

Electrical behavior of sulfur up to 600 kbar—metallic state

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Using a sintered diamond tipped opposed piston apparatus the electrical resistance behavior of sulfur has been studied to pressures well over 500 kbar and to temperature of a few hundred °C. At about 300 kbar the resistance starts dropping below the cell background value of about 10^8 ohm and continues to drop with pressure until about 500 kbar where a steady value of about 10 ohm is reached. In this latter state the dR/dT is positive, indicating metallic character. Temperature cycling the specimen at lower pressures yields negative dR/dT , characteristic of semiconduction. The measured activation energy of semiconduction drops linearly with pressure until the metallic state is reached. The resistivity in the metallic state is about 0.03 ohmcm. The higher temperature behavior in the metallic state was explored by pulse heating for intervals of the order of a hundred microseconds. An abrupt resistance drop occurs at about 600°C which is probably the melting temperature of the metallic phase.

I. INTRODUCTION

When covalently bonded elements and compounds are compressed their bonding electron systems become distorted causing changes and shifts in the relative energy differences between energy states. In some cases the electron systems become unstable and change abruptly to different arrangements that may be truly metallic in character,—as in the cases of Si, Ge, In, Sb, GaP, etc. In other cases the shift of the energy bands with pressure may be continuous over a wide range of pressure, and the gap between valence levels and conduction levels may decrease quite continuously with pressure until the gap reaches zero and the substance takes on a semimetallic character. An example of this is iodine, as reported by Drickamer.¹

Relatively recent high pressure experiments on sulfur by Vereshchagin, *et al.*² in the USSR, and by Notsu³ at Osaka University, Japan, indicate that this element transforms to a relatively highly conducting state at estimated pressures of the order of a megabar. Much earlier (1958) shock compression experiments of Hamann⁴ and of David and Hamann⁵ showed that sulfur and also iodine become quite conductive under shock pressures of roughly 250 kbar and temperatures of approximately 1000 °K. Also in 1958 Slykhouse and Drickamer⁶ reported their measurements of the shift of the edge of the optical absorption band in sulfur with pressure, up to roughly 150 kbar. Their data indicated that the band gap would vanish at a pressure in the range of 400–500 kbar, at which point sulfur should become metallic.

With the advent of an improved Drickamer-type opposed anvil apparatus⁷ in which the center face parts of the cemented tungsten carbide pistons were made of polycrystalline diamond marketed by General Electric under the COMPAX[®] trademark, it became possible to carry out quantitative electrical measurements on specimens of sulfur up to pressures of about 600 kbar and temperatures of a few hundred degrees Centigrade. It has been found that the electrical conductivity of sulfur increases by at least 14 orders of magnitude as the pressure rises from 150 to about 500 kbar, where it attains a steady semimetallic state. Upon decompression from this state it reverts to an electrically insulating state that x-ray diffraction shows to be roughly crystalline,

but the structure has not been worked out successfully.

II. APPARATUS, TECHNIQUES, AND RESULTS

A section of the pressure apparatus is shown in Fig. 1(a). It is an opposed piston type with a confined gasket of pyrophyllite stone between the faces. The main bodies of the pistons are of cemented tungsten carbide, and the very highly stressed regions near the tips are of very strongly sintered diamond powder. The best available pressure calibration tests⁸ utilizing the (α - ϵ) transitions in the FeCo and FeV alloys, observed by shock compression and reported by Loree, *et al.* in 1966,⁹

