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New Melting Law at High Pressures

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Published melting-temperature and compressibility data support the observation that for many substances, and for wide variations in pressure, the relation describing the change of melting temperature with pressure becomes linear when melting temperature is plotted against isothermal volume compression. Linear variation of melting temperature with compression holds for density changes of a factor of 2 in the alkali metals and in sodium chloride. If we assume that iron also exhibits a linear variation of melting temperature with compression for equally large compressions, then this fixes the earth's inner–outer-core boundary temperature at approximately 3724°C, provided that the boundary corresponds to the melting point of iron at a pressure of 3 Mbars.

I. INTRODUCTION

IN an earlier paper[1] the authors reported the discovery that for many substances, and for wide variations in pressure, the relation describing the change of melting temperature with pressure becomes linear when melting temperature is plotted against isothermal volume dilatation instead of pressure, thus

$$T_m = T_m^0(1+C\Delta V/V_0)\,. \tag{1.1}$$

The isothermal dilatation $\Delta V/V_0$ is defined so that it is positive for compressions and varies between zero and unity as the pressure varies from 1 atm to infinity;

$$\Delta V/V_0 = (V_0 - V)/V_0\,. \tag{1.2}$$

In applying (1.1) to a given substance, T_m^0 is the melting point at 1 atm when $V = V_0$, and C is a constant which depends on the particular substance.

The present paper offers further experimental evidence in support of (1.1). Moreover, we have now extended our investigations to include substances which melt with a decrease in volume, and to include pressure ranges in which polymorphic transitions occur.

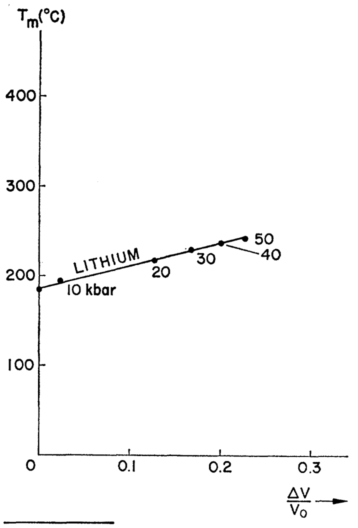

FIG. 1. Melting temperature versus isothermal compression in lithium at 25°C.

2. THE ALKALI METALS

Figures 1–3 show plots of the melting temperature in degrees centigrade versus isothermal compression at 25°C for Li, Na, K, and Rb.[2,3,23] In Fig. 3, the deviation of the Rb data from linearity which begins to become noticeable at 40 kbar may be a possible maximum[4] in the Rb melting curve or it may be due to experimental error in the melting-point and compression measurements. The corresponding analytic expressions[1] are

$$T_m(\mathrm{Li}) = 186(1+1.325\Delta V/V_0)\,°\mathrm{C}, \tag{2.1}$$

$$T_m(\mathrm{Na}) = 97.6(1+6.260\Delta V/V_0)\,°\mathrm{C}, \tag{2.2}$$

$$T_m(\mathrm{K}) = 62.5(1+8.668\Delta V/V_0)\,°\mathrm{C}, \tag{2.3}$$

$$T_m(\mathrm{Rb}) = 38.5(1+13.124\Delta V/V_0)\,°\mathrm{C}. \tag{2.4}$$

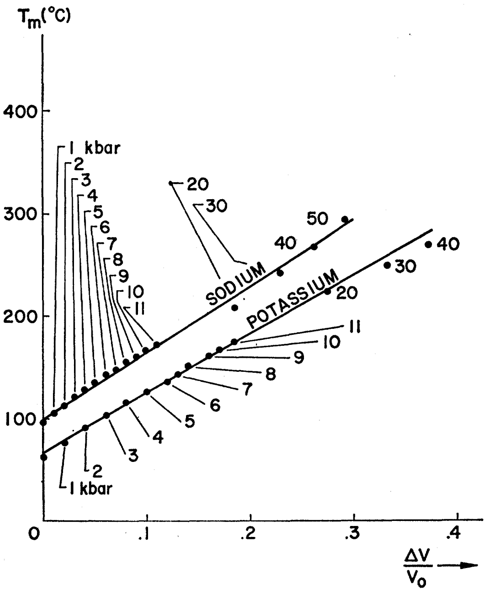

FIG. 2. Melting temperature versus isothermal compression in sodium and potassium at 25°C.

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[1] E. A. Kraut and G. C. Kennedy, Phys. Rev. Letters **16**, 608 (1966).

[2] R. C. Newton, A. Jayaraman, and G. C. Kennedy, J. Geophys. Res. **67**, 2559 (1962).

[3] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 55, 71 (1948); **74**, 425 (1942).

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

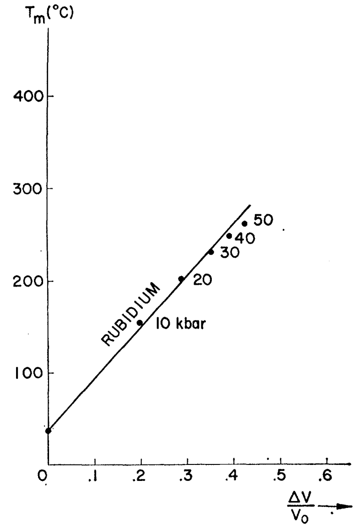

FIG. 3. Melting temperature versus isothermal compression in rubidium at 25°C.

