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Te, Pb

Deviations from the Normal Fusion Curve

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ABSTRACT

The temperature and pressure dependence of the condensed phase equilibria o tellurium, lead telluride, bismuth telluride, and antimony telluride are reported. Particular emphasis is placed on the fusion curves which, in each instance, display a maximum in melting point at elevated pressure. The fractional increase in volume upon melting at zero pressure was determined for each of these substances. The limiting slopes of the fusion curves, at zero pressure, were calculated from the Clapeyron equation.

INTRODUCTION

This paper will describe experimental observations of the condensed phase equilibria of four specific substances at elevated pressure. Particular emphasis will be placed on the effect of pressure on the melting points of these materials, which are tellurium, lead telluride, bismuth telluride, and antimony telluride. But first, by way of introduction, certain general considerations must be reviewed.

The term, fusion curve, refers to the graphical representation of the fusion temperature as a function of pressure. In general, these curves are of two types, called normal and abnormal. Depending on the relative densities of solid and melt, the melting point is expected either to increase continuously with pressure or to decrease. Most commonly, of course, the melt is of lower density and the former, normal, behavior is observed.

However, further complications are conceivable; they are summarized in Fig. 1. The upper curve is a representation of strictly normal behavior, a continuously increasing melting point with pressure. The three remaining curves are suggested modifications of the normal behavior. They were first advanced at a time when experimental observations extended up to only a few thousand atmospheres. They were postulations as to what might be expected at still higher pressures and not experimental curves. Beside each of the curves is shown a name prominently associated with it.

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These postulations include the following: the abrupt termination of the fusion curve in a critical point [1] (analogous to the liquid–vapor transition); the occurrence of a horizontal asymptote at some finite temperature [2], and lastly, a maximum in the melting point separating normal and abnormal segments of the fusion curve [3]. For comparison, the Clapeyron equation is included in Fig. 1; the slope of the fusion curve is thereby related to the volume and entropy changes associated with fusion.

Prof. Bridgman [4] carefully considered these three modifications of the normal curve and concluded that none was to be expected. In his opinion, the fusion temperature would continue to rise with pressure as long as the atomic structure was preserved.

Currently, the maximum static pressure attainable in the laboratory is of the order of one hundred thousand atmospheres. As yet, no evidence is available to support the suggestions of Simon and Schames. However, in the last four years, several examples have been reported of substances that display maxima in melting points at elevated pressure.

The Clapeyron equation requires that, in these instances, the molar volume of the melt must be compressed to a value less than that of the equilibrium solid. Since the entropy of fusion must remain positive at all pressures, the sign of the

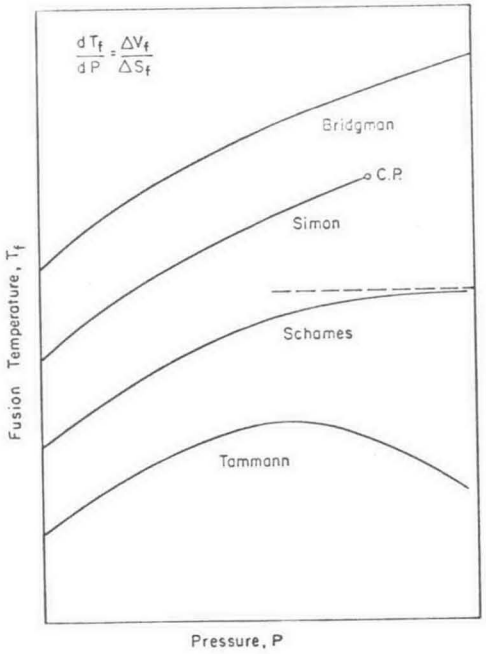

Fig. 1. Classic fusion curves.

slope of the fusion curve must be the same as that of the volume change on f This type of behavior can be expected to occur only under very special circun ces. In addition, its occurrence implies the existence of a more compact, high sure phase whose fusion curve is normal. Otherwise, at some finite pressur extrapolation of the abnormal segment would predict melting at 0 °K.

In 1959, F. P. Bundy [5] of the General Electric Research Laboratory rep an apparent maximum in the melting point of rubidium at 45,000 atmospher 1962, G. C. Kennedy and co-workers [6, 7] at U.C.L.A. indicated that they unable to reproduce the data of Bundy for rubidium, but they did observe m in melting points of each of two phases of cesium (at about 22,500 and 3 atmospheres, respectively). Then in 1963, Bundy [8] provided evidence maximum in the melting point of graphite at high pressure.

In the following four other examples of melting point maxima, observed General Motors Research Laboratories, will be described. In closing, a g explanation will be offered for this unusual behavior in terms of the special c teristics of the substances investigated.

