7. Study on the Elasticity near the Melting Point. Part II. Velocity of Dilatational Wave in Sodium.

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1. Introduction

Study of the elasticity of rocks at the melting point is one of the essential subjects in geophysics, especially with reference to the nature of the earth's interior. Many attempts have been made by several authorities to measure the elastic moduli of rocks at high temperature. Notwithstanding their valuable results, the problem of elasticity near the melting point remained obscure. As the ultrasonic pulse method is considered to be suitable for this problem, an attempt has been made to measure the velocity of ultrasonic compressional wave in the specimen material from room temperature to above the melting point. In a previous paper[1], the author has measured the velocity of ultrasonic pulse in wood's alloy in the wide range of temperature covering the melting point. Discontinuous decrease in velocity was markedly observed at the melting point; however, no further discussion could be made due to the lack of such physical quantities as density variations and compressibility of the specimen meterial.

Therefore, in the present experiment, polycrystalline sodium was tested as a specimen material of which many physical quantities are accurately known.

The ultimate object of the present experiment is the measurement of the variation of the elastic moduli of rocks at elevated temperatures especially at the melting point; however, as a preliminary experiment, the present paper describes the results of experiments on the thermal dependence of the velocity of ultrasonic compressional wave in polycrystalline sodium for the temperature range between room temperature and several degrees above the melting point. Discussion on the rigidity modulus at the melting point is also described.

1) D. SHIMOZURU, *Bull. Earthq. Res. Inst.*, **32** (1954), 271.

2. Experimental procedure

Ultrasonic equipment

Ultrasonic pulse equipment has been constructed for the measurement of the velocity of elastic wave in rocks. The basic instrument is composed of an electronic equipment for generating pulses and one for measuring the transmission time. Trigger pulses, delayed about 10 microseconds by a variable delay line, and amplified by the pulse amplifier are impressed on the driving 1 MC X-cut quartz crystal. The pulse, transmitted through the medium, is received by a similar quartz crystal and amplified and displayed on the screen of a cathode ray oscilloscope which is synchronized with the main trigger.

Specimen material

The sodium specimen was prepared by cutting from the interior of a large coherent block of sodium. It was cut into a cylindrical rod of 4 cm in length and 2 cm in diameter. The specimen was kept carefully so as not to acidify, but was not chemically distilled, being immersed in kerosene in a cylindrical glass vessel as shown in Fig. 1.
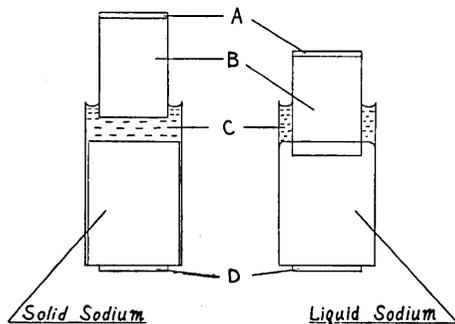
Diameter of the specimen is a little smaller than that of the vessel so as not to compress the specimen due to its large thermal expansion. A cylindrical rod of fused quartz, on the upper end of which a 1 MC X-cut quartz crystal is cemented, is immersed in kerosene. Thus, the ultrasonic compressional wave generated from the quartz crystal and propagated along the fused quartz rod, kerosene, sodium specimen and bottom of the vessel is received by a similar quartz 1 MC crystal cemented to the bottom of the vessel. If the specimen melts, the above procedure becomes inadequate, and the fused quartz is immersed into the melted sodium directly in order to avoid the inaccuracy of the estimation of the transmission length coming from the surface curvature of the fused medium.

Fig. 1.
A: Pulse generating crystal,
B: Cylindrical rod of fused quartz,
C: Kerosene,
D: Pulse receiving crystal.

3. Experimental results and discussion

Measured velocities for the respective temperatures of the ultrasonic longitudinal wave are tabulated in Table I and are illustrated in Fig. 2, together with the variation of density with temperature.

The velocity decreases almost linearly with temperature from room temperature to several degrees below the melting point (=97.6°C). At the neighbourhood of the melting point the velocity begins to drop very sharply. At the melting point, the velocity decreases discontinuously from 2735 m/sec to 2542 m/sec. This discontinuous jump in the velocity at the melting point was also observed in the author's previous experiment[2] in the case of Wood's alloy. In the both experiments, the discontinuous jump in the measured velocity occurs in almost the same manner. It is very interesting that the large drop in the velocity begins from several degrees below the melting point.

