Effect of the non–Coulombic Long-Range Forces and the Next Nearest Neighbor Interactions on the Lattice Properties of Alkali Halide Crystals

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The effect of the non–Coulombic long-range forces and the next nearest neighbor interactions on the lattice properties of alkali halide crystals is calculated using the Electron Gas model and Electron Gas Drude model. It is found that these often neglected interactions make changes in the lattice properties that are indeed small, but by no means negligible.

Introduction

Most of the theoretical methods used for the determination of the structures and cohesive energies of the ionic crystal lattices assume that the total interaction energy is the sum of the Coulombic long-range interactions of all the ions and the short-range repulsive interactions between the nearest neighbor ion pairs only[1]. These mothods thus ignore the non–Coulombic long-range interactions (mainly van der Waals forces) and the short-range repulsions between the ion pairs other than the nearest ones, assuming that the contribution of these interactions is negligible. The Born–Mayer type theory is the classical and still the most widely used, example of this kind. More recent theoretical works continued to adopt the same limitation[2,3].

To be sure, the magnitudes of the interactions thus omitted are small compared with those of the included interactions. But it is far from clear whether their contribution to the lattice properties would be equally negligible, for the lattices are formed through a delicate balance between the long-range attractive forces and the short-range repulsive interactions of almost equal magnitudes. Additional interactions, though small in magnitude, can still cause a significant change in this balance. Yet, the assumption that the contribution of the omitted interactions to the lattice properties is negligible has never been tested directly, by evaluating explicitly the effect of in-

cluding these interactions. For example, Cohen and Gordon[4] evaluated the effect of including only the next nearest neighbor short-range interactions. And although the recent work by Mulhausen and Gordon[5] included the many body effects, they neglected both of the above interactions, giving only some estimation of the effect of the non–Coulombic long-range forces. Moreover, the use by these authors of the scaling parameters of Waldman and Gordon[6] made it difficult to understand the effect of each type of the neglected interaction.

In the present paper, we check the above assumption by calculating the effects of the non–Coulombic long-range interactions and the next nearest neighbor interactios separately on the lattice properties of the alkali halide crystals. The results show that these effects are small, but by no means negligible.

Theory and Calculation

Standard Calculations. In the standard clculations with the above mentioned assumption, the alkali halide crystal energy is given as the sum of the short-range repulsive interactions and the Coulombic Madelung energy:

$$U_{s_1}(R) = a_M/R + 6V_s(R)_{M^+X^-} \cdot \tag{1}$$

Here a_M is the Madelung constant and is -1.747558 for the NaCl(fcc) structure of the alkali halide crystals. $V_s(R)_{M^+X^-}$

Table 1. Equilibrium Bond Distances of Alkali Halide Crystals (in Å)

| System | Crystal Energies Using | | | | Experimental Values (0°K)[b] |
	Eq. (1)[a]	Eq. (2)[a]	Eq. (3)[a]	Eq. (4)[a]	
LiF	1.93	2.01(+0.08)[c]	2.07+(0.14)[d]	2.12(+0.19)[e]	2.014
LiCl	2.47	2.48(+0.01)	2.58(+0.11)	2.59(+0.12)	2.570
LiBr	2.65	2.62(−0.03)	2.77(+0.12)	2.72(+0.07)	2.751
NaF	2.3	2.32(0.00)	2.40(+0.08)	2.41(+0.09)	2.327
NaCl	2.86	2.82(−0.04)	2.93(+0.07)	2.91(+0.05)	2.820
NaBr	3.03	2.97(−0.06)	3.13(+0.10)	3.06(+0.03)	2.989
KF	2.60	2.58(−0.02)	2.67(+0.07)	2.66(+0.06)	2.674
KCl	3.05	3.01(−0.04)	3.11(+0.06)	3.08(+0.03)	3.147
KBr	3.19	3.15(−0.04)	3.29(+0.10)	3.23(+0.04)	3.298
RbF	2.76	2.78(+0.02)	2.85(+0.09)	2.85(+0.09)	2.815
RbCl	3.18	3.14(−0.04)	3.26(+0.08)	3.26(+0.08)	3.291
RbBr	3.32	3.27(−0.05)	3.41(+0.09)	3.41(+0.09)	3.445

[a](1): short range, nearest neighbor. (2): (1) + non–Coulombic long range, nearest neighbor. (3) : (1) + long range, nearest neighbor. (4) : (1) + both [b]Ref. 2. [c](2)–(1). [d](3)–(1). [e](4)–(1).

