severance is the fact that treatment of $Cl_2BC_2H_4BCl_2$ with aqueous sodium hydroxide generates no hydrogen gas, in contrast to the hydrolysis of diboron tetrachloride which yields hydrogen.

The X-ray diffraction data has thus established the molecular geometry and confirmed the formula of $Cl_2BC_2H_4BCl_2$.

This research was supported in part by the Office of Naval Research (Contract N8 onr 66203) and by the Office of Ordnance Research (Contract DA 11 022 ORD 1554). In addition, financial aid of a Fellowship supported by the Shell Oil Company is gratefully acknowledged. We also wish to thank Dr Peter J. Wheatley for his encouragement and assistance.

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X-ray Study of the Alkali Metals at Low Temperatures

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(*Received* 10 *December* 1955)

Using a spectrometer having provision for cold working and X-raying specimens in a high vacuum at low temperatures, it is found that sodium partially transforms on cooling (below 36° K.) or on deforming (below 51° K.) to a close-packed hexagonal structure with stacking faults, having $a = 3{\cdot}767$, $c = 6{\cdot}154$ Å, $c/a = 1{\cdot}634$ at 5° K., this coexisting with body-centered cubic sodium of $a_0 = 4{\cdot}225$ Å. The body-centered cubic form at 78° K. has $a_0 = 4{\cdot}235$ Å. Severe cold work at 5° K. transforms about half of the material to the hexagonal form; subsequent reversion to cubic starts on heating to 60–75° K. and is completed at 100–110° K., or at lower temperatures if there has been no cold work. Reversion can be aided by cold work at 45–100° K. High purity severely deformed sodium recrystallizes at 98° K.

Patterns of lithium that has been cooled can be interpreted similarly, and indicate a phase of close-packed hexagonal structure with parameters $a = 3{\cdot}111$, $c = 5{\cdot}093$ Å, $c/a = 1{\cdot}637$ (which differ from the earlier, tentative ones). This phase coexists with the body-centered cubic phase of $a_0 = 3{\cdot}491$ Å, at 78° K. Confirming the earlier work, hexagonal lithium is converted to face-centered cubic by cold working.

Potassium, rubidium and cesium retain their body-centered cubic structure after cooling and cold working at 5° K., with $a_0 = 5{\cdot}225$, $5{\cdot}585$, and $6{\cdot}045$ Å respectively at 5° K. and with $a_0 = 5{\cdot}247$, $5{\cdot}605$ and $6{\cdot}067$ Å at 78° K.

Introduction

Microscopic tests involving cooling to 1·2° K. have recently shown that there is a martensitic-type transformation at low temperatures in sodium as well as in lithium, but have failed to reveal any in the other alkali metals (Barrett, 1955). Cold working at low temperature promotes a change of phase in lithium (Barrett, 1947; Barrett & Trautz, 1948) and is also suspected of doing so in sodium, judging by a single diffraction peak observed at 78° K. after deformation at 20·4° K. (Barrett, 1948). Diffraction data on the low-temperature phases are few and are complicated by the presence of stacking faults (Barrett, 1950), so that the crystal structure determinations must be regarded as tentative (Barrett, 1947, 1948).

To learn whether cold work at liquid-helium temperatures can induce transformations in the metals potassium, rubidium and cesium which do not transform on simple cooling, and to determine the low-temperature structures of lithium and sodium more reliably, we have performed a number of experiments using apparatus much improved over that used in the earlier work.

The apparatus, designed by E. Long, L. Meyer, C. B. Walker and the author, consists of a cryostat combined with a precision X-ray spectrometer designed by A. H. Compton (1931) and built by the Société Genèvoise; interchangeable X-ray tubes operated on stabilized circuits; Geiger counter; rate meter and recorder.