EXPERIMENTAL TECHNIQUE AND RESULTS

In addition to the direct determination of the melting points of specimens ex to a series of elevated pressures, it is desirable to have some information limiting slope of the fusion curve (at zero pressure) as provided by the Clap equation. This is particularly necessary in the present case because the high sure apparatus used does not lend itself conveniently to experiments at les about 15,000 atmospheres.

In order to perform the required calculation, it was necessary to measu fractional change in volume associated with the fusion of the four substan interest: Te, PbTe, Bi_2Te_3, and Sb_2Te_3. The technique developed [9] fo purpose is shown diagramatically in Fig. 2. This technique is a modification method of "fed" and "unfed" castings first reported in its original form by West [10].

West determined the solidification shrinkage of cast iron by pouring n iron into two molds of effectively identical capacity; however, one mold wa ped after filling whereas the second was provided with a riser (or reservoir o ten iron) to provide compensation for solidification shrinkage. The weights two ingots obtained permit a calculation of the quantity of interest.

The technique shown in Fig. 2 is essentially the same, but it does provide much closer control of the various process variables involved. Pairs of cru are immersed in the melt contained in evacuated glass capsules. The assem then lowered from the center of the furnace to provide for a slow, directional

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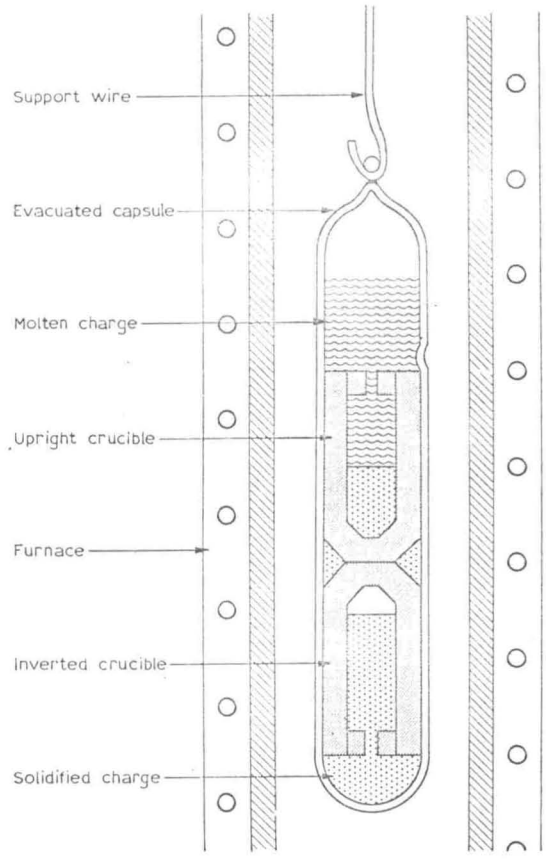

Fig. 2. Technique for determination of fractional volume change upon fusion. (From [9].)

fication (the Bridgman technique of crystal growth). Because of the relative orientation of the two crucibles, the liquid contents of one (the inverted crucible) are isolated from the bulk of the melt by solidification at the entrance port; solidification continues with the formation of a shrinkage void. The upright crucible is continuously fed from the melt and, of course, no void forms. Assuming a reasonable approach to certain idealized conditions [9], the fractional change in volume associated with fusion can be calculated from the relation

$$\frac{V_l - V_s}{V_s} = \frac{W_u - W_i}{W_i},$$

V_l and V_s represent the molar volumes of liquid and solid, respectively, at the melting point; W_u and W_i represent the measured weights of the ingots recovered from the upright and inverted crucibles, respectively.

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PbTe
Bi_2Te_3
Sb_2Te_3

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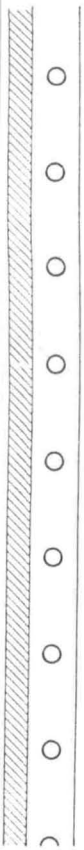

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TABLE I

SUMMARY OF DATA FOR THE FRACTIONAL VOLUME CHANGES ON FUSION

Substance	*Number of determinations*	*Observed mean* $\pm \sigma$
Sn	3	+ 0.030 (Handbook value 0.028)
Te	4	− 0.054 ± 0.002
PbTe	5	− 0.044 ± 0.002
Bi_2Te_3	6	− 0.043 ± 0.002
Sb_2Te_3	4	− 0.064 ± 0.001

Table I summarizes the data obtained. The value for tin was measured to test the reliability of the technique. The result obtained indicates that reasonable accuracy can be expected. In fact, certain rather obvious corrections [9] could be imposed which would bring the observed and handbook values into coincidence.

