The polarizabilities of halide ions in crystals

N C Pyper† and P Popelier‡

† University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK
‡ Department of Chemistry, University of Manchester Institute of Science and Technology,
Sackville Street, Manchester M60 1QD, UK

Abstract. The polarizabilities of the F^-, Cl^- and Br^- ions in their solid lithium and sodium salts in the four-coordinated B3 and eight-coordinated B2 phases are predicted from *ab initio* electronic structure computations. These results plus those for the experimentally observed B1 structures yield insights into the mechanisms by which the in-crystal environment modifies halide polarizabilities.

The anion polarizability in each B2 phase having the cation–anion separation of the B1 structure is reduced compared with that in the B1 phase by the overlap with eight cation neighbours rather than six, these polarizabilities being essentially identical in the corresponding point charge lattices. The greater equilibrium cation–anion separation R_e in the B2 compared with the B1 phase causes each halide polarizability at its R_e to be greater in the B2 phase than in the B1 material. These B2 phase polarizabilities can be accurately predicted from the same function, which describes the dependence of the polarizability on R_e for different salts having the B1 structure. This supplements previous evidence from the caesium halides that these anion polarizabilities are determined solely by R_e, being insensitive to the precise disposition of the cation neighbours.

The halide polarizabilities in the B3 phase are larger than those predicted by the above function describing the dependence of polarizability on R_e. This phase thus differs from B1 or B2 materials, fluorite structured alkaline earth fluorides or MgF_2 in that the halide polarizabilities in the four latter are all essentially determined by R_e through the same function. The halide polarizabilities in the B3 phase differ by exhibiting a specific structural dependence in addition to their R_e variation. A new function describes the R_e dependence of halide polarizabilities in the B3 phase.

1. Motivation

The polarizabilities of ions in crystals are important and useful quantities. Thus the dielectric and optical properties such as the refractive index and dielectric constant at high frequencies are determined by the ion polarizabilities [1–3]. These quantities also govern the polarization energies originating from the charge-induced dipole interactions [4] which arise when an ion resides at a low-symmetry site where there is a non-vanishing electric field. Such interactions not only play an important role in determining the structures of low-symmetry crystals [5] but also make substantial contributions to the energies of formation of defects in high-symmetry materials, which have no such interactions in the perfect crystal [6, 7]. The energetics of even these latter materials contain significant contributions from the inter-ionic dispersive attractions [2, 4, 8] which must therefore be included in accurate treatments of the cohesion and compressibilities [8–10]. Furthermore, the most trustworthy and widely used method [11, 12] for deriving the dipole–dipole dispersion coefficients that govern the

majority of these dispersive attractions, the judicious application of the Slater–Kirkwood formula [13], requires knowledge of the ionic polarizabilities.

It is only during the past dozen years that accurate and trustworthy values have become available for the polarizabilities of a wide range of ions despite much previous work which has been reviewed elsewhere [12, 14]. *Ab initio* electronic structure calculations [15, 16] which took account of the effects of electron correlation not only provided accurate values for the polarizabilities of the gaseous Na^+, K^+, Mg^{2+} and Ca^{2+} ions to supplement the previous high precision result for Li^+ [17] but also showed [15, 16, 18] that the polarizabilities of all these ions remained essentially unchanged on entering an ionic crystal. The molar polarizability, defined as the sum of the polarizabilities of all the ions in a crystal, can be derived through the Clausius–Mossotti relation from the experimentally determined value of the refractive index which has been extrapolated to infinite wavelength [19]. The availability of such molar values enabled the polarizabilities of anions in their salts with any of the above five light cations to be derived [14–16, 18]. For F^- [15, 18], Cl^- [15], Br^- [20] and O^{2-} [16] ions in their salts with the lighter of the above five cations, the anion polarizabilities in crystal were computed *ab initio* with the results agreeing closely with the values deduced from experiment. This agreement is good evidence for the reliability of such in-crystal anion polarizabilities derived from experimental molar polarizabilities assuming gaseous cation values. The anion polarizabilities deduced from experiment in their salts with any of the above five light cations were not only much lower than those of the corresponding free anions but also depended on the counter-cation. It was found that the polarizability α_A of an anion in a series of crystals having the same structure and differing only in the equilibrium closest cation–anion separation R_e by virtue of containing a different cation could be described [14–16] by a relation of the type

$$\log_{10} \alpha_A = A + BR_e^{-2} + CR_e^{-4} \tag{1}$$

where A, B and C are constants depending on only the anion and crystal type. The form of (1) in which C is taken to be zero is called linear, because this relation then implies that the fractional variations of α_A induced by the in-crystal environment depend linearly on R_e^{-2}. The relation (1), whether in its linear or quadratic ($C \neq 0$) form, enabled the polarizabilities of anions in crystals with cations different from the above five to be deduced [14]. The polarizabilities of these other cations could then be derived [14] from the experimental molar polarizabilities. For any cation having an s^2 or a p^6 outermost electronic configuration, essentially the same value was obtained for its polarizability, no matter which of its salts was considered. This confirmed the validity of the values thus deduced and showed that these cation polarizabilities also are independent of their environment in crystal.

Under ambient conditions, all the alkali halides adopt the sixfold-coordinated rock salt (B1) structure except for CsCl, CsBr and CsI, which crystallize in the eightfold-coordinated B2 structure. Nevertheless the value for the polarizability of Cs^+ deduced from the data for either CsCl or CsBr differed by less than 0.1 au from that of 15.36 au derived from the data for CsF, which adopts the same B1 structure as the salts invoked to determine the constants in (1) [14]. Even the cation polarizability deduced from the data for CsI differed from the previous three values by only 0.5 au, which is within the uncertainty of the prediction provided by (1) for the large (over 45 au) polarizability of the iodide ion. These results were taken as evidence that the in-crystal polarizability of a halide ion is essentially independent of the type of crystal structure, being solely determined by R_e. This conclusion was reinforced by two further observations [14]. Firstly for both MgF_2 and CaF_2 the polarizability (about 6 au) of the F^- ion deduced by subtracting the *ab initio* cation value from the experimental molar polarizability agreed closely (to within 0.3 au)

with the α_A predicted by (1) using the values of A, B and C deduced from the alkali halide data. Secondly, combination of fluoride polarizabilities derived by this method with data for SrF_2 and BaF_2 yielded essentially the same cation polarizabilities as those deduced from the molar polarizabilities of SrO and BaO predicting the α_A from equation (1) with the constants determined from data for MgO and CaO. These results for CaF_2, SrF_2 and BaF_2, all of which adopt the fluorite structure, are evidence that the polarizability of a fluoride ion in tetrahedral coordination is determined solely by R_e in exactly the same way as in B1 or B2 structured materials [14]. The result for MgF_2 suggested that this conclusion extended to the threefold-coordinated environment experienced by an anion in a salt adopting the rutile structure.