Experimental methods

Fig. 1 illustrates the design of the lower part of the cryostat, which held the specimen at the temperature of liquid helium (or nitrogen) during an experiment by conduction through a copper rod, *A*, and through the copper block of the specimen holder, *B*. With rod *A* at 4·2° K. and shield *D* at liquid-nitrogen temperature, the specimen at *C* was at 5·0° K. with an uncertainty of about 0·3° K. Radiation shields bolted to the liquid-helium container and the surrounding liquid-nitrogen container enclosed the specimen except for slits for entrance and exit of the X-ray beam, which was about 1·5 mm. wide by 5 mm. high at the specimen. The beam emerged through a nickel filter from a copper target X-ray tube (or occasionally a cobalt target tube); passed through a 0·015 in. slit, through 0·005 in. plastic (Mylar) windows of the cryostat (*F*, Fig. 1), and through another 0·015 in. slit into a Geiger counter. The slits were approximately 6 in. from the spectrometer axis. The cryostat, evacuated to the range 10^{-6}–10^{-7} mm. Hg, was mounted on the X-ray spectrometer, and turned by a synchronous motor at half the rate of the spectrometer arm carrying the counter; the scale of angles on the recorder charts was checked at intervals by signals from an observer viewing the spectrometer scale. The data were plotted by the Nelson–Riley method which provided linear extrapolation curves except at the lowest angles (near b.c.c. 110, or f.c.c. 111 and 200) and were corrected adequately for small specimen-positioning errors.

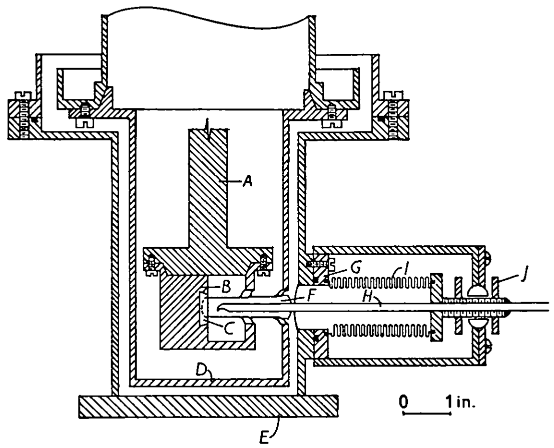

Fig. 1. Lower portion of cryostat. *A*, copper rod leading to liquid-helium chamber; *B*, copper specimen holder; *C*, cavity for specimen; *D*, copper radiation shield bolted to liquid-nitrogen chamber that surrounds helium chamber; *E*, vacuum chamber which sits on X-ray spectrometer; *F*, window for X-ray beam, aligned with windows in *B* and *D*; *G*, ‘O’ ring seal around circular port; *H*, tool for cleaning and working specimen; *I*, sylphon bellows; *J*, ball and socket assembly with adjusting nuts, serving as pivot for tool.

A stainless-steel rod (*H*, Fig. 1) entered the cryostat through a ball-and-socket joint, *J*, and sylphon bellows, *I*, and could be manipulated to cold work the specimen to a depth of a millimeter or so by repeated hammering and rubbing of the surface, meanwhile remaining at the temperature of the specimen. The end of the rod was shaped and sharpened so that if downward strokes were used it would cut off layers from the metal or remove an oxidized surface, in-and-out strokes would cold work the specimen, and upward strokes would rub the surface smooth.

Because of the extreme reactivity of the samples they were loaded into the specimen holder under oil (sometimes in a CO_2 atmosphere) and as rapidly as possible. Trouble with oxidation was not encountered after the cryostat had been evacuated and cooled with liquid nitrogen or liquid helium. When the cryostat was filled to capacity (3 l. nitrogen and 2 l. helium) a temperature of 5° K. could be maintained for about 3½ hr. without refilling.

Materials

Sodium was used in three purities. Samples from stock (Merck) were occasionally used, but most samples were vacuum distilled in pyrex, after which typical spectrographic analyses indicated the following impurities in weight percent: K 0·05; Al 0·001–0·002; Mg $<$ 0·001; Cu $<$ 0·001; Fe $<$ 0·001–0·01; Si $<$ 0·003; Ca $<$ 0·001. Samples of very high purity were supplied by C. T. Ewing, J. A. Grand and P. R. Miller of the Naval Research Laboratory, Washington, D.C., similar to the material used in their work (1952), which had the following spectrochemical analysis: Ag 0·0001–0·001; Li, Si, Ba, Cs, Rb, Ca, Al, Mg, Fe, Cr, Ni, Sn, Pb not detected; the oxide content of the material was less than 0·001% oxygen.

