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The polarizabilities and dispersion coefficients for ions in the solid group IV oxides

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Abstract. The electric-dipole polarizabilities of all the ions in the solid group IV dioxides ZrO_2, CeO_2, ThO_2 and UO_2 are deduced from experimental high-frequency dielectric-constant data. The resulting polarizabilities of 2.76±0.15 au, 5.54±0.15 au and 8.82±0.15 au for Zr^{4+}, Cd^{4+} and Th^{4+}, being unaffected by the crystalline environment, pertain also to these free cations. The polarizabilities of the O^{2-} ions are found to depend on their in-crystal environment, as parameterized by the closest cation–anion separation, in the same way as those of the anions in the M_2O alkali oxides. The ionic polarizabilities are used to derive values with an estimated error of 5% for the coefficients governing the dipole–dipole dispersive attractions between all ion pairs in all four crystals. Taken in conjunction with ion wavefunctions calculated elsewhere, these coefficients are used to compute values, with estimated errors of about 20%, for the coefficients governing the dipole–quadrupole dispersive attractions between all the ions in ThO_2 and UO_2. Values are presented for the parameters governing the damping of these dispersive attractions when the overlap between the wavefunctions of the interacting ions is not negligible.

1. Motivation

The solid dioxides of the group-IV elements zirconium, cerium, thorium and uranium are important both scientifically and technologically. Thus ZrO_2 and CeO_2 are of interest as ceramics (Mackrodt and Woodrow 1986, Butler *et al* 1983), ThO_2 is important not only as nuclear material but also as a solid-state electrolyte and for its use in fluorescent tubes whilst UO_2 is important as a reactor fuel (Catlow 1977, Catlow and Pyper 1979). The interionic forces and cohesive properties of ThO_2 (Harding *et al* 1994a) and UO_2 (Harding *et al* 1994b) have been recently studied theoretically by first using the relativistic integrals programme RIP (Wood and Pyper 1981a, b, 1986) to compute those major portions of the cohesive energy that do not arise from electron correlation and then using the resulting ion wavefunctions to evaluate the important effects of electron correlation. The dispersive or Van der Waals attraction between the ions is one of these correlation effects that had to be evaluated although none of the necessary research has been previously reported since it involved extending the investigation to other group-IV oxides.

The calculation of the dispersion energy requires values for the dipole–dipole and dipole–quadrupole dispersion coefficients, which in turn can currently be evaluated only if numerical values for the polarizabilities of the ions are known. These ionic polarizabilities are also important in their own right because they feature prominently in theories of the refractive index and dielectric constant of ionic materials (Mott and Gurney 1950) as well as providing

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a starting point for describing the collision-induced spectra of ionic melts (Cazzanelli *et al* 1983). Furthermore the dispersion energy cannot be evaluated to a useful accuracy without considering the damping (Kreek and Meath 1969, Jacobi and Csanak 1975) of its standard form in which the leading or dipole–dipole dispersive attraction between two ions varies as the inverse sixth power of their separation. This damping, which originates from overlap of the wavefunctions of the interacting ions, reduces the magnitude of the undamped dispersion energy when this overlap is not negligible. The details of the calculation of this damping have not yet been reported either for ThO_2 or UO_2.

This present paper has two objectives. The first of these is to derive reliable values for the polarizabilities of the ions in the four solids ZrO_2, CeO_2, ThO_2 and UO_2. The four different values for the O^{2-} polarizability to be derived will extend the previous results (Fowler and Pyper 1985) concerning the dependence of the oxide-ion polarizability on its in-crystal environment. The second objective of the present paper is to derive values for both the dipole–dipole dispersion coefficients in all four of these solids and the dipole–quadrupole coefficients and dispersion damping parameters in ThO_2 and UO_2. The latter parameters, one for each ion, determine the functions that damp the dispersive attractions at interionic separations sufficiently short that the overlap of the wavefunctions of the interacting ions is not negligible. The derivation of both the dipole–quadrupole coefficients and the dispersion damping parameters requires the ion wavefunctions, which for the anions depend strongly on the crystalline environment. Accurate anion wavefunctions have to be computed by a process of maximizing the crystal cohesion in a series of RIP computations. Since such computations have only so far been performed for ThO_2 and UO_2 amongst the oxides of present interest, dipole–quadrupole dispersion coefficients and dispersion damping parameters are reported only for these two solids.

2. The ion polarizabilities

2.1. *Derivation of the molar polarizabilities*

Measurements of the dielectric or optical properties of polar crystalline solids directly yield only the polarizability, to be denoted the molar polarizability (α_{cr}), of one entire formula unit. For cubic solids, the quantities α_{cr} can be derived from experimentally determined values of the high-frequency dielectric constant (ε_∞) by using the Clausius–Mossotti relation (Tessman *et al* 1953)

$$\alpha_{cr} = \left[3V_m/(4\pi)\right]\left(\varepsilon_\infty - 1\right)/\left(\varepsilon_\infty + 2\right) \tag{2.1}$$

where V_m, the molar volume, is the volume occupied by one formula unit. The materials ZrO_2, CeO_2, ThO_2 and UO_2 have the cubic fluorite crystal structure with the experimentally determined cell sides (a_0) reported in table 1, from which the molar volumes V_m were derived. These volumes were combined with the measured values of ε_∞ also assembled in table 1 to calculate the molar polarizabilities α_{cr}.