The object of this paper is to deepen our understanding of the in-crystal modifications of halide polarizabilities. Firstly the idea that these quantities are independent of structure, being governed solely by R_e, is tested further by performing *ab initio* quantum chemistry computations of the polarizabilities of halides in a wider selection of crystalline environments. In particular the evidence that the constants in (1) are the same for the B1 and B2 structures has rested hitherto on a very small set of data even though the evidence from this set is impressive. Further evidence is advanced here by computing the polarizabilities of halide ions in some B2 structured alkali salts which experimentally adopt the B1 structure. Similar predictions are presented for the polarizabilities of halide ions in alkali salts in the four-coordinated zinc blende B3 phase, there being hitherto no such information for any material having this structure. Secondly this paper also presents the polarizabilities predicted for halide ions in some model crystalline environments in order to glean further insights into the factors which modify this property in crystal.

2. Theory and computational methods

The properties of an anion in crystal differ from those of the free ion because an electron at a position r_a with respect to the anion nucleus experiences a potential $F_{env}(r_a; R)$, called the environmental potential, which is generated by the nuclei and electrons of all the other ions [10, 12, 21]. After specifying the cubic structure of interest, $F_{env}(r_a; R)$ depends parametrically on just the crystal geometry defined uniquely by the closest cation–anion separation R. The equilibrium R value minimizing the total crystal energy is denoted R_e. It is useful to regard the environmental potential as being composed of two contributions [10, 12, 15, 16, 18, 21], the first being that which would be generated if all the ions excepting the single anion of interest were replaced by point charges each equal to the net charge of the ion occupying that lattice point. This would be the sole contribution to the environmental potential if the wavefunctions belonging to different ions overlapped only negligibly. The second contribution to $F_{env}(r_a; R)$ is the sum of all the corrections to the first which arise from the finite spatial extensions of the wavefunctions of neighbouring ions. These finite extensions not only yield a correction to the electrostatic energy generated by the charge distributions of the other ions but more importantly cause the ion wavefunctions to overlap appreciably. This overlap introduces through the operation of the Pauli principle a repulsive potential which acts strongly on an anion electron in spatial regions where the electron density of neighbouring ions is significant [10, 12, 21].

The influence on an anion of the first contribution to $F_{env}(r_a; R)$ is readily computed using an *ab initio* quantum chemistry program to study the wavefunction for one ion located in a fragment of the point charge representation of the crystal lattice. Here the CADPAC program [22] was used to compute the polarizability of a halide ion located at the centre of a suitably chosen fragment of the point lattice with the outermost charges adjusted so as to

reproduce the spherical average of the environmental potential at the anion nucleus whilst preserving overall electrical neutrality of the entire system of ion plus lattice fragment. Electron correlation was considered by augmenting the coupled Hartree–Fock predictions with corrections from second-order Moller–Plesset perturbation theory applied in its MPE variant (see the appendix). The methods are now standard, being the same as those used [23] to study the polarizabilities of group IIB ions, and differ only in very minor technical details from the earlier work of Fowler and Madden [15, 16, 18]. The full details of the present calculations are reported in the appendix.

The polarizability of an anion subject to the full environmental potential was computed by replacing the closest shell of positive charges in the point lattice by a quantum mechanical description of this shell of cations, each represented by its full nuclear charge plus all its electrons described in the *ab initio* computation by special suitably chosen basis sets. Such a computation yields the polarizability of the entire cluster of anion plus cation shell all embedded in the point charge representation of the remainder of the lattice. The anion polarizability is extracted from that of the cluster by the previously employed methods [15, 16, 18, 23] described in the appendix.

The data in table 1 for halide ions in crystals having the B1 structure show the accuracy to which in-crystal anion polarizabilities are predicted by the Moller–Plesset perturbation method. The computed values agree with the results derived from experiment to within at least around 0.5 au. The latter, taken from the appendix of [23], were deduced by subtracting the known cation polarizabilities from total molar polarizabilities derived from experimental refractive index data. The internuclear separations R used in these computations and reported in the second line of numerical data in table 2 are the experimental R_e values cited [15, 18] excepting the bromide data taken from [24]. All of these halide polarizabilities have been previously investigated [15, 18, 20] by *ab initio* computation with the exception of that of the bromide ion in LiBr. The very slight differences between the present and the previously computed results, discussed in detail in the appendix, arise from the small technical differences between the two series of calculations. The B1 crystals of these halides were reexamined here in order to ensure that the computations for different structures of the same halide are unquestionably fully comparable.

Table 1. Predicted and experimental halide polarizabilities in six-coordinated (B1) salts (au): theory, present *ab initio* results derived from computations including electron correlation contributions for the halide plus six closest cations embedded in a point charge lattice; expt, from [23] calculated by subtracting *ab initio* cation polarizabilities from total molar polarizabilities derived from experimental refractive indices extrapolated to infinite wavelength.

	LiF	NaF	LiCl	NaCl	LiBr	NaBr
Theory	6.126	7.560	19.563	20.617	27.331	28.839
Expt	5.983	6.948	19.412	21.153	26.936	28.826

The small discrepancies between theory and experiment in table 1 cannot be attributed to relativistic effects because the following evidence indicates that these will be minute even for the Br^- ion. Although relativistic coupled Hartree–Fock (RCHF) and corresponding non-relativistic coupled Hartree–Fock (NRCHF) polarizabilities are not currently available for halide ions, the respective RCHF predictions [25] of 10.77 au and 5.457 au for the polarizabilities of Ar and K^+ differ only insignificantly from the corresponding non-relativistic results of 10.76 au and 5.461 au [26]. The RCHF results of 16.47 au and 9.076 au for the polarizabilities of Kr and Rb^+ [25] similarly show only very small differences from

Table 2. Closest cation–anion internuclear separations (au): B1 values are from experiments cited in [15] for fluorides and chlorides and in [24] for bromides; B3 and B2 values are predictions of density functional computations [33] for LiF and B3 NaF, those [34] for B2 NaF and B2 NaCl and those [35] for LiCl, KCl and B3 NaCl.

	LiF	NaF	LiCl	NaCl	KCl	LiBr	NaBr
B3 (4:4)	3.537	4.252	4.436	5.129	5.622		
B1 (6:6)	3.7965	4.3785	4.8566	5.239	5.9451	5.197	5.643
B2 (8:8)	4.240	4.719	5.315	5.669	6.183		

the NRCHF predictions of 16.46 au [26] and 9.146 au [11]. Although, in general, relativistic effects increase with increasing nuclear charge, it has been explained elsewhere [27] why relativity only has a small effect on the properties of the outermost p orbitals of all but the very heaviest elements. It is precisely these orbitals which are responsible for most of the polarizability of each of the halide ions considered here.

3. Results and discussion

3.1. Polarizabilities in the point charge lattices

The polarizabilities predicted from MPE computations for the halide ions in point charge lattices having B1, B2 and B3 structures corresponding to a variety of alkali halides are reported in table 3. All these polarizabilities are considerably reduced from those of the corresponding free ions through the now well understood mechanism described elsewhere [12, 15, 18, 21]. *Ab initio* computations established the polarizabilities of free fluoride and chloride ions to be 15.1 au [28] and 38.1 au [29] respectively whilst that of the free bromide ion is at least 42.9 au [20] with addition of an estimate of the correlation contribution increasing this to about 50 au [30]. In each of the columns headed 'opt B1' in table 3, the computations for each of the three different structures were all performed for point lattices having the same R value, equal to the experimental R_e (table 2) of the B1 structure for the salt appearing as overall heading to the column.