DRICKAMER-TYPE APPARATUS WITH DIAMOND COMPACT-TIPPED ANVILS

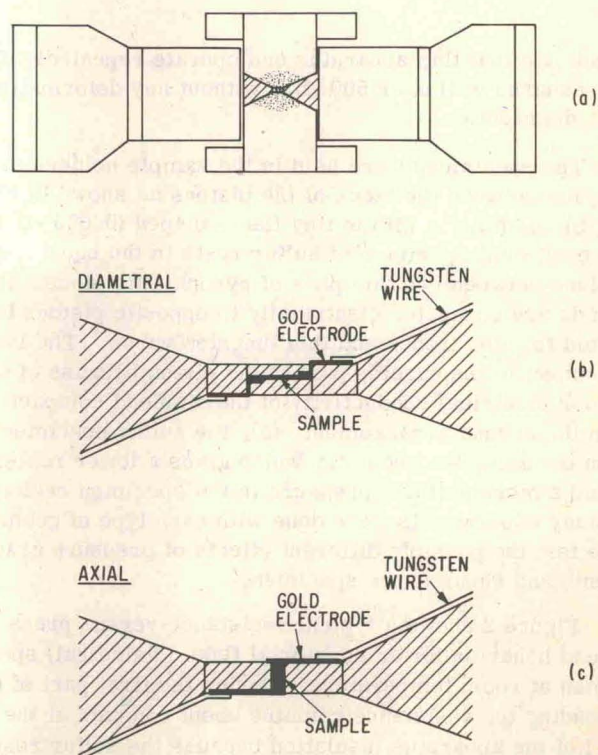


FIG. 1. Opposed diamond-tipped piston apparatus used in this work. (a) Cross section of apparatus; (b) cell arrangement for diametral specimen in equatorial plane; (c) cell arrangement for axial specimen.

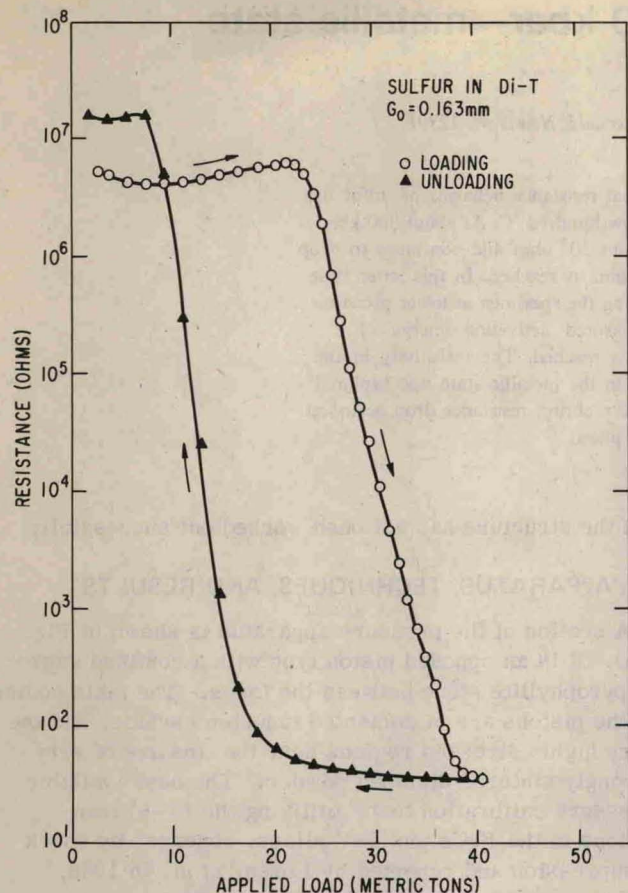


FIG. 2. Resistance vs press ram force for a diametral specimen of sulfur at room temperature.

indicate that this apparatus can operate repeatedly to pressures well over 500 kbar without any deformation or degradation.

The specimens were held in the sample holders in the space between the faces of the pistons as shown in Fig. 1(b) and (c). In (b) the tiny flake-shaped ($0.025 \times 0.43 \times 0.62$ mm) specimen of sulfur rests in the equatorial plane between two thin pills of pyrophyllite stone. Its ends are connected electrically to opposite pistons by gold foil electrodes and thin tungsten wires. The latter connect to the carbide part of the piston because of the poor electrical conductivity of the diamond compact tips. In the second arrangement, (c), the sulfur specimen is on the axis, —a geometry which gives a lower resistance and a more uniform pressure in the specimen region. Many experiments were done with each type of geometry to test the possible different effects of pressure gradients and shear in the specimen.

