

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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¹⁰ F. A. Blum, Jr. and B. C. Deaton (to be published).

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⁴ Stanley E. Babb, Jr., *J. Chem. Phys.* **37**, 922 (1962).