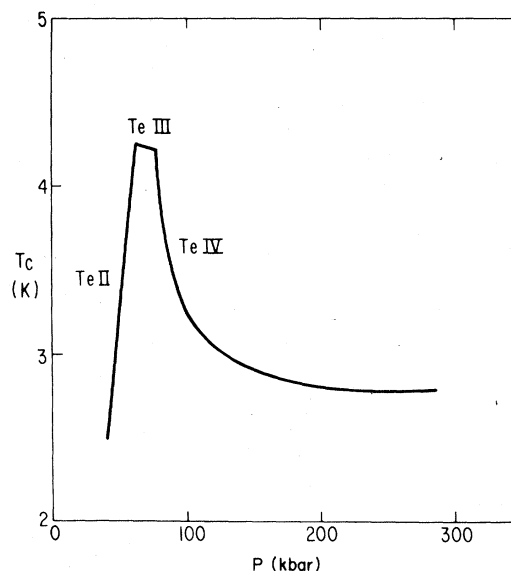


FIG. 3.  $T_c$  vs  $P$  data for Te reported by Berman *et al.* (Ref. 6). The pressure scale used here was in vogue in 1972. On the 1975 pressure scale (Ref. 12) the highest-pressure part of the curve corresponds to about 150 kbars.

tion at room temperature it reverts to a high-pressure semiconducting form.<sup>3</sup> The results for the “amorphous Se” at 170 kbars are presented in Fig. 4. The 0.2-ohm, 10-K curve shows the details of the distinct superconducting transition occurring between about 4.2 and 5.6 K. The 0.02-ohm resistance below 4.2 K is the electrode resistance of the cell. The 1.0-ohm, 300-K curve shows the  $R(T)$  behavior of the “normal” Se metal up to room temperature. Graphical analysis of this latter curve yields a Grüneisen charac-

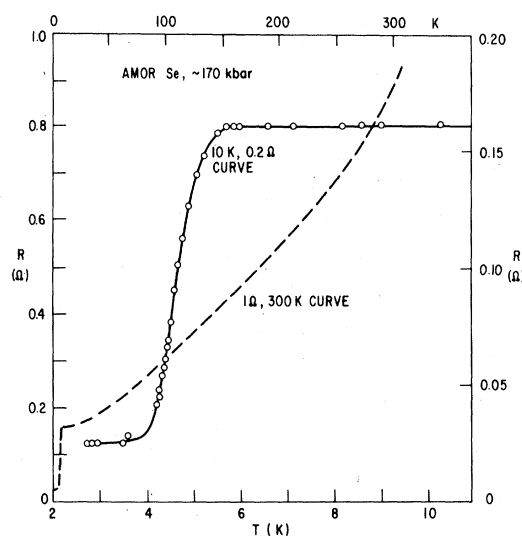


FIG. 4.  $R(T)$  of Se (from amorphous Se) at about 170 kbars in our cryogenic high-pressure cell.

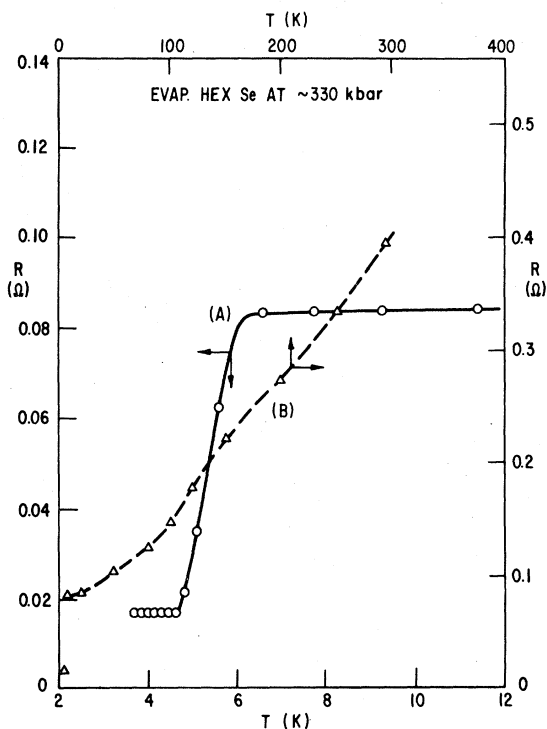


FIG. 5.  $R(T)$  of Se (from hexagonal Se) at about 330 kbars in our apparatus. (A) Low-temperature region showing superconduction transition; (B) full temperature span showing behavior as a normal metal.

teristic temperature,  $\Theta$ , of 234 K which is in the range for usual good metals.

