

Two-body Repulsions in Rare Gas Containing Fluorite Lattices

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An examination of the capability of the δ -function model to account for two-body repulsions occurring in rare gas doped fluorite-type lattices is presented. A previously published work on He dissolution in UO_2 is found to be of doubtful validity. Furthermore, it is shown that the δ -function model is incompatible with available experimental information concerning the lattice parameters and elastic constants of CaF_2 , SrF_2 , and BaF_2 . The poor success of the model in connection with the above alkaline earth fluorides is tentatively attributed to the different characters of closed-shell ion and rare gas atom charge distributions. This explanation is arrived at by attempting to rewrite semiempirical overlap charge potentials in a form similar to the δ -function recipe.

CaF₂-type lattices containing rare gas atoms have been subjected to numerous experimental investigations over the last decade. This interest is due mainly to the technological importance of the fission gas release problem arising with the exploitation of actinide dioxides as nuclear fuels.^{1,2} In connection with theoretical treatments of the above type of crystal defects it would seem profitable to have some simple model which can reproduce in a semiquantitative way the relevant interatomic forces. To the author's knowledge the only published work in this direction is Olander's investigation of helium dissolution in UO_2 .³ Keeping within a central force approximation Olander described the repulsive interactions in the He containing and in the perfect lattice by adopting the δ -function model developed by Frost,⁴ Lipincott,⁵ Weber,⁶ and by Mason and Vanderslice.⁷ The main asset of this model is that it describes diatomic repulsions in terms of a few simple properties of the separate (closed-shell) atoms. This property seems to offer a particularly simple way of estimating atom-ion interactions in rare gas doped ionic lattices; provided the model can be shown to account reasonably well for the central force, repulsive part of the interactions in the host crystal. Although the δ -function recipe has considerable success in predicting the magnitude of forces activated by the overlapping of rare gas atoms at short and medium separations, the issue for calculations on interionic potentials is less clear.

As will be shown presently the problem is hardly resolved by the results of Olander's UO_2 work. The main purpose of the present paper is to attempt to shed some light on this question by examining the applicability of the δ -function prescription to the alkaline earth halides CaF_2 , SrF_2 , and BaF_2 . The reasons for choosing these crystals will be stated in due course.

THE DELTA-FUNCTION MODEL

The model stems from a "toy" theory of the hydrogen atom which replaces the coulomb term in the Schrödinger equation by a δ -function. Proceeding by analogies and by certain plausible intuitive arguments the following recipe has been obtained for the interaction of two closed-shell atoms A - B in the repulsive range

$$\begin{aligned} U_{AB} &= (e^2/a_0)(n_A n_B)^{\frac{1}{2}}(g_A g_B) \exp[-(c_A v_A + c_B v_B)/2] \\ c_A &= g_A [1 - \exp(-c_A v_A)] \\ v_A &= R + 2a_A \exp(-R/a_A) \end{aligned} \quad (1)$$

with similar expressions for c_B and v_B .

Here a_0 is the Bohr radius of the hydrogen atom, $n_{A(B)}$ is the total number of electrons in A(B), $a_{A(B)}$ is the radius of the outermost electronic orbit of A(B), and R is the separation distance between the nuclei of A and B. The parameter $g_{A(B)}$ is a measure of the binding strength of the electrons in A(B), estimated by Mason and Vanderslice from the relation

$$g_{A(B)} = \sqrt{2} \cdot I_{A(B)} / I_H \quad (2)$$

where $I_{A(B)}$ is the ionization potential of the free species A(B) and I_H is the ionization potential of hydrogen. Thus the interatomic repulsive potential can be fully described in terms of a few comparatively simple properties of the separate atoms. On the basis of eqns. (1-2), Mason and Vanderslice found very reasonable agreement with experimental data for both homonuclear and heteronuclear diatomic rare gas complexes at short and medium separation distances. In several cases the results were superior to the ones obtained in more involved quantum mechanical treatments. This success in conjunction with the appealing simplicity of the model probably constitute sufficient reason for attempting to extend the range of applicability to ionic solids.

