Superconductivity of sulfur at high pressure

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A superconducting transition has been observed in the range 14–19 K in the metallic modification of sulfur that occurs at a high pressure at room temperature. A new superconducting state with T_c in the range 26–31 K can be produced by decreasing the pressure to the level of the metal-insulator transition and subsequently increasing it beyond the insulator-metal transition.

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Superconductivity of the metallic modification of sulfur at a high pressure $P \approx 50$ GPa has been observed in Refs. 1–3. Investigation of sulfur is of interest because of its high-temperature superconductivity. Two main reasons make it possible to assume the existence of anomalous superconducting properties of sulfur. First, the polymorphic transformations in sulfur, in particular the transition of sulfur to the metallic state, occur smoothly and over a long period of time.[4-7] In such a case, the metallic and insulator phases can co-exist in the sample; consequently, a metal-insulator boundary, which is conducive for high-temperature superconductivity is produced[8]; second, the sulfur molecules can have the shape of polymer chains,[9] which is of interest because of high-temperature superconductivity.[10]

We present in this paper the results of investigations that were performed using "Carbonado" -type diamond anvils.[11,12] The experimental setup used by us made it possible to vary the forces applied to the anvils from 0 to 1000 kg, to vary the temperature in the range of 2.5 to 350 K, and to perform the experiments in external magnetic fields up to 5 T. Using the chosen design of the anvils, these forces could produce a pressure up to 100 GPa in the sample. The sample is a layer of orthorhombic sulfur (99.9%) with an initial thickness of $\sim$0.1 mm, deposited on a flat "Carbonado" anvil. A combination of high pressures and external magnetic fields[13] was used for an unambiguous determination of the superconducting transition. A correct measurement of the sample temperature is very important in these investigations. In the conducted experiments, the sample temperature was determined with an accuracy of ±0.3 K in the range 4.2–32 K.

The obtained results depend strongly not only on the parameters P and T to which the sample is subjected but also on the path in the P-T (F-T) diagram that leads to these parameters (F is the force applied to the anvils).

I. Figure 1a shows the path corresponding to a transition of the sample to the metallic state at room temperature $1 \rightarrow 2$, followed by a cooling to helium temperature $2 \rightarrow 3$.

Figure 2 shows the trace of the resistance of the sample and of the resistances of the anvils that were connected in series with it, as the temperature was lowered (the transition from point 2 to point 3 in the F-T diagram in Fig. 1b). The anoma-

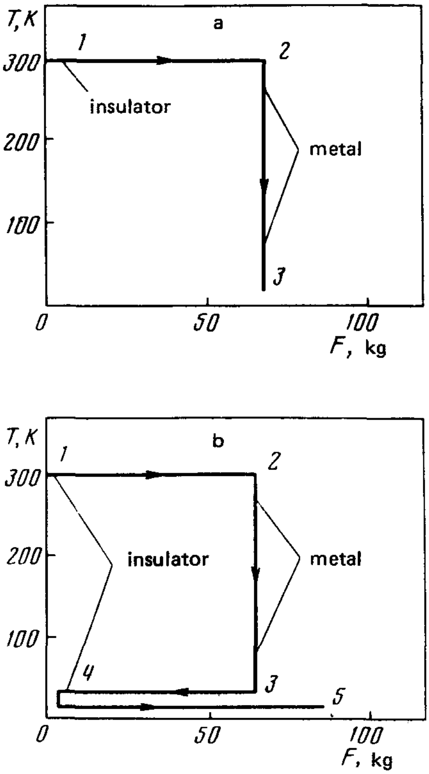

FIG. 1

lous decrease of the resistance in the temperature interval 5–20 K is attributable to the superconducting transition in sulfur. A displacement of the transition toward the lower temperature as a result of application of a magnetic field (Fig. 2) and an increase of the current flowing through the sample confirm this assumption.

T_c was determined at the $0.9\Delta R$ level, where ΔR is the variation of the resistance due to superconducting transition. The critical temperature of the transition in Fig. 2 is 19 K. In the other experiments we observed T_c values in the interval 14–19K. It is characteristic that T_c remains almost the same when the force applied to