Figure 2 shows a typical resistance versus press ram load behavior for an equatorial flake (diametral) specimen at room temperature. During the first part of the loading the resistance remains about constant at the level of the apparatus insulation because the sulfur resistance is much higher than that of the apparatus insulation. At about 22 metric tons loading (approximately 300 kbar) the sulfur specimen begins to conduct better than the apparatus insulation and as the loading increases

the conduction is predominantly by the specimen. At about 38 metric tons loading (almost 500 kbar) the resistance levels out, essentially independent of additional pressure, indicating a fairly saturated semimetallic state with a resistivity of about 0.03 ohm cm. Upon unloading, the resistance increases to the background resistance of the cell. It is known from other experiments by Ruoff and Gupta¹⁰ on sulfur, using special apparatus insulation, that the resistance of the sulfur specimen is at least 10^{14} ohm at about 150 kbar.

It was found that at a given loading the resistance equilibrium of the specimen could be accelerated by increasing the temperature a few tens of $^{\circ}\text{C}$. Figure 3 shows the resistance versus loading behavior when the apparatus was held at 70°C . In order to determine the activation energy of conduction, ΔE^* , of the semiconducting sulfur the loading was held constant at certain levels while the temperature was cycled within the band of $80^{\circ}\text{C} - 25^{\circ}\text{C}$. This was accomplished by wrapping the periphery of the pressure apparatus and its bolster blocks with resistance heating bands and heating the apparatus as a whole while *in situ*, under load, in the hydraulic press. Cool off was effected by turning off the electric heat and blowing room air past the apparatus with a fan. Three such cycling points are indicated on the graph. Figure 4 shows a $\log R$ vs $10^3/T(^{\circ}\text{K})$ plot of the behavior during three successive temperature cycles at 22.5 met-

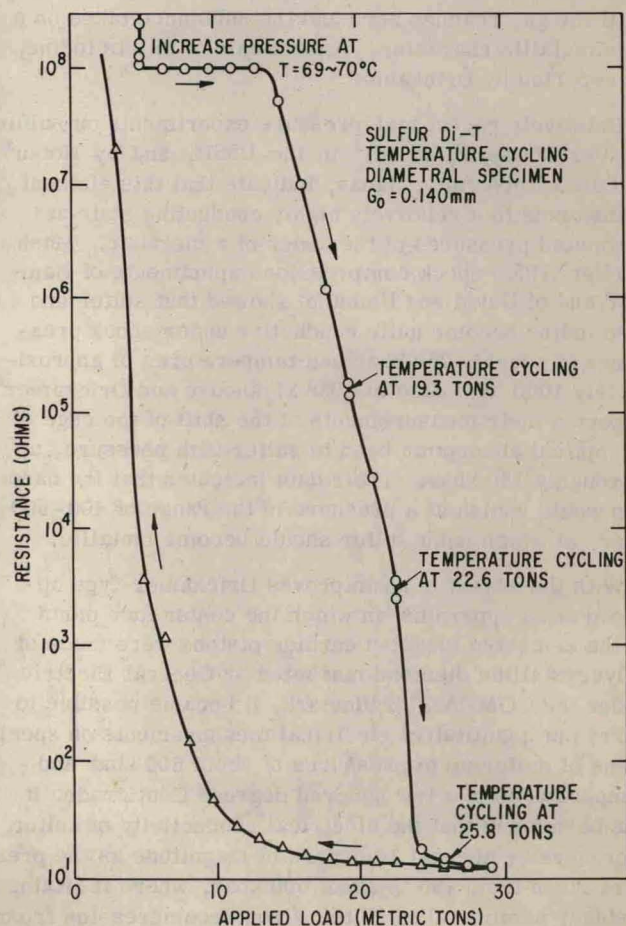


FIG. 3. Resistance vs press ram oil pressure for a diametral specimen of sulfur at 70°C .