Table I.

Temp. °C	Velocity m/sec	Density gr/cm³
27.9	3030	0.9690
28.0	3014	0.9688
58.5	2969	0.9612
60.5	2966	0.9688
71.5	2920	0.9582
73.0	2940*	0.9577
81.5	2915	0.9557
89.0	2900	0.9542
93.5	2838*	0.9527
94.2	2862	0.9525
95.9	2805*	0.9523
96.5	2705	0.9522
97.0	2735*	9.9520
97.9	2542*	0.9286
103.6	2520*	0.9270
110.6	2534*	0.9247

* denotes velocities measured as shown in the right hand side of Fig. 1.

For pulsed compressional waves, generally, the propagation velocity in a bounded medium is not constant, but depends upon the stiffness of the medium as well as the ratio between the radius d of the medium and the wave length Λ. When the ratio d/Λ is very small, the measured velocity is approximately expressed as $(E/\rho)^{1/2}$, where E and ρ are the Young's modulus and the density of the medium. For a large value of d/Λ, the velocity approaches the bulk velocity $(\lambda+2\mu/\rho)^{1/2}$, where λ and μ are the Lame's elastic constants of the medium. When d/Λ is very near to unity, the velocity decreases and seems to approach Rayleigh surface wave velocity. Therefore, the longitudinal velocity will be masked by the surface wave velocity in such a case.

As d/Λ increases, the pulse velocity increases rather sharply, and it becomes constant from a certain value of d/Λ. As this critical ratio

2) D. SHIMOZURU, *loc. cit.*, 1).

of d/Λ is about 2.5 for usual metals, the compressional disturbance may be considered as being propagated in a medium of infinite extent for the ratio greater than 2.5.
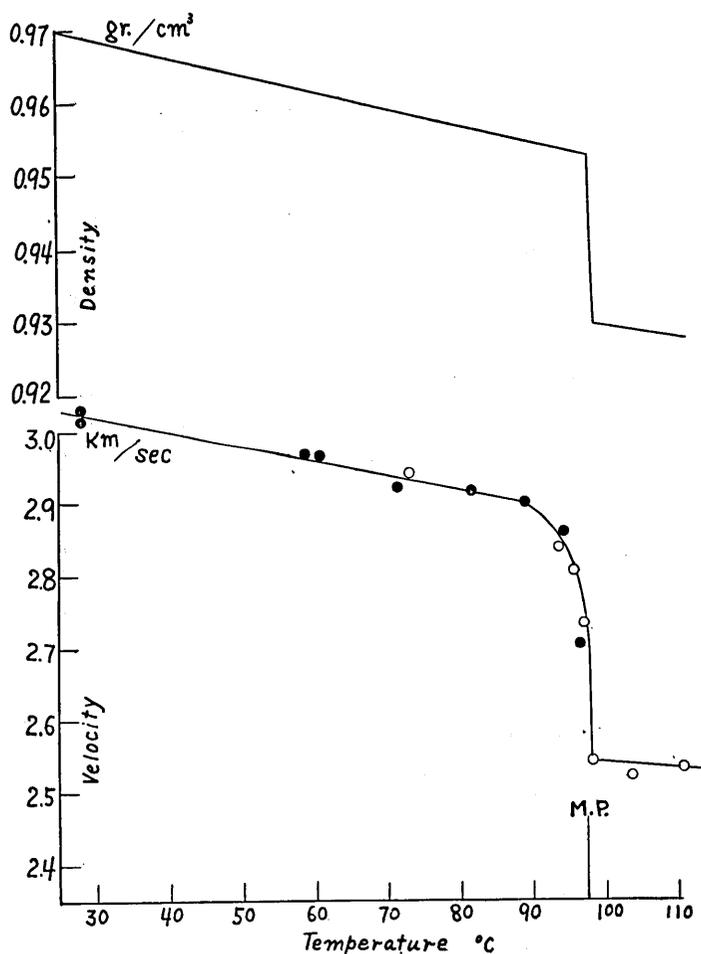

Fig. 2. Density variation with temperature (upper curve) and velocity variation with temperature (lower curve).

In the present experiment, as the ratio d/Λ is considered to be about 3.3, the measured velocity may be sufficiently near the bulk velocity $(\lambda+2\mu/\rho)^{1/2}$ or may be expressed as $\left(K+\dfrac{4}{3}\mu\Big/\rho\right)^{1/2}$, where K, μ are the bulk modulus and the rigidity modulus of the medium.