Although the ε_∞ data for ZrO_2, CeO_2 and UO_2 raise no problems, a different value for ϵ_∞ of ThO_2 can be deduced from the refractive-index measurements of Ellis and Lindstrom (1964). They presented refractive indices (n_λ) of 2.105, 2.110 and 2.135 at respective wavelengths (λ) of 5893 Å, 5461 Å and 4358 Å for a crystal of reported stoichiometry $ThO_{2\pm0.15}$. Even the result at longest wavelength would correspond to an ε_∞ ($= n_\infty^2$) of 4.43 whilst extrapolation of the n_λ values to infinite wavelength using the standard relation (Winchell and Winchell 1964)

$$n_\lambda = n_\infty + C\lambda^{-2} \tag{2.2}$$

Table 1. Unit-cell dimensions (a_0), molar volumes (V_m), closest cation–anion separations (R), high-frequency dielectric constants (ε_∞) and molar polarizabilities (α_{cr}). All dimensional quantities are in atomic units except for cell side, in ångströms.

Salt	a_0 [a]	R	V_m	ϵ_∞ [b]	α_{cr}
ZrO_2	5.191	4.248	235.988	5.09	32.500
CeO_2	5.411	4.428	267.282	4.84	35.822
ThO_2	5.5997	4.582	296.232	4.8	39.520
UO_2	5.4682	4.474	275.848	5.3	38.791

[a] ZrO_2 from Mackrodt and Woodrow (1986); CeO_2 from Butler *et al* (1983); ThO_2 and UO_2 from Wyckoff (1963).

[b] ZrO_2 from Mackrodt and Woodrow (1986); CeO_2 from the square of the average of the two refractive indices reported by Samsonov (1973); ThO_2 from Samsonov (1973) and UO_2 from Ackermann *et al* (1959).

yields an extrapolated value of 2.07 for n_∞ corresponding to $\varepsilon_\infty = 4.28$, differing greatly from the result in table 1. The Ellis and Lindstrom data are also inconsistent with the value of 2.2 reported (Winchell and Winchell 1964) for the refractive index at the wavelength of the sodium D line. The latter value corresponds to a dielectric constant of 4.84, which is slightly greater and thus consistent with the extrapolated ε_∞ value in table 1. Furthermore the highly non-stoichiometric composition with large error reported by Ellis and Lindstrom is very strange as it is difficult to understand how ThO_2 can accommodate such a large excess of oxygen. These difficulties lead us to reject their value.

In the fully ionic description of the oxides of stoichiometry CA_2 of present interest, the molar polarizability is decomposed into cation (α_C) and anion (α_A) contributions according to

$$\alpha_{cr} = \alpha_C + 2\alpha_A. \tag{2.3}$$

However, the polarizabilities of the individual ions can be derived from α_{cr} only by introducing some further independent arguments or data.

2.2. *The derivation of the individual ion polarizabilities*

The key to decomposing the molar polarizabilities (α_{cr}) into their individual cation and anion contributions was provided by accurate *ab initio* quantum-chemistry computations that took into account the effects of electron correlation. The results of such computations furnished accurate values for the polarizabilities of the light cations Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+} and showed that their polarizabilities remain essentially unchanged on entering an ionic crystal (Fowler and Madden 1983, 1984, 1985). Molar polarizabilities of ionic crystals having cubic structures and containing any of these cations have been derived (Wilson and Curtis 1970, Li 1980, Boswarva 1970) through the Clausius–Mossotti relation from experimental values of either ε_∞ or the refractive index that had been extrapolated to infinite wavelength. The polarizabilities of both the halide and the O^{2-} ions in salts with these five cations were then derived (Fowler and Madden 1983, 1984, 1985, Fowler and Pyper 1985) by subtracting the appropriate cation polarizability from α_{cr}. The results showed that, in contrast to the five cations, the polarizability of each of these anions depends quite strongly on the crystal in which its is located, being in all cases much less than that of the free isolated anion. However, it was found that, for a given stoichiometry and type of crystal structure, this environmental variation of anion polarizability could be parameterized by the closest cation–anion separation (R) through relations of the type

$$\log_{10} \alpha_A = A + B/R^2 + C/R^4 \tag{2.4}$$

where A, B and C are constants. Although the polarizability of each halide ion was found to be essentially independent of both the type of crystal structure and the charge carried by the counter-cation and hence to be determined solely by R, the oxide-ion polarizability was found to depend also on the crystal structure. Thus values of α_A in the alkaline-earth oxides MO thereby deduced from experiment are reproduced by (2.4) with $A = 1.706$, $B = -10.31$ and $C = 0$ whereas the α_A values in the alkali oxides M_2O require for their reproduction by (2.4) the different constants $A = 1.270$, $B = -1.762$ and $C = 0$ determined from the data for Li_2O and Na_2O. Use of the alkaline-earth-oxide parameters in (2.4) predicts, in conjunction with the R values in table 1, the polarizability of the O^{2-} ion in ZrO_2, CeO_2, ThO_2 and UO_2 to be 13.635 au, 15.142 au, 16.403 au and 15.521 au respectively whereas use of the alkali-oxide parameters predicts the different set of α_A values presented in table 2. The resolution of this ambiguity requires some independent information on the polarizabilities of the cations in these four salts.

Table 2. Polarizabilities of ions in the group-IV oxides (au). O^{2-} polarizabilities (α_A) are deduced from (2.4) with the alkali oxide A and B parameters and using the R values in table 1. Cation polarizabilities (α_C) are deduced from (2.3) using the α_A values in this table and the molar polarizabilities (α_{cr}) of table 1.

