Sound-wave velocities in liquid alkali metals studied at temperatures up to 150 °C and pressures up to 0.7 GPa

George H. Shaw and D. A. Caldwell

Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minnesota 55455
and Space Science Center, University of Minnesota, Minneapolis, Minnesota 55455

We have measured compressional sound-wave velocities in liquid sodium, potassium, rubidium, and cesium at pressures up to 0.7 GPa and temperatures up to 150 °C, by ultrasonic pulse transmission. The alkali metals are among the simplest of liquids and accurate data on the sound speeds allow the calculation of thermodynamic properties which may be used in the development of the theory of the liquid state. Most previous data are from P-V-T measurements, which are inherently less accurate than ultrasonic measurements. Comparison of the present data with previous room-pressure ultrasonic data shows very good agreement. The present data may also be compared, through calculation of equation-of-state parameters and compressions, with previous piezometric data, some of which extend to pressures higher than those reached in the present experiments. Again the agreement is quite good. The present data show the expected decrease in sound velocity with increasing temperature at all temperatures, with some suggestion that the temperature coefficient may decrease at higher pressures. The calculated values of the bulk modulus (either adiabatic or isothermal) at zero pressure decrease with increasing temperature, and decrease going from sodium to cesium, as expected. The pressure derivative of the bulk modulus at zero pressure (K_0') is close to 4 in all cases, and the isothermal value is greater than the adiabatic value, though not by much. More accurate data will be needed to determine whether K_0' increases or decreases with increasing temperature. The values for the second pressure derivative of the bulk modulus (K_0'') are not well determined; only the data for the highest-pressure runs give any meaningful results. It appears that K_0'' is negative and has a value around -0.01 to -0.03 GPa^{-1}. The value of K_0'' for the highest-temperature run on cesium is the highest measured, at -0.044 GPa^{-1}. This value may indicate the onset of the electronic transition in cesium in the liquid state at pressures well below the transition pressure in the solid. Such a large negative value of K_0'' will produce a marked curvature in the velocity-pressure curve at higher pressures, and possibly a reversal in the pressure derivative of the sound velocity.

INTRODUCTION

We have recently developed a new method for measuring sound velocities in reactive liquids at high pressures and temperatures.[1] Since the alkali metals provide a good test of the device, and are also among the simplest liquids, we have made measurements on four of them (sodium, potassium, rubidium, and cesium) at temperatures up to 150 °C and pressures up to 0.7 GPa. Previous measurements of sound velocities in liquid alkali metals have been restricted to measurements as a function of temperature at room pressure[2-9] and to one set of experiments on rubidium to pressures of 20 000 psi (0.14 GPa) and temperatures up to 200 °C.[10]

Alkali metals are of considerable interest not only because they have a relatively simple liquid state, but because they are also some of the most compressible substances. Thus, the effect of pressure on liquid alkali metals may anticipate the effects of higher pressures on other, less compressible liquid metals at substantially higher pressures. A particularly interesting phenomenon is the occurrence of an electronic transition in cesium, known to occur in the solid at a pressure of about 4.0 GPa,[11] and suspected to occur in the liquid at lower pressures, thus

producing the maximum in the melting curve. Electronic transitions have been proposed for some of the other alkali metals[12] and for iron at very high pressures.[13] While the present experiments cannot hope to thoroughly investigate the effects of such an electronic transition, even for cesium, they do suggest that further work would yield useful information.

EXPERIMENTAL RESULTS

The experiments were carried out with the apparatus previously described.[1] In essence, it is guided stainless-steel bellows with end caps welded onto it (Fig. 1). Access to the interior is through a length of hypodermic tubing which can be sealed. Measurements are made of the transit time of ultrasonic pulses through the end pieces and enclosed liquid metal. After corrections have been made for travel time through the end pieces, and for a number of small dimensional changes due to the effects of pressure and temperature on the bellows, one obtains "effective" sound speeds in the sample. These are corrected for the change in length of the sample due to compression to give the actual, or thermodynamic values of the sound speeds. From these data a variety of thermodynamic pa-
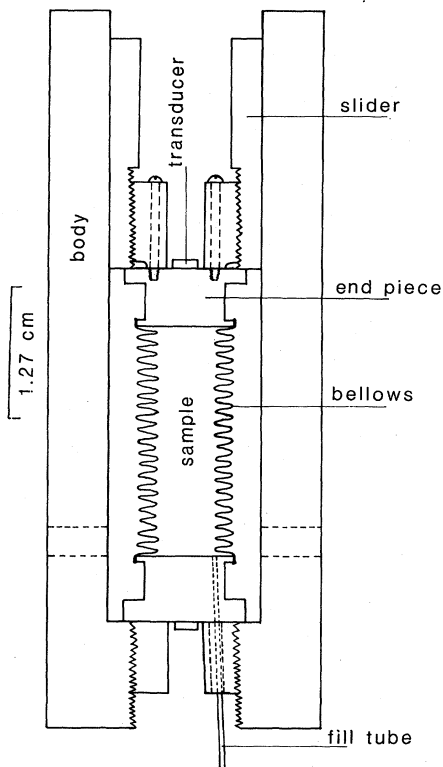

FIG. 1. Sample assembly. Attachment screws have been left off the diagram for the sake of clarity.

