

COMPRESSIBILITY OF SODIUM AT HIGH PRESSURES AND TEMPERATURES AND THE LINDEMANN FUSION CRITERION

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The volume and compressibility of solid sodium as a function of pressure and temperature are measured directly on the fusion curve for the first time. The measurements were performed by means of a piston piezometer. The volume and compressibility measurement errors were of the order of 0.1% and 2%, respectively. The measured values of the compressibilities and volumes were used for the calculation of the Debye temperature of solid sodium along the fusion curve. It is shown that the Lindemann parameter, which characterizes the relative displacement of the atoms from the equilibrium positions, does not remain constant along the fusion curve.

RESULTS are given in the present paper of measurement of the volume of solid sodium over a range of temperatures and pressures directly adjoining the fusion curve. The measurements were made by means of a piezometer with an incompressible piston (Fig. 1). The method of volume measurement used in the present research does not differ in principle from that described by us earlier^[1] and reduces to the determination of the position of the piston relative to the frame of the piezometer for each given pressure.

The experimental method is described briefly below.

The piezometer was filled with sodium by means of a special vacuum system. The amount of sodium in the piezometer was determined by weighing. The piezometer, equipped with a displacement detector, a heater and a chromel-alumel thermocouple, was placed in the channel of a high pressure vessel. Then the heater was turned on and the sodium reduced to the liquid state, after which the process of compression was begun. The temperature was maintained at a given level by means of a servo system.^[2] The pressure in the chamber was produced by compression of silicone oil and measured by a manganin manometer with an accuracy to within $\pm 20 \text{ kg/cm}^2$ in the range up to $15,000 \text{ kg/cm}^2$ and no worse than to within $\pm 100 \text{ kg/cm}^2$ at the highest pressures. Inasmuch as the heater and the thermocouple were inside the high-pressure chamber in our experiments, the value of the temperature, determined by means of the measured values of thermal emf, contained an error due to the effect of the pressure on the thermal emf. In the present case, the necessary correction was made by means of the data of Bridgman^[3], who investigated the fusion curve of sodium under conditions, which avoided the appearance of the error just mentioned. The examples of typical isotherms of compression of sodium are shown in Fig. 2, where regions are clearly seen corresponding to compression of the liquid and solid phases, and also the discontinuous change in the volume upon melting. The results of the measurements of the volume, temperature and pressure, with account of the necessary corrections, and the calculated values of the compressibility are given in the table. The errors of measurement of the vol-

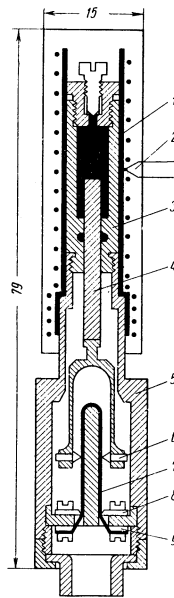


FIG. 1

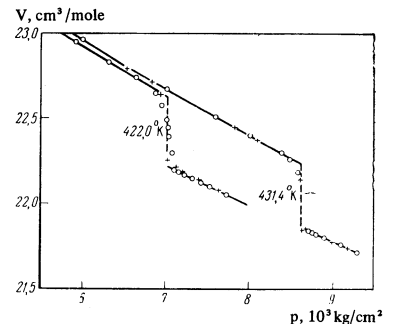


FIG. 2

FIG. 1. Piezometer for the measurement of the volume of sodium at high pressures. 1—heater, 2—thermocouple, 3—frame of piezometer, 4—piston, 5—frame of displacement detector, 6—movable contacts, 7—constantan conductor, 8—fixed contacts, 9—current leads.

FIG. 2. Compression isotherms for sodium.

T, °K	P, kg/cm ²	V, cm ³ /mole	$-\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \cdot 10^{-5}$, cm ³ /kg	θ , °K *	C	$[\frac{C \Delta R^3}{R^3}]^{1/2}$
370.8	0	24.168		167.8	121	0.077
386.6	1940	23.549	1.30	170.1	119	0.078
396.8	3310	23.154	1.23	172.4	118	0.079
411.6	5460	22.597	1.15	175.2	117	0.080
422.0	7070	22.215	1.07	177.2	116	0.080
431.4	8640	21.852	1.02	179.3	116	0.081
440.9	10300	21.507	0.97	181.2	115	0.081
451.4	12270	21.126	0.93	183.0	114	0.082
472.1	16445	20.391	0.80	188.6	114	0.082
494.6	21600	19.605	0.71	194.6	113	0.083
505.8	24370	19.235	0.66	197.9	113	0.083

*Smoothed values of the compressibilities were used for calculation of the Debye temperatures.

ume and compressibility were of the order of 0.1 and 2%, respectively.

The table also contains the values of the Debye temperature, for the calculation of which we used the approximate formula of Blackman.^[4] The required values of the elastic constants were obtained in the following way. The values of the compressibility in the table give the combination C_{11} and C_{12} in the form

$$\beta_r = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{3}{C_{11} + 2C_{12}}.$$

The elastic constants C_{44} and C_{11} are easily computed by means of the well-known formulas of Fuchs,^[5] the validity of which in the case of sodium has recently been reconfirmed.^[6]

The value of the Debye temperature of sodium at atmospheric pressure, calculated by the described method (see table), is in excellent agreement with the value of the high-temperature limit Θ_∞ for sodium given in^[7].

The data in the table are sufficient to prove the applicability of the Lindemann criterion^[8] to the fusion of sodium over a wide range of temperatures and pressures. The Lindemann fusion criterion asserts that at the fusion temperature the ratio of the mean amplitude of the vibrations of the atoms to the interatomic distance is a constant, i.e.,

$$\langle \Delta R^2 \rangle^{1/2} / R_0 = \gamma, \quad (1)$$

where γ is a constant.

In the Debye approximation, the relation (1) can be rewritten in the form

$$mV^{2/3}\Theta^2 / T_m = C^2, \quad (2)$$

where m is the atomic weight, V the molar volume, Θ the Debye temperature, T_m the fusion temperature, C a constant. The quantities C and γ for the case of a body-centered cell are connected by the following relation:

$$\gamma^2 = 4\hbar / C^2 (2/N)^{2/3} k\alpha, \quad (3)$$

where k is the Boltzmann constant, N Avogadro's number, α the mass of the oxygen unit in grams.

The Lindemann relation, which is essentially empirical, is well satisfied for various materials, while the

value of the quantities C and γ from Eqs. (1) and (2) is practically independent of the character of the interaction forces.^[9] This circumstance has allowed wide use of the Lindemann fusion criterion for different estimates in the theory of stability of crystals, the theory of strongly compressed matter, for the consideration of the spatial ordering of an electron gas, and so forth. Very frequently, Eqs. (1) and (2) find application in attempts at an analytic representation of the fusion curve.^[10-12] As is seen from the table, the quantities C and γ from Eqs. (1) and (2) do not remain constant over the pressure range studied. However, the change is small and amounts at most to $\sim 7\%$. Attention should also be paid to the significant decrease in the rate of change of the quantity γ with increase in temperature. It is not excluded that the relation (1) will be exact in the limit of purely repulsive forces. In conclusion, we note that, according to the calculations of^[13] a similar character should be expected for argon upon change in γ .

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