

Equation of state of alkali metals: Sodium

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Experimental data characterizing the equation of state of liquid and solid sodium at pressures up to 22 kbar and temperatures between 370 and 490 K are obtained for the first time with a piston piezometer. The experimental technique and reduction of the experimental data are described and values are presented for the pressure, compressibility, and thermal expansion coefficients of sodium at various volumes and temperatures. It is shown that within the experimental accuracy of the experiments the energy part of compressibility of sodium is independent of temperature. This makes it possible to calculate the zero isotherm and to compare directly the present results with the low-temperature measurements and theoretical calculations.

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INTRODUCTION

In spite of the obvious progress made in the understanding of various properties of metals, the problem of the metallic state still remains one of the most important ones in the physics of condensed matter. Whereas, however, attention was previously focused mainly on the electronic properties of solid metals, at present the center of the stage is occupied by an aggregate of problems connected with investigations of the spectrum of thermal excitations, of the equation of state, of phase transitions, and other properties of both solid and liquid metals.

It should be noted that the theory of many of these problems could not be constructed within the framework of the traditional band-structure calculations, but the recently developed pseudopotential method has made it possible to obtain a number of impressive results,^[1-3] at least as applied to simple nontransition metals. As to the experimental research, the situation here is less comforting. In particular, there is a great lack of precise experimental data on the equation of state, the compressibility, and the elastic constants of various metals in a wide range of temperatures and pressures, making it impossible to verify comprehensively the theoretical schemes and the concrete calculations.

The foregoing holds to a particularly great degree for liquid metals, for which the experimental data at pressures other than atmospheric are practically nonexistent. We note that the development of the theory of liquid metals, which has much in common with the theory of a dense plasma, is made complicated by the need for simultaneously calculating the correlation functions of the ions. Thus, a consistent comparative analysis of the results of the theory and experiment should serve in this case, in addition to all other, as a check on the validity of the approximations used to describe the structure of the liquid metal.

The present paper is a part of the systematic investigations of the equations of state and of the thermodynamics of the melting of alkali metals, carried out at the Crystallography Institute of the USSR Academy of Sciences, and is devoted to the study of the equation of state of liquid and solid sodium in the temperature range from 370 to 490° K at pressures up to 22 kbar. These are the first results obtained in the investigated range temperatures and pressures.

Since this article is the introductory report on this series of studies, it contains a detailed description of the

experimental technique and of the method used to reduce the experimental data. We present the coefficients of the polynomials representing the experimental data, and tabulate the values of the pressure, of the compressibility coefficients, and of the thermal expansion as functions of the volume and of the temperature. The calculated energy and of heat capacity are shown in the figures. Where possible, the a comparison is made with the experimental and theoretical results obtained by others.

EXPERIMENTAL TECHNIQUE

The equations of state of liquid and solid sodium were investigated by a method using a piezometer with a loose piston.^[4-6] The piezometer (see Figs. 1 and 2) is a cylindrical vessel equipped with a piston and a resistive displacement pickup that determines the position of the piston relative to the body of the piezometer. The body of the piezometer contains the compression channel needed to fill the piezometer with the investigated sub-

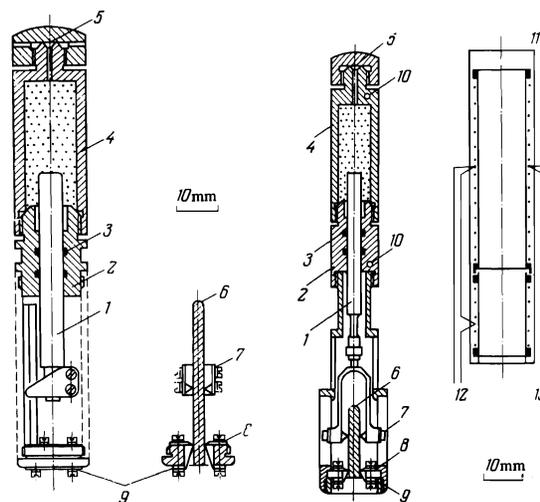


FIG. 1

FIG. 2

FIG. 1. Piezometer for measurements in the external thermostatic control regime: 1—piston, 2—sleeve, 3—leakage-preventing grooves filled with lubricant, 4—body, 5—opening through which the piezometer is filled, 6—constantan wire, 7—movable potential leads, 8—stationary potential leads, 9—current contacts.

