Inter-ionic potentials in solid cubic alkali iodides

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Abstract

A non-empirical fully ionic description, with the anion wavefunctions in their compressed but still spherically symmetrical states optimal for the crystal, is presented for the cohesive energetics of two cubic phases of three solid iodides, KI, RbI and CsI. The non-correlated part of the energy is computed using the RELCRION program which takes full account of relativistic effects. Both the dispersive attractions and energies arising from electron correlations of short range are computed.

For each polymorph stable under ambient conditions, the rock-salt (B1) phases of KI and RbI and the eightfold coordinated (B2) phase of CsI, the cohesion is slightly underestimated. The lattice energy deficits of around 22 kJ mol^{-1} for KI and RbI are reduced to around 13 kJ mol^{-1} for CsI, with overestimations of some 0.2 au in the equilibrium cation–anion separations R decreasing as the metal becomes more electropositive. The prediction that the B2 phase of CsI is more stable (by 6 kJ mol^{-1}) than the B1 polymorph agrees with experiment. For both KI and RbI, the zinc-blende polymorph is predicted to lie some 37 kJ mol^{-1} in energy above the B1 polymorph.

An additional potential, plausibly ascribed to slight covalency, correcting these underestimations is derived semi-empirically.

S Supplementary data are available from stacks.iop.org/JPhysCM/20/085222

1. Motivation

There are two different motivations for the present, essentially non-empirical, study of the cohesive properties of three solid alkali iodides. The inter-ionic pair potentials that are necessarily generated in order to achieve the first objective of this paper are central to the second motivation, that of generating some of the data needed to study alkali iodide nanocrystals.

The first reason for this study is that it is a logical continuation of the previous non-empirical investigations [1], based on a fully ionic description, of the cohesive properties and phase transitions in a range of fluorides [2], chlorides [3–5] and oxides [6–9]. The fully ionic description is defined [1, 10, 11] by the total crystal wavefunction being written as an anti-symmetrized product of individual ion wavefunctions, each of which is spherically symmetric and contains the integral number of electrons consistent with its formal charge. Such a description has been shown to provide an excellent account of the cohesive properties of such solids including the long-standing and challenging problem [12–15] of explaining why solid caesium chloride is eightfold rather

than sixfold coordinated under ambient conditions [3, 4]. It is, therefore, interesting to test the accuracy of such a description for solids which might be expected to show greater deviations from full ionicity than those considered in the previous investigations which did not reveal any evidence for even partial covalency.

The second motivation for the present investigation, and in particular the study of the iodides of potassium, rubidium and caesium, is that each of these salts has been prepared in one or more nanocrystalline forms by encapsulation in single-walled carbon nanotubes [16–20]. Furthermore, the encapsulated structures of both these crystals, as well as other materials, have been accurately determined by recently developed methods in high resolution transmission electron microscopy (HRTEM) [21, 22]. The majority of the encapsulated iodides have structures based on the rock-salt lattice [16–20], although encapsulated CsI crystals based on the eightfold coordinated body-centred cubic (B2) structure have also been observed [18, 20]. All the encapsulated KI, RbI and some of the CsI crystals exhibited, when viewed down the nanotube axis, a fragment of the {001} plane of a rock-salt structured lattice. Each fragment contained either

four or nine ions in cross-section depending on the diameter of the nanotube so that there are four or nine chains of ions respectively. Thus in the four chain (2×2) case, this first plane consists, to within the accuracy of the experiment [17], of a square arrangement of ions with those of the same charge located at the ends of the diagonals. Although each four chain or nine chain structure is based on the rock-salt lattice, the inter-ionic separations are significantly distorted from those of the bulk with the inter-plane separations being significantly reduced whilst those within each plane are appreciably dilated. The first theoretical study [23, 24] of encapsulated KI used semi-empirical inter-ionic potentials [25] dating from the 1970s with the ion–wall interactions scaled from those of the corresponding inert gases. Although this study fulfilled its primary objective of elucidating the mechanism by which the nanotubes became filled by immersion in the molten salt, it could only reproduce the experimentally observed structures if it were assumed that the encapsulating nanotube was surrounded by the bulk material during the microscopy. However, during the HRTEM experiments used to determine the structure, there was no surrounding salt. Furthermore, the structures of the encapsulated salts were shown to remain unchanged on annealing [26]. A density functional study [27] of encapsulated 2×2 KI was unable to reproduce the dilation of the in-plane distances, not unsurprising in view of the inability of such methods to correctly capture the dispersive attractions. Another set of semi-empirically derived inter-ionic potentials [28, 29] included neither the dipole–quadrupole dispersive attractions nor the damping of the dipole–dipole terms and invoked the set of ionic polarizabilities presented by Tessman *et al* [30]. This set is now known [31] both to contain severe inconsistencies and to predict values that cannot stand comparison with modern *ab initio* computations [32–35]. Furthermore the potentials [28, 29] contain semi-empirically determined dispersion coefficients [36] similar to those [37, 38] now known [35] to be too large by factors of around three. These potentials do not, therefore, provide an attractive basis for investigating the structures of the encapsulated iodide nanocrystals.

The difficulties just discussed showed the need to calculate accurate inter-ionic potentials including a correct description of the dispersive attractions. The investigation [39] of the encapsulated nanocrystals, which successfully explained the experimental structures [17, 20] of 2×2 crystals of KI and CsI, relied on the potentials to be described. The computation of such potentials, achieving the second objective of the present work, is necessarily accompanied by an investigation of the cohesion of the bulk crystals, the first objective. A necessary prerequisite of any investigation of the structures of the encapsulated nanocrystals is the use of potentials correctly reproducing the inter-ionic separations of the bulk materials. Furthermore, the potentials presented here were used to test a global analytic theory [40], based on the Born model, of the structures of the non-encapsulated binary ionic nanocrystals. For bulk KI and RbI, both the experimentally observed rock-salt phases are examined as well as the fourfold coordinated zinc-blende structures, the latter being considered because the ions in the four chain

nanocrystals are coordinated by four other ions. For bulk CsI, both experimentally observed structures, namely the rock-salt phase and the eightfold coordinated polymorph having the CsCl structure, are considered.

