PHYSICAL REVIEW VOLUME 137, NUMBER 4A 15 FEBRUARY 1965

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

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(Received 9 September 1964)

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 earlier[2] 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 selenium[4] to 10 kbar and tellurium[1] 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 characteristics 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 Drickamer[6] 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 Drickamer[7] at 130 kbar; it was later confirmed by low-temperature studies that selenium behaves as a metal at 170 kbar.[8] Bridgman[9] 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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† This research was sponsored by the General Dynamics Corporation.

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[1] N. A. Tikhomirova and S. M. Stishov, Zh. Eksperim. i Teor. Fiz. **43**, 2321 (1962) [English transl.: Soviet Phys.—JETP **16**, 1639 (1963)].

[2] F. A. Blum, Jr. and B. C. Deaton, Phys. Rev. Letters **12**, 697 (1964).

[3] W. F. Claussen, *High Pressure Measurement*, edited by A. A. Giardini and E. C. Lloyd (Butterworths Scientific Publications, Inc., Washington, 1963), p. 125.

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

[5] H. G. David and S. D. Hamann, J. Chem. Phys. **28**, 1006 (1958); and S. Joigneau and J. Thouvenin, Compt. Rend. **246**, 3422 (1958).

[6] T. E. Slykhouse and H. B. Drickamer, Phys. Chem. Solids **7**, 275 (1958).

[7] A. S. Balchan and H. G. Drickamer, J. Chem. Phys. **34**, 1948 (1961).

[8] B. M. Riggleman and H. G. Drickamer, J. Chem. Phys. **37**, 446 (1962).

[9] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **81**, 169 (1952).

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

[11] D. L. Ball, in *Proceedings of General Motors Research Laboratories Symposium, September 1963* (Elsevier Publishing Company, New York, 1964: in press).

[12] B. C. Deaton and R. B. Graf, Rev. Sci. Instr. **34**, 45 (1963).

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 earlier[2] 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±1°C and 217±1°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 ±1.5%. Standard room-temperature pressure calibration was utilized[12] and pressures are thought to be accurate to ±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

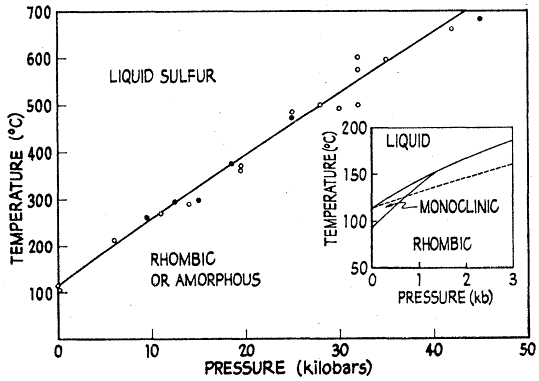

FIG. 1. Melting curve of sulfur. Inset: the solid curve is taken from Ref. 15 and the dashed curve is the low-pressure extrapolation of the reported data.

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

[14] G. W. C. Kaye and W. F. Higgins, Proc. Roy. Soc. (London) **122**, 633 (1929).

[15] G. Tammann, *The States of Aggregation* (D. Van Nostrand Company, Inc., New York, 1925).

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 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]

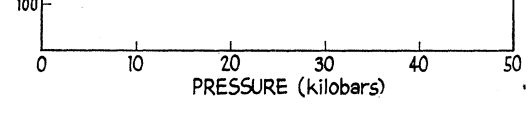

FIG. 2. Melting curve of selenium. The dashed portion of the curve is taken from Ref. 4.

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

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[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).

[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.

