ACKNOWLEDGMENTS

Melting of Sodium Chloride at Pressures to 65 kbar*

JAGANNADHAM AKELLA, S. N. VAIDYA, AND GEORGE C. KENNEDY

Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California 90024

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The melting curve for sodium chloride has been determined to 65-kbar. The present curve is in close agreement with those of Clark and Pistorius. The melting relation proposed by Kennedy has been examined in the light of the new melting data. The plot of melting temperature versus compression is slightly concave towards the $\Delta V/V_0$ axis at higher compression. This phenomenon may be due to a pressure dependence of the Grüneisen constant, but may also be due in part to possible uncertainties in the compression.

INTRODUCTION

THE melting temperature of sodium chloride has been determined by Clark[1] to 18 kbar and by Pistorius[2] to 40 kbar in a piston-cylinder apparatus. Kormer et al.[3] have reported data on melting and compression of NaCl at pressures of 540 and 700 kbar from shock-wave experiments.

A number of workers have reported on the compressibility of sodium chloride using a variety of methods. Bridgman[4] determined the compressibility of sodium chloride by static measurements up to 100 kbar. Dynamic measurements of the compressibility of NaCl have been made by Christian,[5] Al'tschuler et al.,[6] and Kormer.[3] Decker[7] has derived an equation of state for sodium chloride using a Born-Mie lattice model, and Keeler[8] has evaluated and reduced the shock-wave Hugoniot to the 25° isotherm.

The use of sodium chloride for high-pressure calibration has been proposed by some authors. Drickamer et al.[9] have expressed the compression of some metals

and compounds on an NaCl pressure scale. McWhan[10] studied the lattice parameters of quartz as a function of pressure using NaCl as an internal pressure standard. No phase change takes place in NaCl until circa 250 kbar. Probably a continuous single-valued PVT relation and melting curve for NaCl extends to very high pressures. Recent works by Bassett and Takahashi[11] and by Jamieson[12] and others shows that the low-pressure, 20-kbar transition in sodium chloride suggested by some authors does not exist.

In this investigation, the melting curve of sodium chloride has been extended up to 65 kbar using single-stage piston-cylinder apparatus. The melting relation proposed by Kraut and Kennedy[13] has been examined in the light of the new melting data.

Experimental Method

The experiments were carried out in a piston-cylinder apparatus previously described by Cohen et al.[14] Haygarth and Kennedy[15] have shown that the crushing strength of a cemented tungsten carbide piston increases as the unsupported piston length decreases. In order to achieve the amount of piston travel necessary to generate the required pressure and at the same time to control the length of the unexposed piston, the piston

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was fitted with a sliding binding ring in such a way that the binding ring splits the unsupported length of the piston into two segments. By this means, the piston is able to withstand higher stresses, and the available travel of the piston is not hampered in any way, because the piston can move through the sliding binding ring after the ring meets the face of the pressure vessel. The sliding binding ring as well as the stationary binding ring were made of Vascomax 300 steel. These were fitted to the piston with 2% interference. With this new modification pressures up to 80 kbar are achieved in the piston-cylinder apparatus; however, in the present experiments, pressures were limited to 68 kbar because at pressures above this and at the melting temperature of NaCl, rapid breakup of the carbide pressure vessel takes place.

The pressure vessels used in this study in the range 10–40 kbar were of carbide with 13% cobalt binder, Carboloy 55A. The pistons were of Carboloy 883. At pressures above 40 kbar the pressure vessels were carbide with 6% cobalt binder, Carboloy 883, and the pistons were of Carboloy 999 with 3% cobalt binder. It was found that at very high pressures the 883 cores have about $\frac{1}{10}$ the maximum enlargement of the bore that was observed for the 13% cobalt (Carboloy 55A) cores at the maximum pressure. The 999 pistons have a higher crushing strength than the 883 pistons and suffer less radial deformation.