	ZrO_2	CeO_2	ThO_2	UO_2
α_A	14.872	15.140	15.349	15.205
α_C	2.756	5.542	8.822	8.381

Table 3. A comparison of different evaluations of the polarizabilities of the Kr, Xe and Rn isoelectronic sequences (au). Best results are from experiment (Miller and Bederson 1977) for Kr and Xe and deduced (Fowler and Pyper 1985) by a combination of experiment and accurate *ab initio* calculations for Rb^+, Sr^{2+}, Cs^+ and Ba^{2+}. Relativistic coupled Hartree–Fock (RCHF) results are from Johnson *et al* (1983). Relativistic coupled Hartree–Fock–Slater (RCHFS) results are from Feiock and Johnson (1969).

Species	Kr	Rb^+	Sr^{2+}	Y^{3+}	Zr^{4+}
Best	16.8	9.05	5.20		
RCHF	16.5	9.08	5.81	4.05	2.98
RCHFS	23.5	12.89	8.29		4.30
Species	Xe	Cs^+	Ba^{2+}	La^{3+}	Ce^{4+}
Best	27.3	15.3	10.1		
RCHF	27.0	15.8	10.6	7.67	5.83
RCHFS	40.6	23.8	16.1	11.7	8.97
Species	Rn		Ra^{2+}		Th^{4+}
RCHFS	53.3		20.9		11.8

Table 3 presents three different sets of predictions for the polarizabilities of the Kr and Xe isoelectronic sequences. The results labelled 'best' were deduced from experiment and thus include the polarizability contributions arising from electron correlation. The inert-gas results were derived directly from experiment (Miller and Bederson 1977) whereas the cation values were deduced from the α_{cr} values of halides or oxide crystals (Fowler and Pyper 1985). Knowledge of the environmental dependence of the halide and O^{2-} polarizabilities provided by (2.4) enabled these polarizabilities to be predicted for crystals built from cations other than Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+}. The polarizabilities of these other cations were then derived by subtracting the anion polarizability from α_{cr}. For these alkali and alkaline-earth cations as well as Tl^+, the near constancy of the values thus derived for the polarizability of any one of these cations in salts containing different anions not only confirmed the validity of this procedure but also showed that these cation polarizabilities are independent of the crystalline environment. This result taken in conjunction with the subsequent *ab initio* computational prediction (Fowler *et al* 1985) that the polarizability of a gaseous Rb^+ ion is 9.08 au compared with the experimentally deduced in-crystal value of 9.05±0.15 au (Fowler and Pyper 1985) provides strong evidence that the polarizability of every alkali and alkaline-earth cation in any ionic crystal is the same as that of the corresponding isolated gaseous cation. This result coupled with the observation that the electrons in Zr^{4+}, Ce^{4+} and Th^{4+} are more tightly bound than those of the alkali and alkaline-earth cations whilst retaining the same np^6 outermost electronic configuration provides strong evidence that the Zr^{4+}, Ce^{4+} and Th^{4+} polarizabilities are also unaffected by their crystalline environment. No such conclusion is possible for U^{4+} on account of its $5f^2$ open-shell electronic configuration since it has been shown (Fowler and Pyper 1985) that the environment can strongly modify the polarizability of a cation if its crystalline environment lifts the degeneracy exhibited by the outermost electron orbitals in the gaseous state. The above conclusions show that differences between the best values for the ion polarizabilities and the predictions (table 3) of relativistic coupled Hartree–Fock (RCHF) theory for the gaseous ions (Johnson *et al* 1983) arise from the absence in the latter of consideration of the effects of electron correlation. Furthermore the similarity between these two sets of results shows that electron correlation makes only small contributions to the polarizabilities of these cations. These results taken with the RCHF predictions for the polarizabilities of Zr^{4+} and Ce^{4+} are the keys enabling one to determine whether the O^{2-} polarizability in the group-IV oxides depends on R as in the alkali or alkaline-earth oxides.

The assumption that the anion polarizability in the group-IV oxides depends on R in the same way as in the alkaline-earth oxides yields predictions of 5.230 au, 5.538 au, 6.714 au and 7.749 au respectively for the polarizabilities of Zr^{4+}, Ce^{4+}, Th^{4+} and U^{4+} when the α_{cr} results of table 1 and the α_A values reported in the text above are substituted into (2.3). This set of predicted cation polarizabilities is clearly quite erroneous because the value for Zr^{4+} is far too large being not only much greater than the RCHF prediction (table 3) but also larger than the best value for Sr^{2+}. The results in table 3 show, as would be expected, that the polarizability decreases as the nuclear charge increases along an isoelectronic sequence thereby rendering unbelievable a Zr^{4+} polarizability of 5.23 au. This prediction is also unbelievable because it is larger than even the result (Feiock and Johnson 1969) of a relativistic coupled Hartree–Fock–Slater (RCHFS) computation even though the data assembled in table 3 show that this approach always overestimates the polarizability very significantly. Thus both the ratio of the RCHFS to the RCHF and that of the RCHFS to the best polarizabilities lie (table 3) between 1.59 and 1.40. This result in itself suggests that the above Th^{4+} polarizability of 6.714 au is too small because this yields a value of 1.76 for the ratio between the RCHFS and the best polarizability. Overall it can be concluded that α_A in the group-IV oxides does not depend on R as the alkaline-earth oxides.