FIG. 2. Piezometer for measurements in the internal thermostating regime: 1-9—the same as in Fig. 1, 10—openings for the thermocouples, 11—two-section heater, 12—differential thermocouple, 13—control thermocouple.

stance, and a system of annular grooves filled with a high-consistency lubricant (a mixture of flaked graphite and vacuum grease) to prevent leakage of the investigated substance. To compress the substance, the piezometer is placed in a chamber in which hydrostatic pressure is produced by an independent piston system.

It must be emphasized that in such an experimental setup the loose piezometer piston, that separates the investigated substance from the pressure-transmitting medium, moves practically without friction, making the pressures inside and outside the piezometer equal. This circumstance ensures a strictly homogeneous deformation of the piezometer, which is subject only to isotropic and hydrostatic pressure. Thus, the low friction in the piezometer piston system and the uniformity of the deformation ensure the required accuracy in the measurement of the pressure and in the introduction of the corrections for the change of the piezometer volume.

The resistive displacement pickup (see Figs. 1 and 2) consists of a resistance element in the form of a wire of high-resistance alloy, 0.2 mm in diameter, stretched on a steel post and insulated from the latter by a thin layer of mica, and a system of current contacts and movable and stationary potential contacts used to measure the resistance of the wire. The movable contacts are connected with the piston through flat springs that ensure a dependable electric contact and the required rigidity. For a pickup of this design, the ratio of the resistances of the wire sections, measured with the aid of the movable and stationary potential contacts, is determined uniquely by the position of the piston and does not depend on the temperature and on the pressure. The pickup has a sensitivity of 0.5μ and its characteristic remains linear within $\pm 5 \mu$ in the entire range of measured displacements (15–20 mm).

We used two different setups to produce high hydrostatic pressure. The pressure-transmitting medium was gasoline. The first setup (Fig. 3)^[7] yields pressures up to 16 kbar in a high-pressure cell connected with the pressure generator through a thin stainless-steel capillary. This makes it possible to control the piezometer temperature thermostatically, by immersing the high-pressure cell in a thermostat (external thermostatic control), thus easily attaining homogeneity of the temperature field and excluding the need for taking into account the corrections for the effect of pressure on the readings of the thermocouples. The pressure is measured with a manganin manometer, which is a coil of manganin wire, 0.15 mm in diameter, with total resistance 75Ω . The coil is freely mounted on a steatite form and has four leads for the measurement of the resistance by a null method. The manganin manometer is calibrated

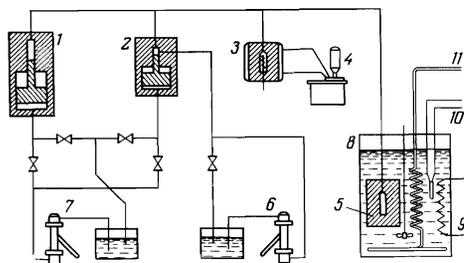


FIG. 3. Schematic diagram of high-pressure system: 1—booster, 2—high-pressure valve, 3—bomb for manganin manometer, 4—thermostat, 5—high-pressure cell, 6, 7—pumps, 8—thermostat, 9—heater, 10—resistance thermometer, 11—refrigerator.

with an absolute loaded-piston manometer. During the course of the measurements, the temperature of the manganin manometer is stabilized by a special thermostat. In the external thermostatic control method, the temperature is maintained within $\pm 0.005^\circ\text{C}$.