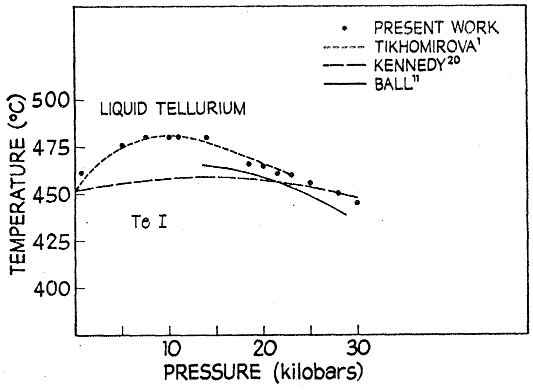

FIG. 3. Melting curve of tellurium determined by DTCA (solid points) compared with other data of indicated source.

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

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[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).

maximum in the melting curve of Glauber's salt ($Na_2SO_4 \cdot 10H_2O$).[15] As a sequel to Tammann's work, Bridgman[24] considered the problem of the general shape of the melting curve in detail in two papers, giving measurements on a number of substances to 12 kbar. On the basis of his experimental results he concluded that the normal shape of the melting curve embodies a monotonic rise in the melting temperature with pressure. Schames[25] proposed that at high pressures the melting curve asymptotically approaches some limiting temperature.

Simon[26] suggested an empirical equation for a melting curve, normal with respect to Bridgman's conclusions. The Simon equation,

$$P_m/a=[T_m/(T_m)_0]^c-1\,,$$

where a and c are positive constants and $(T_m)_0$ is the temperature-axis intercept of the curve, has often been used to fit experimental data. Several investigators have found the Simon equation appropriate only over moderate pressure ranges.[21]

Experimental determinations of melting under pressure in recent years have led to further questioning of the validity of the idea that the normal curve has a positive slope and thus conforms to the general Simon shape. Fusion curves with negative slopes have been reported for bismuth,[21] gallium,[27] water,[15] antimony,[21] silicon,[28] germanium,[29] indium phosphide,[28] indium arsenide,[28] indium antimonide,[28,30] gallium arsenide,[28] gallium antimonide,[28] and aluminum antimonide.[28] Fusion curve maxima have been reported for tellurium, rubidium,[31] cesium,[32] barium,[33] bismuth telluride,[34] lead telluride,[11] antimony telluride,[11] europium,[35] potassium nitrate,[36] and carbon.[37] Jayaraman[35] has just recently reported the first minimum in a fusion curve, that of cerium. Thus, what were once considered anomalous occurrences appear to have become rather widespread phenomena. It therefore appears that the Simon equation does not represent a general fusion curve as it does not allow a maximum, minimum, or negative slope.

The inapplicability of the Simon curve is not surprising if one considers the limitations on its validity. Although originally an empirical relationship, the Simon equation has been derived independently by several investigators.[38,39] All of these theoretical developments assume an isotropic, monatomic solid. However, most of the substances known to possess anomalous melting curves (i.e., not having a slope greater than zero) have rather open, anisotropic crystal structures. Furthermore, Gilvarry[39] has stated that even when theoretically applicable, the Simon equation should be viewed more as an interpolation formula than as a basic fusion equation.[39a]

Voronel[40] also obtained the Simon equation by arbitrarily assuming a linear dependence on pressure of the ratio of the heat of fusion to the volume change, in the Clapeyron equation. More recently Voronel[41] modified the general Simon formula to permit melting curves with negative slopes by introducing an effective temperature (the absolute temperature reduced by an additive constant).

No general fusion-curve equation which would allow maxima and/or minima has been proposed. However, Knopoff has arbitrarily regarded the Simon constants as a function of pressure, thus arriving at a fusion curve allowing maxima.[42] Such an assumption is just a higher order approximation of Voronel's procedure.

At present, it would seem then that a melting curve more specific than the Clapeyron equation, yet maintaining the desired generality, does not exist. Thus, various fusion curve phenomena are best interpreted and correlated in terms of specific characteristics of the material involved and general properties of substances demonstrating similar behavior.

B. Group VI B Melting Curves

As might be expected on the basis of the above discussion, little success was achieved in correlating the results presented here and the Simon equation. Obviously, it cannot be used to represent the tellurium melting data, since it does not allow for a maximum. Although Babb[4] fitted his selenium data up to 10 kbar and found Simon constants of $a=11.1\pm0.7$ kbar and $c=2.04\pm0.1$, the upper portion of the curve shown in

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[24] P. W. Bridgman, Phys. Rev. **3**, 126 (1914); **6**, 1 (1915).