The R value in each of the 'opt B1' columns in table 3 is the same, and hence variations in predicted polarizabilities are caused solely by differences between the geometrical structures of the point lattices. For each R, the polarizability is largest in the B3 structure with the values in the B1 and B2 lattices being extremely similar although the polarizability in the latter is in all cases slightly smaller than in the B1 lattice. These differences are explained [12, 15, 16, 18, 21] by expanding $F_{env}(r_a; R)$ into a series about the anion nucleus in which spherical harmonics centred on this nucleus are used to describe its angular variation, the first and spherically symmetric term $F_{env}^{(0)}(r_a; R)$ depending solely on the radial distance r_a of the electron from this nucleus. Only this first term affects an in-crystal ion [9] in the absence of an externally applied electric field if each of the atomic orbitals is taken to have its usual central field form. Furthermore the basis sets used in the present computations contain only functions of s, p and d symmetries which cannot be mixed at the lattice sites in B1, B2 or B3 phases. Consequently, in the absence of an external electric field, each of the in-crystal atomic orbitals yielded by the present computations has its usual central field form and is influenced by the crystalline environment solely through the spherically symmetric portion of $F_{env}(r; R)$. For each of the three lattices types considered here, $F_{env}^{(0)}(r_a; R)$ is a constant stabilizing potential equal to $-M/R$ for r_a values between

Table 3. Predicted polarizabilities for halide ions in various point charge lattices (au): electron correlation contributions are included in all computations; results labelled 'opt B1' were computed at the equilibrium R values (table 2) for the B1 structure; results labelled 'opt str' were computed at the equilibrium R values (table 2) predicted for the structure (B3 or B2) labelling the rows.

	F^- for LiF dist		F^- for NaF		Cl^- for LiCl		Cl^- for NaCl		Cl^- for KCl dist		Br^- for LiBr	Br^- for NaBr
	opt B1	opt str	opt B1	opt str	opt B1	opt str	opt B1	opt str	opt B1	opt str	opt B1	opt B1
B3	10.023	9.119	12.010	11.589	27.379	24.573	29.499	28.933	32.436	31.224	35.469	37.216
B1	9.141	9.141	10.938	10.938	25.374	25.374	27.498	27.498	30.554	30.554	33.813	35.786
B2	9.065	10.435	10.856	11.855	25.264	27.752	27.372	29.351	30.426	31.252	33.695	35.634

zero and R where M is the Madelung constant. For r_a values larger than R, $F_{env}^{(0)}(r_a; R)$ rises towards zero after several oscillations of smaller magnitude associated with distances between the anion and lattice points other than the closest set at the distance R. Such an environmental potential acts to contract the anion [9, 10] and reduce its polarizability [15, 16, 18, 21]. The constant portion $(-M/R)$ of $F_{env}^{(0)}(r_a; R)$ is least negative, being equal to $-1.638\,055/R$, for a B3 lattice whilst the depths of $-1.747\,564\,6/R$ and $-1.762\,67/R$ in the B1 and B2 lattices respectively are extremely similar [31]. This explains both why the polarizabilities are least reduced in the B3 lattices and why those in the B1 and B2 structures are so similar with a slightly smaller polarizability in the latter. Comparison of each difference (table 3) between the polarizabilities in the B3 (4:4) and B1 (6:6) structures with the corresponding coupled Hartree–Fock results presented in the appendix (table A1) shows that, for F^- and Cl^-, electron correlation increases the differences by about 0.5 au, constituting roughly one half of each difference for the F^- ion but a smaller fraction for the Cl^- case. For the Br^- ion, correlation only enhances these differences by 0.2 au.

The above comparison of halide polarizabilities in different point charge lattices was made taking R to be the same in all three structures. However, the smaller number of cation neighbours in any B3 material will cause its R_e to be less than that of the B1 phase. Similarly R_e for each B2 phase will be larger than that in the B1 material as illustrated by the experimental results that R_e is 6.689 au in the B1 phase of CsCl [32] compared with 6.748 au in the B2 structure [24]. Although neither the B3 nor the B2 phases of the alkali halides considered in tables 1 and 3 are known experimentally under ambient conditions, estimates of their R_e values, reported in the first and third numerical rows of data in table 2, are available from electronic structure calculations [33–35] based on density functional theory. The polarizabilities computed for halide ions in B3 and B2 structured point charge lattices having R values equal to the R_e (table 2) predicted for the actual salts adopting those structures are reported in table 3 in the columns headed 'opt str'. The polarizability in each B2 point lattice having R equal to the R_e of the B2 phase is greater than that for the lattice with the R value equal to the R_e of the B1 phase because expansion of the lattice reduces the depth (M/R) of the constant stabilizing portion of $F_{env}^{(0)}(r_a; R)$ between r_a values of zero and R. These lattice expansions cause the polarizability in the point lattice description of each B2 material to be greater than that in either the B1 or B3 phases of the same material. The reduction in R_e on passing from the B1 to the B3 phase causes the polarizability predicted for each B3 structure at its R_e to be less than that for this phase at the R value equal to the R_e of the B1 material. These polarizabilities are reduced because contraction of the lattice increases the depth of the constant and stabilizing part of $F_{env}^{(0)}(r_a; R)$. For the two lithium salts, the reductions in R_e on passing from the B1 to the B3 phase are sufficient to cause the lowered polarizability in the optimally structured B3 phase to be smaller than in the corresponding B1 material. For the remaining salts these R_e reductions are insufficient to lower the polarizability in each optimal B3 lattice below that in the B1 materials with the result that the B3 values lie between the polarizabilities in the B1 and B2 structures.

3.2. Polarizabilities of halide ions in the full crystal environment

For salts having the B2 or B3 structures, the polarizabilities computed for halide ions subject to the full crystalline environment, thereby including both contributions to $F_{env}(r_a; R)$, are reported in table 4. Comparison of both these results and those in table 1 for the B1 phase with those in table 3 for the corresponding point charge lattices reveals the importance of the second contribution to $F_{env}(r_a; R)$. For both the 'opt B1' and 'opt str' results,

the polarizability in the full environment (table 4) is always significantly less than in the corresponding point lattice. These results further illustrate the now well established polarizability reductions produced by the overlap of the anion with its cation neighbours [15, 16, 18].

For each ion in each compound, the polarizability predicted for the B2 structure at the R_e of the B1 salt, that is the 'opt B1' prediction in table 4, is smaller than that (table 1) for the B1 material. These reductions are seen to result from the greater compressive effects of eight cation neighbours compared with six because the polarizabilities (opt B1 in table 3) predicted in the point B2 and B1 lattices at the same R are essentially identical. The very existence of a significant difference between the predictions for the B2 and B1 structures at fixed R shows that the opt B1 polarizabilities cannot be predicted from a relation of the type (1) with structurally independent A, B and C parameters. This conclusion is reinforced by the significant differences between each anion polarizability in the B1 phase and that predicted (table 4) for the B3 phase at the same R. However it should be stressed that relations of the type (1) have only ever been proposed for anions in crystals at their equilibrium cation–anion separations and that it was never suggested that such relations might describe the polarizability in a crystal having an arbitrary value of R.

