

Compression of the Alkali Metals to 10 000 Atmospheres at Low Temperature

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A technique originally developed by Bridgman has been used to measure the total compressions of the alkali metals (Li, Na, K, Rb and Cs) for pressures up to 10 000 atmospheres at 4.2° and 77°K. The unusual features found were an abnormally low decrease in compressibility with pressure for cesium, probably connected with a smearing out of the electronic transition found at 45 000 atmos at room temperature, and a possible transformation in rubidium at 77°K which resulted in a permanent increase in the room temperature density of about ten percent. A comparison of these data with theoretical work by Bardeen shows better agreement than was obtained with an extrapolation of room temperature data to absolute zero, although the agreement is satisfactory only for sodium. Approximate densities also were obtained at these temperatures, and the agreement with unpublished calculations by Brooks is excellent for all the metals except lithium, where a deviation could be expected to occur.

INTRODUCTION

THE work done in compressing a solid can in general be broken up into two parts: the first involving changes of entropy with volume (heating effects), and the second involving only changes in internal energy. From a theoretical point of view, calculations involving the temperature as an independent variable are extremely difficult, so that theoretical calculations of compressibilities are usually confined to absolute zero where the volume is the only independent variable. Because it is as difficult to extrapolate high-temperature compressibility data to low temperatures as it is to make the initial high-temperature calculations, a proper comparison of theory with experiment can be made only if the range of experimental data is extended into the temperature region where thermal effects will be unimportant.

The substances which are of the greatest theoretical interest are the condensed rare gases and the alkali metals, since they represent, respectively, the simplest dielectric solids and the simplest metals. Because of their low Debye θ 's, it is necessary to go to liquid helium temperatures (4.2°K) to make sure that thermal effects for these substances are negligible, and it is unfortunate that conventional methods for measuring the change in volume with pressure cannot be used in this temperature region. However, exploratory work by Stewart^{1,2} has shown that many of the solidified gases and also the alkali metals are quite plastic at 4.2°K, so that a technique which was used by Bridgman for very high pressure work^{3,4} has been adapted for compressibility work at these temperatures. Results obtained using this method have been published recently for some solidified gases,^{2,5} and the work described below concerns similar measurements on the alkali

metals; lithium, sodium, potassium, rubidium, and cesium.

EXPERIMENTAL DETAILS

The method which was used is essentially that due to Bridgman,⁴ and is illustrated in Fig. 1. The sample was placed in a thick-walled cylinder which was closed at either end by a piston. A compressive force was applied to the pistons, and the motion of the pistons as a function of applied force was used to give, with suitable corrections, the hydrostatic compression of the sample as a function of pressure.

The major problem with this method is to make sure that the sample is plastic enough so that the pressure on the sample is approximately hydrostatic; or, in other words, it must not be possible for an appreciable pressure difference to exist between the ends and sides of the sample. This will be true if the shear yield strength of the sample material is much less than the applied pressure. Stewart's measurements have shown that this is true at 4.2°K for sodium and potassium,¹ and since cesium and rubidium are much more plastic than these at room temperature, it was assumed that they would also be sufficiently plastic at low temperature. Lithium is perhaps less satisfactory and represents a borderline case, so that the results on it must be taken with some reservation.

The major pieces of equipment needed to perform these experiments, other than the sample holder, are a

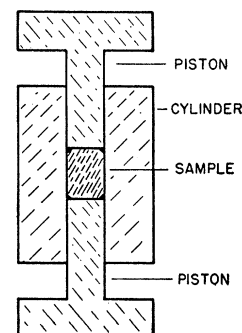


FIG. 1. The type of sample holder used in these experiments.

¹ J. W. Stewart, Doctoral thesis, Harvard University, May, 1954 (unpublished).

² J. W. Stewart, *Phys. Rev.* **97**, 578 (1955).

³ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **74**, 425 (1942).

⁴ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **76**, 1 (1945).

⁵ J. W. Stewart and C. A. Swenson, *Phys. Rev.* **94**, 1096 (1954).

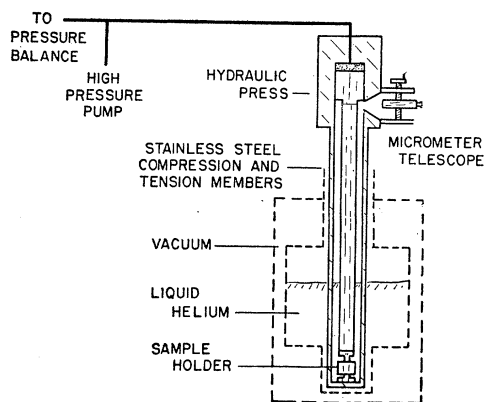


FIG. 2. A sketch of the hydraulic press and the liquid helium (or liquid nitrogen) dewar. The surrounding liquid nitrogen jacket is not shown.