The assembly used in the present experiments (Fig. 1) differs slightly from the conventional type. Talc changes to enstatite + quartz and dehydrates at high temperature. The liberated water generally attacks the thermocouples and the metal capsule, and in order to avoid this a Pyrex glass tube was inserted between the outer talc
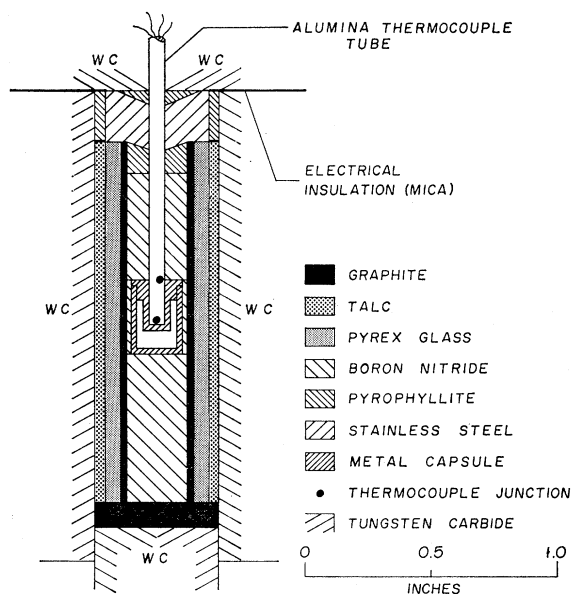
tube and the graphite furnace. Boron nitride filled the graphite furnace. The boron nitride parts were fired at 480°C for 48 h to free them of ammonia and water.

Capsules were made out of tantalum, nickel, and niobium. Nickel capsules apparently contaminated the NaCl and the melting temperatures in them were found to be lower by 5–10°C than those obtained in other capsules.

The sodium chloride used in these experiments was of 99.999% purity and was supplied by Research Organic and Inorganic Chemicals Co. The 1-atm melting point obtained from the present experiments is 800.6°C, whereas the reported 1-atm melting point is 800.5°C. The sodium-chloride crystals were crushed to fine powder and dried at 400°C for 24 h before use.
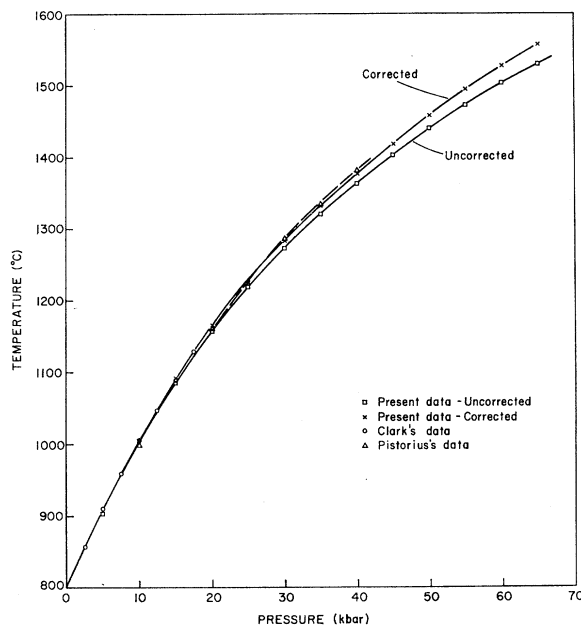

FIG. 2. Melting curve of sodium chloride.

The temperatures were measured with Pt–Pt 10% Rh thermocouples. The melting and freezing at different pressures was detected by differential thermal analysis. The rate of heating and cooling used in the present experiments ranged from 6 to 10°C/sec. At a given pressure the melting and freezing signals were observed at least four times with a typical reproducibility of ±1 to 2°C. Some 120 determinations of the melting temperature were made.

The assembly was initially compressed to the maximum pressure planned for the experiment. The temperature was then taken up to the melting temperature. The melting and freezing temperatures were determined at intervals of 4 kbar on a decompression cycle and on a subsequent compression cycle.

The compression melting curve and the decompression melting curve were separated by ∼2–4 kbar. The fric-

FIG. 1. Furnace assembly.

TABLE I. Parameters of the melting curve of NaCl in the equation

$$t = t_0 + b_1 P + b_2 P^2 + b_3 P^3 + b_4 P^4,$$

together with the derivation of values of b_1 from thermodynamic data.

	t_0 (°C)	b_1 (°C/kbar)	b_2 (°C/kbar^2)	b_3 (10^{-3} °C/kbar^3)	b_4 (10^{-4} °C/kbar^4)	Std. dev. (°C)
Clark	799.6	23.44	−0.383	4.928		4.3
Pistorius	802.5	21.61	−0.201	0.576		2.7
Present work	800.6	21.155	−0.03736	−10.4	2.4	3.4

ΔS (cal/mole °C)	ΔV_f (cc/mole)	$\Delta V_f / \Delta S_f$ (°C/kbar)	b_1 (°C/kbar)
6.3[a]	7.55[b]	29[c]	23.4
6.7[b]	7.55[b]	27[c]	21.6
6.24[d]	7.01[e]	26.8[f]	21.2

[a] F. D. Rossini, S. S. Wagman, N. H. Evans, S. Levine, and I. Jaffe, Natl. Bur. Std. (U. S.) Circ. No. 500 (1952).
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tion was assumed to be symmetrical and the pressure obtained by interpolation. The final pressures are believed to be accurate to within ±0.5 kbar.