It is not necessary to dwell further on the particular values obtained except to emphasize that, in all cases, these substances expand in volume when they melt. They are all expected, therefore, to display normal fusion curves. Previously, Klemm *et al.* [11], reported that tellurium was observed to expand by approximately 2 % on melting. This value was identified as rather uncertain, however, and worthy of redetermination.

Experimental data for the entropy changes on fusion are available for only tellurium [12] and bismuth telluride [13]. Approximations were necessary for the other two materials. Since antimony telluride is isomorphous with bismuth telluride (structure type C33) it seems appropriate to use the entropy value observed for the latter for both compounds. That value is 34 e.u. per mole. In the case of lead telluride, a value of 4.5 e.u. per mole was used in accordance with the available data [14] for other covalently bonded substances with the same structure—that of rock salt (B1).

The high-pressure experiments were performed with a 600 ton tetrahedral anvil apparatus, which was constructed at this laboratory with the consultation of inventor, H. Tracy Hall. A general view of the equipment is shown in Fig. 3.

The apparatus consists of four hydraulic rams slung at the tetrahedral angles. In practice, through the agency of these rams, a force is applied normal to each of the four triangular faces of a small tetrahedron containing the sample. A more detailed description of this type of apparatus is provided elsewhere by Hall [15].

A sectional view of an assembled tetrahedron is shown in Fig. 4. The tetrahedron itself is most commonly constructed of the naturally occurring mineral pyrophyllite, which for a variety of reasons happens to be particularly suited for this purpose. The assembly shown on this slide provides for the measurement of the elec-

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Fig. 3. Tetrahedral anvil apparatus.

trical resistance of the sample during test. A 1/16 in. diameter by 3/8 in. long specimen is capped with tabs which provide electrical access from the load bearing anvils of two of the hydraulic rams. The two remaining anvils provide a current path for the tubular graphite resistance heater which surrounds the sample.

The sample is encased in a suitable insulating material. Most commonly, hot-pressed boron nitride was used. Not shown here, but of considerable importance are the two thermocouples used. The two legs of each couple (platinum/platinum–

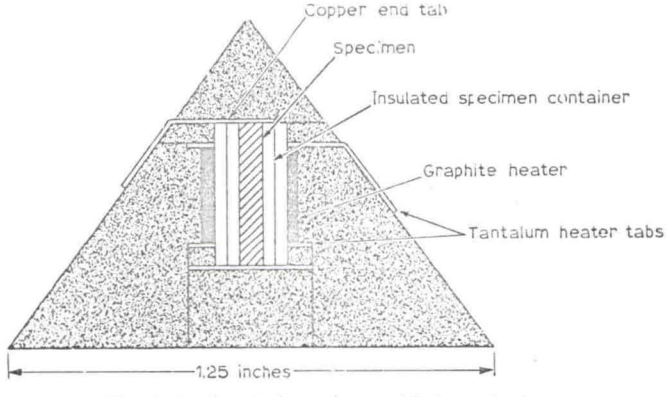

Fig. 4. Sectional view of assembled tetrahedron.

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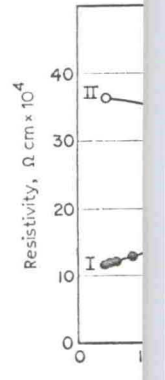

Fig. 5. The effect of temperatur

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rhodium) were enclosed in mullite insulation tubes; these were inserted into holes drilled from the midpoint of an edge of the tetrahedron and directed toward the center. The junction was positioned midway between the inner surface of the heater and the outer surface of the specimen. The legs emerged from between two adjacent anvil faces; in general they remained intact with increasing load.

The pressure calibration [16] of the apparatus was made by noting the hydraulic oil pressures required to produce phase transitions in the metals barium and bismuth as revealed by concomitant changes in electrical resistance. In addition, conventional (one atmosphere) thermocouple conversion tables were used. These practices are customary in the field. It is expected that the reported pressure values are uncertain to about 5 %; the observed temperature values are expected to be somewhat less uncertain.

Changes in electrical resistance provided the most convenient index of phase transformation at high pressure. For purposes of comparison, the effect of fusion (at one atmosphere) on the electrical resistivity of bismuth telluride was determined [16]. The results for two specimens, doped differently, are shown in Fig. 5. The sort of behavior shown is typical of the four nonmetallic substances investigated [17]. An abrupt decrease in resistance accompanies melting. This behavior is to be contrasted with that of metals, where an abrupt increase in resistance occurs on melting. It means that an increase in the number of charge carriers must also occur to compensate for the decreased mobility in the disordered liquid.

