PHYSICAL REVIEW B VOLUME 41, NUMBER 11 15 APRIL 1990-I

Equations of state of alkali hydrides at high pressures

José Luís Martins
Department of Chemical Engineering and Materials Science,
University of Minnesota, Minneapolis, Minnesota 55455

(Received 6 November 1989)

The equations of state of the alkali hydrides LiH, NaH, and KH are calculated as a function of pressure for the $B1$ (NaCl) and $B2$ (CsCl) structures using the pseudopotential and local-density approximations. Contributions of the lattice vibrations to the free energy are treated in the quasiharmonic approximation. The results are in good agreement with experiment, in particular when the vibrational effects are included.

I. INTRODUCTION

The structural phase transition of NaH and KH from the low-pressure rocksalt ($B1$) structure to the high-pressure cesium chloride ($B2$) structure has been observed in diamond-anvil-cell high-pressure experiments.[1,2] However, this transition has not been observed[3-5] for LiH and it has been speculated, using an ionic radii argument, that it may not occur.[6]

Due to the low atomic mass of hydrogen the phonon frequencies in the alkali hydrides are high, and the contribution of the ionic zero-point motion to the enthalpy of the crystal is not negligible. These crystals, therefore, provide an interesting test case for evaluating the influence of the ionic vibration in the equation of state and structural phase transitions when light atoms are present.

In this paper pseudopotential local-density calculations for the equation of state and structural phase transition of LiH, NaH, and KH are presented. The vibrational effects are included in the quasiharmonic aproximation using characteristic phonon frequencies calculated with a frozen-phonon technique. The inclusion of the zero-point-motion free energy improves the agreement between the calculated and measured equations of state. Good agreement with experiment is obtained for the pressure of the rocksalt-to-cesium chloride structural phase transition in NaH and KH. The calculations indicate that the transition in LiH will occur only at very high pressures, in the range of 450 to 500 GPa.

II. THEORY

The motion of the electrons and ions can be decoupled with the Born-Oppenheimer approximation.[7] For a fixed ionic configuration, the total energy of the crystal is calculated with the pseudopotential local-density aproximation with a plane-wave basis set.[8] A nonlocal pseudopotential of the form proposed by Kerker[9] and including a correction[10] for the nonlinearity of the exchange and correlation was used for the alkali ions, while the $1/r$ Coulomb potential was used for hydrogen. The Perdew-Zunger parametrization[11] of the Ceperley-Adler[12] values for the exchange and correlation energy of the homogeneous electron gas were used in the calculations. A kinetic energy cutoff of 36 Ry was used in the plane-wave expansion of the wave functions, and the Brillouin-zone integrations were performed with 10 and 20 special k points, respectively, for the rocksalt and the cesium chloride structures.

The clamped-nucleus (CN) aproximation is obtained when the ionic motion is neglected, that is, when we assume that the atoms stay at the minimum-energy configuration. The clamped-nucleus aproximation is valid in the limit of very large nuclear masses M, when the expansion parameter of the Born-Oppenheimer theory, $\lambda = (m_e/M)^{1/4}$, is small. For hydrogen $\lambda = 0.153$, and the relevant energy scale for vibrational effects, $\lambda^2 \times (27.2\ \text{eV}) = 0.64$ eV, is only 1 order of magnitude smaller than the energy scale relevant for chemical bonding, and is therefore far from negligible. For example, in the hydrogen molecule, the vibrational quantum is $\hbar\omega = 0.54$ eV while the binding energy is 4.47 eV, and in LiH the enthalpy of formation is 0.98 eV while the energy of the transversal-optical phonon is $\hbar\omega_{\text{TO}} = 0.07$ eV.

In the harmonic approximation of lattice dynamics, the interatomic potential is quadratic, and therefore the force constants and phonon frequencies are independent of volume.[7] In the harmonic crystal the zero-point motion adds a constant, independent of volume, to the enthalpy of the crystal and therefore does not modify the equation of state $p(V)$.[13] In the quasiharmonic (QH) approximation, the interatomic potentials are anharmonic, but the force constants and phonon frequencies are determined from the second derivatives of the potential with respect to atomic displacements at constant volume. This procedure introduces the anharmonic dependence of phonon frequencies, $\nu_{\mathbf{q}n}(V) = 2\pi\omega_{\mathbf{q}n}(V)$ on the volume and neglects only the smaller phonon-phonon coupling terms. The zero-point-motion (ZPM) contribution to the energy

$$E_{\text{ZPM}}(V) = \sum_{\mathbf{q},n} \tfrac{1}{2}\hbar\omega_{\mathbf{q}n}(V)$$

depends on the volume, and the equation of state calculated in the quasiharmonic aproximation, $E(V) \approx E_0(V) + E_{\text{ZPM}}(V)$, will be different from the equation of state calculated in the clamped-nucleus aproximation, $E(V) \approx E_0(V)$.