Notice that the slopes of these straight lines are not small numbers and that the linear relationship appears to hold for compressions as large as a half.

We believe that in using the linear relation (1.1) to extrapolate melting data to pressures not readily accessible in the laboratory, the limit of the range over which the linear relation (1.1) can be safely extrapolated is determined not by a maximum pressure but instead by a maximum compression to which one extrapolates. The empirical evidence which we shall present suggests that the pressure-compression range over which (1.1) can be extrapolated is determined by

$$0 \leq \Delta V/V_0 \leq 0.5, \quad (2.5)$$

$$dT_m/dp > 0. \quad (2.6)$$

The condition (2.6) is necessary in order to exclude substances whose melting curves exhibit maxima in the range of extrapolation.

Isothermal compression has been measured in Na along different isotherms[5] ranging from 20 to 359°K. The corresponding melting temperatures computed from the Simon fusion equation[6] are plotted against these isothermal compressions in Fig. 4. The temperature range covered in Fig. 4 corresponds to the range from 20°K to almost the one atomsphere melting point of Na. The data show that increasing the temperature of the isotherm tends to produce a small decrease in the slope of the melting relation (1.1).

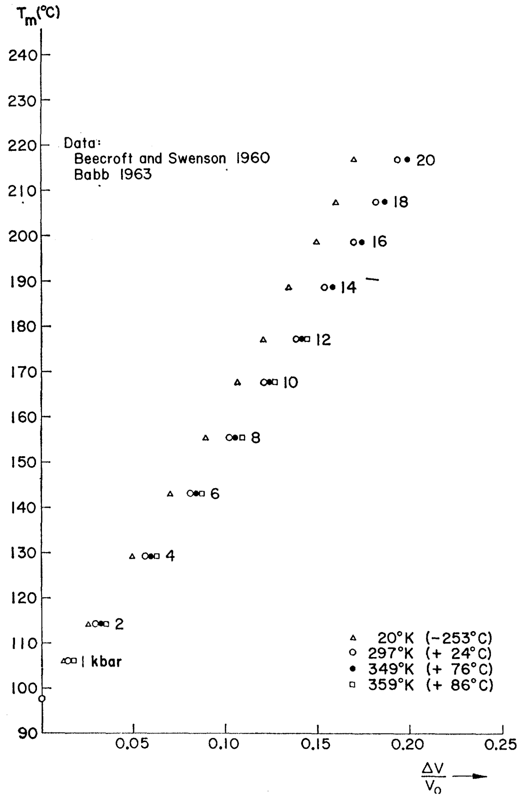

FIG. 4. Melting temperature versus isothermal compression along different isotherms in sodium.

3. IRON

Melting temperatures versus isothermal compression is plotted for Fe in Fig. 5. The compressibility measurements are those of Bridgman[7] on α Fe. The melting data are those of Sterrett, Klement, and Kennedy,[8] and applies to δ Fe. The straight line in Fig. 5 is given by

$$T_m(\text{Fe}) = 1513(1+3.3209\Delta V/V_0)°\text{C}. \quad (3.1)$$

The shock-wave data of Al'tshuler *et al.*[9] suggest that at 3 Mbar and room temperature, $\Delta V/V_0 = 0.440$. This pressure corresponds to the inner-outer core boundary in the earth, and if (3.1) is extrapolated to this value of $\Delta V/V_0$, it yields $T_m = 3724$°C for the melting temperature of iron at 3 Mbar, roughly fixing the inner-outer core boundary temperature in the earth. The use of the linear relation (3.1) in iron for compressions as large as 0.44 seems justified in the light of the observed linearity for compressions of this order in the alkali-metals (Fig. 1), and in sodium cholride (Fig. 6). However, it must be pointed out that the extrapolation of the present data to 3 Mbars disregards the possible occurrence of a maximum in the Fe melting curve, changes in structure, and possible electron promotion effects.

4. SODIUM CHLORIDE

Further evidence regarding the range of compressions over which (1.1) may hold comes from an examination

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[5] R. I. Beecroft and C. A. Swenson, J. Phys. Chem. Solids **18**, 329 (1961).

[6] S. E. Babb, Rev. Mod. Phys. **35**, 400 (1963).

[7] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **77**, 187 (1949).

[8] K. F. Sterrett, W. Klement Jr., and G. C. Kennedy, J. Geophys. Res. **70**, 1979 (1965).

[9] L. V. Al'tshuler, K. K. Krupnikov, B. N. Ledenev, V. I. Zhuchikhin, and M. I. Brazhnik, Zh. Eksperim. i Teor. Fiz. **34**, 874 (1958) [English transl.: Soviet Phys.—JETP **7**, 606 (1958)].