The potassium, vacuum-distilled, had the following spectrochemical analysis: Mg $<$ 0·001, Ca $<$ 0·001, Na approx. 0·5, Cs 0·001, Ti 0·003.

The rubidium was of c.p. grade, from A. D. Mackay, with spectrochemical analysis Mg $<$ 0·001, Fe 0·001, Ca 0·001, Na 0·05, K 0·05, Cs approx. 0·5, Si 0·01, Al 0·001, Cu $<$ 0·001, Ag $<$ 0·001.

The cesium, from Fairmont, had spectrographic analysis Mg $<$ 0·001, Fe $<$ 0·001, Ca $<$ 0·001, Na approx. 0·3, K approx. 1·0.

Results

Structure of sodium at 5° K.

The average value and probable error computed from several determinations of the lattice constant of b.c.c. sodium at 5° K. was 4·225±0·001 Å, assuming the wavelength of Cu $K\alpha$ = 1·54177 Å. The individual experiments leading to this value were as follows. One high-purity sample scraped free of oxide at 175° K. and cooled to 5° K. gave a_0=4·225±0·001 Å, based on 7 good Cu $K\alpha$ reflections. Another high-purity sample scraped at 155° K., cooled and cold worked at 5° K., gave a_0 = 4·223±0·002 Å, based on 4 Co $K\alpha$ reflections (Co $K\alpha$ = 1·79019 Å). A distilled sample scraped near 150° K., cooled to 5° K., gave a_0 = 4·226±0·001 Å, based on 7 reflections; cooled a second time, it gave a_0 = 4·229±0·003 Å, based on 5 reflections; another scraping and working at 200° K. followed by cooling to 5° K. gave a_0=4·224±0·002 Å (based on the 4 highest-angle reflections). The uncertainties in each determination were estimated by the uncertainty in drawing a linear extrapolation line on a Nelson–Riley plot, ignoring the 110 line which was seldom reliable; the average value of these determinations of a_0 agreed with the weighted mean, and was also in agreement with two experiments on sodium from the original stock before distillation in the laboratory, each of which gave a_0=4·225±0·001 Å, one being cooled to 5° K. the other cooled and cold worked at 5° K. after scraping at 78° K.

The results indicate that the effect of the differing purities of the specimens on the lattice dimensions is less than the probable error of the determinations. In view of this, it was possible to compute the ideal angles for each of the b.c.c. lines from the average lattice constant and to use these angles to calibrate each pattern. The diffraction lines that appeared in addition to the b.c.c. lines in runs made at liquid-helium temperature, while few and weak, nevertheless lead convincingly to a structure for the transformation product.

All of the cold worked samples yielded strong diffuse scattering on both sides of the b.c.c. 110 lines, as in Fig. 2, with a peak at spacing d = 3·07 Å. The position of this peak and the intense background scattering near it immediately suggest a close-packed structure with stacking faults, the peak being either f.c.c. 111 or c.p.h. 002.

If the structure were deformation-faulted f.c.c., one would expect a broadened and displaced f.c.c. 200 line; yet no trace of one was seen. The normal position for such a line would have been that corresponding to d = 2·66 Å whereas the diffuse band did not extend this far. A second reason for excluding the f.c.c. solution was the diffuse scattering that was observed in the range between d = 3·07 Å and 3·26 Å. On the basis of deformation-faulted f.c.c. this would have to be ascribed to the tail of the fault-broadened f.c.c. 111 line, as indicated in Patterson's plot (Patterson, 1952) for f.c.c. patterns; but this interpretation would fail to account for the fact that on several runs there was a definite peak in intensity near d=3·23–3·26 Å, as in Fig. 2. The details just mentioned, however, are consistent with a deformation-faulted c.p.h. structure.

