

## The Variation with Temperature of the Principal Elastic Moduli of NaCl near the Melting Point

LLOYD HUNTER, *Carnegie Institute of Technology, Pittsburgh, Pennsylvania*

AND

SIDNEY SIEGEL, *Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania*

(Received October 31, 1941)

The principal elastic moduli of single crystal rods of NaCl were measured over the temperature range 20°C to 804°C, the melting point. The measurements were carried out by means of a tripartite piezoelectric oscillator consisting of a quartz crystal driver, an intermediate fused silica bar, and the NaCl specimen. The shear constants  $C_{44}$  and  $(C_{11} - C_{12})$  decrease nearly linearly with temperature, reaching non-zero values at the melting point. The compressibility increases with temperature, but exhibits a sudden drop within a few degrees of the melting point. The results are compared with certain predictions based on Born's theory of the stability of crystal lattices.

THERE are few data in the literature on the behavior of the elastic moduli of crystals in the neighborhood of their melting point. Various suggestions dealing with this problem have been made,<sup>1</sup> and Born<sup>2</sup> has developed a theory concerning the stability of crystal lattices in which the temperature variation of the shear constants near the melting point is an important feature.

This paper is a report of a series of measurements of the elastic moduli of NaCl over the range 300°K to 1077°K, the melting temperature. Previous writers<sup>3</sup> have reported the variation with temperature of these quantities over the range 80°K to 480°K.

### SPECIMENS

Artificial crystals, grown from the melt, were used.<sup>4</sup> Specimen rods of either circular or square cross section were prepared, 3 to 7 cm long, all having a lateral dimension of 0.476 cm. The square rods were prepared by grinding on a lapping plate, the round by carefully turning on a lathe. The rod axis was made to coincide with either a  $[100]$  or a  $[110]$  direction to better than 30'. Since a five degree error in orientation produces only about one percent error in modulus, the error in modulus produced by a 30' error in

orientation is seen to be negligible. In all, fourteen crystals were prepared.

### EXPERIMENTAL METHOD

The experimental method is a dynamical one, making use of a composite piezoelectric oscillator.<sup>3</sup> Since it was necessary to make measurements at 800°C, above the  $\alpha \rightarrow \beta$  transformation of quartz at 577°C, it was not feasible to use simply a two-

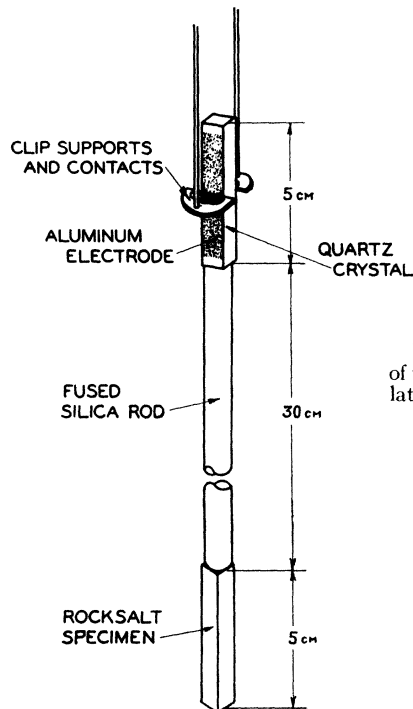


FIG. 1. Diagram of three-part oscillator.

<sup>1</sup> L. Brillouin, *Phys. Rev.* **54**, 916 (1938).

<sup>2</sup> M. Born, *J. Chem. Phys.* **7**, 591 (1939).

<sup>3</sup> L. Balamuth, *Phys. Rev.* **45**, 715 (1934); F. C. Rose, *Phys. Rev.* **49**, 50 (1936); M. A. Durand, *Phys. Rev.* **50**, 449 (1936).

<sup>4</sup> Obtained from the Harshaw Chemical Company.

part oscillator, in which the quartz crystal is maintained at the same temperature as the specimen. The composite oscillator in these experiments consisted of a quartz rod 5 cm long, cemented to one end of a clear fused silica rod 30 cm long; at the other end of the latter the NaCl specimen was cemented. The cement used at the quartz-silica interface was red shellac applied while molten. At the silica-NaCl interface a cement consisting of a paste of sodium silicate and finely divided calcium carbonate was used. This cement dries satisfactorily in 72 hours at room temperature.

