to exhibit x-ray characteristics identical to those reported in the literature[16] for so-called plastic sulfur. It seems probable, therefore, that all data taken after the first temperature cycle were actually indicative of melting of plastic sulfur instead of rhombic. These points are shown by the open circles in Fig. 1 and it is seen that they correspond closely to the rhombic melting data. Within the limits of experimental error there appears to be no difference in the melting-point curves of rhombic and plastic sulfur. Since the data presented here extrapolate to the atmospheric-pressure melting point and since the transformation points of the rhombic and plastic forms agree within experimental error, it is felt that the data given do represent melting rather than just a rhombic to plastic transition, as such. Owing to the scatter, the data of Fig. 1 are well represented by a straight line; the solid line shown has a slope of 15°C/kbar.

In order to arrive at the exact nature of the transformation of the rhombic sulfur to the plastic variety, further studies were made. It was found that at ambient conditions the plastic sulfur (formed by melting the rhombic under pressure) spontaneously reverted to the rhombic structure over a period of a few days. Samples of sulfur subjected to pressure and temperature conditions just short of those required to melt them (as indicated by the currently reported data) remained in the rhombic phase. Samples subjected to various temperatures exceeding the melting point, at the pressure in question, were all transformed to the plastic form. Without exception, all samples subjected to pressure and temperature conditions exceeding those required for melting were found to exist in the plastic form when returned to ambient conditions. Various reasonable rates of temperature change used in crossing the melting curve seemed to have no effect on the transformation to the plastic form.

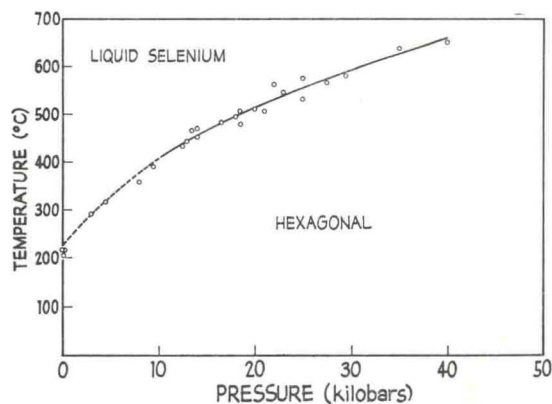It is interesting to note that Bridgman[17] observed

FIG. 2. Melting curve of selenium. The dashed portion of the curve is taken from Ref. 4.

[16] N. S. Gingrich, J. Chem. Phys. 8, 29 (1940); and C. W. Tompson and N. S. Gingrich, ibid. 31, 1598 (1959).
[17] P. W. Bridgman, Phys. Rev. 48, 825 (1935).

that combined shear and hydrostatic pressure initiated this same conversion of sulfur to the "amorphous, sticky variety," whereas hydrostatic pressure alone failed to do so. This further supports the conclusion that the data presented are indicative of melting and the transition to the plastic form is a secondary effect related to the recrystallization process. Pressure inhibition of the atmospheric pressure, 160°C liquid "change point" may explain the formation of plastic sulfur upon melting and cooling under pressure, since the formation process is apparently related to the recrystallization of the phase of liquid sulfur existing above the atmospheric "change point."[17a]

Since the thermal conductivity of all forms of sulfur is comparatively very low,[13] the magnitudes of the discontinuities (indicative of melting) in the temperature dependence of ΔT upon melting of the plastic sulfur were very small, as one would expect, since the thermal conductivity[13] is about a factor of 3 smaller for plastic than for rhombic sulfur. The DTCA signals for sulfur were sometimes completely masked by recorder "ac pick-up" from the heater and transient effects in the signal during the approach to temperature equilibrium. These problems became so acute that we were unable to obtain reliable data on sulfur above 45 kbar.

B. Selenium

Selenium, like sulfur, exists in several allotropic forms, the most stable room-temperature crystal structure being hexagonal with the atoms arranged in spiral chains.[18] A glassy, amorphous form of selenium can be produced by cooling the liquid. This form has no well-defined freezing point and shows a glassy consistency which is retained at room temperature.

The experimental data on the melting of selenium are shown in Fig. 2. The dashed line represents the data of Babb[4] to 10 kbar and the agreement with our data is quite good. The solid line is what is considered the best fit to the experimental points.

The DTCA signals obtained upon melting of selenium were quite strong, though not as well defined as those for tellurium. However, the signals indicative of freezing were very small and often not seen at all. Also, the magnitude of the signals decreased with increasing pressure and were at times masked by the experimental difficulties discussed in the section on sulfur. We were unable to obtain reliable data above 40 kbar.

In order to establish whether the failure to obtain

[17a] Note added in proof. By application of the theory of equilibrium polymerization, A. Eisenberg [J. Chem. Phys. 39, 1852 (1963)] has shown that the transition temperature associated with this "change point" decreases with increasing pressure, becoming equal to the melting temperature at about 0.8 kbar. Thus above 0.8 kbar liquid sulfur is the high-viscosity form which crystallizes in the plastic modification upon cooling. Presuming this theoretical result to be valid, the connection between the formation of plastic sulfur and the recrystallization process appears established.
[18] A. von Hippel, J. Chem. Phys. 16, 372 (1948).

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 Bridgman[17] 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. Bridgman[9] and, more recently, Ball[11] 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 authors[2] 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, Tammann[23] 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 a

[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).
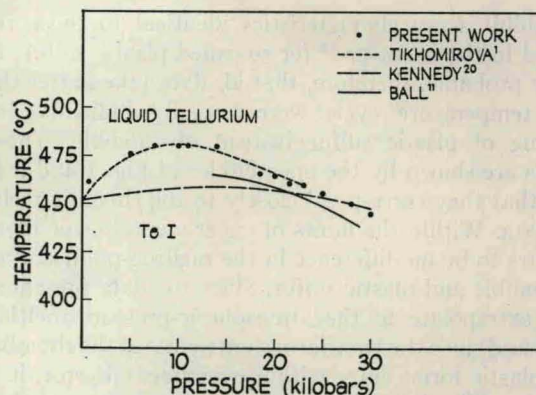
[22] See Bridgman's survey of this early work: P. W. Bridgman, Phys. Rev. **3**, 126 (1914).
[23] G. Tammann, Ref. 15, pp. 27–36; and *Kristallisieren und Schmelzen* (J. A. Barth, Leipzig, 1903).