hydraulic press with long supports to compress the sample holder at low temperature, a means for measuring both the initial length and the changes in length of the sample, and a dewar vessel for containing liquid helium or liquid nitrogen. These essential parts of the apparatus which was used are sketched in Fig. 2. The force on the sample holder was calculated from the oil pressure (given by the pressure balance) and the area of the hydraulic piston, while apparent changes in the length of the sample were indicated by the motion of the hairline as measured by the micrometer telescope (sensitivity about 0.002 mm). The maximum force available was four tons, which corresponds roughly to 10 000 atoms pressure on a 0.250-in. diameter sample.⁶

In principle, the taking of compression data at liquid nitrogen or liquid helium temperatures was quite simple, since it was only necessary to increase the pressure and record the motion of the hairline. However, three basic corrections had to be made which formed a large part of the readings actually taken; namely, the corrections for friction, background stretch (that is, the motion of the hairline with no sample in the holder), and the expansion of the holder under hydrostatic pressure. In order to guard against systematic errors in making these corrections, sample holders of two different sizes were used for each of the five alkali metals.

The holders were similar to that shown in Fig. 1, with the outside diameter of the cylinder being in all cases 0.875 in. Two holders were used with inside diameters of 0.250 in.; the first was made from hardened tool steel, and the second from hardened beryllium copper. A piston on the original steel holder was broken midway through the runs, and when difficulty arose in trying to replace it due to repeated breakage, a beryl-

lium copper holder of the same dimensions was substituted. These holders were useful for sample pressures from 1500 to 10 000 atmos, and will be referred to below as the "small" holders. The other or "large" holder, with twice the piston area (0.354-in. diameter), was also made from hardened tool steel and was used for pressures from 750 to 5000 atmos. The background stretch correction was relatively about twice as great for the "large" as for the "small" holder, while the friction and expansion corrections were less.

The effects of friction are illustrated by the hysteresis loop in Fig. 3, where the experimental data for one cesium run are plotted. As the pressure was increased slowly and monotonically by placing weights on the pressure balance, the friction opposing the motion of the piston built up fairly quickly until it reached a steady value. When a maximum pressure was reached (determined only by the danger of permanently deforming the apparatus), the pressure was slowly reduced, so that the direction of this frictional force was reversed. It did not reverse instantaneously, but eventually became constant again in the opposite direction at slightly lower pressures. This was shown by the fact that the pressure increasing and pressure-decreasing curves were parallel for intermediate pressures, and in this region the true pressure corresponding to a given displacement could be calculated as the mean of the two curves, as is shown.⁴ The dotted curve which gives this average pressure was extrapolated to higher pressures beyond the parallel region on the assumption that the friction remained at a constant value.

At low pressures, the friction decreased, and the true pressure was again the mean for a given displacement. If there was no permanent deformation of the sample,⁷ the reading at zero pressure was unchanged, although because of uncertainties in the friction, this did not necessarily correspond to the true sample length at zero pressure. To eliminate this effect and to allow a determination of the sample length to be made, a calibration setting of the hairline (taken with respect to a fiducial mark on the hydraulic head and corrected for friction) was always recorded at a pressure at 1500 atmos, to be compared with a similar setting with no sample in the holder. This length (good to about 0.03 mm) and the weight of the sample were then used to calculate a density at 1500 atmos which was subsequently extrapolated to zero pressure by using the $\Delta V/V$ data. It is worth noting that the absolute values of the lengths as obtained in this way were far less accurate than changes in lengths, since hairline settings could be reproduced to about 0.002 mm when the pressure was released and then reapplied during a given run. Great care was always taken to ensure that the

⁶ A more detailed description of this apparatus, which was similar to that described in reference 5, will be found in C. A. Swenson, *J. Inst. Soc. Am.* (to be published), and also in the U. S. Army Office of Ordnance Research Technical Memorandum, TM-55-1 (unpublished).

⁷ There was always a zero shift on the initial compression due to the compacting of the material in the sample. For this reason, the sample was subjected to full pressure several times ("seasoned") at each temperature until the zero remained constant after cycling.

temperature gradient down the support members was constant during each run and reproducible from run to run, since any change in gradient could affect both the background stretch correction and the calibration setting of the hairline, as well as cause spurious changes in readings.

The major source of the friction has been discussed by Bridgman,³ and is undoubtedly due to polycrystalline grains of the sample being forced to move with respect to each other. This is supported by the fact that the friction increased with decreasing temperature. It is interesting to note that at 4.2°K the half-height of the hysteresis loop represented about ten percent of the total change in sample length observed for all the metals except lithium, where it was slightly more. This was surprising, since the lengths, the total compressions, and the sample areas all varied indiscriminately over a factor of at least two. Thus, if the two sides of the loop were parallel to ten percent (as was usual), the effect on $\Delta V/V_0$ was of the order of one percent.

