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Cubic crystal cohesion and geometry-dependent spherical deformations of ions

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Abstract

The cohesive properties of cubic ionic crystals are, in principle, affected by the response of anions to symmetry-preserving changes of their environment away from the equilibrium nuclear geometry. The importance of such a response is investigated by performing non-empirical computations with the Relativistic Integrals program. For each crystal, the properties computed using anion wavefunctions optimal for each nuclear geometry are compared with those predicted using ‘frozen’ potentials in which the same anion wavefunction, one optimal for a near-equilibrium nuclear geometry, is used to compute all the inter-ionic interactions. Use of such ‘frozen’ potentials leaves essentially unchanged the excellent predictions of the fully optimal computations for both the lattice energy and the closest equilibrium cation–anion separation. The bulk compressibility is significantly overestimated by using ‘frozen’ potentials, often by 50% or even 80%, thus destroying the agreement between experiment and the predictions of the fully optimal computations.

1. Introduction

There is abundant experimental and theoretical evidence, reviewed elsewhere [1, 2], that many crystals are essentially fully ionic. Consequently theoretical studies of polar solids using non-empirical ionic models are well founded, being motivated by the many reasons discussed previously [1, 3]. Theoretical investigations using a fully ionic model of both the cohesive and other properties of a wide range of crystals, both those of both cubic structure [3–9] and those of significantly lower symmetry [10–12], have yielded excellent agreement with experimental data. However, it has been shown that such good agreement between theory and experiment is only obtained if the responses of at least the anions [3, 9] and in certain cases also the cations [3, 13, 14] to their in-crystal environments are correctly described. Three different types of response of an ion to its in-crystal environment can be distinguished.

The first way in which an ion can respond to its crystalline environment is by acquiring an electric multipole moment, usually a dipole moment. The importance of this phenomenon for the dielectric and elastic properties of crystals has long been recognized [15, 16], it being often described using the venerable shell model [17]. Furthermore, the significant

quadrupole moments induced on silver cations by non-zero electric field gradients are important in determining the properties of silver salts [13, 14]. More recently, it has been shown [2, 14, 18] that the stabilization experienced by an ion on acquiring a dipole moment through residing on a site of low symmetry at which there is a permanent non-vanishing electric field is often the crucial factor in causing a crystal to adopt its observed structure. Indeed this work [18] overturned the previously widely held belief that the low symmetries of many crystal structures were evidence of partial covalency.

The second way in which an ion responds to its in-crystal environment is through the radial electron density of the ion in the crystal at its equilibrium geometry differing from that of the isolated ion which, however, does not acquire any permanent electric multipole moment. The significance of such changes for the crystal cohesive properties have been conclusively demonstrated by the non-empirical computations [1, 3–9, 19] using the Relativistic Integrals program (RIP) [19, 20] for binary cubic materials. The theoretical basis of these computations rests on the definition [1, 3, 21] of a fully ionic crystal composed of main group elements as one where the electronic wavefunction for the entire solid can be written as an anti-symmetrized product of individual ion wavefunctions each of which, although in general different from that of the corresponding free ion, is spherically symmetric and contains the integral number of electrons consistent with its formal charge. The wavefunctions of different ions are not orthogonal; their overlaps generate the short-range repulsions which oppose the attractive Madelung terms, thereby maintaining crystals at their equilibrium geometries. Even after introducing reliable descriptions of the inter-ionic dispersive attractions, computations [3, 9, 19] using the RIP predicted insufficient crystal cohesion if the short-range inter-ionic interactions were computed from the wavefunctions of the free ions. These deficits in cohesion were manifested by the prediction of lattice energies and bulk compressibilities that were too small compared with experiment with equilibrium lattice spacings that were too large. However, it was shown [3–9] that use of ion wavefunctions which were optimal for their in-crystal environment, although still spherically symmetric, repaired the failures of the free ion model. At each crystal geometry, the energy, called the rearrangement energy, required to convert a free ion into its form optimal for that geometry is more than offset by the reduction of the short-range cation–anion repulsions, thereby predicting a more negative value for the total crystal energy. The non-vanishing of anion rearrangement energies and the contraction of their electron densities reducing cation–anion short-range repulsions are not the only manifestations of the compression experienced by an anion on introduction into a crystal at its equilibrium geometry. Further manifestations of these compressions are the significant in-crystal reductions of both the polarizabilities of anions [22–25] and the dipole–dipole [26] and dipole–quadrupole [7, 27] dispersion coefficients involving these species. Another manifestation of the second type of response of an ion to its in-crystal environment are the modifications of the polarizabilities of cations having d^{10} outermost electronic configurations [25].