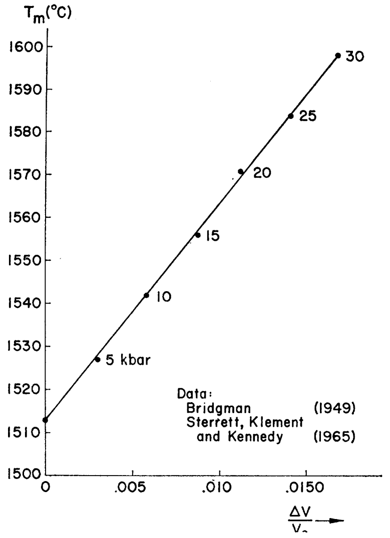

FIG. 5. Melting temperature versus isothermal compression at 25°C in iron.

of published isothermal[10] and shock-wave[11] compressions in NaCl. Figure 6 presents melting-temperature data plotted against isothermal compression data. The melting temperatures from 1 atm to 20 kbar are taken from the experimental data of Clark[12] and those from 20 to 40 kbar are recent experimental data of Pistorius.[13] The compressions from 1 atm to 40 kbar are the static isothermal measurements of Bridgman.[10]

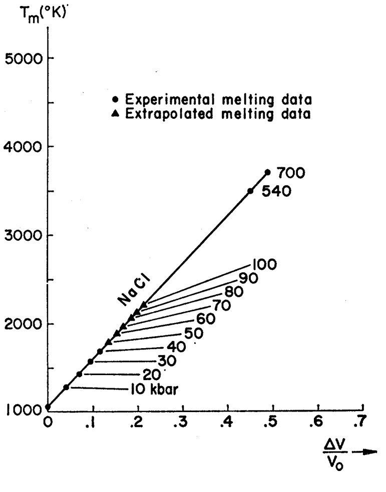

FIG. 6. Melting temperature versus isothermal compression in sodium chloride at 0°C.

Kormer *et al.*[11] have experimentally determined the melting curve of NaCl between 540 and 700 kbar in a shock-wave experiment. In their experiment, NaCl begins to melt at 540 kbar and 3500°K and becomes completely liquid at 700 kbar and 3700°K. The corresponding isothermal compressions at 540 and 700 kbar were calculated using the absolute-zero isotherm for NaCl,

$$P_c = -0.071\delta^{4/3} + 0.052\delta^{5/3} - 0.693\delta^2 + 0.712\delta^{7/3}, \text{ Mbar} \tag{4.1}$$

given by Kormer *et al.*[11] In (4.1), $\delta = V_c/V$, where V_c is the volume of NaCl at $T = 0$°K and $P_c = 0$, and V is the volume of NaCl at $T = 0$°K and pressure P_c. The densities of NaCl were taken as $\rho_c = 2.218$ g/cc at $T = 0$°K and $P_c = 0$, and $\rho_0 = 2.165$ g/cc at room temperature and pressure. Given P_c, δ is calculated from (4.1) and knowing δ, the isothermal compression $\Delta V/V_0$ is then calculated from

$$\Delta V/V_0 = (V_0 - V_c)/V_0 + (V_c/V_0)(1 - 1/\delta). \tag{4.2}$$

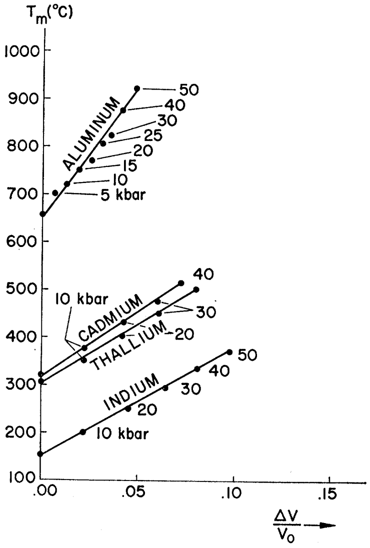

FIG. 7. Melting temperature versus isothermal compression at 25°C in aluminum, cadmium, thallium, and indium.

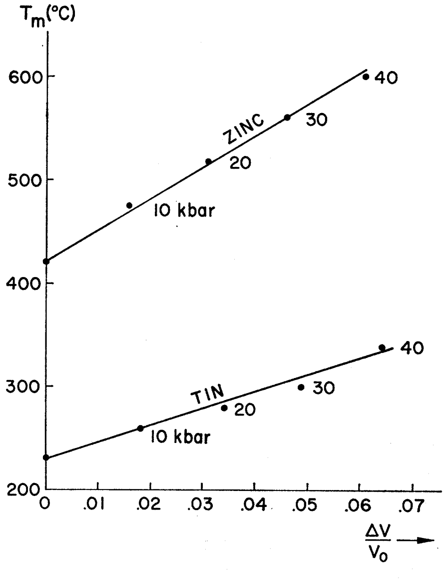

FIG. 8. Melting temperature versus isothermal compression in zinc and tin.

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[10] See Ref. 3.

[11] S. B. Kormer, M. V. Sinitsyn, G. A. Krillov, and V. D. Urlin, Zh. Eksperim. i Teor. Fiz. 48, 1033 (1965) [English transl.: Soviet Phys.—JETP 21, 689 (1965)].

[12] S. P. Clark, Jr., J. Chem. Phys. 31, 1526 (1959).