The calculation of the full phonon spectrum as a function of volume is computationally too demanding. Therefore, a simplified model will be used here to calculate $E_{\rm ZPM}(V)$. The simplest phonon frequency that can be calculated with a frozen-phonon technique is the transverse-optical (TO) phonon at the center of the Brillouin zone. This is, in general, the lowest frequency optical phonon and therefore we can assume that

$$E_{\rm ZPM}(V) \geq 3N\tfrac{1}{2}\hbar\omega_{\rm TO}, \qquad (1)$$

where N is the number of unit cells in the crystal. This corresponds to using an Einstein model for the optical branch (without the transversal-longitudinal splitting) and neglecting the acoustic phonon modes. The inspection of the phonon density of states for LiH shows that the acoustic branches extend almost up to the TO frequency, and that the longitudinal-transversal splitting is very large.[14,15] The result is that the TO phonon is an average frequency for LiH, and

$$E_{\rm ZPM}(V) \approx 6N\tfrac{1}{2}\hbar\omega_{\rm TO}, \qquad (2)$$

will be a reasonable approximation. For NaH the acoustical branches are flatter,[15] and the zero-point-motion energy will be between the values of Eqs. (1) and (2). Although there is no experimental data on the phonon density of states for KH, it should resemble the one for NaH, and its zero-point-motion energy would still be bracketed by Eqs. (1) and (2).

The total energy in the clamped-nucleus aproximation of the alkali hydrides LiH, NaH, and KH in the rocksalt $E_0^{B1}(V)$ and cesium chloride $E_0^{B2}(V)$ structures was calculated for several values of the volume V. These points were fitted to the first-order Birch[16] and Murnaghan[17] equations of state, from which the dependence of the enthalpy and the volume on pressure was obtained for both the $B1$ and $B2$ structures. The condition for the intersection of the two enthalpy curves , $H_0^{B1}(p_{\rm tr}) = H_0^{B2}(p_{\rm tr})$, gives the pressure $p_{\rm tr}$ for the structural phase transition between the $B1$ and $B2$ structures.

To obtain the quasiharmonic equations of state, the frequency of the transverse-optical phonon was calculated for both structures and for several volumes, and Eqs. (1) and (2) were used to estimate the zero-point-motion energy. The quasiharmonic equations of state were then obtained from the fit of $E_0(V) + E_{\rm ZPM}(V)$ to the first-order Birch[16] and Murnaghan [17] expressions.

III. RESULTS AND DISCUSSION

The calculated zero-pressure properties of the alkali hydrides using the CN approximation and the QH aproximation are compared in Table I with the experimental values. The values shown in the table were obtained with a Birch equation of state interpolation of the data points near the minimum of energy and Eq. (2) was used to estimate the zero-point-motion energy. The lattice constants are in good agreement (a few percent) with experiment, while the values for the enthalpy of formation are less accurate. The disagreement between the two experimental values of the bulk modulus, B_0, and of its pressure derivative, B_0', for NaH indicate that the experimental values for these quantities are unreliable and cannot be used to evaluate the reliability of the calculations.

TABLE I. The calculated equilibrium properties of the alkali hydrides, lattice constant (a_0), bulk modulus (B_0), enthalpy of formation (ΔH), pressure derivative of the bulk modulus (B_0'), transverse-optical-phonon frequency at the Brillouin-zone center ($\nu_{\rm TO}$), and the Grüneisen parameter of that phonon mode ($\gamma_{\rm TO}$), are compared with the experimental values.