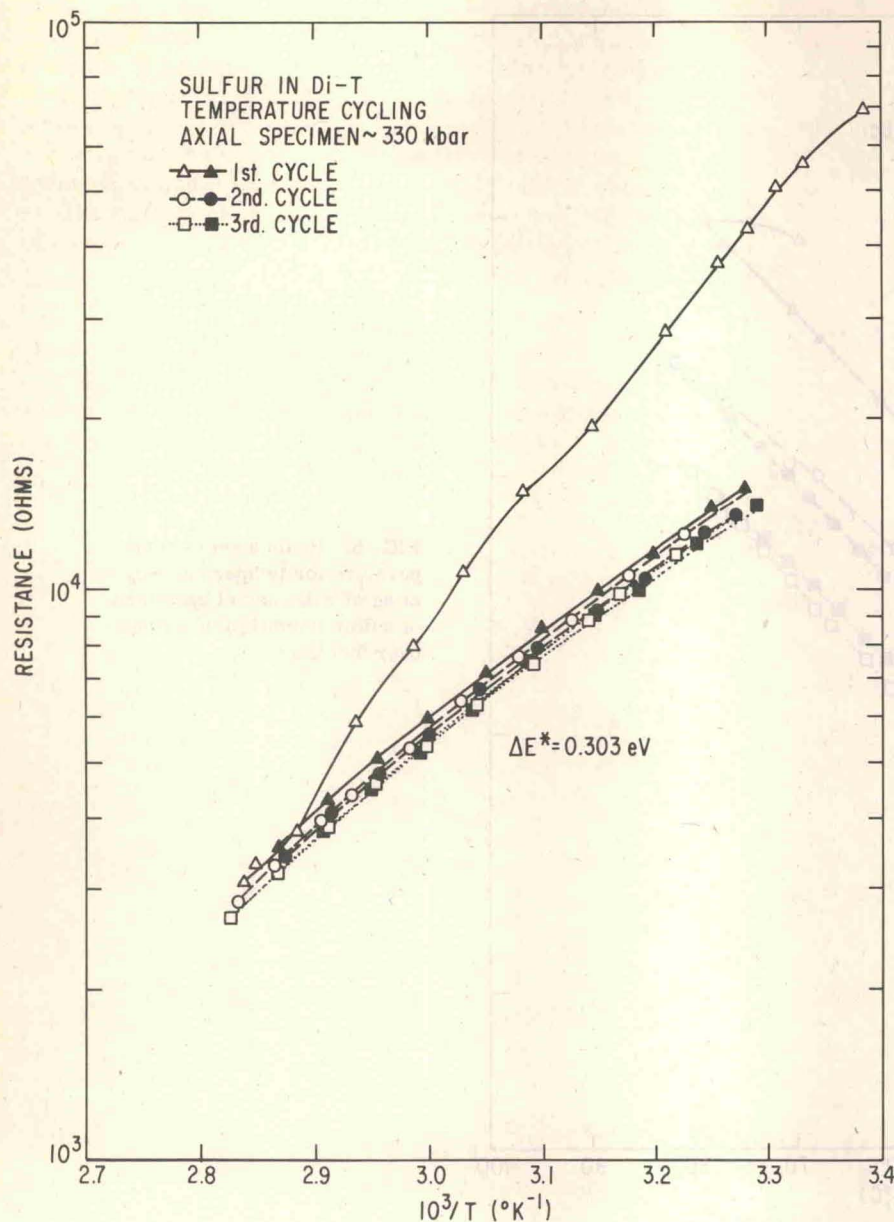


FIG. 4. $\text{Log} R$ vs $10^3/T$ ($^{\circ}\text{K}$) plot for temperature-cycling of axial specimen of sulfur 330 kbar pressure.

ric tons ram loading (~ 330 kbar). The slope of the $\text{log} R$ vs $10^3/T$ line on this graph corresponds to an activation energy of conduction, ΔE^* , of 0.303 eV.

Figure 5 shows the resistance versus temperature behavior at about 500 kbar pressure where the specimen is in the semimetallic state. In this state the specimen shows a positive linear increase of resistance with temperature characteristic of a metallic state. In this case the temperature coefficient of resistance is $7.2 \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$, which is about a fifth that of common metals like copper or aluminum.

After carrying out a dozen different temperature cycling experiments at various pressure levels in the semiconducting regime, using both diametral-type and axial-type specimen geometries, the ΔE^* data points obtained cluster around a straight line that crosses the $\Delta E^* = 0$ line at roughly 480 kbar, the point at which the specimen goes over into the semimetallic regime, as

shown in Fig. 6. The scatter of the data points on this plot is due mainly to the uncertainty of the actual pressure. Even with the greatest care in preparing the gaskets and measuring the G_0 in each case the pressure reproducibility is probably not any better than $\pm 5\%$.

