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Interionic potentials for alkali halides

C R A Catlow[†], K M Diller[‡] and M J Norgett

Theoretical Physics Division, AERE Harwell, UK

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Abstract. We have developed new potentials describing the short-range interactions between ions in the alkali halides. We have used the measured elastic constants to fix the near-neighbour overlap repulsion and study the second-neighbour potentials. The description of the next-neighbour interactions requires the inclusion of large van der Waals attractions, in general accord with latest estimates of these forces. We have used theoretical estimates of the repulsive part of the second-neighbour interaction and added a variable attractive part to fit the crystal data. We have first used a conventional Buckingham potential, but a more flexible form is required to provide a completely coherent picture of these interactions in the whole series of alkali halides.

1. Introduction

The alkali halides are the most widely studied materials with ionic bonding. There exist extensive and accurate data on the gaseous molecules, the solids and the molten salts. The properties of these phases can be related to their simple, interionic interactions. Conversely, such potentials may be tested by setting their predictions against a wide range of data. Thus better potentials evolve by including more extensive information in their derivation.

It has become increasingly clear in recent years that presently available potentials are not wholly satisfactory. They reproduce the perfect-crystal data only in part and assume forms of potential that may well be too restrictive. In this paper, we propose new potentials for the alkali halides. To this end, we require a rather broad review of the diverse and independent developments in this field. In particular, we survey first the limitations of present potentials. We then consider in greater detail the specific information that is available from particular data and the way in which our knowledge of the potentials may be extended. To this end, we emphasize the relations between analogous interactions and examine the extent to which common potentials may be applied in a variety of substances.

The earliest potentials sought principally to explain the cohesive energy of ionic solids. In the Born model, the Coulomb binding is opposed by repulsive forces arising from the overlap of completely filled electronic shells. The parameters in some assumed form of near-neighbour, overlap interaction (typically $V(r) = a/r^n$ or

[†] On attachment from Department of Theoretical Chemistry, South Parks Road, Oxford; present address: Department of Chemistry, University College, Gower Street, London WC1.

[‡] On attachment from Department of Metallurgy and Materials Science, Parks Road, Oxford.

$V(r) = A \exp(-r/\rho)$, although arbitrary variants have been explored: see e.g. Thakur (1975)) may be adjusted to give the correct compressibility and lattice constant at equilibrium.

The most detailed refinement of this approach is the work of Fumi and Tosi (1964) and Tosi and Fumi (1964). The model is extended to include overlap interactions between second neighbours, but the number of the parameters in the model is reduced by relating different potentials according to the formula $V_{ij}(r) = c_{ij}b \exp[(r_i + r_j - r)/\rho]$; here the c_{ij} are Pauling factors depending on the ion charges, and r_i and r_j are characteristic ion radii. Fumi and Tosi first fitted optimum radii assuming a common b and ρ for all halides, and then adjusted ρ separately for each substance. Room-temperature data were corrected for thermal contributions using an equation of state. Fumi and Tosi also included the van der Waals interactions estimated by Mayer (1933).

All potentials of this type give good cohesive energies, which are dominated by the Madelung term, but the Fumi-Tosi potentials fail more critical tests. These authors (Tosi and Fumi 1962) were themselves aware of the difficulties encountered in explaining the relative stability of the NaCl and CsCl structures with consistent potentials. Recently, Ree and Holt (1973) have shown that the Fumi-Tosi potentials predict poor values for the elastic constants over a range of temperature, even towards absolute zero. Adams and McDonald (1974) have used the more detailed Monte-Carlo technique to predict properties of the solid at room temperature, with the same unsatisfactory results. This same method has also been applied to study the behaviour of the molten salts using Fumi-Tosi potentials (Woodcock and Singer 1971, Lewis *et al* 1975). There are small but significant differences between the computed and measured values, especially of pair-distribution functions. It would thus appear that the radius relation between nearest- and next-nearest-neighbour interactions, as assumed by Fumi and Tosi, is invalid. It gives potentials that are unsatisfactory for predicting properties that depend more sensitively on the separate interactions than the lattice equilibrium equation and compressibility.

Detailed information on both interactions is available as force constants (that is, as derivatives of the first- and second-neighbour potentials) from an analysis of the lattice dynamics of the halides. However, such an analysis requires a proper consideration of the ionic polarization and particularly its coupling with the overlap repulsions. The simplest successful description of the dynamical properties of ionic materials is the shell model of Dick and Overhauser (1958). Each ion comprises two distinct entities, a charged core and shell, which are coupled harmonically and isotropically. Cochran (1971) has reviewed the application of this model to the parameterization of the lattice dynamics of ionic crystals (and the extensions of the model, to which we return).

The information provided by the analysis of the lattice dynamics—that is, short-range force constants, core and shell charges and core-shell coupling constants—is more readily available in the elastic and dielectric constants. For alkali halides, there is the added advantage that the derivation of short-range force constants and shell parameters may be separated because the elastic distortion of the lattice generates no polarization. Thus force constants may be found uniquely from elastic data, and shell parameters derived subsequently from the dielectric properties.

However, before the elastic constants can be used to provide improved two-body potentials, the contribution of many-body interactions must be assessed. Their effect is most obviously apparent in the observed difference between c_{12} and c_{44} , which must be equal for a material with the NaCl structure in equilibrium under central, pairwise interactions. The magnitude of this Cauchy violation is apparent from the low-tempera-

Table 1. Data used in fitting potentials and shell parameters.

