PHYSICAL REVIEW B VOLUME 29, NUMBER 2 15 JANUARY 1984

In-crystal polarizabilities of alkali and halide ions

P. W. Fowler
The University Chemical Laboratory, Lensfield Road, University of Cambridge, Cambridge CB2 1EW, United Kingdom

P. A. Madden*
The Royal Signals and Radar Establishment, St. Andrew's Road, Great Malvern, Worcestershire WR14 3PS, United Kingdom

(Received 14 June 1983)

Ab initio values for the polarizabilities of the F^-, Cl^-, H^-, Li^+, Na^+, and K^+ ions have been calculated, both for the isolated ions and in the crystalline environment appropriate to alkali halide crystals. The in-crystal values agree well with those deduced from refractive-index data. They are similar to the isolated ion values for the cations, but much smaller for the anions. The origins of this anion effect are resolved by the separate consideration of the influence of the electrostatic crystal field and of the overlap with the six nearest cation neighbors. The consequences of the effect on the transferability of in-crystal polarizabilities between different substances are discussed.

I. INTRODUCTION

In a recent paper[1] we considered the relationship between the polarizability of an isolated fluoride ion and of a fluoride ion in the crystalline environment appropriate to lithium fluoride. In-crystal ionic polarizabilities are obtained experimentally from the refractive index of the crystal by way of the Clausius-Mossotti relationship. It has been known for many years that for the alkali and halide ions their values are reasonably transferable[2,3] over the range of alkali-halide crystals. Polarizabilities of isolated ions have not been directly measured, but good estimates have been obtained from *ab initio* calculations. For anions these values are much larger than the corresponding in-crystal values; in the case of the fluoride ion in LiF they differ by a factor of 2.5.[1] For cations the effect of the crystalline environment is much smaller; measured, in-crystal polarizabilities[3] agree with isolated-ion values from *ab initio* calculations.[4,5]

In a previous paper we resolved the effect of the crystalline environment into contributions from three physically distinct sources.

(1) Crystal-field effects which result from the purely Coulombic interactions of a lattice of point charges with the electrons of the ion under consideration. As Hurst[6] and Mahan[7] have shown, the effect of the electrostatic potential is to compress an anion and expand a cation and hence to make an anion less polarizable and a cation more so. In our calculations[1] the crystal-field effects are simulated by placing the ion at the center of a cubic lattice of bare point charges. For LiF the result was a reduction in the F^- polarizability[1] from the isolated-ion value of 2.31 Å^3 to 1.33 Å^3, whereas the Li^+ value was very slightly increased. The reduction in the correlation contribution to the F^- polarizability was particularly marked, from 0.73 to 0.25 Å^3.

(2) Overlap compression of the charge cloud of the ion through its interaction with the charge clouds of its neighbors. In orbital terms this effect results from the interaction between the orbitals of the ion and the *occupied* orbitals of the neighbors. This feature may be exploited to isolate[1] the overlap compression of the anion polarizability from the results of calculations on a cluster of ions in the lattice. For LiF the result was a further decrease in the F^- polarizability to 0.92 Å^3 (which agrees very well with the experimental in-crystal value[3]). Again the effect on the correlation contribution was large; it changed from 0.25 to 0.11 Å^3.

(3) Charge-transfer effects: In orbital terms these arise from the delocalization of electrons from one ion into the unoccupied orbitals of another. In an *ab initio* calculation this physical effect may be masked by an artifact of the calculations known as the basis-set superposition error (BSSE).[8] For F^- in LiF we were able to establish that the charge-transfer contributions to the in-crystal polarizability were small.[1]

In this paper we shall apply these ideas to obtain in-crystal polarizabilities for the H^-, Cl^-, Li^+, Na^+, and K^+ ions. In addition we shall investigate the transferability of the in-crystal polarizability between different substances.

The *ab initio* methods and the basis sets used in the calculations are described in Sec. II. In Sec. III we obtain crystal-field polarizabilities for all the ions of interest as a function of the lattice constant, and we find that the *cation* polarizability is scarcely affected by the crystal environment. We then examine the effect of overlap compression on the anion polarizability at the Hartree-Fock level by performing calculations for F^-, Cl^-, and H^- ions surrounded by Li^+ and Na^+ neighbors. In Sec. V we consider the effect of overlap compression on the correlation contribution. From the results of this extensive series of calculations we have noted an empirical relationship between environmental effects on the Hartree-Fock and correlation contributions to the polarizability. This relationship is discussed in Sec. VI; it enables us to estimate correlation contributions for systems which are too large for a direct calculation [for example, the F^--$(Na^+)_6$ cluster]. By combining these results we are able to give theoretical values for the selected ions in a

