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Lattice Properties of Alkali Halides

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From an appropriate form of the interaction potential energy function the values of the cohesive energy, atomization energy, Grüneisen parameter, Anderson–Grüneisen parameter, and pressure and temperature derivatives of elastic constants have been computed for twenty alkali halide crystals. In the present calculation, the contribution of the van der Waals term has been taken into account, but the uncertainty in the values of the van der Waals constant does not hamper the results. The electron affinities of the halogen atoms have also been evaluated. In most cases the agreement between calculated and experimental values is satisfactory.

Introduction

The interaction potential energy function plays an important role in solid-state physics. Several empirical and semi-empirical potential energy functions are available, but they have been severely discredited by Dobbs & Jones (1957) and Thakur (1973). Several theoretical potential energy functions are also available, but they are inadequate for accurately reproducing experimental results. Thakur (1973) has suggested a new form of interaction potential energy function, which is well tested for alkaline earth chalcogenides (Thakur, 1974; Thakur & Pandey, 1975). In the present work, this new potential energy function (Thakur, 1973) has been utilized to calculate the properties of alkali halide crystals.

For better results the van der Waals term has also been taken with the new potential (Thakur, 1973), which is given by

$$\varphi(r) = -\frac{\alpha e^2}{r} - \frac{C}{r^6} + B \log\left[1 + \frac{p}{r^4}\right] \qquad (1)$$

where α is the Madelung constant, e the electronic charge, $\varphi(r)$ the potential energy of an ion pair interacting with each other and with the rest of the lattice, C the coefficient of the van der Waals term, r the internuclear separation, and B and p are potential parameters. The potential parameters have been computed by the method of Kachhava & Saxena (1963).

Cohesive energy

The cohesive energy of alkali halide crystals has been calculated by a method which takes the van der Waals term into account but does not use the values of the van der Waals coefficient (C) which are highly uncertain. The application of crystal stability and compressibility conditions to (1) yields

$$\varphi(r_0) = -x - \frac{C}{r_0^6} + B \log\left[1 + \frac{p}{r_0^4}\right] \qquad (2)$$

$$0 = x + \frac{6C}{r_0^6} - \frac{4Bp}{(r_0^4+p)}\,. \qquad (3)$$

and

$$3fr_0^2 = -2x - \frac{42\,C}{r_0^6} + \frac{4Bp(5r_0^4+p)}{(r_0^4+p)^2} \qquad (4)$$

where $x = (\alpha e^2/r_0)$, $f = (3kr_0/\beta)$, k is the crystal parameter, β the compressibility and r_0 the equilibrium internuclear distance in the lattice.

Eliminating B and C from (2)–(4) one gets

$$6\varphi(r_0) = \frac{\left[3(r_0^4+p)^2 \log\left(1 + \frac{p}{r_0^4}\right) - 2p(r_0^4+p)\right](3fr_0^2 - 5x)}{8p(r_0^4+2p)} + 5x\,. \qquad (5)$$

Thus if $\varphi(r_0)$ is known, the cohesive energy per mole, W, is computed from

$$W = -[N\varphi(r_0) + \varepsilon] \qquad (6)$$

where N is Avogadro's number and ε is the zero point energy.

The values of the cohesive energy computed from (5) and (6) are listed in Table 1 with the experimental values.

Atomization energy

The atomization energy of ionic crystals is of interest since it gives a better idea of the stability than the cohesive energy. Only a limited attempt has been made by Sanderson (1967) to calculate the atomization energy. Recently Thakur (1974) has made a successful attempt to compute the atomization energy of alkaline earth oxides from the potential energy function with the relation

$$E_a = W + E - I \qquad (7)$$

where E_a is the atomization energy of oxide XO, E is the electron affinity of O^{2-} ions and I is the ionization energy to produce X^{2+} ions.

The computed values of the atomization energy from (6) and (7) are reported in Table 1 with the experimental values of Sanderson (1967).

Electron affinity

The values of the electron affinity of halogen atoms for different crystals have been calculated from (7) with the experimental values of E_a and are listed in Table 1 with the experimental values of Berry & Reimann (1963) and Schmidt–Böcking & Bethge (1973).

Grüneisen parameter (γ) and Anderson–Grüneisen parameter (δ)

The Grüneisen parameter (γ) is given by

$$\gamma = -\frac{r_0\varphi'''(r_0)}{6\varphi''(r_0)} \tag{8}$$

where $\varphi''(r)$ and $\varphi'''(r)$ refer to the second and third derivatives of $\varphi(r)$, respectively.

The calculated values of γ from (1) and (8) are given in Table 2. The values of δ computed from the second

Table 1. *Theoretical and experimental values of the cohesive energy, atomization energy and electron affinity of alkali halide crystals* (kJ mol^{-1})

Crystals	W (calc) equation (6)	W (exp)	E_a (calc) equation (7)	E_a (exp) Sanderson	E (calc) equation (7)	E (calc) average	E (exp)
LiF	1011·17	1004·58	820·69	849·39	355·78		
NaF	906·22	892·87	739·17	757·30	345·21		327·1*
KF	802·48	792·03	712·83	732·20	346·45	343·78	
RbF	767·82	759·81	693·65	711·28	344·71		332·4†
CsF	732·66	726·76	686·53	686·18	327·73		
LiCl	827·69	843·08	663·26	690·36	380·23		
NaCl	767·16	772·78	626·16	640·15	367·12		353·1*
KCl	688·94	684·50	625·34	648·52	376·31	369·30	
RbCl	675·13	684·50	627·01	635·97	362·09		348·1†
CsCl	644·26	660·24	624·18	631·78	360·73		
LiBr	780·35	801·24	558·03	623·42	360·63		
NaBr	729·80	735·97	530·91	581·58	345·91		295·2*
KBr	669·67	677·81	548·18	594·13	341·19	344·71	
RbBr	644·70	661·07	538·70	585·76	342·31		324·3†
CsBr	625·45	637·22	547·48	585·76	333·52		
LiI	720·17	753·12	512·32	539·74	337·13		
NaI	679·17	695·80	494·75	502·08	317·04		309·7*
KI	630·89	639·32	523·87	523·00	308·84	315·54	
RbI	611·46	626·34	519·92	518·82	308·61		295·4†
CsI	590·15	608·35	526·65	523·00	306·06		

* Schmidt–Böcking & Bethge (1973). † Berry & Reimann (1963).