Substance	Lattice constant (Å) [†]	Elastic constants (10 ¹¹ dyn cm ⁻²)				Dielectric constants [‡]		Transverse-optic frequency (cm ⁻¹) [‡]
		<i>c</i> ₁₁	<i>c</i> ₁₂	<i>c</i> ₄₄	Reference	ε ₀	ε _∞	
LiF	1.996	12.46	4.24	6.49	(a)	8.50	1.93	318
LiCl	2.539	6.074	2.27	2.692	(b)	10.83	2.79	221
LiBr	2.713	4.721	1.590	2.052	(c)	11.95	3.22	187
LiI	2.951	—	—	—	—	—	3.89	151.5
NaF	2.295	10.85	2.290	2.899	(b)	4.73	1.75	262
NaCl	2.789	5.733	1.123	1.331	(b)	5.45	2.35	178
NaBr	2.954	4.800	0.986	1.070	(b)	5.78	2.64	146
NaI	3.194	3.761	0.798	0.781	(d)	6.62	3.08	124
KF	2.648	7.570	1.35	1.336	(b)	5.11	1.86	201.5
KCl	3.116	4.832	0.54	0.663	(e)	4.49	2.20	151
KBr	3.262	4.17	—	0.52	(f)	4.52	2.39	123
KI	3.489	3.38	0.22	0.368	(e)	4.68	2.68	109.5
RbF	2.789	6.527	1.255	0.952	(g)	5.99	1.94	163
RbCl	3.259	4.297	0.649	0.493	(b)	4.53	2.20	126
RbBr	3.410	3.863	0.474	0.4085	(b)	4.51	2.36	94.5
RbI	3.628	3.210	0.36	0.2920	(b)	4.55	2.61	81.5

[†] Lattice constants are values extrapolated to 0 K, from Ghate (1965).

[‡] Dielectric constants and transverse-optic frequencies are 2 K values from Lowndes and Martin (1969).

References to elastic constants, which are generally helium-temperature measurements, are:

- (a) Briscoe and Squire (1957).
- (b) Lewis *et al* (1967).
- (c) Marshall and Cleavelin (1969).
- (d) Claytor and Marshall (1960).
- (e) Norwood and Briscoe (1958).
- (f) Galt (1948).
- (g) Cleavelin *et al* (1972).

ture values of the elastic moduli in table 1. Strictly, the identity $c_{12} \equiv c_{44}$ should apply, even for central forces, only to a static lattice; thus more appropriate elastic constants should be obtained by extrapolation from high temperatures. The measured results at helium temperatures are, in fact, only slightly different from the harmonic values of $c_{44} - c_{12}$ quoted by Roy *et al* (1972). Nonetheless, the diagnosis of many-body effects from the Cauchy violation may still be erroneous because of the over-simplified treatment of the thermal contributions. Ree and Holt (1973) find no conclusive evidence for many-body effects from their more detailed study of the temperature dependence of elastic constants.

Despite this uncertainty, a variety of models have been proposed that include explicit or implied many-body interactions (see the reviews by Cochran (1971) and Basu *et al* (1974)). These have been used to provide refined descriptions of the lattice dynamics of the alkali halides. It was supposed that this was desirable because of inadequacies in the simple shell model. These have, however, been largely resolved by the work of Bilz *et al* (1975) who have reinterpreted the shell model in a more satisfactory way that largely dispenses with the need for more sophisticated models. Nonetheless, the force-constant analyses based on the various models including non-central forces are important. Thus, because they lead to essentially identical conclusions about the form of the

pair interactions, we are convinced that the elastic constants may be analysed to give pair potentials that are not critically dependent on the residual uncertainties about many-body forces. Essentially, we can eliminate many-body effects by choosing different combinations of elastic constants, but the actual choice is not of primary importance.

The various models including many-body effects may be most simply classified as to whether they include only the result of the fully symmetric distortion about an ion or consider alternatively asymmetric distortions. Of the first type is the charge exchange model of Verma and Singh (1969), based most closely on the quantum mechanical description of binding in ionic crystals due to Löwdin (1956) and Lundqvist (1952, 1955, 1957). It is equivalent as a parameterization scheme to the breathing-shell model of Schröder (1966). In the latter, the many-body effects arise from the symmetric deformation of the ion shells. Regarded as a mechanical model, this requires $c_{44} > c_{12}$; however, this is not a basic constraint on the model as a parameterization of lattice dynamics. Basu and Sengupta (1968) have exploited this in their deformable shell model, which again includes only many-body contributions arising from symmetric deformation of the environment of any ion. In all these cases, there are non-central contributions to volume-changing deformations, but none to the shear moduli $\frac{1}{2}(c_{11} - c_{12})$ and c_{44} . On the contrary, many-body effects from asymmetric distortions of the ions or their environment give no contribution to the bulk modulus (see Sangster (1974a); the term deformable shell model is usually restricted to the case of asymmetric distortion, in contrast to the usage of Basu and Sengupta (1968)).

The proponents of the various models have made essentially equivalent analyses of the elastic constants of the alkali halides. The various results of Goyal and Verma (1974), Sarkar and Sengupta (1973) and Sangster (1973, 1974a) all show the expected repulsive interaction of near neighbours. However, the second-neighbour force constants require either very weak repulsive interactions between like ions or, alternatively, van der Waals potentials much stronger than the Mayer predictions. This result is, significantly, independent of the treatment of many-body effects and applies even for a wide range of assumed ionic charges (see Goyal and Verma 1974).

There have been earlier but less direct intimations that larger, attractive, second-neighbour interactions may be important in alkali halides. That this explains the relative stability of the NaCl and CsCl phases was known to May (1937, 1938). There have been several attempts to re-estimate the appropriate van der Waals potentials by Hajj (1966), Lynch (1967), Ladd (1974) and Jain *et al* (1976). Ladd's results are clearly erroneous, invoking polarizabilities from static rather than high-frequency dielectric constants. The other analyses seem to be convincing and confirm the need for stronger attractive potentials.

Such stronger, attractive interactions must clearly be included in improved potentials. The first question is whether we may, with this development, re-establish a consistent picture of first- and second-neighbour overlap interactions using a radius scheme to relate the different repulsive potentials. But it is very unlikely that this would be meaningful. The ability to derive a unique set of radii depends entirely on reliable estimates of the second-neighbour overlap interactions. It is clear from the appropriate form of interaction $V_{ij}(r) = b \exp [(r_i + r_j - r)/\rho]$ that no near-neighbour potential is changed by adding to all cation radii a constant which is subtracted from the anion radii. However, because at the separations found in the crystal the second-neighbour interactions are predominantly attractive, they provide only marginal information on the repulsive part of the potential and hence the magnitude of suitable ionic radii.

