

strong DTCA signals upon decreasing the temperature past the apparent melting point was indicative of a failure of the selenium to recrystallize, x-ray diffraction studies of the material, before and after the pressure-temperature treatment, were made. It was found that only the hexagonal form was present after melting under pressure. It is felt therefore that Fig. 2 depicts the melting points of hexagonal selenium.

With reference to the possibility of forming glassy amorphous selenium by melting under pressure (analogous to sulfur), it is interesting to note that Bridgman¹⁷ observed that combined shear and hydrostatic pressure transformed amorphous selenium to the hexagonal form. This is just the opposite of what he observed in the case of sulfur.

C. Tellurium

Tellurium crystallizes in a hexagonal chain structure similar to that of selenium.¹⁸ Several high-pressure phases are known to exist. Bridgman⁹ and, more recently, Ball¹¹ found two high-pressure modifications, their room-temperature transition pressures being about 44 and 70 kbar. A thorough investigation of the semiconductor-to-metal transition at 44 kbar by the authors will be published elsewhere.¹⁰ Kabalkina *et al.*,¹⁹ recently reported an apparent structural change from A8 to A7 at 15 kbar and room temperature, as determined by x-ray diffraction studies. Since the pressure dependence of the volume was found continuous in this range, the transition would be one of second order. However, more recently, McWhan and Jamieson,²⁰ making similar x-ray diffraction studies, failed to observe the conditions necessary for the existence of such a transition. Also, their compressibility measurements do not indicate a transition.

The melting of tellurium as a function of pressure has been reported recently by the authors² and others.^{1,11,21} Tellurium was one of the first materials known to exhibit a melting-curve maximum.¹ The melting points for Te I, as determined by DTCA measurements, are shown in Fig. 3. Considering the accuracy involved, these data are found to agree reasonably well with those of other investigators as shown in Fig. 3. The maximum in the melting curve as determined by DTCA occurs at about 10 kbar and 480°C.

The DTCA signals for Te I melting were quite strong as noted previously,² the thermal conductivity of tellurium increasing upon melting. We were unable to obtain reliable indications of the melting of tellurium at pressures above the triple point at 29 kbar and 445°C.

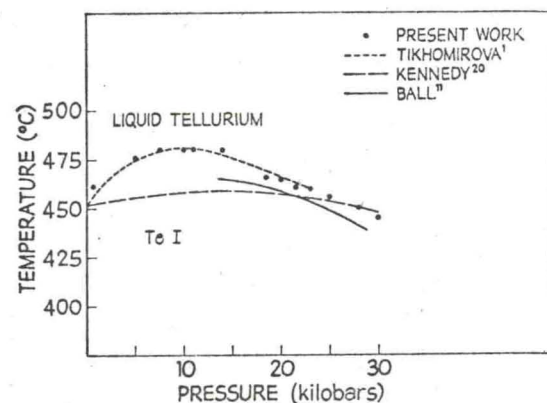


Fig. 3. Melting curve of tellurium determined by DTCA (solid points) compared with other data of indicated source.

IV. DISCUSSION

A survey of the literature revealed that no generally accepted point of view for interpretation of melting curves has been established. It was therefore felt that a brief review and evaluation of the various viewpoints would contribute in a positive manner to an understanding of the data at hand. Section A of the discussion comprises the above-mentioned review, while Sec. B contains specific discussion of the data presented here with the discourse of Sec. A in mind.

A. The General Melting Curve

Thermodynamically, the slope of the melting curve is described by the Clapeyron equation

$$dT_m/dP_m = \Delta V/\Delta S,$$

where T_m and P_m are the temperature and pressure of melting, ΔV is the molar volume change upon melting, and ΔS is the molar entropy change upon melting. This equation restricts in no way the general shape of the melting curve. However, since ΔS is always positive the slope of the melting curve has the same sign as the volume change.

On the assumption that a general shape for all melting curves could be obtained, speculation as to its nature began quite some time ago. Planck, Poynting, and others,²² very early, pointed to the possibility of the melting curve ending in a critical point, analogous to this phenomenon for vaporization curves. Somewhat later, Tammann²³ viewed fusion curves known at that time as segments of general closed curves in the pressure-temperature plane, thus admitting the possibility of minima as well as maxima in the curves. He considered his extensive melting-curve data at pressures to 3 kbar indicative of the idea that the so-called normal melting curve would have a maximum, and he actually found

¹⁹ S. S. Kabalkina, L. F. Vereshchagin, and B. M. Shulenin, Zh. Eksperim. i Teor. Fiz. 45, 2073 (1963) [English transl.: Soviet Phys.—JETP 18, 1422 (1964)].

²⁰ D. B. McWhan and J. C. Jamieson (private communication).

²¹ G. C. Kennedy and R. C. Newton, *Solids Under Pressure*, edited by W. Paul and D. M. Warschauer (McGraw-Hill Book Company, Inc., New York, 1963).

²² See Bridgman's survey of this early work: P. W. Bridgman, Phys. Rev. 3, 126 (1914).

²³ G. Tammann, Ref. 15, pp. 27–36; and *Kristallisieren und Schmelzen* (J. A. Barth, Leipzig, 1903).