FIG. 2. Thermodynamic sound velocity in sodium as a function of pressure. The dots are individual data points, and the curves are sketched in. The upper curve is for 109.4 °C and the lower curve is for 148.9 °C.

rameters can be calculated, provided that auxiliary thermodynamic data are available at room pressure at different temperatures.

Some of the experimental runs were made with increasing and decreasing pressure, but in general, no attempt was made to get data with both increasing and decreasing pressure. Where such measurements were made, there is agreement to better than 0.1%. The data are internally consistent in that results at different temperatures show smooth variations with temperature, whether the data were obtained with increasing pressure or decreasing pressure. While the precision of the present data set is estimated to be better than 0.1%, the accuracy is limited to ±0.5%, largely due to difficulties in measuring the length of the sample and determining first arrival times on the oscilloscope trace. Transit times were measured using a mercury delay line.[14] The sample lengths at zero pressure were measured with vernier calipers. Temperature was maintained by an external heater on the pressure vessel, proportionally controlled to within 0.1 °C, and calibrated against American Society for Testing Materials standard thermometers accurate to 0.1 °C. The pressure medium outside the bellows was pentane. Pressure was measured on a Heise gauge and is accurate to 0.1% of full scale (0.7 GPa).

Data for each of the alkali metals are shown in Figs. 2—5. The data shown have been corrected for all thermal and pressure effects on the apparatus, and for the
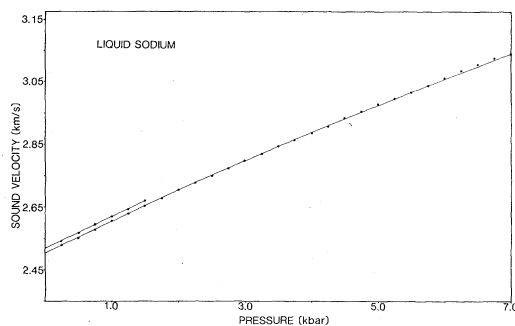
compression of the sample. They are, therefore, the true, or thermodynamic, velocities. The curves shown are not the result of least-squares fits, but are included to make it easier to see the trends in the velocities. Least-squares fits were carried out for the uncorrected velocities as part of the data analysis, as described below. The figures do not show all of the data for each metal. The temperature effect is so small that the data would be crowded on the scale of the figure. The complete data set (excluding repeated data at the same temperature and pressure) is given for each metal in Tables I—IV. These tabular data have not been corrected for sample compression, and are given so that alternative data treatments may be applied by others.

The internal consistency of the data is obvious from the figures. There is more apparent scatter for sodium as shown in the figures, but this is mainly due to the higher absolute value of velocity for sodium. The precision of the present method is clearly shown in that the small velocity differences due to temperature changes are readily distinguishable in the data.

The velocities plotted in Figs. 2—5 can be obtained from the data of Tables I—IV. Polynomial fits to the "effective" velocity data are required in order to calculate the
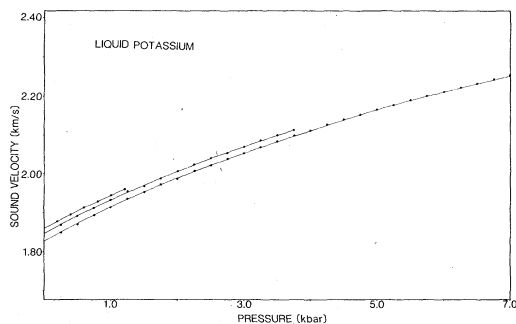

FIG. 3. Thermodynamic sound velocity in potassium as a function of pressure. The dots are individual data points, and the curves are sketched in. The upper curve is for 84.8 °C, the middle curve is for 114.2 °C, and the lower curve is for 150.1 °C.

FIG. 4. Thermodynamic sound velocity in rubidium as a function of pressure. The dots are individual data points, and the curves are sketched in. The upper curve is for 60.1 °C, the middle curve is for 108.3 °C, and the lower curve is for 150.1 °C.
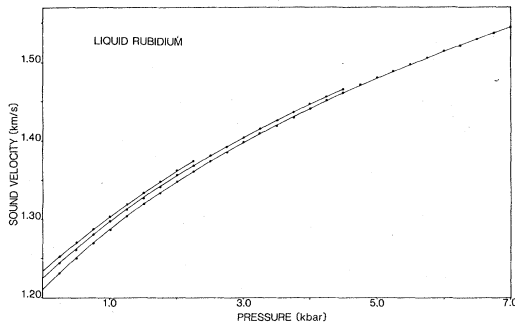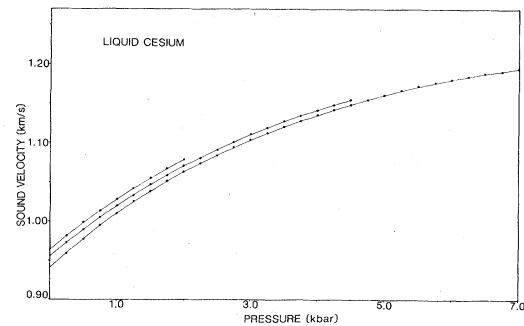