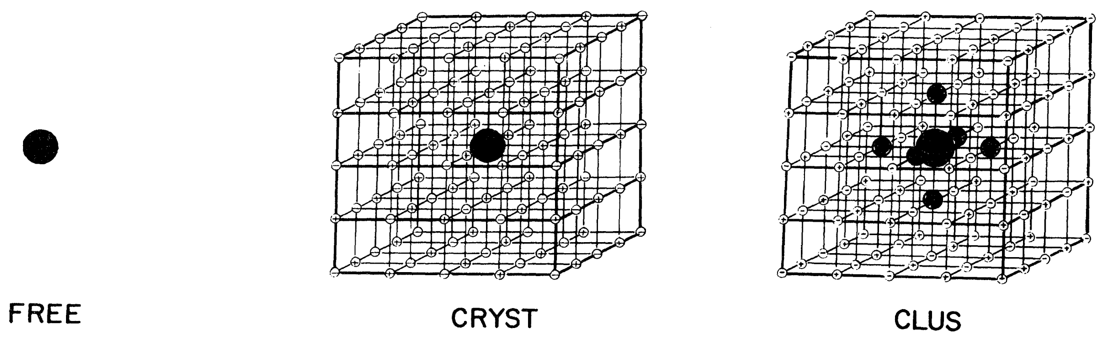

FIG. 1. Model environments of an ion. CRYST refers to crystal, CLUS to cluster.

variety of crystalline environments; they are compared with experimental results in Sec. VII.

II. METHODS

All calculations used the HONDO program[9] as extended by Amos (Cambridge). The general method has been described in Ref. 1. At the uncorrelated level, polarizabilities were obtained by coupled Hartree-Fock (CHF) theory, or equivalently by finite-field perturbation with corrections for hyperpolarizability. Electron-correlation effects were included by the Møller-Plesset (MP) perturbation theory taken to second order. Polarizabilities were obtained by finite-field perturbation of the MP corrections to the dipole moment. There are two ways of defining the MP series for the dipole moment,[10] either as the expectation value of the dipole operator or as the field derivative of the energy. We denote the corresponding polarizabilities as MPD and MPE, respectively.

Truncation of these series at second order is expected to give a good account of the correlation correction to the CHF polarizability for the halide ions. There is evidence of mutual cancellation of third- and fourth-order MPE corrections for isolated F^- (Ref. 11) and Cl^-.[12] For the H^- ion this cancellation does not occur, and we have extended the treatment of the correlation correction by taking the MPE series to fourth order and comparing it with the results of full configuration-interaction (CI) calculations.

The anion basis sets were chosen to give a good free-ion energy and polarizability at both CHF and MP levels. For F^- we used basis II of Ref. 11, consisting of 66 contracted Gaussian functions $[12s8p5d]$. For Cl^- we used basis II of Ref. 12 minus the most diffuse s orbital, giving 76 contracted Gaussian-type orbital (GTO) functions $[13s11p5d]$. For H^- an uncontracted, $(12s10p2d)$ basis was constructed by a geometric continuation of the $(10s)$ H-*atom* basis,[13] adding 10 p functions with the same exponents as the most diffuse s functions, 2 extradiffuse p functions (exponents 0.0070 and 0.0035) and 2 d functions, one function optimizing the CHF polarizability of the ion in the crystal field (exponent 0.516 666) and one function the correlation contribution (exponent 0.172 222).

The cation basis sets were chosen as follows. A $(13s9p5d)$ basis for Na^+ was taken from Ref. 5. The $(14s9p5d)$ basis for K^+ consisted of the $(14s9p)$ *atomic* basis[14] with a set of d polarization functions with exponents $(32\zeta, 9\zeta, 3\zeta, \zeta, \zeta/3)$ and $\zeta = 0.48$. The Li^+ $(13s6p5d)$ set was generated from the $(13s)$ *atomic* basis,[13] and each p exponent is twice a diffuse s exponent and each d exponent 3 times a diffuse s exponent. Some smaller basis sets for Li^+ and Na^+ were used in calculations on ion clusters and will be described later in this section.

The aim of our calculation was to explore the effects of various features of the crystal environment upon the ionic polarizability. A series of model systems (shown in Fig. 1) was used to resolve these effects. The first is the isolated ion, denoted FREE. Second, the crystal field of a particular salt was simulated by placing the ion (nucleus, electrons, and basis functions) at the center of a cubic lattice of point charges with spacing equal to the experimental lattice parameter. Fractional charges on the faces of the cube were used to maintain zero overall charge. A cube including 125 lattice sites was found to give adequately converged results.[1] Calculations of this type are labeled CRYST.

At the next level of sophistication (cluster, denoted by CLUS) a central anion was surrounded by the six nearest neighbors (nuclei, electrons, and basis functions) and the rest of the finite lattice as point charges. Both $(Li^+)_6X^-$ and $(Na^+)_6X^-$ clusters were treated in this way.

In order to keep the CLUS calculations to a manageable size the neighbors of the central ion were represented in smaller basis sets than above. We used projected basis sets, as described in Ref. 1, which give an accurate representation of the cationic charge density and hence of the effect of nearest-neighbor overlap on the central anion.

For Li^+ contracted basis sets $(10s5p) \rightarrow [1s1p]$ and $(10s5p) \rightarrow [1s]$ were constructed.[1] Their essential feature is that the larger $[1s1p]$ set has the same self-consistent-field (SCF) energy and CHF polarizability as the uncontracted $(10s5p)$ set, whereas the smaller $[1s]$ set has the same energy but *zero* polarizability.

For Na^+ the basis set was restricted to $(11s8p)$ by removing diffuse functions from the full $(13s9p5d)$ basis. The SCF eigenvectors for Na^+ in the CRYST model of NaX were then used to construct a highly contracted minimal basis $(11s8p) \rightarrow [2s1p]$ with an SCF energy only 0.0007 a.u. higher than for the full $(13s9p5d)$ basis. The

TABLE I. Polarizability of F^- in various electrostatic environments (in a.u.).