The c.p.h. faulted structure that is derived from all lines of the pattern, as well as from the details mentioned above, predicts a 100 line at 3·262 Å that is broadened by fault streaks which extend out from the 100 line on the high-θ side only, a 002 line that is unbroadened, and a 101 line at 2·882 Å that is broadened on both sides, these features being in suitable agreement with observation. It further predicts that lines having hexagonal indices $H-K = 3n$, where n is an integer, will be unbroadened, and the best lines in the patterns are, in fact, found to be of this class rather than the broadened class $H-K = 3n\pm1$. The strongest of the unbroadened hexagonal lines was the line 110, which was well separated from other lines, was observed to be symmetrical, and was in its expected position. If this line were the 220 line of faulted f.c.c. it would have been composed of 6 sharp components together with 6 components broadened and shifted to the high-θ side (Patterson, 1952), whereas if it is the c.p.h. 110 it contains no broadened components and should be unshifted. Similarly, another line of this class that was found on a few runs was the c.p.h. 004; this, too, was found at the calculated position as expected for an unbroadened line, yet if it had been a line from faulted f.c.c. it would have had indices 222 and would have consisted of 6 components broadened and shifted to the low-θ side together with 2 sharp components. It is therefore concluded that no appreciable amount of the cold worked material is f.c.c. in structure.

Table 1 lists the diffraction lines due to the new

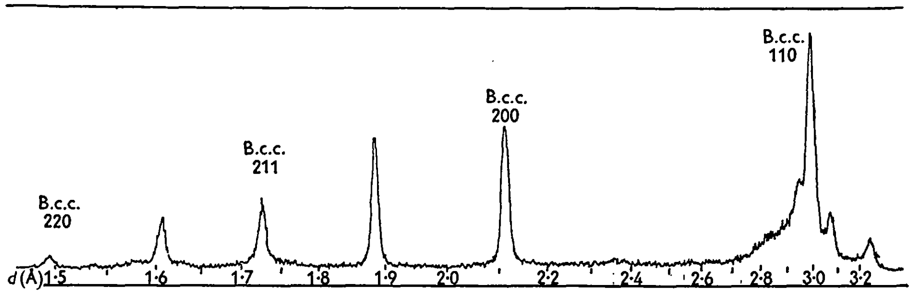

Fig. 2. Portion of diffraction pattern from sodium at 5° K. after cold working. Corrected spacings indicated; Cu $K\alpha$ radiation (filtered).

Table 1. *New reflections from sodium at* 5° K. *after cold working; filtered* Cu $K\alpha$ *radiation*

$I_{\text{obs.}}$	H.c.p. indices	$d_{\text{obs.}}$ (Å)	$d_{\text{calc.}}$ (Å)
s	100	3·25	3·262
s	002*	3·070	3·076
vs	101	2·8–2·9	2·882
s	110*	1·883	1·883
vw	103	1·746	1·736
vw	200	1·629	1·631
m	112*	1·606	1·606
vw	201	1·578	1·576
vw	004*	1·538	1·538
w	210	1·232	1·233
w	211	1·207	1·209
w	114*	1·1916	1·1914

* Reflections that stacking faults should leave unbroadened; the least-squares analysis of these gives a=3·767, c=6·153 Å, c/a=1·633. C.p.h. reflections not observed: 102, 202, 104, 203, 105, 212.

phase in distilled sodium cold worked at 5° K. (The specimen had previously been scraped, cooled to 5° K., and heated to 125° K. before the final cooling.) To find the most probable value of the lattice parameters, the unbroadened lines, marked with asterisks in the table, were used for a least-squares computation, yielding a = 3·767, c = 6·153 Å, c/a = 1·633. The agreement between predicted and observed spacings is satisfactory in spite of the general weakness of the pattern and the partial overlapping of some lines. The extent of the agreement brings to mind Christian's calculations (Christian, 1954) showing that deformation faults in c.p.h. structures do not shift the position of the intensity maxima from their position in unfaulted crystals (a statement, however, that should not be applied to the innermost lines of a c.p.h. powder diffraction pattern). Reflections that were expected and not observed were of the class that should be broadened by faults, thus weakened in maximum intensity, i.e. those for which the indices $H-K = 3n\pm1$. The observed intensities in general are in at least fair agreement with expectations for the proposed structure if account is taken of the effect of faults on the various peak intensities.

