Superconductivity of sulfur at high pressure

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At a pressure 200 kbar sulfur becomes superconducting at a temperature 5.7±0.1 K.

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The elements of group VI of the periodic system (sulfur, selenium, tellurium, and polonium) exhibit a sequence of changes in their physical properties. One of the best insulators (up to 10^{17} Ω-cm) sulfur, which crystallizes under usual conditions into structures formed of ring configurations, gives way to the semiconducting selenium and tellurium, with crystal structure made up of zig-zag chains, and metallic polonium with cubic primitive lattice. A similar sequence of properties is demonstrated by these elements also under the influence of high pressures, which increase with the position of the element in the group.[1]

Tellurium becomes metallic at 40 kbar and selenium at 130 kbar. The metallization of sulfur in shock waves, with a decrease of resistivity to 0.03 Ω-cm, was observed at 220–260 kbar.[2] Extrapolation of the energy gap to zero from the measurements of the dependence of the edge of the optical absorption, with correction to allow for the modern pressure scale, yields for the metallization of sulfur a value 180–240 kbar.[3] Relatively recent measurements of the resistivity give contradictory estimates of the pressure at which the sulfur becomes metallic. This pressure is 0.5–1Mbar according to data of one group of authors,[4,6] and 175–285 kbar according to others.[7,8]

After observing superconductivity of the metallic phase of tellurium and selenium,[9,10] Matthias regarded the superconductivity of the metallic phase of sulfur as a natural to the extent that it is usual for nontransition metals with two and more valence electrons.[11] Our measurements have shown that sulfur, just as its neighbors in the group, exhibits superconducting properties under conditions of high pressures and low temperatures.

We measured the dependence of the resistivity of sulfur of analytically pure grade on the temperature at a given pressure in a bomb with fixed piston. The pressure cell comprised flat Bridgman anvils of VK-3M metal-ceramic alloy, produced by a special technology, with a working-area diameter 1.5 mm. The selenium sample was extruded to 0.2 mm diameter and placed in the central opening of a pellet of pyrophillite 0.3 mm high. The electric contact was through the plungers of the anvils. Figure 1 shows the dependence of the resistivity of sulfur on the load at room temperature. For different samples, the abrupt decrease of the resistance begins at an anvil load of 8–9 tons and ends at 10–11 tons, and the accompanying decrease of resistivity is by ~5 orders of magnitude. The pressure of the transition is estimated at 200–240 kbar on the basic of the jumps of the resistivity of ZnS (150 kbar) and GaP (220 kbar), recorded on the same pair of anvils. The pressure of the transition in the sulfur is only an estimate, since it depends, at constant pellet thickness, on the number of the loadings of the given pair of plungers, on the release of the pressure at a fixed load, and on other features of a chamber of this type.

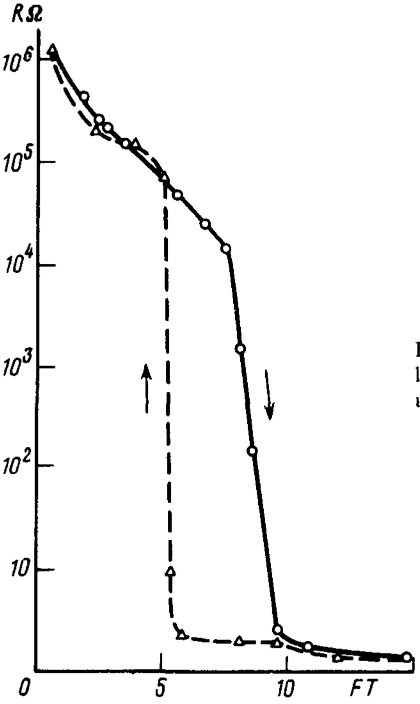

FIG. 1. Dependence of the resistivity of sulfur on the load at room temperature (circles–loading, triangles–unloading).

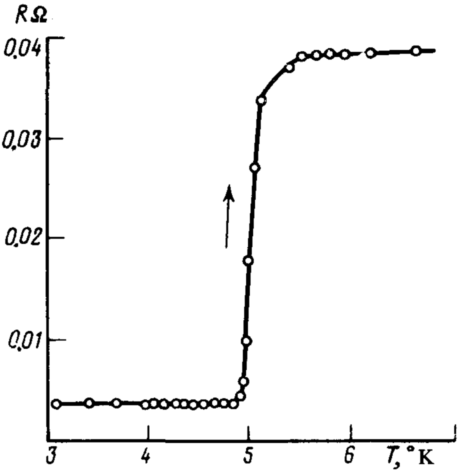

FIG. 2. Plot of superconducting transition of sulfur under pressure.

For the low-temperature measurements, the load on the plungers was fixed at a value substantially increasing the point at which the resistivity curve flattens. The resistance of the sample was in this case 0.1 Ω (0.002 Ω-cm). The large mass of the chamber ensured a slow heating from 4.2 K when the chamber was raised above the helium level. The temperature was measured by two gold (iron)–copper thermocouples arranged symmetrically as close as possible to the sample. Figure 2 shows the jump of the resistivity, observed when the bomb was heated and responsible for the transition of the sulfur into the superconducting state. The transition temperature for the given pressure, averaged for several cooling and heating cycles, is equal to 5.7 ± 0.1 K, and in each case it was determined from the start of the transition. The width of the transtion, 0.5 K, is evidence of the sufficient homogeneity of the pressure in the chamber and of the phase composition of the sample. The sample resistance at low temperatures prior to the transition is 0.04 Ω, and the residual resistance after the transition is 0.004 Ω and corresponds to the resistance of the current path through the plungers and other parts of the chamber.

An anomalously large value (8.0×10^{-5} K/bar) and a positive sign of the baric derivative of T_c were obtained for the high-pressure phase of tellurium (Te-II).[12,13] If the analogy with tellurium is extended also to the superconducting properties of the high-pressure phase of sulfur S-II, then the appreciable difference between the values of the superconducting temperature of sulfur as obtained by our measurements (5.7 K) and the measurements of our colleagues[14] (9.7 K) can be attributed to a difference amounting to only 50 kbar.

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