Electrical behavior of sulfur up to 600 kbar—metallic state

K. J. Dunn and F. P. Bundy

Corporate Research and Development, General Electric Company, Schenectady, New York 12301
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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 resisitivity in the metallic state is about 0.03 ohm cm. 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 Notsu[3] 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 Hamann[4] and of David and Hamann[5] 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 Drickamer[6] 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 apparatus[7] 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 tests[8] utilizing the ($\alpha - \epsilon$) transitions in the FeCo and FeV alloys, observed by shock compression and reported by Loree, *et al.* in 1966,[9]

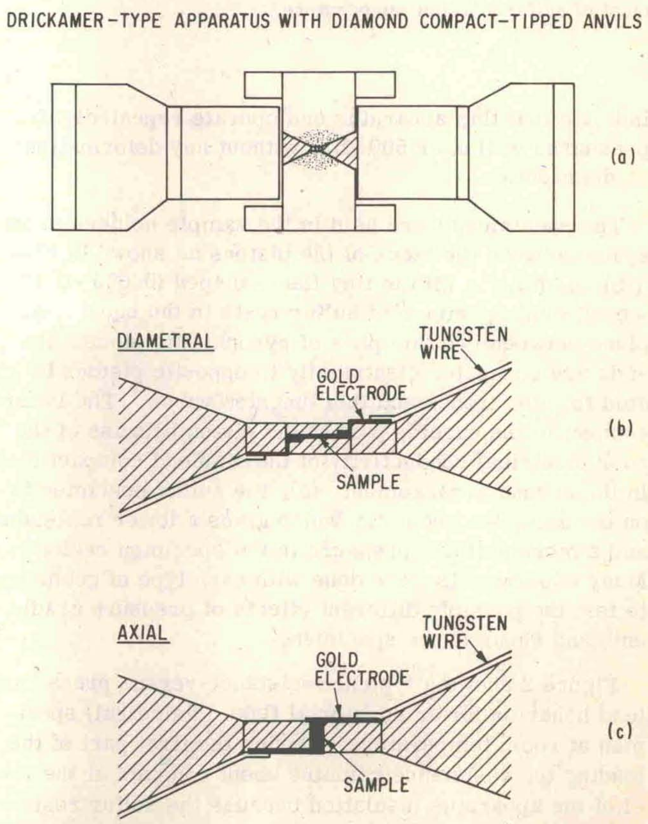

FIG. 1. Opposed diamond-tipped piston apparatus used in this work. (a) Cross section of apparatus; (b) cell arrangement for diametral specimen in equatorial plane; (c) cell arrangement for axial specimen.

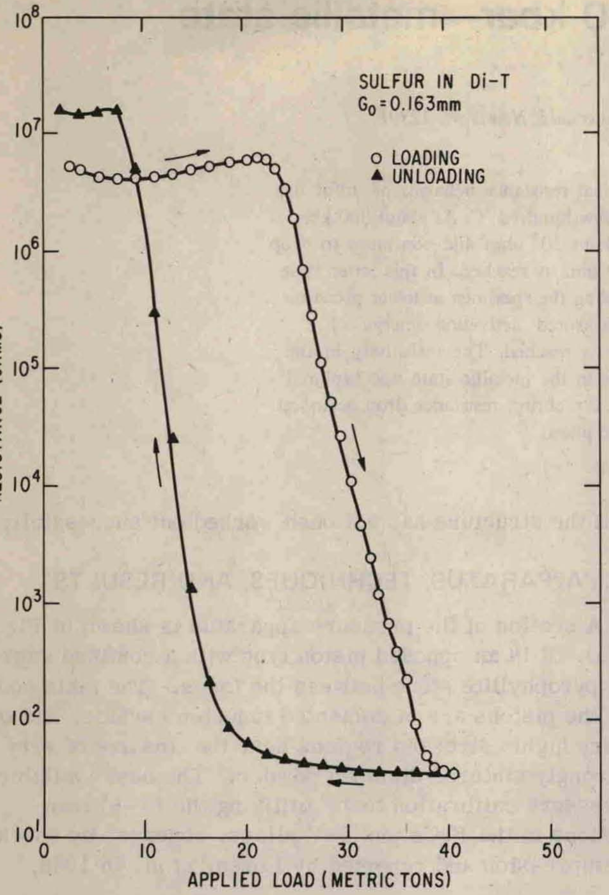

FIG. 2. Resistance vs press ram force for a diametral specimen of sulfur at room temperature.

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 ($0.025\times0.43\times0.62$ 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 Gupta[10] 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 °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 °C–25 °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 logR vs $10^3/T$(°K) plot of the behavior during three successive temperature cycles at 22.5 met-

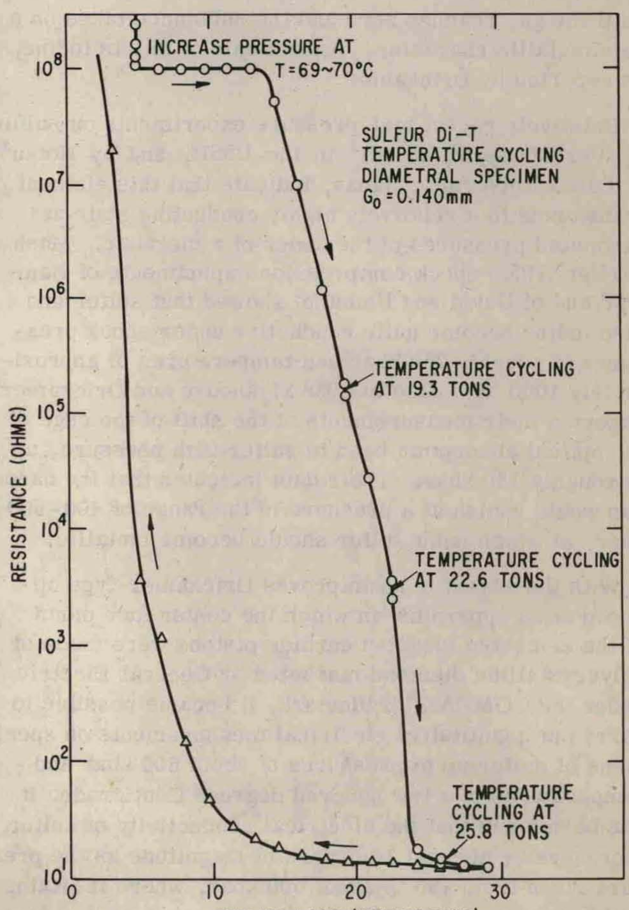

FIG. 3. Resistance vs press ram oil pressure for a diametral specimen of sulfur at 70 °C.