The group-IV-oxide polarizabilities presented in table 2 derived assuming the R dependence of those in the M_2O alkali oxides yield, when combined with the α_{cr} values of table 1, the cation polarizabilities assembled in table 2. The two values for which an independent check is available, namely those for Zr^{4+} and Ce^{4+}, are both seen to be most reasonable, being very similar to the RCHF results in table 3. Furthermore the prediction of values less than the RCHF results corresponds to a negative contribution to the polarizability from electron correlation, which occurs when the effects of angular correlation are more important than those of the radial correlation (Reinsch and Mayer 1978). The results assembled in table 3 show that angular correlation becomes relatively more important than radial correlation as nuclear charge increases along an isoelectronic sequence with the former having become greater than the latter for even the doubly charged species, which therefore have negative correlation polarizabilities. This shows the reasonableness of the predicted negative correlation polarizabilities of Zr^{4+} and Ce^{4+}. These considerations enable it to be concluded that the polarizabilities of the ions in the group-IV oxides have the values presented in table 2 with the oxide-ion polarizability depending on the crystalline environment as defined by the closest cation–anion separation R in the way that it does in the M_2O alkali oxides.

The oxide polarizability varies more strongly with R in the alkaline-earth oxides than in the M_2O alkali oxides so that, for small R, α_A is predicted to be smaller in the former, thus accounting for the derivation of a larger Zr^{4+} polarizability if α_A is taken to vary as in the alkaline-earth oxides. At larger R, the alkaline-earth oxides α_A values are larger than those in the M_2O alkali crystals with the consequence that smaller Th^{4+} and U^{4+} polarizabilities are predicted if α_A is taken to vary as in the alkaline-earth oxides. Since the two functions (2.4) describing the R dependence of α_A intersect at an R value very close to 4.428 au, the cation–anion separation in CeO_2, the two different assumptions for α_A yield essentially identical predictions for the polarizability of Ce^{4+}.

The new value of 8.822 au for the Th^{4+} polarizability accords well with the trend of increasing polarizability on passing from Zr^{4+} through Ce^{4+} to Th^{4+}. The value of 1.41 for the ratio of the RCHFS prediction to this new result falls within the range of ratios shown by the other species in table 3. The value of 36.937 au for α_{cr} of ThO_2 that would be derived through (2.1) if one used the untrustworthy ε_∞ value of 4.28 generated by the data of Ellis and Lindstrom (1964) would predict an α_C of 4.131 au using the alkaline-earth-oxide parameters in (2.4) but an α_C of 6.239 au if the M_2O alkali-oxide parameters were used. The first result, being less than the Ce^{4+} polarizability, can be dismissed whilst even the second value is too similar to that of Ce^{4+} to be credible. This further analysis reinforces our preference for the Samsonov (1973) experimental data for ThO_2. Our work shows that the value of 14.320 au for the Th^{4+} polarizability derived (Colbourn and Mackrodt 1983) by empirical fitting to properties of solid ThO_2 should be discounted even though the value of 14.752 au for the oxide polarizability is not unreasonable, being not dissimilar to the value in table 2.

The new results (table 2) for the polarizabilities of the ions in UO_2 show that the values previously derived (Catlow 1977) from two slightly different models should be discounted because the reported U^{4+} polarizabilities of 30.37 au and 25.64 au are quite clearly far too large whilst the corresponding results of 6.21 au and 9.65 au for the oxide polarizability are much too small. The latter values can be compared with the smallest known oxide polarizability of 11.345 au, which is that in MgO (Fowler and Madden 1985, Pyper 1986) whilst also noticing that all other known values are greater than 14.0 au (Fowler and Pyper 1985).

The cation polarizabilities derived previously by subtracting from α_{cr} values anion polarizabilities predicted from relations of the type (2.4) were shown to have an error of about ±0.15 au (Fowler and Pyper 1985), which suggests that the polarizabilities newly reported in table 2 will be subject to the same error. However any errors in the cation values will be correlated with those of its oxide partner because the weighted sum (2.3) of the polarizabilities is equal to α_{cr}. The actual values used to derive the dispersion coefficients used in the computations (Harding *et al* 1994a, b) are reported rather than values rounded down to this error.

3. The dispersion energy

3.1. The dipole–dipole dispersion coefficients

The dipole-dipole dispersion coefficient controls that portion of the dispersive interaction that arises from the attraction between the dipole induced on one ion by a dipole instantaneously present on a second ion (Buckingham 1967). For one ion of type X and another of type Y separated by a distance r_{XY}, this portion varies as $-C_6(XY)r_{XY}^{-6}$ for separations sufficiently large that the overlap between the wavefunctions of the two ions is negligible.

The literature concerning dipole–dipole coefficients for ions in crystals was very confused before the mid-1980s and contained for any given ion pair a wide range of values for the $C_6(XY)$ coefficient whilst none of this literature provided any criteria for assessing the reliability of the different values. These difficulties were resolved both by making a thorough examination (Pyper 1986) of values known accurately for pairs of isolated species as well as by performing *ab initio* quantum-chemistry computations (Fowler *et al* 1985) for pairs of in-crystal ions with the crystalline environment described using a model whose reliability was proven by earlier work (Fowler and Madden 1983, 1984, 1985) on ion polarizabilities. The confused earlier situation as well as the present much better state of understanding have been reviewed (Pyper 1990, 1991).