The greater value of R_e in each B2 phase compared with the B1 material explains why, for the B2 phase, each 'opt str' polarizability (table 4) is larger than the 'opt B1' prediction. Furthermore the anion polarizability ('opt str') predicted for each B2 phase at its R_e is greater than that (table 1) in the B1 material. This shows that, on passing from the B1 to the B2 structures, the effect of increasing R_e with its concomitant tendency to reduce the confining nature of $F_{env}(r_a; R)$ more than outweighs the extra repulsive contributions introduced into $F_{env}(r; R)$ by increasing the anion coordination. The third and fourth rows of numerical data in table 4 show the anion polarizabilities predicted from both the linear ($C = 0$) and quadratic forms of (1) using the R_e values (table 2) optimal for each structure with the constants A, B and C derived [14] from data on B1 crystals and presented in table 5. The quadratic fits, which are preferable to the linear ones, reproduce the *ab initio* anion polarizabilities in the B2 materials to within at least 0.4 au. Since such discrepancies are no greater than those between the *ab initio* and experimental results for the B1 crystals, the data in table 4 for the B2 materials are evidence that the polarizabilities of halide ions in the B1 and B2 phases are independent of structure, being solely determined by R_e. Furthermore, for the halide polarizabilities in the B2 phases of LiF, NaF, LiCl and NaCl, the respective differences of 0.379, 0.401, 0.202 and -0.400 au between the *ab initio* results and the predictions of equation (1) are semi-quantitatively similar to those of 0.143, 0.612, 0.151 and -0.536 au between the *ab initio* and experimental halide polarizabilities for the B1 crystals. If the latter discrepancies are taken as a measure of the error in each *ab initio* computation and subtracted from the *ab initio* B2 results, one predicts anion polarizabilities of 6.936, 7.323, 21.151 and 22.288 au in the B2 phases of respectively LiF, NaF, LiCl and NaCl, in ever closer agreement with the predictions of equation (1). These results all suggest for the B2 phase that at least half the difference between each *ab initio* value and that from the relation (1) arises from the former and hence that the predictions of (1) are accurate to within 0.2 au. This provides even stronger evidence to supplement the previous results [14] for caesium halides that the anion polarizabilities in the B1 and B2 phases do not depend on the structure but are solely determined by R_e.

The computations, described in the appendix, for the potassium salts do not provide any evidence contrary to the conclusions of the last paragraph even though the interpretation of the K^+ results is limited by technical difficulties. It should be pointed out that the significant reduction in anion polarizability on passing at fixed R from the B1 phase at its R_e to the

Table 4. The polarizability of halide ions in four- and eight-coordinated salts with Li^+ and Na^+ (au): all results are for the in-crystal anion interacting with both the point charge lattice and the full electron charge distribution of cation neighbours; results in first two numerical rows are *ab initio* predictions, that labelled opt B1 being computed at the equilibrium R value of the 6:6 material, the row labelled opt str containing the results computed at the equilibrium R predicted for the structure (B3 or B2) labelling the column; third and fourth numerical rows are predictions of (1) using the parameters (table 5) derived for the B1 materials using the quadratic function (row quad) and the linear function $C = 0$ (row linear).

	LiF		NaF		LiCl		NaCl		LiBr		NaBr	
	B3 (4:4)	B2 (8:8)	B3 (4:4)	B2 (8:8)	B3 (4:4)	B2 (8:8)	B3 (4:4)	B2 (8:8)	B3 (4:4)	B2 (8:8)	B3 (4:4)	B2 (8:8)
opt B1	7.295	5.648	8.644	6.936	21.771	18.277	22.998	19.502	29.743	25.780	31.229	27.060
opt str	6.510	7.079	8.282	7.935	19.198	21.302	22.393	21.752				
quad (1)	5.602	6.700	6.721	7.534	17.422	21.100	20.463	22.152				
linear (1)	5.335	6.816	6.838	7.594	17.635	21.083	20.455	22.156				

Table 5. Parameters describing through equation (1) the R dependence of in-crystal F^- and Cl^- polarizabilities (au): results derived for B1 structured materials (first two numerical rows) from [14]; results in third row (this work) derived for the *ab initio* predictions of table 4 (row labelled opt str) for the B3 materials at their predicted equilibrium R values.

	Fluorides			chlorides		
	A	*B*	*C*	*A*	*B*	*C*
quad B1	1.201	−9.204	44.30	1.473	−3.370	−23.48
linear B1	1.077	−4.377	0.0	1.502	−5.030	0.0
linear B3	1.1530	−4.2464	0.0	1.5486	−5.2212	0.0

B2 phase shows that care is needed in interpreting the previous statement [14] that halide polarizabilities are essentially determined only by the size, that is the distance over which $F_{env}^{(0)}(r_a; R)$ is constant, of the confining environmental potential and are insensitive to the precise distribution of the cation neighbours. This statement is true only when comparing halide polarizabilities for different phases each at its equilibrium cation–anion separation.

The reductions of R_e that occur on passing from the B1 to the B3 phase explain why each 'opt str' anion polarizability for the B3 structure is less than the 'opt B1' value predicted using the R_e of the B1 crystal. However, for LiF, NaF and NaCl, these R_e reductions are insufficient to offset the greater repulsive contributions to $F_{env}(r_a; R)$ arising in the B1 phase from six cation neighbours as opposed to four in the B3 structure. Consequently each 'opt str' polarizability in the B3 phase is still greater than that in the B1 crystal. For LiCl, however, the reduction of R_e in the B3 compared with the B1 phase is sufficiently great that the 'opt str' polarizability in the B3 phase is less than that in the B1 crystal. However all the polarizabilities predicted for the B3 phase by using equation (1) with the A, B and C parameters [14] determined from B1 structured crystals are significantly less than the 'opt str' *ab initio* predictions for the B3 phase. These differences do not mirror those between the *ab initio* and experimental results for the B1 crystals and are in any case too large to be ascribed to inaccuracies in the *ab initio* computations for the B3 materials. This shows that halide polarizabilities in the B3 phase cannot be predicted from (1) using the previous parameters [14]. Halide polarizabilities in B3 materials are thus revealed to depend explicitly on this structure in not varying with R_e in the same common fashion previously found [14] for all the B1 and B2 phases, fluorite structured alkaline earths and MgF_2. It is beyond the scope of the present investigation to attempt to elucidate the reasons for this different behaviour in the B3 phase. The 'opt str' *ab initio* F^- and Cl^- polarizabilities in the B3 phase determine the A and B parameters reported in the last line of table 5 for the linear form of (1) applicable to this structure. These parameters enable the polarizabilities of the F^- and Cl^- ions in their B3 structured salts with other cations to be predicted.