The second setup (Fig. 4) is intended for measurements at higher pressures (up to 30 kbar) and constitutes a booster with double mechanical support.^[8] The piezometer designed for measurements in an expanded temperature range (Fig. 2) is equipped with an autonomous heating, and in the course of the measurements the temperature of the loaded units of the apparatus remains close to the ambient temperature (internal thermostatic control).

Under the conditions of internal thermostatic control, the measurement accuracy can be strongly influenced by distortions produced in the temperature field by the intense heat exchange between the piezometer and the pressure-transmitting medium. To decrease the temperature gradients in the working zone of the piezometer, which are particularly undesirable when a phase transition in the investigated substance is registered, a two-section heater is used and is controlled by two automatic thermal regulators. The pickup of the thermal regulator of the principal section of the heater is the control thermocouple (see Fig. 2), while that of the auxiliary section, used to equalize the temperature, is a differential thermocouple. The temperature of the investigated substance is measured with a chromel-alumel thermocouple located in the opening of the piezometer body. The axial temperature gradients in the working cavity of the piezometer are monitored by an additional thermocouple. The accuracy with which the specified temperature is maintained in the internal thermostatic control regime is $\pm 0.02^\circ\text{C}$.^[9]

The specific demands on the measurements in the internal thermostatic regime have necessitated introduction of a number of design features in the displacement pickup (see Fig. 2), to reduce the influence of the temperature drops in the high-pressure cell channel on the measurement accuracy. In particular, the axial symmetry of the pickup contributes to a decrease of the

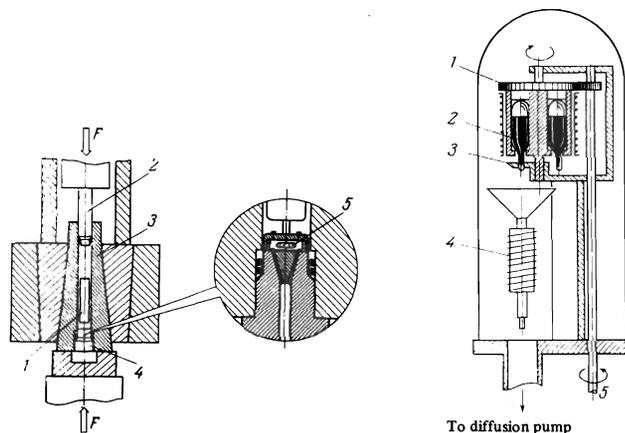


FIG. 4

FIG. 5

FIG. 4. High-pressure cell with variable mechanical support: 1—piezometer, 2—piston, 3—cone, 4—electric lead-in bushing, 5—manganin resistance manometer.

FIG. 5. Device for filling the piezometer with the investigated metal: 1—drum, 2—glass cells with sodium, 3—support for opening the cell, 4—piezometer with funnel and heater, 5—shaft to rotate the drum.

deformations of the latter under conditions of an inhomogeneous temperature field. The resistance element of the displacement pickup is a constantan wire having a very small thermal coefficient of resistivity, and the pickup itself is placed below the heater and is located in the "cold" part of the high-pressure-cell channel. The effectiveness of these measures was verified experimentally in special experiments with the moving contacts of the displacement pickup fixed relative to the body of the piezometer, at various heater temperatures and various pressures. It turned out that at temperatures on the order of 250°C, in the working zone of the piezometer, the error introduced into the readings of the displacement pickup by the inhomogeneities of the temperature field did not exceed $\pm 5 \mu$.

In the second setup for the pressure measurement we used a manganin manometer of 800 Ω resistance, made in the form of a freely wound coil of 0.05 mm silk-insulated wire. The manometer resistance was measured by a bridge method. During the course of the experiment, the manometer was located in a special cavity of the multichannel electric lead-in bushing (see Fig. 4), in which the temperature did not exceed 50°C. This ensured a measurement accuracy not worse than ± 25 bar at pressures up to 15 kbar (in the pressure interval in which calibration with the aid of a loaded-piston manometer was possible). At higher pressures, the pressure accuracy depends principally on the accuracy with which the calibration curve of the manganin manometer is extrapolated to higher pressures (up to 30 kbar) and is estimated by us at ± 40 bar.