Figure 5 presents our results for Se metal at about 330 kbars, derived from hexagonal Se. The 0.14-ohm, 12-K curve shows the details of the superconduction transition occurring between about 4.7 and 6.2 K. The other curve gives the  $R(T)$  behavior on up to room temperature, and this leads to a  $\Theta$  of 358 K, a value higher than the one for 170 kbars, suggesting a stiffer lattice.

*Sulfur.* The 1978 report by Yakovlev *et al.*,<sup>10</sup> which suggests a superconduction transition in sulfur, was based on experiments using a film of sulfur between an indenter of "carbonado" diamond and a flat "carbonado" diamond anvil. During loading of the specimen at room temperature the resistance decreased by several decades and leveled out in the saturated semimetallic state. When held at this loading and cooled, a drop of resistance from 2.02 to 2.00 ohms was observed, reproducibly, just below 10 K. The background resistance of the anvil system at the low temperature was stated to be about 2 ohms, and the drop of resistance was interpreted as a superconduction transition in the metallic sulfur.

The 1978 experiments of Yevdokimova and Kuzemskaya<sup>11</sup> utilized opposed piston cemented tungsten carbide apparatus. They reported a sharp

drop of resistance of several decades at about 200 kbars, beyond which it leveled out indicating a saturated metallic state. When this system was cooled at pressure, they observed a sharp drop of resistance at about 5.5 K which had all the characteristics of a superconduction transition. The  $R(T)$  curve they published is almost identical to that shown here in our Fig. 4 for 170-kbar Se. They could explain the large difference between their  $T_c$  and that of Yakovlev *et al.*<sup>10</sup> only by assuming a rather large difference in pressure between the two types of experiments, and a large pressure dependence of  $T_c$  for metallic sulfur.

We carried out five different cryogenic ultrahigh-pressure experiments with pure sulfur specimens, one with  $S_{99}Se_1$ , and one with  $S_{90}Se_{10}$ . The details of specimen and electrode materials, geometry, pressure, duration, etc., are presented in Table I. The specimen geometry and arrangements were as shown in Ref. 7. In 6 of the experiments the specimen was in the form of a thin flake about 0.025 mm thick positioned in the center of the cell parallel to the pressure faces of the pistons. The electrodes were in contact with the ends so that the resistance measurement was in a direction perpendicular to the axis of compression (transverse geometry). In one pure sulfur experiment the specimen was cylindrical and coaxial with the pistons, the specimen being initially about 0.15 mm in diameter and 0.12 mm long. In this case the resistance path was parallel to the axis of compression (axial geometry).

The specimen of the first experiment was of 99.999%-pure orthorhombic sulfur in contact with Pt-foil electrodes. It was compressed at room temperature to about 440-kbars pressure where it gradually settled into a fairly stable semimetallic state with a resistance of about 17  $\Omega$  (over 100 times the electrode resistance). Its resistance behavior as it warmed up from liquid-He temperature is shown in Fig. 6. The same resistance pattern was followed quite accurately in the second warm-up, showing the behavior to be stable and repeatable. The noteworthy features were the minimum in the 150-K region (quite unexpected), and the jog in the 10-K region (where we had anticipated a first-order resistance drop due to superconduction, somewhat like those for Se and Te). The subsequent experiments with other sulfur specimens verified that this is indeed the pattern of resistance behavior for sulfur in this pressure regime.

To investigate the possibility that the 200-kbar metallization of sulfur reported by Yevdokimova and Kuzemskaya<sup>11</sup> might result from starting with a different allotropic form of sulfur we tried two experiments using specimens pressed from pure "precipitated sulfur," and one experiment starting with monoclinic sulfur. Both of the "precipitated sulfur" experiments used transverse geometry and gold foil

TABLE I. Parameters of cryogenic ultrahigh-pressure sulfur runs carried out.