M^+	CHF	MPD	MPE	M-X Distance
FREE	10.654	4.958	6.090	
Cs^+	9.780	3.789	4.368	5.6824
Rb^+	9.489	3.484	3.968	5.3290
K^+	9.201	3.202	3.609	5.0512
Na^+	8.291	2.412	2.642	4.3785
Li^+	7.300	1.715	1.835	3.7965

TABLE II. Polarizability of Cl^- in various electrostatic environments (in a.u.).

M^+	CHF	MPD	MPE	M-X Distance
FREE	31.468	3.805	5.608	
Rb^+	28.162	2.416	3.332	6.2191
K^+	27.522	2.207	3.036	5.9451
Na^+	26.655	1.661	2.300	5.2390
Li^+	23.705	1.178	1.679	4.8566

CHF polarizability is, of course, zero for the $[2s\,1p]$ basis.

The advantage of "projected" basis sets of this type is that they enable us to make a realistic calculation of basis-set superposition effects (BSSE). In calculations on a cluster it is important to eliminate spurious contributions to the polarizabilties from BSSE.[15] In the conventional counterpoise treatment the polarizability of each subsystem would be evaluated in the full supersystem basis. This method effectively collapses the electrons and nuclei of one subsystem, leaving its basis functions free for occupation by the electrons of the other system. The result is an overestimate of the contribution from orbitals which, in the supersystem, are occupied. With the use of the basis sets described above we can remove these orbitals and perform the calculation of the polarizability of the central ion in a basis extended only by the virtual orbitals (if any) of the neighbors. This gives a much better estimate of the superposition effects on the anion polarizability.[1]

For the effect of superposition on the polarizability of the cage of six cations we use a more approximate treatment. The total BSSE arising from anion basis functions is approximately a sum of s, p, and d contributions. The estimated error is found by removing the s (for H^-) or s and p (for F^- and Cl^-) contributions because these are expected to be dominated by the occupied anion orbitals. In a case where the true superposition error is known, this estimate was found to be reliable.[1]

III. CRYSTAL-FIELD EFFECTS

In Tables I—III we give the results of a series of calculations on the effect of the electrostatic crystal field on the polarizabilities of F^-, Cl^-, and H^-. These calculations are of the CRYST type, as described in Sec. II. Row one of each table refers to the free ion. The lattice parameters used in the calculations were taken from Refs. 3 and 16; the salts considered all have the simple NaCl structure. The first three columns give the polarizability at the CHF level and the correlation corrections obtained from second-order MP perturbation theory (MPD and MPE, as defined in Sec. II). In Table III we also give the third- and fourth-order correlation corrections to the polarizability of H^-, and the results of full CI CRYST calculations which should be compared with the totals (MPE + MP3 + MP4).

As the strength of the crystal field increases (i.e., as the lattice parameter decreases) the CHF polarizability is rapidly reduced. The corresponding decrease in the correlation correction is even more marked. For the free F^- and Cl^- ions there is evidence[11,12] of cancellation of the higher-order terms in the MP series; this indication of rapid convergence is supported by the reasonable agreement between MPE and MPD values for the free ions. The agreement of MPE and MPD values improves in the crystal field so that the second-order MP treatment should give a good estimate of the full correlation correction in the crystal.

For the H^- ion the correlation corrections are large and the convergence of the MP expansion is poor, as shown by the values of the third- and fourth-order terms and by the poor agreement of MPD and MPE. This may be traced to the fact that free H^- is unbound at the Hartree-Fock level (cf. the "CHF" value for the polarizability is for a *restricted* Hartree-Fock calculation.[17]) However, in the crystalline environment the hydride ion becomes bound at the Hartree-Fock level, and we see a massive reduction in the correlation contributions. The term-by-term convergence of the MP expansion remains poor, and so in order to arrive at a realistic estimate of the correlation correction we

TABLE III. Polarizability of H^- in various electrostatic environments (in a.u.).

M^+	CHF	MPD	MPE	MP3	MP4	CI	M-X distance
FREE	89.874	16.166	33.677	13.250	12.243	(113)[a]	
Cs^+	39.935	1.325	2.707			8.720	6.0282
Rb^+	36.584	1.068	2.168				5.7070
K^+	33.148	0.842	1.697	1.608	1.008	5.558	5.3857
Na^+	24.961	0.443	0.863	0.872	0.536		4.6109
Li^+	17.612	0.202	0.380	0.425	0.248	1.257	3.8362

[a] Estimate from restricted Hartree-Fock limit for free H^- is 93 a.u. (Refs. 4 and 17); exact (with correlation), 206 a.u. (Refs. 4 and 18).

TABLE IV. Crystal-field effects on the polarizabilities of cations (in a.u.).

	CHF	MPD	MPE
Free Li^+	0.1892	0.0022	0.0026
Li^+ in LiH	0.1892	0.0022	0.0026
Free Na^+	0.9444	0.0562	0.0595
Na^+ in NaF	0.9447	0.0563	0.0597
Free K^+	5.3986	−0.0933	−0.0264
K^+ in KF	5.4038	−0.0921	−0.0260

have performed a full CI calculation with our basis for H^- in the CRYST environments appropriate to LiH, KH, and CsH. For the free ion a full CI polarizability is available.[18,4] The results of these calculations are given in Table III. For the free ion the MPE series summed through fourth order (59 a.u.) recovers only 52% of the full correlation contribution to the polarizability (113 a.u.). In contrast, the corresponding values for the LiH CRYST calculation are 1.05 and 1.26 a.u. (i.e., 84%). In both free and all CRYST calculations, MPE is 30% of the total correlation correction (cf. Fig. 4).