FIG. 5. Thermodynamic sound velocity in cesium as a function of pressure. The dots are individual data points, and the curves are sketched in. The upper curve is for 49.7 °C, the middle curve is for 108.3 °C, and the lower curve is for 150.1 °C.

bulk modulus and its pressure derivatives for each metal at each temperature. For the lower temperatures, with limited pressure ranges, second-order polynomials were sufficient to fit the data. Because of the high compressibilities of the alkali metals, third- and even fourth-order polynomials were required for the higher pressure ranges at the higher temperatures. The order to fit needed was determined by calculating fits for successively higher orders, until the standard error of the fit was close to the estimated precision of the experiment. It is possible that a

higher-order fit might be justified in some cases, but it should not lead to a meaningful change in the results. Table V gives the least-squares-fitting parameters for each metal at each temperature.

Using the parameters in Table V and auxiliary thermodynamic data given in Table VI, it is possible to calculate the values of the adiabatic and isothermal bulk moduli and their pressure derivatives at zero pressure given in Table VII. The appropriate equations, given in Shaw and Caldwell,[1] generally follow the method of Overton[15] and

TABLE I. Sound velocities in liquid sodium. All corrections have been made except for the length change of the sample due to pressure.

Pressure (GPa) \ Temperature (°C)	109.4	129.7	148.9
0.025	2.544	2.537	2.529
0.050	2.571	2.562	2.552
0.075	2.596	2.585	2.579
0.100	2.621	2.611	2.608
0.125	2.645	2.634	2.632
0.150	2.673	2.660	2.656
0.175		2.684	2.681
0.200		2.711	2.706
0.225		2.734	2.731
0.250		2.758	2.752
0.275		2.780	2.776
0.300		2.805	2.802
0.325		2.827	2.822
0.350		2.850	2.847
0.375		2.869	2.869
0.400		2.890	2.890
0.425		2.912	2.915
0.450			2.937
0.475			2.957
0.500			2.982
0.525			2.998
0.550			3.019
0.575			3.040
0.600			3.064
0.625			3.087
0.650			3.107
0.675			3.127
0.700			3.142

TABLE II. Sound velocities in liquid potassium. All corrections have been made except for the length change of the sample due to pressure.

Pressure (GPa) \ Temperature (°C)	84.8	100.0	114.2	150.1
0.020	1.897			
0.025		1.895	1.891	1.873
0.040	1.926			
0.050		1.934	1.932	1.912
0.060	1.959			
0.075		1.974	1.972	1.955
0.080	1.990			
0.100	2.018	2.011	2.010	
0.120	2.048			
0.125		2.048	2.047	2.033
0.150		2.086	2.080	2.069
0.175		2.121	2.119	2.107
0.200		2.157	2.155	2.142
0.225		2.189	2.189	2.177
0.250			2.223	2.213
0.275			2.255	2.245
0.300			2.288	2.278
0.325			2.321	2.311
0.350			2.353	2.343
0.375			2.382	2.375
0.400				2.406
0.425				2.438
0.450				2.469
0.475				2.498
0.500				2.526
0.525				2.556
0.550				2.586
0.575				2.614
0.600				2.641
0.625				2.668
0.650				2.694
0.675				2.723
0.700				2.750

TABLE III. Sound velocities in liquid rubidium. All corrections have been made except for the length change of the sample due to pressure.

Pressure (GPa) \ Temperature (°C)	60.1	78.8	108.3	130.9	150.1
0.020	1.267				
0.025		1.268	1.260	1.253	1.249
0.040	1.293				
0.050		1.302	1.294	1.287	1.284
0.060	1.318				
0.075		1.334	1.327	1.321	1.319
0.080	1.343				
0.100	1.367	1.364	1.360	1.353	1.352
0.120	1.391				
0.125		1.395	1.390	1.385	1.384
0.150		1.424	1.419	1.416	1.414
0.175		1.454	1.449	1.444	1.444
0.200		1.482	1.479	1.474	1.474
0.225		1.508	1.506	1.502	1.503
0.250			1.533	1.531	1.531
0.275			1.559	1.557	1.558
0.300			1.585	1.584	1.585

TABLE III. (*Continued*).

Temperature (°C) Pressure (GPa)	60.1	78.8	108.3	130.9	150.1
0.325			1.611	1.610	1.611
0.350			1.636	1.634	1.636
0.375			1.660	1.659	1.660
0.400			1.685	1.684	1.686
0.425			1.709	1.708	1.711
0.450			1.732	1.733	1.735
0.475				1.756	1.758
0.500				1.778	1.781
0.525				1.801	1.805
0.550				1.824	1.827
0.575				1.847	1.850
0.600				1.868	1.872
0.625					1.894
0.650					1.915
0.675					1.936
0.700					1.957

TABLE IV. Sound velocities in liquid cesium. All corrections have been made except for the length change of the sample due to pressure.

