

## Theory of binding of ionic crystals: Application to alkali-halide and alkaline-earth-dihalide crystals\*

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The ion-pair interaction potentials obtained by using the model presented in our previous paper are applied to some ionic crystals. The calculated lattice properties of alkali-halide and alkaline-earth-dihalide crystals agree quite well with experimental data. The polymorphic transitions of alkali-halide crystals at high pressures are also successfully described by the calculations.

### I. INTRODUCTION

Recently, we developed a model to calculate the interactions between closed-shell atoms, ions, and molecules.<sup>1</sup> In this model, the electron density of the system is taken as the sum of the two separate densities, and the non-Coulombic part of the interaction potential is calculated using the electron-gas energy expression from this density. Using this model, we have calculated interaction potentials for many ion pairs.<sup>2</sup> The potentials thus obtained have been used in the treatment of ionic compounds such as alkali-halide and alkaline-earth-dihalide molecules and they have predicted quite accurate molecular properties. In this paper we treat ionic crystals using these ion pair potentials.

We make the following three basic assumptions in addition to the assumptions already introduced in the calculation of the pair potentials: (a) the systems are made of free ions; (b) the interactions of ions are pairwise additive, i.e., the total interaction is the sum of all the pair interactions, neglecting the many-body interactions<sup>3</sup>:

$$V = \sum_{\substack{a,b \\ \text{(pairs)}}} V^{ab}(R_{ab}) \quad ; \quad (1)$$

(c) the short-range interactions are restricted to the nearest-neighbor pairs only:

$$V = \sum_{\substack{a,b \\ \text{(all} \\ \text{pairs)}}} \frac{n_a n_b}{R_{ab}} + \sum'_{\substack{a,b \\ \text{(nearest-} \\ \text{neighbor} \\ \text{pairs)}}} V_S^{ab}(R_{ab}) \quad , \quad (2)$$

where  $n_a$  and  $n_b$  are the ionic charges and the prime in the summation indicates the summation over the nearest-neighbor pairs only.

This summation can then be carried out using the standard techniques<sup>4</sup> and the total interaction energy, which is called the crystal energy, is expressed in terms of the nearest-neighbor distance  $R$ ,

$$V(R) = -\alpha_M/R + n_S V_S(R) \quad . \quad (3)$$

Here,  $\alpha_M$  is called the Madelung constant and  $n_S$  is the number of nearest neighbors. From  $V(R)$ , we can obtain the equilibrium internuclear distances, the dissociation energies to the free ions, and other properties of the ionic crystals.

So far, there have been two types of nonexperimental approaches to treat the alkali-halide crystals since the early decades of this century. The classical approach, which was founded by Madelung<sup>5</sup> and by Born,<sup>6</sup> was formulated by Born and Mayer.<sup>7</sup> The crystal energy was expressed in a form as Eq. (3) using an exponential term,  $Ae^{-aR}$  for  $V_S(R)$ , with the parameters  $A$  and  $a$  to be determined empirically. This approach has been used extensively<sup>8</sup> to describe many properties of the alkali-halide crystals, often with the modifications to include the van der Waals forces. The *a priori* quantum-mechanical approach, on the other hand, was initiated by Hylleraas<sup>9</sup> and by Landshoff.<sup>10</sup> It was firmly formulated later by Löwdin,<sup>11</sup> who expressed the cohesive energy, or the crystal energy at the equilibrium, in three separate contributions, the electrostatic, the exchange, and the overlap parts. He also developed numerical methods to evaluate these terms using the free-ion Hartree-Fock wave functions. This approach has also been used often<sup>12</sup> to obtain the lattice properties of the alkali-halide crystals, also usually in modified forms, where the free-ion wave functions are scaled, using a parameter to be treated by the variation principle, to account for the deformations of the electron densities of the free ions in crystals.<sup>13</sup> Both the approaches have been fairly successful in their predictions of the crystal-lattice properties. Our simple method is related to both of these approaches.