[13] C. W. F. T. Pistorius (private communication).

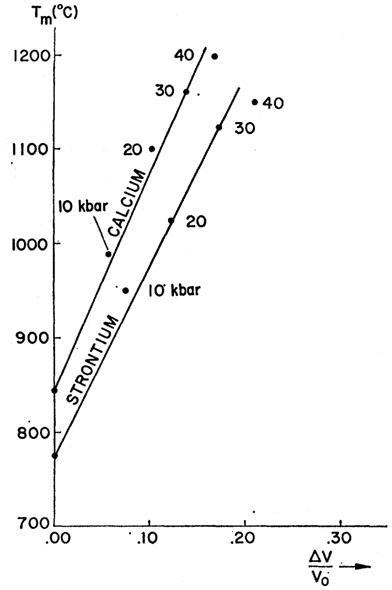

FIG. 9. Melting temperature versus isothermal compression at 25°C in calcium and strontium.

It is assumed that above 500 kbar $\Delta V/V_0$ along the 0°K isotherm is essentially the same as $\Delta V/V_0$ along a room-temperature isotherm. The results of the calculation give $\Delta V/V_0=0.45$ at $P=540$ kbar and $\Delta V/V_0=0.49$ at $P=700$ kbar. The corresponding points are plotted in Fig. 6. Remarkably, these shock points fall right on the extrapolated straight line passing through the experimental static data.

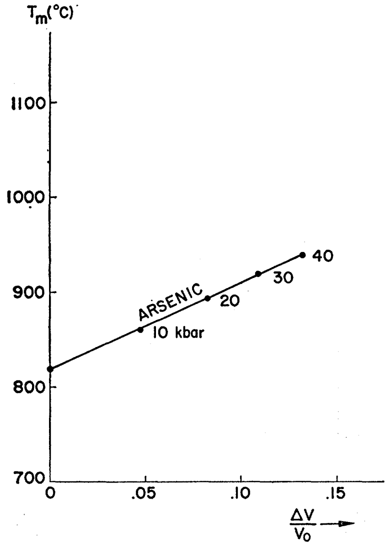

FIG. 10 Melting temperature versus isothermal compression in arsenic at 25°C.

Since Bridgman's static measurements in NaCl extend to 100 kbar, we have shown these points in Fig. 6 as triangles in order to emphasize that the corresponding melting temperatures between 40 and 100 kbar are extrapolated from Clark's[12] 20-kbar data using the Simon equation[6]

$$T_m(\text{NaCl})=1073(1+P/16.7)^{1/2.7}\ {}^{\circ}\text{K}. \tag{4.3}$$

The linearity of the NaCl plot (Fig. 6) for compressions as large as a half is consistent with the alkali-metal observations and lends some support to the choice of (1.1) over the Simon fusion equation[14];

$$P_m/a=(T_m/T_0)^c-1 \tag{4.4}$$

for extrapolating melting data to hydrostatically unattainable pressures. It is interesting to note in Fig. 6 that the first 70 kbar of pressure increase produces as large a melting temperature change as the next 700 kbar.

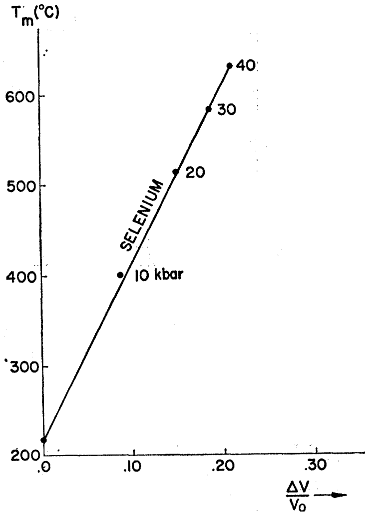

FIG. 11. Melting temperature versus isothermal compression in selenium at 25°C.

5. SOME OTHER NORMAL MELTING SUBSTANCES

A substance exhibits normal melting behavior within a given pressure range provided that it melts with an increase in volume throughout that range. Such behavior is exhibited by Al, Cd, Tl, and In in the range from 1

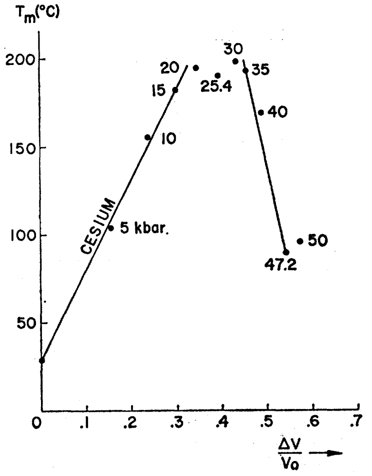

FIG. 12. Melting temperature versus isothermal compression in cesium at 25°C.

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[14] F. E. Simon and G. Glatzel, Z. Anorg. Allegem. Chem. 178, 309 (1929).