In Table IV we give the results of our calculations on the polarizabilities of the free Li^+, Na^+, and K^+ ions and on the CRYST polarizabilities of these ions. In all cases the increase in the cation polarizability on entering the lattice is less than 0.1%. Both the correlation correction and its change in the crystal field are small. The negative sign of MPE and MPD for K^+ is perhaps surprising, but we note that negative correlation polarizabilities have been found for atoms on the left-hand side of the first[19] and second[20] rows of the Periodic Table: Reinsch and Meyer[20] interpret this as a predominance of angular over radial correlation.

IV. OVERLAP COMPRESSION AT THE CHF LEVEL

The crystal-field calculations have demonstrated the insensitivity of the cation properties to environmental effects. The anion polarizabilities, on the other hand, are seen to be highly sensitive to the presence of neighboring ions, even as represented by point charges. In this section we investigate the additional effects on the anion polarizability due to the overlap of cation and anion charge distributions. These effects may be isolated[1] from a calculation of the polarizability of a cluster consisting of the anion of interest surrounded by the six neighboring cations, the whole being embedded in a lattice of point charges. The polarizability of the cluster may be written

$$\alpha_{\mathrm{CLUS}}=6\alpha_{\mathrm{CRYST}}(M^+)+\alpha_{\mathrm{CRYST}}(X^-)+\alpha_{\mathrm{DID}}(M^+\,|\,X^-)+\alpha_{\mathrm{DID}}(M^+\,|\,M^+)+\alpha_{\mathrm{INT}}\,,$$

where α_{CRYST} is the polarizability in the crystal field calculated in Sec. III and $\alpha_{\mathrm{DID}}(A/B)$ gives the total contribution to the cluster polarizability of the dipole—induced-dipole (DID) interactions between species A and B. α_{INT} contains all the contributions to the cluster polarizability including the anion-cation overlap compression (the term of interest) but also possible cation-cation overlap and basis-set superposition terms.

The utility of the cluster calculations for the elucidation of the anion overlap terms rests upon the fact that the cation charge distribution is so insensitive to its environment. This means that the properties of the in-cluster cation are very similar to those of the CRYST cation and the distortion of these properties by overlap is small: α_{INT} (where INT refers to term of interest) is then dominated by the terms of interest and the basis-set superposition terms. Pursuing the same reasoning we may represent the lowest order, nonvanishing contribution to $\alpha_{\mathrm{DID}}(M^+/X^-)$ (i.e., the X^--M^+-X^- term[1]) by

$$\alpha_{\mathrm{DID},\alpha\beta}(M^+\,|\,X^-)=12[\alpha_{\mathrm{CRYST}}(X^-)]^2\times\alpha_{\mathrm{CRYST}}(M^+)R^{-6}\delta_{\alpha\beta}\,.$$

For the Li^+ clusters we have performed a series of calculations which use the $[1s\,1p]$ basis described in Sec. II to separate the different contributions to α_{INT}. We begin by calculating the polarizability $[\alpha(6Li^+)]$ of six Li^+ ions with the central anion replaced by a point charge. In all cases the polarizability of this cluster is just 6 times the CRYST polarizability of a single Li^+ ion, showing that the $\alpha_{\mathrm{DID}}(Li^+/Li^+)$ and the Li^+-Li^+ contributions to α_{INT} for the full $Li_6^+\,X^-$ cluster are negligible. Since the X^- and $[1s\,1p]$ Li^+ basis sets give a good description of the polarizability of these ions we do not expect a large enhancement of the anion polarizability by basis-set superposition. This was checked by the methods described in Sec. II. The $X^-\rightarrow M^+$ superposition errors (the arrow denotes the flow of electrons from X^- into the available M^+ orbitals) were evaluated by our modified counterpoise method[1] and found to be negligible. The $M^+\rightarrow X^-$ errors were found from a conventional counterpoise calculation,[15] so that the latter should be regarded as upper limits. The net in-crystal anion polarizability at the CHF level is given by the last row in the table (i.e., the result of subtracting rows 2—4 from row 1 in Tables VI—VIII).

In dealing with the Li^+ clusters we are able to exploit the fact that for this two-electron ion we can accurately represent the ground-state and electric-field-perturbed wave functions with the use of just two basis functions. For the Na^+ clusters in a basis of tractable size it is only possible to represent the ground-state wave function accurately. Whilst this suffices for the description of the overlap compression term it leads to substantial $M^+\rightarrow X^-$ superposition errors in the polarizability. With a minimal $[2s\,1p]$ basis for the Na^+ ions (see Sec. II) $\alpha_{\mathrm{CRYST}}(Na^+)$ and the DID contributions to the cluster polarizability vanish. Also the $X^-\rightarrow M^+$ superposition error obtained by the modified counterpoise method is exactly zero.[1] To estimate the remaining $M^+\rightarrow X^-$ superposition error we

TABLE V. Correlation contributions to the cluster polarizability of $(Li^+)_6(X^-)$ (in a.u.).