The effect of pressure on the emf of the Pt–Pt 10% Rh thermocouples is large around 1000°C and above. This effect also depends upon the difference between the seal and the sample temperature. A separate experiment was conducted using the same type of assembly with a dummy capsule to determine the difference between the seal and the sample temperature. Between 1000 and 1500°C the difference ranged from 830 to 1270°C. The value for the pressure effect on the thermocouples as given by Hanneman and Strong[16,17] is approximately +55° at 1500°C and 60 kbar. However, we have used the corrections as determined in this laboratory which suggest an effect only about one-half as great. The correction[18] for the effect of pressure on thermal emf is 4°C at 1000°C and 10 kbar and 26°C at 1530°C and 65 kbar. In Fig. 2 both corrected and uncorrected melting data are presented.

EXPERIMENTAL RESULTS

The present experimental results are presented along with those of Clark and Pistorius in Fig. 2. The agreement between the two sets of results is good. At 40 kbar, Pistorius's maximum pressure, his curve lies 2°C above ours.

The curve for the melting temperature was calculated from the equation

$$t = t_0 + b_1 P + b_2 P^2 + b_3 P^3 + \cdots$$

fitted to the 120 experimental values by least squares.

The parameters for the fifth-order polynomial are presented in Table I. The standard deviation for the higher-order polynomials did not show substantial change.

The melting temperatures are given in Table II. The initial slope of melting is 0.0212°C/bar. The value calculated from the Clausius-Clapeyron equation $dT/dP = \Delta V / \Delta S$ is 0.028°±0.001°C/bar.

In our experiments the suggested transition at 10–20 kbar was not observed. This result is in accordance with that of Bridgman,[4] Bassett and Takahashi,[11] Jamieson,[12] Johnson,[19] Perez-Albuerne, and Drickamer,[20] and Pistorius.[2] Johnson[19] has pointed out that the x-ray diffraction lines attributed to high-pressure phases of NaCl by Evdokimova and Vereschagin[21] were probably due to

TABLE II. Melting points of NaCl.

Pressure (kbar)	T_m (°C) (Uncorr.)	T_m (°C) (Corr.)
0	800.6	800.6
5	904	906
10	1000	1004
15	1085	1090
20	1158	1165
25	1219	1227
30	1273	1283
35	1320	1332
40	1362	1377
45	1403	1419
50	1440	1458
55	1474	1494
60	1504	1527
65	1530	1556

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the intrusion of a lithium plug contaminated with its hydroxide into the x-ray beam.

Volume Compression and Melting

Kraut and Kennedy[13] showed that the melting temperature T_m and the compression of the solid phase $\Delta V/V_0$ at the same pressure can be correlated in accordance with the equation

$$T_m = T_m{}^0(1+C_1|\Delta V/V_0|), \qquad (1)$$

where $T_m{}^0$ and V_0 are the melting temperature and specific volume of the solid at 1 atm. The melting Eq. (1) seems to describe approximately the compression and melting data on several metals, alkali halides,[13] and solidified gases.[22] Furthermore, by combining the Lindemann equation $\theta^2 V^{2/3} = C_2 K T_m$ and the Grüneisen relation $\gamma = \partial \ln\theta/\partial \ln V$, the constant C_1 in Eq. (1) can be shown to be equal to $2(\gamma-\frac{1}{3})$.[23,24] Equation (1) can therefore be rewritten as

$$T_m = T_m{}^0[1+2(\gamma-\tfrac{1}{3})|\Delta V/V_0|]. \qquad (2)$$

Using the available data on metals, alkali halides, and solidified gases, Eq. (2) is shown to agree with the thermal value of γ, i.e.,

$$\gamma = V\alpha/K_T C_V, \qquad (3)$$

where V is the specific volume, α is the coefficient of volume thermal expansion, and K_T is the isothermal compressibility. Recent determinations of melting of alkali metals to 80 kbar,[25] silver halides,[26] and the present paper of sodium chloride, have been made to examine this relationship more closely.