		a_0 (a.u.)	B_0 (GPa)	ΔH (eV)	B_0'	$\nu_{\rm TO}$ (THz)	$\gamma_{\rm TO}$
LiH	Theory (CN)	7.37	40	1.11	3.3	20.6	1.5
	Theory (QH)	7.63	31		3.5	17.7	1.6
	Experiment	7.72[a]	33.6[a]	0.92[b]		17.6[c]	
NaH	Theory (CN)	9.02	27	0.53	3.7	16.6	1.8
	Theory (QH)	9.30	20		4.1	13.9	2.2
	Experiment	9.28[d]	19.4 ± 2[d] 14.3 ± 1.5[e]	0.53[f]	4.4 ± 0.5[d] 7.7 ± 1.0[e]	~15[g]	
KH	Theory (CN)	11.03	15	0.33	4.2	14.8	2.0
	Theory (QH)	11.32	12		4.2	12.6	2.2
	Experiment	10.83[e]	15.6 ± 1.5[e]	0.5[h]	4.0 ± 0.5[e]		

[a] See Ref. 3.
[b] F. D. Rossini *et al.*, Circ. Bur. Stand. **500** 431 (1952).
[c] See Ref. 14.
[d] See Ref. 2.
[e] See Ref. 1.
[f] C. R. Fuget and J. F. Masi, N.S.A. **12**, 3720 (1958).
[g] See Ref. 15.
[h] J. Kasarnowsky, Z. Phys. **61**, 263 (1930).

The pressure-versus-volume equation of state for LiH, NaH, and KH are shown in Figs. 1–3. The agreement between experiment and theory is very good for the pressure-versus-volume curves, and for the pressures and volume changes at the structural phase transitions. The effects of zero-point-motion are small but not negligible and their inclusion improves the agreement between theory and experiment. The theoretical curves are Murnaghan equation-of-state interpolation of the calculated values over a wide range of pressures.[18] In the figures, the solid curves correspond to the clamped-nucleus aproximation, while the two dashed curves correspond to using the two different estimations [Eqs. (1) and (2)] of the zero-point-motion in the quasiharmonic aproximation. As discussed previously the two dashed lines should bracket the curve that would be obtained if the full phonon density of states was used to calculate the zero-point-motion energy.

The quasiharmonic aproximation has two effects on the equation-of-state curves. First, the equilibrium volume V_0 is larger, displacing the equation of state towards the bottom of the figure. Second, for a fixed volume, it increases the pressure displacing the equation-of-state curves towards the right of the figure. It is seen from the figure that the first effect dominates, and the quasiharmonic equation of state is softer than the clamped-nucleus equation of state.

Examination of the figures also show that the equation of state is better described in the quasiharmonic aproximation, in particular, there is an improvement in the agreement between theory and experiment for the transition pressures and volume changes associated with the $B1$ (NaCl) to $B2$ (CsCl) structural phase transition.

The equation of state of LiH has been measured[3] up to 4 GPa. The diffraction pattern has been observed up to compressions of $V/V_0 = 0.78$ in an experiment where the pressure has not been measured,[5] and the reflectance spectra has been observed up to 48GPa in an experiment where the volume compression was not measured.[4] Although these experiments did not measure the equation of state, they indicate that the rocksalt-to-cesium chloride structural phase transition does not occur in LiH below 48 GPa. According to our calculations, the phase transition should occur around 450 to 500 GPa at a compression of one-quarter of the original volume. This is

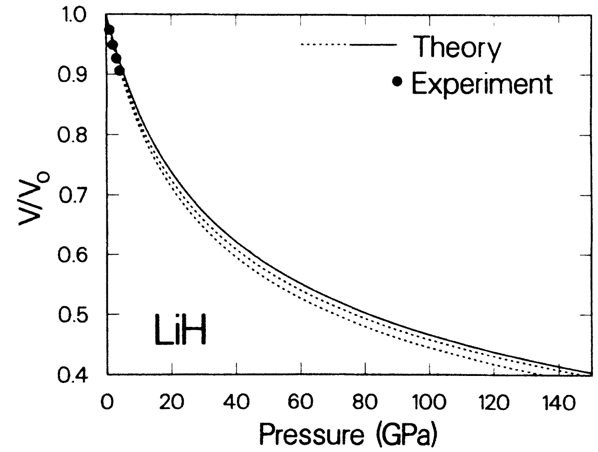

FIG. 1. The calculated equation of state, relative volume vs pressure, for LiH is compared with experiment. The solid curve is calculated with the clamped-nucleus approximation, while the two dashed lines are calculated in the quasiharmonic approximation using the two limits for the zero-point energy given by Eqs. (1) and (2). The solid dots are the experimental values of Ref. 3.