It was shown (Fowler *et al* 1985, Pyper 1986) that the most accurate way of deriving values of $C_6(XY)$ coefficients for in-crystal ions is to use the Slater–Kirkwood (1931) formula

$$C_6(XY) = \tfrac{3}{2}\alpha_X\alpha_Y/\left[(\alpha_X/P_X)^{1/2} + (\alpha_Y/P_Y)^{1/2}\right] \qquad (3.1)$$

provided that the electron numbers P_X and P_Y of ions X and Y are suitably chosen. It was shown that the electron number for each ion should be chosen such that (3.1) precisely reproduces the exact dipole–dipole dispersion coefficient $C_6(ZZ)$ of the inert gas (Z) isoelectronic with the ion from the exact polarizability α_Z for that gas. The Ne electron number required for the O^{2-} ion is 4.455 (Pyper 1986) whilst the Kr and Xe values needed for Zr^{4+} and Ce^{4+} presented in table 4 are taken from the same source. The $C_6(XY)$ coefficients for ZrO_2 and CeO_2 calculated through (3.1) from these P_X values and the polarizabilities of table 2 are presented in table 4.

Table 4. Dipole–dipole dispersion coefficients and cation electron numbers for group-IV oxides (au). Dispersion coefficients are calculated from the Slater–Kirkwood (1931) formula using the ion polarizabilities of table 2, tabulated cation electron numbers and an O^{2-} electron number of 4.455 deduced as described in the text.

Salt	P_C	$C_6(CA)$	$C_6(AA)$	$C_6(CC)$
ZrO_2	7.305	25.183	90.790	9.274
CeO_2	7.901	46.945	93.255	27.504
ThO_2	8.0	69.888	95.193	55.585
UO_2	10.0	69.184	93.857	57.545

The electron numbers of Th^{4+} and U^{4+} cannot be derived using data for the isoelectronic inert gases since these are not available. Consequently the required P_X values have to be deduced by relating the properties of the individual orbitals to their contributions to the polarizability, it being clear that the largest contributions will originate from the most diffuse and loosely bound orbitals. If the average-energy approximation is made to the standard perturbation-theory expression (Buckingham 1967) for the contribution of an orbital i to the polarizability, this contribution is found to be $2\langle r^2\rangle_i/(3e_i)$ (Vinti 1932) if, for the average excitation energy, one makes the natural choice of the orbital binding energy (e_i), defined to be positive for a bound orbital. This shows that the more diffuse an orbital (i) as measured by the mean square distance $\langle r^2\rangle_i$ of the electron from the nucleus the larger its contribution to the polarizability, which is also seen to be enhanced by a reduction of e_i. The mean square radii and binding energies of the outermost orbitals in Th^{4+} and U^{4+} are compared in table 5 with those of Rb^+ and Xe, chosen as control systems of known electron number. Two results suggest that both the 6s and 6p electrons in Th^{4+} contribute significantly to its polarizability: first the value (7.901) for P_X of Xe and second the value (7.305) for P_X of Rb^+ taken in conjunction with the result (Fowler *et al* 1985) of *ab initio* quantum-chemistry computations that 99.5% of its polarizability comes from the eight outermost electrons with each 4s and 4p electron contributing some 12.5% regardless of its l quantum number. The implication that P_X for Th^{4+} is at least eight is supported by the result that the electron numbers of the inert gases increase monotonically down the group with all eight outermost electrons contributing fully to α_{Xe}. These results also show that the d electrons belonging to the shell having principal quantum number $(n-1)$ one less than that (n) of the eight outermost electrons make only negligible contributions to the polarizabilities of Rb^+ and Xe. These $(n-1)$d orbitals have values of $\langle r^2\rangle_i/e_i$, which are very small compared with those of the outermost ns and np orbitals. The result that the 5d electrons in Th^{4+} have a similarly small value of $\langle r^2\rangle_i/e_i$ indicates strongly that these electrons do not contribute significantly to the polarizability and should not therefore be considered in the derivation of the Th^{4+} electron number. This conclusion taken in conjunction with the previous arguments shows that the electron number of Th^{4+} should be taken to be eight.

Table 5. Valence-orbital properties of Rb^+, Xe, Th^{4+} and U^{4+}. All results are in atomic units and are computed using the Oxford Dirac–Fock programme (Grant *et al* 1980); orbital eigenvalues (e_i) are positive for a bound orbital. Results for orbitals with non-zero orbital angular momentum (l) are averages over the properties of the two relativistic orbitals (Grant *et al* 1970) having the same l but different total angular momentum $j = l \pm \frac{1}{2}$. U^{4+} results are from single-manifold $2J+1$ weight EAL calculations (Rose *et al* 1978).