The purity of the investigated sodium was not less than 99.99% by weight. The main impurity was potassium.

The piezometers were filled with sodium in a vacuum on the order of 10^{-6} Torr with the aid of the setup illustrated in Fig. 5. The amount of matter placed in the piezometer was determined by weighing and was of the order of 3 and 1.5 g for the first and second piezometer, respectively.

As a rule, the experiments were performed in the isothermal regime. In the calculation of the sodium volume we took into account corrections for the compressibility of steel in accord with Bridgman's data^[10] (see^[6] for details). To calculate the initial volume of the piezometer, we used the value of the volume of liquid sodium, equal to 24.967 cm³/mole at 400°K and atmospheric pressure according to the data of Gol'tsova.^[11] Typical isotherms obtained as a result of these measurements are shown in Fig. 6. The accuracy, determined on the basis of the theoretical formula (see^[6]) with allowance for the errors in the measurements of the pressure and temperature, is $\pm 0.15\%$ or ± 0.03 cm³/mole.

REDUCTION OF THE EXPERIMENTAL DATA AND DISCUSSION OF THE RESULTS

For convenience in the analysis, the experimental P-V-T data, totaling 120 and 200 experimental points characterizing the equation of state of the solid and liquid phases, respectively, were approximated by polynomials in the form^[12]

$$P = \sum_{ij} a_{ij} V^{-i} T^j.$$

The rms approximation error was in this case much smaller than the summary error of the experimental

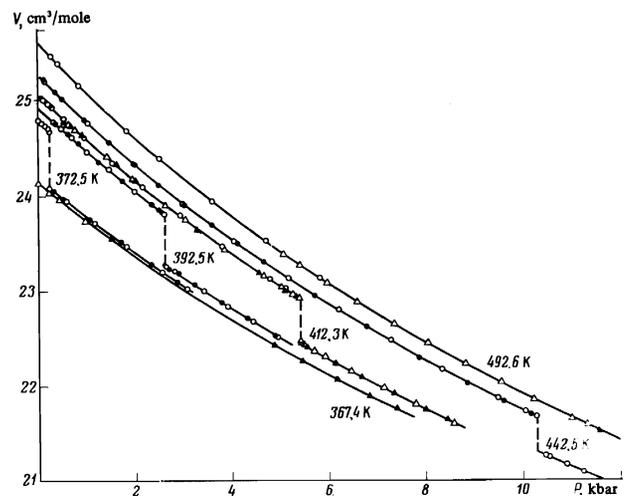


FIG. 6. Typical compression isotherms of sodium. The dark circles and triangles correspond to data obtained as the pressure was lowered.

values of the pressure, which, as can be judged from the volume-measurement error, reaches 60–100 bar.

The polynomial representation of the experimental data was used to calculate the pressure, the isothermal compressibility, and the thermal expansion of the sodium, the values of which are given in Tables I–III. The same polynomials together with the data by others^[13,14] have made it possible to calculate the internal energy and the heat capacity of the sodium (see Figs. 7 and 8). We note that the accuracy of the calculated values of the heat capacity can be estimated at 2–3% for liquid sodium and at about 5% for solid sodium.