4. Conclusion

The polarizabilities of the fluoride, chloride and bromide ions in their solid lithium and sodium salts have been investigated by *ab initio* electronic structure computations. For the Br^- ion in the experimentally observed six-coordinated rock salt B1 phase of LiBr, the computed polarizability agrees with the trustworthy value derived from experimental refractive index data to the same high accuracy found previously [15, 18, 20] for the B1 phase of the other lithium and sodium halides. The principal object of the present work

was to study the polarizabilities of these halide ions in the two experimentally unknown phases having the eightfold-coordinated CsCl B2 structure and the fourfold-coordinated zinc blende B3 structure. These polarizabilities are of interest for two reasons. The first of these, motivating the investigations of the B2 phase, was to test further the previous conclusion [14] that halide polarizabilities in this phase are essentially identical to those in the B1 structure. This study also formed part of the second and wider reason, which was to extend the range of materials for which halide polarizabilities are reliably known, and thus gain further understanding of the environmental influences on these properties.

In the B2 phase having R value equal to the R_e of the B1 crystal, the interaction with eight cation neighbours rather than six significantly reduces the polarizability of each halide ion compared with that in the B1 salt. However each halide polarizability in the B2 phase at its R_e is larger than that in the B1 material because the R_e increase on passing from the B1 to the B2 structure more than outweighs the concomitant increase in the number of closest cation neighbours. These B2 phase polarizabilities were shown to be reproduced accurately by the same relation (1) which describes the R_e dependence of the anion polarizability in B1 crystals. This supplements the evidence [14] from the caesium halides that the environmental modifications of polarizabilities of halides in the B1 and B2 phases are essentially determined solely by R_e, being independent of the detailed structure provided that only materials at their R_e are considered.

The polarizability computed *ab initio* for a fluoride or chloride ion in a crystal having the B3 structure at its R_e was found to be significantly greater than that predicted by the relation (1) parametrized from data for the B1 phase. This shows that halide polarizabilities in the B3 phase differ not only from those in the B1 and B2 materials but also from those in the fluorite structured alkaline earth fluorides or in MgF_2, which has the rutile structure. The polarizabilities of halide ions in all the four latter structures are similar in being determined to within at least 0.3 au solely by R_e and in being thus insensitive to the precise distribution of cation neighbours. The present results for the B3 materials have revealed a phase to which this structural independence of halide polarizabilities does not extend. The *ab initio* fluoride and chloride polarizabilities for the B3 phase provide the data needed to derive the parametrization (table 5) of the relation (1) through which the polarizabilities of halide ions in B3 structured salts with other cations can be predicted.

Appendix. The *ab initio* computations

A.1. Basis sets

All the *ab initio* computations were performed with the CADPAC program [22]. The polarizabilities were derived by adding to the prediction of coupled Hartree–Fock (CHF) theory the contribution from electron correlation, the correlation polarizability, yielded by the MPE variant of second-order Moller–Plesset perturbation theory. In the MPE method the polarizability is derived from the energy predicted in the presence of a perturbing external electric field whereas the alternative MPD approach considers the dipole moment in the presence of this field [36]. However, for both cations and in-crystal anions these two methods yield similar numerical predictions [15, 18, 36]. For the latter the MPD and MPE results are similar because the large correlation polarizabilities of free anions are markedly reduced by the crystalline environment to become comparable with those of neutral or cationic species. This similarity of the MPD and MPE predictions does not extend to free anions because their polarizabilities are not very well described by MP2 theory. The Gaussian basis sets were those used previously [15, 18, 20] to study the B1 phases of the

alkali halides with any small modifications introduced here only because the contraction depth of the version of CADPAC used is limited to ten functions. The halide basis sets were all identical to those used previously [15, 18, 20], that for the fluoride ion being the uncontracted 12s8p5d set designated basis II in [37]. For the chloride ion, the uncontracted 13s11p5d set used differed from that called basis II in [38] only by deletion of the most diffuse function of s symmetry. For the bromide ion, the uncontracted 16s12p6d2f set used was that called basis I in [20] generated by extending a 16s12p4d1f set of primitives from [39] with exponents generated by a geometrical progression with a common ratio of 1/3. The polarizability of 38.310 au predicted here for a free bromide ion by using CHF theory is in full agreement with that of 38.3 au found previously [20] for this basis. Here we report the prediction of 41.725 au afforded by the MP2 method corresponding to a correlation polarizability of 3.415 au. A larger basis, basis II, yielded a CHF polarizability of 42.9 au [20] from which a free bromide polarizability of 46.3 au is predicted by addition of our correlation contribution of 3.4 au. The correlation polarizability of diffuse free anions is underestimated by the MP2 method as evidenced by the MPD and MPE predictions of 3.805 au and 5.608 au [15] for a free chloride ion compared with the currently most accurate value of 6.6 au derived by subtracting the CHF result [15] from the full prediction of 38.1 au [29]. The present result of 46.3 au for a free Br^- ion coupled with the knowledge that this is almost certainly an underestimate, provides further evidence to support the previous conclusion [30] that this polarizability is probably about 50 au.

For Li^+, the contracted basis used in the cluster computations for a halide plus its six closest lithium neighbours was generated from the uncontracted 10s5p set from [18] derived by deleting the three most diffuse s functions from the 13s set of [40] with the p exponents being twice those of the five most diffuse s functions from the 10s set. The single s function in the contracted basis was the Li^+ 1s Hartree–Fock atomic orbital resulting from a computation for one free Li^+ ion using the uncontracted basis. The single contracted p function was the p symmetry component of the single occupied Hartree–Fock orbital resulting from a computation using this uncontracted basis for an Li^+ ion in the presence of a uniform electric field. This [1s1p] contracted basis yields a CHF polarizability of 0.188 au in extremely close agreement with the exact CHF result of 0.189 au [41]. This contraction procedure, introduced in the CHF calculations of [18], was also used here in the MP2 computations, the latter being previously treated [15, 18] by using just the 1s Hartree–Fock atomic orbital. The Na^+ basis was a [2s1p] contraction consisting of the free ion Hartree–Fock orbitals generated using the uncontracted 10s9p basis produced by deleting all the d functions as well as the most diffuse and two most contracted s functions from the 13s9p5d set from [42]. The K^+ basis was a [3s2p] contraction consisting of the occupied Hartree–Fock atomic orbitals produced for the free cation by using the uncontracted 10s9p basis generated by deleting the most diffuse and the three most contracted s functions from the 14s9p basis from [43]. For both Na^+ and K^+, the small differences from the previous contractions [15] originated from the limitation to a contraction depth of ten functions in the CADPAC version used.

A.2. The point charge lattices

All three point charge lattices were constructed such that the entire system of single ion plus point lattice was electrically neutral whilst reproducing the constant portion of the spherically symmetric part $F_{env}^{(0)}(r_a; R)$ of the environment potential occurring for $r_a \leqslant R$.

For the B1 structure, a $5 \times 5 \times 5$ fragment of the lattice was used so that the anion was surrounded by 124 point charges. The charges at the eight corners of this fragment

were chosen to be -0.1065 au whilst the remaining charges on the faces were taken to be 0.2971 au, thereby ensuring that the two above conditions are satisfied. This procedure, adopted in [30], differs from that used previously [15, 18] where all the charges on the faces were scaled to the same common value to ensure overall electrical neutrality. The earlier procedure will not exactly reproduce the constant portion of $F_{env}^{(0)}(r_a; R)$.

