Polymorphic Transition in LiH†

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The transition pressure at which LiH would be expected to go from a NaCl to a CsCl structure is calculated to be 3050 and 3800 kg/cm² by using two different potential functions. Also the transition pressures are calculated for KCl and RbI to be 22 500 and 5400 kg/cm², respectively, which are in good agreement with the observed values.

A QUANTUM-MECHANICAL calculation of the metallic transition pressure in LiH assuming no initial transition to the denser CsCl structure has been carried out by Behringer.[1] It is possible that this assumption is unwarranted.

The variation of the molecular volume with pressure is given by

$$p=-\frac{\partial E_{\mathrm{mol}}}{\partial v}=-\frac{\partial E_{\mathrm{mol}}}{\partial a}\frac{da}{dv},$$

where a is the nearest Li-H distance and $E_{\mathrm{mol}}=L\varphi$, L being Avogadro's number. The potential function[2] φ is taken as

$$\varphi=A\exp(-a/\rho)-\alpha e^2/a, \tag{1}$$

or as

$$\varphi=A/a^n-\alpha e^2/a, \tag{2}$$

where α is the Madelung constant, ρ is a constant which for saline metal hydrides is equal to $0.46_5\times10^{-8}$ cm,[3,4] n is the Born exponent taken as 5.0 for LiH,[5] and A is found from $(\partial\varphi/\partial a)_{a=a_0}=0$. These equations then lead to

$$p=\frac{\alpha e^2}{3Ka^2}\left[\frac{e^{(a_0-a)/\rho}}{a_0^2}-\frac{1}{a^2}\right] \tag{3}$$

and

$$p=\frac{\alpha e^2}{3Ka^3}\left[\frac{a_0^{n-1}}{a^n}-\frac{1}{a}\right], \tag{4}$$

from Eqs. (1) and (2), respectively. The term K is a structure factor.[6] The values of a_0 for LiH are 2.04 Å for the NaCl structure[7] and 2.12 Å for a CsCl structure. The a_0 for the CsCl case is calculated from the sum of the tabular radii[8] with a coordination number correction for the cation.[9]

TABLE I. Summary of results.

	Transition pressures (kg/cm²)				$\Delta v/v_0$	
	Obs.[a]	Calc.	Calc. by others		Obs.[a]	Calc.
KCl	20 060	22 500[b]	74 000[d]	31 400[e]	0.085	0.080
RbI	4050	5400[b]	22 000[d]		0.035	0.032
LiH	···	3050[b]	···		···	0.0035
		3800[c]				0.0039

[a] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 1 (1948).
[b] From Eq. (3).
[c] From Eq. (4).
[d] R. B. Jacobs, Phys. Rev. **54**, 468 (1938).
[e] See reference 6.

Similar calculations were also extended to KCl and RbI using the appropriate value of $\rho=0.345$ Å. The results are tabulated in Table I.

The value of ρ used is that which gives the best agreement between calculated and observed lattice energies[5] and cannot be expected to express the repulsive energy adequately at high pressures. The agreement between calculated and observed transition pressures is quite good considering the empirical nature of ρ.

If ρ is increased from 0.345 to 0.374 Å in the case of RbI, the transition pressure will be increased to 5860 kg/cm², while for LiH, if $\rho=0.345$ Å, the transition pressure will be decreased to 2400 kg/cm². For an uncertainty of ±0.01 Å in ρ, the transition pressure will vary by ±50 for LiH and ±230 kg/cm² for RbI.

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