OLANDER'S CALCULATION

Owing to the unstableness of O^{2-} in a free state Olander could not achieve a complete determination of the model parameters by using eqn. (2) and therefore decided to treat $g_{\text{O}^{2-}}$ and $g_{\text{U}^{4+}}$ as adjustable quantities to be fixed from observed values of the lattice parameter and the compressibility. In addition Olander stated that at the relatively large distances in question the δ -function model can conveniently be reduced to a simple exponential form

$$U_{AB} = (e^2/a_0)(n_A n_B)^{\frac{1}{2}}(g_A g_B) \exp[-(g_A + g_B) \cdot R/2] \quad (3)$$

The underlying approximation, $v_A = v_B = R$ and $c = g$, was assumed to have a negligible effect on the numerical results. The present author feels that this simplification can, perhaps, be justified for crystal interactions also when smaller internuclear distances are involved. The effective separation distance v implies a certain shift of the δ -functions away from the nuclei, which feature was proposed by Mason and Vandarslice on the basis of an analogy with Hurley's floating orbital calculations.⁸ In the variational LCAO approach adopted by Hurley the centres of the atomic orbitals are displaced from the nuclei by amounts depending on the internuclear separation. As was proved by Hurley this "floating" of orbitals makes his model satisfy the Hellmann-Feynmann electrostatic theorem.^{9,10} Proceeding to a comparison of a " δ -function solid" with an "LCAO solid" we note that in a uniform compression of the fluorite-type lattice, which was the only state of strain considered by Olander, the point symmetry about the ion sites ($m3m$ and $\bar{4}3m$ for cation and anion positions, respectively) is sufficiently high to prevent any shift of atomic orbitals away from the ion nuclei. Thus the previously mentioned analogy does not require the δ -functions to shift off the nuclei in this case. Conceivably the difference between R and v may implicitly account for other effects than the shift suggested by the electrostatic theorem in the diatomic case. However, in a solid where each atom or ion interacts with several partners simultaneously such effects would not necessarily be additive, and *a priori* there seems to be no strong reason for preferring eqn. (1) to eqn. (3). At all events eqn. (3) provides a description of repulsive potentials quite similar to the familiar Born-Mayer rule.¹¹ However, in the present context the simplified δ -function model would seem to be the more useful. As remarked by Olander . . . "there is no obvious way of mixing the Born-Mayer potential with a rare gas potential to obtain the ion-atom interaction".

Utilizing Kirkwood-Müller theory^{12,13} Olander included also dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole dispersive forces in his model. The required numerical values of magnetic susceptibilities were directly obtained from literature tabulations, while the dipole polarizabilities were estimated with screening constant calculations and literature data used as guidance.

The predicted cohesive energy deviated from the value obtained by feeding the relevant experimental and estimated data into a Born-Haber cycle¹⁴ by $\sim 0.7\%$, which result most certainly must be considered satisfactory. Also the obtained He solubility was in order of magnitude agreement with observed values.^{15,16} However, there are various approximations of unknown validity underlying the results obtained by Olander. Hence, the success of the calculations of lattice energy and solubility might be fortuitous. That this remark is not overly pessimistic is born out by a scrutiny of the model. Without adding any essential approximations to the ones already introduced by Olander the elastic constants c_{11} and c_{12} implied by his model can be obtained by the long-wave method¹⁷ or, alternatively, by considering two simple homogeneous deformations: uniform compression and the shear deformation defined by $e_{xx} = -e_{yy}$, all other strain components equated with zero.¹⁸ By performing a few simple desk calculations Olander's potentials were found to imply: $c_{11} = 4.77 \times 10^{12}$ dyne \cdot cm⁻² and $c_{12} = -0.06 \times 10^{12}$ dyne \cdot cm⁻². The experimentally