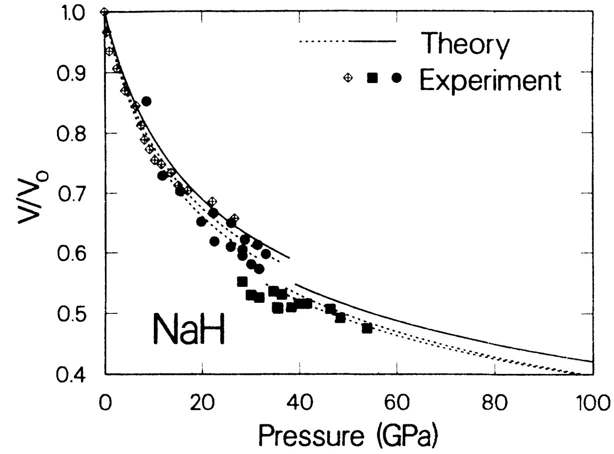

FIG. 2. The calculated equation of state, relative volume vs pressure, for NaH is compared with experiment. The solid curve is calculated with the clamped-nucleus approximation, while the two dashed lines are calculated in the quasiharmonic approximation using the two limits for the zero-point-energy given by Eqs. (1) and (2). The crossed diamonds are the experimental values of Ref. 1 for the rocksalt structure, the solid dots are the experimental values of Ref. 2 for the rocksalt structure, and the squares are the experimental values of Ref. 2 for the cesium chloride structure.

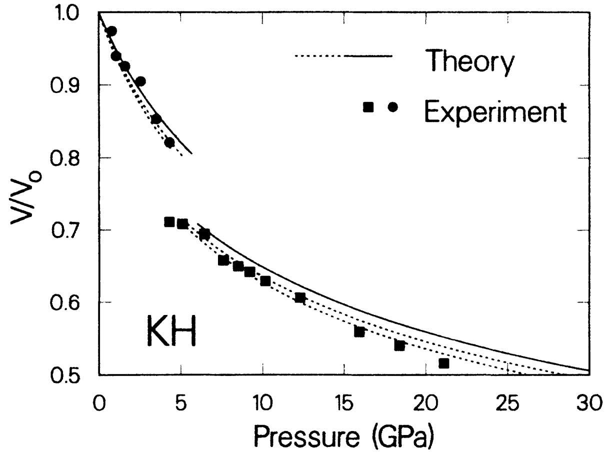

FIG. 3. The calculated equation of state, relative volume vs pressure, for KH is compared with experiment. The solid curve is calculated with the clamped-nucleus approximation, while the two dashed lines are calculated in the quasiharmonic approximation using the two limits for the zero-point energy given by Eqs. (1) and (2). The solid dots are the experimental values of Ref. 1 for the rocksalt structure, and the squares are the experimental values of Ref. 1 for the cesium chloride structure.

roughly twice the value of the highest pressures currently achieved in diamond-anvil cells. The caveat of this type of calculation is that the enthalpy was not calculated for other possible structures of LiH and therefore one cannot rule out the possibility of other structural phase transitions appearing at lower pressures.

The equation of state of NaH has been measured twice[1,2] in recent years using diamond-anvil cells up to 28 and 58 GPa. The rocksalt-to-cesium chloride structural phase transition was observed in the second experiment[2] at $p_{\mathrm{tr}} = 29.3 \pm 0.9$ GPa and a volume fraction $V/V_0 = 0.61 \pm 0.01$. The equation of state of KH was measured up to 24 GPa in a diamond-anvil cell,[1] with a phase transition observed at about 4 GPa. In those experiments the pressure was measured with the ruby fluorescence technique and the lattice constant determined by energy dispersive x-ray diffraction. We show in Figs. 2 and 3 the experimental data points (omitting for the sake of clarity the error bars) and compare them to the calculated equation of state.