The third type of response of an ion to its in-crystal environment consists of those changes in the electronic structure and properties of an ion which are generated when a cubic crystal undergoes a small but uniform expansion or contraction from its equilibrium geometry. The second type of response, discussed in the last paragraph, could be regarded as the special case of this third kind in which the crystal is expanded to an infinite size so that each of its constituent ions becomes essentially isolated. Thus the third type of response is similar to the second in that the ion does not acquire any permanent electric multipole moment. The theoretical studies [3–9] of the cohesive properties of cubic crystals using the RIP have accounted for the third type of environmental response by using, at each geometry considered, the ion wavefunctions optimal for that geometry. However, unlike the case for the first two types of environmental response whose importance is now well documented, there has been no previous elucidation of

the significance for the crystal cohesion of this third type of environmental influence, namely effects generated by differences between the ion wavefunctions optimal for any geometry and those optimal for the equilibrium geometry. The purpose of this present paper is to fill this gap in our knowledge by showing explicitly how the cohesive properties of cubic crystals are influenced by this third type of environmental modification of ionic properties.

2. Results

The importance of the third type of response of an ion to its environment in crystal is elucidated by comparing the crystal cohesive properties computed taking account of such a response with the predictions resulting when this is ignored. These two types of prediction were generated by using the fully ionic description, computing the inter-ionic potentials with the RIP with subsequent introduction of electron correlation effects. The short-range correlations were derived from density functional theory [1] whilst the calculation of the inter-ionic dispersive attractions included their damping [1, 3, 28] which arises when the overlap between an interacting pair of ions is not negligible. The cation wavefunctions, computed using the Oxford Dirac–Fock program [29], were taken to be the same as those of the free ions because there is abundant evidence, reviewed elsewhere [1, 25], that cations having a p^6 outermost electronic configuration are essentially unaffected by their in-crystal environments. The wavefunctions of the anions were computed using one of the two currently most sophisticated descriptions of their in-crystal environments, namely the ODMFS or OEMFS models [5, 8, 9]. Thus the crystal cohesive energies were computed as a function of the closest cation–anion separation R , the only variable needed to define the geometry of a cubic crystal of given structure, by using the already documented methods [1, 3–5, 8, 9] based on the energy expression (1) presented in the next section. The predictions derived by using, at each R , the anion wavefunctions optimized for that crystal geometry have been designated ‘optimal’ [30, 31]. For each crystal, predictions derived by using at all inter-ionic separations the same anion wavefunction, namely that optimal for an R -value close to R_e , denoted R'_e , are designated ‘frozen’ [30, 31]. Comparison of the predictions derived from the ‘optimal’ wavefunctions with those predicted using the ‘frozen’ ones will therefore reveal the importance of the third type of response of the anions to variations in their in-crystal environment.

The lattice energies (D_e), equilibrium inter-nuclear separations (R_e) and compressibilities (B) predicted using the ‘optimal’ wavefunctions and presented in table 1 in the columns headed ‘Optimal’ are just those previously reported [5, 7–9]. The results for both ThO_2 and CsCl were derived using the later more accurate values [7, 9] for the dipole–quadrupole dispersion coefficients as well as, for CsCl , the other small refinements reported elsewhere [9]. These results thus differ from those presented in [4, 6]. The predictions for all three quantities D_e , R_e and B derived from the ‘optimal’ wavefunctions agree well with the experimental results. The slight discrepancy between theory and experiment for the CsCl lattice energy arises, as discussed elsewhere [9], from the omission of the Axilrod–Teller three-body dispersion energy. These optimal results should be compared with those presented in the table in the columns headed ‘Frozen’ which were derived for each crystal by using its ‘frozen’ anion wavefunction, so that in each such calculation the same anion wavefunction was used to compute at all R both the short-range cation–anion interaction and the short-range anion–anion term. Since, for each crystal, the R'_e -value used to compute the ‘frozen’ wavefunction is so close to the experimental R_e , it is not surprising that the predictions for both D_e and R_e derived using this wavefunction are so similar to the ‘optimal’ results. However, each bulk compressibility B is significantly overestimated by the computation using the ‘frozen’ wavefunction. Although the overestimation is only about 20% for CaF_2 since the fluoride ion is only moderately