The data obtained at high pressure were not so well defined as those shown here. This is because the resistance measured was that of the entire length of the specimen along which a temperature gradient occurred (from the center to the ends). Still in most cases, a readily detected, reproducible and reversible index of fusion was provided.

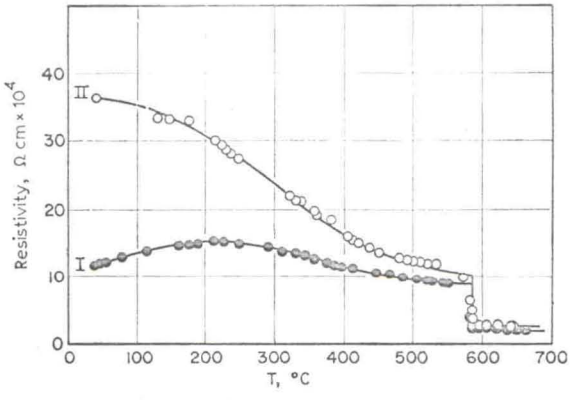

Fig. 5. The effect of temperature on the electrical resistivity of bismuth telluride (Bi_2Te_3) at one atmosphere. (From [16].)

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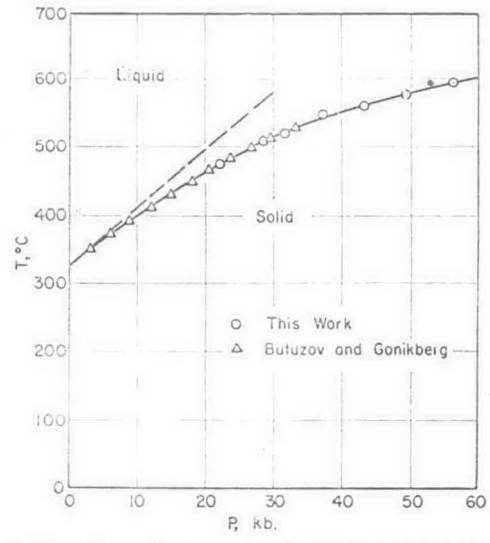

Fig. 6. The effect of pressure on the melting point of lead.

The overall reliability of the technique was tested by determining the effect of pressure on the melting point of lead. Fig. 6 shows the results, which is a normal fusion curve. The agreement with earlier data, obtained elsewhere [18], appears adequate. Also shown is the limiting slope provided by the Clapeyron equation. In Fig. 6, the unit of pressure used is the kilobar (abbreviated kb). This unit is now customarily used in the field. One kilobar equals 10^9 dynes/cm^2, but, for our purposes, it may be regarded as equivalent to one thousand atmospheres.

Fig. 7 summarizes the data obtained for the condensed phase equilibria of tel-

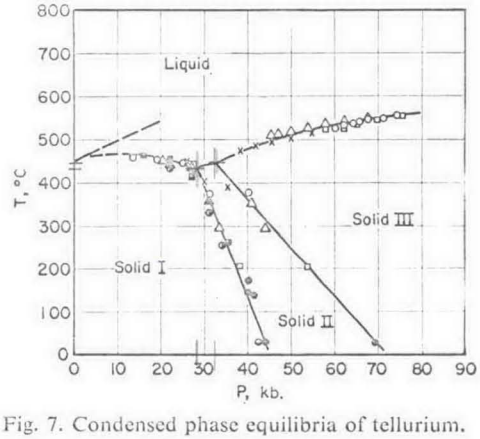

Fig. 7. Condensed phase equilibria of tellurium.

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lurium as functions of temperature and pressure. Each individual run is identified with a different symbol.

Comparison of the Clapeyron slope and the data obtained shows the occurrence of a broad maximum in melting point for the low pressure phase—called here solid I. The melting curve for solid III is normal. The two solid phase transformations proceed with a decrease in electrical resistance; they also are relatively rapid and reversible. Solid III melts with an increase of specimen resistance.

Other data are available from two sources. The existence of the two high pressure phases of tellurium was first shown by Bridgman [19] at relatively low temperatures (below 200 °C). The transition points, which are given as filled circles in Fig. 7, were obtained by measurement of the specimen volume as a function of pressure. Bridgman's data for the volume changes on transformation together with the slopes of the phase boundaries permit a calculation of the latent heats associated with the transitions. These are 290 cal/g-atom and 85 cal/g-atom for the solid phase transitions I–II and II–III, respectively.