Two types of oscillator were used—one for longitudinal, and another for torsional vibrations. In the former, both the X-cut quartz crystal and the NaCl specimen were of square section. In the latter, the Y-cut quartz rod and NaCl specimen were both round, 0.476 cm in diameter. In both cases the silica rod was circular in section, having been ground to a diameter of  $0.476 \pm 0.003$  cm over its entire length. Figure 1 is a diagram of a typical longitudinal oscillator.

The oscillator is suspended vertically on the axis of a tube furnace 64 cm long, 4 cm bore, with the NaCl specimen at the center of the furnace, maintained at the desired elevated temperature. The quartz crystal is situated above the end of the furnace, nearly at room temperature.

The theory of such a three-part oscillator has been developed by Rose.<sup>3</sup> The resonance frequency  $f_0$  of one of the normal modes of longitudinal or torsional vibration, is measured by means previously described. The resonance frequency  $f_3$  of one of the normal modes of the NaCl specimen is obtained by means of the equation

$$f_3 = f_0 + (m_1/m_3)(f_0 - f_1) + (m_2/m_3)(f_0 - f_2), \quad (1)$$

where  $f_1$  is the fundamental frequency of the quartz crystal,  $f_2$  is the frequency of one of the normal modes of the silica rod, and  $m_1$ ,  $m_2$ , and  $m_3$  are the masses of the quartz, silica, and NaCl bars, respectively. This equation is an approximation, valid under the condition

$$f_0 = f_1 = f_2 = f_3 \quad (2)$$

to about 5 percent. This condition was always fulfilled experimentally.

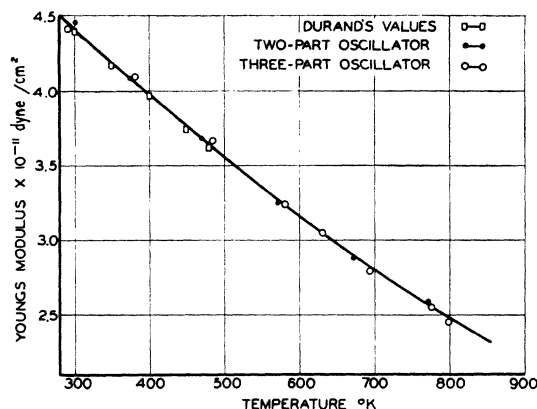


FIG. 2. Comparison of the data obtained with a two-part and a three-part oscillator with those of Durand.

From the values of  $f_3$  obtained from Eq. (1), the appropriate elastic modulus  $M$  is obtained by means of the equation

$$M = \lambda^2 f_3^2 \rho \quad (3)$$

where  $\rho$  is the density of the specimen and  $\lambda$  the wave-length in the NaCl specimen. The wave-length is always  $2L/n$ , where  $L$  is the length of the specimen and  $n$  a small integer determined from an approximate knowledge of the modulus. The length at any temperature  $T^\circ\text{C}$  is obtained from the room temperature length by means of the coefficient of linear expansion

$$\alpha = 4.45 \times 10^{-5} + 2.49 \times 10^{-8}(T - 200) + 6.52 \times 10^{-14}(T - 200)^3$$

given by Walther, *et al.*<sup>5</sup>

In these experiments a temperature gradient of nearly  $30^\circ\text{C}/\text{cm}$  may exist in the silica rod, which is therefore elastically inhomogeneous, since its elastic moduli vary with the temperature. The quantity  $f_2$  of Eq. (1) is determined in a preliminary run in which a two-part oscillator, consisting only of the quartz crystal and the silica rod is suspended in the furnace with the silica rod occupying the identical position that it does during an actual run on a three-part oscillator. Furthermore, to ensure that the *relative spatial distribution* of vibration nodes and the temperature along the silica rod does not change appreciably during a three-part oscillator run, the length

<sup>5</sup> A. K. Walther, W. P. Haschkowsky, and P. G. Strelkow, *Physik. Zeits. d. Sowjetunion* **12**, 35 (1937).