2. Ionic description

2.1. Methods

2.1.1. The uncorrelated potentials. The methods used in the fully ionic description are identical with those described [1, 4] and used previously [1–7, 9]. Hence these need only be outlined in detail sufficient to define the quantities whose numerical values are reported.

The first step is to derive the individual ion wavefunctions whose anti-symmetrization yields the wavefunction for all the electrons in the crystal composed of equal numbers of cations (C) and anions (A). There is abundant evidence [1, 31–35, 41] that cations with p^6 outermost electronic configurations are essentially unaffected by their environment in-crystal, as evidenced by the constancy of their charge distributions [1, 32–34] and polarizabilities [31–35]. The cation wavefunctions, therefore taken to be same as those of a free cation, were computed using the Oxford Dirac–Fock program [42]. This, using a Dirac Hamiltonian and four component orbital wavefunctions, ensures a fully relativistic description.

Anions are significantly affected by their environment in-crystal, being less polarizable [31–33, 35, 43, 44] with charge distributions contracted [1, 32, 33, 43] compared to those of the free ion. These polarizability reductions and contractions depend on both the inter-nuclear distance [44–46] and polymorph [44, 46, 47] in any one crystal as well as on the cation in comparisons of different crystals at their equilibrium geometries [31–34, 44, 46, 47]. Furthermore any dispersion coefficient involving an anion is smaller than the corresponding value with the free anion as shown by *ab initio* computations for both the dipole–dipole [35] and dipole–quadrupole dispersive attractions [48]. For the present investigations of KI, RbI and CsI, the anion wavefunctions were computed using the RELCRION program [49] and the OHSMFS in-crystal model [5, 6]. This model describes the interaction of the anion electrons with their environment in-crystal by adding to the Fock Hamiltonian for an electron in the free ion, a model operator, the OHSMFS term, depending on two constants A and q. These are determined by the variational criterion that the crystal cohesive energy $U_L^0(R)$ computed using this uncorrelated description is minimized. For a crystal of stoichiometry CA, this energy, measured relative to the sum of the energies of the free ions, is given by [1, 10, 11]

$$U_L^0(R) = N_f \left\{ -\frac{M}{R} + E_{re}^0(R) + n_{CA} V_{sCA}^0(R) \right.$$
$$\left. + \tfrac{1}{2}[n_{AA} V_{sAA}^0(x_{AA}R) + n_{CC} V_{CC}^0(x_{CC}R)] \right\} \qquad (2.1)$$

after neglecting the very small short-range interactions between pairs of ions more distant than the closest cation–anion, anion–anion and cation–cation terms. The geometry

Table 1. Fitted short-range cation–cation interactions $V_{sCC}(r_{cc})$ (au). (Note: constants A_1, b_1, A_2 and b_2 defined by equation (2.3). Rb^+ values taken from [5].)

Cation C	A_1	b_1	A_2	b_2	χ^2
K^+	75.6692	0.717 528	−65.929	0.727 383	7.105×10^{-10}
Rb^+	170 958.0	0.351 755	−0.061 54	0.961 563	3.942×10^{-11}
Cs^+	27 460 800.0	0.317 341	−0.000 310	2.104 27	8.226×10^{-11}

of a cubic crystal is defined by the closest cation–anion separation R. Each integer n_{XY} is the number of closest Y ions neighbouring one ion of type X. All the terms in the curly brackets { . . . } are expressed in atomic units per ion or per ion pair whilst N_f is a constant converting a binding energy per ion into one per mole. In (2.1), M is the Madelung constant and $E_{re}^0(R)$ is the positive rearrangement energy needed to convert one isolated anion in its ground state into the state optimal for the crystal with geometry defined by R. The potential $V_{sXY}^0(x_{XY}R)$ is the energy of interaction of one ion of type X with one of type Y, separated by a distance $x_{XY}R$, measured relative to the sum of the energies that ions X and Y would have when isolated if they still had the wavefunctions optimal for the crystal with geometry defined by R.

The relativistic integrals program (RIP) [50, 51] yields fully relativistic results for the short-range two-body interactions which are exact for the wavefunctions input to the program. The two OHSMFS parameters are determined using RELCRION program which, incorporating both the RIP [50, 51] and Oxford–Dirac Fock [42] programs, enables $U_L^0(R)$ to be evaluated for any given A and q which are then automatically variationally optimized. The optimal values of these parameters are reported for all the phases of all the crystals in table S1 of the supplementary material (available at stacks.iop.org/JPhysCM/20/085222). Tables S2–S7 (available at stacks.iop.org/JPhysCM/20/085222) of this material present the $E_{re}^0(R)$ as well as the closest cation–anion and anion–anion interactions $V_{sCA}^0(R)$ and $V_{sAA}^0(x_{AA}R)$. For both Rb^+ [5] and Cs^+ [4], the cation–cation terms $V_{sCC}^0(x_{CC}R)$ have been reported elsewhere whilst for K^+ this potential is almost negligible, the least negligible value for the phases considered here being a mere 0.000 059 au for $R = 5.0$ au in the rock-salt phase.

2.1.2. The contributions from electron correlation. The total cohesive energy $U_T(R)$ predicted with the inclusion of electron correlation is given by [1, 11]

$$U_T(R) = U_L^{nd}(R) + U_{disp}(R) + U_{AT}(R) \qquad (2.2)$$

where $U_L^{nd}(R)$ is given by an expression identical to (2.1) except that each term, excluding $-M/R$, is augmented by a contribution from electron correlations of short-range to yield totals distinguished from their uncorrelated counterparts in (2.1) by the absence of the superscript ^{0}. In (2.2), $U_{disp}(R)$ is the total two-body dispersion energy whilst $U_{AT}(R)$ is the total energetic contribution arising from the Axilrod–Teller triple dipole dispersive interactions.