[25] L. Schames, Z. Physik. Chem. (Leipzig) **87**, 369 (1914).

[26] F. Simon, Trans. Faraday Soc. **33**, 65 (1937); and Z. Elektrochem. **35**, 618 (1929).

[27] A. Jayaraman, W. Klement, Jr., R. C. Newton, and G. C. Kennedy, J. Chem. Phys. **24**, 7 (1963).

[28] A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, Phys. Rev. **130**, 540 (1963).

[29] H. T. Hall, J. Chem. Phys. **59**, 1144 (1955).

[30] M. D. Banus, R. E. Hanneman, and A. N. Mariano, Appl. Phys. Letters **2**, 35 (1963).

[31] F. P. Bundy, Phys. Rev. **115**, 274 (1959).

[32] G. C. Kennedy, A. Jayaraman, and R. C. Newton, Phys. Rev. **126**, 1363 (1962).

[33] A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, Phys. Rev. Letters **10**, 387 (1963); and B. C. Deaton and D. E. Bowen, Appl. Phys. Letters **4**, 97 (1964).

[34] D. L. Ball, Inorg. Chem. **1**, 805 (1962).

[35] A. Jayaraman, Bull. Am. Phys. Soc. **9**, 534 (1964); and Phys. Rev. **137**, A179 (1965).

[36] B. B. Owens, Bull. Am. Phys. Soc. **9**, 147 (1964); and S. E. Babb, Jr., and P. E. Chaney, *ibid.* **9**, 534 (1964).

[37] F. P. Bundy, J. Chem. Phys. **38**, 618 (1963).

[38] C. Domb, Phil. Mag. **42**, 1316 (1951); J. de Boer, Proc. Roy. Soc. (London) **A215**, 5 (1952); and L. Salter, Phil. Mag. **45**, 369 (1954).

[39] J. J. Gilvarry, Phys. Rev. **102**, 325 (1956).

[39a] *Note added in proof.* For a further discussion of the shortcomings of the Simon equation, see S. E. Babb, Jr., Rev. Mod. Phys. **35**, 400 (1963).

[40] A. V. Voronel, Zh. Techn. Fiz. **28**, 2630 (1958) [English transl.: Soviet Physics—Tech. Phys. **3**, 2408 (1958)].

[41] A. V. Voronel, Fiz. Metal. Metalloved. **9**, 169 (1960) [English transl.: Phys. Metals Metallog. USSR **9**, 7 (1960)].

[42] Newton *et al.*, refer to Knopoff's unpublished work: R. C. Newton, A. Jayaraman, and G. C. Kennedy, J. Geophys. Res. **67**, 2559 (1962).

TABLE I. Comparison of experimental melting curve slopes with those calculated on the basis of the Clapeyron equation.

	Atmospheric pressure values				
Element	Melting point T_m(°K)	Entropy of melting $S\left(\frac{\text{cal}}{\text{°K g atom}}\right)$	Relative volume change on melting $\Delta V/V$	Clapeyron $\frac{dT_m}{dP_m}\left(\frac{\text{°K}}{\text{kbar}}\right)$	Experimental $\frac{dT_m}{dP_m}\left(\frac{\text{°K}}{\text{kbar}}\right)$
S (rhombic)	386	1.06[a]	0.055[b]	32	30[d]
Se	490	3.04[b]	0.159[b]	21	24
Te	725	5.80[b]	0.054[c]	4.6	5.4

[a] Estal D. West, J. Am. Chem. Soc. **81**, 29 (1959).
[b] O. Kubaschewski, Trans. Faraday Soc. **45**, 931 (1949).
[c] See Ref. 11.
[d] See Ref. 15.

