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New Theory of Repulsion and Structural Stability in Ionic Crystals

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An ionic crystal is viewed as a collection of compressible ions in polyhedral, space-filling cells. Repulsion arises solely from the increased compression energy at the cell faces. Eighteen parameters (two per ion) are determined from the lattice spacings and compressibilities of the twenty alkali halides. These explain for the first time the observed structures of all these crystals as well as their thermal and pressure transitions—a significant advance over previous semiempirical theories.

Most theories of cohesion in ionic crystals concentrate on calculating the repulsive forces, since the attractive interactions are well understood. Born's semiempirical theory^{1,2} models the repulsion energy by simple functions of r , the interionic spacing [e.g., $A \exp(-r/\rho)$], using two parameters per crystal fitted from experimental data. Among many later extensions,²

Tosi and Fumi³ have carried out detailed calculations on the alkali halides using 27 parameters for seventeen crystals.⁴ Although they obtain a good fit with experimental interionic spacings (r_0) and compressibilities (K_0), their theory, in common with all Born-type approaches, requires some of the parameters to be determined only from the experimental data on the crystals of in-

terest, thus ruling out predictions on new systems.

This defect is rectified in our recent theory⁵ where we abandon the traditional concept of incompressible spherical ions. Instead, we assume the following:

(a) Each ion has a compression energy which is a function of its size. The repulsion energy in an ionic crystal arises *solely* from the compression energies of the individual ions. For a binary cubic ionic crystal, the lattice energy per pair of ions is therefore written in the form

$$W_L(r, r_+, r_-) = -\alpha e^2/r - c/r^6 - D/r^8 + W_+(r, r_+) + W_-(r, r_-), \quad (1)$$

where the first three terms are the electrostatic and van der Waals interaction energies, r_+ and r_- are the "radii" of the two ions, and $W_+(r, r_+)$ and $W_-(r, r_-)$ are their compression energies. Since nearest neighbors are assumed to be in contact, we have

$$r = r_+ + r_- . \quad (2)$$

Internal equilibrium further requires that

$$(\partial W_L / \partial r_+)_r = (\partial W_L / \partial r_-)_r ; \quad (3)$$

r_+ and r_- are *variables* which depend on the compressing force acting on the ions and so the "radius" of an ion varies from crystal to crystal and with pressure in the same crystal.

(b) The compression energy of an ion is taken to be the sum of contributions $A \exp(-r_i/\rho)$ from each contact it makes with its neighbors, where r_i is the "radius" of the ion in the direction of the contact. For the cation, for instance, we write

$$W_+(r, r_+) = n_1 A_+ \exp(-r_+/\rho_+) + n_2 A_+ \exp(-br/\rho_+), \quad (4)$$

where A_+ and ρ_+ are repulsion parameters associated with the ion, n_1 and n_2 are, respectively, the number of nearest and next nearest neighbors, and $2br$ is the distance between the ion and its next nearest neighbor. The ion is therefore not spherical, its "radius" being r_+ and br , respectively, in the direction of unlike nearest and like next-nearest neighbors. This picture is strikingly borne out by the electron density map of NaCl.⁶

The theory has two parameters, A and ρ , associated with each ion and so only eighteen parameters are needed for the twenty alkali halides. Once obtained from one set of crystal data, the parameters of an ion can be used in any other crystal in which it occurs. This lends predictive

power to the theory. For instance, the same parameters have been used in both the NaCl and high-pressure CsCl phases of alkali halides such as KCl.⁵ Moreover, the theory has successfully explained the r_0 and K_0 values of a number of perovskitelike crystals⁷ without introducing any new adjustable parameters, but using only A and ρ values determined from data on other simpler crystals.

Although the above theory has the unique feature of transferability of parameters from one crystal to another, it fails to solve another long-standing problem, viz., the relative stability of different crystal modifications of ionic crystals. In the oft-studied alkali halides, *all* Born-type theories have two significant discrepancies (of Table II): (i) CsCl, CsBr, and CsI are wrongly predicted to occur in the NaCl structure. (ii) Some of the lithium and sodium halides are found to be more stable in the ZnS structure.⁸

The most probable reason for the above discrepancies is that the repulsion energy at any contact between two adjacent ions is not a function of their separation alone but is also reduced by the proximity of other contacts. Clearly, this effect favors structures of higher coordination. One unsatisfactory way of incorporating this effect is by introducing more parameters. However, using a physically more appealing approach, requiring no extra parameters, we have completely resolved the problem of the relative stability of structures in the alkali halides.

In the new picture, we associate a face of contact at each point where two neighboring ions touch. The faces surrounding an ion would then form a polyhedron and the crystal would consist of two kinds of polyhedral cells filling space. This is a natural extension of the Wigner-Seitz cell concept.⁹ Where two like ions touch, the polyhedral face is required by symmetry to be the midplane. However, where two unlike ions touch, the plane can be anywhere between them, since the "radii" r_+ and r_- are variables and not necessarily equal [though relations (2) and (3) continue to hold].¹⁰ A few typical ionic polyhedral cells are shown in Fig. 1.