After the work summarized by Fig. 7 had been completed, it was learned that G. C. Kennedy *et al.* [20] had also investigated the high pressure phase equilibria of tellurium. They used the technique of differential thermal analysis with a piston-cylinder type of apparatus. Their results, although not contained in Fig. 7, are essentially coincident with the phase boundaries shown up to the maximum pressure they investigated (50 kb). The second solid transition (II–III) was not observed,

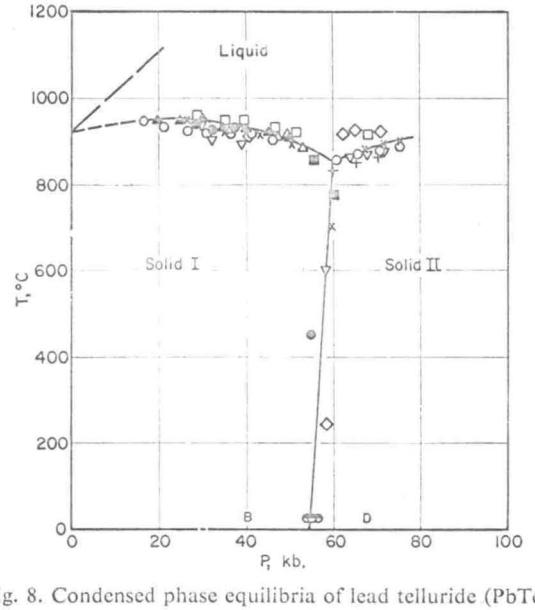

Fig. 8. Condensed phase equilibria of lead telluride (PbTe).

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but this is perhaps due to the relatively small latent heat associated with it. Of most importance is the fact that they also observed the maximum in melting point for the low pressure phase.

Fig. 8 summarizes the data obtained for the condensed phase equilibria of lead telluride. Again it appears that a maximum in melting point must occur when the calculated limiting slope is compared with the data taken above 20 kb. The calculated slope appears too great in comparison with the experimental points; it is possible that the approximation used for the entropy of fusion is unrealistic. That value was approximately 2 e.u./g-atom. The correct value could conceivably be as high as 6 or 7 e.u./g-atom in view of the comparable values displayed by tellurium and bismuth telluride.

In Fig. 8 a triple point is shown at about 60 kb. The data for the fusion temperatures of solid II are particularly scattered; still the normal type of fusion curve appears appropriate.

It is probable that the high pressure phase is of the cesium chloride (B2) structure; however, direct evidence is not available. At least the slope of the phase boundary is consistent with this possibility. Other compounds which possess the cesium chloride structure at low temperature do, at constant pressure, transform to the rock salt structure (B1) at some elevated temperature. The same sequence would occur here in the case of lead telluride.

Other data are available for the solid–solid transition pressure at room temperature. These were provided by Bridgman [21] and, more recently, by Drickamer [22]; their points are shown in Fig. 8 as "B" and "D", respectively. In this instance, the three available determinations are in considerable disagreement.

The next example is bismuth telluride; the fusion curve is given in Fig. 9. A more detailed description of these results is provided elsewhere [16].

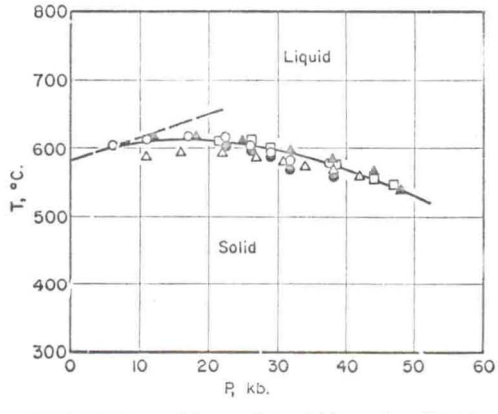

Fig. 9. The effect of pressure on the melting point of bismuth telluride (Bi_2Te_3). (From [16].)

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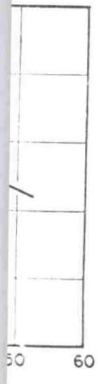

telluride (Bi_2Te_3). (From [16].)

Solid Bi_2Te_3 possesses a special sort of structure (C33) in which the atoms of the same element are distributed in layers; five layer bundles are joined by Van der Waals bonds. However, for our purposes it is sufficient to regard the structure as a slight distortion of the rock salt structure which it resembles in terms of coordination and symmetry on the short range.

The data show a rather broad maximum at about 15 kb. The subsequent abnormal segment to the fusion curve implies that a high pressure phase will be encountered although no direct evidence was encountered for its existence. The data do not extend beyond about 50 kb because the index of fusion used was no longer adequate. With increases in pressure, the resistance change associated with fusion grew smaller and less abrupt. Finally, it was no longer sufficient to define the melting temperature and remained so up to the maximum pressure investigated, 75 kb.

