

a 0.20-in.-diam. graphite heater with stainless-steel current leads, inside of which was placed a 0.18-in. cylinder of boron nitride which served to transmit pressure to the 0.06-in. cylindrical sample. A pair of chromel-alumel thermocouples, one at the center of the sample ( $T_a$ ) and the other imbedded in the sample container at a distance of 0.03 in. from the edge of the sample ( $T_b$ ), were used to make DTCA measurements. DTCA measurements consist of observation of the temperature difference  $\Delta T = T_b - T_a$  as a function of the center temperature  $T_a$ . If the thermal conductivity of the sample differs in magnitude on each side of a phase boundary, the transition between phases will be reflected by a discontinuous shift in the temperature dependence of  $\Delta T$ . Suitable conditions of experiment, with a theoretical analysis such as presented earlier<sup>2</sup> allow a qualitative measure of the sample thermal conductivity at elevated pressure and temperature.

The DTCA signals indicative of melting of the samples were not discontinuous in the mathematical sense. All signals obtained had a width on the  $T_a$  scale greater than zero. The midpoint of this temperature spread was taken as the melting point.

The thermocouple at the center of the sample was not, in general, electrically insulated from the sample. It is conceivable that temperature gradients along the sample length could create thermoelectric emfs affecting the measured thermocouple output. However, experiments with electrically insulated center thermocouples indicated that such effects are well within experimental error for the materials in question.

Powder samples of S, Se, and Te were used in the experiments, the powder being compacted around the center thermocouple. Reagent grades of sulfur and selenium from Fisher Scientific Co. were used. The sulfur and selenium were 99.5% and 99.9% pure, respectively. The atmospheric-pressure melting points of these materials were found to be  $114 \pm 1^\circ\text{C}$  and  $217 \pm 1^\circ\text{C}$  for S and Se, respectively. The tellurium stock was obtained from American Smelting and Refining Co., and was 99.999% pure. The S and Se starting materials were investigated by x-ray diffraction and each was shown to consist primarily of the crystalline form of the elements. Division of the portions of the sulfur soluble and insoluble in carbon disulfide at  $-80^\circ\text{C}$  indicated that the material consists of about 75% crystalline and 25% amorphous forms.<sup>13</sup>

All experimental data were automatically recorded on X-Y recorders. Standard thermocouple conversion tables were used and no attempt was made to correct for the effect of pressure on the output of the thermocouples. The temperatures are believed to be accurate to about  $\pm 1.5\%$ . Standard room-temperature pressure calibration was utilized<sup>12</sup> and pressures are thought to

be accurate to  $\pm 2.5\%$  above 20 kbar and  $\pm 0.5$  kbar below 20 kbar.

### III. RESULTS

#### A. Sulfur

Sulfur exists in a complex multiplicity of solid and liquid phases.<sup>13,14</sup> The stable room-temperature crystal structure is rhombic. At atmospheric pressure and  $95^\circ\text{C}$  rhombic sulfur transforms to a solid monoclinic form which then melts at  $115^\circ\text{C}$ . Liquid sulfur is found to experience a "change point" at  $160^\circ\text{C}$  where its physical properties are strikingly altered. If liquid sulfur above  $160^\circ\text{C}$  is rapidly cooled to room temperature, a sticky, amorphous variety is formed. This amorphous sulfur transforms spontaneously into the stable crystalline form existing at the temperature being maintained, the rate of transformation depending on the temperature.

The effect of pressures up to 3 kbar on the melting of sulfur and the rhombic to monoclinic transition has been reported by Tammann.<sup>15</sup> His results are shown in the inset in Fig. 1. It was found that the rhombic to monoclinic phase boundary intersects the melting curve forming a triple point at 1.3 kbar and  $155^\circ\text{C}$ , as shown in the inset in Fig. 1. At pressures above 1.3 kbar, the rhombic sulfur is the stable form and the melting point curve will be that of rhombic sulfur.

The present melting data on sulfur under pressure are shown in Fig. 1. The filled circles represent points taken on the initial temperature cycle, while the open circles are data points taken after the sulfur had been previously melted. Examinations of sulfur samples which had been melted at pressure showed that the original rhombic sulfur was transformed to the sticky amorphous form. This amorphous sulfur was studied by x-ray diffraction at atmospheric pressure and found

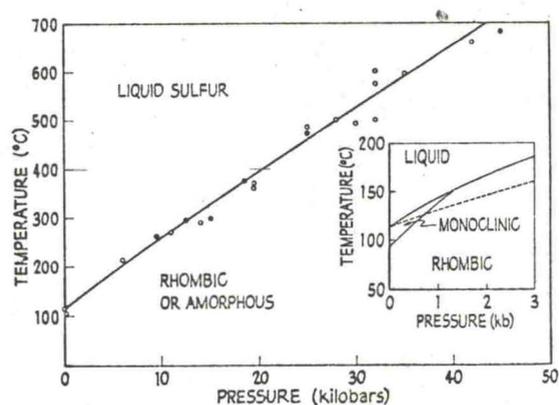


FIG. 1. Melting curve of sulfur. Inset: the solid curve is taken from Ref. 15 and the dashed curve is the low-pressure extrapolation of the reported data.

<sup>14</sup> G. W. C. Kaye and W. F. Higgins, Proc. Roy. Soc. (London) 122, 633 (1929).

<sup>15</sup> G. Tammann, *The States of Aggregation* (D. Van Nostrand Company, Inc., New York, 1925).

<sup>13</sup> *The Sulphur Data Book*, edited by William N. Tuller (McGraw-Hill Book Company, Inc., New York, 1954), p. 4.