Our treatment is parallel to the Born-Mayer theory in its form of Eq. (3). However, since it uses the *a priori* short-range pair potential  $V_S(R)$  instead of the empirically obtained exponential term, our approach is purely theoretical and it eliminates some difficulties which the empirical Born-Mayer theory often encounters. By fitting the parameters in  $V_S(R)$  to experimental data, the Born-Mayer approach depends heavily on these experimental

quantities. Although the predictions of other quantities agree with the independent experimental determinations fairly well, this good agreement is usually restricted to the properties near equilibrium, and furthermore, the simple exponential term cannot represent the true  $V_s(R)$  over a wide range of distances. Our purely theoretical  $V_s(R)$  is free from these limitations and we can treat properties such as the effects of high pressure and the properties in the alternative crystal structures with equal accuracies.

The common feature of our method and of Löwdin's, on the other hand, is more of a physical nature. Both methods, in their original formulations, treat the crystal as the aggregates of free ions and then describe these free ions with their Hartree-Fock wave functions, which has recently been proved to be quite accurate in describing the experimentally determined electron distributions in the crystal, NaCl, for example.<sup>14</sup> However, using the electron-gas energy expression in terms of local-electron density, our approach is considerably simpler than Löwdin's. The separation of the crystal energy into the different contributions is much more transparent in our formulation than in Löwdin's, where somewhat ambiguous separation into the exchange and the overlap contributions is present, which then makes the physical interpretation of the terms rather difficult. Our derivation of the final expression for the crystal energy is also quite straightforward once the two principal assumptions, i. e., the electron-gas approximation and the free-ion assumption, are made, whereas Löwdin's approach introduces approximations of different degrees at various stages. The error introduced into our model by using the electron-gas energy expression should be less than 10% as can be seen from our recent study of the electron-gas approximation<sup>15</sup> and this is not serious considering the other errors introduced by using the free-ion assumption and by the other assumptions made in Löwdin's approach. As can be seen in Table I, our predictions from the simple treatment are of about the same accuracy as Löwdin's more complicated approach for the crystals he treated. Our results are often better than his, especially for the values of the bulk modulus, although later modifications of Löwdin's method by scaling the free-ion wave functions have improved his results.

In Sec. II, we present our predictions of the equilibrium lattice properties of the alkali-halide crystals in NaCl structure and compare them with the experimental data. In Sec. III, we treat the alkali-halide crystals in CsCl structure and discuss the polymorphic transition at high pressure. We have treated some alkaline-earth-dihalide crystals using the same method and the results are given in Sec. IV.

## II. EQUILIBRIUM PROPERTIES OF ALKALI-HALIDE CRYSTALS IN NaCl STRUCTURE

We have carried out the crystal calculations on 12 alkali-halide crystals, using Eq. (3) with the ionic pair short-range potentials reported in Ref. 2. In this section we assume the known NaCl structure (fcc) for all the alkali halides treated,<sup>16</sup> (see Sec. III for calculations on the CsCl structure). The Madelung constant  $\alpha_M$  and the number of the nearest neighbors  $n_s$  are known for many crystal structures.<sup>17</sup> For the NaCl structure,  $\alpha_M = 1.747558$  and  $n_s = 6$ . Therefore, the crystal energy is given as

$$V^{\text{NaCl}}(R) = -1.747558/R + 6V_s(R) \quad (4)$$

From this we have obtained the nearest-neighbor separations  $R_e$  and the cohesive energies  $D_e$  for these crystals. Another interesting equilibrium property of the crystal is the bulk modulus, which is defined by<sup>18</sup>

$$B = \left( v \frac{d^2V(R)}{dv^2} \right)_{R=R_e}, \quad (5)$$

where  $v$  is the volume occupied by a molecule. Using  $v = 2R^3$  for the NaCl structure, we obtain