These difficulties are quite clearly exemplified in the study by Müller and Norgett

(1972, 1973) of potentials suitable to the caesium halides. The elastic constants required large second-neighbour attractions. If these were consistently extended to act also between immediate neighbours, no reasonable radius scheme could account for all the measured elastic moduli. The conclusion is that one must look separately at the two types of interaction or, ultimately, consider more flexible potential forms that are valid in both the overlap and attractive regions. It is, of course, already well known that a simple addition of repulsive and attractive terms gives unsatisfactory potentials for the inert gases (see Barker 1976).

Thus, elastic-constant data provide information on the magnitude of the repulsive part of the near-neighbour interaction and the attractive part of the next-nearest-neighbour potential. More comprehensive potentials require more general information on each interaction in other ranges of separation. There are alternative sources of such data. Thus the molecules have smaller anion-cation separations and avoid the complications of next-nearest-neighbour contributions, but give data more difficult to interpret because of ion polarization. In fact, the solid-state potentials seem always to give adequate descriptions of the molecules (see Sangster (1974b) and Smith (1972) for reviews). Conversely, the molecular data contribute little additional information not available by analysis of the solid properties.

On the contrary, the recent quantum mechanical calculations of interionic potentials do seem to be a valuable additional source of information, particularly for the strongly repulsive region. The chief difficulty is assessing the validity of various approximate methods. These are best tested by a comparison of the appropriate calculated potentials with inert-gas scattering data; Smith (1972) provides a convenient review of this field. For argon, it seems that the best single-configuration Hartree-Fock calculations (Gilbert and Wahl 1967) overestimate the repulsion, presumably because of neglect of correlation. There is better agreement of experiment with calculations based on the Thomas-Fermi-Dirac method (see e.g. Wedepohl 1967). The semi-classical calculation of the interaction energy uses formulae for the kinetic and exchange contributions which are functions of the electron-gas density. The main improvement over earlier calculations is the substitution of accurate Hartree-Fock charge densities for the ions, in preference to less valid Thomas-Fermi-Dirac estimates. Gordon and Kim (1972) have calculated potentials for argon-argon in this way that are in excellent agreement with gas-scattering results.

The same methods have already been applied to ionic systems with excellent effect. Kim and Gordon (1974) and Cohen and Gordon (1975) have calculated very satisfactory potentials for alkali halides. Keeton and Wilson (1973) have computed interactions for $\text{Ca}^{2+}-\text{F}^-$ in excellent agreement with the crystal potentials of Catlow and Norgett (1973). The method thus seems particularly suited to studying interactions between ions in regions where the crystal data are irrelevant, for example the overlap of like ions in alkali halides. The crystal data can then be used to assess the attractive part of the next-neighbour interactions. We use these semi-classical, electron-gas potentials in this way.

The object of this study will be to develop potentials by using a wide range of data corresponding to different interionic separations. So far, we have shown the value of combining elastic-constant data with theoretical calculation. At first we consider each substance separately. But the same second-neighbour interactions between like ions appear in a series of halides; for example, the $\text{Cl}^- - \text{Cl}^-$ interaction contributes in LiCl, NaCl, KCl and RbCl at different separations. The second stage is therefore to derive potentials that may be consistently applied to every halide. This requires a revision not of the appropriate parameters in one of the conventional interaction forms but rather a

critical consideration of the form of interaction itself. We consider these developments in the next section and then provide a corresponding set of shell parameters to describe the dielectric properties of the halides.

2. New potentials

We will deduce two sets of pair potentials for the alkali halides based on the elastic constants and equilibrium equations. We have already shown that such potentials have general features independent of the form assumed for the many-body interactions, which are probably unimportant. However, we must base our analysis on some combination of elastic constants; thus we follow Sangster (1973) and use the breathing-shell formalism. This does not imply a restriction to $c_{44} > c_{12}$ but rather defines a fit based on the shear moduli c_{44} and $\frac{1}{2}(c_{11} - c_{12})$. The appropriate defining equations for the elastic constants are in the Appendix, to aid discussion.

The shear moduli are directly related to measured sound velocities; thus their use avoids the large experimental errors in c_{12} . The thermal contributions are simpler and there is no confusion of isothermal and adiabatic constants. Hence there is less problem in using measured low-temperature moduli rather than harmonic values; the differences are only of the order of the errors in measurement. The lattice is set in equilibrium at a separation found by extrapolating the measured room-temperature lattice constant. The equilibrium separations and measured elastic constants are in table 1. (There are no low-temperature elastic moduli for LiI, and c_{12} for KBr is not known below 140 K.)

The three independent measured quantities for each halide depend on four force constants (see Appendix 1, where the notation is defined). They may be fixed uniquely by using additional dielectric data if only one ion is polarized or calculated from some assumed potential with fewer parameters. Alternatively, we may combine data from different substances.

It is simplest in either circumstance to consider first the interaction of next-nearest neighbours. We can eliminate B , the near-neighbour tangential force constant, from the equilibrium equation and the expression for c_{44} (see Appendix 1). This gives a relation between the gradient and curvature of the second-neighbour interactions and measured quantities for each halide. The analysis is equally valid for a deformable shell model because the expression for c_{44} is unchanged (see Sangster 1974a).

The second-neighbour force constants have contributions from both anion-anion and cation-cation interactions. Despite this complication, it is clear that the second-neighbour interactions deduced from the values of c_{44} and the equilibrium equation have the expected form. There is an attractive region at large separations with negative curvature and the potential passes through a point of inflexion to a minimum at smaller distances. Thus we find negative curvatures for second-neighbour interactions in K^+ and Rb^+ salts with large ion separations, small curvatures for the Na^+ salts and positive potential curvature for the Li^+ salts as the anions begin to overlap.

Our own recent experience with fluorite materials (Catlow and Norgett 1973) is that there is no way of extrapolating from data appropriate to the minimum of the potential and beyond to determine the repulsive interaction region. Rather we require absolute estimates of the overlap potential. Previously, we have used a Hartree-Fock calculation for $F^- - F^-$ (Catlow and Hayns 1972); however, we now believe that this gives too strong a repulsion (see Catlow *et al* 1977). We now use estimates of the repulsive part

of the eight second-neighbour interactions using the less well-founded but more successful electron-gas methods but without including any estimate of correlation. These potentials are accurately represented by an exponential in the range of interest.