X^-	F^-	Cl^-	H^-
MPD	0.762	0.333	0.074
MPE	0.852	0.634	0.124

TABLE VI. Effect of nearest-neighbor overlap on the CHF polarizability of F^- (in a.u.).

M^+	Li^+	Na^+
M^+ basis	$[1s\,1p]$	$[2s\,1p]$
α_{CLUS}	6.560	6.782
$\alpha[(M^+)_6]$	1.126	0
α_{DID}	0.040	0
BSSE $M^+ \rightarrow F^-$	<0.001	0.50
Net $\alpha(F^-)$	5.394	6.372

TABLE VIII. Effect of nearest-neighbor overlap on the CHF polarizability of H^- (in a.u.).

M^+	Li^+	Na^+
M^+ basis	$[1s\,1p]$	$[2s\,1p]$
α_{CLUS}	11.426	15.584
$\alpha[(M^+)_6]$	1.126	0
α_{DID}	0.219	0
BSSE $M^+ \rightarrow H^-$	<0.001	0.50
Net $\alpha(H^-)$	10.081	15.084

take that part of the conventional counterpoise estimate which arises from the virtual anion orbitals, as described in Sec. II.

V. OVERLAP COMPRESSION AND THE CORRELATION CORRECTION IN LITHIUM SALTS

In Table V we show the MPE and MPD estimates of the correlation polarizabilities of $(Li^+)_6(X^-)$ clusters. The basis sets used were as in Sec. IV, except that in the LiF and LiCl calculations the polarization functions on the cation were omitted. With these basis sets the cation contribution to the correlation correction to the cluster polarizability is very small (<0.005 a.u.). We may therefore identify the numbers in Table V as correlation corrections to the in-crystal polarizability of F^- and Cl^- in their lithium salts (given in the last rows of Tables VI and VII).

In the case of H^- we have shown that truncation of the MP series at second order is inadequate. However we also showed that for free and CRYST anions the second-order MPE term was a constant 30% of the full correlation correction. From the reduction of the CRYST values by overlap (Table VIII) we infer that the full CI CRYST correlation correction will be reduced by overlap compression to 0.4 a.u. This is the number which we shall combine with the CHF polarizability for H^- in LiH from the last row of Table VIII.

VI. ENVIRONMENTAL SUPPRESSION OF CORRELATION POLARIZABILITY

Our calculations have shown two effects of the crystal environment on the polarizability of an anion. First, α, the total polarizability of the ion, is reduced from the free-ion value. Second, Δ, the ratio of the correlation polarizability to the CHF polarizability, is reduced even though the correlation *energy* is not sensitive to the environment.[1]

TABLE VII. Effect of nearest-neighbor overlap on the CHF polarizability of Cl^- (in a.u.).

M^+	Li^+	Na^+
M^+ basis	$[1s\,1p]$	$[2s\,1p]$
α_{CLUS}	20.115	20.552
$\alpha[(M^+)_6]$	1.126	0
α_{DID}	0.096	0
BSSE $M^+ \rightarrow Cl^-$	<0.001	0.32
Net $\alpha(Cl^-)$	18.893	20.232

We can use the results presented in Secs. III—V to follow the suppression of the correlation polarizability through a series of environments. In Figs. 2—4 α_{CHF} is plotted against α_{MPE} and α_{MPD} for each of the three anions. The computed points may be joined by a smooth curve which passes through the results of both CRYST and CLUS calculations. The curves for different anions are similar in shape. Figure 4 also shows the results of the full CI calculations on H^- in the CRYST environment. As we have already noted the MPE value is a constant fraction of the full CI polarizability contribution so that the CI and MPE curves have the same shape. As the crystal field becomes stronger (i.e., as the lattice parameter decreases) Δ declines smoothly and then overlap compression causes a steeper drop towards values characteristic of the isoelectronic inert-gas atom.[1]

Apart from their intrinsic interest these curves are useful in that they allow us to estimate the (small) correlation

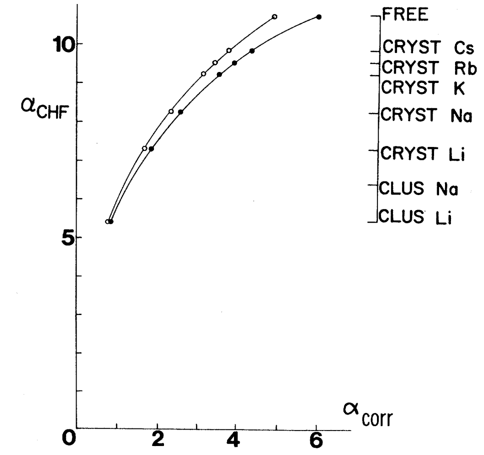

FIG. 2. Variation of CHF and correlation polarizability of F^- with environment. ○ is an MPD value, ● an MPE value. Units given in a.u. Definitions of CRYST and CLUS as in Fig. 1.