Two types of experiments were carried out heating the specimen while in the semimetallic state by passing heating current through it. First, by passing direct current through it continuously under steady state thermal conditions;—and second, by application of a very short single pulse of direct current the duration of which was of the order of the thermal relaxation time of the cell. In the first type experiment temperatures up to about $300 \text{ }^{\circ}\text{C}$ were generated in the specimen as estimated from the power input, the dimensions of the specimen and the cell, and the thermal conductivity of pyrophyllite. In the second case the thermal transient characteristics of the cell had to be established and a spe-

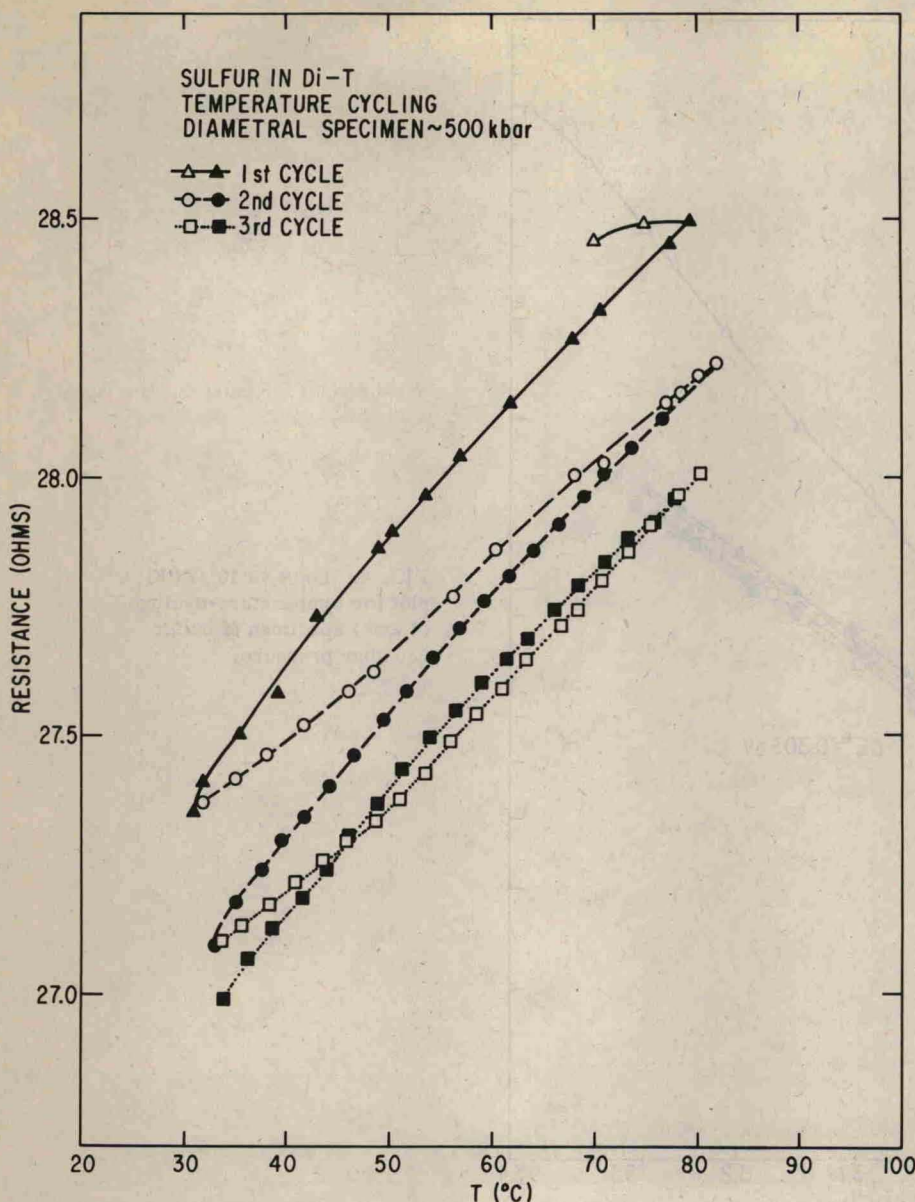


FIG. 5. Resistance vs temperature for temperature-cycling of a diametral specimen of sulfur (metallic) at a little over 500 kbar.

cial pulse-heating circuit devised to match, so that the heating energy could be inserted in a time period of the order of the thermal relaxation time of the cell.