Having fixed the repulsive part of the second-neighbour interaction, we can now use the information from c_{44} and the equilibrium equation to fix the attractive part. Initially, we considered each substance separately and used a conventional parameterized potential. Subsequently, we considered the trends in the potentials so deduced and found a more consistent representation of the second-neighbour interactions. However, this requires a more flexible form of potential. We consider the two sets of potentials independently and then compare them in a final subsection.

2.1. First potential set

We derive separate second-neighbour interactions for each substance. With the limited data available, it seemed sensible to use a conventional Buckingham potential for all next-neighbour interactions with $V_{ii}(r) = A_{ii} \exp(-r/\rho_{ii}) - C_{ii}/r^6$. The C_{ii} parameters measure effective van der Waals interactions in the sense that these interactions are cut off beyond second neighbours. Using the calculated values of A_{ii} and ρ_{ii} , we may then fix the sum $C_{++} + C_{--}$ for each substance directly from the equilibrium equation and the value of c_{44} .

The value of $C_{++} + C_{--}$ varies markedly. For Rb^+ and K^+ salts, the total is much greater than the sum of the appropriate Mayer values of the van der Waals coefficients. For Na^+ and Li^+ salts, there is damping of the attractive interaction. Indeed, for LiI , for which there are no elastic data, we set $C_{++} + C_{--}$ to zero by analogy with the other lithium salts. To obtain separate anion-anion and cation-cation interactions, we must divide $C_{++} + C_{--}$ appropriately. The peculiar variation of this factor as the cation changes in the halide series gives no indication how this should be done. We have thus arbitrarily divided the van der Waals interactions equally between anion and cation. This was merely an expedient to provide a set of potentials for calculation without the more serious limitations of the Fumi-Tosi potentials.

With an assumed second-neighbour interaction, we can fit A and ρ in a near-neighbour potential of Born-Mayer form $V(r) = A \exp(-r/\rho)$ for any substance with measured elastic constants. By analogy with the second-neighbour interactions, we have assumed complete quenching of the van der Waals interactions between adjacent, overlapping ions. To obtain potentials for all the halides, we have used a more complex simultaneous fit, based on a radius scheme, to compensate for the missing data. We set $V(r) = b \exp[(r_i + r_j - r)/\rho]$ with a single b value for all halides and a unique radius r_i for each ion. Varying b , r_i and ρ_{ij} introduced a more restricted variable set and hence could give potentials for each substance. The radii define only near-neighbour interactions and are thus undefined up to a constant to be added to all cation radii and subtracted from the anions; the radii thus have no physical significance. The simultaneous fit in fact involves only weak coupling between solutions for different substances and these potentials are best regarded as specific to each halide.

We made one further variation in the model, by adjusting the ion charge. This is a feature of many lattice dynamical models, but it is known generally to give models with insufficient binding. We thus investigated the effect of altering the ion charge, subject to the constraint that the model still gives reasonable cohesive energies. In every case, this led to a small but hardly significant reduction in ion charge; the potentials actually

correspond to the 'best fit' charges in table 2. We did not retain this feature in the subsequent study.

The most satisfactory feature of the potentials, unlike those of Fumi-Tosi, is that they reproduce the elastic shear constants, typically to 1 or 2%; there are a few cases where

Table 2. Potential parameters—set 1.

$$\begin{aligned} V_{+-}(r) &= A_{+-} \exp(-r/\rho_{+-}), \\ V_{++}(r) &= A_{++} \exp(-r/\rho_{++}) - C/r^6, \\ V_{--}(r) &= A_{--} \exp(-r/\rho_{--}) - C/r^6. \end{aligned}$$

A_{++} , ρ_{++} , A_{--} and ρ_{--} depend only on the particular interaction; these are values obtained using a calculated potential. The fitted parameters A_{+-} , ρ_{+-} and C , the effective second-neighbour van der Waals interaction, depend on the substance, as does the ion charge Z . The parameters were fitted assuming that $V_{+-}(r)$ acts only between near neighbours and $V_{++}(r)$ and $V_{--}(r)$ between second neighbours.

(a) Cation-cation interactions.

Potential	A_{++} (eV)	ρ_{++} (Å)
Li ⁺ -Li ⁺	1153.8	0.1364
Na ⁺ -Na ⁺	7895.4	0.1709
K ⁺ -K ⁺	3796.9	0.2603
Rb ⁺ -Rb ⁺	6808.1	0.2704

(b) Anion-anion interactions.

Potential	A_{--} (eV)	ρ_{--} (Å)
F ⁻ -F ⁻	1127.7	0.2753
Cl ⁻ -Cl ⁻	1227.2	0.3214
Br ⁻ -Br ⁻	2948.2	0.3164
I ⁻ -I ⁻	5502.5	0.3066

(c) Ion charge Z , cation-anion interaction parameters and effective van der Waals interaction.

Substance	Z ($ e $)	A_{+-} (eV)	ρ_{+-} (Å)	C (eV Å ⁶)
LiF	0.981	485.6	0.2614	12.71
LiCl	0.995	1380.6	0.2786	0.34
LiBr	0.992	1662.8	0.2882	0.01
LiI	0.979	8894.7	0.2617	0.0
NaF	0.981	1594.2	0.2555	11.68
NaCl	0.988	2314.7	0.2903	29.06
NaBr	0.988	2593.1	0.3014	42.08
NaI	0.988	3705.5	0.3099	27.38
KF	0.969	2426.8	0.2770	44.60
KCl	0.994	4117.9	0.3048	124.9
KBr	0.988	2944.0	0.3295	183.8
KI	0.994	5842.4	0.3264	285.9
RbF	0.960	2209.3	0.2945	69.83
RbCl	0.991	3559.9	0.3233	201.2
RbBr	0.998	4169.9	0.3321	261.4
RbI	0.999	5282.0	0.3431	400.6

the error reaches $\sim 5\%$. There are larger errors specifically for LiF ($\sim 10\%$), where a slightly wrong value of the lattice constant was used in the fit. With the subsequent development of more realistic potentials and the general independence of the potentials from substance to substance, it did not seem worth rectifying this error. With this exception, the predicted lattice strains are also very small.