$$B = \frac{1}{18R_e} \left( \frac{d^2V(R)}{dR^2} \right)_{R=R_e}. \quad (6)$$

Our results of  $R_e$ ,  $D_e$ , and  $B$  are given in Table I with the experimental determinations and also with the predictions by Löwdin's approach.<sup>12</sup> The agreement of our results with the experimental values is generally good.  $R_e$  values lie within 0.1 Å of the experimental results, while  $D_e$  values are usually, with a few exceptions, within 10 kcal/mole of the experimental values extrapolated to 0 °K. The experimental values of the bulk modulus vary considerably with temperature and the 0 °K extrapolation has been done only for some compounds. Our values agree rather well with these extrapolated values. In the cases where 0 °K values are not available, our values are generally higher than the room-temperature values by about 10–20%, which is roughly the amount of increase given by the 0 °K extrapolation. Since the bulk modulus is a measure of the second derivative of the potential with respect to the distance, which depends very heavily on the short-range potential, the kind of agreement we have found here provides an independent support for our short-range potential at distances near the crystal  $R_e$ . Our potential is expected to be more accurate at shorter distances, where the long-range forces are not important. Therefore, we may conclude that our  $V_s(R)$  is a good representation of the true short range potential over the entire range of the

TABLE I. Equilibrium properties of some alkali-halide crystals in NaCl structure.

	$R_e(\text{\AA})$			$D_e(\text{kcal/mole})$			$B(10^{11} \text{ dyn/cm}^2)$			Expt. <sup>a</sup> (298 °K)						
	Present	Calc.	Expt. 0 °K <sup>c</sup>	Present	Calc.	Expt. 0 °K <sup>d</sup> (298 °K) <sup>e</sup>	Present	Calc.	Löwdin <sup>b</sup>							
LiF	1.93	2.40 <sup>e</sup>	(2.02) <sup>f</sup>	2.014	260.2	199.5 <sup>e</sup>	(242) <sup>f</sup>	246.8	(242) <sup>f</sup>	246.8	(242.3)	9.3 ± 0.1	2.5 <sup>e</sup>	(5.9) <sup>f</sup>	7.2 <sup>g</sup>	(6.5) <sup>h</sup>
LiCl	2.47	2.69 <sup>e</sup>		2.570	206.1	187.7 <sup>e</sup>		201.8		201.8	(198.9)	3.6 ± 0.1	2.38 <sup>e</sup>			(3.5) <sup>i</sup>
LiBr	2.66			2.751	192.3						(189.8)	2.70 ± 0.05				(2.57) <sup>j</sup>
NaF	2.31	2.29	(2.43) <sup>j</sup>	2.317	222.3	205.1	(210.2) <sup>j</sup>	217.9		217.9	(214.4)	5.3 ± 0.2	2.70	(4.1) <sup>j</sup>	5.17 <sup>k</sup>	(4.86) <sup>l</sup>
NaCl	2.86	2.75		2.820	182.7	183.2		185.3		185.3	(182.6)	2.42 ± 0.03	2.17		2.74 <sup>l</sup>	(2.47) <sup>m</sup>
NaBr	3.04			2.989	172.6			174.3		174.3	(173.6)	2.19 ± 0.03				(1.94) <sup>n</sup>
KF	2.60			2.674	204.1			194.5		194.5	(189.8)	3.8 ± 0.1				(3.19) <sup>o</sup>
KCl	3.05	3.09		3.147	175.3	166.9		169.5		169.5	(165.8)	2.25 ± 0.05	1.67		1.97 <sup>h</sup>	(1.78) <sup>h</sup>
KBr	3.20			3.298	167.2			159.3		159.3	(158.5)	1.7 ± 0.5 <sup>m</sup>			1.79 <sup>g</sup>	(1.54) <sup>g</sup>
RbF	2.77			2.815	194.0						(181.3)	3.3 ± 0.1			(2.7) <sup>i</sup>	
RbCl	3.19			3.291	169.4						(159.3)	1.9 ± 0.5 <sup>m</sup>			(1.6) <sup>i</sup>	
RbBr	3.32			3.445	161.9						(152.6)	1.9 ± 0.5 <sup>m</sup>			(1.38) <sup>i</sup>	

<sup>a</sup>Experimental values are obtained from the measurement of elastic constants  $C_{11}$  and  $C_{12}$  using the relation  $B = \frac{1}{3}(C_{11} + 2C_{12})$ . See, e.g., Ref. 18, Chap. 4.

<sup>b</sup>Reference 11. Values in parentheses are obtained using the scaled wave functions of free ions, Ref. 12.

<sup>c</sup>Data compiled by Tosi, Ref. 4, p. 44.

<sup>d</sup>Extrapolated to 0 °K by L. Brewer, quoted by Kittel, Ref. 18, p. 98.