Run No.	Specimen Material	Specimen Geometry	Electrode material	$P$ (kbar)	Days under $P$	No. of warm-ups
1	99.999% orthorhombic (OR) sulfur Precip. powder	Transverse	Pt foil	440	11	2
2	pure OR sulfur Precip. powder	Transverse	Au foil	440	16	2
3	pure OR sulfur Pure	Transverse (short gap)	Au foil	440	13	2
4	monoclinic sulfur 99.999%	Transverse	Au foil	540	10	2
5	OR sulfur	Axial	Pt foil	490	28	6
6	$S_{99}Se_1$	Transverse	Pt foil	450	11	2
7	$S_{90}Se_{10}$	Transverse	Au foil	440	8	2

electrodes. In the second experiment the gap between the electrodes spanned by the specimen was made only about one-tenth the diameter of the pressure faces of the pistons in order to practically eliminate any possibility of pressure gradient within the specimen. X-ray diffraction analysis of the "precipitated sulfur" showed it actually to be the usual orthorhombic type. These two runs were carried out at about 440 kbars. Except for the magnitudes of the resistances associated with the different lengths of the specimens these two experiments showed the same behavior which was very similar to that of the pure orthorhombic sulfur.

The fourth experiment used monoclinic sulfur formed by annealing a specimen of ultrapure orthorhombic sulfur *in situ* before closing the pressure cell. This specimen, like the others, required standing for hours at pressure over 400 kbars and at temperature 10–20°C above room temperature to cause it to settle into a saturated semimetallic state. This experiment was run at a pressure of about 540 kbars, the highest in this series. The resistance-temperature behavior was about the same as the others.

A room-temperature compression experiment was done with a specimen of amorphous sulfur made by quenching sulfur from its hot "ropy" phase. This specimen required the same high pressure to force it into the semimetallic state as did the others, and therefore time was not taken to subject it to a cryogenic test.

To test the possibility that the direction of the electrical path in the specimen relative to the axis of

compression might have an effect in a complex material like sulfur, the fifth experiment used pure orthorhombic sulfur in a small coaxial cylindrical space in the cell between the piston faces. This experiment was run at about 480 kbars, and involved six temperature scans over a total time period of 28

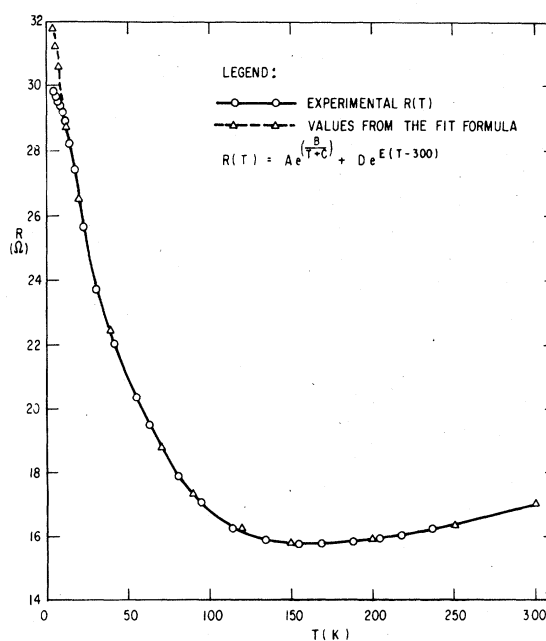


FIG. 6. Our  $R(T)$  results for pure orthorhombic sulfur at about 440 kbars. Experimental values and the two-term analytical fit curve are compared.