Figure 7 shows the volume dependence of the quantity $U - 3RT$ for liquid and solid sodium at various temperatures. The quantity U is the internal energy of the sodium after subtracting the total energy taken at $T = 0^\circ\text{K}$ and atmospheric pressure (by total energy at $T = 0$ and atmospheric pressure, which we denote by U_0 , we mean the sum of the cohesion energy and the ionization potential; for sodium its value is ~ 145 kcal/mole). The stratification of the $U - 3RT$ isotherms, observed in Fig. 7, is evidence of the existence of an anharmonic contribution to the internal energy and to the heat capacity (Fig. 8) of the sodium in both the liquid and the solid phases. It is surprising that in the case of liquid sodium the anharmonic contribution is rather small; this indicates once more the effectiveness of the phonon approach to the dynamics of liquid metals.^[15]

Attention should be called to the very low temperature dependence of the volume coordinate of the minima of the $U(V)$ curves and to the proximity of this coordinate to V_0 , where V_0 is the volume of the solid sodium at $T = 0$ and $P = 1$ atm (Fig. 7). It is obvious that this is a direct consequence of the smallness of the contribution of the thermal energy to the total energy of the sodium at temperatures close to the melting point. A measure of this contribution can be, e.g., the ratio of the melting temperature to the total energy at $T = 0$. At atmospheric pressure the ratio T_m/T_0 (T_m is the melting temperature and U_0 is the total energy expressed in degrees) is ~ 0.005 for sodium. We indicate for comparison that the corresponding ratio for argon reaches ~ 0.1 .

We turn now to consideration of compressibility. Fig. 9 shows plots of the isothermal compressibility $-V^{-1}(\partial V/\partial P)_T$ against the volume for liquid and solid

TABLE I. Pressure P (kbar) of liquid (L) and solid (S) sodium.

V_L , cm ³ /mole	T, K							V_S , cm ³ /mole
	493.15	473.15	453.15	433.15	413.15	393.15	373.15	
19.5	22.642	—	—	14.181	13.914	13.646	13.378	20.5
20.0	19.459	19.166	—	11.659	11.392	11.126	10.859	21.0
20.5	16.620	16.332	—	9.409	9.143	8.877	8.610	21.5
21.0	14.082	13.798	13.510	—	7.132	6.867	6.602	22.0
21.5	11.809	11.530	11.247	—	5.334	5.069	4.805	22.5
22.0	9.772	9.497	9.218	8.934	—	3.459	3.195	23.0
22.5	7.942	7.671	7.396	7.117	—	—	1.753	23.5
23.0	6.296	6.029	5.758	5.483	5.203	—	0.458	24.0
23.5	4.815	4.552	4.284	4.013	3.736	3.456	—	—
24.0	3.480	3.220	2.957	2.688	2.416	2.139	—	—
24.5	2.276	2.020	1.759	1.494	1.225	0.952	0.674	—
25.0	1.188	0.936	0.679	0.417	0.151	—	—	—
25.5	0.206	—	—	—	—	—	—	—

TABLE II. Isothermal compressibility $-V^{-1}(\partial V/\partial P)_T$, 10^{-6} of liquid and solid sodium.

V_L , cm ³ /mole	T, K							V_S , cm ³ /mole
	493.15	473.15	453.15	433.15	413.15	393.15	373.15	
19.5	7.61	—	—	9.14	9.14	9.14	9.14	20.5
20.0	8.32	8.34	—	10.00	10.00	10.01	10.01	21.0
20.5	9.09	9.11	—	10.94	10.94	10.95	10.95	21.5
21.0	9.92	9.94	9.96	—	11.96	11.97	11.97	22.0
21.5	10.82	10.84	10.86	—	13.07	13.07	13.08	22.5
22.0	11.78	11.80	11.83	11.85	—	14.27	14.28	23.0
22.5	12.81	12.84	12.87	12.90	—	—	15.58	23.5
23.0	13.93	13.97	14.00	14.04	14.07	—	17.00	24.0
23.5	15.14	15.18	15.22	15.26	15.30	15.34	—	—
24.0	16.44	16.49	16.53	16.58	16.62	16.67	—	—
24.5	17.85	17.90	17.95	18.00	18.06	18.11	18.17	—
25.0	19.36	19.42	19.49	19.55	19.61	—	—	—
25.5	21.01	—	—	—	—	—	—	—

TABLE III. Thermal expansion $V^{-1}(\partial V/\partial T)_P$, 10^{-3} of liquid and solid sodium.