Temperature (°C) Pressure (GPa)	49.7	71.8	89.4	108.3	130.9	150.1
0.020	0.995					
0.025		0.997	0.991	0.988	0.980	0.975
0.040	1.020					
0.050		1.029	1.024	1.021	1.015	1.010
0.060	1.045					
0.075		1.060	1.056	1.053	1.048	1.045
0.080	1.069					
0.100	1.093	1.090	1.086	1.084	1.080	1.077
0.125		1.119	1.116	1.113	1.110	1.108
0.150		1.147	1.144	1.142	1.139	1.137
0.175		1.174	1.171	1.169	1.167	1.165
0.200		1.200	1.199	1.197	1.195	1.193
0.225			1.223	1.221	1.221	1.220
0.250			1.249	1.248	1.247	1.246
0.275			1.273	1.272	1.272	1.272
0.300			1.298	1.297	1.297	1.297
0.325				1.320	1.320	1.320
0.350				1.343	1.343	1.344
0.375				1.364	1.366	1.366
0.400				1.386	1.389	1.389
0.425				1.406	1.409	1.410
0.450				1.427	1.429	1.431
0.475					1.450	1.452
0.500					1.470	1.473
0.525					1.491	1.494
0.550					1.511	1.514
0.575					1.530	1.533
0.600					1.548	1.552
0.625						1.571
0.650						1.588
0.675						1.605
0.700						1.624

TABLE V. Least-squares-fitting parameters for the polynomial velocity-pressure curves for each liquid metal: $V = A + BP + \frac{1}{2}CP^2 + \frac{1}{6}DP^3 + \frac{1}{24}EP^4$. The errors are all $\pm 1\sigma$ values resulting from the least-squares fits of the data. These values represent the precision of the experiment. The accuracy of the experiment results in a larger error in the value of A of $\pm 0.5\%$. Error calculations used $\pm 0.5\%$ as the 2σ value for A.

T (°C)	A	$\pm 1\sigma$	B (10^{-1} km/sec kbar)	$\pm 1\sigma$	C (10^{-2} km/sec kbar^2)	$\pm 1\sigma$	D (10^{-3} km/sec kbar^3)	$\pm 1\sigma$	E (10^{-4} km/sec kbar^4)	$\pm 1\sigma$
Sodium										
109.4	2.519	0.002	1.01	0.06	0.2	0.7				
129.7	2.508	0.001	1.06	0.01	−0.5	0.1				
148.9	2.503	0.001	1.05	0.008	−0.4	0.02				
Potassium										
84.8	1.863	0.001	1.65	0.03	−1.7	0.5				
100.0	1.854	0.001	1.64	0.02	−1.3	0.1				
114.2	1.852	0.001	1.62	0.01	−1.1	0.1				
150.1	1.832	0.001	1.68	0.01	−1.4	0.1	1.6	0.2		
Rubidium										
60.1	1.241	0.0002	1.33	0.01	−1.3	0.1				
78.8	1.235	0.0004	1.36	0.01	−1.3	0.1				
108.3	1.225	0.0005	1.42	0.01	−1.8	0.1	3.2	0.4		
130.9	1.218	0.0006	1.43	0.01	−1.7	0.1	2.5	0.2		
150.1	1.215	0.0008	1.44	0.01	−1.6	0.1	2.1	0.2		
Cesium										
49.7	0.969	0.0005	1.33	0.02	−1.8	0.3				
71.8	0.964	0.0004	1.34	0.01	−1.6	0.1				
89.4	0.959	0.0008	1.34	0.01	−1.4	0.1				
108.3	0.954	0.0008	1.38	0.02	−1.8	0.1	2.6	0.3		
130.9	0.945	0.0007	1.43	0.02	−2.1	0.1	3.2	0.2		
150.1	0.939	0.0007	1.50	0.01	−2.8	0.1	8.6	0.8	−17	2

TABLE VI. Thermodynamic properties of the liquid alkali metals needed for data reduction. All data after Kim *et al.* (Ref. 2) unless otherwise indicated.

Liquid alkali metal	Temperature (°C)	Density (g/cm^3)	α (10^{-6}/deg)	C_p (j/g deg)	$\frac{1}{\alpha^2}\left[\frac{\partial \alpha}{\partial T}\right]_{P=0}$	$\frac{1}{\alpha K_T}\left[\frac{\partial K_T}{\partial T}\right]_{P=0}$
Sodium						
	109.4	0.9243	238	1.377	2.26	−3.81
	129.7	0.9198	241	1.367	2.24	−3.85
	148.9	0.9156	243	1.358	2.22	−3.87
Potassium						
	84.8	0.8228	269	0.815	1.87	−4.09
	100.0	0.8194	271	0.812	1.85	−4.14
	114.2	0.8163	273	0.808	1.83	−4.16
	150.1	0.8082	278	0.799	1.80	−4.27
Rubidium						
	60.1	1.4690	274	0.398	1.92	−3.99
	78.8	1.4614	277	0.394	1.90	−4.04
	108.3	1.4494	282	0.388	1.87	−4.12
	130.9	1.4402	285	0.384	1.84	−4.18
	150.1	1.4323	288	0.381	1.82	−4.22
Cesium						
	49.7	1.8283	284	0.267	1.53	−4.17
	71.8	1.8168	287	0.263	1.46	−4.23
	89.4	1.8076	289	0.261	1.41	−4.29
	108.3	1.7977	291	0.258	1.36	−4.36

TABLE VI. (*Continued*).