In contrast, the Simon equation

$$(P-P_0)/a = (T/T_0)^{c-1},$$

which is traditionally used to represent melting at high pressure, does not give a good fit of the experimental data over an extended pressure range, and the values of the constants a and c cannot be satisfactorily related to measurable physical quantities.

The compression values of NaCl from Bridgman's[4] static experiments to 100 kbar, Keeler's[8] shock-wave data to 200 kbar, Decker's[7] calculations based on the Born-Mie equation of state, and Jeffery's x-ray results are represented in Fig. 3. Bridgman's and Keeler's compression values agree within 1% at 100 kbar, whereas Decker's values are higher by about 10%. Bassett et al.[27] and McWahn[12] have pointed out that Decker has

possibly overestimated the compression values. Decker used in his calculation an initial compressibility of $(4.27\pm0.04)\times10^{-3}$ obtained by measurement of echo-travel-time method.[28] The revised value from ultrasonic interferometry obtained by Slagle and McKinstry[29] is 4.21×10^{-3} kbar^{-1}. This reduction in K_0 from 4.27 to 4.21×10^{-3} reduces Decker's values by about 3% above 200 kbar. We have used a different approach to place Decker's values on the recently revised pressure scale. Jeffery et al.[30] have used Decker's equation to determine pressures at the Bi I-II, Bi III-V, and Ba I-II transitions simultaneously with x-ray compression values for NaCl. The transition pressure determined in these experiments were 24.8 ± 08 kbar for the Bi I-II transition, 73.8 ± 1.3 kbar for the Bi III-V transition, and 53.8 ± 1.2 kbar for the Ba I-II transition Kennedy and La Mori's[31] value of the Bi I-II transition pressure measured in rotating piston apparatus is 25.38. Hydemann[32] found the Bi I-II transition pressure equal to 25.499 kbar in a piston-cylinder apparatus with a dead-weight piston gauge for pressure measurement. Recently, Bi III-V and Ba I-II transition pressures have also been determined by observing the discontinuity in electrical resistance of a sample wire embedded in AgCl pressure medium. The pressure of the Bi III-IV transition determined from these experiments is 77.5 ± 0.5 kbar,[33] and that of Ba I-II transition is 55 ± 0.5 kbar.[34] Using the revised values of the transition pressures, and the values of compressions $\Delta V/V_0$ at the transition as determined by Jeffery et al.,[30] we have replotted the x-ray values of their work (Fig. 3). These x-ray compression values are higher than the shock-wave or the Bridgman values by about 6% at 100 kbar.

The plot of melting temperature of NaCl versus the compression values of Bridgman, Keeler, and Decker are shown for the corrected melting temperatures in Fig. 4. The plots are linear at low compressions and begin to curve down towards the $\Delta V/V_0$ axis at high compressions. The curvature is more pronounced for Decker's compression values. The plot of the corrected values of T_m versus the compression values of Bridgman shows only a small curvature at high pressures.

The value of γ obtained from the initial slope of T_m versus Bridgman's $\Delta V/V_0$ values is 2.78. The value of γ calculated in this manner is too high because $\Delta V/V_0$ values at room temperature were used in Eq. (2). To correct for the compressions measured at room tempera-

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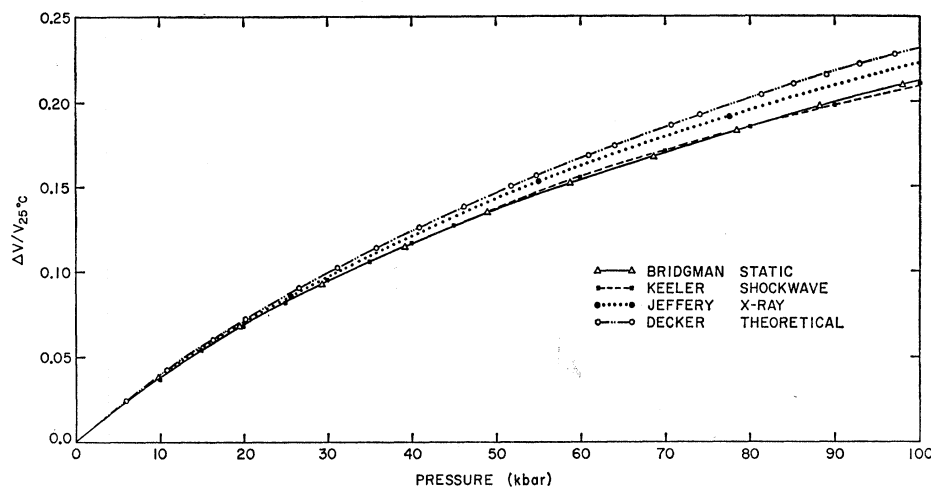[30] R. N. Jeffery, J. T. Barnett, H. B. Vanfleet, and H. T. Hall, J. Appl. Phys. **37**, 3172 (1966).