However, there remain very substantial difficulties with these potentials. The equal division of the van der Waals interaction between second neighbours is unjustified and unsatisfactory. The variation in the potential acting between the same ions in different materials leads at the very least to ambiguities when an ion is substituted into a different environment. More seriously, we have not represented the most obvious effect which is the continuous quenching of the van der Waals interaction as the ions overlap. This cannot be represented satisfactorily by a Buckingham potential. Clearly we should enquire whether more flexible forms of potential are appropriate, especially as it is known that such forms are required to represent the interaction of the rare gases (see Barker 1976). Such an enquiry led to our second set of potentials.

2.2. Second potential set

We have studied the application of a general, arbitrary potential to represent the interaction of the second neighbours in the alkali halides. We join a polynomial of third order to the expected $-C/r^6$ interaction, dominant at large separations. Three coefficients in the polynomial are fixed by requiring continuity in function and two derivatives at the junction point r_a . The fourth coefficient is determined by fixing the minimum in the polynomial at r_m . The form of the interaction in the region $r > r_a$ depends only on C , and in the region $r_a > r > r_m$, the potential is independent of the form of interaction for $r < r_m$. The various regions are shown in figure 1.

It is thus simplest to begin by identifying systems where $r > r_a$ for both anion-anion and cation-cation interactions. The overlap of both second neighbours is least when the ion radii are nearly equal. In this case, we expect that $C_{++} + C_{--} = C_i$, deduced from the value of c_{44} and the equilibrium condition, will have separate, characteristic anion and cation parts. We find this behaviour in the series KCl, KBr, RbCl, RbBr, where $C_i^{KBr} - C_i^{KCl} = C_i^{RbBr} - C_i^{RbCl}$ and $C_i^{RbCl} - C_i^{KCl} = C_i^{RbBr} - C_i^{KBr}$ to good accuracy.

However, to fix independent anion and cation parts of C_i , we need one additional condition. We provisionally scale the interactions for $Br^- - Br^-$ and $Cl^- - Cl^-$ in constant proportion to the Mayer van der Waals values, taking an average over all the halides. Our values in table 3 are 2.2 times the mean Mayer results. We then derive parameters for $F^- - F^-$ and $I^- - I^-$, assuming an unmodified sum rule for second-neighbour van der Waals interactions in KF and RbI, where the ion sizes are not too different. Our scaling hypothesis is justified when we find a value 2.3 times the Mayer value for $I^- - I^-$ and 2.5 times the Mayer value for $F^- - F^-$. (There is in fact little initial flexibility if the value of C_{--} for the $F^- - F^-$ interaction is not to be negative.)

Our view of the quenching of the van der Waals interactions by overlap is supported when we find that C_i for RbF and KI lies below the value predicted by adding contributions from anion and cation. We expect quenching of the $Rb^+ - Rb^+$ interaction in RbF and of the $I^- - I^-$ attraction in KI because of ion overlap.

This effect is represented in our potentials by the substitution of the polynomial potential for the $1/r^6$ form when $r < r_a$ and quantitatively by adjusting the value of r_a and r_m for each particular potential. We consider first the anion-anion interactions. We can certainly neglect interactions between $Li^+ - Li^+$ and $Na^+ - Na^+$ to good order and

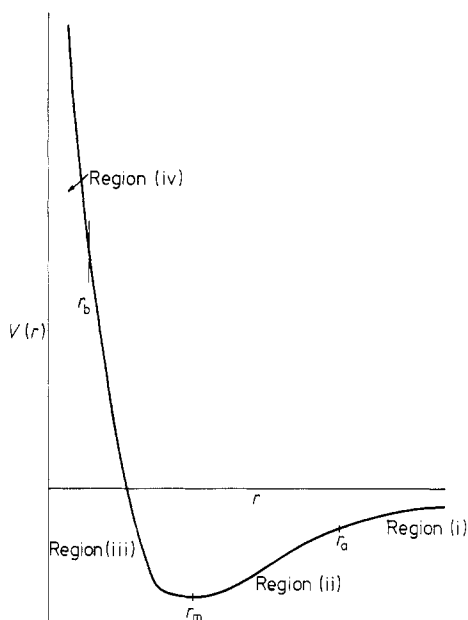


Figure 1. Schematic plot of composite potential showing various regions: Region (i), $r > r_a$, $V(r) = -C/r^6$; Region (ii), $r_a > r > r_m$, $V(r)$ is a third-order polynomial; Region (iii), $r_m > r > r_b$, $V(r)$ is a fifth-order polynomial; Region (iv), $r_b > r$, $V(r) = A \exp(-r/\rho)$. The polynomials are determined so as to be continuous in function, gradient and second derivative at r_a , r_m and r_b . The minimum is fixed at r_m .

Table 3. Potential parameters—set 2.

(a) Second-neighbour interactions.

- (i) $r > r_a$ $V(r) = -C/r^6$.
 (ii) $r_a > r > r_m$ $V(r)$ is a third-order polynomial, continuous in function and two derivatives with the potential in region (i) at r_a and with a minimum at r_m .
 (iii) $r_m > r > r_b$ $V(r)$ is a fifth-order polynomial, continuous in function and two derivatives with potential (ii) at r_m and potential (iv) at r_b .
 (iv) $r_b > r$ $V(r) = A \exp(-r/\rho)$.

Interaction	$C(\text{eV } \text{\AA}^6)$	$r_a(\text{\AA})$	$r_m(\text{\AA})$	$A(\text{eV})$	$\rho(\text{\AA})$	$r_b(\text{\AA})$
K^+-K^+	52.0	(3.69)	(3.17)	(3796.9)	(0.2603)	(2.57)
Rb^+-Rb^+	208.8	3.993	3.442	(6808.1)	(0.2704)	(2.78)
F^--F^-	26.8	3.457	2.833	1127.7	0.2753	2.0
Cl^--Cl^-	165.4	4.103	3.551	(1227.2)	(0.3214)	(2.69)
Br^--Br^-	274.4	4.379	3.737	(2948.2)	(0.3164)	(2.90)
I^--I^-	566.4	4.965	3.813	(5502.5)	(0.3066)	(3.21)

Note: (i) All like interactions between Li^+-Li^+ and Na^+-Na^+ were ignored in fitting potentials.