Fig. 10 summarizes the data for the final example, antimony telluride, which is identical in structure with bismuth telluride. In this case, however, definite evidence was obtained for a new phase which is formed at high pressure and can be retained metastably at ambient conditions.

The behavior shown in the lower pressure range is similar to that observed previously. At about 50 kb there occurs a triple point with the intersection with what is presumed to be a normal fusion curve for the high pressure phase. Unfortunately, the data in this region are particularly scattered.

The solid-I–solid-II transition was observed only at relatively high temperatures, and, in each instance, the transition was irreversible. The conditions at which it occurred are shown in Fig. 10 as filled symbols, which are contained within the expected region of stability of the high pressure phase. These points were revealed by permanent increases in specimen resistance. In addition, the analysis of the recovered specimens by X-ray diffraction after exposure to the indicated conditions

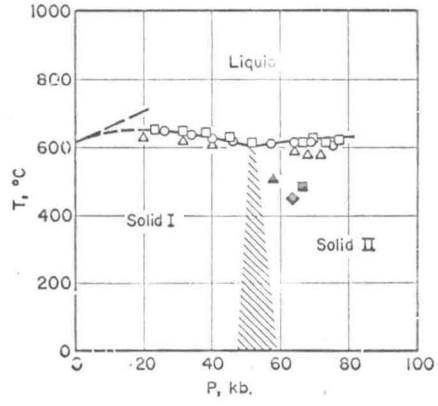

Fig. 10. The condensed phase equilibria of antimony telluride (Sb_2Te_3).

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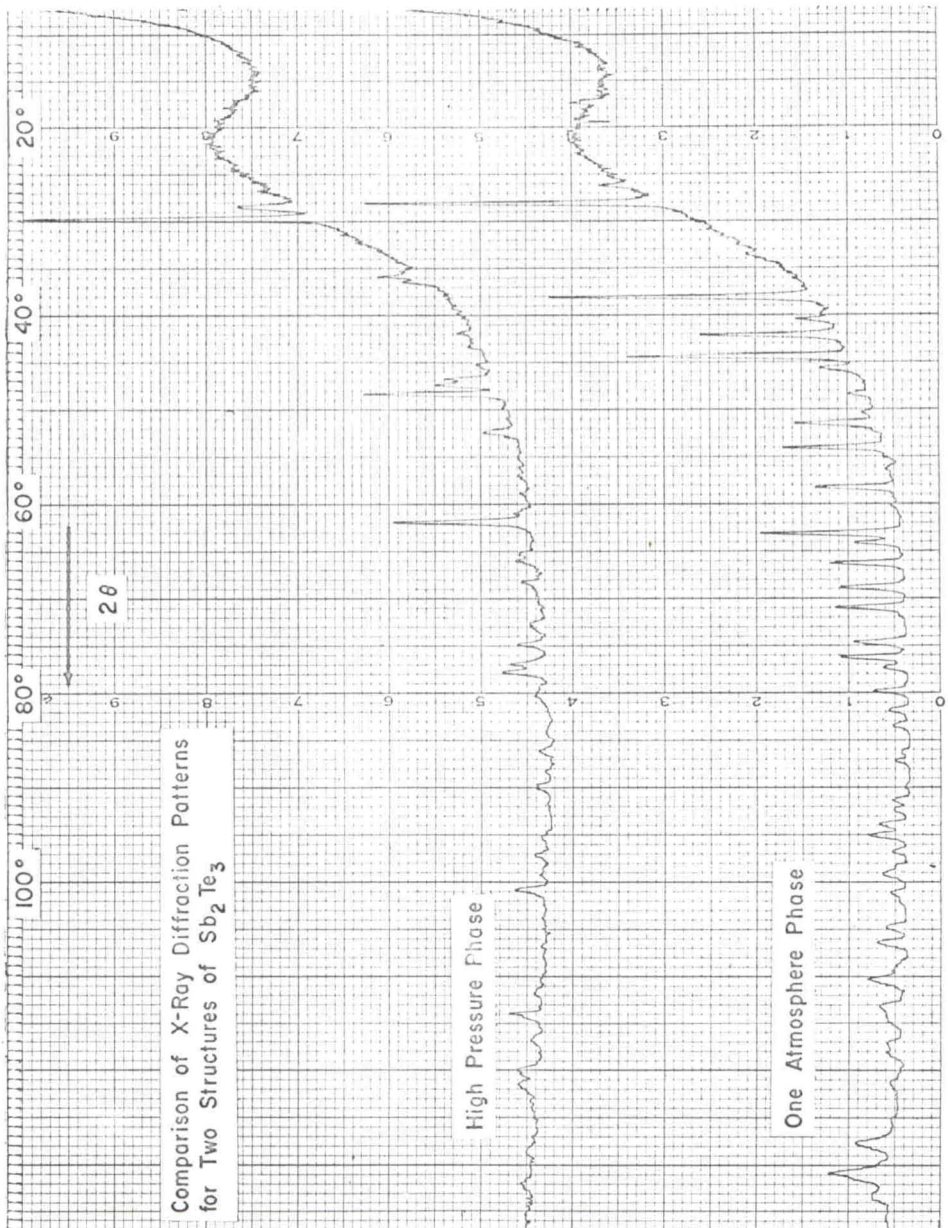