The background stretch due to the hydraulic press and the sample-holder pistons was determined by performing an identical experiment at each temperature for each holder in the absence of a sample. The resulting curves were quite linear, and gave a total compression in 10 000 atmos, which was reproducible to about one-half percent. The magnitude of this correction is shown also in Fig. 3, where it can be seen to represent about thirty percent of the data which was taken. This was the most favorable case, and the correction varied with sample material and length until in the least favorable cases (short samples of lithium and sodium) it represented about sixty percent of the data. This introduced an uncertainty into the final calculations of less than two percent.

The last correction, that due to the expansion of the sample holder under hydrostatic pressure, had to be determined experimentally. The sample holders were filled with a soft metal (such as lead, indium or thallium), and a measurement of the room temperature compression of this metal was taken as described in the aforementioned. The difference between the total compression as given by using the background stretch and friction corrections only, and the true value as given in the more accurate results of Bridgman,⁴ was assumed to be due to the cylinder expansion. This difference was measured as a function of length for each holder at room temperature and was extrapolated to 77° and 4.2°K by assuming that it was inversely proportional to the Young modulus of the metal.⁸ This correction at room temperature amounted to less than 0.005 in $\Delta V/V_0$ for the full compression in the large holder, while the maximum effect was about 0.020 in $\Delta V/V_0$ for the small beryllium copper holder. The inaccuracy in $\Delta V/V_0$ due to this

⁸ Unpublished results at this laboratory have shown that the increase in Young's modulus for steel and beryllium copper as the temperature is decreased is roughly ten percent from room temperature to 77°K and practically zero from 77°K to 4.2°K.

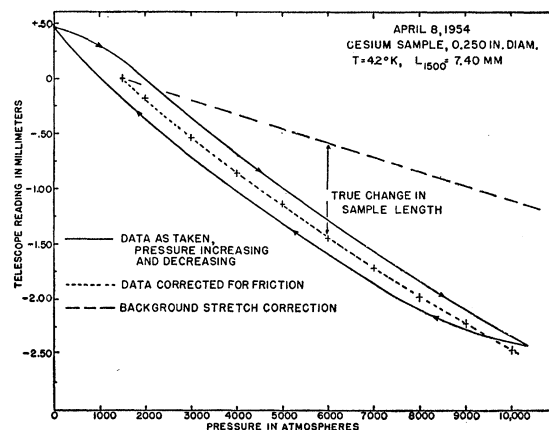


FIG. 3. Typical experimental data obtained in a cesium run at 4.2°K.

cause can be shown to be absolute, independent of the compression to a first approximation, and it was never greater than 0.001. It was consequently more serious for the least compressible metals, lithium and sodium. The necessity for determining the correction in this manner means that the results quoted are relative to Bridgman's results. Making a correction in this way also serves to eliminate errors due to small effects which might otherwise be overlooked.

A fourth correction, due to thermal expansion, was not serious except in the density calculations. The volume change between room temperature and 4.2°K was assumed to be $-0.5(\pm 0.3)$ percent for the steel holders, and $-0.9(\pm 0.3)$ percent for the beryllium copper holders. The weights of the samples were obtained by weighing the holders when empty and when full, and the volume was calculated from the value of the length at 1500 atmos extrapolated to zero pressure. The values of the densities so obtained for each holder usually agreed to about one-half percent, and the experimental accuracy is estimated to range from 0.5 percent for the heavier metals to one percent for lithium.

The metals were obtained from A. D. Mackay, Inc., who estimated the purities as 99.9 percent for the sodium, rubidium, and cesium, and as better than 99 percent for the lithium and potassium. Except for the lithium, they were furnished in evacuated glass ampules containing from 0.5 to 1 gram. These were broken and manipulated under dry benzene into a glass funnel arrangement which could be evacuated and in which the metal was melted from the ampule into the cylinder (closed at its bottom by its lower piston), either under vacuum or in a helium atmosphere. The sample holder was then cooled considerably below room temperature so that the top piston could be placed in the cylinder. The chances for the introduction of oxide were very slight, since all operations were done as quickly as possible, and no film was ever observed on the metal surfaces after melting. The lithium was immersed in

benzine while being cut with a cork borer and placed in the sample holder. After the pistons had been fitted into the holder, it was removed from the bath and dried in a chamber using a vacuum pump.

There was some difficulty with extrusion of the more plastic metals between the piston and cylinder walls, even though they were an excellent fit, so small, triangular brass rings which were pressed into the cylinder were used as an additional seal (see Fig. 1). A correction was made to allow for these in the final calculations.

CALCULATION OF THE RESULTS

The values for $\Delta V/V_{1500}$ which were obtained for each metal in each sample holder, suitably corrected, were plotted against pressure on a large sheet of graph paper, and a smoothed curve drawn through them for each temperature. The lower pressure limit of 1500 atmos for the small holders and 750 atmos for the large holder was caused by a limitation in the minimum weight which could be used on the pressure balance. No great effort was made to rectify this, since at lower pressures the friction was changing so rapidly. The agreement of the two curves between 1500 atmos and 5000 atmos was never worse than five percent of $\Delta V/V_{1500}$, and was usually much better, giving a considerable confidence in the correctness of the data obtained and the corrections made.