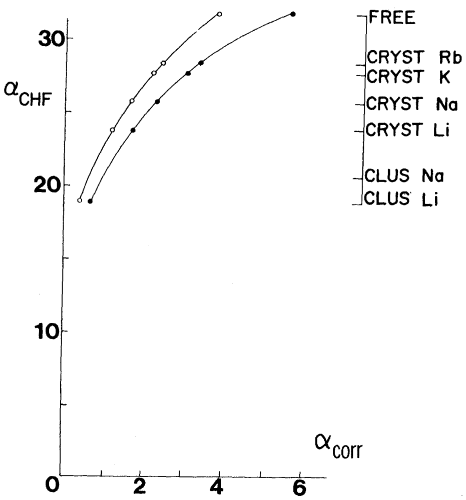

FIG. 3. Variation of CHF and correlation polarizability of Cl^- with environment. Symbols and units same as Fig. 2. Definitions of CRYST and CLUS as in Fig. 1.

polarizability for the NaX clusters, where only a SCF calculation was feasible. Correlation corrections are read off the curves at the computed values of α_{CHF} for NaX clusters. Our final values for the correlation contributions to the in-crystal polarizabilities of all three anions in their lithium and sodium salts are collected in Table IX.

TABLE IX. Correlation contributions to the in-crystal polarizability of X^- in LiX and NaX (in a.u.). For F^- and Cl^- we have taken the simple average of MPD and MPE. For H^- these are the estimated full CI results.

X^-	F^-	Cl^-	H^-
In LiX	0.79	0.48	0.4
In NaX	1.2	0.7	1.0

VII. COMPARISON WITH EXPERIMENT

As a result of our series of calculations we have arrived at a set of *ab initio* in-crystal polarizabilities for three cations (Table X) and three anions (Table XI), and in Table XII we compare these with "experimental" values which were derived as we now describe. For the cations Li^+, Na^+, and K^+ we have found no significant difference between in-crystal and free-ion values. We can be confident that the Li^+ and Na^+ values are consistent with other *ab initio* results. Our K^+ value is larger than a previous *ab initio* value of 0.789 Å^3 (Ref. 21) and agrees with the empirical estimate of 0.79 Å^3.[3]

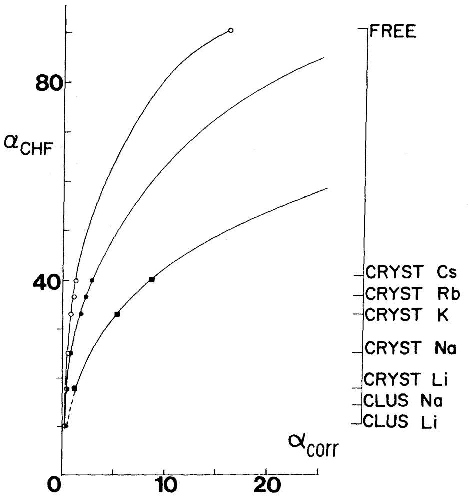

FIG. 4. Variation of CHF and correlation polarizability of H^- with environment. ■ is a full CI value, and other symbols and units are the same as Fig. 2. Definitions of CRYST and CLUS as in Fig. 1.

The pair polarizabilities of alkali halides, as obtained from refractive-index data, have been critically reviewed by Wilson and Curtis.[3] By subtracting our cation polarizabilities for Li^+ and Na^+ from their recommended experimental values we obtain in-crystal polarizabilities for the F^- and Cl^- ions in their lithium and sodium salts. For the hydrides we have used the Clausius-Mossotti formula on the refractive indices of LiH (Ref. 22) NaH (Ref. 23) to obtain in-crystal polarizabilities for H^- in LiH and NaH. The NaH value refers to the sodium *D* wavelength and would be expected to decrease on extrapolation to infinite wave length. As Table XII shows the *ab initio* values are in good agreement with experiment for F^- and Cl^-, and less so for H^-.

A calculation based on the refractive index of KH (Ref. 23) and our theoretical K^+ polarizability gives a value of 2.21 Å^3 for the polarizability of H^- in KH. Our theoretical value for H^- in NaH is therefore clearly too high. This may be due to the lack of next-nearest-neighbor overlap in our CLUS calculations. The very large radius of H^- found in the CLUS calculations (see below) suggests that these effects may be more important for H^- than for F^- and Cl^-. The experimental results for H^- do not show the monotonic increase of α with lattice parameter found for F^- and Cl^-.

We have found that an anion has a polarizability which is strongly affected by its environment so that the simple idea of a single in-crystal polarizability for each ion[2] is not supported by our results. It is well known that the use of constant in-crystal polarizabilities leads to serious incon-

TABLE X. Theoretical values for cation polarizabilities (in a.u.).

Ion	α
Li^+	0.192
Na^+	1.00
K^+	5.34

TABLE XI. Theoretical values for in-crystal polarizabilities of anions (in a.u.).

Anion	Crystal	α
F^-	LiF	6.18
	NaF	7.57
Cl^-	LiCl	19.4
	NaCl	20.9
H^-	LiH	10.5
	NaH	16.1

sistencies in the empirical values, e.g., the "constant" polarizability of the oxide ion O^{2-} deduced in Ref. 2 ranges from 0.9 to 3.2 Å^3 depending on the crystal considered, indicating a strong environmental effect.