days. This number of scans was made because at the end of a warm-up when the temperature approached room value the resistance would drift down slowly with elapsed time suggesting more complete conversion to the semimetallic form after a cold period, or possibly slow plastic deformation of the specimen itself toward shorter length and broader diameter. Such drift was never observed at temperatures below about 250 K. In this experiment, even after the sixth warm-up there was still a very slow settling of the resistance with time after the temperature exceeded about 285 K. This may be seen at the high-temperature end of the curve in Fig. 7 which shows the resistance-temperature behavior of this "axial" specimen on the sixth warm-up when it certainly was quite settled into the semimetallic state. This specimen shows the same general resistance-temperature behavior as the "transverse geometry" ones, except that the ratio of the resistance at lower temperatures to the minimum resistance ran much higher than in the other cases, and the  $R/R_{\min}$  ratio for temperatures above the minimum ran lower than in the other cases. The room-temperature resistivity of this specimen after the sixth warm-up was about the same as for the other specimens. The fact that in all the warm-up cycles of the axial specimen the low-temperature  $R/R_{\min}$  ratios were practically the same, and also several times larger than the corresponding ratios for the transverse specimens, leads us to believe that there may be a real difference in the low-temperature conduction mechanism in the axial as

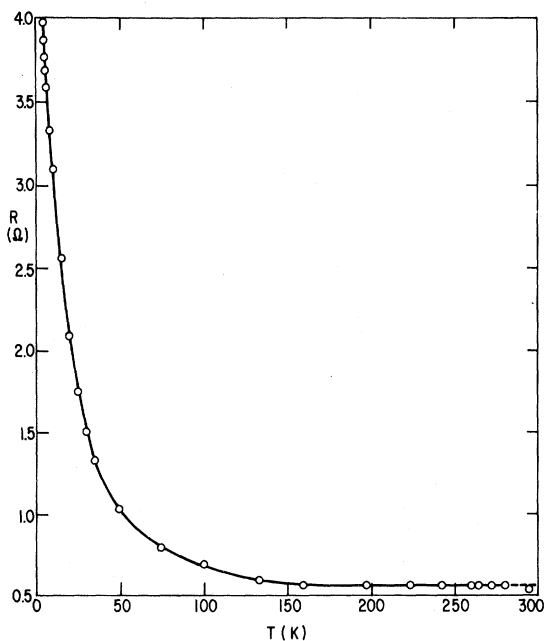


FIG. 7. Our  $R(T)$  results for the sixth warm-up of an axial specimen of pure orthorhombic sulfur.

contrasted to the transverse direction. Such an effect could be due to preferred orientation of crystal or molecular axes in the new phase.

To test the possibility that relatively small amounts of Se as an impurity in sulfur might have a pronounced effect on the low-temperature behavior of the high-pressure phase, two such experiments were carried out, one using  $S_{99}Se_1$ , and the other using  $S_{90}Se_{10}$ . Although these two elements are miscible there was some practical difficulty in the preparation because of the gummy phase of sulfur in the 200°C range where Se melts, and because of loss by vaporization at higher temperatures. The specimens were prepared by heating together weighed amounts of the components in a small test tube without good control over vapor escape. The specimen material prepared in this manner may not have been homogeneous on a molecular scale, or of exactly the initial weight ratios.

Conversion of the  $S_{99}Se_1$  specimen to a nearly saturated semimetallic form in our apparatus required the same high pressures as did the pure sulfur. The resistance-temperature behavior of the pressurized  $S_{99}Se_1$  specimen at about 450 kbars was like that of pure sulfur except that below about 15 K the resistance dropped away in a much more pronounced manner. This behavior was repeated accurately on the second warm-up, which indicates that it was reversible and reproducible. The behavior of the  $S_{90}Se_{10}$  came out to be essentially like that for pure sulfur. Again, the same pattern was obtained in both warm-ups. More experiments using very carefully prepared mixture specimens would be required to establish the effect of small amounts of Se molecularly dispersed in sulfur. It may be that trace amounts can have pronounced effects.

The consistency and reproducibility of our experimental data for sulfur lead us to believe that they were reliable, and that they justified some effort to understand them in terms of some of the possible physical models. The resistance versus time behavior at room temperature during the initial compression to very high pressure indicated that the new semimetallic phase forms slowly, and that there could be some residual semiconducting phase. Our experience with Se also indicated two-phase behavior when under "intermediate-pressure" conditions. It was logical therefore to consider that the high-pressure sulfur specimens might consist of two phases, one semiconducting and one semimetallic. Also in view of the Soviet reports,<sup>10,11</sup> together with the known superconducting behavior of the metallic forms of Te and Se, it was reasonable to expect superconductive behavior from semimetallic sulfur at sufficiently low temperature.