At each point on the surface of the ionic polyhedron, we associate a compression energy density $(B/2\pi) \exp(-r'/\sigma)$, where r' is the distance of the point from the center and B and σ are parameters. The compression energy of the cation, for instance, is therefore the surface integral

$$W_+(r, r_+) = (B_+/2\pi) \int \exp[-r(s)/\sigma_+] ds . \quad (5)$$

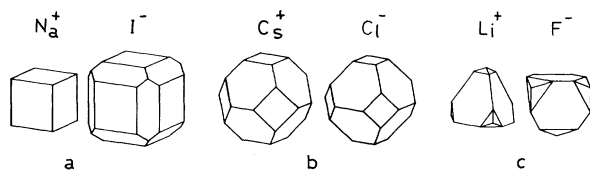


FIG. 1. Ionic polyhedral cells to scale. (a) NaI (*B1*) (b) CsCl (*B2*), and (c) LiF (hypothetical *B3*).

Though arbitrary, the above form of the compression energy has the realistic property that the energy is maximum at the centers of the polyhedral faces and reduces towards the edges. Equation (5) therefore is approximately of the form (4), becoming closer at larger interionic distances. Moreover, since in (5) the compression energy of each face depends on its area and shape, the effect of the coordination number has also been allowed for.

It should be pointed out that the only modification introduced in this new extension of the theory is in the *form* of the compression energy. We still have only two parameters and still retain the predictive power associated with the theory.

The equilibrium lattice spacing of a crystal at 0°K and 0 pressure is calculated by solving the equation

$$dW_L/dr = 0 \quad (6)$$

subject to conditions (2) and (3). The compressibility K_0 can then be obtained from d^2W_L/dr^2 . For finite temperatures and pressures, we have employed the Hildenbrand² equation of state

$$dW_L/dV = -P + T\beta/K, \quad (7)$$

where $V (=xr^3)$ is the volume, P the pressure, T the temperature, β the thermal expansivity, and K the compressibility. To calculate $T\beta/K$

TABLE I. Repulsion parameters of the alkali and halogen ions (see text).

Ions	$B(\text{ergs})$	$\sigma(\text{\AA})$
Li ⁺	5.131×10^{10}	0.060 15
Na ⁺	7.787×10^9	0.085 01
K ⁺	1.665×10^{10}	0.099 57
Rb ⁺	5.036×10^{11}	0.087 55
Cs ⁺	1.957×10^{11}	0.103 82
F ⁻	1.057×10^7	0.173 22
Cl ⁻	3.677×10^7	0.187 35
Br ⁻	4.119×10^7	0.198 91
I ⁻	4.582×10^7	0.214 73

at high temperatures and pressures, we have assumed that the Grüneisen constant $\gamma = V\beta/C_V K$ (C_V taken to be the classical value of $6k_B$) is independent of temperature and pressure.¹¹

The parameters B and σ of the nine ions Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, F⁻, Cl⁻, Br⁻, and I⁻ were determined by least-squares fitting of the experimental values of r_0 and K_0 (including high-pressure data) of the alkali halides.¹² These parameters (listed in Table I) fit the data to rms errors of 0.62% and 5.9% in r_0 and K_0 . This is better than the fit of 0.71% and 6.5% obtained with our earlier theory⁵ (using the same number of parameters), showing that the modification introduced here is in the right direction.

Using Eq. (6) and the parameters of Table I the free energy (including zero-point energy calculated from the Debye approximation) of the alkali halides has been calculated for the NaCl, CsCl, and ZnS structures. All the twenty crystals are correctly predicted to be stablest in their observed structures (Table II), a dramatic improve-

TABLE II. Structures predicted for the alkali halides by different theories. Calculations carried out by us based on the potentials of Huggins-Mayer (given in Ref. 2) (HM), Tosi-Fumi (Ref. 3) (TF), Narayan-Rasaseshan (Ref. 5) (NR), and the present theory (PT). *B1*, NaCl structure; *B2*, CsCl structure; *B3*, ZnS structure. Crosses are marked against wrong predictions.

