

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

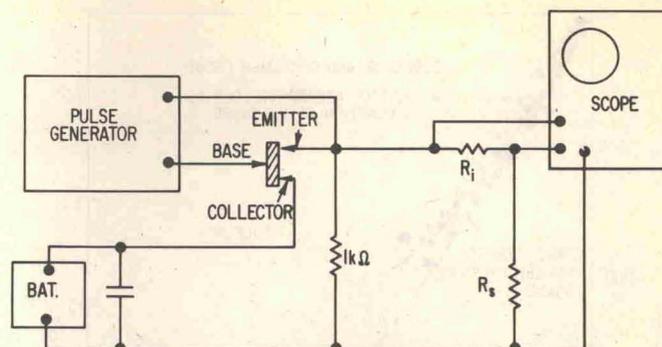


FIG. 7. Transistor-switched circuit for pulse-heating specimens in the diamond-tipped opposed piston apparatus.

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-

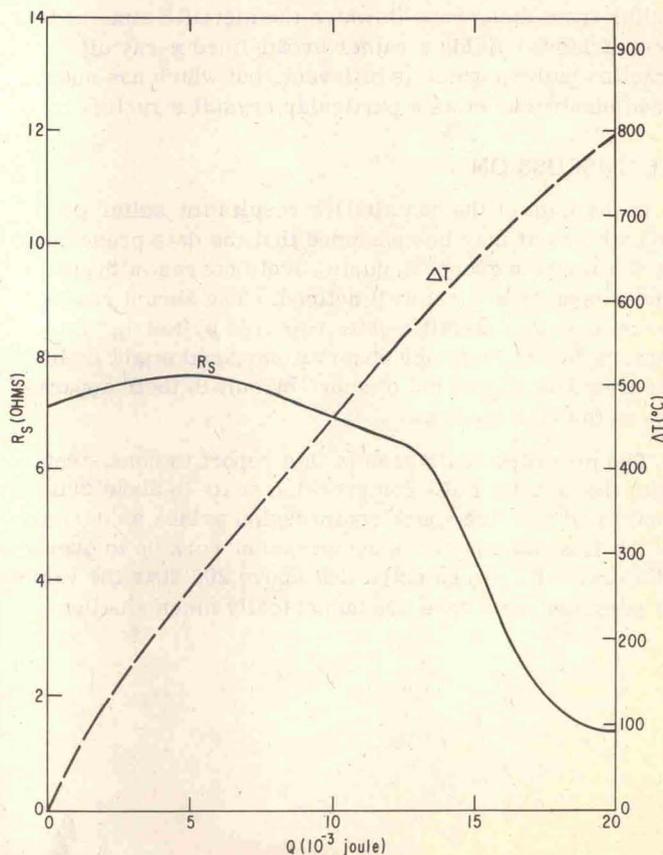


FIG. 8. R_s (ohms) and temperature rise, ΔT °C, vs energy insertion, Q , for a metallic sulfur specimen at $P > 500$ kbar, pulse-heated at about the 100 watt power level.

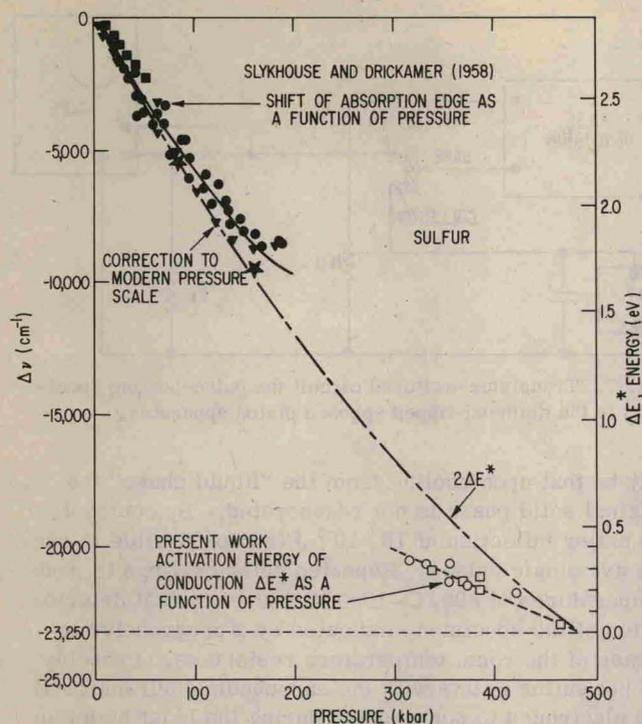


FIG. 9. Absorption edge shift, and activation energy plotted against pressure, for elemental sulfur.

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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