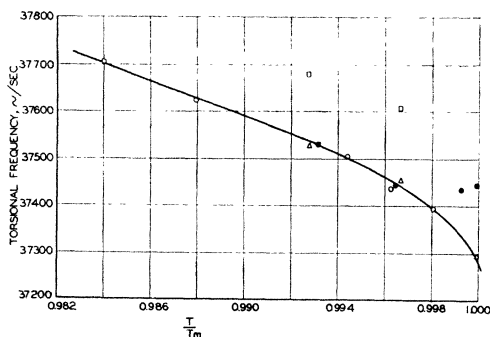


FIG. 3. Typical behavior of the natural frequency of a NaCl specimen near the melting point. Description in the text.

of the NaCl specimen is always so adjusted that condition (2) is fulfilled to 2 percent or better. This is accomplished in the following manner. The length of the NaCl specimen is first chosen so that this condition is met over the range 20°C to 200°C. Then its length is reduced successively three times, so that the condition is fulfilled over the ranges 200° to 400°, 400° to 600°, and 600° to the melting point at 804°.

Equation (1) was derived under the assumption that all parts of the oscillator are elastically homogeneous, an assumption not valid here because of the temperature gradient along the silica rod. To establish the validity of the method, Young's modulus of a [100] NaCl specimen was measured by means of a conventional two-part oscillator consisting of a quartz crystal and NaCl specimen, with the entire oscillator maintained at the elevated temperature. Data were taken from 20° to 530°C. The identical specimen was then made part of a three-part oscillator and measured over the same temperature range. Figure 2 shows the results of this experiment. The open circles are the measurements made with the three-part oscillator; the closed circles were obtained with the two-part oscillator, and the squares are results obtained by Durand.<sup>3</sup> The agreement establishes the validity of data obtained with the three-part oscillator in the fashion described above.

Throughout these experiments the temperature was measured with a Pt vs. Pt-10 percent Rd thermocouple, of which the hot junction was closely adjacent to the NaCl specimen. This couple was calibrated against the temperatures of

boiling water, freezing Sn, Zn, Pb, Al, and NaCl. It was checked before and after each run against freezing NaCl, and could be checked *in situ* through the discontinuous behavior of the resonance frequency of the composite oscillator as the NaCl specimen melted.

In obtaining the data, both heating and cooling curves were taken whenever possible. In general these checked to better than 0.2 percent, but at high temperatures, within a few degrees of the melting point, the curves were not closely reproducible. In order to accurately determine the true curve in this region, several cycles of heating and cooling were carried out. Figure 3 shows the result of one such experiment. The resonance frequency of torsional vibration for one of the [100] crystals is plotted against  $T/T_m$ , the ratio of the absolute temperature to the melting point on that scale. Each measurement, represented by a point in Fig. 3, was made only after the furnace windings had been constant in temperature to better than 0.2°K for at least an hour, to ensure that the temperatures of the silica rod and the NaCl specimen were steady. The heating or cooling from one point to the vicinity of the next, prior to the establishment of thermal equilibrium at the new point, usually took only a few minutes.

The open circles represent data taken on heating, the last point on this heating cycle being

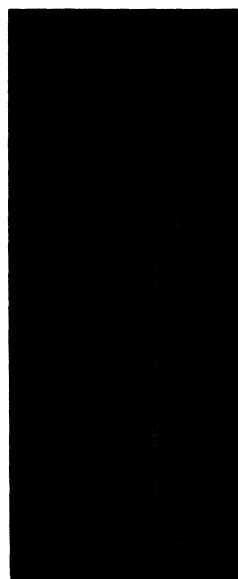


FIG. 4. Photograph of a NaCl specimen in its original condition, and one which had been held at the melting point for six hours.

at  $T/T_m = 0.9980$ . The specimen was then cooled to  $T/T_m = 0.9932$ , giving the closed circle there and demonstrating that the point at 0.9980 was still on a reproducible part of the curve. The remaining closed circles were obtained on heating, and the specimen cooled from  $T/T_m = 0.9999$  to the first square at  $T/T_m = 0.9927$ . The specimen was heated finally to  $T/T_m = 0.9965$ , giving the last square.