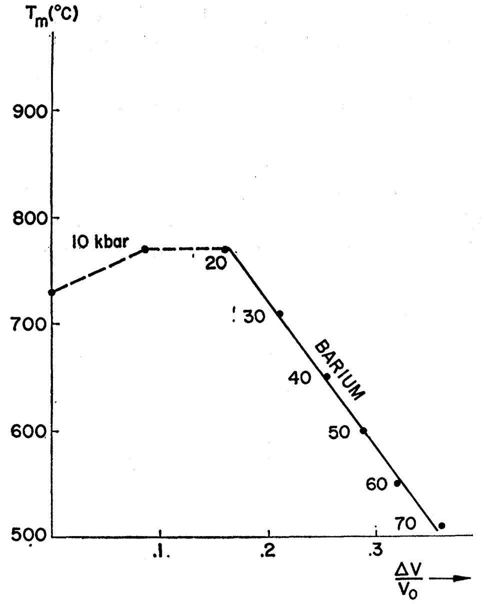

FIG. 13. Melting temperature versus isothermal compression in barium at 25°C.

atm to 40 kbar. The corresponding melting temperature[15,16] versus isothermal compression[7,10] plots are shown in Fig. 7. The data for Zn [10,15] and Sn [10,17] appear in Fig. 8, and Ca and Sr [3,18] are shown in Fig. 9. In the case of Ca and Sr, the compressibilities used are for the fcc phase while the melting points are for the bcc polymorph. Normal melting behavior is also exhibited by As [10,19] and Se [3,20] to 40 kbar, and the corresponding straight lines appear in Figs. 10 and 11.

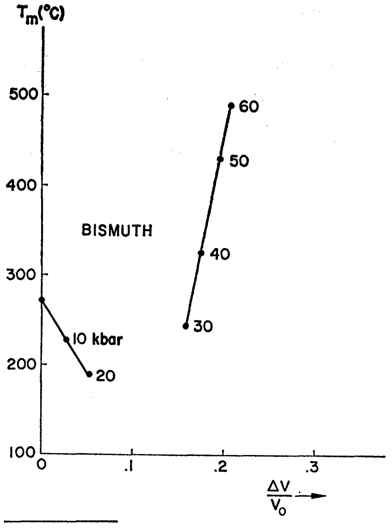

FIG. 14. Melting temperature versus isothermal compression in bismuth at 25°C.

6. THE EFFECT OF POLYMORPHISM ON THE TEMPERATURE-COMPRESSION MELTING RELATION

The previous experimental data suggest that for a pressure interval along which dT_m/dp is positive and monotonically decreasing, the corresponding $(T_m, \Delta V/V_0)$ plot is a straight line. The question then arises as to what happens to this straight line at a phase change.

For example, consider cesium. The fusion curve for cesium metal has been studied up to 50 kbar.[21] It shows two maxima, one at approximately 22.5 kbar and 197°C, and a second at about 30 kbar and 198°C. Bridgman[22] has reported two phase transitions in cesium at room temperature. He located a small transition with a volume discontinuity of about 2% at approximately 23 kbar, and a large discontinuity with a volume change of about 10% at 42 kbar. Bardeen[23] has suggested that the 23-kbar transition is one in which the cesium atoms are rearranged in a cubic close-packed configuration. The 42-kbar transition is probably the result of an electron-shell collapse, in which a 6*s* electron moves to a vacant 5*d* shell.[24] Figure 12 shows melting temperature of Cs [21] versus isothermal compression.[3] The detailed structure of the regions of Fig. 12 where the slope changes sign cannot be resolved with the presently available compressibility data on Cs. More compressibility measurements using much smaller pressure increments are called for.

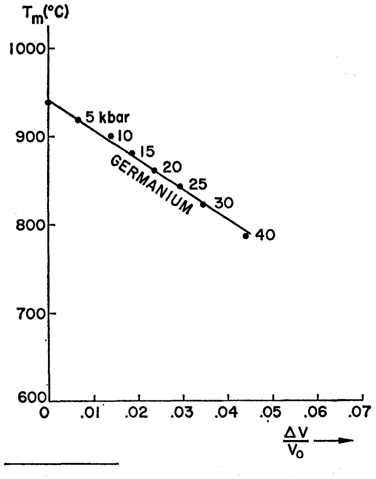

FIG. 15. Melting temperature versus isothermal compression in germanium at 25°C.

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[15] B. J. Alder, G. C. Kennedy, and R. C. Newton, *Solids Under Pressure*, edited by W. Paul and D. Warschauer (McGraw-Hill Book Company, Inc., New York, 1963), Chap. 7.

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

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

[18] A. Jayaraman, W. Klement Jr., and G. C. Kennedy, Phys. Rev. **132**, 1620 (1963).

[19] W. Klement Jr., A. Jayaraman, and G. C. Kennedy, Phys. Rev. **131**, 632 (1963).

[20] W. Klement Jr., L. H. Cohen, and G. C. Kennedy, J. Phys. Chem. Solids **27**, 171 (1966).

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

[22] P. W. Bridgman, Phys. Rev. **60**, 351 (1941).

[23] J. Bardeen, J. Chem. Phys. **6**, 372 (1938).

[24] R. Sternheimer, Phys. Rev. **78**, 235 (1950).