V_L , cm ³ /mole	T, K							V_S , cm ³ /mole
	493.15	473.15	453.15	433.15	413.15	393.15	373.15	
19.5	1.13	—	—	1.22	1.22	1.22	1.22	20.50
20.0	1.21	1.23	—	1.33	1.34	1.34	1.34	21.00
20.5	1.30	1.32	—	1.46	1.46	1.46	1.46	21.50
21.00	1.40	1.42	1.44	—	1.59	1.59	1.59	22.00
21.5	1.50	1.52	1.55	—	1.73	1.73	1.73	22.50
22.0	1.60	1.63	1.66	1.69	—	1.88	1.88	23.00
22.5	1.72	1.75	1.78	1.82	—	—	2.05	23.50
23.0	1.84	1.88	1.91	1.95	1.99	—	2.23	24.00
23.5	1.97	2.01	2.05	2.09	2.13	2.17	—	—
24.0	2.11	2.16	2.20	2.24	2.28	2.33	—	—
24.5	2.26	2.31	2.36	2.40	2.45	2.50	2.54	—
25.0	2.43	2.48	2.53	2.58	2.63	—	—	—
25.5	2.60	—	—	—	—	—	—	—

sodium at various temperatures. The same figure shows a few experimental data taken from the literature, and the results of certain theoretical calculations.

Attention is called to the slight (~2%) difference between the values of the compressibility of the liquid and solid phases at fixed values of the volume and the rather small temperature dependence of the compressibility for both liquid sodium and especially for solid sodium (the temperature dependence of the compressibility of solid sodium was too small to be plotted in Fig. 9). So weak a temperature dependence of the compressibility is in general not unusual for solids,^[10] but in the case of liquids this dependence is as a rule more pronounced (see, e.g., the corresponding results for argon^[17]). Obviously, the explanation of the foregoing facts lies, on the one hand, in the predominant contribution of the potential energy to the free energy of the sodium and its volume derivatives, and on the other in the low dependence of the potential energy of alkali metals on the character of the arrangement of the ions, and this in fact was one of the causes of the success of the calculations of the alkali-metal energy by the Wigner-Seitz method.

The statements made above can be regarded as con-

FIG. 7. Dependence of the internal energy on the volume at different temperatures for liquid and solid sodium. U—internal energy of sodium after subtracting the total energy taken at T = 0°K; R—universal gas constant.

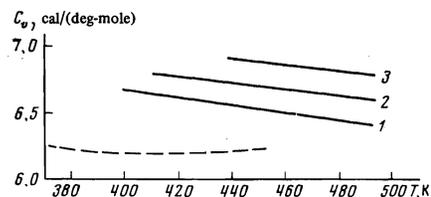
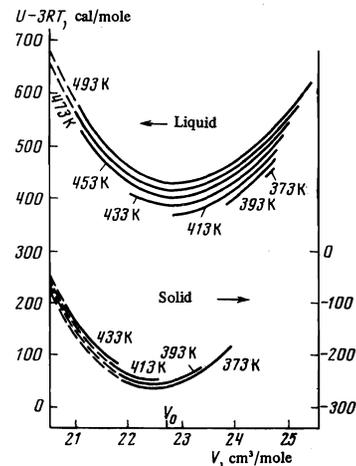


FIG. 8. Heat capacity C_V of liquid and solid sodium vs. temperature: 1, 2, 3—isochores at V equal to 25, 23.5, and 22 cm³/mole, respectively; dashed—isochores of solid body.

firmed by the interesting result that follows from an analysis of the data listed in Table II. It turns out that the temperature contribution made to the compressibility of the solid and liquid sodium is determined only by the entropy part of the free energy, and consequently the energy part of the compressibility is independent of temperature within the limits of experimental accuracy. In this case, having at our disposal complete thermodynamic information, we can easily calculate the temperature-independent or the energy part of the compressibility.