Fig. 2 departs significantly from the Simon equation using these constants. For sulfur the error involved in arriving at values for a and c is so large that such a calculation is meaningless. Mills and Grilly[43] have observed similar difficulties in arriving at unique and accurate values for a and c. Considering the complexity of the crystal lattices of S, Se, and Te, and the previous discussion, the failure of the Simon curve to fit the data presented is not surprising.

Knowledge of the volume change and latent heat upon melting at atmospheric pressure permits the calculation of the initial slope of the fusion curve from Clapeyron's equation. Table I gives, for the Group VI B elements, a comparison of the experimental initial slopes and the initial slopes calculated using the Clapeyron equation and latent heats and volume changes of indicated source. The agreement between the two slopes is good considering the accuracy of the ΔV and ΔS values given. Also given in Table I are the atmospheric-pressure melting points.

One of the most interesting characteristics of the data presented is the maximum in the melting curve of tellurium. The Clapeyron equation requires ΔV to be zero at the maximum and negative at all points in this phase beyond the maximum. Thus, at pressures beyond the maximum, the density of the liquid at the melting point is greater than that of the solid. Two immediately apparent explanations for a melting curve maximum are: (1) increases in the coordination of the liquid concomitant with pressure at such a rate that the density of the liquid becomes greater than that of the solid; and (2) a solid-state phase boundary intersecting the melting curve at the maximum. Since support for the latter alternative has not, in general, been found, most observers have turned to the former. Ball[11] and Jayaraman[35] have supported the first alternative as constituting the most fruitful approach.

In the case of tellurium, Kalbakina *et al.*,[19] have explained the melting curve maximum by the existence of an apparent second-order phase transition at 15 kbar and room temperature. However, as previously pointed out, McWhan and Jamieson[20] failed to observe this transition, even with careful compressibility measurements made using an x-ray diffraction apparatus. Also, measurements of electrical resistance and electronic energy gap by the authors[10] gave no indication of this transition. There is, therefore, some doubt concerning the presence of this phase transition.

Several investigations of the structure and properties of liquid tellurium at atmospheric pressure have been undertaken.[44–46] X-ray studies[44] indicate that the chain structure with covalent bonding and a coordination number of 2 is retained just above the melting point. Due to this persistence of the chain structure, hole conduction dominates conduction by electrons, the Hall coefficient and thermoelectric power being positive.[46] As the temperature is increased, the number of covalent bonds (and thus holes) decreases and the number of tellurium ions and free electrons increases. The Hall coefficient is found to reverse sign at about 575°C, showing that electrons are beginning to dominate the conduction process. The semiconducting behavior is observed up to 625°C where the resistivity becomes constant, remaining so until 670°C at which point metallic behavior begins.[46] Furthermore, liquid tellurium has a minimum[47,48] in the temperature dependence of its volume. Mokrovskii and Regel[47] observed kinks in the dependence of the electrical resistance and viscosity on the temperature, at the temperature of the volume minimum. All of the above properties of liquid tellurium can be understood by considering its structure.[46] Just above the melting point, the chain structure dominates. As the temperature increases the chains are progressively broken, yielding ionized atoms and electrons free to conduct. Johnson[45] successfully developed an expression for the electrical conductivity of tellurium

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[44] R. Buschert, I. G. Geib, and K. Lark-Horovitz, Phys. Rev. **98**, 1157(A) (1955); Bull. Am. Phys. Soc. **1**, 340 (1956).

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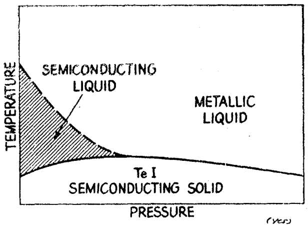

FIG. 4. Qualitative phase diagram for tellurium showing the quasiphase boundary of the liquid state.

as the weighted sum of a metallic and a semiconductive component, the weight being a statistical Boltzmann factor governing the probability of the dissociation of the chain bonds. Therefore, the onset of metallic conduction can be interpreted as the temperature at which dissociation of the chain structures in the liquid has become prevalent and the liquid becomes progressively a disordered array of atoms with a metallic type conduction and bonding.