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FIG. 3. Volume compression of sodium chloride.

ture we adopt the following scheme.[24] Since γ is very nearly independent of temperature,

$$\gamma = (V\alpha/K_T C_V)_{\mathrm{RT}} = (V\alpha/K_T C_V)_{T_m}.$$

Furthermore, variation in C_V is only a few percent; hence $(K_T)_{T_m} = (\alpha V)_{T_m}/(\alpha V)_{\mathrm{RT}}(K_T)_{\mathrm{RT}}$ in other words, $|\Delta V/V_0|$ in Eq. (2) should be replaced by $[(\alpha V)_{T_m}/(\alpha V)_{\mathrm{RT}}]|\Delta V/V_0|$. When this correction is applied using the thermal-expansion data of Enck et al.,[35] $\gamma = 1.77$ is obtained. This is in agreement with the thermal value of $\gamma = 1.74$.[36]

DISCUSSION

The T_m-versus-$\Delta V/V_0$ plot of NaCl shows curvature towards the compression axis at high pressure (Fig. 4). This behavior has also been noticed in lithium, potassium, indium, and in some other cases. A possible explanation of this curvature is that it results from the volume and temperature dependence of γ in Eq. (2). The Grüneisen constant at pressure P and temperature T_m can be written as

$$\gamma = \gamma_0 + \left(\frac{\partial \gamma}{\partial V}\right)_T \Delta V + \left(\frac{\partial \gamma}{\partial T}\right)_V (T_m - T_m^0),$$

where γ_0 is the Grüneisen constant at temperature T_m^0 and volume V_0 of solid.

This can be rewritten as

$$\gamma = \gamma_0 + \gamma_0 \frac{\partial \ln\gamma}{\partial \ln V} \frac{\Delta V}{V_0} + \frac{\partial \ln\gamma}{\partial \ln T}(T_m - T_m^0)\frac{\gamma_0}{T_m^0}$$

or

$$\gamma = \gamma_0 + \gamma_0 \frac{\partial \ln\gamma}{\partial \ln V} \frac{\Delta V}{V_0} - 2\gamma_0(\gamma_0 - \tfrac{1}{3})\alpha T_m^0 \frac{\partial \ln\gamma}{\partial \ln V} \frac{\Delta V}{V_0}. \quad (4)$$

[35] F. D. Enck, D. G. Engle, and I. I. Marks, J. Appl. Phys. 36, 839 (1965).
[36] C. M. Kachhava and S. C. Saxena, J. Chem. Phys. 44, 986 (1963).

Anderson[37] has shown that [Eq. (14) of his paper]

$$\partial \ln\gamma/\partial \ln V = \delta_T - \beta_T + 1,$$

where $\delta_T = (1/\alpha\beta_T)(\partial\beta_T/\partial T)_P$, $B_T(P,T) = B_T(0,T) + \beta_T P$, and $B_T = (K_T)^{-1}$ is the isothermal bulk modulus. Using Anderson's Eq. (2), namely, $\delta_T \simeq \beta_T$, a relationship which he has shown holds for many solids, we obtain
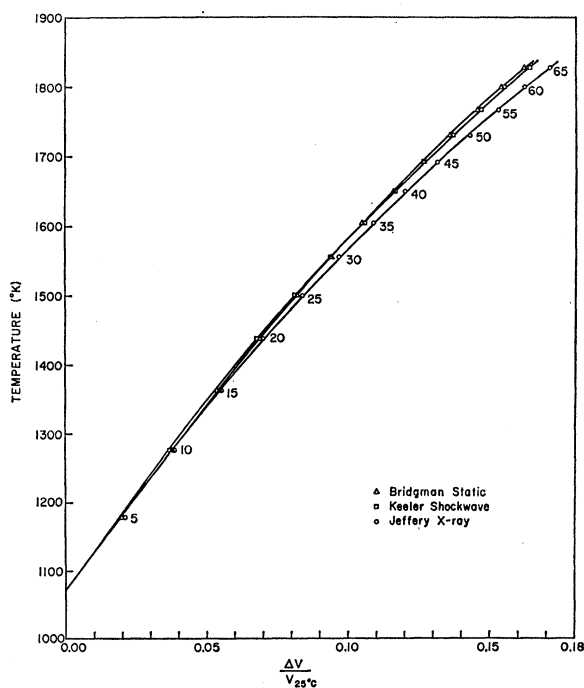
$$\partial \ln\gamma/\partial \ln V = 1.$$