<sup>e</sup>Large errors may be due to the inaccurate Hartree-Fock wave functions used for  $\text{Li}^+$  ion.

<sup>f</sup>Mansikka and Bystrand, Ref. 12.

<sup>g</sup>Data compiled by C. Kittel, in *Phonons*, edited by R. W. H. Stevenson (Oliver and Boyd, London, 1966).

<sup>h</sup>Data compiled by H. B. Huntington, *Solid State Phys.* **7**, 213 (1958).

<sup>i</sup>Data compiled by K. S. Aleksandrov and T. V. Ryzhova, *Sov. Phys.-Crystallogr.* **6**, 228 (1961).

<sup>j</sup>Vallin *et al.*, Ref. 12.

<sup>k</sup>J. Vallin, K. Marklund, J. O. Sikström, and O. Beckman, *Ark. Fys.* **32**, 515 (1966).

<sup>l</sup>R. Q. Fugate and D. E. Schuele, *J. Phys. Chem. Solids* **27**, 493 (1966).

<sup>m</sup>Large uncertainties are due to the large oscillations of the crystal energies at distances near the equilibrium separation.

TABLE II. Comparison of some alkali-halide crystals in two different structures.

	NaCl structure (fcc)		CsCl structure (bcc)	
	$R_e$ (a. u.)	$D_e$ (a. u.)	$R_e$ (a. u.)	$D_e$ (a. u.)
LiF	3.65	0.4146	3.83	0.4007
LiCl	4.66	0.3284	4.87	0.3187
LiBr	5.02	0.3064	5.24	0.2978
NaF	4.37	0.3541	4.56	0.3449
NaCl	5.40	0.2910	5.61	0.2847
NaBr	5.74	0.2749	5.92	0.2690
KF	4.92	0.3251	5.07	0.3197
KCl	5.77	0.2793	5.95	0.2753
KBr	6.04	0.2664	6.22	0.2626
RbF	5.23	0.3091	5.37	0.3050
RbCl	6.03	0.2699	6.18	0.2668
RbBr	6.27	0.2580	6.48	0.2549

distances of interest. However, the good accuracy of our short-range potential at relatively large distances, despite its failure to account for the long range forces, should not be overemphasized, because it is partly due to the absence of the induction forces in crystals because of the crystal symmetry.

The error of our predictions should be assigned to various sources such as the imperfect descriptions of the dispersion forces, the next-nearest-neighbor interactions and the nonadditivity of the total interaction energy, in addition to the assumptions already made in the calculations of  $V_S(R)$ . Although our predictions of the ion pairs which constitute the next-nearest neighbors are now available,<sup>2</sup> the distances corresponding to the next-nearest-neighbor pairs are rather large, and the predictions of our  $V_S(R)$  can not be trusted at such large distances because of their failure to account the dispersion forces properly. The imperfect description of the dispersion force in the nearest-neighbor pair interactions also is a significant source of error. Therefore, it appears to be more logical to improve the treatment of the dispersion forces first before introducing the next-nearest-neighbor interactions. This will require a considerable amount of work beyond the present stage of the theory and therefore we stay within the limit of the nearest-neighbor approximation in this paper, as was stated at the beginning.

The accuracy of Löwdin's quantum-mechanical predictions of  $R_e$  and  $D_e$  values, especially after the scaling of the free ion wave functions, is about as good as our results. However, his predictions of the bulk modulus are generally poorer than ours, which then suggests that his prediction of the crystal energy becomes poorer than ours as one moves from the equilibrium distances. There is no obvi-

ous physical reason for this larger error in his treatment. It is possible that his approximate formulation of the final expression for the cohesive energy and the numerical techniques actually used involve larger errors than the error we have introduced by the electron gas approximation. It has to be also emphasized again that our method involves a much simpler procedure than Löwdin's.