Effects of Long-Range and Next Neighbor Interactions

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is the short-range potential at the interionic distance R between alkali ion (M⁺) and the halide ion (X⁻).

The Effect of the Next Nearest Neighbor Interactions. In the above structure of the alkali halide crystals there are additional ion–pair interactions of $M^+ - M^+$ and $X^- - X^-$ pairs with the interionic distances of $\sqrt{2}$ times the closest $M^+ - X^-$ distances. To obtain more accurate cohesive energy these "next nearest neighbor" pair interactions have to be included in the above equation. Thus we have, instead of Eq. (1),

$$U_{s_2}(R) = \alpha_M/R + 6V_s(R)_{M^+X^-} + 6V_s(\sqrt{2}R)_{M^+M^+}$$
$$+ 6V_s(\sqrt{2}R)_{X^-X^-} \cdot \qquad (2)$$

The difference between U_{s_2} and U_{s_1} represents the contribution of the next nearest neighbor interactions.

The Effect of the Non–Coulombic Long-range Interactions. To include the effect of the non–Coulombic long-range interactions we have to replace the short-range potential V_s (R) in Eqs. (1) and (2) by a new potential V (R) which includes the non–Coulombic long-range interactions. Thus the alkali halide crystal energy becomes

$$U_1(R) = \alpha_M/R + 6V(R)_{M^+X^-} \qquad (3)$$

if only the nearest neighbor interactions are included, and

$$U_2(R) = \alpha_M/R + 6V(R)_{M^+X^-} + 6V(\sqrt{2}R)_{M^+M^+}$$
$$+ 6V(\sqrt{2}R)_{X^-X^-} \qquad (4)$$

when the next nearest neighbor pairs are taken into consideration. The effect of the non–Coulombic long-range interaction, then, is obtained through the differences between U_1 and U_{s_1} or U_2 and U_{s_2}.

Calculation. The potentials to be used in Eqs. (1)–(4) are calculated by the Electron Gas Model[7] for V_s and by the Electron Gas Drude Model[8] for V. (The procedures for the calculation are described in the original references.) These models are known to yield reasonably accurate potential values for the interactions between closed-shell atoms and ions. Each of the Crystal energies thus obtained – U_{s_1}, U_{s_2}, U_1, U_2 – is used in determining the equilibrium bond distances (R_e) and the binding energies (D_e). We also calculated the bulk moduli (B) of the alkali halide crystals for each of the four crystal energies using the following formula:

Table 2. Binding Energies of Alkali Halide Crystals (in kcal/mole)

System	(1)[a]	(2)[a]	(3)[a]	(4)[a]	Experimental 0°K[b](298°K)[c]
LiF	260.1	257.9(−2.2)	246.0(−14.1)	242.9(−17.2)	246.8(242.3)
LiCl	206.0	214.7(+8.7)	197.2(−8.8)	203.2(−2.8)	201.8(198.9)
LiBr	192.3	204.6(+12.3)	184.6(−7.7)	194.5(+2.2)	(189.8)
NaF	222.2	224.8(+2.6)	214.5(−7.7)	215.7(−6.5)	217.9(214.4)
NaCl	182.6	189.4(+6.8)	177.2(−5.4)	182.3(−0.3)	185.3(182.6)
NaBr	172.5	181.0(+8.5)	167.2(−5.3)	174.1(+1.6)	174.3(173.6)
KF	204.0	206.6(+2.6)	197.6(−6.4)	200.2(−3.8)	194.5(189.9)
KCl	175.2	180.6(+5.4)	172.3(−2.9)	175.9(+0.7)	169.5(165.8)
KBr	167.2	174.0(+6.8)	163.7(−3.5)	169.6(+2.4)	159.3(158.5)
RbF	194.0	196.4(+2.4)	187.8(−6.2)	190.7(−3.3)	(181.3)
RbCl	169.4	173.8(+4.4)	165.4(−4.0)	169.7(+0.3)	(159.3)
RbBr	161.9	167.6(+5.7)	158.8(−3.1)	164.3(+2.4)	(152.6)

[a]See Table 1. [b]Values extrapolated to 0°K by L. Brewer: C. Kittel, *Introduction to Solid State Physics*, 3rd edn. (Wiley, New York, 1966), p. 98. [c]Ref. 1

Table 3. Bulk Moduli of Alkali Halide Crystals (in dyn/cm² × 10¹¹)