It will be observed that the two squares and the last closed circle lie on a curve parallel to the original, reproducible heating curve, but are

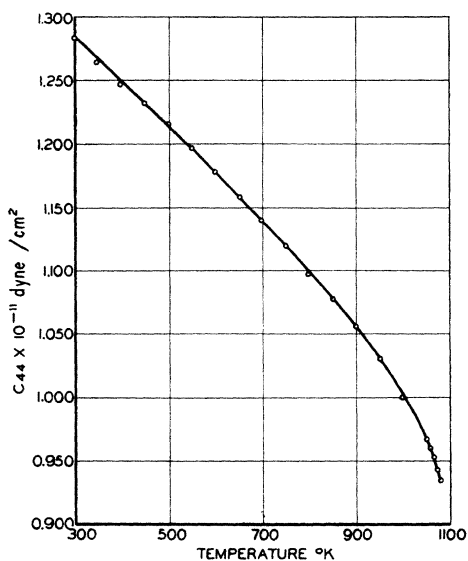


FIG. 5. The variation of  $C_{44}$  with temperature.

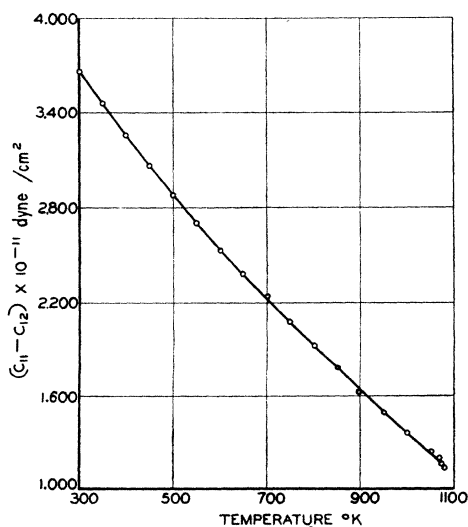


FIG. 6. The variation of  $(C_{11} - C_{12})$  with temperature.

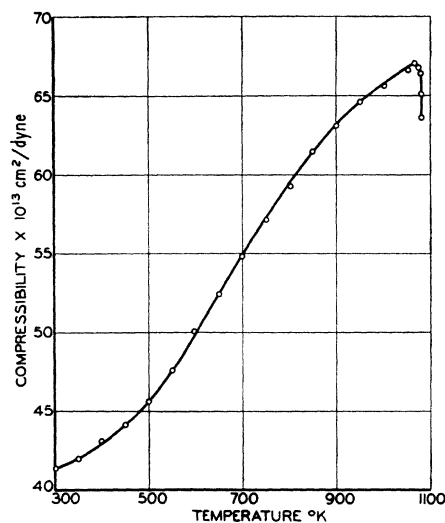


FIG. 7. The variation of the compressibility  $K$  with temperature.

displaced upwards from it. It is, therefore, assumed that the true position of these points is represented by the three triangles, and that the data are best represented by the curve which passes through the open circles, the first two closed circles, and the triangles. This method of determining the true curve near the melting point was employed in every set of measurements made near the melting point. The anomalous behavior of the measured frequencies is probably due to slight changes in the dimensions of the NaCl specimen due to plastic flow under its own weight near the melting point.

The photograph of Fig. 4 shows the initial appearance of the square specimens, and the appearance of a  $[110]$  crystal which had been held at the melting point for six hours, during which time frequency measurements were made continually. As the geometrical shape of the specimen changed slowly, the frequency drifted in an erratic manner, but was never more than a few percent from its initial value. The logarithmic decrement of the NaCl specimen at the melting point was of the order of  $10^{-3}$ . It is felt that this experiment demonstrates conclusively that the material behaves as an elastic solid right up to the melting point.

## RESULTS

Four elastic moduli were measured, Young's modulus  $E$  and the rigidity modulus  $G$ , in the