determined single crystal values are: $c_{11} = (3.95 \pm 0.02) \times 10^{12}$ dyne·cm⁻² and $c_{12} = (1.21 \pm 0.02) \times 10^{12}$ dyne·cm⁻². The latter results were obtained from room-temperature, adiabatic measurements,¹⁹ whereas the predicted values refer to 0°K. A comparison of the calculated elastic constants with available experimental data pertaining to lower temperatures²⁰ would hardly be meaningful in view of the onset of appreciable magnon-phonon interactions.^{20,21} A hypothetical UO₂ crystal with magnetic effects quenched would be expected to behave similarly to the diamagnetic ThO₂, the room-temperature single crystal elastic constants of which are:²² $c_{11} = (3.67 \pm 0.04) \times 10^{12}$ dyne·cm⁻², $c_{12} = (1.06 \pm 0.02) \times 10^{12}$ dyne·cm⁻². Measurements on a polycrystalline ThO₂ specimen indicate an increase in the elastic constants of the order of a few percent when the temperature is lowered to 0°K.²³ Therefore, the values calculated on the basis of Olander's potentials are likely to be in strong disagreement with what might loosely be referred to as the lattice contribution to the low-temperature elastic constants of UO₂. The success of the calculation of cohesive energy probably serves to demonstrate the insensitivity of this quantity to inaccuracies in the approach to interionic potentials. With regard to the calculated He solubility the following remarks apply. For an interstitial He atom occupying an octahedral hole in the f.c.c. U⁴⁺ lattice the leading term in the potential energy part of the defect energy is contributed by the difference between the repulsive and dispersive interactions associated with the He atom and its eight nearest neighbour O²⁻ ions. In Olander's calculations these two energy quantities are of almost equal magnitudes, and the accuracy of the result of the subtraction is strongly dependent on the quality of the atom-ion potentials. Since the latter were estimated, in part, from the obtained perfect lattice potentials, the calculated "static" defect energy must be considered to be of doubtful validity. Furthermore, the treatment of vibrational contributions to the defect free energy is open to questioning. The interstitial He atoms were considered to behave as independent Einstein oscillators with an associated frequency of $\sim 8 \times 10^{12}$ sec⁻¹. According to the lattice dynamics calculations carried out by Dolling *et al.*²⁴ on the basis of their inelastic neutron scattering measurements the frequency spectrum of UO₂ exhibits no gap and has an upper edge at $\sim 20 \times 10^{12}$ sec⁻¹. The He oscillators, therefore, are located on the frequency axis at a point corresponding to a non-vanishing density of UO₂ phonon states. According to Wagner's generalization²⁵ of the Lifshitz theory of vibrations in defect lattices²⁶ the "interstitial" Green's function matrix has a pole at 8×10^{12} sec⁻¹. The occurrence of this pole within the band is likely to induce a strong perturbation of band mode frequencies in the immediate vicinity of the He oscillator frequency. Accordingly, one might well expect the single oscillator treatment to break down.

We conclude that the results of Olander's calculations do not furnish sufficient reasons for advocating the use of the δ -function recipe to interactions in solids. Since the rule originates in work on rare gas potentials an application to ionic crystals would, presumably, have to rely on the frequently invoked analogy between closed-shell ions and rare gas atoms. Apart from the caution that should generally be observed when depicting a crystal lattice as an array of "individual" ions the above analogy is particularly hazardous when O²⁻ ions are involved.²⁷⁻²⁹ Therefore, rather than attempting to improve Olander's

calculations by readjusting the model parameters it is probably better to examine the applicability of the δ -function prescription to crystals which, with a higher degree of plausibility, might be referred to as being of the "simple ionic type".

APPLICATION TO ALKALINE EARTH FLUORIDES

In order to investigate further the prospects of the δ -function model it is instructive to see whether it may be reconciled with previous overlap charge (OC) calculations concerning the alkaline earth fluorides CaF_2 , SrF_2 , and BaF_2 .³⁰ A study of the behaviour of rare gases in these lattices may prove to be a valuable first step towards an understanding of the corresponding processes taking place in the isomorphous actinide dioxides; the latter compounds probably being less amenable to a theoretical analysis. Experimental work on rare gas release rates in CaF_2 and BaF_2 has already been reported.³¹⁻³³ Moreover, the present author has recently prepared extensive numerical tabulations of data required in performing a static Kanzaki-type³⁴ and a dynamic Green's function-type^{25-26,35} analysis of defect induced effects in the three crystals. These data will be made available in a forthcoming paper.

The OC calculations referred to above have been described at length elsewhere³⁰ and the details need not be repeated here. It suffices to note that the calculation scheme is based on a semiempirical version^{30,36} of the Heitler-London method within the S^2 approximation.²⁷ The magnitude of three-body forces and the steepness of short-range, central force repulsions are estimated from the dependence of overlap charge magnitude on the separation distance between overlapping ions. The non-orthogonality of (free ion) orbitals centred on adjacent lattice sites gives rise to a shift in charge density when reckoned on the density obtained by a superposition of free ion densities. Within the S^2 approximation this density shift can be divided into separate distributions, overlap charges, each one associated with a particular pair of ions. For a number of diatomic complexes of closed-shell ions it is found that the magnitude of overlap charge, q_{AB} , as a function of R_{AB} can be reasonably well fitted by a simple relation