These values of $\Delta V/V_{1500}$ were then extrapolated to zero pressure by means of an expression derived by

Birch from Murnaghan's theory of finite strain⁹:

$$P = (3/2\beta_0)[y^7 - y^5][1 - \xi(y^2 - 1)], \quad (1)$$

where $y = (V_0/V)^{1/3}$, V is the volume at the pressure P , V_0 is the volume at zero pressure, β_0 is the initial compressibility [$\beta = -(1/V_0)(\partial V/\partial P)_T$], and ξ is an adjustable constant which must be found by trial and error. For this extrapolation, β_0 is actually β_{1500} , and V_0 is V_{1500} . Good fits were found for moderate values of ξ except for the case of lithium.

$\Delta V/V_0$ could then be calculated from the values of V_{1500}/V_0 which were found. These compressions are plotted as a function of pressure in Fig. 4 for all the alkali metals at both 77° and 4.2°K, while the actual 4.2° smoothed data are given in Table I. It must be emphasized that the differences in the $\Delta V/V_0$'s between 1500 and 10 000 atmos are known more accurately than those from zero to 1500 atmos, since these latter are due to an extrapolation. The probable error in $\Delta V/V_0$ was estimated to be less than three percent at

TABLE I. The smoothed results for the compression experiments on the alkali metals.

P (atmos)	Li	Na	K	Rb	Cs
0	0.000	0.000	0.000	0.000	0.000
500	0.004	0.007	0.014	0.016	0.022
1000	0.007 ⁵	0.013	0.028	0.031	0.044
1500	0.011	0.020	0.039	0.046	0.063
2000	0.014	0.026	0.049	0.060	0.081
3000	0.021	0.038	0.070	0.084	0.113
4000	0.028	0.049	0.090	0.106	0.141
6000	0.040	0.070	0.123	0.142	0.188
8000	0.051	0.088	0.152	0.171	0.229
10 000	0.061	0.105	0.177	0.196	0.263
$\beta_{0,77}(10^{-5} \text{atmos}^{-1})$	0.88	1.56	2.96	3.88	4.93
$\beta_{0,4.2}(10^{-5} \text{atmos}^{-1})$	0.78	1.39	2.88	3.48	4.41
$\xi_{0,77}$	-2.5	-0.9	0	-0.3	+0.4
$\xi_{0,4.2}$	-2.0	0	0	-0.15	+0.6
$\rho_{0,300}(\text{g/cc})$	0.53 ⁴	0.971	0.862	1.53(1.71)	1.90
$\rho_{0,77}(\text{g/cc})$	0.56 ⁹	1.01 ⁵	0.91 ⁵	1.64(1.79)	2.09
$\rho_{0,4.2}(\text{g/cc})$	0.56 ⁴	1.01 ⁹	0.92 ⁵	1.63	2.13

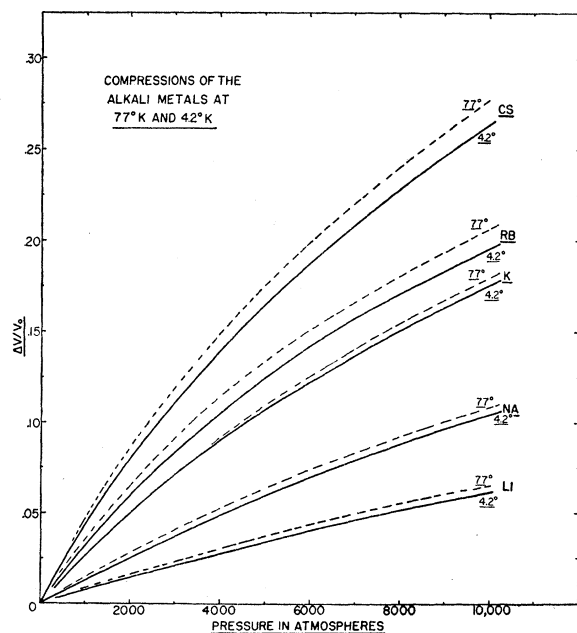


FIG. 4. The P - V relationships to 10 000 atmos for the alkali metals at both 77° and 4.2°K.

10 000 atmos for potassium, rubidium, and cesium, and to be slightly higher for lithium and sodium. This corresponds to an error in the pressure for a fixed $\Delta V/V_0$ of less than five percent. The data for lithium are the least dependable, both because of its low compressibility, and its lack of plasticity at 4.2°K. Final $\Delta V/V_0$ curves were again fitted to Eq. (1) in order to obtain compressibilities at zero pressure, and the resultant values of β_0 and ξ are given in Table I for both 77° and 4.2°K.

The average densities at 77° and 4.2°K as found in these experiments are also given in Table I, together with the room temperature densities.¹⁰ In general, within the limits of error, the density was greater at 4.2° than at 77°K, although as would be expected, the change was quite small. The agreement with the 77°K x-ray

⁹ F. Birch, *J. Geophys. Research* **56**, 227 (1952).