TABLE I. *Adiabatic elastic moduli of NaCl.*

T°K	T/T <sub>m</sub>	Elastic Moduli × 10 <sup>13</sup> cm <sup>2</sup> /dyne			Elastic Constants × 10 <sup>11</sup> dynes/cm <sup>2</sup>		K × 10 <sup>13</sup> cm <sup>2</sup> /dyne
		S <sub>11</sub>	-S <sub>12</sub>	S <sub>44</sub>	C <sub>44</sub>	C <sub>11</sub> -C <sub>12</sub>	
300	0.2784	22.80	4.50	78.09	1.281	3.663	41.4
350	0.3248	23.95	4.98	79.08	1.265	3.457	42.0
400	0.3712	25.23	5.46	80.14	1.248	3.258	43.1
450	0.4176	26.63	5.96	81.22	1.231	3.068	44.1
500	0.4640	28.18	6.49	82.37	1.214	2.884	45.6
550	0.5104	29.92	7.03	83.61	1.196	2.706	47.6
600	0.5568	31.85	7.58	84.87	1.178	2.536	50.1
650	0.6032	33.84	8.18	86.32	1.158	2.380	52.4
700	0.6496	35.95	8.85	87.79	1.139	2.232	54.8
750	0.6960	38.35	9.67	89.39	1.119	2.082	57.0
800	0.7424	41.14	10.68	91.08	1.098	1.930	59.3
850	0.7888	44.30	11.91	92.84	1.077	1.779	61.4
900	0.8352	47.86	13.42	94.74	1.056	1.632	63.1
950	0.8816	51.74	15.11	97.09	1.030	1.496	64.6
1000	0.9285	56.37	17.24	100.0	1.000	1.359	65.7
1050	0.9749	61.60	19.67	103.5	0.966	1.230	66.8
1055	0.9796	62.15	19.93	104.0	0.961	1.218	66.9
1060	0.9842	62.71	20.20	104.6	0.956	1.206	66.9
1065	0.9889	63.31	20.48	105.1	0.952	1.193	67.1
1067	0.9907	63.55	20.59	105.3	0.950	1.188	67.1
1070	0.9935	63.92	20.76	105.6	0.947	1.181	67.2
1072	0.9954	64.19	20.90	105.8	0.945	1.175	67.2
1073	0.9963	64.35	21.01	106.0	0.943	1.172	67.0
1074	0.9972	64.53	21.13	106.2	0.942	1.167	66.8
1075	0.9981	64.72	21.28	106.4	0.940	1.163	66.5
1076	0.9991	64.93	21.50	106.6	0.938	1.157	65.8
1077	1.0000	65.18	21.98	107.1	0.934	1.134	63.7

[100] and [110] directions. In all, twenty-five individual temperature runs were made on the fourteen crystals used. A cubic crystal has three independent elastic moduli; these are related to the measured quantities by the equations

$$\begin{aligned}
 1/E_{[100]} &= S_{11}, \\
 1/E_{[110]} &= \frac{1}{2}(S_{11} + S_{12} + \frac{1}{2}S_{44}), \\
 1/G_{[100]} &= S_{44}, \\
 1/G_{[110]} &= S_{11} - S_{12} + \frac{1}{2}S_{44}.
 \end{aligned}
 \tag{4}$$

For each of the moduli measured, a smooth curve was drawn best fitting all of the data

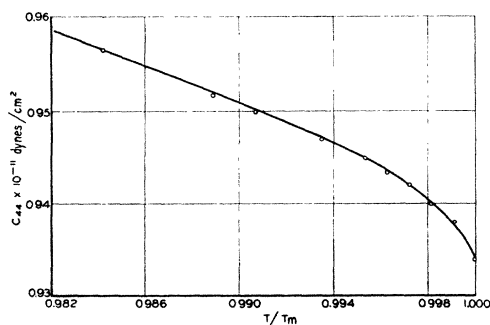


FIG. 8. The variation of  $C_{44}$  near the melting point.

obtained on that modulus. At the temperatures tabulated in Table I, the best set of values of  $S_{ij}$  was computed by means of a graphical method of averaging the data obtained from the curves. These values are tabulated in the 3rd, 4th, and 5th columns of Table I. Another set of elastic constants, obtainable from the  $S_{ij}$ 's by simple linear relationships, is of primary physical significance. These are  $C_{44}$ ,  $(C_{11}-C_{12})$ , and the compressibility  $K$ . The first two of these are pure shear constants, the last a pure dilation constant. These quantities are tabulated in the last three columns of Table I.

In Figs. 5, 6, and 7, the elastic constants are plotted against temperature over the range 300° to 1077°K. In Figs. 8, 9, and 10, the behavior of these constants in the last 20° before the melting point is shown on a magnified scale.