Table 1. Influence of environmental model on crystal binding. Lattice energies (D_e) in kJ mol^{-1} , closest equilibrium cation–anion separations (R_e) in au and bulk compressibilities (B) in 10^{10} N m^{-2} . For sources of experimental data, see the papers cited for the optimal results. Note that for ThO_2 the ‘experimental’ D_e derived in [6] from a thermodynamic cycle involved values for the third and fourth ionization potentials of thorium calculated by augmenting the predictions of *ab initio* relativistic Hartree–Fock computations with semi-empirical estimates of the contributions arising from electron correlation. Results labelled ‘Frozen’ were derived using, at all R , the wavefunction optimal for the distance R'_e close to the experimental R_e . Results labelled ‘AA froz’ used optimal rearrangement energies and cation–anion interactions but the frozen anion–anion interaction. Results labelled ‘Optimal’ used at each R the wavefunction optimal for that R . The R'_e -values were 3.981, 4.544, 4.5, 6.75 and 4.5 au for MgO, CaO, ThO_2 , CsCl and CaF_2 respectively.

	MgO				CaO			
	Frozen	AA froz	Optimal [5]	Experiment	Frozen	AA froz	Optimal [5]	Experiment
D_e	3038	3040	3038	3038	2645	2646	2645	2644
R_e	4.001	3.918	3.994	3.974	4.568	4.567	4.536	4.537
B	27.0	20.8	19.9	17.5	18.7	12.6	11.7	11.3
	ThO_2				CsCl			
	Frozen	AA froz	Optimal [7]	Experiment	Frozen	AA Froz	Optimal [9]	Experiment
D_e	8119	8140	8140	8100	664	664	664	659, 656
R_e	4.582	4.590	4.587	4.582	6.728	6.757	6.755	6.748
B	33.0	19.3	18.4	19.3	4.92	2.69	2.69	
	CaF_2							
	Frozen	AA froz	Optimal [8]	Experiment				
D_e	2631	2632	2631	2630				
R_e	4.471	4.449	4.457	4.448				
B	10.53	9.63	8.90	8.825				

affected by its in-crystal environment, the fractional discrepancies increase on passing to more environmentally sensitive chloride and oxide ions. Thus the ‘frozen’ calculations overestimate the B -values of the three oxides and CsCl by factors of between 50% and 80%. This shows that, in general, an anion responds very significantly to small variations in its in-crystal environment away from the equilibrium crystal geometry and hence such a response must be considered if crystal properties other than D_e and R_e are to be accurately predicted.

For each crystal, the predictions assembled in the table in the columns headed ‘AA froz’ were derived by using the wavefunction optimal at each R to compute both the anion rearrangement energy and the short-range cation–anion repulsion but used the ‘frozen’ anion–anion interaction. Such computations are of interest not only because they reveal the relative significance of freezing the anion–anion interaction compared with freezing all the interactions but also because they were found to provide [10–12, 14, 30] the most appropriate basis for the first compressible ion model calculations. The ‘frozen’ anion–anion short-range interactions have been reported in detail elsewhere, in [31] for the oxides and CaF_2 and in [9] for CsCl and also NaCl. Comparison of the predictions in the table columns headed ‘AA froz’ with both those derived using the fully optimal (‘Optimal’ columns) and entirely frozen (‘Frozen’ columns) wavefunctions shows that the overwhelming degradation of the predictions and overestimation of the compressibility in the fully ‘frozen’ computations is caused by the failure to use optimal values for the rearrangement energy and short-range cation–anion repulsions. By contrast, the inaccuracies introduced by replacing just the ‘optimal’ anion–anion interaction by its ‘frozen’ counterpart are quite minor. The success of previous compressible ion model descriptions of

MgO, CaO [11, 30] and CaF₂ [10] relied on this result which had to be elucidated during the course of those researches. Any small differences between the results in the table columns headed ‘AA froz’ and those previously reported arise simply because the compressible ion model fits to the *ab initio* RIP results, although very good, were not, of course, quite perfect.