¹⁰ J. D'Ans and E. Lax, *Taschenbuch für Chemiker und Physiker* (Springer-Verlag, Berlin, 1949), p. 211.

data of Simon and Vohsen¹¹ is satisfactory, although their results give slightly lower densities.

An exception for rubidium (noted by the figures in brackets at room temperature and 77°K) deserves special mention, and a rather detailed account of its occurrence. The small and large holders were both filled with rubidium and run at 4.2°K, giving results for $\Delta V/V_{1500}$ and the density which agreed quite well with each other. The next day, the small sample was run at 77°K, giving the density of 1.64 g/cc which is recorded. The large sample and holder were then placed in the press and cooled, after which the pressure was increased slowly to "season" the sample, as was the usual practice. At a sample pressure of a few hundred atmos, a sharp crack was heard, with a coincidental decrease in the sample length of about ten percent. The resulting $\Delta V/V_{1500}$ curve agreed very well with the same curve for the small sample holder, in spite of the difference in density (1.64 to 1.79 g/cc) and consequent change in V_{1500} .

When the holder was warmed to room temperature and its length and weight checked, a sample density of 1.71 g/cc was obtained in place of the correct 1.53 g/cc which was obtained for the small holder. This sort of phenomenon was not found for any other substance, and could not be reproduced in two other runs with different fillings of rubidium. The weight was checked twice, and gave good agreement at 4.2°K with the small holder, so that an error here seems unlikely. Since an error in the measurement of a length at room temperature to a few percent is unlikely, this isolated effect is reported as unexplained, and as being a *possible* new form of rubidium of higher density, stable at room temperature.

Before the sample was destroyed (in the firm belief that the sample holder had changed its characteristics), an attempt was made to measure the melting point of the material in the sample holder. Normally, rubidium melts at about 38°C, while no evidence of melting was found as high as 100°C. A slight decrease of density was found after this heating, which is probably significant. These effects may have some connection with the rather strange, irreversible effects which have been found by Pearson in the thermal expansion of rubidium,¹² and also by others in its specific heat¹³ and electrical resistance.¹⁴

DISCUSSION OF THE RESULTS

The 4.2°K data of Table I were extrapolated to 50 000 atmos and were replotted as molar volumes in Fig. 5 to compare them with the room temperature results given by Bridgman.¹⁵ This extrapolation of over

¹¹ F. Simon and E. Vohsen, *Z. physik. Chem.* **133**, 165 (1928).

¹² F. M. Kelley and W. B. Pearson, *Can. J. Phys.* **33**, 17 (1955).

¹³ T. M. Dauphinee and H. Preston-Thomas (unpublished results). See reference 12.

¹⁴ D. K. C. MacDonald, *Phil. Mag.* **43**, 479 (1952).

¹⁵ P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1949), second impression, p. 178.

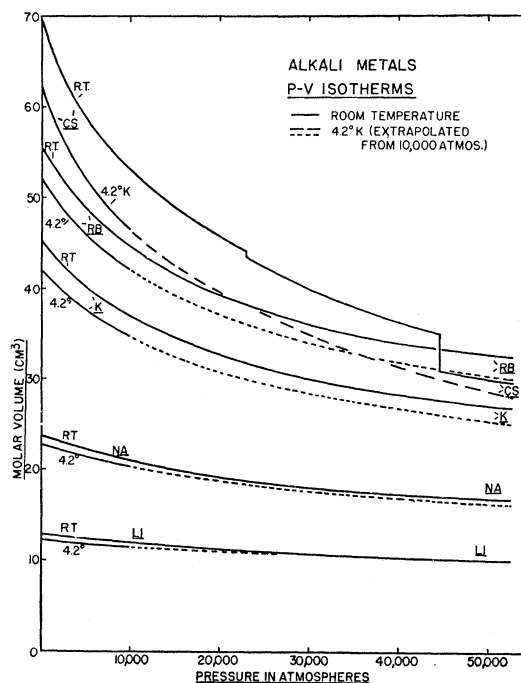


Fig. 5. A comparison of the extrapolated low temperature data for the alkali metals with the data obtained by Bridgman at room temperature.

a factor of five in pressure, made by using Eq. (1), is qualitatively justified by the success which Birch has had in fitting this function to compression data for pressures up to 100 000 atmos.⁹ Birch found that most substances obeyed the simpler form of Eq. (1) given by $\xi=0$, and this is the case for sodium, potassium and rubidium to 10 000 atmos at 4.2°K. If this behavior is to be taken as "normal" (realizing that Eq. (1) is semiempirical in nature), then one can conclude that lithium is too hard ($\xi<0$) with its compressibility dropping off more rapidly than one would expect, and that cesium is too soft ($\xi>0$), with its compressibility dropping off more slowly than "normal" with increase of pressure. While the data for lithium are suspect because of the mechanical strength of the metal, there is no reason to mistrust either the actual data or the extrapolation for cesium.