Crystal	Observed structure	Predicted structure			
		HM	TF	NR	PT
LiF	<i>B1</i>	<i>B3</i> ×	<i>B3</i> ×	<i>B3</i> ×	<i>B1</i>
LiCl	<i>B1</i>	<i>B3</i> ×	<i>B3</i> ×	<i>B3</i> ×	<i>B1</i>
LiBr	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>
LiI	<i>B1</i>	<i>B1</i>	<i>B3</i> ×	<i>B3</i> ×	<i>B1</i>
NaF	<i>B1</i>	<i>B3</i> ×	<i>B3</i> ×	<i>B3</i> ×	<i>B1</i>
NaCl	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B3</i> ×	<i>B1</i>
NaBr	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>
NaI	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B3</i> ×	<i>B1</i>
KF	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>
KCl	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>
KBr	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>
KI	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>
RbF	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>
RbCl	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>
RbBr	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>
RbI	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>
CsF	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>	<i>B1</i>
CsCl	<i>B2</i>	<i>B1</i> ×	... ^a ×	<i>B1</i> ×	<i>B2</i>
CsBr	<i>B2</i>	<i>B1</i> ×	... ^a ×	<i>B1</i> ×	<i>B2</i>
CsI	<i>B2</i>	<i>B1</i> ×	... ^a ×	<i>B1</i> ×	<i>B2</i>

^aRef. 4.

TABLE III. Transition pressures in the rubidium, potassium, and sodium halides predicted by different theories. BMJ, Jacobs (Ref. 16) using Born-Mayer parameters (given in Ref. 2); TF, calculated by us using Tosi-Fumi (Ref. 3) parameters; PT, present theory.

Crystal	Observed transition pressure (kbar)	Calculated transition pressure (kbar)		
		BMJ	TF	PT
RbCl	4.9 (Ref. 17)	39	31.4	5.8
RbBr	4.5 (Ref. 17)	30	24.6	10.3
RbI	4.0 (Ref. 17)	22	14.5	12.1
KCl	19.5 (Ref. 17)	74	64.1	22.1
KBr	17.6 (Ref. 17)	59	40.2	23.3
KI	17.8 (Ref. 17)	49	35.8	36.2
NaCl	300 (Ref. 18)	74	100	167
	< 257 (Ref. 19)			
NaBr	> 200 (Ref. 20)	53	220	197
NaI	> 200 (Ref. 20)	44	380	455

ment over earlier theories. Although the improvement in fit of r_0 and K_0 is small in terms of rms deviations, there is actually a much greater qualitative improvement. In the earlier theory, the calculated values of r_0 were systematically too high in the B2 structures and too low in the B1 structures. The differences were only about 0.5%, but the problem of the relative stability of phases is so sensitive to these differences that the results there were quite inaccurate. These systematic deviations are not present in the new theory, which explains the marked improvement in the predictions of the alkali halide structures.

Calculations with the present theory, using Eq. (7) and a Debye model for thermal effects,¹³ indicate that CsCl is the only crystal to undergo a thermal transition below its melting point, in agreement with observation. The calculated transition temperature of 890°K is also close to the experimental value of 734°K.¹⁴ The only existing attempt¹⁴ to explain the thermal transition in CsCl employs a large number of adjustable parameters fitted to the transformation data themselves.

The transition pressures predicted by the present theory in the rubidium, potassium and sodium halides are listed in Table II along with the experimental pressures and the values predicted by other theories.¹⁵ The present results are distinctly superior. There is, however, a systematic deviation increasing from the chlorides to the iodides.

In parallel with the semiempirical approaches, many quantum mechanical theories have also been

tried using free-ion wave functions. These approaches are parameter free, but the calculations^{21,22} are often laborious and require considerable sophistication (like three-body interaction). A notable exception is the recent electron-gas approach²³ which, though simple, leads to good results. Strangely enough, the electron-gas approach assumes rigid overlapping ions while our present model assumes nonoverlapping deformable ions. In spite of this, since the chief region of overlap is near the surface of contact, the form of the repulsion energy may be similar in the two approaches. A serious defect in all the quantum mechanical theories is that the predicted transition pressures in the sodium halides are unreasonably low.

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NMR in Spinning Samples of Biaxial Liquid Crystals

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Magnetic resonance measurements on a spinning sample of deuterated *n*-heptyloxyazoxybenzene (HOAB- d_{30}) are presented. The resulting spectral patterns for the deuterated terminal methyl groups display the biaxial character of the smectic-C phase. Values for those biaxial order parameters which survive under free molecular rotation are directly determined from the shape of the spectral patterns. Parameters expressing biased rotation are also present and contribute significantly to the biaxiality.

In spite of the intense interest in the nature of molecular orientational order in liquid crystals, uncertainty still remains concerning its role in the biaxial character of the smectic-C, S_C , phase. The lack of experimental data on molecular order is evidenced by the numerous and varied models¹ that have been proposed for this phase. Some of these models are principally based on the biaxial property, while others are not. Experimentally, the biaxial condition is

most readily observed optically by the characteristic "baseball" figure seen conoscopically under a polarizing microscope.² While this has been a common method of identification, little quantitative information has come from these studies. NMR techniques, on the other hand, have more potential for quantitative measurements; however, they suffer from the fact that the biaxiality is not readily observed in the usual NMR measurement of spectral splittings where the samples