

Properties of Group VI B Elements Under Pressure. I. Melting Curves of S, Se, and Te†

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The melting curves of S, Se, and Te have been determined to 45 kbar by differential thermal-conductivity analysis in a tetrahedral anvil apparatus. The data for sulfur show that the melting point increases approximately linearly from 114°C at atmospheric pressure to about 700°C at 45 kbar. Rhombic sulfur melted under pressure is found to crystallize upon solidification in the amorphous plastic form, which can be retained metastably at atmospheric pressure. The selenium melting curve is slightly concave toward the pressure axis and rises from 220°C at atmospheric pressure to 650°C at 40 kbar. A maximum in the melting curve of tellurium is observed at about 10 kbar and 480°C. These experimental results are discussed in relation to the current ideas on the general nature of melting curves. The maximum in the melting curve of tellurium is explained in terms of coordination in the liquid state and the existence of a liquid-state structural change of a statistical nature, which appears to divide the liquid into a metallic and a semiconducting phase. It is predicted that selenium, and, perhaps, sulfur also have maxima in their melting curves. The normalized change in resistivity upon melting ($\Delta\rho/\rho$) is correlated with the atmospheric-pressure melting-curve slopes m_0 for a number of elements. A plot of m_0 versus ($\Delta\rho/\rho$) shows that the data for the elements considered, except the alkali metals and the Group VI B elements, very roughly define a linear relationship. The sign of m_0 and ($\Delta\rho/\rho$) is the same for all elements considered except S, Se, and Te. A general relation between the change upon melting in the short-range order of the atomic distribution and the sign of m_0 is also discussed. The semimetals, for which $m_0 < 0$, undergo striking changes in short-range order, whereas the metals, for which $m_0 > 0$, exhibit a continuity of short-range order.

I. INTRODUCTION

ATMOSPHERIC-PRESSURE physical properties of sulfur, selenium, and tellurium have been thoroughly investigated for quite a number of years. Very little data, however, have been reported on the high-pressure-high-temperature behavior in either sulfur or selenium, and only recently a maximum in the high-pressure melting curve of tellurium was discovered.¹ We report here measurements on the melting curves of S, Se, and Te to 45 kbar and 700°C. The experimental technique utilized has been described earlier² and involves a newly developed, simplified version of differential thermal conductivity analysis (DTCA).³ The present data agree well with previous determinations of the high pressure melting curves of selenium⁴ to 10 kbar and tellurium¹ to 30 kbar. No results on the high-pressure melting of sulfur above 3 kbar have been reported. The present study shows that pressure affects the melting points of S, Se, and Te in a very striking manner and indicates the ready applicability of the DTCA technique for determination of phase boundaries of electrically insulating materials.

One of the most interesting high pressure character-

istics of the Group VI elements S, Se, and Te is that each approaches a metallic state under extreme pressure conditions. No static high-pressure resistance measurements on sulfur have been reported, but possible metallic conduction at a shock pressure of 230 kbar has been observed.⁵ Optical studies by Slykhouse and Drickamer⁶ on the sulfur forbidden-band gap indicate that its conduction will become metallic at about 400 kbar. A transition in selenium to a state of high electrical conductivity was observed by Balchan and Drickamer⁷ at 130 kbar; it was later confirmed by low-temperature studies that selenium behaves as a metal at 170 kbar.⁸ Bridgman⁹ first noted a semiconductor-to-metal transition in tellurium which has later been confirmed to be at about 43 kbar.^{10,11} It is interesting, also, to note that the next member of Group VI B, polonium, is metallic at atmospheric pressure.

II. EXPERIMENTAL PROCEDURE

The experiments were performed using a tetrahedral anvil high-pressure apparatus and techniques described previously.^{2,12} The pyrophyllite tetrahedrons contained

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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 $\Delta T \equiv T_b - T_a$ 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 ΔT . Suitable conditions of experiment, with a theoretical analysis such as presented earlier² 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°C indicated that the material consists of about 75% crystalline and 25% amorphous forms.¹³

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 utilized¹² and pressures are thought to

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

III. RESULTS

A. Sulfur

Sulfur exists in a complex multiplicity of solid and liquid phases.^{13,14} The stable room-temperature crystal structure is rhombic. At atmospheric pressure and 95°C rhombic sulfur transforms to a solid monoclinic form which then melts at 115°C . Liquid sulfur is found to experience a "change point" at 160°C where its physical properties are strikingly altered. If liquid sulfur above 160°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.¹⁵ 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°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

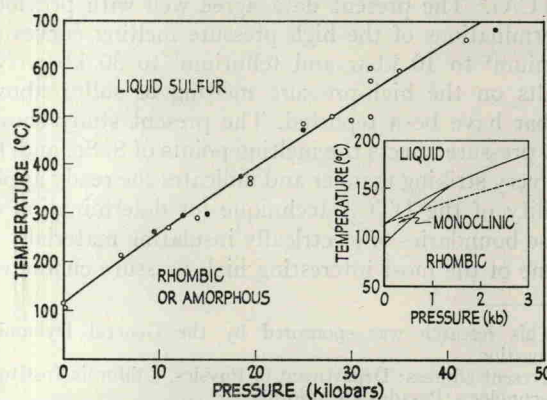


FIG. 1. Melting curve of sulfur. Inset: the solid curve is taken from Ref. 15 and the dashed curve is the low-pressure extrapolation of the reported data.

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