

Equation of state of sodium at pressures up to 30 GPa

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The equation of state of sodium has been studied by an x-ray method at pressures up to 30 GPa at 303 K for the first time, through the use of a diamond-anvil technique. The possibility of using this equation of state to construct a high-pressure scale is discussed.

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Since the classic paper of Wigner and Seitz,¹ sodium has been the acid test for any theory advanced to describe the metallic state of matter. It is thus particularly interesting to study the physical properties of sodium under extreme conditions.

A further motivation for such studies is the problem of the high-pressure scale. The "ruby" scale,^{2,3} which is presently used widely, is based on the equations of state of several substances (NaCl, Cu, Mo, Pd, and Ag), none of which are known accurately. The accuracy of the ruby scale is thus extremely limited ($\pm 6\%$ up to 100 GPa and $\pm 15\%$ at $P = 150$ GPa; Ref. 3), and this circumstance often robs high-pressure research of its physical significance.

Some workers (the present authors included) hold the opinion that a high-pressure scale must ultimately be based on calculations from "first principles" of the equation of state of some model substance. At present, this goal cannot be achieved because of the poor accuracy of strictly "first-principles" calculations. We believe that a compromise approach is more promising: to use a physically transparent theory with a small number of adjustable parameters. Interesting in this regard are pseudopotential

calculations with adjustment of the parameters of the pseudopotential on the basis of experimental data, so that the equations of state and other properties of alkali metals can be described with an accuracy essentially equal to the experimental accuracy.^{4,5} Among the alkali metals, sodium is the most obvious candidate for the role of the "carrier substance" of the high-pressure scale, because of the simple electronic structure of sodium and the absence of phase transitions, at least at pressures up to several tens of gigapascals.

In this letter we report an x-ray study of the equation of state of sodium at pressures up to 30 GPa, a pressure corresponding to a compression by a factor greater than two.

For the experiments we used a diamond-anvil apparatus developed especially for the purpose. The design of this apparatus is similar in principle to the designs of Refs. 6 and 7. The working surfaces of the diamond anvils (0.25 carats), made from jewelry-quality diamonds, were 0.7 mm in diameter. From the resulting diamond cell we were able to obtain x-ray diffraction patterns of polycrystalline samples at a maximum diffraction angle of 40–70°, through the use of a slit with the appropriate dimensions in one of the supports below the diamond anvils.

The sample was compressed through the use of a metal interlayer (Inconel) with an aperture 200 μm in diameter, compressed beforehand to a thickness of 30 μm . To produce polycrystalline samples, we subjected the original sodium (99.99% pure by weight) to a mechanical treatment consisting of repeated extrusion through a small gap ($\sim 50 \mu\text{m}$).

The x-ray measurements were taken by a photographic method in filtered Mo $K\alpha$ radiation (50 kV \times 80 mA). The visible focus of the x-ray tube was 0.5 \times 0.5 mm in size, and the exposure time was ~ 200 h. Three Bragg reflections were recorded stably under these conditions. The distance from the sample to the photographic film was determined with the help of a calibration device: 20- μm aluminum foil cemented to the support surface of the diamond anvil (inside the slit).

The pressure was determined from the shift of the R_1 luminescence line of ruby and the calibration curve of Ref. 3. During the x-ray and optical measurements, the diamond cell was held at a regulated 30 °C.

We must emphasize that even after the most thorough mechanical treatment of the original sodium it is difficult to produce polycrystalline samples with a high degree of dispersion. As a result, there are significant errors in the determination of the lattice constants of sodium. The maximum error in the values of the specific volume is thus on the order of 1%. The error in the pressures due to the error in the measurement of the wavelength of the ruby R_1 line (ignoring the error in the pressure scale) is ± 0.07 GPa.

The experimental data obtained (20 points) are described well by a polynomial

$$P = a\rho + b\rho^2 + c\rho^4, \quad (1)$$

where P is the pressure in gigapascals, $\rho = 1/V$, V is the volume in cubic centimeters per mole, $a = -169.646$, $b = 3960.42$, and $c = 30734.5$. The rms error of this approximation is 0.0848 GPa.