On the basis of the present study and resistance measurements on tellurium,[10] it is felt that the maximum in the melting curve of tellurium is intimately connected with the above behavior and structure of liquid tellurium. Measurements of the resistance of tellurium in the liquid state at pressures above the pressure of the melting-curve maximum show that conduction is metallic in nature at temperatures just above the melting point. On the basis of the above structure model for liquid tellurium, this indicates that pressure inhibits the preservation of the chain structure upon melting. The minimum in the volume versus temperature curve for liquid tellurium at atmospheric pressure indicates that the volume occupied by the atoms in the chain structure is greater than that occupied by an equal number of atoms in the structure of metallic-type conduction. Therefore, a lowering of the characteristic temperature associated with the change to metallic bonding is exactly what is expected. This lowering is entirely equivalent to the above-mentioned pressure inhibition of the temperature range in which the chain structure exists. As a consequence, it is felt that liquid tellurium undergoes a relatively ill-defined structure change which is inhibited by pressure. It now seems possible to establish the existence of a liquid state quasiphase[49] boundary, qualitatively shown by the dashed line in Fig. 4. The pressure inhibition of this quasitransition is responsible for a marked increase in coordination with pressure, possibly of such a nature as to yield densities of the liquid state greater than those of the corresponding solid. This semiconducting liquid to metallic liquid quasiphase transition is thus quite possibly a factor contributing to the melting curve maximum for tellurium.

An attempt to establish an effective boundary for the liquid semiconducting phase by resistance measurements was made. Since this range of pressures and temperatures constitutes a region in which it is difficult to make measurements in our apparatus, we were unable to obtain reliable and consistent results. However, the metallic conduction of liquid tellurium at pressures above 10 kbar appears consistently.

Liquid-state studies of selenium at atmospheric pressure indicate that the chain structure is retained above the melting temperature and that liquid selenium remains a semiconductor with predominant electrical conduction by holes.[50,51] Blum *et al.*[51] also indicate the expectation that, at higher temperatures, liquid selenium will become metallic in nature. Because of the close similarity between the structure and properties of selenium and tellurium, it is believed that selenium will exhibit a melting-curve maximum analogous to that observed for tellurium. This maximum, if actually observed, could quite possibly be due to the dissociation of the chain structure in selenium at high pressures such as appears to be the case for tellurium.

A. von Hippel[18] has pointed to the progressive crystal structure development of the Group VI B elements. Recent x-ray investigations by McWhan and Jamieson[20] have shown that at pressures just above 40 kbar tellurium transforms to the β-polonium structure. It therefore seems possible that pressure will serve to bring all the Group VI B elements to the same crystal structure, i.e., the metallic polonium structure. On this basis, one is tempted to predict a melting-curve maximum for sulfur. However, the situation may be more complicated for sulfur than the above argument indicates, as pressure would first, perhaps, have to induce transformation to the chain-like hexagonal structure of Se and Te before transformation to the β-polonium structure could occur.

It is interesting to note that Bi, Sb, and Ge, which have melting curves with negative slopes, undergo a decrease in resistivity ρ upon melting followed by a metallic-type conduction in the liquid state,[52] just as tellurium does from 10 to 29 kbar. The possibility of correlation of the sign of the slope of the melting curve with the nature of the changes in resistivity upon melting is immediately apparent. Sutra,[53] and Schneider and Heymer[52] have found that an approximately linear relationship exists between the normalized change in resistivity $(\Delta\rho/\rho)$ and the relative volume change $(\Delta V/V)$ upon melting, for a number of elements. Since the Clapeyron equation relates ΔV to the slope of the melting curve and ΔS, the obvious extension of the above correlation is a comparison of $(\Delta\rho/\rho)$ and the initial

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[49] The statistical nature of the liquid structure change as indicated by the work of Johnson (see Ref. 45) rules out the possibility of giving this change the status of a true phase boundary.