### III. CsCl STRUCTURE; POLYMORPHIC TRANSITION AT HIGH PRESSURES

We assumed in Sec. II the NaCl structure in the calculation of all the alkali-halide crystals reported in Table I. However, it is known that the heavier alkali-halide crystals containing the  $\text{Cs}^+$  ion exist in a more closely packed CsCl structure (bcc).<sup>19</sup> Due to the lack of the Hartree-Fock wave function of the  $\text{Cs}^+$  ion, we are not able to treat the actual cesium halide crystals, which are known to exist in the CsCl structure. However, we have repeated the calculations in the CsCl structure for the alkali-halide crystals treated in Sec. II, where the crystal energy is represented by<sup>17</sup>

$$V^{\text{CsCl}}(R) = -1.76268/R + 8V_S(R) \quad (7)$$

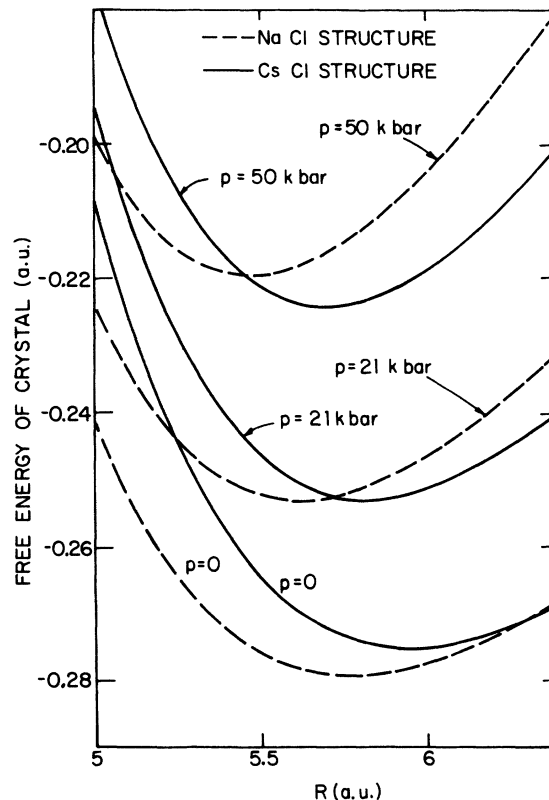


FIG. 1. KCl crystal energy in two different structures at different pressures.

TABLE III. Transition pressures of some alkali-halide crystals from the NaCl structure to the CsCl structure (in kbar).

	Present work	Semiempirical <sup>a</sup>	Experimental values <sup>b</sup>					
			I	II	III	IV	V	VI
LiF	550	310	>100 <sup>c</sup>					
LiCl	160	110	>100					
LiBr	110	105	>100					
NaF	142	200	>100		>200			16.8 <sup>d</sup>
NaCl	49	74	20		>250	29	>50	18 <sup>e</sup>
NaBr	35	53	>100					
KF	51	88	>100	20				
KCl	21	36	20	19.7	20	20	20	
KBr	17.0	29	19	18.1		18.5		
RbF	30	68	>100	11.8				
RbCl	14.0	31	5.5	4.9				5.4 <sup>f</sup>
RbBr	12.4	25	5.0	4.5				

<sup>a</sup>Reference 8a, p. 162.

<sup>b</sup>Experimental values are taken from the following sources: I: compiled by Born and Huang in Ref. 8a, p. 162; II: Ref. 23a; III: Ref. 23b; IV: shock-induced transitions by D. B. Larson, Ref. 23b, p. 459; V: E. A. Perez-Albuerné and H. G. Drickamer, *J. Chem. Phys.* **43**, 1381 (1965); VI: miscellaneous data.

<sup>c</sup>>100" means that no transitions were found below 100 kbar.

<sup>d</sup>C. W. F. Pistorius and L. J. Admiraal, *Nature* **201**, 1321 (1964).

<sup>e</sup>V. V. Evdokimova and L. F. Vershchagin, *Sov. Phys.-Solid State* **4**, 1438 (1962).

<sup>f</sup>L. H. Adams and B. L. Davis, *Proc. Nat. Acad. Sci.* **48**, 982 (1962).