It was found that all 7 of the experimental  $R(T)$  curves for S and S-Se mixtures could be fitted quite accurately in the 15–300-K temperature range using

a two-term expression of the form:

$$R(T) = A \exp[B/(T + C)] + D \exp[E(T - 300)]$$

where the first term represents a semiconductorlike component, and the second term a metal-like component. The  $E$  is the temperature coefficient of resistance of the hypothetical metallic component and  $D$  its resistance at 300 K. The  $B$  and  $C$  are fictitious temperatures relating to the hypothetical semiconducting component. Each experimental case required a different set of constants. The closeness of fit to an experimental  $R(T)$  curve is shown by the triangular points in Fig. 6.

If in such a hypothetical model the conducting path consists of a complex chain grid of metallic and semiconducting links, then upon the metallic links becoming superconducting the total resistance would decrease abruptly by the amount of the resistance of the metallic component. In all the experimental cases the resistance change in the 12-K jog region was not large enough to be accounted for in this manner, and therefore the model cannot be completely correct.

Another possibility is that the sulfur specimen at very high pressure is a single phase of linear conducting molecules in a polycrystalline state in which the electrical conduction process consists of linear metallic conduction along the molecules with hopping of electrons from molecule to molecule, as in a Mott model.<sup>18</sup> In this model at low temperatures the resistance would follow the  $T^{-1/4}$  relationship characteristic of "variable range hopping." In Fig. 8 we plot the experimental data from 4 of the pure sulfur experiments as  $\ln R$  vs  $T^{-1/4}$ . It is seen that there are two temperature ranges in which approximate linearity occurs, the main one extending from about 150 down to 15 K, and a second one with distinctly smaller slope below about 12 K. According to the theory of variable range hopping<sup>18</sup> the slope,

$$\frac{d(\ln R)}{d(T^{-1/4})} = \left( \frac{1.5}{k \alpha^3 N(E)} \right)^{1/4}$$

where  $k$  is the Boltzmann constant,  $\alpha$  is the rate of falloff of the envelope of the wave functions for the weakly localized states, and  $N(E)$  is the density of states at the Fermi level. To account for the two different slopes there would have to be two different regimes of  $\alpha^3 N(E)$ , and these in turn would have to be caused by different crystal or electronic arrangements of the specimen. At temperatures as low as 10 K, crystal-structure rearrangement would be improbable, and therefore the change of regimes in the 12-K region would more likely be electronic in nature. This would be a matter for theorists to consider.

In consideration of the possibility of the sulfur behavior being of the type referred to as Anderson "Fermi glass," the data from the same four experiments are plotted in Fig. 9 as  $\ln R$  vs  $1/T$ . In these

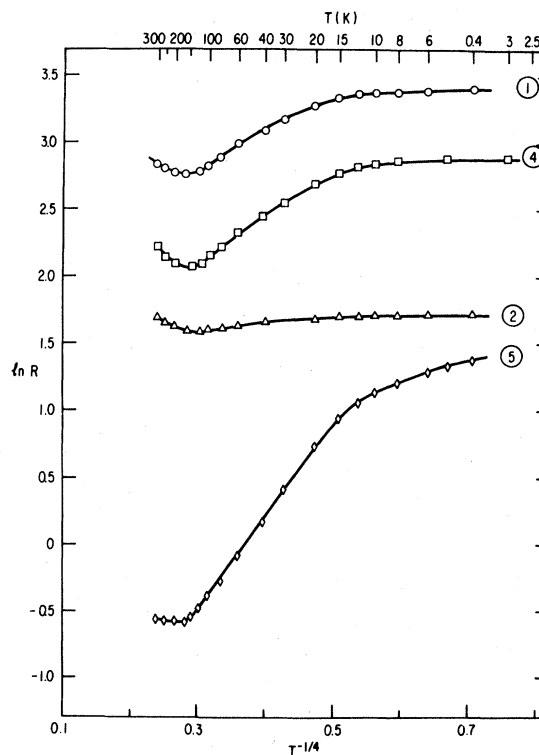


FIG. 8. Plots of  $R(T)$  behavior of various sulfur specimens on a  $\ln R$  vs  $T^{-1/4}$  basis. (1) Orthorhombic, transverse geometry, 440 kbars; (2) precipitated powder orthorhombic, transverse geometry, 440 kbars; (4) monoclinic, transverse geometry, 540 kbars; (5) orthorhombic, axial geometry, 490 kbars.

plots the only segment that can be considered very linear is that below about 12 K where the slopes are so small that they would correspond more to a condition of extended states rather than to localized states, according to Mott.