Figure 9 shows the energy parts of the compressibility β' for solid and liquid sodium. It can be seen that the contribution of the temperature-dependent part of the compressibility of sodium to the total compressibility is indeed small. Just as in the case of the complete compressibility, the difference of the values of β' at fixed values of the volume for a liquid and a crystal is quite small, 1.5% on the average; this time, however, the value of β' for crystalline sodium lies systematically below the corresponding value for the liquid. It is this result which is natural in view of the possible difference between the ion energy in the crystalline and liquid states of the alkali metal.^[18]

On the basis of the results of the present investigation we can draw the following practical conclusion. The point is that the independence of the energy part of the compressibility of the temperature actually provides us with information on the compressibility of sodium at T = 0, and this in turn enables us to calculate the equation of state at T = 0 if we know at least one value of the volume at arbitrary pressure. This result is quite important, since more accurate measurements of the compressibility are possible at high temperatures than at helium temperatures. This circumstance can make the comparative analysis of the theoretical and experimental data more effective.

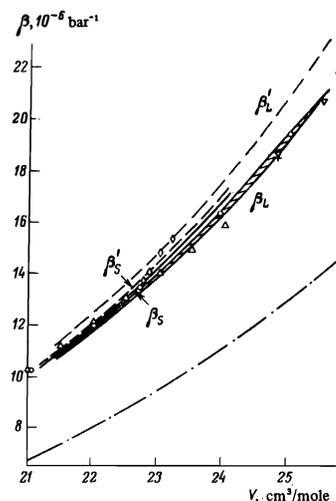


FIG. 9. Compressibility of liquid (L) and solid (S) sodium vs. volume. $\beta' = [\beta^{-1} + TV(\partial^2 S/\partial V^2)_T]^{-1}$, solid curves and dashed—our data; \triangle —^[22], \diamond —^[23], \square —^[24], \square —^[25], \circ —^[19], dash-dot—data of ^[20].

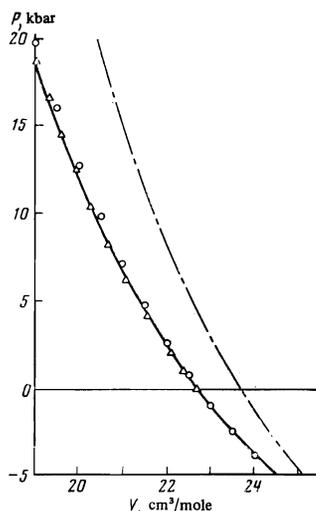


FIG. 10. Isotherm of sodium at $T = 0^\circ\text{K}$. The notation is the same as in Fig. 9.

Figure 9 shows the results of calculations of the compressibility of solid sodium with the aid of the pseudopotential method in second-order perturbation theory^[19] and the analogous results of calculations^[20] performed within the framework of the theory of an inhomogeneous electron gas. These data can be compared directly with the values of β' calculated on the basis of the present measurements. The good agreement of the calculations of Brovman et al.^[19] with experiment is perfectly obvious but for the sake of correctness it must be indicated that in that reference the pseudopotential parameters were fitted to the experimental data. At the same time, the agreement between experiment and Tong's calculations, which are fully based on first principles, are much less satisfactory.¹⁾

Figure 10 shows the results of the calculation of the zeroth isotherm of sodium use the value of β' and the x-ray diffraction data^[21] for zero volume in comparison with the results of direct measurements^[22] and theoretical calculations.^[19,20] As seen from Fig. 10, the method of calculating the zeroth isotherm using high-temperature data gives rather good results, although the accuracy of the measurements^[22] is insufficient to assess the details.

We note in conclusion that the proximity of the values of the compressibility of liquid and solid sodium probably indicates that it is possible to describe the contribution of the indirect interaction between ions via the conduction electrons to the compressibility within the framework of a theory close to the average-field theory. This question, however, calls for a separate discussion.

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