(ii) Data in brackets may be varied independently without altering the elastic constants or equilibrium properties of any substance as determined using these potentials.

Table 3.—continued

(b) Near-neighbour potentials. $V(r) = A \exp(-r/\rho)$.

Substance	$A(\text{eV})$	$\rho(\text{\AA})$
LiF	393.7	0.2767
LiCl	336.1	0.3489
LiBr	300.9	0.3774
LiI	—	—
NaF	1189.8	0.2677
NaCl	872.7	0.3341
NaBr	778.0	0.3579
NaI	789.1	0.3829
KF	1958.8	0.2865
KCl	4660.8	0.3007
KBr	4172.7	0.3177
KI	4968.3	0.3328
RbF	961.2	0.3334
RbCl	3527.5	0.3240
RbBr	5537.5	0.3217
RbI	6255.4	0.3367

hence, using the known value of C_{--} for the F^- – F^- interaction, deduce r_a and r_m from the data for LiF and NaF. In the same way, we fix details of the Cl^- – Cl^- potential using data on LiCl and NaCl, and the Br^- – Br^- potential from LiBr and NaBr. To fix the I^- – I^- potential, we use NaI and KI, including the settled K^+ – K^+ van der Waals interaction for KI.

Except for the F^- – F^- potential, the interactions are fixed only in the region $r > r_m$, which covers the next-neighbour separations found in all substances except LiF. Thus, only in the latter case need we make any assumption as to the form of the potential in the overlap region. We have in fact used a fifth-order polynomial joined smoothly at the minimum and to the calculated, exponential, overlap potential at 2.0 Å. For F^- – F^- , this gives a smoothly varying interaction and is supported by defect studies on fluorite crystals (Catlow *et al* 1977). But we can actually learn very little about the potential in this region from crystal data as, even in LiF, the F^- – F^- separation is very close to the minimum.

We have used all available data to fix the potentials. The validity of the procedure is confirmed rather by the coherent overall pattern of results. Thus the minima correspond quite closely to the minima in the potentials of the isoelectronic rare gases (table 4(a)). The ions are seemingly smaller despite the smaller nuclear charge, but the ions are also more polarizable. This strengthens the van der Waals interactions and reduces the separation at which overlap and attractive forces balance. In any case, the most significant feature is the regular trend.

The potential minima also scale regularly with the ion radius. The ratios of the potential minima to Fumi–Tosi ion radii in table 4(b) vary from 2.36 for F^- – F^- through 2.21 for Cl^- – Cl^- , 2.15 for Br^- – Br^- to 1.98 for I^- – I^- . Even the ratio shows a trend. There is a similar regularity in the spline points, although these influence the potential only slightly within wide limits. The spline points never trespass into a region where this quenches an interaction which we initially assumed unmodified.

We use scaling arguments to fix the remaining potential parameters. For cation–

Table 4. Comparison of potentials.

(a) Comparison of minima for second-neighbour ion-ion and isoelectronic rare-gas potentials.

Ion potential	Minimum (Å)	Isoelectronic rare-gas potential	Minimum (Å)	Reference
F ⁻ -F ⁻	2.833	Ne-Ne	3.102	(a)
Cl ⁻ -Cl ⁻	3.551	Ar-Ar	3.761	(b)
Br ⁻ -Br ⁻	3.737	Kr-Kr	4.007	(c)
I ⁻ -I ⁻	3.813	Xe-Xe	4.362	(c)

References to gas potentials:

(a) Farrar *et al* (1973).(b) Barker *et al* (1971).(c) Barker *et al* (1974).

(b) Comparison of potential parameters with ion radii.

Ion	Radius r_0 (Å)	r_a/r_0	r_m/r_0	r_b/r_0
K ⁺	1.539	(2.40)	(2.06)	(1.67)
Rb ⁺	1.667	2.40	2.06	(1.67)
F ⁻	1.199	2.88	2.36	1.67
Cl ⁻	1.608	2.55	2.21	(1.67)
Br ⁻	1.736	2.52	2.15	(1.67)
I ⁻	1.924	2.58	1.98	(1.67)

(i) Radii are from Fumi and Tosi (1964).

(ii) Numbers in brackets were assumed and in fact were used to fix the relevant parameters in table 3.

(c) Comparison of hardness factors ρ (Å) for near-neighbour interactions.

	—This work—		From Gilbert (1968)	Electron-gas calculation
	Set 1	Set 2		
LiF	0.2614	0.2767	0.248	
LiCl	0.2786	0.3489	0.307	
LiBr	0.2882	0.3774	0.328	
LiI	0.2617	—	0.358	0.355
NaF	0.2555	0.2677	0.258	0.286
NaCl	0.2903	0.3341	0.317	0.327
NaBr	0.3014	0.3579	0.338	0.337
NaI	0.3099	0.3829	0.368	0.356
KF	0.2770	0.2865	0.285	
KCl	0.3048	0.3007	0.343	
KBr	0.3295	0.3177	0.364	
KI	0.3264	0.3328	0.395	0.357
RbF	0.2945	0.3334	0.294	
RbCl	0.3233	0.3240	0.352	
RbBr	0.3321	0.3217	0.373	
RbI	0.3431	0.3367	0.404	0.357

cation interactions, we have van der Waals quenching only in RbF. We cannot fix r_a and r_m separately even for Rb^+-Rb^+ , and hence set $r_a/r_m = 1.16$, the value for Cl^--Cl^- and essentially for Br^--Br^- . The parameters for Rb^+-Rb^+ then show much the same pattern as the anions. The minimum is at a smaller separation than for Cl^--Cl^- , the correct ratio using Goldschmidt radii but opposite to that predicted by Fumi-Tosi radii. This can have no real significance. We then fix minimum and spline points for K^+-K^+ in the same ratios to the Fumi-Tosi radii. One feature of the cation-cation interactions is perhaps significant. The van der Waals parameters exceed the Mayer values by a factor larger than that found for the anions. But the later analyses of Lynch (1967) and Hajj (1966) support this result.