The thermal relaxation time of the cell was established approximately by application of the classical solution of the "hot slab in a cold medium" heat diffusion problem. In the calculation the heat capacity and thermal conductivity of pyrophyllite measured at about 50 kbar were used, together with the cell dimensions, to find the temperature distribution versus time. The results indicated that the "half cool-off time" of the specimen slab is about 25 μ sec in this case. Because of this fast heat leakage the input heating pulse needs to be less than 50–100 μ sec.

The electric circuitry for the single pulse heating is illustrated in Fig. 7. R_s is the specimen to be heated inside the pressure cell. R_i is a noninductive "current resistor," the IR_i drop of which gives the current signal to the oscilloscope. The oscilloscope is a two-chan-

nel, chopped-beam, unit in which the single sweep is triggered by the onset of the pulse, and the dual trace is photographed by an appropriate camera. The power for the pulse is provided by a 45 V "B" battery with a large capacitor in parallel to minimize the terminal voltage drop during the pulse. The "switch" is a silicon transistor (D44H11) capable of switching up to 80 V and a maximum current of 20 A. The trigger pulse generator is adjustable to give pulses of desired voltage and duration, single or repetitive. In an experiment the specimen in the apparatus is brought up to the desired pressure and resistance state, then connected into the pulse circuit and pulsed once to approximately the desired temperature peak, the camera film recording the voltage and current on the specimen against time. From the oscillogram the instantaneous resistance and power can be determined from E/I and $E \times I$ derived from the E and I readings. The $E \times I$ versus time curve is integrated to give the accumulated input energy, Q , versus time, τ . Then R can be plotted against Q as shown in

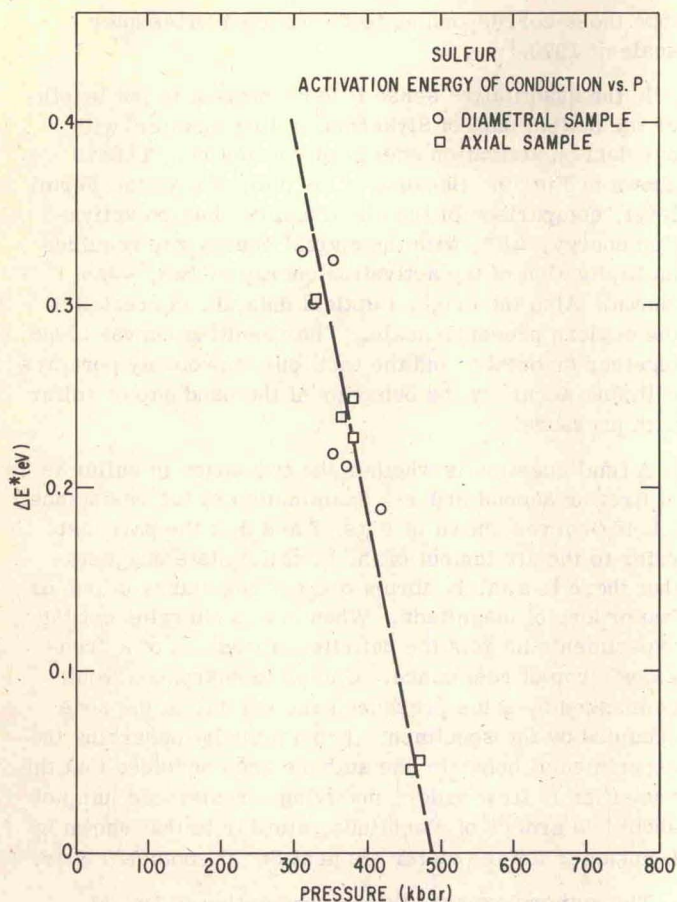


FIG. 6. Activation energy of conduction, ΔE^* , for sulfur vs pressure, derived from temperature cycling experiments.

Fig. 8. The major inflection of the $R(Q)$ curve at about 13×10^{-3} J is reproducible in successive heating pulses and is most likely an indication of the onset of melting.