The short-range correlation contribution to each of the two-body terms in (2.1) was computed using the density

functional theory (DFT) of a uniform electron gas as implemented by Gordon and Kim [52]. The resulting total cation–anion and anion–anion interactions $V_{sCA}(R)$ and $V_{sAA}(x_{AA}R)$ are reported in tables S2–S7 of the supplementary material (available at stacks.iop.org/JPhysCM/20/085222). Each of the computed cation–cation interactions, $V_{sCC}(x_{CC}R)$, could be reproduced as a function of cation–cation separation r_{CC} to at least one part in 10^7 by the expression

$$V_{sCC}(R) = A_1 \exp\left(-\frac{b_1}{r_{CC}}\right) + A_2 \exp\left(-\frac{b_2}{r_{CC}}\right). \qquad (2.3)$$

The resulting parameters A_1, b_1, A_2 and b_2 are presented in table 1.

The correlation contribution $E_{re}^{corr}(R)$ to the rearrangement energy was evaluated from

$$E_{re}^{corr}(R) = B_{corr}[E_A^{Ccorr}(R) - E_{Af}^{Ccorr}] \qquad (2.4)$$

[2] where E_{Af}^{Ccorr} is the correlation energy of free anion evaluated using the Cowan modification [53] of the DFT treatment [52] of a uniform electron gas. This modification ensures that the correlation energy of a one electron system is predicted to be zero. $E_A^{Ccorr}(R)$ is the similarly evaluated correlation energy of one isolated anion retaining the wavefunction optimal for the crystal with cation–anion separation R. In (2.4), B_{corr} is a scaling factor which, ideally, should be derived as the ratio of the exact total correlation energy of a free anion to the prediction derived from the Cowan DFT modification. For the F^- and Cl^- ions B_{corr} was found to be 0.576 [2] and 0.544 [4] respectively. Since the total correlation energy of the iodide ion is not known, B_{corr} was taken to be 0.544 since the values for F^- and Cl^- indicate that this parameter, for the halide ions at least, is only weakly dependent on nuclear charge. The total rearrangement energies $E_{re}(R)[= E_{re}^0(R) + E_{re}^{corr}(R)]$ are presented in tables S2–S7 of the supplementary material (available at stacks.iop.org/JPhysCM/20/085222).

The total crystal dispersion energy $U_{disp}(R)$ is given by summing over all pairs of ions the dispersive attraction within each pair. In the theory of Jacobi and Csanak [54], which takes account of the damping of the dispersive attractions when the overlap of the charge densities of the interacting ions ceases to be negligible, each pair attraction is determined by the dispersion coefficients and the damping parameters, one of the latter for each type of ion. The dipole–dipole $C_6(XY)$ dispersion coefficients (tables 2 and 3) were evaluated from the Slater–Kirkwood formula [55] with each electron number P_X taken to be that which exactly reproduces the exact $C_6(XX)$ from the exact polarizability (α_X) of the iso-electronic inert gas.

Table 2. Homonuclear two- and three-body dispersion constants and auxiliary data (au). (Note: derivation of coefficients described in the text. Cation–cation results for Rb^+ from [5] and for Cs^+ from [4]. Expectation values for each phase computed from anion wavefunctions at R values close to R_e. These R values are 6.5 au (B3 KI), 6.7 au (B1 KI), 6.875 au (B3 RbI), 7.0 au (B1 RbI) and 7.5 au (both CsI phases).)

Ion X	α_X	P_X	$\langle r^2 \rangle$	$\langle r^4 \rangle$	K_{XX}	C_6 (XX)	C_8 (XX)	ν (XXX)	d_X
K^+	5.339	6.106	14.479	62.230	1.403	22.863	413.593	91.549	2.423
Rb^+	9.05	7.305	20.454	115.899	1.403	55.188	1 316.209	374.857	2.282
Cs^+	15.28	7.901	29.438	226.535	1.403	125.918	4 078.437	1 443.02	2.130
I^- (B3 KI)	—	—	47.013	623.331	1.285	633.610	32 385.243	21 322.085	1.251
I^- (B1 KI)	44.869	7.901	46.581	599.491	1.285	633.610	31 435.492	21 322.085	1.445
I^- (B3 RbI)	—	—	47.456	638.619	1.285	653.732	33 913.673	22 462.558	1.239
I^- (B1 RbI)	45.814	7.901	46.548	594.929	1.285	653.732	32 209.124	22 462.558	1.517
I^- (B1 CsI)	—	—	47.135	613.732	1.285	670.670	33 664.217	23 440.923	1.507
I^- (B2 CsI)	46.602	7.901	46.820	595.193	1.285	670.670	32 866.970	23 440.923	1.509

Table 3. Heteronuclear dipole–dipole, dipole–quadrupole and three-body dispersion coefficients (au). (Note: dipole–quadrupole dispersion coefficients derived from the Starkschall–Gordon formula using in all cases scaling factors $K^{DQ}(CA) = 1.352$ and $K^{QD}(CA) = 1.394$.)

CA	Structure	C_6(CA)	C_8^{DQ}(CA)	C_8^{QD}(CA)	ν (CCA)	ν (CAA)
KI	B3	108.294	2911.878	973.239	496.714	3114.190
KI	B1	108.294	2826.482	973.239	496.714	3114.190
RbI	B3	176.630	4820.401	2092.762	1345.851	5325.081
RbI	B1	176.630	4578.120	2092.762	1345.851	5325.081
CsI	B1	279.664	7384.818	4500.052	3495.289	8889.188
CsI	B2	279.664	7209.928	4500.052	3495.289	8889.188