For both the B2 and B3 lattices, the slightly different procedure of including the neighbours in all successive shells up to and including the seventh was adopted with the necessary coordinates being taken from [44]. The correct charges of unit magnitude were used for the first five shells with those in the sixth and seventh shells being scaled so as to satisfy the two above conditions. For the B2 lattice the resulting charges in the sixth and seventh shells were -1.1195930 au and -0.0715649 au respectively with those for the B3 lattice being -0.9283513 au and 3.320108 au.

A.3. Anion polarizabilities in the point charge lattices

The CHF polarizabilities predicted for anions in the point charge lattices are presented in table A1. The results inclusive of correlation are reported in table 3 of the main text. The prediction of each correlation polarizability is given as the difference between the polarizability in table 3 and the corresponding CHF result in table A1.

Table A1. SCF polarizabilities for halide ions in various point charge lattices (au). Results labelled 4:4 B1 and 8:8 B1 were computed at the equilibrium R values (table 2) for the B1 structure, i.e. are 'opt B1' type calculations of tables 2–4. Results for other rows are for the equilibrium R values (table 2) predicted for the structure labelling the row in the left-hand column, i.e. are 'opt str' type calculations of tables 2–4. Each salt heading a numerical column denotes the material used to generate the R values (dist) for the results in that column. 6:6 pr, previous results for the 6:6 structure from [18] for LiF, from [15] for NaF, LiCl and KCl, from [20] for NaCl and NaBr; note [20] used the slightly different $R = 5.6333$ au for NaBr.

Dist in	F⁻		Cl⁻			Br⁻	
	LiF	NaF	LiCl	NaCl	KCl	LiBr	NaBr
4:4 B1	7.832	8.848	25.327	26.875	28.867	33.744	35.127
4:4 opt	7.321	8.644	23.157	26.470	28.068		
6:6	7.299	8.289	23.698	25.316	27.519	32.213	33.853
6:6 pr	7.300	8.291	23.705	25.655	27.522		33.808
8:8 opt	8.023	8.747	25.509	26.674	28.000		
8:8 B1	7.252	8.245	23.616	25.226	27.433	32.124	33.736

The present results for the polarizabilities in the point B1 lattices are essentially identical with those computed previously [15, 18, 20]. This agreement is gratifying because it shows that the accuracy of these previous results was in no way impaired by any deviations of the spherically symmetric part of the environmental potential from the exact constant result for $r_a \leqslant R$.

A.4. Anion polarizabilities in the lithium salts

For each cluster of anion plus closest shell of Li⁺ neighbours all embedded in the point charge lattice, the polarizabilities α_{clus} computed using both the CHF and MP2 methods are reported in table A2. Each cluster polarizability can be written [18, 30, 45]

$$\alpha_{clus} = \alpha_A + n\alpha_C + \alpha_{did} \tag{A.1}$$

where α_C is the polarizability of one cation, n is the anion coordination number and α_{did} is the contribution from the dipole–induced dipole interactions. The latter is in general composed of both first- and second-order terms, but the former vanish for an anion in the high-symmetry environments considered here. Consequently, α_{did}, equal to the second-order contributions, is given by [45]

$$\alpha_{did} = 2n(\alpha_A)^2\alpha_C R^{-6}. \tag{A.2}$$

Substitution of (A.2) into (A.1) yields the quadratic equation from which the anion polarizabilities α_A were derived from the α_{clus} values in table A2 taking the CHF and correlated polarizabilities (α_C) of Li$^+$ to be 0.188 au and 0.192 au respectively. There is no need to include any basis superposition corrections in (A.1) because the anion basis is so large that α_A will not be altered by the presence of the cation basis whilst each cation has its correct polarizability by virtue of its specially contracted basis.

Table A2. SCF cluster and anion polarizabilities plus MP2 cluster polarizabilities for lithium halides (au): all results are for the in-crystal anion interacting with both the point charge lattice and the full electron charge distribution of cation neighbours; see notes to table A1; the first six numerical columns are SCF results, the last numerical columns (7–9) are MP2 results, these being MPE results in the row labelled 6:6 pr.

	SCF LiF		SCF LiCl		SCF LiBr		MP LiF	MP LiCl	MP LiBr
	α_{clus}	α_A	α_{clus}	α_A	α_{clus}	α_A	α_{clus}	α_{clus}	α_{clus}
4:4 B1	6.848	6.077	21.500	20.699	29.416	28.602	8.090	22.594	30.580
4:4 opt	6.303	5.528	19.314	18.494			7.311	20.040	
6:6	6.535	5.385	20.087	18.898	27.685	26.477	7.398	20.782	28.570
6:6 pr	6.560	5.394	20.155	18.893			7.412	20.749	
8:8 opt	7.532	6.009	21.956	20.396			8.641	22.900	
8:8 B1	6.523	4.994	19.385	17.808	26.691	25.091	7.217	19.891	27.420

For the B1 phase, both the CHF and MP2 predictions are in essentially exact agreement with the previous CHF and MPE results [15, 18, 20]. Such agreement greatly strengthens confidence in all these results in showing that they are insensitive to small technical differences in the computations.

A.5. Anion polarizabilities in the sodium and potassium salts

The cluster polarizabilities predicted by the CHF and MP2 computations for the sodium and potassium halides are reported in table A3. Since the contracted cation basis sets are minimal, the polarizability of each free cation is predicted to be zero. However, the cations in the cluster computation will not have zero polarizability because this will be partially described by the anion basis functions. The polarizability α_{clus} computed for the cluster will therefore be the sum of the required α_A plus the description in the cluster of the polarizability of the first shell of cation neighbours. The latter basis set superposition contribution, denoted α_{BSE}, is the polarizability predicted from a computation including just the first shell of cation neighbours, each described by its minimal contracted basis but including also the anion basis functions all embedded in the point charge lattice with an additional single negative charge located at the position of the anion functions. An upper bound, denoted α'_{BSE}, to the cation superposition polarizability in the cluster is provided by such a counterpoise computation in which all the anion basis functions are included. This will be an overestimate because in the cluster containing the full anion nuclear charge plus

Table A3. Cluster, basis superposition corrections and anion polarizabilities for the Na^+ and K^+ salts (au): the first five numerical columns are the SCF results with the numerical columns 6–10 being MP2 results; results α'_{BSE} and α'_A are derived by including all the anion basis functions, α_{BSE} and α_A are computed omitting all anion basis functions of s and p symmetry from the basis superposition computations; see notes to table A1; results 8:8 opt* are computed at R values of 4.745 au for NaF and 5.759 au for NaCl predicted from the density functional computations [33] and [35], slightly different from those in table 2.