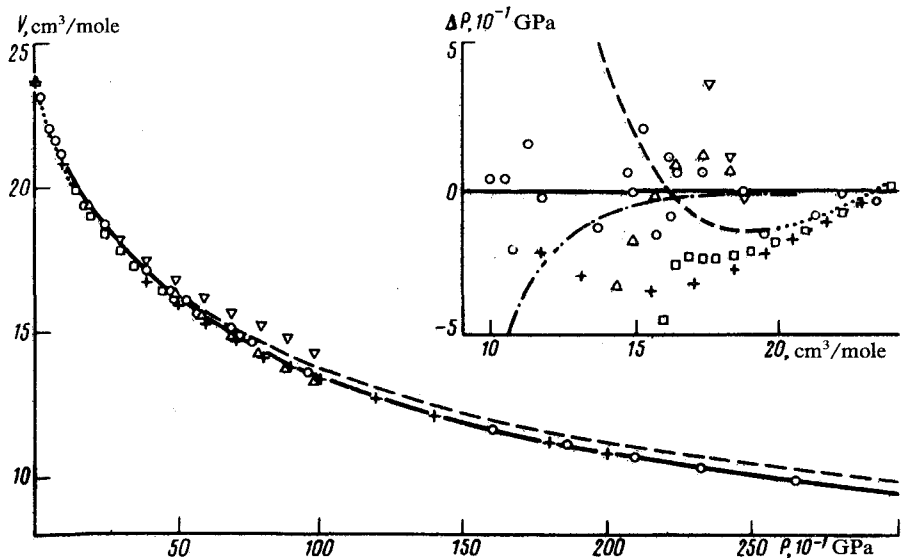


FIG. 1. Compression isotherm of sodium at $T = 303$ K. The inset shows the differences between our experimental points (\circ) and data from the literature, on the one hand, and the smooth function (1), on the other (see the text proper). Dashed curve—Ref. 5, $T = 303$ K; Δ —Ref. 9; ∇ —Ref. 10; \square —Ref. 11; $+$ —Ref. 12; dotted curve—Ref. 8; dot-dashed curve—polynomial (1), with the pressure determined from the scale of Ref. 2; solid curve—the same, but with the pressure from the scale of Ref. 3.

The results of our measurements are shown in Fig. 1 in comparison with data from the literature.^{5,8-12} Also shown here are the deviations of these results from approximating polynomial (1). Figure 2 shows the corresponding pressure dependence of the bulk modulus. It should be noted that the volume of sodium at $P = 0$ and $T = 303$ K found from our x-ray data is essentially the same as the more accurate

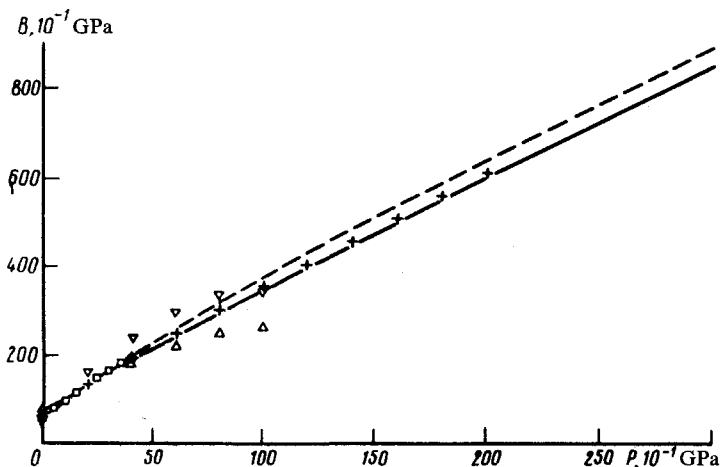


FIG. 2. Pressure dependence of the bulk modulus of sodium. The notation is the same as in Fig. 1.

value $23.76 \text{ cm}^3/\text{mole}$ from Ref. 8). We accordingly used the results of Ref. 8 to convert the data of Refs. 5 and 9–12 to absolute values.

The information on the equation of state of sodium available in the literature includes (a) the results of static experiments by Brigman^{9,10} and by Vaidya *et al.*¹¹ (at room temperature), (b) a compression isotherm calculated by Grover *et al.*¹² for $T = 298 \text{ K}$ from measurements of the Hugoniot adiabat,^{13,14} and the results of pseudopotential calculations by Vaks *et al.*⁵

It can be concluded from Fig. 1 that our results agree with the experiments of the first group, except those of Ref. 10, within the experimental error ($\pm 9\%$ in the pressure, where the error of the calibration curve is taken into account³). Nevertheless, in comparing the bulk moduli calculated from our data with those from Ref. 9 (Fig. 2) we find a significant discrepancy at $P > 5 \text{ GPa}$.

We find an extremely good agreement between our measurements and the experimental results of Ref. 12 on shock compression, although the results of Ref. 12 actually describe the compression of liquid sodium.¹⁾ The importance of this agreement should not be overrated, however, since the high-pressure scale which we used³ is based on the equations of state of several metals (as mentioned above), which—like the data of Ref. 12—were calculated from shock-wave experiments.

Comparison of our data with the pseudopotential calculations of Ref. 5 (Figs. 1 and 2) shows that up to 16 GPa the theoretical equation of state of sodium agrees with the experimental results within the experimental error.

At high pressures, however, the calculations of Ref. 5 are clearly at odds with our experimental data. From Fig. 2 we see that the experimental bulk moduli are lower than the calculated values. This discrepancy is apparently the first indication that the simple pseudopotential theory based on a local pseudopotential in second-order perturbation theory begins to fail at compressions $\Delta V/V_0 \approx 0.5$. We do not rule out the possibility that primarily the hard-core approximation must be discarded at high densities. It can be hoped that the present study will stimulate an investigation of this question.

In conclusion we wish to emphasize that the difference between the experimental and calculated values is, on the whole, small, and there is the hope that a suitable modification of the theory will lead to a better agreement with experiment. In this case the equation of state of sodium may play a central role in the construction of a high-pressure scale based on a physical theory.

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¹⁾According to our estimates, based on the results of Ref. 8, the compression isotherms of liquid and solid sodium can differ by no more than 0.25 GPa.

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