Liquid alkali metal	Temperature (°C)	Density (g/cm³)	α (10^{-6}/deg)	C_p (j/g deg)	$\dfrac{1}{\alpha^2}\left[\dfrac{\partial\alpha}{\partial T}\right]_{P=0}$	$\dfrac{1}{\alpha K_T}\left[\dfrac{\partial K_T}{\partial T}\right]_{P=0}$

$\dfrac{1}{\alpha^2 K_T}\left[\dfrac{\partial^2 K_T}{\partial T^2}\right]_{P=0} \approx 0$ for all, on the basis of the present measurements.

$\dfrac{1}{\alpha}\left[\dfrac{\partial K_{T'}}{\partial T}\right]_{P=0} \approx 0$ for all, on the basis of the present measurements.

All data, except $\dfrac{1}{\alpha K_T}\left[\dfrac{\partial K_T}{\partial T}\right]_{P=0}$ are from equations given by Kim *et al.* (Ref. 2).

$\dfrac{1}{\alpha K_T}\left[\dfrac{\partial K_T}{\partial T}\right]_{P=0}$ from the present work.

TABLE VII. Calculated values of the bulk moduli and their pressure derivatives at zero pressure. The listed errors are $\pm 2\sigma$ from error propagation using the values in Table V.

Liquid alkali metal	Temperature (°C)	K_{s0} (GPa)	$\pm 2\sigma$	K_{s0}'	$\pm 2\sigma$	K_{s0}'' (GPa^{-1})	$\pm 2\sigma$
Sodium	109.4	5.87	0.06	3.6	0.6	0.019	0.074
	129.7	5.79	0.06	3.8	0.1	−0.011	0.008
	148.9	5.74	0.06	3.7	0.1	−0.006	0.004
Potassium	84.8	2.86	0.03	3.9	0.2	−0.025	0.038
	100.0	2.82	0.03	3.9	0.2	−0.012	0.014
	114.2	2.80	0.03	3.8	0.1	−0.008	0.007
	150.1	2.71	0.03	3.8	0.1	−0.014	0.008
Rubidium	60.1	2.26	0.02	3.8	0.1	−0.017	0.011
	78.8	2.23	0.02	3.8	0.1	−0.013	0.008
	108.3	2.18	0.02	3.9	0.1	−0.027	0.010
	130.9	2.14	0.02	3.9	0.1	−0.022	0.009
	150.1	2.11	0.02	3.9	0.1	−0.018	0.009
Cesium	49.7	1.72	0.02	3.6	0.2	−0.026	0.030
	71.8	1.69	0.02	3.6	0.1	−0.018	0.009
	89.4	1.66	0.02	3.5	0.1	−0.012	0.010
	108.3	1.64	0.02	3.6	0.2	−0.022	0.017
	130.9	1.59	0.02	3.7	0.2	−0.025	0.014
	150.1	1.57	0.02	3.9	0.1	−0.045	0.016

Liquid alkali metal	Temperature (°C)	K_{T0} (GPa)	$\pm 2\sigma$	K_{T0}'	$\pm 2\sigma$	K_{T0}'' (GPa^{-1})	$\pm 2\sigma$
Sodium	109.4	5.33	0.05	3.7	0.6	0.015	0.074
	129.7	5.22	0.05	3.9	0.1	−0.010	0.008
	148.9	5.14	0.05	3.8	0.1	−0.007	0.004
Potassium	84.8	2.57	0.03	4.1	0.2	−0.025	0.038
	100.0	2.52	0.03	4.0	0.2	−0.013	0.014
	114.2	2.49	0.02	4.0	0.1	−0.010	0.007
	150.1	2.38	0.02	4.1	0.1	−0.016	0.008

TABLE VII. (Continued).

Liquid alkali metal	Temperature (°C)	K_{s0} (GPa)	±2σ	K_{s0}'	±2σ	K_{s0}'' (GPa^{-1})	±2σ
Rubidium	60.1	2.06	0.02	3.9	0.1	−0.018	0.011
	78.8	2.02	0.02	4.0	0.1	−0.014	0.008
	108.3	1.95	0.02	4.1	0.1	−0.026	0.010
	130.9	1.90	0.02	4.1	0.1	−0.022	0.009
	150.1	1.86	0.02	4.1	0.1	−0.020	0.009
Cesium	49.7	1.57	0.02	3.8	0.2	−0.026	0.030
	71.8	1.53	0.02	3.8	0.1	−0.020	0.009
	89.4	1.50	0.02	3.8	0.1	−0.016	0.010
	108.3	1.47	0.01	3.9	0.2	−0.025	0.017
	130.9	1.42	0.01	4.0	0.2	−0.028	0.014
	150.1	1.39	0.01	4.2	0.1	−0.044	0.016

Barsch[16] modified for (1) the special geometry of the present experiment, (2) the need for only one sound speed, and (3) the required extension to get the second pressure derivative of the bulk modulus. After calculating these values it is possible to use an isothermal equation of state[20] at each temperature to calculate compressions for the liquid metals. These compressions then allow the calculation of the length changes required to get the true sound speeds at elevated pressures, which are the results shown in Figs. 2—5.