The results of this calculation are given in Table II. For all the systems treated, the NaCl structure has been found to be of lower energy than the CsCl structure, which agrees with the experimental fact that all the alkali halides treated here exist at low pressures in the NaCl structure. The results also show the expected trend, the energy difference between the two structures being rather large for the lighter alkali halides and becoming smaller as one goes to the heavier species such as RbCl and RbBr. However, without performing the cesium halide crystal calculations to find them in the CsCl structure, we still can not conclude that our theory predicts the correct structure for the cesium halide crystals. The Born-Mayer semiempirical approach usually overestimates the stability of the NaCl structure and often predicts the NaCl structure even for the cesium halides.<sup>20</sup> It would be most interesting to test our model on the cesium halides to see if the theory predicts the correct structure, thus accounting for the very delicate difference of the crystal energies in different structures at different distances.

A similar type of test of such delicate energy difference can, however, be achieved by calculating the polymorphic transition pressures of the alkali-halide crystals. It has been known that some alkali-halide crystals undergo transition from the NaCl structure to the CsCl structure at very high pressures.<sup>20</sup> This can be explained in terms of the free energy  $F$ , defined by

$$F = E + pv - TS \quad (8)$$

using the standard symbols for the thermodynamic variables. Using  $v = 2R^3$  for the NaCl structure and  $v = 8R^3/3^{3/2}$  for the CsCl structure, we express the free energy per molecule at 0 °K,

$$F^{\text{NaCl}}(R) = V^{\text{NaCl}}(R) + 2R^3p \quad (9a)$$

and

$$F^{\text{CsCl}}(R) = V^{\text{CsCl}}(R) + (8/3\sqrt{3})R^3p \quad (9b)$$

Although, at  $p = 0$ , the free energy of the CsCl structure is higher than the NaCl structure for the crystals treated here, the free energy of the CsCl structure eventually becomes lower than the NaCl structure at pressures higher than a certain transition pressure. Figure 1 shows this for the case of KCl crystals, where the transition takes place at  $p = 21$  kbar. The transition pressures obtained for the alkali-halide crystals are given in Table III.

Since the discovery of this polymorphic transition in the alkali-halide crystals by Slater<sup>21</sup> and the pioneering work of Bridgman,<sup>22</sup> there have been many high-pressure experiments to study the polymorphic transitions of the alkali-halide crystals.<sup>23</sup> However, except for some species for which values of the transition pressures are well established at relatively low pressures, the experiments have not yet been able to determine the transition pressures accurately and there have been uncertainties and conflicting measurements among the experiments. We put the experimental values of the transition pressure in Table III.

Although these values have been determined most-

ly at room temperatures, they are expected to be fairly close to the 0 °K values, since the transition pressure is known to be almost independent of temperature.<sup>24</sup> The experimental transition pressure values for NaCl given in Table III provide a good example of the large discrepancies among different experiments, which are mainly due to the difficulty of applying the high pressure isotropically to the crystals and also due to the very slow rate of transition between the two structures. There have also been semiempirical approaches<sup>25</sup> to treat this, generally along the line of the Born-Mayer theory. However, these attempts have succeeded only in showing a certain qualitative trend among the various alkali halides, and for the cases of KCl, KBr, RbCl, and RbBr, for which the experimental transition pressures are known rather accurately, the semiempirical predictions are nowhere near the experimental values.

We put the predictions from a typical semiempirical work by Born and Huang<sup>26</sup> in Table III. Although our *a priori* predictions also seem to remain only qualitative, they are much better predictions of the experimental values compared with these semiempirical predictions. For KCl and KBr, our predictions agree almost exactly with the established experimental values. For RbCl and RbBr, they are larger than the experimental values by more than a factor of 2, but they are still large improvements over the semiempirical values. For the other alkali halides we need more reliable experimental determinations to find the real accuracy of our predictions.

Meanwhile, we can take our predictions for these systems in a rather optimistic way. Although the errors in our predictions for RbCl and RbBr appear to be large, it is due to a very small error in energy differences. At the pressure of 5 kbar, which corresponds to the transition pressure of RbCl and RbBr, the calculated crystal energies of RbCl and RbBr in the NaCl structure are lower than the corresponding energies in the CsCl struc-

TABLE IV. Structures of some alkaline-earth-dihalide crystals.