	Rb^+		Xe		Th^{4+}		U^{4+}	
	e_i	$\langle r^2\rangle_i$	e_i	$\langle r^2\rangle_i$	e_i	$\langle r^2\rangle_i$	e_i	$\langle r^2\rangle_i$
$(n-1)$d	4.844	0.333	2.655	0.894	5.019	0.980	5.553	0.884
ns	1.767	2.469	1.010	4.111	3.240	2.646	3.469	2.395
np	1.010	3.651	0.458	6.167	2.248	3.651	2.377	3.331
5f							1.691	2.043

The properties (table 5) of the U^{4+} orbitals show that the 5d electrons should not be considered in the evaluation of the U^{4+} electron number for the same reasons that these orbitals do not contribute to the Th^{4+} P_X value. This places an upper limit of 10 for the U^{4+} P_X value. The ratio e_{6p}/e_{5f} for U^{4+}, equal to 1.4, is less than that of 2.21 for e_{5s}/e_{5p} in Xe where the 5s orbital fully contributes two electrons to the polarizability. This argument alone shows that the 6p as well as the 5f electrons in U^{4+} contribute fully to the polarizability thereby showing that the electron number is at least eight. This argument is reinforced by the observation that whilst in Xe the 5s orbital is smaller than the 5p, the U^{4+} 6p orbital is larger than the 5f orbital. The U^{4+} 6s orbital is larger than the 5f with an energy ratio e_{6s}/e_{5f} of 2.05, which is slightly less than that, e_{5s}/e_{5p}, in Xe, where the 5s orbital contributes fully to P_X despite being smaller than the 5p. This shows that the U^{4+} 6s electrons will make the same contribution of two to the electron number as that made by the 5f orbitals. All these arguments combine to show that the electron number of U^{4+} is 10.

The $C_6(XY)$ coefficients for ThO_2 and UO_2 predicted from (3.1) using the electron numbers of table 4 and ion polarizabilities of table 2 are assembled in table 4. The previous tests (Fowler *et al* 1985, Pyper 1986) of the accuracy of the Slater–Kirkwood predictions of $C_6(XY)$ coefficients suggest that the results should be in error by no more than 5%. This table reports the actual values resulting from using (3.1) because these were the ones actually used in the computations (Harding *et al* 1994a, b) even though the precision of the values in table 4 exceeds their probable errors.

3.2. The dipole–quadrupole dispersion coefficients

The dipole–quadrupole dispersion coefficient $C_8(XY)$ governs the attraction that arises from the interaction between the quadrupole induced on one ion by a dipole instantaneously present on a second ion (Buckingham 1967). For any pair of ions X and Y, this coefficient is the sum

$$C_8(XY) = C_8^{DQ}(XY) + C_8^{QD}(XY) \tag{3.2}$$

where the contribution $C_8^{DQ}(XY)$ originates from the attraction between the quadrupole induced on ion Y by a dipole instantaneously present on the ion X. For separations sufficiently large that the overlap between the wavefunctions of the two interacting ions is negligible, this attraction is given by $-C_8^{DQ}(XY)/r_{XY}^8$. In (3.2) the quantity $C_8^{QD}(XY)$ similarly governs the attraction resulting from the interaction between the quadrupole induced on ion X by a dipole instantaneously present on ion Y. For $C_8(XY)$ coefficients, the confused situation in the literature before the mid-1980s, reviewed elsewhere (Pyper 1990, 1991), was clarified both by an examination (Pyper 1986) of values known reliably for pairs of isolated atoms and by *ab initio* quantum-chemistry computations (Fowler and Pyper 1986) of values for pairs of in-crystal ions with the environment described by the model used in the earlier work on polarizabilities (Fowler and Madden 1983, 1984, 1985) and $C_6(XY)$ dispersion coefficients (Fowler *et al* 1985) of in-crystal ions.

Ab initio quantum-chemistry computations of $C_8(XY)$ coefficients for the ions in ThO_2 and UO_2 are not currently feasible on account of both the large number of electrons and the importance of relativistic effects in cations of such high nuclear charges. It was shown (Pyper 1986, Fowler and Pyper 1986) that, in the absence of *ab initio* quantum-chemistry computations, the most reliable values for $C_8^{DQ}(XY)$ and $C_8^{QD}(XY)$ coefficients are those derived from the Starkschall–Gordon (1972) formulae

$$C_8^{DQ}(XY) = (\tfrac{3}{2})C_6(XY)\langle r^4\rangle_Y/\langle r^2\rangle_Y \tag{3.3a}$$

$$C_8^{QD}(XY) = (\tfrac{3}{2})C_6(XY)\langle r^4\rangle_X/\langle r^2\rangle_X \tag{3.3b}$$

where $\langle r^n\rangle_X$ is the expectation value of the nth power of the distance of all the electrons from the nucleus of ion X with $\langle r^n\rangle_Y$ being the corresponding quantity for ion Y.