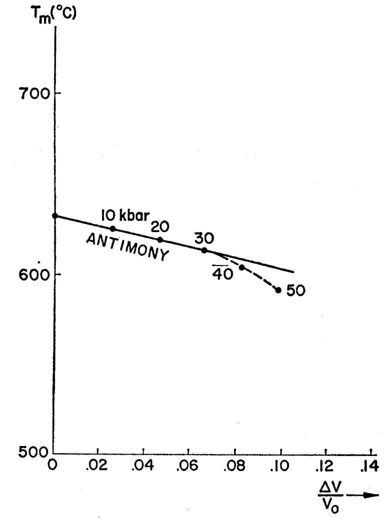

FIG. 16. Melting temperature versus isothermal compression in antimony at 25°C.

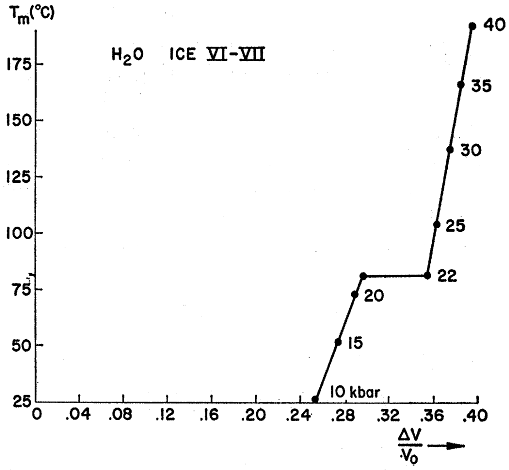

FIG. 17. Melting temperature versus isothermal compression in ice VI and ice VII.

Jayaraman, Klement, and Kennedy[25] have investigated the fusion curve of barium up to pressures of 65 kbar. The corresponding isothermal compression data of Bridgman[3] shows phase transitions near 17 and 59 kbar, at room temperature. The fusion curve obtained by Jayaraman *et al.* does not show the 17-kbar transition, although the 59-kbar transition was detected. The corresponding graphs of melting temperature versus isothermal compression appear in Fig. 13. The broken straight-line segments to 20 kbar indicate a lack of sufficient compressibility data for small pressure increments in this region of the curve.

Figure 14 is the $(T_m, \Delta V/V_0)$ plot for Bi.[10,19] The region between 20 and 30 kbar in Fig. 14 has been left open because of a lack of sufficient compressibility data for this interval. Figure 15 presents the data on Ge [10,17] to 40 kbar.

Like germanium, antimony starts out with a falling melting curve[19] $(dT_m/dp<0)$. It then suffers a sudden discontinuity in slope at about 57 kbar and 567°C corresponding to a triple point. The $(T_m, \Delta V/V_0)$ plot is shown in Fig. 16. It is clear from this figure that the Sb data to 50 kbar cannot be represented by a single straight line.

Figure 17 is a graph of melting temperature versus isothermal compression for ice VI–VII.[26,27] At the triple point near 80°C and 22.4 kbar, ice VI, ice VII, and liquid H_2O coexist.

7. SOLIDIFIED GASES

Some solidified gases appear to obey the linear temperature-compression melting relation (1.1) over the pressure intervals for which experimental data are available. For example, the $(T_m, \Delta V/V_0)$ plot for CO_2 is shown in Fig. 18.[28–30] However, helium and argon do not obey such a rule. The volume of solid helium has been measured as a function of pressure both along a 4°K isotherm and along the helium melting curve.[31,32] Determinations of the helium melting curve have been published by several investigators.[32–34] The data are presented in Fig. 19 and 20. It is clear from an examination of these figures that the melting temperature of solid helium is not a linear function of $\Delta V/V_0$ along the 4°K isotherm or along the melting curve. This observation is particularly interesting in view of the fact that

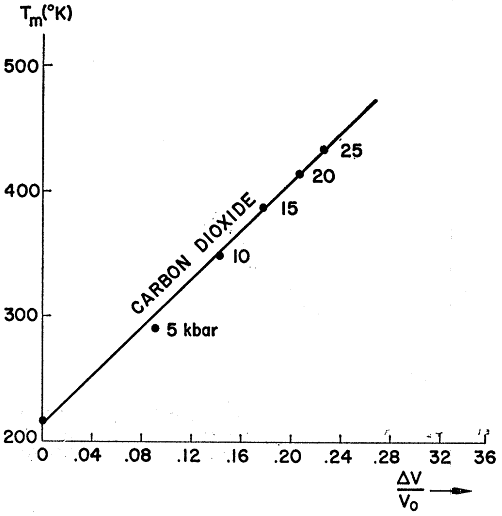

FIG. 18. Melting temperature versus isothermal compression in carbon dioxide.

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[25] A. Jayaraman, W. Klement Jr., and G. C. Kennedy, Phys. Rev. Letters **10**, 387 (1963).

[26] P. W. Bridgman, J. Chem. Phys. **5**, 964 (1937).

[27] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **74**, 399 (1942).

[28] P. W. Bridgman, Phys. Rev. **3**, 126 (1914).

[29] G. C. Kennedy and J. Grace (unpublished).

[30] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **72**, 207 (1938).

[31] J. W. Stewart, J. Phys. Chem. Solids **1**, 146 (1956).