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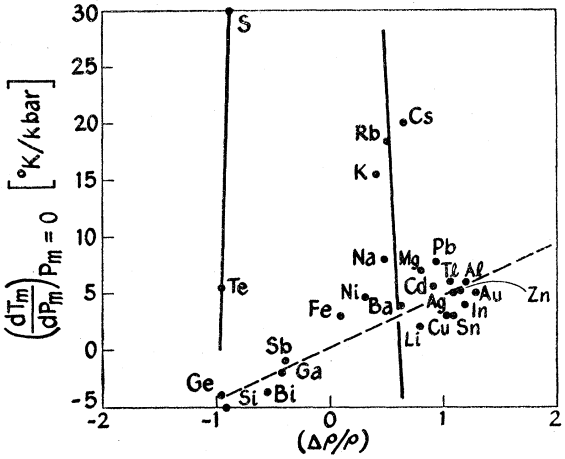

FIG. 5. Correlation of the change in resistivity upon melting with the slope of the melting curve for a number of elements at atmospheric pressure.

slope of the melting curve $m_0 \equiv dT_m/dP_m$ at $P_m = 0$.[54] Figure 5 gives a plot of m_0 versus $(\Delta\rho/\rho)$.[55] A surprising regularity exists in the points lying in close proximity to the dashed line. The alkali metals and Group VI B elements comprise obvious exceptions to this correlation. The most general feature exhibited by Fig. 5 is the direct correspondence between the sign of $(\Delta\rho/\rho)$ and the sign of m_0. This correspondence is violated only by the Group VI B elements for which $(\Delta\rho/\rho) < 0$ and $m_0 > 0$.

To the authors' knowledge, the theoretical investigations concerning the change in resistivity upon melting have dealt only in an approximate manner with metals whose resistivity increases upon melting. Cusack and Enderby[56] have surveyed and evaluated these works which are based largely on Mott's[57] early attempts to relate the change in resistivity to ΔS.

There is one further point of interest concerning the correlation of the initial melting-curve slopes with the general properties of the elements. In general, the melting of a substance is accompanied by marked changes in the long-range order of the crystal structure. However, most liquid metals exhibit a short-range order in close agreement with that of the corresponding solid.[52] While, conversely, the semimetals (e.g., Bi, Ge, and Ga, which have $m_0 < 0$) exhibit decided changes in both short-range and long-range order upon melting.[52] In fact, the x-ray diffraction patterns indicate a short-range order for the semimetals similar to those of the liquid metals.[52] Also, for most of the semimetals $\Delta V < 0$. This is not surprising since the short-range order of the semimetals is similar to that of the more closely packed liquid metals, and one would expect the relative volume of a substance to be more closely related to its short-range than its long-range order. Since $\Delta V < 0$ for these semimetals, $m_0 < 0$. Thus, for a number of elements, there appears to exist a direct relation between the sign of the slope of the melting curve m_0 and the change in short-range order upon melting. Presuming that such a relation is valid for all elements, and recalling that the short-range order for the Group VI B elements is preserved upon melting, we have then a better understanding of the failure of the Group VI B elements to conform to the direct correlation of the sign of $(\Delta\rho/\rho)$ and m_0. Also, it should be noted that the previously given explanation for the maximum in the melting curve of tellurium is in complete accord with this picture of the relation between the relative liquid and solid structures of the elements and the sign of the melting-curve slope. However, an explanation, on the basis of this model, of the maxima in the melting curves of elements with relatively close packed structures, such as barium, is not apparent.

All of the above observations and generalizations are by no means complete in themselves. A thorough survey and investigation of these properties of the elements is needed.

ACKNOWLEDGMENTS

We are indebted to D. N. Peden for help with the measurements and gratefully acknowledge interesting and helpful discussions with A. J. Ehlmann and J. W. Hagemeyer. We wish to thank D. B. McWhan, J. C. Jamieson, and D. L. Ball for permission to refer to their results prior to publication.

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