$$q_{AB} \propto R_{AB} \exp(-g_{AB}R_{AB}) \quad (4)$$

where the parameter g_{AB} can be regarded as a constant for a restricted range of R_{AB} .^{30,36-37} By assumption the steepness parameter of an exponential repulsive potential, U_{AB} , equals g_{AB} , which quantity, in the homonuclear case, can therefore be compared to the result of applying eqn. (2) to the appropriate ionization potential or electron affinity. The OC steepness parameter has been evaluated for some homonuclear pairs of interest in the present context. The results are displayed in Table 1 where the eqn. (2)-values have been included for comparison.

For crystal ions at sites possessing $m\bar{3}m$ or $\bar{4}3m$ point symmetries (dipole) polarization of orbitals is suppressed and eqn. (3) may be regarded as the appropriate form of the δ -function model. Then the I - g 's may directly be compared to the OC- g 's. One sees from Table 1 that (at least for separation distances of interest here) the use of eqn. (2) exaggerates the $\text{M}^{2+} - \text{M}^{2+}$ values

and grossly underestimates the $F^- - F^-$ values as compared to the OC results. The disagreement is not entirely unexpected. In the OC scheme g is determined by the character of the tails of the outer atomic orbitals involved. One may argue that in an isoelectronic series . . . $A^{2+}B^+C D^-$ the ionization potential, and thereby g as defined by eqn. (2), decreases upon going through the series in the sequence stated, and that the tails of the outer orbitals become increasingly diffuse in the same order. Thus a decrease in the steepness of the repulsive potential from $A^{2+} - A^{2+}$ to $D^- - D^-$ is predicted by both definitions of g . On the other hand the outer orbitals often penetrate quite deeply into the core even in the case of negative ions. If this is the case, a non-negligible contribution to I is determined by the behaviour of the outermost orbital within the core region. Generally this would seem to preclude a quantitative characterization of the slope of the orbital tail by the simple relation, eqn. (2), as born out by Table 1 for the ions included. For rare gas atoms the I - g 's should be compared to the OC- g 's pertaining to the region $4.5 \lesssim R \lesssim 5.5$. In this region the difference between R and the effective separation distance v is unimportant and eqn. (1) reduces to the exponential relation, eqn. (3). The agreement between the two sets of g values is tolerable. If it were not, the OC scheme would be rendered dubious since eqn. (2) works rather well in the case of rare gas atoms.

Table 1. Homonuclear steepness parameters.

He—He ^a	2.44(3.5—4.5)	2.49(4.5—5.5)	2.56(<i>I</i>)
Ne—Ne ^b	2.38(3.5—4.5)	2.42(4.5—5.5)	2.24(<i>I</i>)
Ar—Ar ^b	1.66(3.5—4.5)	1.77(4.5—5.5)	1.64(<i>I</i>)
Ca ²⁺ —Ca ^{2+c}	2.91(4.5—5.0)	3.18(6.0—7.0)	5.33(<i>I</i>)
Sr ²⁺ —Sr ^{2+d}	2.40(4.5—5.0)	2.66(7.5—8.0)	4.49(<i>I</i>)
Ba ²⁺ —Ba ^{2+d}	2.00(4.8—5.0)	2.34(8.0—8.5)	3.86(<i>I</i>)
F ⁻ —F ^{-b}	1.51(4.5—5.0)	1.48(5.0—5.5)	0.36(<i>I</i>)

Numbers enclosed in brackets indicate the respective ranges of internuclear separation in a.u. (*I*) denotes results obtained from eqn. (2). The upper index of the pair designations refers to the origin of the adopted wave functions: ^aRef. 38, ^bRef. 39, ^cRef. 40, ^dRef. 30.

Table 2. Heteronuclear steepness parameters in the range $4.5 \lesssim R \lesssim 5.0$ a.u.

	Ne	Ar	F ⁻	Ca ²⁺	Sr ²⁺	Ba ²⁺
He	2.44(2.45)	2.07(2.13)	1.73(1.99)	2.67(2.70)		
Ar	2.06(2.09)			2.17(2.34)		
F ⁻				1.93(2.21)	1.82(1.95)	1.71(1.75)

The bracketed numbers refer to g values obtained as $g_{AB} = \frac{1}{2}(g_{AA} + g_{BB})$.