[32] J. S. Dugdale and F. E. Simon, Proc. Roy. Soc. (London) **218**, 291 (1953).

[33] D. W. J. Langer, J. Phys. Chem. Solids **21**, 122 (1961).

[34] R. L. Mills and E. R. Grilly, Phys. Rev. **99**, 480 (1955).

Dugdale and Simon[32] were able to fit their experimental melting data in helium over a pressure range involving compressions as large as a half, using the Lindemann melting law.[35] A similar situation obtains in argon.[31,36,37] The (T_m, $\Delta V/V_0$) plot for argon is shown for isotherms at 65 and 77°K in Fig. 21. As is the case in helium, the linear relation between T_m and $\Delta V/V_0$ breaks down for argon, although the Lindemann melting relation[35] correctly describes the melting behavior of argon.[37]

8. DISCUSSION

The temperature compression melting relation

$$T_m = T_m^0\{1 + C\Delta V/V_0\}\,°\mathrm{C} \tag{8.1}$$

has been recently criticized by Ross and Alder[37] and by Gilvarry.[38] Ross and Alder[37] object to (8.1) on the grounds that it does not fit the results of their computer experiment on argon, whereas the Lindemann law[1,35]

$$T_m = Cm\Theta_D^2 V_m^{2/3}, \tag{8.2}$$

does. Secondly, they suggest on the basis of their analysis of three argon isotherms that the actual relation between melting temperature and compression is

$$T_m = T_m^0 \exp(\alpha\Delta V/V_0), \tag{8.3}$$

and that therefore (8.1) is an approximation to (8.3) and should only be used for small values of $\Delta V/V_0$, certainly much smaller values than those appropriate to the interior of the earth.

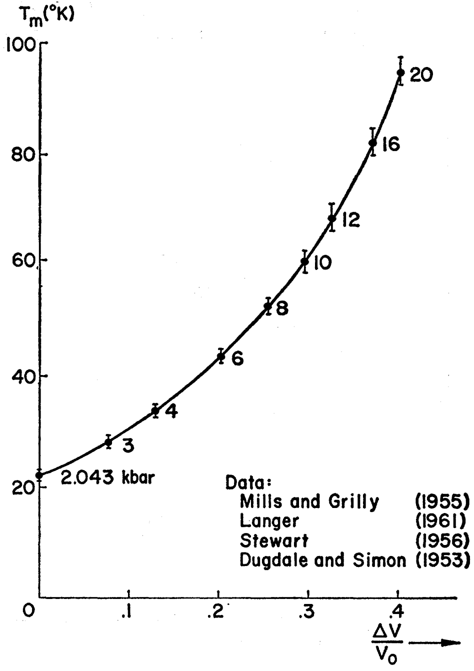

FIG. 19. Melting temperature versus isothermal compression in helium I at 4°K.

Consider the case of potassium which Ross and Alder[37] have chosen to discuss. Assuming that (8.1) represents the first two terms of the Taylor series expansion of (8.3), one obtains

$$T_m = 335.5 \exp(1.6147\Delta V/V_0)\ °\mathrm{K}, \tag{8.4}$$

on comparing (2.3) and the expansion of (8.3), taking into account the two different temperature scales. At 50 kbar the measured compression[3] in potassium is $\Delta V/V_0 = 0.405$ and the observed melting temperature[2] is 281°C. The Ross and Alder relation (8.4) makes the unlikely prediction that at 50 kbar, potassium melts at 372°C. It seems clear that the accuracy of (8.1) for changes in density as large as a factor of 2, as observed in the alkali metals and in sodium chloride, makes the interpretation of (8.1) as the first two terms in the Taylor series expansion of (8.3) unlikely. Ross and Alder also object to (2.3) because it predicts a potassium melting temperature of 604°C at infinite pressure. Their relation (8.4) would give a melting temperature of 1411°C for potassium at infinite pressure. They give no indication of why they think the latter value preferable.

Gilvarry[38] has derived (8.1) from the Lindemann law under the assumption that the isothermal compression $\Delta V/V_0$ is sufficiently small. This suggests that for large compressions, i.e., of the order of 0.4 or more, the melting temperature predicted by the Lindemann law should differ significantly from that predicted by the linear relation (8.1). We agree. Consider the case of sodium chloride. Figure 22, taken from the shock wave experiment of Kormer *et al.*,[11] shows that solid NaCl is compressed along the shock adiabat until it begins to melt at about 3500°K and 540 kbar. Instead of continuing along the Hugoniot, the melting process continues along the melting curve. This curve has a smaller slope, since part of the shock-wave energy goes into the latent heat of melting instead of into increasing the temperature. Melting continues until the NaCl becomes com-

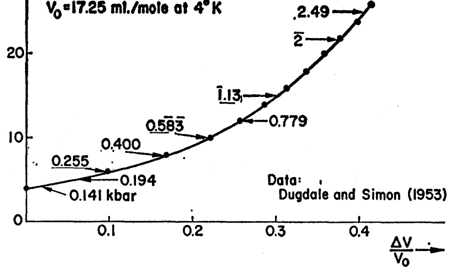

FIG. 20. Melting temperature versus compression along the melting curve of helium I.