This procedure is known to yield values correct to within 5% [1, 35]. The cation polarizabilities (α_C, table 2) are reliably known from a combination of *ab initio* computation and analysis of experimental refractive index data [31–35]. The anion polarizability (α_A) in each salt, for which experimental data is available, was derived by subtracting α_C from the molar polarizability of the crystal as presented by Wilson and Curtiss [56]. Since there is no experimental data available for either the zinc-blende structured polymorphs of KI and RbI or for the rock-salt phase of CsI, each anion polarizability was taken to be the same as that in the phase stable under ambient conditions. The polarizability of any iodide ion is sufficiently large that the required values cannot be deduced from the expression [31] relating polarizability to the equilibrium bond length shown to be reliable for fluorides, chlorides and bromides [4]. The dipole–quadrupole C_8^{DQ}(XY) and quadrupole–dipole C_8^{QD}(XY) dispersion coefficients were derived by scaling [2] the values predicted by the Starkschall–Gordon formula [57]. The required electronic expectation values, $\langle r^2 \rangle$ and $\langle r^4 \rangle$, presented in table 3, were computed considering only the six outermost electrons as justified previously [1, 48]. The scaling factors K(CC), K(AA), K^{DQ}(CA) and K^{QD}(CA) have been found [2] to quite insensitive to nuclear charge but to be slightly more dependent on the total ion charge. They were therefore taken to be those derived from a comparison of the *ab initio* and Starkschall–Gordon formula predictions for the ions pairs in the rock-salt phase of NaCl [2]. The dispersion damping parameters were evaluated as previously. The cation values were calculated from the orbital eigenvalues produced by Dirac–Fock calculations for the free cations [1] with the anion ones being derived [6] from the spatial decay of the in-crystal anion OHSMFS Dirac–Fock wavefunctions.

The Axilrod–Teller triple dipole dispersion coefficients [58, 59] were calculated from the ion polarizabilities using the Midzuno–Kihara formula [60, 61]. Values thus derived are known to have errors no greater than 5% [35].

2.2. Results

2.2.1. The inter-ionic potentials. The rearrangement energies and short-range cation–anion interactions, presented in the supplementary material (available from stacks.iop.org/JPhysCM/20/085222), show the same trends as those already elucidated for a wide range of other ionic crystals [1–7, 9]. Thus both $E_{re}^0(R)$ and $E_{re}(R)$ increase with decreasing R in each structure, with increasing coordination number at constant R and counter cation and with increasing cation size at constant R and coordination number. Both $V_{sCA}^0(R)$ and $V_{sCA}(R)$ decrease with increasing coordination number at constant R and counter cation and with increasing cation nuclear charge at constant R and coordination number.

Almost all of the standard modelling programs based on potential functions cannot handle separate rearrangements energies. Since the GULP program [62], used to model [39] the encapsulated iodides, falls into this category, it was necessary to define [3] for each crystal the cation–anion effective potential $V_{sCA}^{eff}(R)$ as

$$V_{sCA}^{eff}(R) = V_{sCA}(R) + \frac{1}{6}E_{re}(R). \quad (2.5)$$

This definition ensures that the total energy (2.2) of a rock-salt structured bulk crystal is reproduced by standard expressions for $U_L^{nd}(R)$ in which no rearrangement energies appear explicitly.

It has been suggested to us that it would be interesting to compare the potentials presented here with those [29, 63]

derived many years ago by empirical fitting to a wide range of experimental data. It should be pointed out that, at the time of these earlier works, reliable values were not known for either the vast majority of ionic polarizabilities or interionic dispersion coefficients. Consequently some credence was given to a set [36] of such coefficients most of whose members are now known from accurate *ab initio* computations [35] to be in error by factors of three or four. The successful reproduction [29, 63] of a wide range of experimental data, although constituting very strong evidence that the total potentials are trustworthy for the bulk crystals, does not provide any evidence for the reliability of the individual short-range and dispersive contributions.

One example of the observation just made is provided by the assumption in the derivation of both sets of potentials presented in [63] that the closest cation–anion dispersive attractions are negligible. This assumption can now be seen to be unsustainable because the present trustworthy calculations show that the attraction between one cation and one anion is $-0.001\,603$ au for KI at $R = 6.7$ au and $-0.002\,401$ au for RbI at $R = 6.875$ au. The neglect of these dispersive attractions in [63] caused each of the empirically deduced cation–anion short-range repulsions to be only $2/3$ of the effective potentials (2.5) derived from the $V_{sCA}(R)$ and $E_{re}(R)$ presented here in the supplementary material (available at stacks.iop.org/JPhysCM/20/085222). However each of the total non-point Coulomb interactions, derived by adding to $V_{CA}^{eff}(R)$ the dispersive attraction calculated from the coefficients and damping parameters presented in tables 2 and 3 for the interaction of one cation with one anion, is very similar but slightly larger than the previous short-range terms. Furthermore, addition of the contribution $V_{CA}^{cov}(R)$ derived here semi-empirically in section 3 brings each of the present and previous total cation–anion potentials into very close agreement at all distances except for those so short as to be of no relevance to experiments performed under ambient conditions. These results are illustrated graphically in the supplementary material (available at stacks.iop.org/JPhysCM/20/085222). Since the two parameters determining the function $V_{CA}^{cov}(R)$ were derived by fitting to experimental data obtained under ambient conditions, it is not known whether $V_{CA}^{cov}(R)$ is reliable for distances less than about 5.5 au. Both the present computations and previous semi-empirical analysis agree in predicting both that the short-range cation–cation interactions $V_{sCC}(\sqrt{2}R)$ are insignificant and that the anion–anion terms $V_{sAA}(\sqrt{2}R)$ in RbI are small. For KI, the *ab initio* results show that $V_{sAA}(\sqrt{2}R)$ is not insignificant for anion–anion distances somewhat smaller than $\sqrt{2}R_e$ in contrast to the previous values [63] computed using the original Gordon–Kim electron gas method. It is explained in the review [11] why the Gordon–Kim method in its original unmodified form underestimates the uncorrelated short-range repulsions originating from the overlap of wavefunctions centred on different atoms. The dispersion coefficients $C_6(CC)$ and $C_6(AA)$ of both the two sets of potentials in [63] are now known to be untrustworthy with those in the second set being in error by about 50%. In the first set, it was assumed that