If the OC method of evaluating steepness parameters is given preference when ions are involved, it becomes pertinent to ask whether eqn. (4) is compatible with the mixing rule $g_{AB} = \frac{1}{2}[g_{AA} + g_{BB}]$ implied by eqn. (3) in the heteronuclear case. As can be seen from Table 2, the arithmetic mean overestimates g_{AB} by an amount which increases with the magnitude of $(g_{AA} - g_{BB})$. For diatomic, heteronuclear rare gas complexes the agreement varies from excellent

(He-Ne) to reasonable (He-Ar). However, when the constituents of the pair have essentially different characters ($F^- - Ca^{2+}$), the agreement is rather poor. Therefore, in the general case it might seem natural to rewrite eqn. (3) in the "homonuclear" form

$$U_{AB} = (e^2/a_0)K (n_A n_B)^{\frac{1}{2}} g_{AB}^2 \exp(-g_{AB} R) \quad (5)$$

K = some value independent of A and B

where g_{AB} is to be evaluated by overlap integral calculations. The above relation preserves the main virtue of the δ -function model; it being still possible to obtain the repulsive potential in a very simple fashion. The second part of eqn. (5) is dictated by the requirement that the prescription should be applicable to atom-ion repulsions. In the case of rare gas doped ionic lattices there is, as far as the author is aware of, no experimentally determined quantity which lends itself to an empirical scaling of atom-ion interactions in a straightforward manner. In so far as eqn. (5) can be regarded as an extrapolation of eqn. (3) the choice $K=1$ would seem to be a plausible conjecture. However, before applying eqn. (5) to atom-ion repulsions the capability of this relation to account reasonably well for the host lattice ion-ion repulsions should be tested. Unfortunately it turns out that the second part of eqn. (5) is incompatible with the available information concerning the lattice parameters and elastic constants of CaF_2 , SrF_2 , and BaF_2 . As will be seen shortly the experimental values of the latter quantities suggest that K depends rather strongly on the type of pair in question. Accordingly K will henceforth be referred to as K_{AB} . In previous calculations³⁰ the observed c_{11} and c_{12} values were exploited in an empirical scaling of the OC potentials. Simultaneously the lattice model was required to be in a stressfree state at the experimental lattice parameter value. The dispersive forces were taken into account by using Kirkwood-Müller theory.^{12,13} By relaxing the restriction imposed by the second part of eqn. (5) the outcome of these calculations may be rewritten in the form prescribed by the first part of eqn. (5). The resulting K_{AB} values are displayed in Table 3. Before commenting on these values it should be remarked that the rare gas potentials obtained by setting K_{AB} equal to unity nearly coincide with those predicted by eqn. (3). This, in turn, implies good agreement with experimental values of the interaction energy at internuclear separations where polarization effects are relatively unimportant. Hence the K_{AB} values shown in Table 3 seem to indicate that a certain modification of a rare gas type potential is required in the case of ion-ion interactions. It is tempting to ascribe the deviations of ion pair K_{AB} values from unity to the characteristics of the outer ion orbitals. Comparing a $F^- - F^-$ pair to a pair of rare gas atoms one would expect the diffusiveness of the $F^- - 2p$ orbital to give a comparatively large weight to the attractive contributions (exchange energy among others) counteracting the repulsion caused by the interaction of the overlap charge with the nuclear charges. Hence K_{F-F} should be less than unity as born out by Table 3. By reversing the argument one obtains $K_{M^{2+}M^{2+}} > 1$. Unfortunately, the present OC model is not sufficiently elaborate to allow one to obtain a meaningful estimate of the supposedly small $M^{2+} - M^{2+}$ repulsions in the three crystals. Turning to the $M^{2+} - F^-$ pairs it should be

Table 3. K -factors pertaining to nearest ($M^{2+}-F^-$) and second nearest ($F^- - F^-$) repulsive interactions.