	Structure	$n_s$	$\alpha_M$
CaF <sub>2</sub>	fluorite <sup>a</sup>	8	5.03879 <sup>b</sup>
MgF <sub>2</sub>	rutile <sup>c</sup>	6	4.8100 <sup>b,d</sup>
BeCl <sub>2</sub>	SiS <sub>2</sub> <sup>e</sup>	4	4.086 <sup>b</sup>
CaCl <sub>2</sub>	distorted rutile <sup>f</sup>	6	4.803 <sup>b,d</sup>

<sup>a</sup>Reference 16, Vol. 1, (IV, a1).

<sup>b</sup>Reference 17c.

<sup>c</sup>Reference 16, Vol. 1, (IV, b1).

<sup>d</sup>Based on the averaged nearest-neighbor distance.

<sup>e</sup>Reference 16, Vol. 1, (IV, e14).

<sup>f</sup>Reference 16, Vol. 1, (IV, b2).

TABLE V. Equilibrium properties of some metal dihalide crystals.

	$R_e(\text{Å})$		$D_e(\text{kcal/mole})$	
	Calc.	(Expt.)	Calc.	(Expt.) <sup>a</sup>
CaF <sub>2</sub>	2.30	(2.360) <sup>b</sup>	649	(623 ± 4)
MgF <sub>2</sub>	1.97	(1.987) <sup>b,c</sup>	706	
BeCl <sub>2</sub>	2.04	(2.017) <sup>b</sup>	562	
CaCl <sub>2</sub>	2.67	(2.750) <sup>b</sup>	531	(534 ± 2)

<sup>a</sup>Compiled by P. George and D. S. McClure, Adv. Inorg. Chem. 1, 381 (1959).

<sup>b</sup>Reference 17c.

<sup>c</sup>Averaged value of 1.968 (2) and 1.997 (4).

ture only by about 1.2 kcal/mole. Since our predictions are based on the energy values through Eqs. (9), we have to take this error in the energy scale as the characteristic error for our predictions, instead of the relative error in terms of the ratio of the predicted transition pressure to the experimental transition pressure. Unlike the semiempirical potentials, our potential is not restricted to the region near the equilibrium separation and it is expected to be even better at shorter distances. Therefore we may argue that our predictions for other cases will involve comparable errors in energy, a few kcal/mole also, unless we have any particular reason to believe that the other alkali halides should be less accurately described by our model. The free energy has a term  $p v$ . Thus, if we assume the same error in energy  $\Delta E$  for two different alkali halides *A* and *B*, the errors in pressure  $\Delta p_A$  and  $\Delta p_B$  will be related roughly by

$$\Delta E = \Delta p_A v_A = \Delta p_B v_B \quad (10)$$

or

$$\Delta p_B = \Delta p_A v_A / v_B \quad (11)$$

In the worst case for LiF, where the equilibrium separation near the transition point is only about half the corresponding distance for RbBr, the error in the transition pressure will be about eight times as large as the corresponding error for RbBr. But this will be only about 50 kbar, which amounts to a 10% error in terms of the transition pressure.

#### IV. ALKALINE-EARTH-DIHALIDE CRYSTALS

We have done calculations on some alkaline-earth-dihalide crystals with known simple structures. In Table IV, we list their structures and the necessary data for the calculations. Some crystals have slightly distorted structures and therefore they contain several "nearest"-neighbor distances, which are slightly different from one

another. We have based our calculations on the averaged nearest-neighbor distances for these distorted structures.

The results are given in Table V with the values from experiments. Since the experimental data for crystals are more reliable than the molecular data of these species which exist only at very high

temperatures, the comparison of our crystal results with the experimental data provides a more reliable means to check our potentials for these systems. The results agree reasonably well with the experimental values, even for the calcium dihalides, which showed a discrepancy in the molecular case.<sup>2</sup>

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<sup>1</sup>R. G. Gordon and Y. S. Kim, *J. Chem. Phys.* **56**, 3122 (1972).

<sup>2</sup>Y. S. Kim, Ph.D. thesis (Harvard University, 1973) (unpublished), Sec. III-2; Y. S. Kim and R. G. Gordon, *J. Chem. Phys.* (to be published).

<sup>3</sup>For a general discussion of the nonadditivity of intermolecular forces and some brief discussions of many body forces, see H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces*, 2nd ed. (Pergamon, New York, 1971), Chap. 5.

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