Additional runs made with sodium of various purities, cold worked at 5° K. and computed by least squares using the best of the unbroadened lines, confirmed the above conclusions. A high-purity sample agreed well in the 100-002-101 region, but reflections of higher indices were too weak for precision measurement. A distilled sample gave a = 3·767, c = 6·157 Å, computed from the 002, 110, 112 and 114 lines. A sample from stock gave a = 3·766, c = 6·152 Å, using 110, 112, 004 and 114 lines.

Samples cooled and run at 5° K. without cold working were interpreted similarly. These had less diffuse scattering, indicative of less frequent faulting, and c.p.h. lines of lesser intensity. In some runs there were a few peaks that were due to Laue spots and that disappeared when the specimen was rotated independently of the Geiger counter. A distilled specimen provided 10 lines that could be indexed as in Table 1, and a least-squares calculation based on lines 110, 112, and 114 gave a = 3·769, c = 6·155 Å. The same lines from a high-purity specimen likewise gave a = 3·769, c = 6·155 Å.

The difference between the parameters of the cold worked specimens and those that were simply cooled is not believed to be significant when judged on the basis of the uncertainty in individual determinations. Therefore the mean and the probable error were computed from all determinations and are, for 5° K.,

$$a = 3{\cdot}767\pm0{\cdot}001,\ c = 6{\cdot}154\pm0{\cdot}001\ \text{Å},$$
$$c/a = 1{\cdot}634\pm0{\cdot}001\ .$$

The volume of the unit cell containing 2 atoms is 75·625 Å^3 and the calculated density is 1·010 g.cm.$^{-3}$. This may be compared with the b.c.c. unit cell at 5° K., which has a_0 = 4·225 Å, a volume of 75·419 Å^3 and a calculated density 1·012 g.cm.$^{-3}$, a difference in density of 0·2% which is of the order of the experimental uncertainty. The distance of closest approach of atoms changes from 3·659 Å in the b.c.c. structure to 3·767 Å in the c.p.h., a difference of 2·9%, which is a reasonable change to accompany the change in coordination number.

The relative peak heights of broadened and unbroadened lines, and the obvious widening of the 101 and 100 peaks in particular, make it clear that the density of stacking faults is very high in the c.p.h. phase after cold work, perhaps reaching an order of magnitude of 2 faults in 10 planes in some instances. It is less but still appreciable in samples that were simply cooled.

Structure of sodium at 78° K.

The lattice parameter of b.c.c. sodium at liquid-nitrogen temperature (78° K., −195° C.) was determined by the following experiments. Two runs on high-purity sodium that had been cold worked at 5° K. and then raised to 78° K. gave a_0 = 4·228 and 4·236 Å respectively with Co $K\alpha$ radiation taken as of wavelength 1·79019 Å. These contained weak lines from transformed material as well as the b.c.c. Two runs with distilled sodium cooled to 78° K. after scraping at 140° K., free of transformed material, each gave a_0 = 4·238 Å using Cu $K\alpha$ radiation. These determinations lead to the value a_0 = 4·235±0·002Å.

Transformation and reversion characteristic of sodium

The beginning of transformation on cooling, M_s, occurs at 36° K., as was shown metallographically with large-grained unrestrained samples (Barrett, 1955), and the transformation progresses with lowering temperature. The amount transformed by cooling to 5° K. was computed from the areas of the c.p.h. 110 peak and the b.c.c. 200 and 211 peaks, after correcting for the Lorentz, polarization, multiplicity, and structure factors. A high-purity sample previously scraped and annealed at 175° K. was 7% transformed on cooling to 5° K.

As in the earlier studies of lithium and lithium–magnesium alloys, cold working below M_s promotes the transformation, while cold working above the highest temperature at which transformation is induced by strain (M_d) tends to suppress the transformation on subsequent cooling. Thus a sample of sodium from stock, that had been cold worked at 78° K. and immediately cooled to 5° K., contained only about 3% c.p.h. phase. When this sample was then peened and rubbed at 5° K., the c.p.h. phase was immediately increased to approximately 43%. Another sample (high-purity metal) was 30% transformed after cold work at 5° K.