The accuracy of the present results can be assessed by comparison with ultrasonic data obtained by others. Our experiments were not designed to get data at room pressure, but the comparison of our data, extrapolated to zero pressure, with data collected at zero pressure is quite good. Such comparisons are shown in Figs. 6—9. Most of the previous data in these figures are results from high precision ultrasonic interferometry. Using the most recent results[2] we calculated predicted velocity values at the temperatures of our experiments and then calculated the rms deviation between the two sets at the 18 points available. The value was approximately 0.2%. Kim et al.[2] estimate their accuracy at 0.5%, as do we. The figures give

0.5% error bars on our data. It is clear that the data are in very good agreement.

The data on rubidium may also be compared with the data of Rosenbaum,[10] who made ultrasonic velocity measurements at temperatures up to 200 °C and pressures up to 20000 psi (0.14 GPa). The comparison is made in Fig. 10 for two temperatures, 60.1 °C and 150.1 °C. The comparison is reasonably good. The differences in the sound speeds at room pressure are well within the experimental accuracy. The differences in the slopes of the two sets of curves result mainly in different values for the first pressure derivative of the bulk modulus. At 60.1 °C the present data give a value of K_{s0}' of 3.8 while Rosenbaum's equations give a value of 4.2, and at 150.1 °C the present value of K_{s0}' is 3.9 compared to 4.4 from Rosenbaum's data. At 20000 psi (0.14 GPa) the difference between Rosenbaum's velocities and the present results amounts to about 2%, which is a bit greater than the combined errors, suggesting that there is a real difference between the two data sets. The values of K_{s0}' calculated from the present data at each temperature, for each of the alkali metals, are lower than the values calculated from Rosenbaum's equations for rubidium. This suggests that Rosenbaum's re-
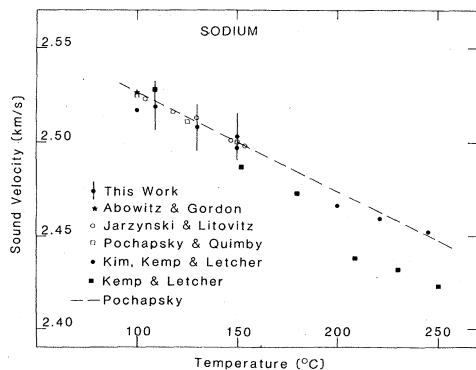

FIG. 6. Sound velocity in sodium as a function of temperature at room pressure. The data of K. A. Kemp and S. V. Letcher [Office of Naval Research Technical Report No. 1 (1968)] are taken as reported in Kim et al. (Ref. 2).
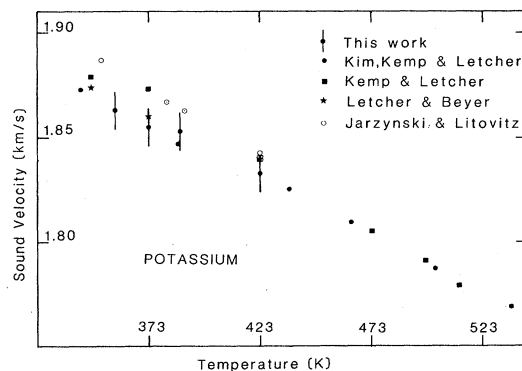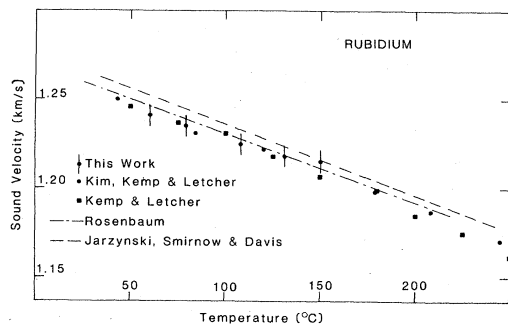

FIG. 7. Sound velocity in potassium as a function of temperature at room pressure. The data of K. A. Kemp and S. V. Letcher [Office of Naval Research Technical Report No. 1 (1968)] are taken as reported in Kim et al. (Ref. 2).

FIG. 8. Sound velocity in rubidium as a function of temperature at room pressure. The data of K. A. Kemp and S. V. Letcher [Office of Naval Research Technical Report No. 1 (1968)] are taken as reported in Kim et al. (Ref. 2).

FIG. 10. Sound velocity in rubidium as a function of pressure compared with the results of Rosenbaum (Ref. 10). The upper two curves are for a temperature of 60.1 °C and the lower two curves are for a temperature of 150.1 °C.

sults lead to too rapid a rise in sound speed with pressure, or that the present results for all the metals lead to too slow an increase in sound speed with increasing pressure. Alternatively, rubidium may be a special case, with slightly higher values for K'_{s0} than that for the alkali metals as a group.