$C_6(CC) = C_6(AA)$ so that, although the latter are also in error by about 50%, the C_6 (CC) coefficients, whose true values are much smaller, were too large by factors of up to 21. For KI the total, $C_6(CC) + C_6(AA)$, of [63] is some 50% and larger than the total derived from the data in table 2 and, furthermore, the dispersion damping was neglected in [63]. Nevertheless, the present total dispersive attraction between second nearest neighbours is similar to the corresponding semi-empirical results for distances in the vicinity of R_e as shown by the figures in the supplementary material (available at stacks.iop.org/JPhysCM/20/085222). This similarity arises because the present inclusion of the dipole–quadrupole dispersive attractions corrects for the previous overestimation of the dipole–dipole terms. For RbI, the previous [63] total $C_6(CC) + C_6(AA)$ is some 90% larger than that derived from table 2. This causes the previous total second nearest neighbour dispersive attraction to be somewhat greater than that predicted here as shown by the figure in the supplementary material (available at stacks.iop.org/JPhysCM/20/085222).

A second set [29] of semi-empirical potentials dating from the 1970s used dispersion coefficients [36] most of which are now known to be error by factors of about four, the dipole–dipole coefficients being too large with the dipole–quadrupole coefficients being underestimated by the same factor. The consequent serious overestimation of the dipole–dipole dispersive attractions compounded by the neglect of the dispersion damping more than outweighed the underestimation of the dipole–quadrupole attractions thus causing the total dispersive attractions in [29] to be between and 3 and 4 times larger than the present totals. Consequently, the semi-empirically determined short-range cation–anion repulsions are significantly larger than the present $V_{CA}^{eff}(R)$. However each sum of the previous cation–anion short-range and dispersive interactions is less than the present results even if the $V_{CA}^{cov}(R)$ term is included. This shows that the crystal cohesion is only satisfactorily described by the potentials of [29] if the fractional ionic charges, each less than unity used in that work, are introduced.

Although the previous semi-empirical potentials [29, 63] in totality yielded a good description of the bulk rock-salt crystals, the contributions of short-range and dispersive interactions in an encapsulated nanocrystal are unlikely to be in the same ratio as in the bulk solids. It should therefore be expected that the semi-empirical potentials would be unsuitable for studying the nanocrystals on account of both the significant differences between the semi-empirical and *ab initio* short-range terms as well as the large differences between the previous [29, 63] and present dispersive attractions.

2.2.2. The crystal cohesive properties. The present predictions, derived from (2.2), for the crystal cohesive properties, as manifested by the lattice energy $D_e[-U_R(R_e)]$, closest equilibrium cation–anion separation R_e and bulk modulus B, are compared with experiment in tables 4 and 5.

The results computed without including the Axilrod–Teller energy $U_{AT}(R)$ were derived from the function $U_L(R)$ which differs from (2.2) only in the omission of $U_{AT}(R)$.

Table 4. Experimental and predicted cohesions of KI and RbI. (Note: lattice energy D_e in kJ mol^{-1}, equilibrium closest cation–anion separation R_e in au and bulk modulus B in 10^{10} Nm^{-2}. Experimental D_e at 0 K: KI [66–68], RbI [67, 68]. Experimental R_e at 0 K from [69]. Experimental B at 4.2 K derived as $(C_{11} + 2C_{12})/3$: KI [70], RbI [71].)

| | KI | | | | RbI | | | |
| | B3 (4:4) | Rock-salt B1 (6:6) | | | B3 (4:4) | Rock-salt B1 (6:6) | | |
	$U_L(R)$	$U_L(R)$	$+U_{AT}(R)$	Expt	$U_L(R)$	$U_L(R)$	$+U_{AT}(R)$	Expt
D_e	590.9	627.3	624.2	648, 649, 650	570.2	608.9	605.5	630, 632
R_e	6.649	6.813	6.843	6.608	6.945	7.059	7.095	6.863
B	0.698	1.286	1.264	1.273	0.678	1.084	1.024	1.310

Table 5. Experimental and predicted cohesion of CsI. (Note: lattice energy D_e in kJ mol^{-1}, equilibrium closest cation–anion separation R_e in au and bulk modulus B in 10^{10} Nm^{-2}. Experimental D_e at 0 K from [66–68]; R_e at 0 K from [69] and B at 4.2 K from [72] derived from $(C_{11} + 2C_{12})/3$.)

| | Rock-salt B1(6:6) | | CsCl type B2 (8:8) | | |
	$U_L(R)$	$+U_{AT}(R)$	$U_L(R)$	$+U_{AT}(R)$	Expt
D_e	585.7	581.6	594.3	587.6	604, 610, 613
R_e	7.398	7.430[a]	7.529	7.598	7.375
B	1.216	1.111	1.346	1.136	1.441

[a] Experimental value at room temperature, when the phase is metastable, is 7.238 au [69].

The results for KI and RbI predict, as would be expected, that the phase observed at room temperature, the B1 rock-salt structured polymorph, is more stable than the B3 fourfold coordinated phase having the zinc-blende structure. For CsI, the calculations correctly predict that the B2 eightfold coordinated phase having the CsCl structure observed at ambient temperatures, has a lower energy than the B1 structured polymorph. The difficulties of correctly predicting that the former phase is more stable have been fully discussed previously [3, 4, 12–15].