	$CaF_2^{(1)}$	$CaF_2^{(2)}$	SrF_2	BaF_2
$M^{2+} - F^-$	2.649(2.168)	2.608(2.127)	2.169(1.846)	1.986(1.754)
$F^- - F^-$	0.380(0.513)	0.479(0.611)	0.386(0.443)	0.346(0.227)

$CaF_2^{(1)}$ refers to results obtained from the use of the experimental, 4°K elastic constants reported by Huffman and Norwood.⁴¹ More recent measurements^{42,43} indicate that the roomtemperature c_{12} value of Huffman and Norwood is too high by 0.09×10^{12} dyne \cdot cm⁻². A lowering of their c_{12} value at 4°K by the same amount led to the above $CaF_2^{(2)}$ results. The SrF_2 and BaF_2 results were obtained from the low-temperature elastic constants reported by Gerlich.^{44,45} The braced values resulted from a neglect of three-body overlap charge forces.

remarked that the outermost p orbitals of the metal ions become increasingly extensive in the order Ca^{2+} , Sr^{2+} , Ba^{2+} .³⁰ Thus one expects $K_{Ca^{2+}F^-} > K_{Sr^{2+}F^-} > K_{Ba^{2+}F^-}$ in agreement with Table 3. Altogether the trend in the Table 3 results is in qualitative agreement with the so-called Pauling factors appearing in Born-Mayer potentials.¹¹ However, the empirically obtained K_{AB} factors depend more strongly on the net ionic charges than do the Pauling factors.

DISCUSSION

Olander claims the δ -function formulation to be equally valid for ions and atoms provided that appropriate values of g can be determined.³ If the OC calculations can be regarded as even qualitatively indicative the above assertion is not vindicated. This rather disappointing result may to a certain extent depend on the various uncertainties and approximations inherent in the OC scheme invoked. However, the possible uncertainty in the low-temperature c_{12} value of CaF_2 (see footnote to Table 3) and the probable inaccuracy of Kirkwood-Müller theory (see footnote to Table 4) do not appreciably affect the trend in K_{AB} values, as is apparent from Tables 3-4. Furthermore, one sees from these tables that, with the exception of $K_{F^-F^-}(BaF_2)$, the inclusion of three-body forces originating in overlap charges leads to K_{AB} factors which deviate more strongly from unity than do the ones resulting from a central force model.

Table 4. Influence of uncertainties in van der Waals potentials on K -factors for $CaF_2^{(2)}$.

$\alpha_{F^-} \times 10^{24}$ cm ⁻³ =	1.40	0.80	0.60
$M^{2+} - F^-$	2.608(2.127)	2.433(1.952)	2.366(1.885)
$F^- - F^-$	0.479(0.611)	0.241(0.374)	0.178(0.311)

The use of Kirkwood-Müller theory is likely to exaggerate the magnitude of dispersive forces.¹² A diminishing of the calculated dispersive forces is conveniently effected by employing a F^- polarizability, α_{F^-} , smaller than the free ion Hartree-Fock value of 1.40×10^{-24} cm³.⁴⁶ The above results display the attendant effect on K -factors. The braced values refer to a neglect of three-body overlap charge forces.

A conspicuous objection to OC calculations based on free ion wave functions arises from the neglect of distortions which may be induced on the ions when they are brought from a free to a crystalline state. The careful analysis of X-ray Bragg reflection data carried out by Maslen⁴⁷ seems to confirm the essentially ionic character of CaF_2 . However, due to the insensitivity of such data to the outer parts of the crystal constituents Maslen's work does not reveal the deformations which are likely to take place in these regions. Since the steepness parameters are determined primarily by the orbital tails, the pronounced dependency of K_{AB} on the nature of A and B may conceivably be a fortuitous feature produced by the combination of inadequate g_{AB} values with the observed c_{11} , c_{12} , and lattice parameter values. Giving the δ -function model the benefit of the doubt it was attempted to reconcile eqn. (1) and eqn. (3) with the latter experimental quantities in an entirely empirical fashion by treating the g 's as fitting parameters. In addition, the Kirkwood-Müller dispersive potentials were made adjustable by allowing the electronic dipole polarizability of F^- , α_{F^-} , to vary. The remaining parameters needed when specifying the dispersive potentials were fixed at the numerical values adopted in previous calculations.³⁰ The model was forced to predict correct values for the lattice parameters of CaF_2 , SrF_2 , and BaF_2 . Subjected to this restriction the sum of squares of relative c_{11} and c_{12} errors were minimized with respect to the fitting parameters. Since the results obtained by using eqn. (1) were consistently inferior to those stemming from the use of eqn. (3), only the latter will be commented upon here. A "best" set parameters could not be found for any of the three crystals owing to the existence of several local minima of the sum of squares in the space of fitting parameters. The results may briefly be described as follows.