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[35] F. A. Lindeman, Physik Z. **11**, 609 (1910).

[36] P. H. Lahr and W. G. Eversole, J. Chem. Eng. Data **7**, 42 (1962).

[37] M. Ross and B. J. Alder, Phys. Rev. Letters **16**, 1077 (1966).

[38] J. J. Gilvarry, Phys. Rev. Letters **16**, 1089 (1966).

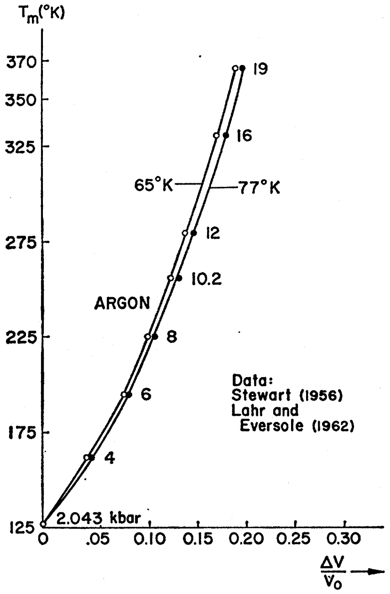

FIG. 21. Melting temperature versus isothermal compression in argon.

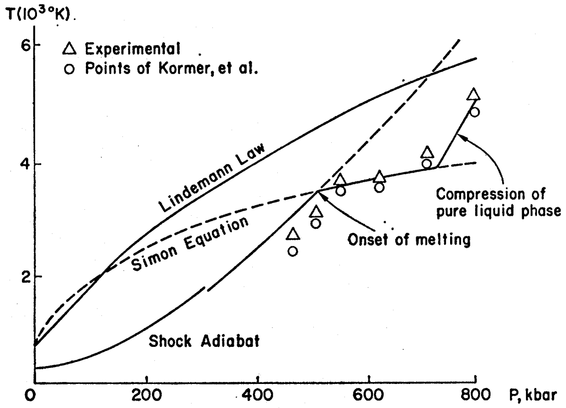

FIG. 22. Melting temperature versus pressure in sodium chloride.

pletely liquid at about 700 kbar and 3700°K. At this point, the slope suddenly increases again, corresponding to compression of the pure liquid phase of NaCl. For comparison, the prediction of the Lindemann law (8.2) is also shown in Fig. 22. In the treatment of Kormer *et al.*,[11] the dependence of the Debye temperature Θ_D on the density of NaCl is calculated using the formula of Dugdale and MacDonald.[39] A discussion of the validity of such a calculation has been given by Rice, McQueen, and Walsh,[40] and by Gilvarry.[41] At 700 kbar the Lindemann law predicts a melting temperature 35% higher than observed. Equation (8.1) correctly predicts the 700 kbar observed melting temperature using only experimental data to 40 kbar. Furthermore, Kormer *et al.*[11] find that the Lindemann law gives values of dT_m/dp which are too small at low pressures and too large at high pressures to be consistent with the NaCl data.

The results of Cohen, Klement, and Kennedy[42] on the melting of Cu, Ag, and Au give further support to the observation that the Lindemann law predicts melting temperatures which are too high in comparison with the observed values at high pressure. Gilvarry[38] suggests that (8.1) represents an interpolation or extrapolation relation in the same sense as the Simon equation,

$$P_m/a=(T_m/T_0)^c-1. \tag{8.5}$$

The latter can also be derived from the Lindemann law with the aid of an equation of state such as the Murnaghan equation.[43] In addition to the well-known inability of the Simon equation (8.5) to represent melting curves exhibiting maxima and to represent the melting curves of substances in which the liquid is more dense than the solid, the Simon equation also suffers from a glaring disadvantage as an extrapolation formula. Whenever the Simon equation (8.5) is fitted to experimental melting data over a range smaller than that actually measured and the resulting extrapolation then compared with experiment, the Simon equation invariably yields a higher melting temperature than is actually observed. Consider the case of NaCl. Clark's[12] melting data to 20 kbar are fitted by the Simon equation (4.3).[6] At 40 kbar Clark's extrapolated 20-kbar data yield a melting temperature of 1317°C, while Pistorius[13] observes a melting temperature of 1312°C. Similarly, the melting temperature of NaCl at 700 kbar is observed[11] to be 3700°K, while the extrapolated melting temperature given by (4.3) is 4292°K. We cannot agree with Gilvarry's conclusion[38] that (8.1) represents an extrapolation formula in the same sense as the Simon equation (8.5). For any range of P, V, and T and in any substance for which both the Simon equation and (8.1) hold, the latter gives a superior extrapolation to that obtained from the Simon equation.

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[39] J. S. Dugdale and D. K. C. MacDonald, Phys. Rev. **89**, 832 (1953).

[40] M. H. Rice, R. G. McQueen, and J. M. Walsh, Solid State Phys. **6**, 1 (1957).

[41] J. J. Gilvarry, Phys. Rev. **102**, 331 (1956).

[42] L. H. Cohen, W. Klement Jr., and G. C. Kennedy, Phys. Rev. **145**, 519 (1966).

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