3. Discussion

The inadequacies of computations using frozen wavefunctions do not imply that the approach widely called the rigid ion model in the literature is necessarily similarly deficient. The terminology ‘rigid ion model’ is normally applied to descriptions in which the ions are taken to be non-polarizable so that they cannot respond to their in-crystal environments in the first of the three ways listed here, that is by developing any permanent electric multipole moments. The short-range interactions in rigid ion models are usually determined semi-empirically by fitting an assumed analytic form for this repulsion so that appropriate experimental data are reproduced. The effects arising from the response of anion wavefunctions, charge distributions and hence short-range cation–anion repulsions to the changes in the in-crystal environment may well be implicitly included in rigid ion model fits even though these procedures do not explicitly recognize the existence of ion rearrangement energies or the third type of environmental response of an ion to variations in its in-crystal environment. Thus the negative molar binding energy $U_L(R)$ of a cubic crystal of formula CA_m composed of cations (C) and anions (A) and having geometry defined by the closest cation–anion separation R is the difference between the total crystal energy and the sum of the energies of one mole of free cations and m moles of free anions. For oxides, the m moles of free anions actually consists of m moles of free singly charged O[−] ions and m moles of free electrons. The molar binding energy is given by [1, 3]

$$U_L(R) = N_f \{-M/R + mE_{re}(R) + n_{CA}V_{sCA}(R) + (1/2)[mn_{AA}V_{sAA}(x_{AA}R) + n_{CC}V_{sCC}(x_{CC}R)]\} + U_{disp}(R). \quad (1)$$

All the energies 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. Here M is the Madelung constant, n_{XY} is the number of closest neighbouring ions of type Y ($X = C$ or A) surrounding one ion of type X and x_{XY} is a geometric constant, determined by the crystal structure, which yields the separation between an ion of type Y and a closest neighbour of type X as $x_{XY}R$. The quantity $E_{re}(R)$ is the rearrangement energy needed to convert one free anion into its compressed form optimal for the crystal with geometry defined by R . Each short-range interaction $V_{sXY}(x_{XY}R)$ is, disregarding the point Coulomb term $q_Xq_Y/(x_{XY}R)$ where q_X is the net charge of ion X, the energy of a pair of ions, one of type X and one of type Y, separated by a distance $x_{XY}R$ measured relative to the sum of the energies that the ions X and Y would have at infinite inter-nuclear separation if they were then to retain their wavefunctions optimal for the crystal with geometry defined by R . Both $E_{re}(R)$ and each $V_{sXY}(x_{XY}R)$ are sums of a major part computed using the RIP plus a correlation correction evaluated using density functional theory as described elsewhere [1, 3, 5]. The summation over all pairs of ions of the dispersive attractions within each pair yields for the one mole of crystal the total two-body dispersion energy $U_{disp}(R)$ calculated as described elsewhere [1, 3, 7–9]. The expression (1) for the cohesive energy can be cast into a form in which the rearrangement energy is absorbed into an effective cation–anion pair potential $V_{sCA}^{eff}(R)$:

$$U_L(R) = N_f \{-M/R + n_{CA}V_{sCA}^{eff}(R) + (1/2)[mn_{AA}V_{sAA}(x_{AA}R) + n_{CC}V_{sCC}(x_{CC}R)]\} + U_{disp}(R) \quad (2)$$

with

$$V_{sCA}^{eff}(R) = V_{sCA}(R) + (m/n_{CA})E_{re}(R). \quad (3)$$

Since the cohesive energy in rigid ion models is fitted to expressions of the type (2), the resulting quantities conventionally considered to be short-range cation–anion interactions are actually effective cation–anion interactions of the type (3). Thus, if only one crystal structure is considered, the rigid ion model fit does implicitly account for the third type of influence of the in-crystal environment on ion wavefunctions. However, the explicit presence of the cation coordination number n_{CA} in the form (3) shows that the effective potential will not be fully transferable to a different polymorph of the same compound even if the anion wavefunctions in the two polymorphs were sufficiently similar that the individual terms $V_{sCA}(R)$ and $E_{re}(R)$ were to remain essentially unchanged. It has been shown [4, 9] that it is the coordination dependence of the $V_{sCA}^{eff}(R)$ which causes theories assuming structure-independent effective cation–anion interactions to be unable to predict that the eightfold-coordinated structure of CsCl has an energy slightly lower than the rock-salt-structured polymorph.