FIG. 4. Melting temperature of sodium chloride versus volume of the melting solid.
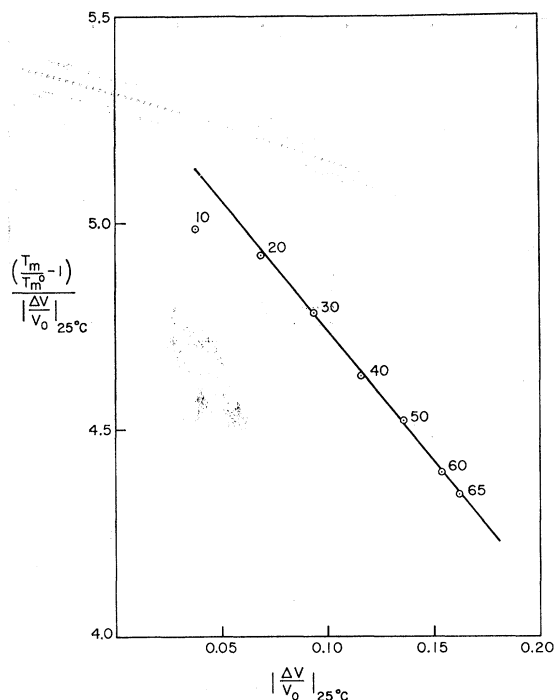
[37] O. L. Anderson, J. Geophys. Res. 72, 3661 (1967).

FIG. 5. Plot of $(T_m/T_m{}^0-1)/|\Delta V/V_0|_{25°C}$ versus $|\Delta V/V_0|_{25°C}$.

From Eq. (4),

$$\gamma=\gamma_0+\gamma_0(1-2(\gamma_0-\tfrac{1}{3})\alpha T_m{}^0)(\Delta V/V_0).\qquad(5)$$

α is typically $\sim10^{-5}/°C$ and $T_m\sim10^3\ °C$, so that the second term is very small as compared to the first term. As was mentioned earlier, the temperature derivative of γ, namely, $\partial\ln\gamma/\partial\ln T\simeq T_m{}^0\alpha$, is indeed very small as compared with the volume derivative $\partial\ln\gamma/\partial\ln V$, which is nearly equal to 1. This has also been found experimentally by Anderson. Leaving out the second term in Eq. (5) we have

$$\gamma=\gamma_0(1+\Delta V/V_0),\qquad(6)$$

which on substitution in Eq. (2), gives

$$T_m=T_m{}^0[1-2(\gamma_0-\tfrac{1}{3})(\Delta V/V_0)-2\gamma_0(\Delta V/V_0)^2].\quad(7)$$

Using the present melting data on NaCl and Bridgman's $\Delta V/V_0$ values, a plot of $(T_m-T_m{}^0)/T_m{}^0(\Delta V/V_0)$ was made in accordance with Eq. (7), and is shown in Fig. 5. The plot is linear, and the value of γ_0 obtained from its slope is 3.15. When the correction for conversion of $\Delta V/V_0$ values from room temperature to T_m is applied, $\gamma=1.08$ is obtained. This is much smaller than the thermal value of $\gamma=1.74.$[36]

In conclusion, the plot of T_m versus $\Delta V/V_0$ is linear to moderately large compressions and the value of γ_0 obtained from the initial slope of this plot agrees with the value obtained from thermal data. The curvature in T_m versus the $\Delta V/V_0$ plot at high pressure can be accounted for by taking into consideration the pressure dependence of the Grüneisen constant. This gives the correct sign for the effect, though the magnitude is different from the observed value. It seems that there are some other factors which influence the quadratic term in Eq. (7). The present experimental data may also not be as reliable as their precision suggests insofar as the calculation of this curvature goes. The compression values for NaCl still may have substantial uncertainties, and the accuracy in T_m is limited by the uncertainties in applying the correction for the pressure effect on the thermocouples.

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