i) CaF_2 : The relative error in c_{11} could be made no smaller than 10 %, as compared to an experimental uncertainty of 0.8 %, ⁴¹ while the c_{12} error remained within the (speculated) uncertainty in the experimental value (see footnote to Table 3). For any positive value of α_{F^-} g_{F^-} exceeded 1.6 while $g_{\text{Ca}^{2+}}$ kept below 1.8.

ii) SrF_2 : c_{11} and c_{12} values correct to within the stated uncertainty in the observed values, 0.2 %, ⁴⁴ could be obtained for positive α_{F^-} -values below 0.8 Å³. Within this range $g_{\text{F}^-} > 1.9$ and $g_{\text{Sr}^{2+}} < 1.5$.

iii) BaF_2 : Although the correct c_{11} value could be realized for $1.1 \lesssim \alpha_{\text{F}^-} \lesssim 1.2$ Å³, the c_{12} error consistently exceeded 15 % (experimental uncertainty 0.2 %).⁴⁵ In particular, for α_{F^-} -values which led to a correct c_{11} value the c_{12} error was found to be ~ 20 %. Whatever the value of α_{F^-} , g_{F^-} kept within the range 1.9 – 2.1 while $1.2 \lesssim g_{\text{Ba}^{2+}} \lesssim 1.3$.

Considering the amount of flexibility inherent in the calculation procedure the fit to c_{11} and c_{12} must, in the cases of CaF_2 and BaF_2 , be regarded as very poor. To the extent that the anticipated distortion effects can be discussed in terms of the Madelung field⁴⁷⁻⁴⁸ or, alternatively, by placing the crystal ions in "effective" potential wells,^{49,50} one expects a contraction of anions and an extension of cations as compared to ions in their free states. Although the deviations of the above g values from the Table 1 results seem to be in qualitative agreement with this picture, the adjusted $g_{\text{M}^{2+}}$ parameters are likely to be smaller than can be accounted for by invoking the effects of

crystalline environments. For $g_{\text{Ba}^{2+}}$, in particular, the obtained range $1.2 \lesssim g_{\text{Ba}^{2+}} \lesssim 1.3$ suggests a "loosening" of Ba^{2+} sufficiently drastic to give it an anionlike character. As compared to free ions a $g_{\text{Ba}^{2+}}$ value in this range would seem to require the existence of a "crystal" Ba^{2+} ion with outer parts surpassed in diffusiveness only by the rather extreme case of H^- . On the basis of a Hartree-Fock calculation of the $1s\text{H}^-$ orbital⁵¹ the OC scheme predicts a g_{H^-} value of ~ 0.6 .

Altogether it seems doubtful whether the relations eqn. (1) and eqn. (3) are capable of representing adequately the short-range repulsions in CaF_2 , SrF_2 , and BaF_2 . Rather than reflecting distortion effects the trend in the adjusted g parameters is probably caused by the omission of K_{AB} factors in the δ -function model. The latter statement is supported by the following argument. To the extent that an "ionic" lattice model may be regarded as realistic the experimental elastic constants require the major part of short-range interactions to be associated with nearest neighbour $\text{M}^{2+} - \text{F}^-$ interactions. Predominance of nearest neighbour interactions is suggested also by the available experimental information on the effects of anharmonicity on CaF_2 and BaF_2 neutron diffraction intensities.^{52,53} When a $K_{\text{F-F}}$ factor smaller than unity is neglected, a small $\text{F}^- - \text{F}^-$ repulsion can be realized only by adopting a large g_{F^-} value. This, in conjunction with the omission of a $K_{\text{M}^{2+}\text{F}^-}$ factor larger than unity, forces the fitting process to select an unduly small $g_{\text{M}^{2+}}$ value in order that a reasonably large $\text{M}^{2+} - \text{F}^-$ interaction may be maintained. The accompanying increase in $\text{M}^{2+} - \text{M}^{2+}$ repulsions is largely offset by the comparatively large distance between neighbours of the third order.

CONCLUSION

The experimental situation concerning rare gas location in ionic lattices is still in a state of flux^{1,2,54}. Hence, highly refined and laborious quantum mechanical calculations of defect energy and related quantities would seem to be premature at the present stage. In anticipation of more experimental information simple exploratory investigations of the type reported by Olander³ are very much in demand. It is doubtful, however, whether a straightforward description of the relevant interactions in terms of the δ -function model is sufficiently realistic. Work on alternative potential models is now in progress.

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