A number of tests were made to determine the M_d temperature. Using high-purity sodium, it was found that peening and rubbing at 204, 78, and 62° K. produced no transformation; the amount of c.p.h. present, if any, must have been less than 2% of the b.c.c. material, but samples cold worked and X-rayed at 50° K. and at 51° K. each gave a small peak at the position expected for the c.p.h. 110, indicating that transformation to the extent of about 3% was induced by deformation at this temperature. For the conditions employed, sodium therefore has M_d at 51° K.

Reversion to the b.c.c. form while a specimen is warming up takes place over a range of temperatures that is dependent on the mechanical history of the specimen. A sample of distilled sodium that had been cooled to 5° K. without cold work began to lose the low-temperature phase abruptly when the temperature on warming passed 45° K., and lines from the phase steadily decreased over a temperature interval of about 45° K. until they finally disappeared at 87° K. The c.p.h. phase persisted to higher temperatures in samples cold worked at helium temperature. In one experiment of this kind there was a slight decrease in peak intensity in warming from 5° K. to 60° K., then a more rapid decline to completion at 100° K.; in another, reversion was rapid from 45° K. to 110° K., and in the experiment of Fig. 3 reversion was rapid in the range 75–110° K. (sodium from stock). There was evidence that reversion was appreciable only while temperatures were increasing, at least at temperatures below the liquid-nitrogen range.

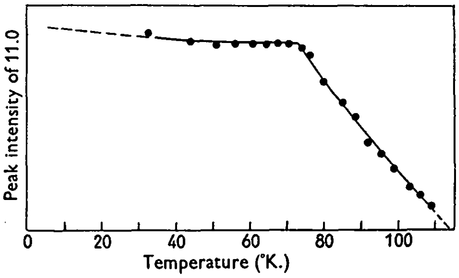

Fig. 3. Diffraction from hexagonal sodium versus temperature during warming after cold work at 5° K.

A test was made to see if hexagonal sodium could be forced to revert to b.c.c. by applying plastic deformation at a temperature too low for reversion on normal heating. A sample containing about 43% c.p.h. as a result of deformation at 5° K. was cold worked vigorously as it warmed through the temperature interval 42–46° K. When tested immediately thereafter, only 6% of the sample remained in the c.p.h. form, whereas warming unaccompanied by deformation would have caused but slight reversion at this temperature (for example, the amount indicated in Fig. 3). In another experiment, cold working at 78° K. removed all trace of the hexagonal 110 reflection, in a sample that had been nearly half hexagonal at 5° K., yet normal heating to this temperature would not have caused complete reversion, nor would storage at this temperature for a period of several days.

The recrystallization temperature of sodium

A test for recrystallization was developed as follows. The Geiger counter was held stationary at the correct angle for a strong reflection, and the specimen chamber was rotated through the normal position at its usual rate. If the specimen was in the cold worked condition a smooth record would be obtained on the chart, but the recorded line would become jagged when recrystallized grains of sufficient size appeared in the specimen during the warm-up period.

Using this method, a high-purity sample of sodium that had been cold worked severely by peening and rubbing at 5° K. and had rested at 78° K. for 18 hr., was warmed at a rate of approximately 1° K. per minute with the counter set for the b.c.c. 200 line. The first appearance of recrystallization was at 98° K. and it was apparent that some fairly large grains were present by the time 105° K. had been reached.

Lithium

The observation that faulted hexagonal sodium has an axial ratio so exactly that of the close packing of spheres led to the suspicion that hexagonal lithium, which likewise forms from b.c.c. on simple cooling and has a high density of faults, might have a similar axial ratio, even though the original tentative analysis of the data had led to different conclusions (Barrett, 1947, 1948; Barrett & Trautz, 1948; Barrett, 1950). Upon comparison of the original charts the similarities with the sodium charts were striking. Too few lines were recorded for the indexing to be as certain as with sodium, but it was immediately apparent that the indices used for sodium would account satisfactorily also for the corresponding lines in the lithium patterns.