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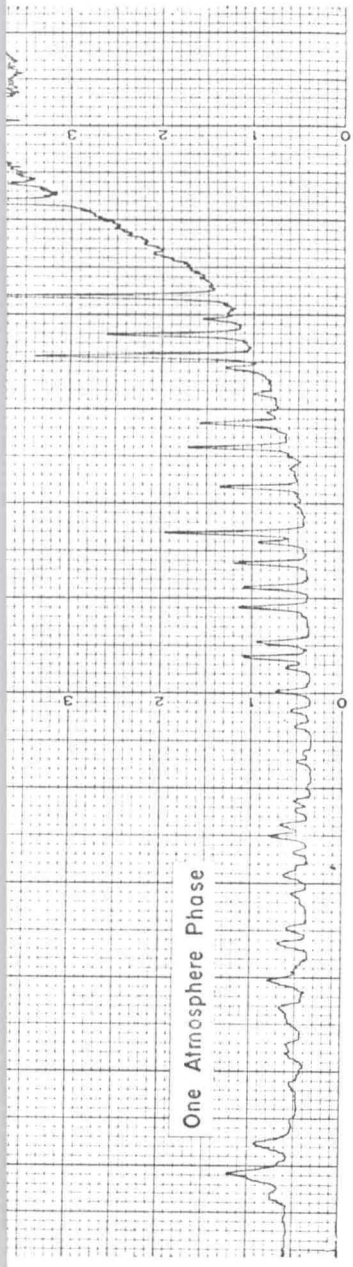

of pressure and temperature revealed a characteristic pattern unlike that displayed by the starting material.

The formation of the new phase is sluggish and requires a relatively high temperature to proceed at a detectable rate. As a result, it was not possible to determine the position of the phase boundary. Only the approximate position is shown in a manner intended to imply that the sign of the slope is not known.

When a phase is capable of persisting metastably at low pressure, it is natural to suspect that it will not be formed rapidly at elevated pressure where it is stable. Numerous examples could be cited of this behavior, which might be explained as follows. The potential energy barrier separating the two structures, and permitting a retention of the metastable one, is not likely to disappear with increases of pressure at constant temperature. If the volume of the activated complex associated with the barrier is greater than that of the high pressure phase, the magnitude of the barrier restricting formation under equilibrium conditions will be even greater than that permitting the retention of the metastable phase at one atmosphere.

Fig. 11 shows the comparison between the X-ray diffractometer patterns of the conventional and the new structure recovered from high pressure. The transformation appears essentially complete, but a duration of three months at room temperature is sufficient for a substantial retransformation of the new structure. Two hours at 500 °C are sufficient to destroy completely the new structure and reproduce the original X-ray diffraction pattern. It is hoped ultimately to establish the precise structure of the new phase, but this has not been possible as yet.

INTERPRETATION OF RESULTS

Experimental evidence has been presented for the occurrence of maxima in the melting points of four substances at elevated pressure. These substances are tellurium, lead telluride, bismuth telluride, and antimony telluride. Reference was made also to other examples of this behavior which were observed elsewhere.

Before attempting some sort of general explanation for the unusual behavior observed, it seems appropriate to distinguish between two sorts of examples. These are the metallic substances (rubidium and cesium) as contrasted with the nonmetallic examples, such as those reported here.

The two metals are body-centered cubic structures as solids; they are more closely packed than any of the nonmetallic examples. It has been suggested [6] that an unusually high compressibility of the liquid metals (Cs and Rb) may be associated with pressure induced electronic transitions. In both cases, empty inner orbitals are available which are, energetically, fairly close to the bonding s-electrons. Whatever the merits of this argument, it seems untenable in the case of the nonmetallic examples of melting point maxima.

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The nonmetallic substances, whose fusion curves were presented above, all possess relatively open structures as solids. The maximum coordination number is six. Perhaps the structure of tellurium merits special mention. The solid is composed of spiral chains. Each atom is bonded covalently to two neighbors; the chains are held together by van der Waals attraction. It is suggested that the bonding in the melt is significantly different than the equilibrium solid because of the decrease in electrical resistance observed in each instance. It was mentioned earlier that an increase in charge carriers was required; another way of saying this is that the bonding is different.