We now have a complete description of the next-neighbour interactions in the region $r > r_m$, independent, except for F^--F^- , of the form of potential assumed for the overlap region.

In all other cases, we have no data appropriate to this latter region. It is, nonetheless, convenient to provide a complete interaction. As for F^--F^- , we join a fifth-order polynomial at r_b to an exponential potential based on the electron-gas calculation and join smoothly at the minimum. The point r_b is scaled with the appropriate ion radius, based on $r_b = 2.0 \text{ \AA}$ for F^--F^- .

With a complete representation of the second-neighbour potentials, we finally fix the parameters A and ρ in a Born-Mayer potential to describe the near-neighbour interactions. We use the two pieces of crystal data remaining for each substance. We propose no further potential for LiI and set $c_{12} = c_{44}$ for KBr to determine $c_{11} - c_{12}$.

2.3. Comparison of the potentials

We thus have two sets of potentials, essentially equivalent in their valid description of the elastic shear properties but, nonetheless, with substantial differences. For example, in the first set of potentials given in table 2, the next-neighbour van der Waals interaction in LiBr is totally quenched and the interaction is repulsive. In the second set of potentials, the separation of Br^--Br^- in LiBr corresponds to the potential minimum. The difference is apparent in the calculated cohesive energies but not clearly because of the dominance of Coulomb terms. However, such variations clearly emphasize the significant influence of the assumed form of interaction and the need to check this from data on different substances.

Such assumptions also affect the interaction deduced for immediate neighbours. Where the van der Waals interaction is unquenched, the two sets of near-neighbour potentials are closely analogous. For the Li^+ and Na^+ salts, however, the hardness factors ρ show very different behaviour in the two sets of potentials. With a Buckingham second-neighbour interaction, the ρ 's for all the Li^+ and Na^+ salts are rather similar. With our alternative, more realistic, second-neighbour potential, the value deduced for ρ increases substantially for the heavier anions.

We now discuss the validity of this trend separately for the light and heavy cations. For Li^+ and Na^+ salts, we seek independent verification of the observation that ρ is largely independent of cation but increases for larger anions. In table 4(c), we compare our two sets of ρ values with an analysis of a limited range of electron-gas calculations and Gilbert's (1968) values deduced from molecular data. We select these latter values since, unlike in many other analyses, they were deduced using a potential omitting near-neighbour van der Waals interactions; they thus compare strictly with our own results. The best solid-state, molecular and calculated potentials agree rather closely.

However, for the K^+ and Rb^+ salts, there is a discrepancy. The molecular and calculated potentials show the same trend to larger ρ with heavier anion while the solid-state potentials show smaller, more constant ρ values. A possible explanation is the neglect of the attractive parts of the anion-cation interaction, which should be much smaller for Li^+ and Na^+ salts.

If the actual potential falls below a limiting exponential, the parameters deduced assuming such a form will vary depending on the separation that is used for fitting. The solid-state potential is fixed to the gradient and curvature of the interaction. Specifically, the effective ρ value is the ratio of gradient to curvature. It is zero at the minimum but exceeds the limiting value on the repulsive side of the minimum where the curvature is decreased and the gradient increased as the actual potential falls below the limiting exponential form. Thus, in such a region, we might expect a wide and unpredictable variation in the fitted potential.

Clearly, then, the near-neighbour interactions are susceptible to further refinement, but not on the basis of alkali-halide data alone. The interaction can be studied over a wider range of separation by a simultaneous analysis of solid and molecular alkali halides, but only if the molecular polarization is correctly described. It may be more important to study the anion-cation interactions at larger separations if such distances are in fact found in other materials. The perovskite fluorides look promising; for example, the KF separation in $KMgF_3$ is 3.44 \AA compared with 2.65 \AA in KF. But clearly such information is available only from a comprehensive examination of their properties. Meanwhile, the exponential interactions are a convenient if limited representation.

3. Shell-model parameters

If our models are to be complete in that they describe dielectric as well as elastic properties of the alkali halides, then we must present a set of shell parameters. These are essentially the shell charges Y and spring constants k .

As we have observed in defining potentials, there is a great convenience in a set of parameters that refer specifically to each ion and are independent of its environment. It is well known (Tessman *et al* 1953) that we may divide the high-frequency ionic polarization into unique anion and cation parts and deduce characteristic ion polarizabilities. Equally, Cochran (1959) has shown that the static dielectric properties may be analysed to a quite good approximation, using unique shell parameters for each ion.

We have therefore varied a single shell charge and spring constant for each of the eight ions forming our series of sixteen isostructural halides. The optimum values given in table 5 give a best fit to the optical and static dielectric constants and the transverse-optic frequency of all sixteen halides. The fit is therefore of sixteen variables to forty-eight pieces of independent data; the low-temperature experimental values used in the fit are found in table 1.

The two sets of values in table 5 correspond to our two different choices of short-range interaction which influence the dielectric properties to some degree. However, the differences are rather small. The fits are in fact very satisfactory in that they reproduce the optic dielectric constants to about 2%, the static dielectric constants and optic frequencies to about 5%.

However, it is rather more difficult to ascribe a physical basis to the parameters. The clearest interpretation must involve a discussion of the ion polarizabilities, which are given in the table with the parameters. The polarizabilities quoted are free-ion polariz-

Table 5. Shell-model parameters.