It is evident from the experimental results and the physical analysis presented here that high-pressure sulfur is not a good classical metal, and that it is not subject to superconduction at temperatures down to 2.7 K. However it certainly undergoes a definite change in the mode of electrical conduction in the 12-K region of temperature. Some postpressurization crystallographic evidence<sup>19</sup> suggests that the high-pressure sulfur may consist of crystallites of linear spiral molecules which might be linear metallic conductors while under pressure. Such a model could account for the semimetallic resistance behavior at higher temperatures, a resistance minimum, and a kind of semiconducting behavior at the lower temperatures where some kind of hopping mechanism between the linear molecules or crystallites would become dominant. This idea is supported by the experimental observation that there is a large difference in the  $dR/dT$  in the 15–120-K temperature range for

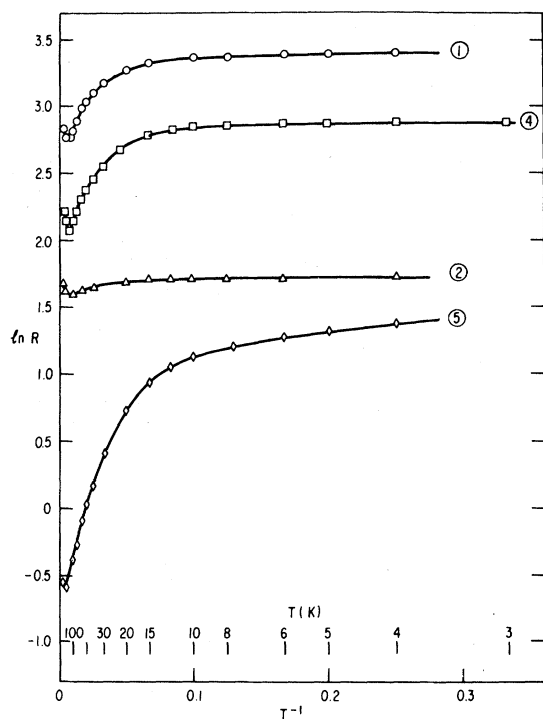


FIG. 9. Plots of  $R(T)$  behavior of various sulfur specimens on a  $\ln R$  vs  $T^{-1}$  basis. Curve identification same as in Fig. 8.

sulfur specimens measured parallel to the compression axis as compared to those measured perpendicular to it. This effect could be associated with the preferred orientation of needle (or platelike) crystallites in any uniaxial pressure apparatus. Even if the electron-hopping model is the correct one in the

300–12-K temperature range an additional explanation is still needed for the change in mode of conduction from 12 K on down.

In respect to the experimental results for sulfur reported recently by the Soviets, our results and those of Yakovlev *et al.*<sup>10</sup> are in rough agreement, but we have never observed the behavior reported by Yevdokimova and Kuzemskaya.<sup>11</sup>

#### IV. GENERAL COMMENT

Of the three group VIA elements studied in this experimental investigation Te is definitely the most metallic, and S the least so. Above about 300 kbars Se is also quite metallic, but in the range of about 120 to 250 kbars the metallic phase has competition with a high-pressure semiconducting phase. Consequently in experimenting with Se in the midpressure region the initial allotropic form and the pressure-temperature time path to the final state is important. As our present quantitative results on sulfur show, sulfur is not very metallic at 500 kbars. One can only speculate by analogy, or by theory, about how much pressure would be required to compress sulfur to a true metallic state. On the basis of this trend in the family of elements one might expect the lightest member, oxygen, to require several megabars of pressure to render it metallic.

#### ACKNOWLEDGMENTS

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