The electrical and structural properties of molten tellurium have been investigated relatively extensively [17, 23, 24]. Here metallic conductivity is encountered at some temperature above the melting point. This has been analyzed in terms of the ultimate loss of the chain structure with the adoption of the metallic type of bonding. An increase in coordination number resulting from the non-directional character of bonds is suggested [24].

An explanation of the observed maxima in melting points at elevated pressure can only be given in rather general terms such as the following. It seems possible that, in the melt, the total number of neighboring accessible sites (both occupied and unoccupied) is greater than the coordination number appropriate to the solid. For the compounds the ordered arrangement of the solid is probably lost. With increases in pressure, the number of vacant sites, as well as other sources of disorder, are expected to decrease. With pressure increases then, the coordination number could increase providing for the attainment of densities greater than those realizable for the solid.

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23. A. S. EPSTEIN, H. FRITZCH
24. R. C. BUSCHERT, *Ph. D. T*

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A. R. UBBELOHDE (*Imperi*
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A. R. UBBELOHDE:
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W. TILLER:
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Discussion

A. R. UBBELOHDE (*Imperial College, London, England*):

Of course, in liquid sulfur there are two types of molecules in the liquid, aren't there?

D. L. BALL:

There are rings and chains.

A. R. UBBELOHDE:

Does tellurium have only a single molecular structure in the melt?

D. L. BALL:

My understanding of the data in the literature is, yes. There have been studies of the liquid by X-ray diffraction, and they interpret their results this way—as predominately chains.

W. TILLER (*Westinghouse, Pittsburgh, Pa.*):

This would be supported by the ease of growing tellurium crystals, as distinct from its cousin, selenium, which is difficult, because of its ring and chain structure.

A. R. UBBELOHDE:

More attention should perhaps be paid to the growth evidence than to that from X-rays, because it seems unlikely that the resolving power of radial distribution curves would pinpoint 5 % or thereabouts of a rival molecular structure.

W. TILLER:

Certainly in selenium, when you go to the pressures required to change its melting temperature to that of tellurium, associated with 1 atmosphere pressure, the liquid also appears to consist predominantly of chains.

A. SCHNEIDER (*Göttingen University, Germany*):

Might I, from the view of chemical bonding, add the following questions to the extraordinary and highly interesting results of Dr. Ball's works: Have you any information about the values of the electrical conductivity or the Hall-effect of the high-pressure phase of Sb_2Te_3 in comparison with the low-pressure phase? What sort of temperature dependence of the measured values did you find in the two cases, respectively, or would you predict?

D. L. BALL:

The limited, available data are based on measurements made at room temperature on two specimens of the metastable material. In both instances the starting material possessed a resistivity of $2.4 \times 10^{-4}\ \Omega$ cm and a thermoelectric power (relative to copper) of $+85\ \mu V/°C$. The recovered specimens each displayed a resistivity of about $1.3 \times 10^{-3}\ \Omega$ cm and a thermoelectric power of about $-30\ \mu V/°C$. No determinations have yet been made of the pressure and temperature dependence of these properties for the new structure.

N. F. MOTT (*University of Cambridge, England*):

Near the melting point the conductivity depends very little on doping, doesn't it?

D. L. BALL:

Yes, that is true.

R. A. MURIE (*Allison Div., GMC*):

On the recovered specimens have you run any differential thermal analysis to see if there is any phase transition at lower temperatures back to a more stable structure?

D. L. BALL:

No attempts at differential thermal analysis were undertaken; the quantity of material recovered is small and, thus, this technique would be rather difficult. The slow formation of the stable structure at room temperature and the rapid formation at elevated temperature were shown by X-ray diffraction.

F. P. BUNDY (*G. E., Schenectady, N. Y.*):

Did you try to make any temperature–pressure excursions; for example, going at room temperature into the high-pressure solid phase, then melting that at pressure, and then lowering the pressure and temperature to allow freezing at lower pressure?

D. L. BALL:

No excursions were ma
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load.

F. P. BUNDY:

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do not give much attentic
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D. L. BALL:

No excursions were made with decreasing pressure at constant temperature. I regarded the pressure calibration of the apparatus as reliable only for increasing load.

F. P. BUNDY:

I would like to comment on this point. I used to think, too, that you couldn't trust the pressure calibration on the unloading part of the cycle. Recently I had need of getting some information on descending pressure excursions. When I went back and plotted the calibration data on unloading, which we usually record but do not give much attention, I found it more consistent than we had thought. It may not be as good as the up-load calibration, but I wouldn't ignore it.