The structural dependences of the anion sizes and hence of short-range cation–anion interactions are modelled in a simplistic way by the well established breathing shell model [32]. However, this model was motivated not by the considerations underlying the computations using the RIP but by the need to take account of those many-body effects which explicitly manifest themselves in the non-equality between the two elastic constants C_{12} and C_{44} . Thus this theory is concerned with those many-body contributions to the energy of a cubic crystal which arise when its geometry is distorted such that the cubic symmetry is destroyed. Such environments are implicitly referred to in theoretical treatments of these two elastic constants. The present work was not concerned with such distorted geometries but with those preserving cubic symmetry. The most direct demonstration of the importance of the response of an ion to cubic symmetry-preserving changes in its environment is provided by the results presented in the table in the present paper.

4. Conclusions

Non-empirical computations based on the fully ionic model of the cohesive properties of cubic crystals have shown the importance of taking into account the changes in the properties of anions when such a crystal undergoes uniform expansions or contractions from its equilibrium nuclear geometry. Failure to account for these changes in anion properties yields predictions for the bulk compressibility of a crystal which are often more than 50–80% too large.

References

- [1] Pyper N C 1991 *Adv. Solid State Chem.* **2** 223
- [2] Madden P A and Wilson M 1996 *Chem. Soc. Rev.* **25** 339
- [3] Pyper N C 1986 *Phil. Trans. R. Soc. A* **320** 107
- [4] Pyper N C 1994 *Chem. Phys. Lett.* **220** 70
- [5] Pyper N C 1995 *Phil. Trans. R. Soc. A* **352** 89
- [6] Harding J H, Lindan P J D and Pyper N C 1994 *J. Phys.: Condens. Matter* **6** 6485
- [7] Pyper N C and Popelier P 1995 *J. Phys.: Condens. Matter* **7** 5013
- [8] Pyper N C 1995 *J. Phys.: Condens. Matter* **7** 9127
- [9] Pyper N C 2002 *J. Chem. Phys.* at press
- [10] Wilson N T, Wilson M, Madden P A and Pyper N C 1996 *J. Chem. Phys.* **104** 8068
- [11] Wilson M 1997 *J. Phys. Chem. B* **101** 4917
- [12] Castiglione M J, Wilson M and Madden P A 1999 *J. Phys.: Condens. Matter* **11** 9009
- [13] Wilson M, Costa-Cabral B J and Madden P A 1996 *J. Phys. Chem.* **100** 1227
- [14] Wilson M and Madden P A 1997 *Discuss. Faraday Soc.* **106** 339

-
- [15] Mott N F and Gurney R W 1950 *Electronic Processes in Ionic Crystals* (Oxford: Oxford University Press)
- [16] Harding J H 1991 *Rep. Prog. Phys.* **53** 1403
- [17] Dick D G and Overhauser A W 1958 *Phys. Rev.* **112** 90
- [18] Wilson M and Madden P A 1994 *J. Phys.: Condens. Matter* **6** 159
- [19] Wood C P and Pyper N C 1986 *Phil. Trans. R. Soc. A* **320** 71
- [20] Wood and Pyper N C 1981 *Chem. Phys. Lett.* **81** 395
- [21] Abarenkov I V and Antonova I M 1970 *Phys. Status Solidi* **38** 783
- [22] Fowler P W and Madden P A 1983 *Mol. Phys.* **49** 913
- [23] Fowler P W and Madden P A 1984 *Phys. Rev. B* **29** 1035
- [24] Fowler P W and Madden P A 1985 *J. Phys. Chem.* **89** 258
- [25] Fowler P W and Pyper N C 1985 *Proc. R. Soc. A* **398** 377
- [26] Fowler P W, Knowles P J and Pyper N C 1985 *Mol. Phys.* **56** 83
- [27] Fowler P W and Pyper N C 1986 *Mol. Phys.* **59** 317
- [28] Jacobi N and Csanak Gy 1975 *Chem. Phys. Lett.* **30** 367
- [29] Grant I P, McKenzie B J, Norrington P H, Mayers D F and Pyper N C 1980 *Comput. Phys. Commun.* **21** 207
- [30] Wilson M, Madden P A, Pyper N C and Harding J H 1996 *J. Chem. Phys.* **104** 8068
- [31] Pyper N C 2001 *J. Chem. Phys.* **114** 4390
- [32] Catlow C R A, Faux I D and Norgett 1976 *J. Phys. C: Solid State Phys.* **5** 415