The above presentation of the Starkschall–Gordon (1972) formula implies that all the electrons should be included in the evaluation of the expectation values $\langle r^4\rangle$ and $\langle r^2\rangle$. However since the inner electrons make only negligible contributions to both the static polarizabilities and the polarizabilities at imaginary frequency whose Casimir–Polder-type integrals yield exactly the dispersion coefficients (Mavroyannis and Stephen 1962, Buckingham 1967), it seems illogical to include the contributions of these inner electrons in the evaluation of the expectation values in (3.3). Indeed numerical tests of the accuracy of (3.3) for pairs of inert-gas atoms and isoelectronic ions in ionic solids showed both that the inclusion of all the electrons in the evaluation of the $\langle r^n \rangle_X$ significantly degraded the quality of the predictions and that consideration of only the six outermost p electrons yielded significantly more accurate results. For systems isoelectronic with Ne and Ar the inclusion of only these electrons is entirely consistent with the values of their electron numbers P_X because these have been shown to be 4.455 and 6.106 respectively (Pyper 1986). For systems isoelectronic with Kr and Xe, the respective electron numbers of 7.305 and 7.901 would seem to suggest that one should include in the evaluation of $\langle r^2 \rangle_X$ and $\langle r^4 \rangle_X$ the contributions from the two outermost *n*s electrons in addition to those of the outermost *n*p electrons. Since the ratio $\langle r^4 \rangle / \langle r^2 \rangle$ for the *n*s orbital is smaller than that for the *n*p orbital, the inclusion of the former in addition to the latter reduces the predictions of (3.3). However it was found that the Starkschall–Gordon formula always slightly underestimated the $C_8(XY)$ coefficients and that this underestimation was least if the expectation values were calculated using just the outermost *n*p orbitals even where electron-number arguments might suggest the inclusion of the *n*s-orbital contribution. Hence only the contributions of the 6p electrons are included in the calculation of the Th^{4+} expectation values in (3.3) whilst only those of the 2p electrons are included in the oxide-ion terms. Table 6 presents the relevant expectation values computed from Dirac–Fock wavefunctions of the isolated cations and oxide-ion wavefunctions computed with the important modifications resulting from their in-crystal environment treated using the optimized environmental model described elsewhere (Pyper 1994, Harding *et al* 1994a). Table 7 presents the dipole–quadrupole dispersion coefficients computed from the $C_6(XY)$ coefficients of table 4 and the expectation values of table 6 evaluated considering only the Th^{4+} 6p electrons.

Table 6. Orbital expectation values needed for the derivation of dipole–quadrupole dispersion coefficients (all in atomic units). $\langle r^n \rangle_S$ denotes the average *n*th power of the distance from the nucleus of all electrons in shell S. 2p data for the oxide-ion 2p electrons; all other data for the cations. U^{4+} results derived from the ground level hence the $\langle r^2 \rangle$ 5f value if slightly different from twice the result in table 5.

	ThO_2			UO_2			
	6s	6p	2p	6s	6p	5f	2p
$\langle r^2 \rangle_S$	5.293	21.905	15.141	4.789	19.987	4.004	15.356
$\langle r^4 \rangle_S$	19.761	114.856	74.841	16.209	96.087	14.662	77.475

Table 7. Dipole–quadrupole dispersion coefficients and dispersion damping parameters for ThO_2 and UO_2 (au). Dipole–quadrupole dispersion coefficients calculated using the Starkschall–Gordon (1972) formula from the dipole–dipole dispersion coefficients of table 4 and orbital expectation values in table 6 as described in the text. Cation (d_C) and oxide (d_A) dispersion damping parameters are derived as described in the text.

Salt	$C_8^{DQ}(CA)$	$C_8^{QD}(CA)$	$C_8(AA)$	$C_8(CC)$	d_C	d_A
ThO_2	518.178	549.673	1411.599	874.358	3.751	2.451
UO_2	523.577	479.058	1420.599	769.930	3.540	2.343

The deduction in the last subsection that the electron number of U^{4+} is 10 might suggest that the 6s, 6p and 5f electrons should all be considered in the evaluation of the expectation values in (3.3). However the reasoning presented to justify omitting the 6s contribution from Th^{4+} still applies in the U^{4+} case. The dipole–quadrupole coefficients for UO_2 presented in table 7 were therefore calculated including only the 6p and 5f contributions to the U^{4+} expectation values.

For systems having $n\text{p}^6$ outermost electronic configurations, tests (Pyper 1986, Fowler and Pyper 1986) showed that the Starkschall–Gordon predictions for dipole–quadrupole coefficients were invariably too small, usually by about 20% although this underestimation could occasionally reach 30%. The ThO_2 and UO_2 dipole–quadrupole coefficients presented in table 7 should be expected to have a similar accuracy. The values in table 7, being those used in the computations (Harding *et al* 1994a, b) of the cohesive energies, are reported to a greater precision than their expected errors.

3.3. The total crystal dispersion energy

The total dispersion energy ($U_{\mathrm{disp}}(R)$) of an entire crystal with nuclear geometry defined by R is evaluated, after neglecting the three-body Axilrod–Teller (1942) and higher-order multibody contributions expected to be small, by summing over all ion pairs (a, b) the dispersive attraction within each pair. Denoting the total number of ions by N, the result is

$$U_{\mathrm{disp}}(R) = -\sum_{a=1}^{N-1}\sum_{b=a+1}^{N}\sum_{n=6,8}\chi_n^{ab}(r_{ab})C_n(ab)r_{ab}^{-n}. \tag{3.4}$$

The quantities $\chi_n^{ab}(r_{ab})$ are the dispersion damping functions, which are unity at large distances r_{ab} where the overlap of the wavefunctions of the two interacting ions is negligible. However the $\chi_n^{ab}(r_{ab})$ become less than one when this overlap is non-negligible and decrease with decreasing r_{ab}, thus reducing the magnitudes of the undamped energies $-C_n(ab)r_{ab}^{-n}$. For distances r_{ab} at which overlap is appreciable the $\chi_n^{ab}(r_{ab})$ decrease rapidly with increasing n, thus ensuring that terms in (3.4) having high n are unimportant. These terms are also unimportant at large r_{ab} due to their r_{ab}^{-n} dependence even though the damping function is close to unity. Hence only the $n = 6$ and $n = 8$ terms in (3.4) needed to be retained in the computations of Harding *et al* (1994a, b). The only damping functions deviating significantly from unity are those damping the attractions within the closest cation–anion, the closest anion–anion and the closest cation–cation pairs. After using this result in (3.4), $U_{\mathrm{disp}}(R)$ reduces to the expression (2.22) of Pyper (1986) with the dispersion sum constants entering (2.22) being given in the last row of table 2 of that paper. However the result (2.22) still contains the functions $\chi_n^{ab}(r_{ab})$ for the closest ion pairs listed above.