Wilson and Curtis[3] proposed a relationship between the in-crystal polarizability α of an anion in a salt and the lattice constant R_e,

$$\log_{10}\alpha = \log_{10}\alpha^0 - kR_e^{-2} ,$$

where α^0 is the polarizability of the free ion. The equation is based on the idea that the change in the ionic volume from one substance to another may be related to the change in ionic polarizability. It has been used to estimate the polarizabilities of isolated ions by extrapolating a plot of $\log_{10}(\alpha)$ vs R_e^{-2} to infinite lattice constant,[3] giving results which although higher than earlier empirical estimates are still well below the results of sophisticated *ab initio* calculations on the free ions. For our own purposes the Wilson and Curtis plot gives a way of representing our data graphically to compare the sizes and transferability of the different physical effects in the crystal. The use of the relationship to extrapolate to the free-ion polarizability is *not* supported by our calculations.

Figures 5–7 show plots of $\log_{10}(\alpha)$ vs R_e^{-2} for the three anions we have studied. CRYST and CLUS polarizabilities at CHF and correlated levels of theory are plotted. The results for the free ions are given on the vertical axis and the experimental in-crystal results (Table XII) are represented by closed circles. The calculated points have been joined by a solid line to aid the eye, and the line through the two CLUS points has been extrapolated to $R_e = \infty$ with the dashed line.

TABLE XII. In-crystal anion polarizabilities and comparison with experiment (in Å^3).

X^-	MX	Theoretical[a]	Experimental[b]
F^-	LiF	0.92	0.89
	NaF	1.12	1.03
Cl^-	LiCl	2.87	2.88
	NaCl	3.10	3.14
H^-	LiH	1.56	1.86
	NaH	2.39	1.80

[a] Present work, Table XI.

[b] Derived (see text) from refractive-index data.

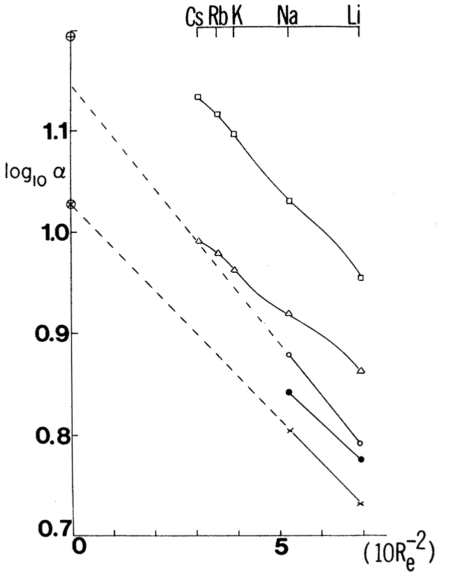

FIG. 5. Variation of polarizability of F^- with lattice parameter. $\text{Log}_{10}\alpha$ (a.u.) is plotted vs $10R^{-2}$ a.u.$^{-2}$ ● represents experiment; ○, correlated CLUS; × CHF CLUS; □, correlated CRYST; △, CHF CRYST; ⊕, correlated FREE; ⊗ CHF FREE.

The slopes of the CRYST and CLUS curves are very similar, which might be taken to imply an electrostatic origin for the effects which cause the in-crystal polarizability of an anion to change between different substances. However, if we perform a calculation on a cluster consisting of an F^- ion surrounded by six Li^+ ions at the crystal lattice spacing (i.e., remove all the point charges from a CLUS calculation) then the polarizability of the cluster changes by only 0.07% from the value for the same cluster in the crystal. These observations can be rationalized by considering all the environmental effects as a confinement of the anion charge density to a region whose size

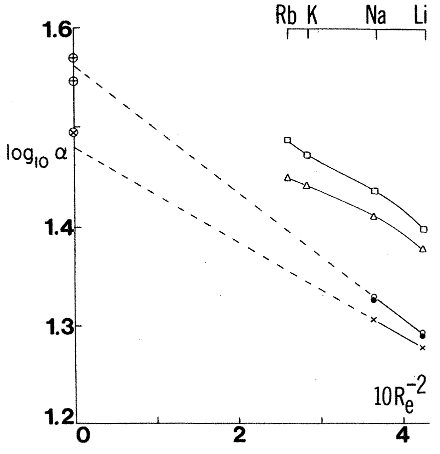

FIG. 6. Variation of polarizability of Cl^- with lattice parameter. Symbols and units same as Fig. 5.