A Nelson–Riley extrapolation on five individual runs from the previous series and one from the present instrument gave an average value of the lattice constant of b.c.c. lithium at 78° K. as 3·491±0·002 Å, the individual values being 3·493, 3·496, 3·484, 3·492, 3·489, 3·490 Å. This agrees well with the value given in the 1948 paper when corrected for the difference in wavelength value used, i.e. $3{\cdot}486\times1{\cdot}54177/1{\cdot}5393 = 3{\cdot}492$ Å; though it is larger than the value 3·482 Å expected from the work of other investigators who used lithium of higher purity than the 99·45 and 99·86% used here. Using the b.c.c. lines as an internal standard, corrected spacings for the hexagonal 110 and 112 lines (the only lines that were sufficiently separated, unbroadened and unshifted by faults) were read off from each of the best charts for the specimens cooled to 78° K. without straining. When the lattice parameters were computed from these the following mean values were obtained:

$$a = 3{\cdot}111\pm0{\cdot}001,\ c = 5{\cdot}093\pm0{\cdot}009\ \text{Å},$$
$$c/a = 1{\cdot}637\pm0{\cdot}003\ .$$

The individual a and c parameters were, respectively, 3·111, 5·080; 3·115, 5·098; 3·108, 5·067; 3·111, 5·127 Å. The volume of the unit cell computed from the average parameters is 42·545 Å^3 for b.c.c. and 42·687 Å^3 for the hexagonal phase at 78° K.

It was confirmed in experiments on the present apparatus that cold work at low temperatures produces f.c.c. material at the expense of the c.p.h. and the b.c.c.

Potassium

No transformation was induced in potassium by cooling to 78, 66, or 5° K. The samples were pressed into the sample holder under oil at room temperature, then cooled to 78° K. and scraped clean at that temperature.

No strain-induced transformation resulted when cooling was followed by cold working at 5° K., in spite of several attempts of this kind. The intensities of individual lines of the b.c.c. pattern were about half those of sodium. Both filtered Cu $K\alpha$ and filtered Co $K\alpha$ radiation were used.

The following values for the lattice constant of the b.c.c. phase were obtained by Nelson–Riley extrapolation:

At 78° K.: 5·242, 5·251, 5·247 Å; average value, 5·247±0·002 Å.
At 66±2° K.: 5·236 Å with estimated error of ±0·004 Å.
At 5° K.: 5·223, 5·223, 5·228 Å; average value 5·225±0·002 Å.

Rubidium

No transformation was induced in rubidium by cooling to 5° K., by cold working at 78° K. or at 5° K., or by cold working at 5° K. and warming to 78° K. The sample was pressed into place under oil, cooled to 78° K. and scraped clean at this temperature before making the runs.

The lattice constants of the b.c.c. phase, from Nelson–Riley extrapolation of the data, were as follows:

At 78° K.: 5·605, 5·605 Å; estimated error ±0·001 Å.
At 5° K.: 5·585, 5·585, 5·584 Å; estimated error ±0·001 Å.

Determinations reported earlier are summarized by Kelly & Pearson (1955) who obtained $a_0 = 5{\cdot}607$, 5·609, 5·612 Å for three specimens at 77° K., with estimated accuracies ‘approaching 1 in 5000’.

Cesium

No transformation was induced in cesium by cooling to 5° K., by cold working at 5° K., or by subsequent warming to 78° K. The sample was cast into place under oil in an atmosphere of CO_2 with the holder at about 0° C., and was scraped after cooling in the cryostat to liquid-helium temperature.

The lattice constants of the b.c.c. phase, from Nelson–Riley extrapolation of the data were as follows:

At 78° K.: 6·069, 6·054, 6·066, 6·079, 6·065, 6·068 Å; average, 6·067±0·002 Å.
At 5° K.: 6·046, 6·057, 6·039, 6·040 Å; average 6·045±0·002 Å.