Another comparison is possible using piezometric data giving pressure-volume isotherms. Bridgman[17] made one set of measurements on liquid cesium at 75 °C up to about 0.2 GPa, and Makarenko et al.[18] report measurements on sodium, potassium, and cesium (both solid and liquid) at temperatures up to 220 °C and pressures up to 2.2 GPa. Jarzynski[19] made measurements on liquid rubidium using an accurate ultrasonic dilatometer to pressures up to 20 000 psi and temperatures up to 200 °C. Compressions were calculated from the values in Table VII using the second-order Murnaghan equation of state.[20] Figure 11 shows the comparisons. The agreement is quite good, well within the experimental uncertainties.

DISCUSSION

The present set of experiments provides values of the zero-pressure bulk moduli (in Table VII) which are accurate to about ±1.0%. This accuracy is based upon estimated errors in the measurements. The values for the first and second pressure derivatives of the bulk moduli
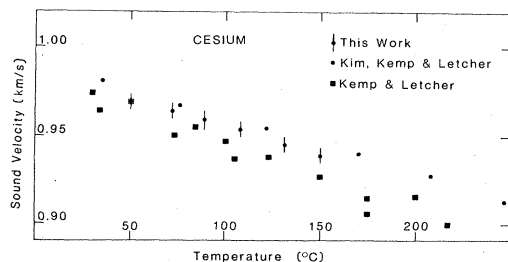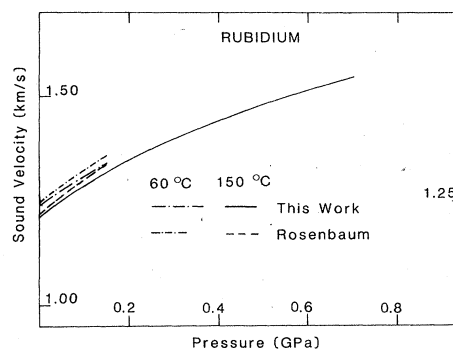
(at zero pressure), and the associated errors are also given in Table VII. The errors for the derivatives are calculated from the standard errors of the least-squares fits of the velocity data and the estimated error in K_0. This procedure was adopted since the errors in the pressure derivatives are more a reflection of the precision of the experiment, rather than its accuracy. The 2σ values for the errors are given in Table VII. They are about 3—5 % for K'_0. The error in K''_0 is so large for the small pressure
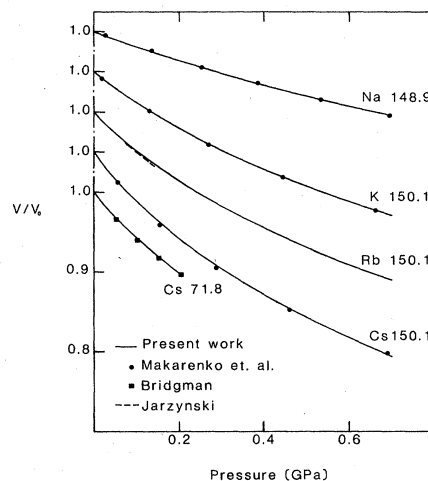

FIG. 11. Compression curves for the liquid-alkali metals. Compressions calculated from the present data using the second-order Murnaghan equation. Comparisons are made with piezometer determinations of Makarenko et al. (Ref. 18) for sodium, potassium, and cesium for the highest temperature runs, where the pressure range is the greatest. The data of Makarenko et al. were interpolated to the comparison temperatures. Their data were also extrapolated to get the data point at the highest pressure in each case. A comparison is also shown with the rubidium data of Jarzynski (Ref. 19) as calculated from his equation at 150.1 °C. A separate curve is also given for cesium at 71.8 °C and comparison made with Bridgman's (Ref. 17) data for cesium at 75 °C.

FIG. 9. Sound velocity in cesium as a function of temperature at room pressure. The data of K. A. Kemp and S. V. Letcher [Office of Naval Research Technical Report No. 1 (1968)] are taken as reported in Kim et al. (Ref. 2).

range of the low-temperature experiments as to make the calculated K_0'' of little use. However, the greater pressure range at higher temperatures results in errors which provide a useful constraint on the values of K_0''. Since K_0'' is not likely to vary by much over the temperature range under investigation here, the more accurately determined values from the higher temperature experiments should probably be used in any calculations. Such an approach was used in all calculations done in this paper. We also note that the values of K_0'' for each metal, calculated at all temperatures, are in good agreement within the stated errors, with the exception of the highest temperature values of K_0'' for cesium, which will be discussed further below. This unusually large value of K_0'' for the highest pressure run for cesium was not used in the equation-of-state calculations for the lower temperature data on cesium.

The values of bulk modulus present no special surprises. The most compressible of the liquid metals is cesium and the least compressible is sodium. Bulk modulus decreases with increasing temperature in all cases, for both adiabatic and isothermal moduli. The first pressure derivatives of the bulk moduli all have values near 4, which is not unexpected for a condensed phase. The isothermal values are greater than the adiabatic values for all of the metals. A value of zero for the temperature derivative of K_0' is probably as good a value as any, based upon the present data. There is no clear trend in K_0' going from sodium to cesium.