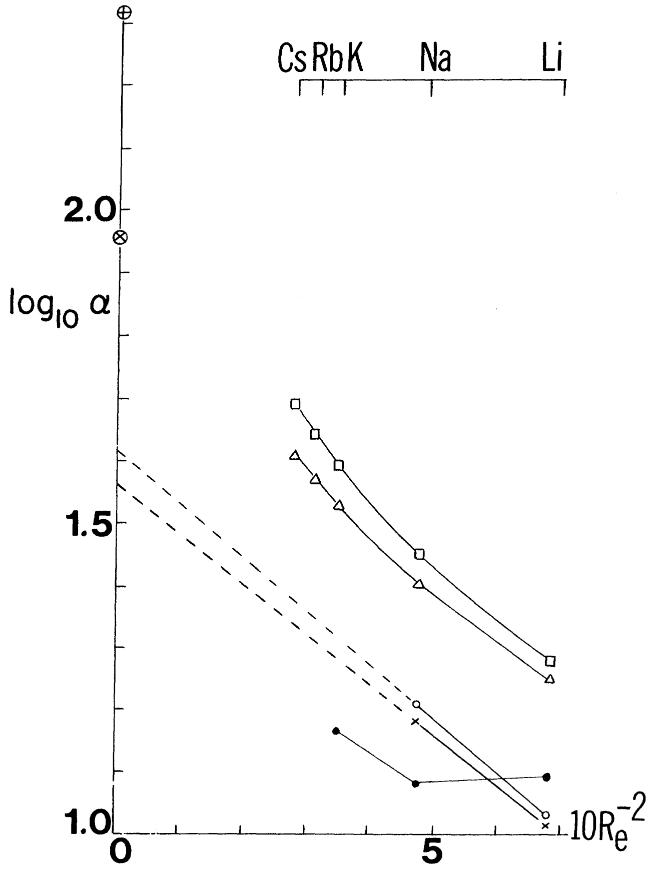

FIG. 7. Variation of polarizability of H$^-$ with lattice parameter. Symbols and units same as Fig. 5.

TABLE XIII. Environmental effects on the mean-square radius of an electron in an anion (in a.u.). Calculated at the SCF level.

Environment	H$^-$	F$^-$	Cl$^-$
FREE X^-	9.37	1.60	2.14
CRYST CsX	7.16	1.58	
RbX	6.90	1.57	2.10
KX	6.62	1.57	2.10
NaX	5.85	1.54	2.07
LiX	4.95	1.50	2.04
CLUS NaX	4.50	1.45	1.97
LiX	3.75	1.42	1.94

varies with the lattice parameter. This simple physical idea underlies the use of the "Watson sphere" to simulate the confining effect of the crystalline environment.[24]

Confinement of the charge density might be expected to affect other properties of the ionic charge cloud; a measure of the "size" of the ion is the mean-square radius $\langle r^2\rangle$. In Table XIII we present values of $\langle r^2\rangle$ for the anions in a variety of crystalline environments. This ground-state property is seen to be less sensitive to environment than is the polarizability. Kirkwood[25] proposed a simple proportionality between α and the square of $\langle r^2\rangle$. Reinsch and Meyer[20] found a modified form of the relationship to hold for the first row atoms Li to Ne, provided α was divided by the number of valence electrons. With the use of our data we find that the best straight-line fit to a plot of $\ln(\alpha)$ vs $\ln(\langle r^2\rangle)$ gives a slope of ~ 2 for H$^-$ and ~ 6 for F$^-$ and Cl$^-$. For H$^-$ the Kirkwood relationship works well, but for the heavier anions $\langle r^2\rangle$ varies more slowly than predicted. In $\langle r^2\rangle$, for these ions, the confinement by the crystal of the outer electrons (which predominantly determine the polarizability) is masked by the unchanging core. Thus the Kirkwood relationship gives a qualitative description of environmental effects on H$^-$ for which there is no core.

ACKNOWLEDGMENT

The authors thank the United Kingdom Science and Engineering Research Council for financial support.

---

*To whom correspondence should be addressed.

[1] P. W. Fowler and P. A. Madden, Mol. Phys. 49, 913 (1983).
[2] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. 92, 890 (1953).
[3] J. N. Wilson and R. M. Curtis, J. Phys. Chem. 74, 187 (1970).
[4] A. J. Sadlej, J. Phys. Chem. 83, 1653 (1979).
[5] G. H. F. Diercksen and A. J. Sadlej, Theor. Chim. Acta 61, 485 (1982).
[6] R. P. Hurst, Phys. Rev. 114, 746 (1959).
[7] G. D. Mahan, Solid State Ionics 1, 29 (1980).
[8] S. F. Boys and F. Bernardi, Mol. Phys. 19, 553 (1970).
[9] M. Dupuis, J. Rys, and H. F. King, Quant. Chem. Prog. Exch. 13, 403 (1981).
[10] R. D. Amos, Chem. Phys. Lett. 88, 89 (1982).
[11] G. H. F. Diercksen and A. J. Sadlej, Mol. Phys. 47, 33 (1982).
[12] G. H. F. Diercksen and A. J. Sadlej, Chem. Phys. Lett. 84, 390 (1981).
[13] F. B. van Diujneveldt, IBM Research Report RJ945 (1971) (unpublished).
[14] A. J. H. Wachters, J. Chem. Phys. 52, 1033 (1970).
[15] P. D. Dacre, Mol. Phys. 45, 1 (1982).
[16] R. M. McKay, in *Comprehensive Inorganic Chemistry,* edited by A. F. Trotman-Dickinson (Pergamon, New York, 1973), Vol. 1.
[17] K. T. Chung and R. P. Hurst, Phys. Rev. 152, 35 (1966).
[18] R. M. Glover and F. Weinhold, J. Chem. Phys. 65, 4913 (1976).
[19] H.-J. Werner and W. Meyer, Phys. Rev. A 13, 13, (1976).
[20] E.-A. Reinsch and W. Meyer, Phys. Rev. A 18, 1793 (1978).
[21] J. Lahiri and A. Mukherji, Phys. Rev. 155, 24 (1967).
[22] E. Staritzky and D. I. Walker, Anal. Chem. 28, 1055 (1956).
[23] *CRC Handbook of Chemistry and Physics,* 62nd ed., edited by R. C. Weast (CRC, Boca Raton, Florida, 1981).
[24] R. E. Watson, Phys. Rev. 111, 1108 (1958).
[25] J. G. Kirkwood, Phys. Z. 33, 57 (1932).