This "softness" in cesium and a possible explanation can be seen in the curves of Fig. 5. The two transitions for cesium shown in the room temperature curve are due to a change in crystal structure from body centered cubic to face centered cubic at 23 000 atmos, and a presumed change in electronic structure (a 6s electron moving into a 5d orbit) at 45 000 atmos.^{15,16} The crystallographic transformation is too small to be of significance for the extrapolation, but the excess softness of the cesium seems to be connected with a smearing out of the electronic transition, as is seen by the

¹⁶ R. Sternheimer, *Phys. Rev.* **78**, 235 (1950).

coincidence of the room temperature and 4.2° isotherms at 50 000 atmos. The 77°K data indicate that the softening effect also exists at this temperature, and it would be interesting to obtain experimental isotherms at 77°K and higher to try to discover what the behavior of the transition is as a function of both pressure and temperature. Electrical measurements in this same region would also be of interest.

The curves of Fig. 5 give some grounds for speculation on the suspected rubidium transition. First, it is of the same order of magnitude (10 percent) as the cesium transition, and, according to the theoretical work of Sternheimer,¹⁶ there is no *a priori* reason for excluding rubidium from having the same type of transition. If a more stable form of rubidium did exist, with a higher density and a similar $P-V$ curve, it would remove the crossing of the Rb and Cs isotherms which has been commented on by Bridgman,¹⁷ and would place rubidium in its "proper" position at high pressure between potassium and cesium. The grounds for conclusions like these are very vague at the moment, but they do give guidance for the direction of future experimental work. The only other known transitions in the alkali metals are shear-sensitive at low temperatures and occur in lithium¹⁸ and sodium,^{19,20} but since the volume changes are very slight, they would not show up in this work.

The 77°K data were not plotted in Fig. 5, since they tended to coincide with the 4.2°K data at pressures above 5000 atmos. The relative contributions to the pressure of the internal energy and the entropy terms have been discussed by Bridgman,^{21,22} and it is of interest to try to estimate the entropy contribution for relatively low pressures near 80°K, where it should be small. The thermodynamic relationship,

$$TdS = PdV + dU, \quad (2)$$

can be rewritten at constant temperature to give

$$P = T \left(\frac{\partial S}{\partial V} \right)_T - \left(\frac{\partial U}{\partial V} \right)_T \\ = - \left[T \frac{(\partial V / \partial T)_P}{(\partial V / \partial P)_T} + \left(\frac{\partial U}{\partial V} \right)_T \right]. \quad (3)$$

In this expression, the first term vanishes at low temperatures, where the pressure is determined solely by the volume derivative of the internal energy. At higher temperatures, it would be possible to calculate the magnitude of the first term if thermal expansion data as a function of pressure and temperature were

available, but, except for some average values at room temperature, these data do not exist for the alkali metals. Bridgman has estimated that at room temperature $(\partial U / \partial V)_T = 0$ at pressures of a few thousand atmospheres for sodium and one would expect this term to increase rapidly with decreasing volume, while the first term decreases in importance. The indications are, however, that the entropy term is still significant at room temperature for pressures of 50 000 atmos.

There is a second way of estimating the relative importance of this entropy term. The total work done in an isothermal compression can be calculated from the integral of $-PdV$, part of which appears as heat $(-\int TdS)$, and the rest of which appears as a change in the internal energy. In general, the entropy decreases with pressure with the total decrease limited by the third law of thermodynamics, since the entropy can never be less than its value at absolute zero for a system in thermodynamic equilibrium. Thus, if the value for the entropy difference between absolute zero and a given temperature is known for zero pressure $[(S - S_0)_{p=0}]$, then it is possible to calculate the maximum heat which can be evolved in a reversible isothermal compression at that temperature as $Q \leq T(S - S_0)_{p=0}$.

If this calculated heat is large compared with the total work done in the compression, it is highly probable that the entropy contribution to the pressure will be considerable. If, however, the two are comparable, then one would expect that the substance has been compressed to the point where the contribution of its entropy term is negligible, since $T(\partial S / \partial V)_T$, or the thermal expansion, will decrease with pressure, and $(\partial U / \partial V)_T$ will increase.

These quantities have been calculated for the alkali metals and are given in Table II. The values of $T(S - S_0)_{p=0}$ decrease by a factor of about ten from room temperature to 77°K and are negligible at 4.2°K,²³ while (except for the previously discussed softness of cesium) the work done in a compression to 10 000 atmos changes only slightly. Thus, one would expect a relatively large pressure difference between the room temperature and 77° isotherms for a given value of the molar volume, but only a slight change between 77° and 4.2°K. This, in fact, is what is observed. In effect, the molar volumes obtained for 10 000 atmos and 77°K would seem to differ only slightly from those at 10 000 atmos and 4.2°K, so that preliminary experimental work in the higher pressure region can probably be done as profitably at 77° as 4.2°K.