At the melting point, the density decreases from $0.9519\,\mathrm{gr/cm^3}$ to

0.9287 gr/cm³ as the consequence of the sudden expansion on melting. From the measured velocity and the corresponding density, the change of stiffness $\left(K+\dfrac{4}{3}\mu\right)$ is calculated for each temperature. Fig. 3 shows the change of $\left(K+\dfrac{4}{3}\mu\right)$ with temperature thus calculated. $\left(K+\dfrac{4}{3}\mu\right)$ also shows a catastrophic drop in the neighbourhood of the melting point. It means that the stiffness of the medium largely decreases from several degrees below the melting point. From the theory of the liquid state or of the study of the nature of the earth's core, the rigidity modulus at the melting point is the most interesting.

If the thermal variation of adiabatic bulk modulus $(\partial K_s/\partial T)$ is known, the thermal variation of adiabatic rigidity modulus $(\partial\mu_s/\partial T)$ can be calculated from Fig. 3 up to the melting point.

Supposing that Mie's formula

$$\phi(r)=-\frac{a}{r^m}+\frac{b}{r^n}\,,$$

Fig. 3.   Change of stiffness with
temperature.

gives an adequate potential curve for sodium, Grüneisen[3] derived the following equation from simple thermodynamical considerations, i.e.

$$-\frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_p=m+n+6/3\,.$$

Using thermodynamical identity between adiabatic bulk modulus and isothermal bulk modulus $\dfrac{1}{\alpha K_s}\left(\dfrac{\partial K_s}{\partial T}\right)_p=\gamma+\dfrac{1}{\alpha K_T}\left(\dfrac{\partial K_T}{\partial T}\right)_p\,,$ and
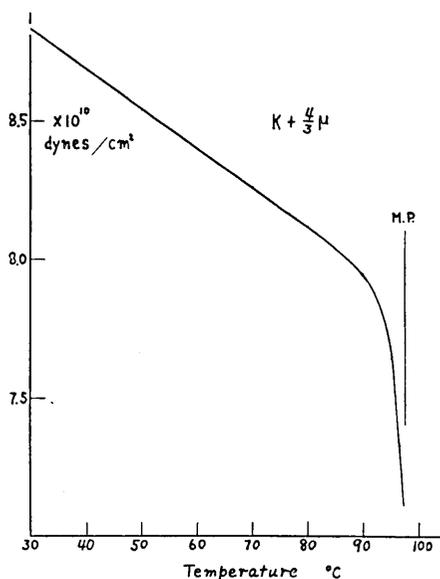
$\gamma=m+n+3/6\,,$

3)   Grüneisen, *Handb. der Phys.*, **10** (1926), 33.

we get finally as the temperature dependence of adiabatic bulk modulus as follows ;

$$\frac{1}{\alpha K_s}\left(\frac{\partial K_s}{\partial T}\right)_p = -\frac{m+n+9}{6} \ .$$

For body-centred cubic structure the average value of $(m+n)$ is 7, (perhaps $m=2$, $n=5$).

Therefore, we have

$$\frac{1}{\alpha K_s}\left(\frac{\partial K_s}{\partial T}\right)_p = -2.67 \ .$$

The above considerations, however, give unreliable conclusions because of the obscurity of the value of m and n in Mie's formula.

Next, we consider $(\partial K_s/\partial T)_p$ in another way.
From thermodynamical identities, the following relations hold,

$$\frac{1}{\alpha K_s}\left(\frac{\partial K_s}{\partial T}\right)_p = \gamma + \frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_p = \gamma - \frac{1}{\alpha \beta_T}\left(\frac{\partial \beta_T}{\partial T}\right)_p = \gamma + \frac{1}{\alpha \beta_T}\left(\frac{\partial \alpha}{\partial p}\right) ,$$

where $\gamma \cdots\cdots\cdots$ Grüneisen's parameter,
           $\beta \cdots\cdots\cdots$ compressibility,
           $\alpha \cdots\cdots\cdots$ coefficient of linear thermal expansion.