	SCF					MP2				
	α_{clus}	α'_{BSE}	α_{BSE}	α'_A	α_A	α_{clus}	α'_{BSE}	α_{BSE}	α'_A	α_A
NaF										
4:4 B1	7.308	0.609	0.316	6.699	6.992	8.972	0.637	0.328	8.335	8.644
4:4 opt	7.094	0.641	0.332	6.453	6.762	8.628	0.673	0.346	7.955	8.282
6:6	6.876	0.906	0.498	5.970	6.378	8.077	0.947	0.517	7.130	7.560
6:6 pr	6.782				6.372					
8:8 opt	7.266	1.046	0.586	6.220	6.680	8.539	1.085	0.604	7.454	7.935
8:8 opt*	7.308	1.034	0.580	6.274	6.728	8.609	1.072	0.597	7.537	8.012
8:8 B1	6.678	1.207	0.668	5.471	6.010	7.629	1.262	0.693	6.367	6.936
NaCl										
4:4 B1	21.900	0.406	0.213	21.494	21.687	23.218	0.420	0.220	22.798	22.998
4:4 opt	21.411	0.428		20.983		22.625	0.443		22.182	
6:6	20.116	0.595	0.335	19.521	19.781	20.963	0.616	0.346	20.347	20.617
6:6 pr	(20.552)				(20.232)					
8:8 opt	21.150	0.672	0.374	20.478	20.776	22.137	0.692	0.385	21.445	21.752
8:8 opt*	21.598	0.647	0.360	20.951	21.238	22.681	0.667	0.371	22.014	22.310
8:8 B1	18.929	0.812	0.451	18.117	18.478	19.517	0.840	0.465	18.677	19.052
KCl										
4:4 B1	29.610	7.688	4.629	21.922	24.981	31.997	8.444	5.177	23.553	26.820
4:4 opt	28.903	8.518	4.846	20.385	24.057	31.131	9.396	5.450	21.735	25.681
6:6	30.825	11.125	6.552	19.700	24.273	32.961	12.170	7.255	20.791	25.706
8:8 opt	32.937	13.322	8.263	19.615	24.674	35.090	14.471	9.081	20.619	26.009
8:8 B1	32.375	14.160	8.411	18.215	23.964	34.425	15.416	9.268	19.009	25.157
NaBr										
4:4 B1	30.054	0.297	0.157	29.757	29.879	31.390	0.306	0.161	31.084	31.229
6:6	28.072	0.443	0.244	27.629	27.828	29.090	0.456	0.251	28.634	28.839
6:6 pr					27.58					28.59
8:8 B1	26.585	0.596	0.328	25.989	26.257	27.397	0.613	0.337	26.784	27.060

all the anion electrons not all the anion basis functions are available for the incomplete description of the cation polarizability, since some of these are partially used to describe the occupied anion orbitals.

For the F^- and Cl^- ions, a lower bound, denoted α_{BSE}, to the superposition correction in the full cluster is provided by a counterpoise computation in which only anion basis functions of d symmetry are included. The anion functions of s and p symmetries are excluded from this superposition computation on the grounds that these functions are used in the full cluster computation to describe the atomic orbitals occupied by the anion electrons. Table A3 reports the basis superposition corrections α'_{BSE} and α_{BSE} computed by these two methods and the anion polarizabilities α'_A and α_A derived by subtracting α'_{BSE} and α_{BSE} respectively from α_{clus}. For the sodium salts, both α'_{BSE} and α_{BSE} are small, the anion polarizabilities α_A derived from the lower bound (α_{BSE}) for the superposition correction being reported in the main text. Currently there is insufficient information to discriminate between the α'_A and α_A predictions although the latter were previously regarded [15, 16, 18]

as slightly preferable. In any case the predictions α'_A and α_A only differ by 0.3 au at most. Technical problems caused the absence from table A3 of a value for α_{BSE} for B3 structured NaCl at its R_e. The α_A value reported in the main text was calculated by deriving the required α_{BSE} by scaling the 'opt B1' α_{BSE} by the ratio of the 'opt str' and 'opt B1' α'_{BSE} values, thereby producing an MP2 'opt str' α_{BSE} of 0.232 au. Division of each α'_{BSE} or α_{BSE} by the coordination number yields the polarizability that one cation acquires through the basis superposition effect. For each salt, this value clearly decreases with increasing cation–anion separation but more interestingly essentially the same result is obtained if R is held constant as in the comparison of the three 'opt B1' computations. It is in principle possible to write α_{clus} as the sum of α_A plus α_{BSE} plus a dipole–induced dipole correction given by (A.2) with α_C equal to α_{BSE} divided by the coordination number. One would then derive α_A from the resulting quadratic equation. It was not considered worthwhile to adopt this procedure because any changes in the predictions for α_A are significantly less than the small uncertainties arising from the different choices (α'_{BSE} or α_{BSE}) for the cation superposition polarizabilities. Thus the largest single cation superposition polarizability for the latter choice, that in the 'opt str' calculation for the B3 phase of NaF, is only 0.079 au. There are two sets of 'opt str' results for the B2 phase, corresponding to slightly different predictions for the R_e values. There are no significant differences between the two sets and only one of these is reported in the main text.

For NaBr, the α'_{BSE} results were computed as before by including all the bromide basis functions whilst only the functions of s and p symmetries were excluded in the calculation of α_{BSE}. However, in contrast to F$^-$ and Cl$^-$ cases, the latter does not provide a rigorous lower bound to the cation superposition polarizabilities because d orbitals are occupied in the Br$^-$ ion. A true lower bound is only provided by the counterpoise computation in which all Br$^-$ functions are excluded excepting those of f symmetry. For the B3, B1 and B2 phases, such MP2 computations yielded 0.019, 0.029 and 0.039 au respectively for the total polarizability of all the cations in the first coordination shell. Each of the corresponding CHF values was identical to three decimal places to the MP2 result. Clearly, the bromide polarizabilities predicted by using these superposition corrections will not differ significantly from those derived using the α_{BSE} which are reported in the main body of the text.

It has not so far been technically possible to generate suitably contracted cation basis sets which will reproduce the full polarizabilities of either Na$^+$ or K$^+$. This necessitated using unpolarizable contracted cation bases, thereby introducing a cation basis superposition error into the computed α_{clus}. The latter had then to be corrected by further calculations aiming to evaluate the unwanted superposition contributions. Although these could not be precisely determined, both their upper (α'_{BSE}) and lower (α_{BSE}) bounds and the differences $\alpha'_{BSE} - \alpha_{BSE}$ were sufficiently small for Na$^+$ that halide polarizabilities in sodium salts could be accurately predicted. However, the greater polarizability of K$^+$ (5.339 au [15]) compared with Na$^+$ (1.002 au [15]) caused the superposition corrections in potassium salts to be sufficiently large as to preclude definitive computations of the anion polarizabilities. Thus, for the B1 phase of KCl, the upper and lower limit MP2 superposition corrections α'_{BSE} and α_{BSE} of 12.170 and 7.255 au (table A3) yield anion polarizabilities of 20.619 and 26.009 au compared with the experimentally deduced α_A of 22.856 au [23]. However, as would be expected, the two computed results do bound the true value. The two *ab initio* values are only changed to 20.558 and 25.492 au respectively on including a dipole–induced dipole term in α_{clus}, taking α_C to be α'_{BSE} or α_{BSE} divided by the coordination number. These results all show that the present calculations by themselves cannot provide useful predictions for the polarizabilities in the B2 and B3 phases. However it is not unreasonable to suggest that the computations can provide sensible predictions for the differences between

the anion polarizabilities in the alternative phases. The polarizability of Cl^- in the B2 phase at its R_e would then be predicted to be 23.159 au by adding to the 22.856 au α_A for the B1 structure the difference of 0.303 au between the MP2 predictions for α_A in the B2 and B1 phases. Since this result is so similar to that of 23.377 au produced by the relation (1) using the A, B and C parameters derived from the B1 phase data, the present computations for KCl do not provide any evidence contrary to the conclusions drawn from the results for the lithium and sodium salts. Similarly a value of 22.831 au is deduced for the polarizability of the Cl^- ion in the B3 phase of KCl at its R_e by adding the difference of -0.025 between the computed MP2 α_A in the B3 and B1 phases to the experimental B1 phase value. The resulting polarizability of 22.831 au value is larger than that of 22.023 au predicted from the relation (1) using the B1 phase A, B and C parameters. Thus there is again no evidence to counter the conclusion drawn from the lithium and sodium salts that halide polarizabilities in the B3 phase exhibit an explicit structural dependence.