²³ The room temperature values of the entropy were taken from J. D'Ans and E. Lax, *Taschenbuch für Chemiker und Physiker* (Springer-Verlag, Berlin, 1949), pp. 214-256. The low-temperature entropies for lithium and potassium were estimated from the Debye θ 's given in the survey of F. M. Kelley and D. K. C. MacDonald [Can. J. Phys. **31**, 147 (1953)]. The entropy at 77°K for sodium was taken from G. L. Pickard and F. E. Simon [Proc. Phys. Soc. (London) **59**, 1 (1948)], while the rubidium and cesium data are from unpublished results of Dauphinee and Preston-Thomas (reference 13), kindly furnished by Dr. Martin of the National Research Council, Canada.

¹⁷ Reference 15, p. 182.

¹⁸ C. S. Barrett and O. R. Trautz, Trans. Am. Inst. Mining Met. Engrs. **175**, 579 (1948).

¹⁹ C. S. Barrett, Am. Mineralogist **33**, 749 (1948).

²⁰ John Rayne, Phys. Rev. **95**, 1428 (1954).

²¹ Reference 15, p. 172.

²² P. W. Bridgman, Revs. Modern Phys. **7**, 1 (1935).

While speculations as to the change of internal energy with temperature are amusing, the chief value in obtaining experimental results at temperatures where the entropy term is negligible lies in a comparison with theoretical calculations. Very little has been done along these lines which is quantitative enough in nature to allow a check with the experimental results of Table I.²⁴ Some time ago, Bardeen reported detailed calculations for lithium and sodium using the Wigner-Seitz model, while also giving an analysis of Bridgman's room temperature results for all of the alkali metals in terms of a semiempirical model.²⁵ Even though the latter is probably too simple, it is of interest to repeat Bardeen's analysis using the data in Table I and his quoted experimental values for the cohesive energy at absolute zero. Very briefly, Bardeen assumed that the energy of a simple metal is given by

$$E_{\text{coh}} = Ay^3 + By^2 - Cy, \quad (4)$$

where $y = (V_0/V)^{1/3}$, and the first and third terms refer to the energy of the electron in its lowest state, while the second term represents the Fermi energy. By using values for V_0 , β_0 and E_{coh} at absolute zero and zero pressure, it is possible to evaluate the constants A , B , and C , and to compare them with theory.²⁵ This comparison is made in Table III, lines 3 to 7. As would be expected, the agreement is better than was obtained by Bardeen's use of the extrapolated room temperature values. In particular, all the constants now have the expected sign, and vary in the expected direction.

By evaluating $P = -(\partial E/\partial V)_P$, Bardeen derived the following expression from this three-constant energy equation²⁵:

$$PV_0 = y^4(y-1)[2A + 2B/3 + a(y-1)], \quad (5a)$$

or

$$P = y^4(y-1)[3/\beta_0 + A(y-1)/V_0]. \quad (5b)$$

The second term in the brackets in (5b) is quite small (of the order of a few percent at most), so that the shape of the $P-V$ curve is almost uniquely determined

TABLE II. The work done in compressing the alkali metals to 10 000 atmos at 298° and 4°K, compared with the maximum heat which can be produced in an isothermal compression for the same metals at 298° and 77°K. The 4.2°K entropies, and hence the heat developed in a reversible compression at 4.2°K (not shown), are negligibly small.

	Li	Na	K	Rb	Cs
	(All calculations in calories per mole)				
$-\int_{p=0}^{p=10\,000} PdV$					
{ 298°K	90	270	(800)	(1050)	1350
{ 4°K	84	260	770	1020	2000
$T(S-S_0)_{p=0^a}$					
{ 298°K	2000	3640	4530	5000	5900
{ 77°K	100	344	520	726	880

^a See reference 23.

²⁴ F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. 10.

²⁵ J. Bardeen, *J. Chem. Phys.* **6**, 364, 372 (1938); also F. Seitz, reference 24, p. 381-3.

TABLE III. Comparison of the experimental results with theory. a is the lattice constant. The parameters A , B , and C are defined in Eq. (4).

	(Units)	Li	Na	K	Rb	Cs
a (exp)	(10 ⁻⁸ cm)	3.43	4.22	5.20	5.56	5.92
a (th)	(10 ⁻⁸ cm)	3.31	4.25	5.19	5.57	5.90
A (exp)	(10 ¹² ergs/mole)	0.46	1.48	1.60	2.08	1.94
B (exp)	(10 ¹² ergs/mole)	5.76	3.06	1.92	0.72	0.63
B (th)	(10 ¹² ergs/mole)	2.73	1.81	1.39	1.03	0.91
C (exp)	(10 ¹² ergs/mole)	12.90	10.56	8.74	7.68	7.08
C (th)	(10 ¹² ergs/mole)	12.7	9.82	8.00	7.46	6.91
Theoretical pressure						
in atmos for						
$P_{\text{exp}} = 10\,000$ atmos						
		8900	9500	9250	9000	11 400

once β_0 has been specified. The easiest method for comparison here is to compute the theoretical pressure which would correspond to the value of (V_0/V) given by an experimental pressure of 10 000 atmos. This comparison is shown in the last line of Table III. The indications are that all the metals except cesium are less compressible than would be expected from the observed β_0 and theoretical curve, while cesium is too compressible, in agreement with the earlier conclusion. The deviations are outside the limits of experimental error (± 500 atmos) and can be interpreted as meaning that the three constant equation does not provide the correct form of the pressure-volume curve. This is not surprising in view of the approximations involved. In particular, when these calculations are compared with Bardeen's earlier work, the anomaly found for rubidium disappears, although anomalies appear for lithium and cesium.