The deviations among the individual runs on a single specimen averaged about 0.2 percent, except near the melting point, where the maximum deviations in the true curve, obtained by repeated cycles of heating and cooling as described before, were about 0.1 percent. The curves for different specimens agreed to better

than 0.3 percent in every case, and to better than 0.1 percent near the melting point. The moduli  $S_{11}$ ,  $S_{12}$ , and  $S_{44}$  are therefore reliable, respectively, to 0.3 percent, 2.0 percent, and 0.3 percent in the main body of the curves, and to 0.1 percent, 0.4 percent, and 0.1 percent near the melting point. The shear constants  $C_{44}$  and  $(C_{11} - C_{12})$  are good to 0.3 percent over most of the range, and to 0.1 percent near  $T_m$ . The compressibility  $K$  is reliable to about 2 percent over the entire range of measurement.

The present results overlap those of Durand in the interval 20°C to 230°C. The two sets of values of  $S_{11}$  check to 0.2 percent, of  $S_{12}$  to 4 percent, and of  $S_{44}$  to 1 percent. The differences may be due to the fact that his crystals were natural, these artificially prepared. The isothermal compressibility has been measured by Voigt,<sup>6</sup> Madelung and Fuchs,<sup>7</sup> Slater,<sup>8</sup> and Rose.<sup>3</sup> Their values are, respectively, 41.3, 41.2, 42.0, 41.9 × 10<sup>-13</sup>. The present value at 20°C is 43.0 × 10<sup>-13</sup> cm<sup>2</sup>/dyne.

#### DISCUSSION

The curves of Figs. 8 and 9 show clearly that the shear moduli  $C_{44}$  and  $(C_{11} - C_{12})$  both have definite non-zero values at the melting point. This is probably the most important conclusion to be reached from these experiments. Born's

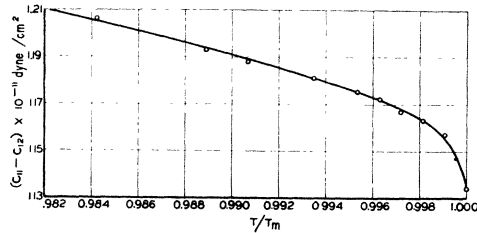


FIG. 9. The variation of  $(C_{11} - C_{12})$  near the melting point.

theory cannot be compared quantitatively with these results because his calculations are for a body-centered cubic lattice, but both theory and experiment yield results for  $C_{44}$  that are qualitatively similar in form. Durand's suggestion that  $(C_{11} - C_{12})$  vanishes at the melting point is seen to be erroneous.

<sup>6</sup> W. Voigt, *Lehrbuch der Kristallphysik*, p. 741.

<sup>7</sup> E. Madelung and R. Fuchs, *Ann. d. Physik* **65**, 289 (1921).

<sup>8</sup> J. C. Slater, *Phys. Rev.* **23**, 488 (1924).

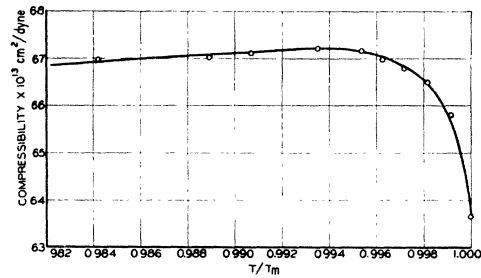


FIG. 10. The variation of  $K$  near the melting point.

Born's work has been extended by Fürth.<sup>9</sup> A relationship between the compressibility at the melting point, the coefficient of expansion  $\alpha$ , and the specific volume  $V$ ,

$$K/\alpha V = 3.4 \times 10^{-9} \quad (5)$$

is obtained. The experimental value of this ratio is  $7.2 \times 10^{-9}$ . A further result obtained by Fürth for the b.c.c. lattice is the relation

$$\frac{C_{11}(0) - C_{11}(T_m)}{C_{11}(0)} = 0.57. \quad (6)$$

With the value  $C_{11}(0) = 5.96 \times 10^{11}$  dynes/cm<sup>2</sup> given by Durand, and the present value  $C_{11}(T_m) = 2.34 \times 10^{11}$  dynes/cm<sup>2</sup>, the value 0.61 is obtained for this ratio. On these two points it would appear that the theory agrees to a good approximation with experiment.

A more severe comparison is afforded by the temperature variation of the compressibility at temperatures far below the melting point. Fürth gives the relation

$$(T_m/K)(\partial K/\partial T) = 1.17.$$

The experimental values of this quantity are given in Table II.