The lattice energies of the lowest energy phases of KI, RbI and CsI predicted with the inclusion of $U_{AT}(R)$ are underestimated by 25, 25 and 16 kJ mol^{-1} respectively. These differences are only slightly reduced to 23, 21 and 10 kJ mol^{-1} if $U_{AT}(R)$ is not considered. These discrepancies, particularly those for KI and RbI, are significantly larger than those found for the LiF, NaF, NaCl, AgF, PbF$_2$ [1], MgO, CaO [6, 7], CaF$_2$ [2], RbCl [5] and CsCl [4] systems previously examined for which the predicted D_e values differed from experiment by no more than 5 kJ mol^{-1} at most. The equilibrium cation–anion separations (tables 4 and 5) in all three iodides are overestimated compared with experiment by at least 0.2 au, excepting that for CsI without considering $U_{AT}(R)$ where the discrepancy is reduced to 0.15 au. These overestimations of R_e are relatively small in fractional terms, being some 3%, excepting the 2% error for CsI without considering $U_{AT}(R)$. Nevertheless these 0.2 au discrepancies are significantly larger than any of those arising in the previously examined crystals just listed including that of ThO$_2$ [9] for which no fully experimental value for D_e is available. The largest overestimation for any of these R_e is that of 0.065 au for RbCl if that of 0.077 au for LiF is legitimately discounted on the grounds that this computation used for the anion environment in-crystal the older RVMW model which is now known [4, 6]

to provide a less accurate description than the later ODMFS, OEMFS or OHSMFS models.

Re-examination of the calculations for these three iodides should initially focus on the contributions from electron correlation both because the evaluation of the non-correlated terms is essentially variational and because the former are more significantly different from the corresponding quantities in the materials studied previously. Since, however, there is no significant qualitative difference in the short-range two-body correlation terms, it is the two remaining correlation contributions, $E_{re}^{corr}(R)$ (2.4) and the dispersion energy, that need to be considered. The evaluation of $E_{re}^{corr}(R)$ should be re-examined because the value of B_{corr} was taken to be the same as that for the Cl$^-$ ion. Both this value (0.544) and that of 0.576 for the F$^-$ ion were derived as the ratio of the exact free ion total correlation energy to that of the total correlation energy predicted from the Cowan modification of the density functional theory of a uniform electron gas (equation (12) of [2], (4.2) of [6]). The former energies were derived using experimental values for all the ionization potentials. The B_{corr} value for the I$^-$ ion cannot be evaluated by this method because experimental data is only available for the first few ionizations. In the test computation to be reported, B_{corr} is increased to 0.8. Any larger B_{corr} value can be rejected because this would cause the total rearrangement energy $E_{re}(R)$ to become negative for some distances. The dispersion energies for the iodides are larger than those for most of the systems previously studied. For example, $U_{disp}(R)$ for the B2 phase of CsI is some 90 kJ mol^{-1} around its equilibrium geometry of 7.375 au compared with 79 kJ mol^{-1} for CsCl near its equilibrium separation. The values of the dispersion coefficients themselves, being derived from well established methods, are less open to question than those of the damping parameters d_C and d_A. It is now well established [1] that neglect of the dispersion damping produces $U_{disp}(R)$ energies

too great in magnitude, thereby causing the crystal cohesion to be overestimated, as manifested by too large D_e values and too small R_e distances. Consequently, one test of the accuracy of the implementation of the present fully ionic model is provided by a computation with B_{corr} increased to 0.8 and the dispersion damping neglected. However, for KI, the system showing the greatest underestimation of the cohesion, such a calculation fails to rectify this difficulty, the predicted D_e and R_e values being 640.2 kJ mol^{-1} and 6.679 au respectively. For KI the damped dispersion is some 82% of its undamped value around R_e with corresponding figures of 85% and 88% for RbI and CsI. These fractions are similar to those of 85% and 84% for the B2 and B1 phases of CsCl.

The above considerations indicate that the discrepancies between theory and experiment should not be ascribed to weaknesses in the implementation of the fully ionic model. This suggests that there are non-negligible contributions to the cohesion of these iodides that lie outside the present fully ionic description. Not only are these underestimations only manifested for the iodides, being absent for the fluorides, chlorides and oxides previously examined, but also they decrease as the metal becomes increasingly electropositive. These two observations suggest that the cohesion of each of the iodides is increased above that provided by fully ionic binding by a covalent contribution, in which the iodide 5p electrons become slightly delocalized into the empty ns and np orbitals of the metal of which the cation outer shell contains six electrons in $(n − 1)$p orbitals. This suggestion should not be taken as evidence against the conclusion drawn from the studies [64, 65] of materials that had earlier been thought to be significantly covalently bonded on account of the symmetries of their structures being much lower than cubic. The charge-induced dipole interactions shown to be capable of explaining these structures [64, 65] involve energies much larger than 20 kJ mol^{-1} or less discrepancies for the cubic iodides. Furthermore, any such covalency in the alkali iodides must be sufficiently small that, at most, it affects the polarizabilities of the ions only minimally. Thus, it has been shown [44] in an extensive series of *ab initio* computations, using methods of proven reliability [32–35, 43, 47], that the fully ionic description accurately predicts the polarizability of the iodide ion in both NaI and KI.

3. Additional cohesion

The significance of the relatively small discrepancies of around 3% between experiment and the present computations for the cohesion of the three iodides might, for some purposes, be debatable. However the overestimation of the R_e values by some 0.25 au means that the inter-ionic potentials yielding these predictions are not sufficient by themselves to use in modelling the encapsulated alkali iodide nanocrystals. The evidence presented in the last section suggests that these discrepancies do not arise from inaccuracies in implementing the fully ionic description but that there are additional sources of cohesion lying outside this approach. The small additional attractive interaction needed to provide a complete set of potentials for investigating the encapsulated nanocrystals

Table 6. The cohesive properties with inclusion of semi-empirical addition potential $V_{CA}^{cov}(R)$. (Note: lattice energy D_e in kJ mol^{-1}, equilibrium closest cation–anion separation R_e in au and bulk modulus B in 10^{10} Nm^{-2}. Bracketed results were assumed in the fitting procedure.)