System	(1)[a]	(2)[a]	(3)[a]	(4)[a]	Exp.[b]
LiF	9.34	9.69(+0.35)	8.81(−0.53)	9.06(−0.28)	8.67
LiCl	3.62	4.57(+0.95)	3.25(−0.37)	3.87(+0.25)	3.54
LiBr	2.75	3.79(+1.04)	2.33(−0.42)	3.02(+0.27)	—
NaF	5.36	5.78(+0.42)	6.36(+1.00)	6.65(+1.29)	5.14
NaCl	2.43	2.96(+0.53)	2.51(+0.08)	2.85(+0.42)	2.85
NaBr	2.19	2.58(+0.39)	1.35(−0.84)	1.63(−0.56)	2.29
KF	3.90	4.29(+0.39)	3.86(−0.04)	4.41(+0.51)	3.42
KCl	2.27	2.63(+0.36)	2.35(+0.08)	2.50(+0.23)	2.02
KBr	2.09	2.33(+0.24)	1.54(−0.55)	1.32(−0.77)	1.80
RbF	3.44	3.73(+0.29)	3.46(+0.02)	3.67(+0.23)	—
RbCl	2.09	2.34(+0.25)	1.46(−0.63)	3.01(+0.92)	1.85
RbBr	1.80	2.22(+0.42)	1.14(−0.66)	1.90(+0.10)	1.59

[a]See Table 1. [b]Ref. 2 and Ref. 4.

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$$B = \frac{1}{18R_e}\left(\frac{d^3U(R)}{dR^2}\right)_{R=R_e} \qquad (5)$$

In determining both the minima and the second derivatives of the potentials, the least squares method was used.

Results and Discussion

The values of R_e, D_e and B calculated using the method discussed above are presented in Tables 1-3. The changes made in these values by the inclusion of the next nearest neighbor short–range interaction (2), of the nearest neighbor non–Coulombic long–range force (3), and of both (4), are noted in parentheses. We also provide the available experimental values.

The results show that the inclusion of these often neglected interactions indeed makes small changes in the bond distance and the binding energy of the alkali halide crystals. They are of the order of, but usually less than, 0.1 Å for the bond distances and 10 Kcal/mole for the binding energies. But these are by no means "negligible" numbers. In particular, the values of the bulk modulus, which is far more sensitive to the crystal energy than the other two properties, show much larger variations. The changes do not bring any significant improvement in comparision with the exprimental values. This comparision may not be meaningful, however, because the Electron Gas model crystal interaction energy that we have chosen for U_{s_i} in Eq. (1) contains other sources of error, possibly of similar magnitudes. What is more important are the magnitudes of the changes. They show that we can not neglect these interactions in any treatment of the alkali halide crystals that aims at an accuracy better than the above sort.

The changes also show some consistent trends. For most of the systems the next nearest neighbor short-range forces shorten the bond distances and increase the binding energies. On the other hand, the non-Coulombic long-range interactions cause the bond distances to increase thereby decreasing the binding energies. The effect of these interactions on the bulk moduli fails to show such a clear trend.

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Photophysical Properties of 1,3–Dimethylnaphtho[1,2–e]uracil

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The solvent change and salt do not affect the fluorescence quantum yield of 1,3–dimethylnaphtho[1,2–e]uracil indicating the considerable energy gap between the lowest singlet (π, π^*) and (n, π^*) states in the compound. The results are consistent with the strong quenching of fluorescence by ethyl iodide. Fluorescence quantum yield is nearly independent of temperature, probably due to the relatively inefficient internal conversion. Unusual spectral difference is observed in isopentane and ethanol at 77K. The temperature dependence of emission in isopentane and in ethanol suggests that the increase of charge transfer character by the conformational change in isopentane leads to the structureless and red–shifted fluorescence, while in ethanol the decrease of the charge transfer character by the hydrogen bonding interaction results in the structured and blue–shifted fluorescence along with phosphorescence at the low temperature. Temperature dependence of emission in poly (methylmethacrylate) matrix indicates that $T_1 \rightarrow S_0$ radiationless decay is an important process responsible for the strong temperature dependence of phosphorescence.

Introduction

Many photophysical and photochemical studies for the heterocyclic compounds have served to emphasize the important role of the (n, π^*) state in the efficiente radiationless decay compared with parent aromatic hydrocarbons.[1-3] It is now strongly suspected that an increase in Frank–Condon vibrational overlap factor by the vibronic interaction between the lowest energy (π, π^*) and (n, π^*) singlet states leads to an efficient $S_1 \rightarrow S_0$ internal conversion for many nitrogen heterocyclic and aromatic carbonyl compounds in the condensed phase.[4]

We previously observed that (n, π^*) state gives significant