The dispersion damping functions $\chi_n^{ab}(r_{ab})$ having $n = 6$ or $n = 8$ needed here have been derived (Pyper 1986, 1994) from the general formalism presented by Jacobi and Csanak (1975). For interaction of two like species (a) each dispersion damping function depends, in addition to the interionic separation, on just a single dispersion damping parameter d_a characteristic for that species. The functions $\chi_n^{ab}(r_{ab})$ damping the dispersive attractions between two unlike species depend on the same two damping parameters d_a and d_b that control the damping of the interactions between the two like species. Although in general the damping parameters depend on n, it has been shown (Pyper 1986) that, for the interaction of systems having $n\text{p}^6$ outermost electronic configurations, the damping parameters are the same for the dipole–dipole and dipole–quadrupole dispersive attractions. Each dispersion damping parameter is the sum of a term d_{ag} originating from the ground state plus a term (d_{ae}) determined by the lowest excited state (e) having the correct symmetry to contribute to the sum-over-states perturbation-theory description of the corresponding dispersion energy (Lassettre 1965, Csanak and Taylor 1972)

$$d_a = d_{ag} + d_{ae}. \tag{3.5}$$

Since the cation wavefunctions are unaffected by their in-crystal environment, their damping parameters are determined by the eigenvalues e_{ag} and e_{ae} of the outermost orbitals in respectively the ground state and excited state e of the free cation (Pyper 1986, 1994) according to

$$d_{ag} = \surd(2e_{ag}) \tag{3.6a}$$

for a = cation.

$$d_{ae} = \surd(2e_{ae}) \tag{3.6b}$$

Here each eigenvalue is expressed in atomic units (au) and is defined to be positive for a bound orbital. The anion dispersion damping parameters are determined by the exponential decreases of the radial parts $(P_{ag}(r_a)/r_a)$ and $(P_{ae}(r_a)/r_a)$ of the wavefunctions of the outermost orbitals in respectively the ground state and excited state e at distances r_a significantly greater than those at which these two orbital wavefunctions attain their maxima. It is these decreases through which the two contributors d_{ag} and d_{ae} to d_a are determined (Pyper 1994):

$$[P_{ag}(r_a)/r_a] \propto \exp(-d_{ag}r_a) \tag{3.7a}$$

$$[P_{ae}(r_a)/r_a] \propto \exp(-d_{ae}r_a). \tag{3.7b}$$

Although for the free-cation wavefunctions the d_{ag} and d_{ae} values derived from (3.6) are the same as those predicted from (3.7), this is not the case for the oxide-ion wavefunctions for the reasons discussed elsewhere (Pyper 1994). Hence the oxide-ion dispersion damping parameters d_A must be derived using the results (3.7) and cannot be calculated from the orbital eigenvalues according to (3.6). The excited state (e) in (3.5) is the ^1P term of the $2p^53s$ configuration for the oxide ion but belongs to the $6p^56d$ configuration of Th^{4+} and the 5f6d configuration of U^{4+}. Both cation (d_C) and oxide (d_A) dispersion damping parameters are presented in table 7.

4. Conclusion

Accurate values for the polarizabilities of all ions in the quadrivalent group-IV oxides ZrO_2, CeO_2, ThO_2 and UO_2 have been derived. The results are expected to be accurate to within ±0.15 au. The results for Zr^{4+} and Ce^{4+} slightly refine the previous predictions (Johnson *et al* 1983) of relativistic coupled Hartree–Fock theory whilst we have deduced the first trustworthy values for Th^{4+} and U^{4+}. The polarizabilities of the closed-shell cations Zr^{4+}, Ce^{4+} and Th^{4+} deduced from the present in-crystal data will apply in all other ionic crystals as well as to the free cations. It is not currently known whether the value deduced for U^{4+} in solid UO_2 is sensitive to the particular in-crystal environment and by how much the polarizability of a free U^{4+} ion differs from our in-crystal value. The polarizability of the doubly charged O^{2-} ion in these four solids has been shown to depend on the crystal geometry, as defined by the closest cation–anion separation R, in the same way as the anion polarizability in the M_2O alkali oxides.

The ion polarizabilities deduced in this paper were used to predict through the Slater–Kirkwood formula values of the dipole–dipole dispersion coefficients between all three types of ion pair in each of the four solids. Since these values should be expected to be accurate to at least 5%, not only will they be useful in any future modelling of ZrO_2 and CeO_2 but they also serve to document the coefficients used in the previous calculations of the cohesion of both ThO_2 (Harding *et al* 1994a) and UO_2 (Harding *et al* 1994b). This documentation of the calculation of the dispersion energy of ThO_2 and UO_2 has been completed by deriving values both for the dipole–quadrupole dispersion coefficients for all ion pairs in these two solids and for the dispersion damping parameters. The dipole–quadrupole dispersion coefficients are probably underestimated by about 20%. The dispersion damping parameters are needed to calculate the functions that damp the standard undamped multipolar form of the dispersion energy at interionic separations sufficiently short that the overlap of the wavefunctions of the interacting ions is not negligible. It has been conclusively shown that the cohesive properties of polar solids cannot be accurately computed unless this damping is taken into account (Pyper 1986).

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