	D_e	R_e	B	Q	ζ
KI B1(6:6)	640.6	(6.606)	(1.283)	16.39	1.25
RbI B1(6:6)	623.6	(6.862)	(1.310)	9.09	1.15
CsI B2(8:8)	600.7	7.376	1.437	25 000.0	1.80

will therefore be derived by adding a two-parameter model potential to the cation–anion short-range interactions already derived on the fully ionic basis. For each bulk crystal in its polymorph stable under ambient conditions, these two parameters will be determined by demanding that the experimental values of both R_e and the bulk modulus (B) are reproduced. The latter property, rather than the lattice energy, is used in the fitting because B governs the energy change when the bulk crystal undergoes small displacements from equilibrium. The Axilrod–Teller energy, $U_{AT}(R)$, is excluded from these calculations because it is small and moreover its inclusion would slow very considerably the modelling of the encapsulated nanocrystals using the GULP program [62].

The most plausible explanation for the underestimations in the fully ionic model is a small covalent contribution to the binding, arising from the fully ionic wavefunction becoming mixed with excited states in which one I$^-$ 5p electron is transferred to the valence ns orbital of the neutral alkali metal. An expression for the energy originating from this covalency is introduced just within the closest cation–anion pairs, being expressed as $n_{CA} V_{CA}^{cov}(R)$, where $V_{CA}^{cov}(R)$ is the interaction within one such pair. Any covalent contribution to the binding, has been shown to be small, some 20 kJ mol^{-1} at most, out of some 600 kJ mol^{-1} of total cohesion. This justifies its treatment by perturbation theory when the energy lowering of each electron, belonging to an I$^-$ ion in zeroth order, will be given by the reciprocal of an energy denominator multiplied by the square of a matrix element of the Fock operator linking the occupied anion and vacant cation orbitals. Invoking the approximation that this matrix element, the resonance integral, is proportional to the overlap integral, and combining this proportionality constant with the excitation energy, enables $V_{CA}^{cov}(R)$ to be written

$$V_{CA}^{cov}(R) = -Q\{[1 + \zeta R + \tfrac{1}{3}(\zeta R)^2]\exp(-\zeta R)\}^2. \quad (3.1)$$

Since the two parameters Q and ζ are derived by fitting to experimental data, the energies $V_{CA}^{cov}(R)$ will not be sensitive to the precise form of the fitting function provided that this is not physically unreasonable. The overlap integral in square brackets in (3.1) was therefore, to avoid introducing unnecessary complexity, taken to be that for two hydrogenic 1s orbitals. The resulting values for the Q and ζ parameters are presented in table 6 together with the predicted lattice energies not included in the fitting procedure.

It should be noted that, whilst the fitting will ensure that (3.1) with the parameters in table 6 provides a good description for R values both in the vicinity of R_e and at large

R, its mathematical form causes it to become unreliable at very short distances. However, the total crystal energies at such distances are sufficiently large as to render them irrelevant through not being accessible either thermally or through the application of any reasonable pressure. Although for KI, the lattice energy predicted with the inclusion of the contribution $n_{CA} V_{CA}^{cov}(R)$ still deviates slightly from experiment, the faithful reproduction of R_e and B will ensure that the potentials computed here, after the inclusion of (3.1), are suitable for studying the encapsulated iodide nanocrystals.

4. Conclusion

The non-empirical description of KI, RbI and CsI based on the assumption of full ionicity has been shown to leave unaccounted a small fraction of the binding which decreases with decreasing electronegativity of the metal. This fraction is about 3% for KI and RbI decreasing to 2% for CsI. The equilibrium cation–anion separations in the experimentally observed rock-salt phases of the two former iodides are overestimated by about 0.25 au whilst the prediction for that of the B2 polymorph of CsI is too large by 0.15 au. These cohesion underestimations contrast the results of the calculations for the fluorides, chlorides and oxides which showed no such disagreements with experiment. This suggests that the discrepancies for the iodides could arise from small covalent contributions to the binding.

The dominant contributions to the binding, those captured by the fully ionic description, have been calculated using physically soundly based methods of proven reliability. For each crystal in its ground state polymorph, these have been augmented with the small residual contribution to the binding derived by demanding that the experimentally observed closest cation–anion separations and bulk moduli are reproduced. The introduction of all these potentials provides a sound basis from which to develop models for the nanocrystals of the iodides encapsulated in single-walled carbon nanotubes. This approach minimizes the magnitude of that component of the total binding deduced by fitting to experimental data whilst maximizing the portion containing components each of which is physically soundly based with parameters thereby guaranteed to be realistic.