Here it is seen that the quantity  $(T_m/K) \times (\partial K/\partial T)$  is not a constant at low temperatures but does become somewhat constant at intermediate temperatures.

The changes in compressibility observed in the last 10° before the melting point are considerably

TABLE II.

$T^\circ\text{K}$	300	400	500	600	700	800	900	1000
$(T_m/K)(\partial K/\partial T)$	0.57	0.78	1.06	1.23	1.18	1.06	1.05	1.08

<sup>9</sup> R. Fürth, *Proc. Camb. Phil. Soc.* **37**, 34 (1941).

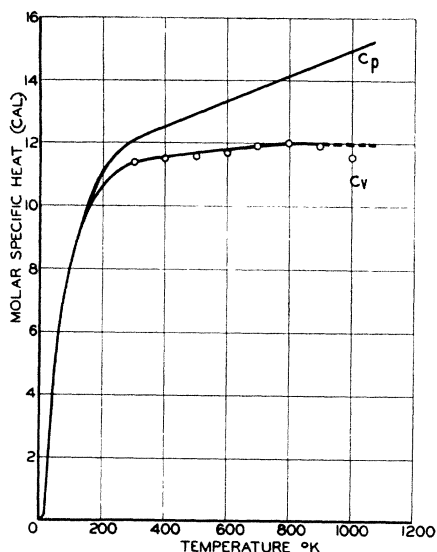


FIG. 11. The variation of  $C_v$  with temperature.

larger than the errors in the measurements, and the drop in  $K$  must be considered to be a real effect. This behavior may at first sight seem to be anomalous, implying that the lattice becomes harder to compress in the immediate neighborhood of the melting point. It should be pointed out, however, that the adiabatic compressibility is plotted in Fig. 10. The isothermal compressibility is larger by an amount  $9\alpha^2 VT/C_p$ , and since it appears that  $\alpha$  increases rapidly near the melting point, it is quite probable that the isothermal compressibility increases monotonically up to the melting point. The present results for the compressibility can be used to determine

more reliably than has been hitherto possible the behavior of the specific heat at constant volume, at elevated temperatures. The experimental values of  $C_p$  must be corrected by a term  $9\alpha^2 VT/K = C_p - C_v$  to yield  $C_v$ .

Eücken and Dannöhl,<sup>10</sup> using an extrapolated value of  $K$ , obtained an anomalously low value of  $C_v$  at high temperatures, about 2 calories per mole lower than the Dulong and Petit value. Their curve for  $C_v$  reaches 12 calories/mole at 600°K, but then drops off to 10 calories/mole at  $T_m$ .

The present data for  $K$ , together with the previously quoted values of  $\alpha$  and data for  $C_p$  given by Kelley<sup>11</sup> yield results shown in Fig. 11. This curve of  $C_v$  rises to 12 calories/mole at 700°K, and as far as can be determined from the rather uncertain values of  $\alpha$  and  $C_p$  available near the melting point, maintains the Dulong and Petit value up to the melting point.

The experimental method described here should lend itself to other problems of this kind, and the present work is being extended to other types of crystals.

One of us (Lloyd Hunter) wishes to thank the directors of the Westinghouse Research Laboratories for extending to him permission to use their facilities, and Drs. Otto Stern and O. C. Simpson of Carnegie Institute of Technology for much helpful advice and encouragement.

<sup>10</sup> A. Eücken and W. Dannöhl, *Zeits. f. Electrochemie* **40**, 789 (1934).

<sup>11</sup> K. K. Kelley, U. S. Bureau of Mines Bulletin, No. 371.

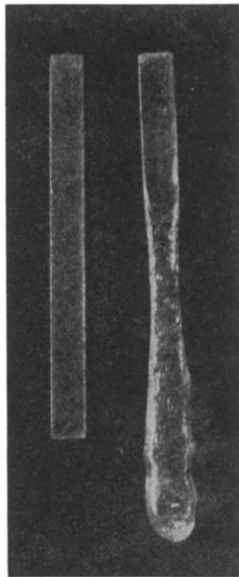


FIG. 4. Photograph of a NaCl specimen in its original condition, and one which had been held at the melting point for six hours.