More recently, Brooks has published an outline of some new and more exact calculations on the alkali metals which are currently being refined.²⁶ The latest, unpublished, values for the lattice constant as given by these calculations²⁷ agrees well with the experimental values at 4.2°K (see lines 1 and 2 in Table III), except for the case of lithium, where the free electron approximation of the theory does not really apply.

CONCLUSIONS

The information about the density and pressure-volume relationships for the five alkali metals near absolute zero is useful chiefly as a basis for comparison with theory, and the check with Brooks' calculations for lattice parameter at absolute zero is reassuring, and gives promise for the future. The existence of an excessive softness for cesium, which seems to be an indication of a smearing out of the large room temperature electronic transition found at high pressure, and the probable existence of another modification of rubidium, ten

²⁶ H. Brooks, *Phys. Rev.* **91**, 1027 (1953).

²⁷ H. Brooks (unpublished results). The author is indebted to Professor Brooks for allowing him to quote these results prior to publication.

percent more dense than normal, would indicate that these data should be extended to pressures of at least 25 000 and preferably 50 000 atmos. This is not quite the formidable task which it would appear to be, since the similarity of the 4.2° and 77°K isotherms above 5000 atmos shows that for pressures above this figure these metals are effectively at absolute zero at liquid nitrogen temperatures. It also would be of interest to obtain isotherms at temperatures between 77°K and room temperature, especially for cesium, so that the effect of temperature on the internal energy could be calculated.

The agreement with Bardeen's theoretical model is acceptable only for sodium, with the deviations, especially in the shape of the $P-V$ curve, outside experi-

mental error. It is to be hoped that more refined calculations will show a better agreement between theory and experiment.

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Surface Adsorption and Migration Energies for KCl^\dagger

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The binding and migration energies for a K^+ ion on a (100) KCl surface are calculated. It is found that the most stable K^+ site is about an interionic lattice spacing above a Cl^- surface ion and the binding energy is 0.68 ev. The activation energy for lateral diffusion is 0.23 ev and the estimated vibration frequencies are 10^{12} sec^{-1} along the surface and 2.8×10^{12} sec^{-1} normal to the surface. From these figures it is shown that the mean path length of the ion is about 2×10^{-4} cm; the binding energy for an adsorbed KCl molecule is found to be about 0.36 ev. This leads to the conclusion that the molecule will travel at most a few lattice spacings before evaporating. Some effects of this on crystal growth and additive coloring are discussed briefly.

I. INTRODUCTION

BASIC to most problems concerning defects in crystals is the energy required to form the defect and the energy required for it to migrate through the crystal.

One defect (although perhaps not usually considered as such) of interest is an adsorbed ion or molecule on a crystal surface. Possibly the simplest materials of importance for which a study of adsorbed particles can be readily carried out are the alkali-halides with a $NaCl$ -type lattice. Typical problems, involving the binding and diffusion energies for these solids are crystal growth from a vapor phase (or, conversely, evaporation) and the detailed mechanism of additive coloring from the metal vapor. The first step, in calculating the total energies involved, is to find the energies for an isolated defect of one kind only. This problem will be considered in the present paper. Thus (although there will be dislocation ledges on the surface¹), the configuration con-

sidered will be a perfectly smooth (100) surface with a single ion or molecule adsorbed. For the numerical results the crystal will be taken as KCl and the adsorbed ion will be considered as K^+ ion. This has the advantage that covalent effects are small, so that the semiempirical Born-Mayer interaction energies may be used.²

In this case, an important problem is that of evaluating the long-range energy contributions. To facilitate such evaluations, use has been made of the convergence transformation developed in a previous paper.³ This is of special value for the lattice polarization energy contribution which is quite long-range in character, although it is convenient to so transform even the short-range overlap repulsive energy. As mentioned in reference 3, this lattice sum transformation permits many non-Coulomb interactions to be handled as easily as those of a Coulombic nature.⁴ A secondary purpose of the present paper is to demonstrate this.

[†] This paper is based on work performed at Cornell University, Ithaca, New York, under a predoctoral Cornell Aeronautical Laboratory Fellowship.

¹ Burton, Cabrera, and Frank, *Trans. Roy. Soc. (London)* **243**, 299 (1951).

² N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), second edition.

³ J. E. Hove and J. A. Krumhansl, *Phys. Rev.* **92**, 569 (1953).

⁴ J. E. Lennard-Jones and B. M. Dent, *Trans. Faraday Soc.* **24**, 92 (1928).