References

[1] Pyper N C 1986 *Phil. Trans. R. Soc.* A **320** 107
[2] Pyper N C 1995 *J. Phys.: Condens. Matter* **7** 9127
[3] Pyper N 1994 *Chem. Phys. Lett.* **220** 70
[4] Pyper N C 2003 *J. Chem. Phys.* **118** 2308
[5] Pyper N C, Kirkland A I and Harding J H 2006 *J. Phys.: Condens. Matter* **18** 683
[6] Pyper N C 1995 *Phil. Trans. R. Soc.* A **352** 89
[7] Pyper N C 1996 *J. Phys.: Condens. Matter* **8** 5509
[8] Pyper N C and Popelier P 1995 *J. Phys.: Condens. Matter* **7** 5013
[9] Harding J H, Lindan P J D and Pyper N C 1994 *J. Phys.: Condens. Matter* **6** 6485
[10] Abarenkov I V and Antonova I M 1970 *Phys. Status Solidi* **38** 783
[11] Pyper N C 1991 *Adv. Solid State Chem.* **2** 223
[12] Hund F 1925 *Z. Phys.* **34** 833
[13] May A 1937 *Phys. Rev.* **52** 339
[14] May A 1938 *Phys. Rev.* **54** 629
[15] Tosi M P and Fumi F G 1962 *J. Phys. Chem. Solids* **23** 359
[16] Meyer R R, Sloan J, Dunin-Borkowski R E, Kirkland A I, Novotny M C, Bailey S R, Hutchinson J L and Green M H L 2000 *Science* **289** 1324
[17] Sloan J, Novotny M C, Bailey S R, Brown G, Xu C, Williams V C, Friedrichs S, Flahaut E, Callender R L, York A P E, Coleman K S, Green M H L, Dunin-Borkowski R E and Hutchinson J L 2000 *Chem. Phys. Lett.* **329** 61
[18] Sloan J, Kirkland A I, Hutchison J L and Green M H L 2002 *Chem. Commun.* 1319
[19] Sloan J, Friedrichs S, Meyer R R, Kirkland A I, Hutchison J L and Green M H L 2002 *Inorg. Chim. Acta* **330** 1
[20] Sloan J, Kirkland A I, Hutchison J L and Green M H L 2003 *Comptes Rendus* **4** 1063
[21] Kirkland A I, Saxton W O and Chand G 1997 *J. Electron Microsc.* **46** 11
[22] Meyer R R, Kirkland A I and Saxton W O 2002 *Ultramicroscopy* **92** 89
[23] Wilson M and Madden P A 2001 *J. Am. Chem. Soc.* **123** 2101
[24] Wilson M 2002 *J. Chem. Phys.* **116** 3027
[25] Sangster M J C and Dixon M 1976 *Adv. Phys.* **23** 247
[26] Brown G, Bailey S R, Novotny M, Carter R, Flahaut E, Colemna K S, Hutchison J L, Green M H L and Sloan J 2003 *Appl. Phys.* A **76** 457
[27] Sceats E L, Green J C and Reich S 2006 *Phys. Rev.* B **73** 125441
[28] Sangster M J L, Schroder U and Atwood R M 1978 *J. Phys. C: Solid State Phys.* **11** 1523
[29] Sangster M J C and Atwood M 1978 *J. Phys. C: Solid State Phys.* **11** 1541
[30] Tessman J R, Kahn A H and Shockley W 1953 *Phys. Rev.* **92** 890
[31] Fowler P W and Pyper N C 1985 *Proc. R. Soc.* A **398** 377
[32] Fowler P W and Madden P A 1983 *Mol. Phys.* **49** 913
[33] Fowler P W and Madden P A 1984 *Phys. Rev.* B **29** 1035
[34] Fowler P W and Madden P A 1985 *J. Phys. Chem.* **89** 258
[35] Fowler P W, Knowles P J and Pyper N C 1985 *Mol. Phys.* **56** 83
[36] Jain J K, Shankar J and Khandelwal D P 1976 *Phys. Rev.* B **13** 2692
[37] Hajj F 1968 *J. Chem. Phys.* **44** 4618
[38] Shankar J, Agrawal G G and Singh R P 1978 *J. Chem. Phys.* **69** 670
[39] Bichoutskaia E N and Pyper N C 2008 *Phys. Rev.* B submitted
[40] Bichoutskaia E N and Pyper N C 2006 *J. Phys. Chem.* B **110** 5936
[41] Madden P A and Wilson M 1996 *Chem. Soc. Rev.* **25** 339
[42] Grant I P, McKenzie B J, Norrington P H, Mayers D F and Pyper N C 1980 *Comput. Phys. Commun.* **21** 207
[43] Fowler P W and Tole P 1990 *J. Chem. Soc. Faraday Trans.* **86** 1019
[44] Bichoutskaia E N and Pyper N C 2007 *J. Phys. Chem.* C **111** 9548
[45] Pyper N C 1998 *Mol. Phys.* **95** 1
[46] Jemmer P, Fowler P W, Wilson M and Madden P A 1998 *J. Phys. Chem.* A **102** 8377
[47] Pyper N C and Popelier P 1997 *J. Phys.: Condens. Matter* **9** 471
[48] Fowler P W and Pyper N C 1986 *Mol. Phys.* **59** 317
[49] Pyper N C and Harding J H 2008 in preparation
[50] Wood C P and Pyper N C 1981 *Chem. Phys. Lett.* **81** 395
[51] Wood C P and Pyper N C 1986 *Phil. Trans. R. Soc.* A **320** 71
[52] Gordon R G and Kim Y S 1972 *J. Chem. Phys.* **56** 3122
[53] Cowan R D 1967 *Phys. Rev.* **136** 54

[54] Jacobi N and Csanak Gy 1975 *Chem. Phys. Lett.* **30** 367
[55] Slater J C and Kirkwood J G 1931 *Phys. Rev.* **37** 682
[56] Wilson J N and Curtiss R M 1970 *J. Phys. Chem.* **74** 187
[57] Starkschall G and Gordon R G 1972 *J. Chem. Phys.* **56** 2801
[58] Axilrod B M and Teller E 1942 *J. Chem. Phys.* **11** 299
[59] Axilrod B M 1951 *J. Chem. Phys.* **19** 724
[60] Midzuno Y and Kihara T 1956 *J. Phys. Soc. Japan* **11** 1045
[61] Tang K T 1969 *Phys. Rev.* **177** 108
[62] Gale J D 1997 *J. Chem. Soc. Faraday Trans.* **93** 629
[63] Catlow C R A, Diller K M and Norgett M J 1977 *J. Phys. C: Solid State Phys.* **10** 1395
[64] Wilson M and Madden P A 1994 *J. Phys.: Condens. Matter* **6** 159
[65] Madden P A and Wilson M 1996 *Chem. Soc. Rev.* **25** 339
[66] Johnson D A 1968 *Some Thermodynamic Aspects of Inorganic Chemistry* (Cambridge: Cambridge University Press) p 21
[67] Weast R C (ed) 1979 *CRC Handbook of Physics and Chemistry* 59th edn (Boca Raton, FL: CRC Press)
[68] Weast R C (ed) 2003 *CRC Handbook of Physics and Chemistry* 84th edn (Boca Raton, FL: CRC Press)
[69] *Landolt–Börnstein New Series* 1966 Group III, vol 1 (Berlin: Springer)
[70] Norwood M H and Briscoe C V 1958 *Phys. Rev.* **112** 45
[71] Lewis J T, Lehoczky A and Briscoe C V 1967 *Phys. Rev.* **161** 877
[72] Vallin J, Beckman D and Salama K 1964 *J. Appl. Phys.* **35** 1222