A.6. Comparison with previous B1 phase results

The present results for α_{clus} and α_A for the B1 phase agree well (table A3) with those few previously computed [15, 20] values as were explicitly reported. The close agreement between the two sets of results again shows the unimportance of the slight technical differences between the calculations. The previous [15] results for NaCl in table A3 are bracketed because subsequent work [20] suggested that the former might be subject to slight revision.

Table A4. A comparison of present and previous anion polarizabilities predicted for B1 salts with inclusion of electron correlation (au): previous results in columns headed MPD and MPE, denoting the two different methods for computing polarizability, are from [18] for LiF, from [14] for NaF, LiCl and NaCl and from [20] for NaBr; values in brackets are the averages reported in [15] of the MPD and MPE results.

	Point lattice			Full cluster		
	MPD	MPE	Present	MPD	MPE	Present
LiF	9.015	9.135	9.141	6.156	6.246	6.126
NaF	10.703	10.933	10.938	(7.572)	(7.572)	7.560
LiCl	24.883	25.384	25.374	19.226	19.527	19.563
NaCl				(20.932)	(20.932)	20.617
NaBr				28.62	28.59	28.839

The data assembled in table A4 compare the present and previous Moller–Plesset perturbation predictions for the anion polarizabilities in the B1 phase including both contributions to the environmental potential. There are only small differences between the previous MPD and MPE results with the latter showing close agreement with the present predictions, which are of the MPE type. The previous values in brackets in table A4 are the averages of the MPD and MPE results, these not having been reported individually.

References

[1] Fajans K and Joos G 1924 *Z. Phys.* **23** 388
[2] Mayer J E 1933 *J. Chem. Phys.* **1** 270
[3] Mott N F and Gurney R W 1950 *Electronic Processes in Ionic Crystals* (Oxford: Oxford University Press)
[4] Buckingham A D 1967 *Adv. Chem. Phys.* **12** 107

[5] Wilson M and Madden P A 1994 *J. Phys.: Condens. Matter* **6** 159
[6] Mott N F and Littleton M J 1938 *Trans. Faraday Soc.* **34** 485
[7] Harding J H 1991 *Rep. Prog. Phys.* **53** 1403
[8] Pyper N C 1994 *Chem. Phys. Lett.* **220** 70
[9] Pyper N C 1986 *Phil. Trans. R. Soc.* A **320** 107
[10] Pyper N C 1995 *Phil. Trans. R. Soc.* A **352** 89
[11] Fowler P W, Knowles P J and Pyper N C 1985 *Mol. Phys.* **56** 83
[12] Pyper N C 1991 *Adv. Solid State Chem.* **2** 223
[13] Slater J C and Kirkwood J G 1931 *Phys. Rev.* **37** 682
[14] Fowler P W and Pyper N C 1985 *Proc. R. Soc.* A **398** 377
[15] Fowler P W and Madden P A 1985 *Phys. Rev.* B **29** 1035
[16] Fowler P W and Madden P A 1985 *J. Phys. Chem.* **89** 2581
[17] Glover R M and Weinhold F 1977 *J. Chem. Phys.* **66** 191
[18] Fowler P W and Madden P A 1983 *Mol. Phys.* **49** 913
[19] Tessman J R, Kahn A H and Shockley W 1953 *Phys. Rev.* **92** 890
[20] Fowler P W and Tole P 1990 *J. Chem. Soc. Faraday Trans.* **86** 1019
[21] Mahan G D 1980 *Solid State Ion.* **1** 29
[22] 1992 *'CADPAC': the Cambridge Analytic Derivatives Package* issue 5 Cambridge. A suite of quantum
     chemistry programmes developed by Amos R D with contributions from Alberts I L, Andrews J S,
     Colwell S M, Handy N C, Jayatilaka D, Knowles P J, Kobayashi R, Koga N, Laidig K E, Malsen P E,
     Murray C W, Rice J E, Sanz J, Simandiras E D, Stone A J and Su M D
[23] Pyper N C, Pike C G, Popelier P and Edwards P P 1995 *Mol. Phys.* **86** 995
[24] Wilson J N and Curtiss R N 1970 *J. Phys. Chem.* **74** 187
[25] Johnson W R, Kolb D and Huang K N *At. Data Nucl. Data Tables* **28** 333
[26] McEachran R P, Stauffer A D and Greita S 1979 *J. Phys. B: At. Mol. Phys.* **12** 3119
[27] Rose S J, Grant I P and Pyper N C 1978 *J. Phys. B: At. Mol. Phys.* **11** 1171
[28] Nellin C, Roos B J, Sadlej A J and Siegbahn P E M 1982 *J. Chem. Phys.* **77** 3607
[29] Kello V, Roos B J and Sadlej A J 1988 *Theor. Chim. Acta* **74** 185
[30] Pyper N C, Pike C G and Edwards P P 1992 *Mol. Phys.* **76** 353
[31] Benson G C and van Zeggeren F 1957 *J. Chem. Phys.* **26** 1083
[32] *Landolt–Bornstein New Series* 1966 Group III vol 1 (Berlin: Springer)
[33] Muhlhausen C and Gordon R G 1981 *Phys. Rev.* B **23** 900
[34] Hemley R J and Gordon R G 1985 *J. Geophys. Res.* **90** 7803
[35] Muhlhausen C and Gordon R G 1981 *Phys. Rev.* B **24** 2147
[36] Amos R D 1982 *Chem. Phys. Lett.* **88** 89
[37] Dierckson G H F and Sadlej A J 1982 *Mol. Phys.* **47** 33
[38] Dierckson G H F and Sadlej A J 1981 *Chem. Phys. Lett.* **84** 390
[39] Werner H J and Rosmus P 1980 *J. Chem. Phys.* **73** 2319
[40] Van Duijneeveldt F B 1971 *IBM Research Report* RJ945
[41] McEachran R P, Stauffer A D and Greita S 1979 *J. Phys. B: At. Mol. Phys.* **12** 3119
[42] Dierckson G H F and Sadlej A J 1982 *Theor. Chim. Acta* **61** 485
[43] Watchers A J H 1970 *J. Chem. Phys.* **52** 1033
[44] Stoneham A M 1975 *Theory of Defects in Solids* ch 1 (Oxford: Oxford University Press)
[45] Fowler P W 1990 *Mol. Simul.* **4** 313