The specimen temperature rise at a time τ after the beginning of the heat pulse may be calculated from the energy insertion, $Q(\tau)$, by allowing for the heat leakage during that time corresponding to the heating power level, and assuming from the relationship of Dulong and Petit that the molecular heat capacity is about 6 cal mole⁻¹ deg⁻¹ °C (since we do not know by measurement the heat capacity of metallic sulfur). Using these relationships the $\Delta T(Q)$ curve shown in Fig. 8 is obtained. Comparison of the inflection point of the $R(Q)$ curve with the $T(Q)$ curve gives a ΔT of about 575 °C, or a T of 600 °C for the temperature of the onset of the 13×10^{-3} J "phenomenon" (probably melting).

The temperature coefficient of resistance corresponding to the initial slope of the $R(T)$ line for the initial heat pulse of a given specimen agrees with that derived from static heating just prior to the heat pulse. Thus the two methods are consistent. The minor $R(Q)$ inflection point which appears in Fig. 8 at about 6×10^{-3} J (or about 300 °C) has not been studied enough to determine whether it is real and always reproducible on the first heating pulse. It does not appear in the pulses after the first. It is possible that it corresponds to a solid-to-solid phase change on the first heating, and it

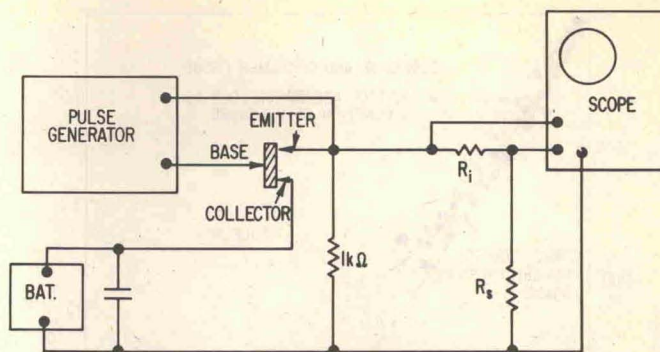


FIG. 7. Transistor-switched circuit for pulse-heating specimens in the diamond-tipped opposed piston apparatus.

may be that upon cooling from the "liquid phase" the original solid phase is not regenerated. By contrast, the major inflection at 13×10^{-3} J is reproducible in successive single pulses. Repeated pulse heatings to peak temperatures of 800 °C–1000 °C cause gradual deterioration of the specimen, indicated by a progressive increase of the room temperature resistance. Probably the hot sulfur reacts with the surrounding cell material and electrodes to some extent during the brief high temperature pulses.

In the room temperature runs it has been found that the retrieved sulfur specimens yield the usual x-ray dif-

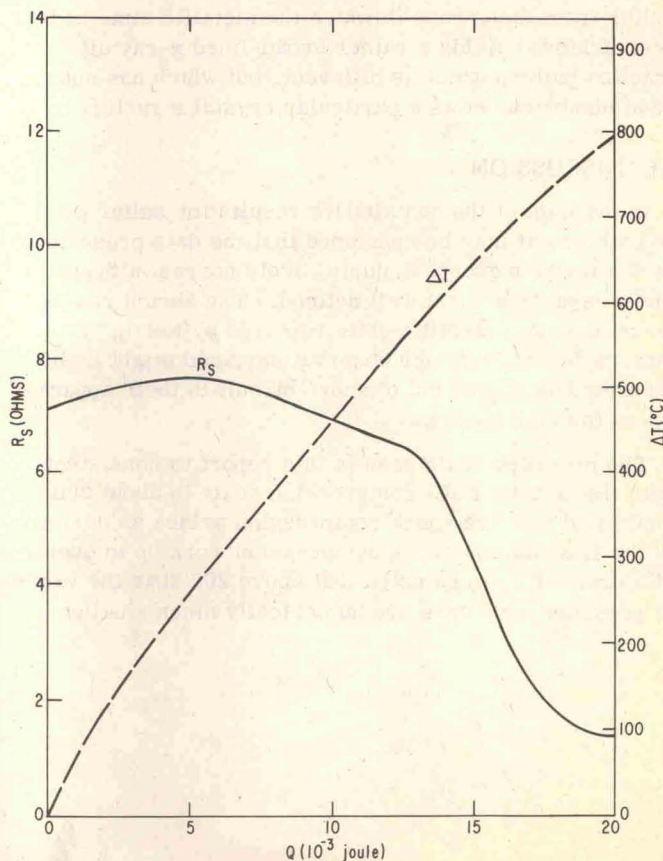


FIG. 8. R_s (ohms) and temperature rise, ΔT °C, vs energy insertion, Q , for a metallic sulfur specimen at $P > 500$ kbar, pulse-heated at about the 100 watt power level.

