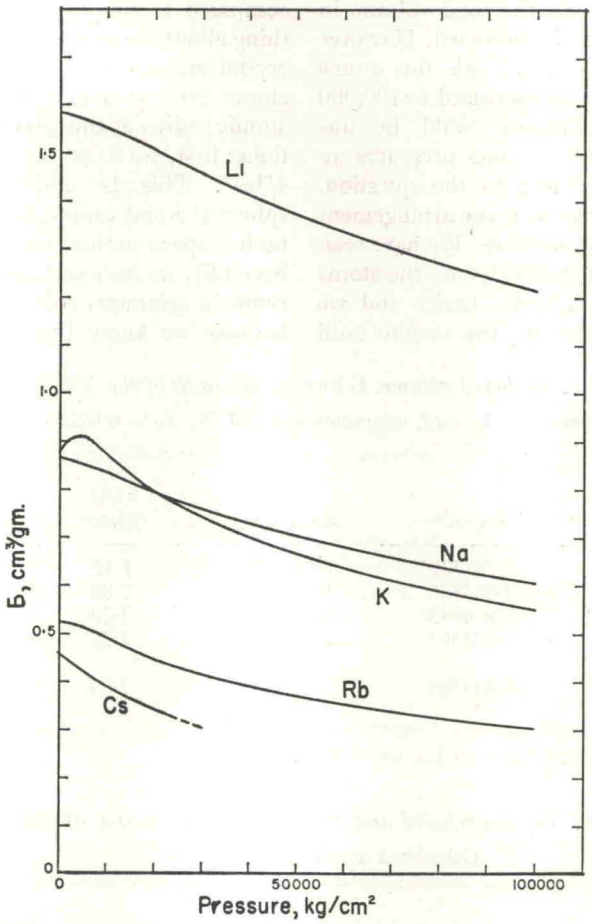

FIG. 4. Pressure vs. excluded volume, Б, for the alkali metals. See text for discussion of potassium curve.

The corresponding formula for a f.c.c. configuration is

$$r = \left(\frac{БM^0}{4\sqrt{(2N_0)}}\right)^{1/3} \tag{17}$$

while for a simple cubic array it is

$$r = \left(\frac{БM^0}{8N_0}\right)^{1/3} \tag{18}$$

We now assume that the associated particles in the solid are large enough so that the end effects are negligible. Using our value of A calculated at the minimum point, we calculate Б at 1 atm. using equation (4). Thus we arrive at the values given in Table 3. As can readily be seen these values are as good as the SLATER[8] or the BRAGG[9] values which are derived from X-ray measurements.

In Fig. 4 is shown a graph of the excluded volume, Б, as a function of the pressure. Whether the maximum in the potassium curve is real, is questionable. However we have already discussed the fact that the potassium values are not good. The excluded volume decreases because as the particles decrease in size the internal volume is released and becomes part of the defect volume. As the pressure increases the defect volume also decreases. This means that the decrease in volume with increase in pressure is generally due to a squeezing out of defect volume. In Table 4 it can be seen that the

excluded volume approaches the total volume in magnitude as the pressure is increased. However the question still remaining is: are the atoms compressed as the pressure is increased to 100,000 kg/cm²? If the atomic radius could be unbiguously calculated at the various pressures an answer might be forthcoming to the question. However the problem is; what is the arrangement of the atoms at increasing pressure? We have seen that we could assume that at one kg/cm², the atoms are arranged in a body-centered lattice and we could get very good values for the atomic radii compared to the X-ray values. We know something about the atoms at one other point. Here the crystal–array symmetry has been disrupted and the atoms exist as 1-mers. We have calculated the atomic radius at this point under several assumptions: first, we have assumed that their volume is $4/3\pi r^3$. This is undoubtedly wrong because spherical atoms cannot be packed in a volume with no free space so that this value should be too high. Secondly, we have calculated the radius as if body-centered symmetry still existed. This also is wrong because we know that this symmetry does not

Table 3. *Excluded volume,* Б *and atomic radii of the alkali metals.*

Pressure = 1 kg/cm², temperature = 300°K, $N_0 = 6{\cdot}02283 \times 10^{23}$

Metal	Б (cm³)	r (Å) (this paper)	r (Å) (Slater)	r (Å) (Bragg)
Lithium	1·585320*	1·43675*	1·45	1·50
Sodium	0·867506	1·75192	1·80	1·77
Potassium	0·876645	2·09854	2·20	2·07
Rubidium	0·524303	2·29461	2·35	2·25
Cesium low pressure form	0·457988	2·54125	2·60	2·37

* Truncated from 20 digits used in calculation.

Table 4. *Total, excluded and defect volumes at* 1 *and* 100,000 *kg/cm².*

Calculated densities at 1 kg/cm²

Metal	Pressure (kg/cm²)	Total volume (v/g)	Excluded volume (Б/gm)	Defect volume (v–Б/g)	Density calculated = $1/v$ at 1 kg/cm²	Density rubber handbook*
Lithium	1	1·86351†	1·58532†	0·27819†	0·537†	0·534 (20°C)
	100,000	1·25508	1·21855	0·03652		
Sodium	1	1·00401	0·86751	0·13650	0·996	0·971 (20°C)
	100,000	0·61963	0·60901	0·01062		
Potassium	1	1·18282	0·87664	0·30617	0·845	0·862 (20°C)
	100,000	0·55689	0·55208	0·00481		
Rubidium	1	0·65739	0·52430	0·13308	1·521	1·532 (20°C)
	100,000	0·30814	0·30594	0·00220		
Cesium	1	0·52446	0·45800	0·06647	1·907	1·8785 (15°C)
	23,000	0·33897	0·33074	0·00824		1·873 (20°C)

* *Handbook of Chemistry and Physics*, 45th ed. (1964–65). The Chemical Rubber Co., Cleveland, Ohio.
† Rounded off from 20 digits.