Values for K_0'' are a bit more difficult to assess, for reasons given above, and evaluation of trends is correspondingly more difficult. It appears that K_0'' for all of the metals is negative at all temperatures. The sole exception is for the lowest temperature run for sodium, which covered a pressure range of only 0.15 GPa, which is too small a range to provide any kind of reasonable value for K_0''. It is not possible to say whether the adiabatic value of K_0'' is greater or less than the isothermal value. Given the poorly constrained results at low temperatures, it is also impossible to define a trend with temperature. If one looks at the highest temperature runs only, for which the determination of K_0'' is best, there is some suggestion that the value becomes more negative going from sodium to cesium.

The highest temperature run on cesium yields a value for K_0'' which is larger than all the other runs on cesium

or the other metals, although the 2σ error bars overlap. If this is a real difference, it may be a manifestation of the electronic transition in cesium which is known to occur in the solid at a pressure of about 4.0 GPa.[11] The electronic transition probably occurs in the liquid at a lower pressure, and probably over a range of pressures rather than at a sharply defined pressure. The decrease in atomic dimension that accompanies the transition results in a pronounced density increase. If this occurs in the liquid at a lower pressure than in the solid, it could be responsible for the maximum in the melting curve of cesium which has been observed experimentally.[11,21] A gradual transition of this type would appear as a marked decrease in the bulk modulus, or at least a lessening of the normal rate of increase with increasing pressure. A relatively large negative value of K_0'' is just what one might expect. It is interesting that the value of K_0' for cesium increases with increasing temperature, while at the highest temperature, K_0'' appears to become more negative. It is difficult to say whether this is actually an indication of the electronic transition in the liquid, but the shape of the melting curve of cesium suggests that the transition in the liquid might be underway at a pressure as low as 2.0 GPa, perhaps less. This is also suggested by measurements of the resistivity of liquid cesium at high pressure.[11] If an electronic transition takes place over a range in pressure in liquid cesium it should have a profound effect on the sound speed. The relatively rapid increase in density due to the transition will be reflected in a lower than usual bulk modulus (higher compressibility). This, coupled with the density increase should lead to a noticeable decrease in sound speed with increasing pressure since $V^2 = K/\rho$. Such an effect is not observed at the highest pressure attained in the present experiments, which only reached 0.7 GPa. However, the pronounced curvature in the velocity-pressure curve, which shows up in the calculated value of K_0'', could be an indication of things to come at higher pressures.

The present results, limited as they are, suggest at least the possibility that a velocity reversal may take place where a liquid is undergoing an electronic transition. In order to better assess the possible effects of such a transition in a liquid, additional measurements on liquid cesium to higher pressures would be useful.

[1] G. H. Shaw and D. A. Caldwell, Rev. Sci. Instrum. 56, 1402 (1985).

[2] M. G. Kim, K. A. Kemp, and S. V. Letcher, J. Acoust. Soc. Am. 49, 706 (1971).

[3] J. Jarzynski, J. R. Smirnow, and C. M. Davis, Jr., Phys. Rev. 178, 288 (1969).

[4] S. V. Letcher and R. T. Beyer, J. Acoust. Soc. Am. 35, 1571 (1963).

[5] J. Jarzynski and T. A. Litovitz, J. Chem. Phys. 41, 1290 (1964).

[6] G. Abowitz and R. B. Gordon, J. Chem. Phys. 37, 125 (1962).

[7] T. E. Pochapsky, Phys. Rev. 84, 553 (1951).

[8] T. Pochapsky and S. Quimby, Phys. Rev. 79, 892 (1950).

[9] O. J. Kleppa, J. Chem. Phys. 18, 1331 (1950).

[10] I. J. Rosenbaum, Ph.D. thesis, American University, 1971.

[11] A. Jayaraman, R. C. Newton, and J. M. McDonough, Phys. Rev. 159, 527 (1967).

[12] M. S. T. Bukowinski, Geophys. Res. Lett. 3, 491 (1976).

[13] M. S. T. Bukowinski, Phys. Earth Planet Int. 13, 57 (1976).

[14] F. Birch, J. Geophys. Res. 65, 1083 (1960).

[15] W. C. Overton, Jr., J. Chem. Phys. 37, 116 (1962).

[16] G. R. Barsch, Phys. Status Solidi 19, 129 (1967).

[17] P. W. Bridgman, Proc. Am. Acad. Sci. 60, 385 (1925).

[18]I. N. Makarenko, H. M. Nikolaenko, and S. M. Stishov, in *Liquid Metals—1976,* edited by R. Evans and D. A. Greenwood (IOP, London, 1977), pp. 79—89.

[19]J. Jarzynski, Philos. Mag. **31**, 1253 (1975).

[20]M. S. Anderson and C. A. Swenson, Phys. Rev. B **28**, 5395 (1983).

[21]G. C. Kennedy, A. Jayaraman, and R. C. Newton, Phys. Rev. **126**, 1363 (1962).