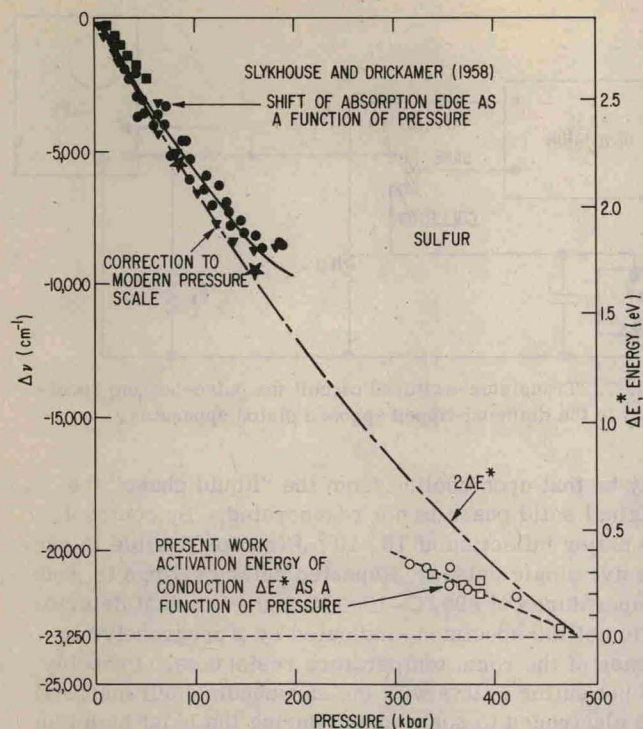


FIG. 9. Absorption edge shift, and activation energy plotted against pressure, for elemental sulfur.

fraction pattern of orthorhombic sulfur, provided it was not pressurized into the metallic region. The retrieved sulfur from those runs in which the metallic state had been achieved yields a rather broad-lined x-ray diffraction pattern which is different, but which has not been identified yet as a particular crystal structure.

III. DISCUSSION

In the light of the quantitative results for sulfur presented here it may be concluded that the data presented by the Russian group² is qualitatively correct although the pressures are not well defined. The abrupt resistance drop to a metallic state reported by Notsu,³ is quite different from our observations, and might be interpreted as some kind of short-circuit in their apparatus at the high loadings.

The pressure scale used in this report is consistent with the current NaCl compression scale to about 300 kbar, and with the shock compression values as derived in the Los Alamos shock compression work up to over 500 kbar. It is to be noted that above 200 kbar the values of pressure used here are numerically much smaller

than those corresponding to the revised Drickamer scale of 1970.¹¹

In the quantitative sense it is of interest to put together the optical data of Slykhouse and Drickamer⁶ with our data on activation energy of conduction. This is shown in Fig. 9. Because of the definition of the Fermi level, comparison of the electrical conduction activation energy, ΔE^* , with the optical energy gap requires multiplication of the activation energy by two,¹—as shown. Also the original optical data are corrected to the modern pressure scale. The resulting curves blend together smoothly, and the total curve probably portrays with fair accuracy the behavior of the band gap of sulfur with pressure.

A final question is whether the transition in sulfur is of first or second order. Examination of the resistance/loading curves shown in Figs. 2 and 3 at the part just prior to the attainment of the metallic state suggests that there is a fairly abrupt drop of resistance of one or two orders of magnitude. When one is carrying out the experiments he gets the definite impression of a "run-away" drop of resistance. Complete sharpness would be masked by some pressure gradient within the zone occupied by the specimen. From actually observing the experimental behavior the authors are convinced that the transition is first order, involving a resistance jump of about two orders of magnitude, similar to that shown by Drickamer for the sister element Se¹ at about 120 kbar.

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