Discussion

This X-ray investigation confirms the conclusions of the earlier metallographic tests (Barrett, 1955) that low-temperature transformations occur in Li and Na, and not in K, Rb, and Cs. It will be noted that cooling induces a partial transformation to c.p.h. in both Li and Na, whereas cold work at low temperatures produces some f.c.c. phase in Li but not in Na and produces no change from the normal b.c.c. structure in K, Rb and Cs. Attempts to induce transformations extended in temperature down to 5° K. in the X-ray work, and to 1·2° K. in the earlier metallographic (simple cooling) experiments; the probability of structure changes at still lower temperatures is negligible, judging by the exceedingly small change with temperature of the free energy of a phase in this temperature range. The results on rubidium also confirm the X-ray tests of Kelly & Pearson (1955), which disclosed no change in crystal structure down to 77° K. (although these authors were led by resistance measurements to suggest that perhaps some electronic transition occurs in some samples of rubidium near 180° K.).

Comparison of the results of the X-ray tests on the alkali metals with observed curves of electrical and thermal conductivity and of thermo-electric force that have been published seems unrewarding at this time for several reasons: these properties are sensitive to impurities, to imperfections such as stacking faults, and to transformations—and transformation temperatures are greatly influenced by inhibiting conditions such as the adherence of a metal to the glass tube in which it is cast. The dependence of M_s upon specimen condition also makes it difficult to correlate these experiments in an exact way with the specific heat anomaly found near 0·8° K. by Rayne (1954), or the anomaly in the Knight shift in the nuclear resonance experiments of Knight (1954), although these anomalies are presumably due at least in part to the transformation.

The free energies of the f.c.c. and c.p.h. phases discussed here would not be expected to differ greatly, and in fact must be highly similar if one is to judge by the occurrence of frequent stacking faults. In sodium, however, the c.p.h. form is definitely predominant in the entire range 51–5° K., both after cooling and after cold working. In lithium, on the other hand, cold work seems to convert c.p.h. to f.c.c., and there does not appear to be any temperature range in which c.p.h. lithium is stable against cold work. It is concluded that none of the alkali metals has the same sequence of phases as strontium, which is reported to have the high-temperature phase, b.c.c., replaced by c.p.h. and then at still lower temperatures by f.c.c., each presumably being stable within its temperature range.

Few c.p.h. metals have c/a ratios as near to the ideal ratio 1·633 for the close packing of spheres as do lithium and sodium. Strontium and calcium with c/a ratios of 1·63 and 1·638 are the nearest; cobalt and magnesium are next with 1·623, and all others are more remote. Axial ratios in the Li–Mg system and a discussion of their theoretical significance are being presented in a separate paper.

It should be pointed out that if the recrystallization temperature is near 100° K. for high-purity sodium, as indicated, neither the formation of hexagonal sodium on cooling nor the reverse transformation on heating is likely to involve movement of high-energy boundaries as in recrystallization. This is confirmed by the absence of indications of isothermal transformation or reversion at liquid-nitrogen temperature and lower. These reversion temperatures are also well below the value $T_0 = Q/41{\cdot}4R = 127°$ K. where Q is the activation energy for diffusion (10,450), a temperature which Nowick (1955) points out divides 'low temperature recovery' from 'high temperature recovery' in most cubic metals. The transitions in this range are thus of the martensitic type, as in lithium.

Much credit for the solution of design and construction problems in the low-temperature apparatus is due to Messrs T. J. O'Donnell and J. Getzholtz. The spectrometer has been furnished by the Physics Department of the University of Chicago. Some of the X-ray data were obtained with the assistance of Y. Baskin, and the spectrochemical analyses were made by Mrs Althea Tompkins. This work was supported in part by Contract N6ori-02004 with the Office of Naval Research.

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Short Communications

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Acta Cryst. (1956). **9**, 677

The structure of anhydrous scandium phosphate.

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(*Received* 29 *May* 1956)

A roughly equimolar mixture of scandium oxide and dilute phosphoric acid, held at 400° C. for periods of a week or more in a hydrothermal bomb, yields anhydrous scandium phosphate in the form of a well crystallized powder. At lower temperatures, a hydrate or mixture of hydrates is produced. For briefer heating periods, the product generally contains unconverted oxide. Powder

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