The behavior of alkali hydrides under pressure is very similar to the alkali halides. The pressure for the $B1$ to $B2$ phase transition is strongly dependent on the cation, but is almost insensitive to the anion (hydrogen or halide). Majewski and Vogl[19] presented an interesting explanation for this effect, which is also observed in other I-VII and II-VI crystals.[20] They approximated the transition pressure by

$$p_{\mathrm{tr}} \approx -[E^{B1}(V_0^{B1}) - E^{B2}(V_0^{B2})]/(V_0^{B1} - V_0^{B2}), \qquad (3)$$

where V_0 is the equilibrium volume of the specified crystal structure. The assumption behind their approximation is that the $E(V)$ curves have the same shape for all crystal structures, but are displaced relatively to each other. They argued then that both the numerator and denominator increase with increasing anion atomic number Z, while the numerator decreases and the denominator increases with increasing Z, with the net result that the transition pressure is insensitive to the anion species and decreases with increasing cation Z. The calculations for NaH and KH show that the transition pressure estimated with Eq. (3) differ by ~25% from the correct values, but nevertheless the trend for the transition pressures seems to be correctly given by that equation. The case for LiH is more delicate because within the precision of our calculations the zero-pressure densities of the $B1$ and $B2$ are the same, leading to a prediction of a very large or even negative transition pressure for LiH. This was noticed by Bashkin et al.[6] who used an ionic radii model to predict that the zero-pressure volume of the $B2$ phase should be larger than the zero-pressure volume of the $B1$ phase. They concluded that the $B1$ phase being the more compact does not have any tendency to transform into the $B2$ phase under pressure (for all other alkali hydrides this ionic radii theory predicts that the $B1$ phase is less compact at zero pressure and that therefore the transition should occur). In the present calculations the compressibility of the $B1$ and $B2$ phases are not identical, and the transformation is predicted to occur at very high pressures in the 450 to 500 GPa range.

IV. CONCLUSION

The calculations of the isothermal equation of state of the alkali hydrides show that the inclusion of the zero-point-motion effect in the quasiharmonic approximation has small but not negligible effects, which improve the agreement of the calculations with experiment. As it is clearly shown in Figs. 1–3 the $E(V)$ curves and the transition pressures and volume changes associated with the $B1$ to $B2$ structural phase transition are well described by the *ab initio* calculations.

This work was supported by a computer time grant from the Minnesota Supercomputer Institute.

---

[1] H. D. Hochheimer, K. Strössner, W. Hönle, B. Baranowsky, and F. Filipek, Z. Phys. Chem. **143**, 139 (1985).

[2] S. J. Duclos, Y. K. Vohra, A. Ruoff, S. Filipek, and B. Baranowski, Phys. Rev. B **36**, 7664 (1987).

[3] D. R. Stephens and E. M. Lilley, J. Appl. Phys. **39**, 177 (1968).

[4] Y. Kondo and K. Asaumi, J. Phys. Soc. Jpn. **57**, 367 (1988).

[5] B. Olinger and P. M. Halleck, Appl. Phys. Lett. **24**, 536 (1974); F. F. Voronov, V. A. Goncharova, and O. V. Stalgorova, Fiz. Tverd. Tela **8**, 1643 (1966).

[6] I. O. Bashkin, T. N. Dymova, and E. G. Ponyatovskii, Phys. Status Solidi B **100**, 87 (1980).

[7] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954).

[8] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

[9] G. P. Kerker, J. Phys. C **13**, L189 (1980).

[10] S. G. Louie, S. Froyen, and M. L. Cohen Phys. Rev. B **26** 1738 (1982).

[11] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[12] D. M. Ceperley and B. J. Adler, Phys. Rev. Lett. **45**, 566 (1980).

[13] By similar arguments it can be shown that the thermal expansion parameter of an harmonic crystal is null.

[14] M. G. Zemlianov, E. G. Brovman, N. A. Chernoplekov, and Iu. L. Shitikov, in *Inelastic Scattering of Neutrons* (IAEA, Vienna, 1965), Vol. 2, p. 431. A. S. Filler and E. Burnstein, Bull. Am. Phys. Soc. **5**, 198 (1960); D. J. Montgomery and J. R. Hardy, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, Oxford, 1965), p. 491.

[15] A. D. B. Woods, B. N. Brockhouse, M. Sakamoto, and R. N. Sinclair, in *Inelastic Scattering of Neutrons* (IAEA, Vienna, 1961), p. 487.

[16] F. Birch, J. Geophys. Res. **83**,1257 (1978).

[17] F. D. Murnaghan, Proc. Nat. Acad. Sci. USA **30**, 244 (1944).

[18] The coefficients of these curves are not the same as those from Table I, which correspond to a fit of the equation of state in a narrow range around zero pressure.

[19] J. A. Majewski and P. Vogl, Phys. Rev. Lett. **57**, 1366 (1986).

[20] C. W. F. T. Pistorius, Prog. Solid State Chem. **11**, 1 (1976).