Table 2. *Theoretical and experimental values of* γ, δ, $(\mathrm{d}B/\mathrm{d}P)_T$ *and* $[\mathrm{d}(\log\beta)/\mathrm{d}T]_P$ *of alkali halide crystals*

	γ		δ		$(\mathrm{d}B/\mathrm{d}P)_T$		$[\mathrm{d}(\log\beta)/\mathrm{d}T]_P \times 10^4$ deg^{-1}	
Crystals	equation (8)	exp*	calc	exp*	equation (9)	exp†	equation (10)	exp†
LiF	1·59	1·99	3·18	3·98	4·18	–	3·24	–
NaF	1·46	1·57	2·92	3·14	3·92	8·7	3·15	2·0
KF	1·57	1·48	3·14	2·96	4·14	6·3	3·46	1·0
RbF	1·59	1·28	3·18	2·56	4·18	4·6	3·18	–
CsF	1·60	–	3·20	–	4·20	4·7	–	–
LiCl	1·54	1·54	3·68	3·08	4·68	6·3	4·07	7·0
NaCl	1·66	1·43	3·32	2·86	4·32	5·3	3·98	6·2
KCl	1·79	1·34	3·58	2·68	4·58	5·4	4·11	3·5
RbCl	1·85	1·25	3·70	2·50	4·70	2·8	4·00	4·0
CsCl	1·99	1·97	3·98	3·94	4·98	–	6·69	–
LiBr	1·67	1·70	3·34	3·40	4·34	6·1	5·01	8·0
NaBr	1·68	1·55	3·36	3·10	4·36	5·3	4·33	4·1
KBr	1·84	1·43	3·68	2·86	4·68	4·8	4·42	4·8
RbBr	1·90	1·27	3·80	2·54	4·80	2·9	4·33	3·8
CsBr	1·83	–	3·66	–	4·66	–	–	–
LiI	1·62	–	3·24	–	4·24	5·3	5·73	5·0
NaI	1·72	1·59	3·44	3·18	4·44	4·5	4·98	1·0
KI	1·92	1·58	3·84	3·16	4·84	4·0	5·18	3·4
RbI	1·90	1·50	3·80	3·00	4·80	2·3	4·90	4·6
CsI	2·01	–	4·02	–	5·02	2·0	–	–

* Born & Huang (1956). † Mathur & Singh (1968).

relationship of Chang (1967) connecting γ and δ are also listed, as well as the experimental values of γ and δ (Born & Huang, 1956).

Variation of bulk modulus with pressure and compressibility with temperature

The application of thermodynamic principles to crystal stability and compressibility conditions of an interaction potential energy function yields

$$\left[\frac{\mathrm{d}B}{\mathrm{d}P}\right]_T = 1 - \frac{r_0^3\beta}{27V}\varphi'''(r_0) \tag{9}$$

where B is the isothermal bulk modulus of elasticity, P the pressure and V the molar volume. The values of $(\mathrm{d}B/\mathrm{d}P)_T$ calculated from (1) and (9) are reported in Table 2 with the experimental values of Mathur & Singh (1968).

From the thermodynamic relations of Chang (1967) it can be shown that

$$\left[\frac{\mathrm{d}(\log\beta)}{\mathrm{d}T}\right]_P = \alpha_v\left[\left(\frac{\mathrm{d}B}{\mathrm{d}P}\right)_T - 1\right] \tag{10}$$

where α_v is the volume coefficient of thermal expansion.

The values of $[\mathrm{d}(\log\beta)/\mathrm{d}T]_P$ calculated from (1), (9) and (10) are reported in Table 2, with the experimental values of Mathur & Singh (1968).

In the calculation the values of r_e and k_e have been taken from Lide, Cahill & Gold (1964), those of r_0 and β from Jain, Saxena & Pandey (1974), and those of α_v from Saxena & Kachhava (1966).

Discussion

It is found that the theoretical values of W, E_a, E, γ, δ, $(\mathrm{d}B/\mathrm{d}P)_T$ and $[\mathrm{d}(\log\beta)/\mathrm{d}T]_P$ agree well with the experimental values. The discrepancies may be explained by the fact that the new function is very sensitive to r; a small uncertainty in the value of r_0 may bring a large change in the values of the calculated parameters. The present method of calculating W removes the effect of uncertainty involved in the values of the van der Waals constant. The agreement between calculated and experimental values of E_a and E confirms that the method suggested for alkaline earth oxides only (Thakur, 1974) can be extended to alkali halide crystals. The successful computation of the temperature and pressure derivatives of the elastic constants suggests a correlation between the ultrasonic method and the interaction potential method for calculating the various properties of the solid.

The agreement for the Grüneisen parameter and Anderson–Grüneisen parameter, which makes use of the third order derivative of the potential function, is a rigorous test of an interaction potential function.

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