According to Bridgman's experiment[4],

$$\frac{1}{\alpha \beta_T}\left(\frac{\partial \beta_T}{\partial T}\right)_p = 4.4 \ .$$

Using the value $\gamma = 1.25$[5] for sodium, we get for the temperature variation of adiabatic bulk modulus divided by αK_s as follows ;

$$\frac{1}{\alpha K_s}\left(\frac{\partial K_s}{\partial T}\right)_p = -3.15 \ .$$

As the coefficient of linear thermal expansion α is 71×10^{-6} in the temperature range between 0°C and 90°C[6],

4)   P. W. BRIDGMAN, *Proc. Amer. Acad.*, **58** (1923), 202.
5)   GRÜNEISEN, *Handb. d. Phys.*, **10** (1926), 33.
6)   P. W. BRIDGMAN, *Proc. Amer. Acad.*, **70** (1935), 94.

$$\frac{1}{K_s}\left(\frac{\partial K_s}{\partial T}\right)_p = -2.24 \times 10^{-4}.$$

According to the compressibility measurement[7], Bridgman shows that the volume change of sodium polycrystal at 30°C is expressed as a function of pressure as follows ;

$$\frac{\Delta V}{V_0} = -159.3 \times 10^{-7}p + 3 \times 10^{-10}p^2 + 1.6 \times 10^{-13}p^3.$$

The above formula would give for the initial compressibility at 30°C over the range of 500 kg as

$$K_{T(30°C)} = 6.277 \times 10^{10} \text{ dynes/cm}^2.$$

If we put the values $T = 303$, $\alpha = 71 \times 10^{-6}$, $\gamma = 1.25$ in the following relation between adiabatic and isothermal bulk modulus

$$K_s/K_T = 1 + T\alpha\gamma ,$$

we obtain the adiabatic bulk modulus at 30°C as follows ;

$$K_{s(30°C)} = 6.446 \times 10^{10} \text{ dynes/cm}^2.$$

Consequently, the thermal variation of the adiabatic bulk modulus is found to be,

$$\left(\frac{\partial K_s}{\partial T}\right)_p = 1.44 \times 10^{10} \text{ dynes/cm}^2 \text{ degree.}$$

Thus, the numerical value above yields the adiabatic bulk modulus for respective temperature. Fig. 4 shows the temperature variation of K_s of polycrystalline sodium up to the melting temperature calculated in this way. At the melting point, the compressibility of solid phase is smaller than that of liquid phase generally. According to Bridgman[8], the change of compressibility $\Delta\beta$ of sodium on melting is found to be,
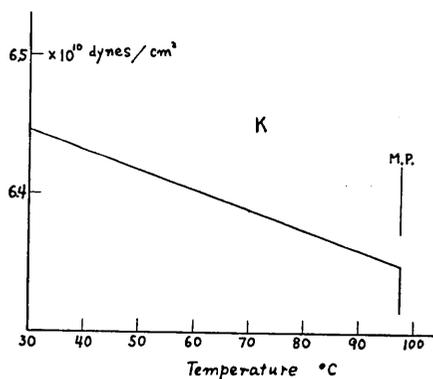
Fig. 4.   Temperature variation of adiabatic bulk modulus.

7) P. W. BRIDGMAN, *Proc. Amer. Acad.*, **58** (1923), 202.
8) P. W. BRIDGMAN, *Phys. of High Press.* (1949), 217.

$$\Delta\beta = \beta_l - \beta_s = 34 \times 10^{-13} \, \mathrm{cm^2/dyne} \,,$$

where β_l · · · · · · · · · compressibility of liquid sodium,

β_s · · · · · · · · · compressibility of solid sodium.

As $\dfrac{1}{\beta_s} = K_s = 6.35 \times 10^{10}$ dynes/cm² at the melting point, we get $\dfrac{1}{\beta_l} = K_l$ $= 5.23 \times 10^{10}$ dynes/cm² for the liquid sodium at the melting point.

From the measured variation of $\left(K + \dfrac{4}{3}\mu\right)$ and the thermal variation of K which is calculated by the above procedure, we get the thermal variation of rigidity modulus μ up to the melting point as shown in Fig. 5. Rigidity modulus which decreases almost linearly with tem-
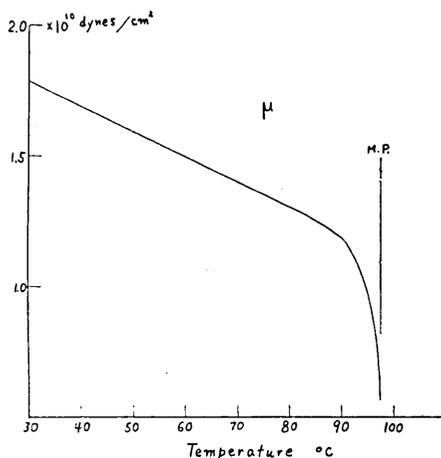

Fig. 5. Temperature variation of adiabatic rigidity modulus.