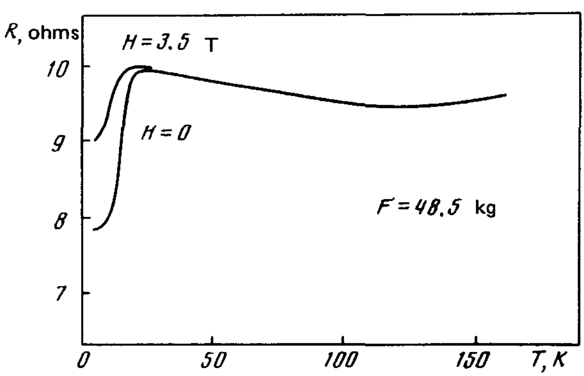

FIG. 2

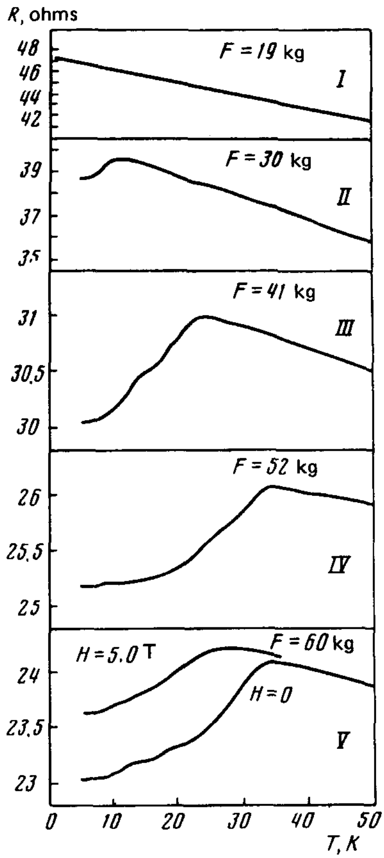

FIG. 3

the anvils is varied. A decrease of T_c to 5 K is observed when the forces are close to the values that correspond to the transition to the insulator state, consistent with the experimental results of Refs. 1-3.

II. Figure 1b shows the path in the F-T diagram corresponding to the transition to the metallic state at room temperature $1 \rightarrow 2$, to the cooling to helium temperatures $2 \rightarrow 3$, to the transition of the sample to the insulator state as a result of decreasing the pressure at helium temperatures $3 \rightarrow 4$, and to a subsequent increase of the pressure at helium temperatures $4 \rightarrow 5$. The results of measurements of the sample resistance $R(T, F = \text{const})$ for the forces $F_I, F_{II}, \ldots, F_V$ along the path segment $4 \rightarrow 5$ (Fig. 1b) are shown in Fig. 3. The semiconductor modification is observed at low forces $F_I = 19$ kg. At $F_{II} = 30$ kg an anomaly characteristic of the superconducting transition appears on the $R(T)$ curve, and at $F_{III} = 41$ kg this anomaly is displaced toward higher temperatures. At $F_{IV} = 52$ kg the displacement of this anomaly toward higher temperatures with an increase in the force virtually ceases (see Fig. 3). The anomaly is displaced toward lower temperatures in a magnetic field (Fig. 3) and also as a result of increasing the current that flows through the sample; this indicates that the anomaly is attributable to the superconducting transition. The maximum temperature of the superconducting transition (Fig. 3) is $T_c = 31$ K.

The maximum values of T_c were in the range 26–31 K in the other experiments in which the samples and anvils were replaced.

Variation of the parameters F and T in the schemes in Figs. 1a and 1b was repeated several times for each of the three sulfur samples and three pairs of "Carbonado" anvils (a total of about 500 times).

It can be concluded from our measurements that 1) the maximum values of T_c obtained as a result of varying the paramenters F and T in accordance with the scheme in Fig. 1a are in the range 14–19 K. 2) The maximum values of T_c obtained as a result of varying the parameters F and T in accordance with the scheme in Fig. 1b are in the range 26–31 K.

We note that the value of T_c decreases to 14–19 K when the metallic modification of sulfur with $T_c \sim 26$–31 K is held at least three days at a constant pressure and room temperature.

A large difference (about 10 K) between the intervals of the maximum critical temperatures T_c of sulfur, which is subjected to a pressure in accordance with the schemes in Figs. 1a and 1b, makes it possible to assume that two sulfur states exist. These may be different polymorphic modifications of metallic sulfur. It is also possible that there is one metallic modification, which is arranged differently in an insulator matrix, as already mentioned at the beginning of this paper.

It should be noted that the anomaly of $R(T)$ observed in the investigation of sulfur at low temperatures (Figs. 2 and 3) does not depend on the rate at which the temperature changes within the interval $dT/dt = (10$ K/sec to 10^{-2} K/sec). This indicates that the anomaly of $R(T)$ is not due to polymorphic transformations (first-order transitions) that occur slowly in sulfur.[4-7]

The dependence of the $R(T)$ anomaly on the magnetic field makes it possible to assume that it is associated with the magnetic transformations in sulfur. Before such assumption is made, however, we must also assume that metallic sulfur is a magnetic material.

On the other hand, all the characteristic features of the $R(T)$ anomaly of sulfur are explained by superconductivity: 1) a sharp increase of the resistance as a result of increasing the temperature; 2) a decrease of T_c with increasing external magnetic field; and 3) a decrease of T_c with increasing current that flows through the sample.

A decrease of the resistance at $T > T_c$ is caused by shunting the metallic sulfur by semiconductor sulfur between the anvils in the high-pressure region.

We note that a similar anomaly of $R(T)$, its behavior in an external magnetic field and as a function of the current were observed in a rounded cone-plane chamber that was used in our experiments with sulfur and in a study of germanium and silicon.[14] The presence of superconductivity in germanium and silicon under pressure was established previously.[15]

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