Ion	Set 1			Set 2			Experiment†
	$Y(e)$	$k(\text{eV } \text{\AA}^{-2})$	$\alpha(\text{\AA}^3)$	$Y(e)$	$k(\text{eV } \text{\AA}^{-2})$	$\alpha(\text{\AA}^3)$	
Li ⁺	0.705	7.989	0.87	1.267	79.85	0.28	0.03
Na ⁺	2.128	96.44	0.66	2.216	125.2	0.55	0.255
K ⁺	-83.55	86032.0	1.14	1076.0	13430000.0	1.21	1.201
Rb ⁺	-125.3	121460.0	1.81	204.6	330300.0	1.77	1.797
F ⁻	-1.339	37.98	0.66	-1.405	36.50	0.76	0.759
Cl ⁻	-2.485	29.38	2.94	-1.984	17.52	3.15	2.974
Br ⁻	-2.705	24.66	4.15	-2.094	13.66	4.50	4.130
I ⁻	-4.087	39.95	5.85	-2.679	15.16	6.63	6.199

† Tessman *et al* (1953).

abilities, that is Y^2/k , since the crystal polarizabilities $Y^2/(k + R)$ depend on the repulsive force constant R . In fact our polarizabilities agree very well with those of Tessman *et al* (1953) except for the small cations where our values are somewhat larger. In these cases, there is the most marked effect of changing the short-range interaction, and the second set of interionic potentials in fact give more reasonable polarizabilities: or at least more satisfactory trends.

The least agreeable feature of these parameters is the rather anomalous trend of the cation shell charges and spring constants, while the ratio Y^2/k remains well defined. The small positive shell charges for Li⁺ and Na⁺ may be explained following Bilz *et al*'s (1975) reinterpretation of the physical content of the model. For K⁺ and Rb⁺, the shell charges are very large. In this case, it is worth observing that the sign of the shell charge is effectively undetermined. In the limit of large Y and k at constant $\alpha^{\text{ion}} = Y^2/(k + R)$, the displacement polarizability of the ion $\alpha^{\text{disp}} = -YR/(k + R)$ is very small. The only physical parameter describing the ion is then α^{ion} . This we have verified by reversing the sign of the shell charge at the end of the fit. It is difficult to account for the vanishing of α^{disp} except by the unlikely coincidence of the actual ion-displacement polarization cancelling the effect of charge redistribution in the anion which Bilz *et al* invoke to explain positive cation-shell charges.

This discussion perhaps is unrealistic in even attempting a physical interpretation of what is basically a convenient parametrization of dielectric properties. We are aware of the criticisms levelled by Pantelides (1975) at the concept of the polarization of independent ions. Also, the work of Zeyher (1975) on the atomic theory of the response of alkali halides demonstrated the need for extensions to the shell model. For many purposes, however, the shell-model parametrization of the dielectric properties remains convenient and adequate and the parameters in table 5 are provided to satisfy just such needs.

4. Conclusions

We have deduced new potentials for the alkali halides based on crystal data. We have provided two sets of interionic interactions. The first set assume a Buckingham potential (exponential minus C/r^6) for the second-neighbour interactions and simple exponentials for near-neighbours. The repulsive part of the second-neighbour interaction is provided

by an electron-gas calculation and all other parameters are fitted to the equilibrium equation for each substance and the elastic shear moduli. We have assumed a very restricted radius relation to derive potentials for LiI where no low-temperature elastic constants are available.

The van der Waals interactions deduced by fitting, as is well known, may be larger than the classical values of Mayer (1933), but only for K^+ and Rb^+ salts. For the Li^+ and Na^+ salts, the interaction is quenched by the overlap of the anions. To describe this effect requires more flexible potential forms. Using flexible potentials, that is, polynomials with specified minima connected to the appropriate limiting forms, we have deduced unique second-neighbour interactions that describe the properties of all the halides. These potentials show regular trends and compare consistently with the latest interactions deduced for the inert gases.

The near-neighbour interactions, which are presently represented simply as exponential potentials, depend quite sensitively on the assumed form of the second-neighbour interaction. Using the better second-neighbour potentials, the near-neighbour potentials for Li^+ and Na^+ salts show clear trends that parallel the behaviour of the interactions deduced from calculation and analysis of the properties of the alkali-halide molecules. In the K^+ and Rb^+ salts, the possible effect of attractive contributions in the anion-cation interaction distorts the exponential potential and leads to variations in the potentials deduced in different ways.

Finally, we have derived shell-model parameters to describe the dielectric properties of the halides, making very satisfactory fits using unique shell charges and spring constants for each ion. These reproduce the optic and static dielectric constants and transverse-optic frequencies of all sixteen halides with the NaCl structure.

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Appendix 1. Elastic constants and equilibrium equation for the NaCl lattice in the breathing-shell model (from Sangster 1973)

Equilibrium equation:

$$B + 2B' = -\frac{2}{3}\alpha Z^2.$$

Elastic constants:

$$\frac{vr_0}{e^2} c_{11} = \frac{1}{2}(A + A' + B') - \gamma - 2.55604 Z^2,$$

$$\frac{vr_0}{e^2} c_{12} = \frac{1}{4}(A' - 5B' - 2B) - \gamma + 0.11298 Z^2,$$

$$\frac{vr_0}{e^2} c_{44} = \frac{1}{4}(2B + A' + 3B') + 1.27802 Z^2,$$

where α is the Madelung constant, Z the ion charge (in units of $|e|$), e the electronic charge, r_0 the anion-cation separation, $v = 2r_0^3$ is the unit-cell volume and γ is the 'breathing' contribution. A , B , A' and B' are force constants related to the derivatives of the short-range interactions; $\phi_{+-}(r)$ acts between anion and cation, and the second-neighbour potentials $\phi_{++}(r)$ and $\phi_{--}(r)$ between like cations and anions, respectively. Then

$$\begin{aligned}\frac{e^2}{2v} A &= \left. \frac{d^2 \phi_{+-}}{dr^2} \right|_{r_0}, \\ \frac{e^2}{2v} B &= \left. \frac{1}{r} \frac{d\phi_{+-}}{dr} \right|_{r_0}, \\ \frac{e^2}{2v} A' &= \left(\frac{d^2 \phi_{++}}{dr^2} + \frac{d^2 \phi_{--}}{dr^2} \right) \bigg|_{\sqrt{2}r_0}, \\ \frac{e^2}{2v} B' &= \left(\frac{1}{r} \frac{d\phi_{++}}{dr} + \frac{1}{r} \frac{d\phi_{--}}{dr} \right) \bigg|_{\sqrt{2}r_0}.\end{aligned}$$

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