Table II.

Material	$-\partial\mu/\partial T \times 10^{-8}$
Na	1.0
Pb	1.1
Zn	1.1
Al	4.7
Ag	2.4
Fe	2.2
Cu	1.7

perature begins to drop very sharply from several degrees below the melting point. Table II. shows the tabulated values of $(\partial\mu/\partial T)_p$ of sodium obtained by the present method as well as that for other materials measured directly by T. Kikuta[9]. At the melting point, the rigidity modulus does not vanish but seems to remain and decrease by a factor of 3 when the temperature is raised from room temperature to the melting point.

Kornfeld[10] has also observed the very large drop of rigidity modulus in the neighbourhood of the melting point in the case of stearine. His result indicates that the approach to the melting point is accompanied by a large drop in μ as may be seen from the following table. (Table III.)

9) T. KIKUTA, Sci. Rep. Tohoku Imp. Univ., **10** (1921), 139.

11) M. O. KORNFELD, C. R. Ac. Sci. U. R. S. S., **36** (1942), 58.

Table III.

$T°K$	88	273	300	314	319	321.5	322.8
$\mu \times 10^{10}$	0.78	0.54	0.34	0.14	0.048	0.014	0.005

The exact theory as to whether or not liquid has rigidity does not exist since the mechanism of fusion is very complicated. But, Born's criterion $C_{44}=0$ for the instability of crystal lattice or his definition of the melting point corresponding to a vanishing value of the rigidity modulus seems to be inadmissible in the light of these experiments.

As for the earth's core, it is very likely that the cause of the opacity of the earth's core for S wave is not due to vanishing rigidity, but to the large absorption of its energy.

It must be stressed finally that the stiffness constants must be considered to be complex on account of the visco-elastic effect of the medium in the present experiment. In such a case, bulk modulus and rigidity modulus are expressed, for instance, as follows;

$$K=K^*-i\omega\eta,$$
$$\mu=\mu^*-i\omega\zeta$$

where K ·········· measured bulk modulus,
  K^* ········· true bulk modulus,
  μ ·········· measured rigidity modulus,
  μ^* ········· true rigidity modulus,
  η ·········· bulk viscosity or voluminal viscosity,
  ζ ·········· shear viscosity or equivoluminal viscosity,
  ω ·········· frequency.

Accordingly, if the frequency of the transmission wave can be changed, true elastic constants and viscosities in the above sense could be measured separately.

4. Summary and Acknowledgment

The velocity of ultrasonic longitudinal pulse transmitted through sodium cylindrical rod was measured as a function of temperature from room temperature to several degrees above the melting point. The velocity decreases almost linearly with rising temperature and begins to decrease largely in the neighbourhood of the melting point. At the melting point, the velocity decreases discontinuously by an amount of

7 %. Thermal variation of rigidity modulus was calculated from thermodynamical considerations using Bridgman's compressibility measurement of sodium. Rigidity modulus, thus calculated, decreases largely in the neighbourhood of the melting point and seems to remain considerable.

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7. 融解点附近の弾性の研究
其の 2. ナトリウム中の縦波の速度

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前論文では Wood 合金が融解する時に，超音波の縦波の速度が jump して減少する事を示したが，今回は問題をもう少し定量的に扱うために種々の物理量の判つている Sodium の多結晶を試料とした．Sodium の場合もやはり速度は，温度が上ると共に減少し，融解点附近になると，その割合が激しく，融解点（＝97.6°C）に於いて，不連続的に速度が減少する．その割合は約 7% である．実験温度範囲で，密度変化が判つているから，測定された速度の値とから，$\left(K+\dfrac{4}{3}\mu\right)$ を計算出来る．$\left(K+\dfrac{4}{3}\mu\right)$ も亦，融解点附近で急激に減少する．Bridgman の圧縮率測定値より，各温度に対する K を計算し，得られた $\left(K+\dfrac{4}{3}\mu\right)$ の値より差引いて，剛性率 μ の温度変化を計算した．それに依ると μ は融解点附近に於いて急激に減少はするが融解点に於て 0 にはならない．此の事は Born 等の考える融解に対する Criterion とは合わない．又，S 波を通さない地球液核の剛性に関しても，一つの data を与えるものと思われる．