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## The cohesion of thorium dioxide

J H Harding†, P J D Lindan‡ and N C Pyper§

† Theoretical Studies Department, AEA Industrial Technology, Harwell Laboratory, Didcot, Oxon OX11 0RA, UK

‡ Department of Physics, University of Keele, Keele, Staffs ST5 5BG, UK

§ Universal Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

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**Abstract.** The cohesion of solid thorium dioxide is calculated within the fully ionic description, calculating exactly, after generating the electronic wavefunctions of the ions, those parts of each inter-ionic potential that do not arise from electron correlation. The wavefunctions of the anions are modified by a potential representing the environment in the crystal. This gives rise to a substantial contribution to the lattice energy. Density-functional theory is used to evaluate the contributions from electron correlation. The dispersion term is evaluated separately. The lattice energy, lattice parameter and bulk compressibility calculated here are in excellent agreement with experiment supporting the ionic description of thorium dioxide.

### 1. Introduction

Interest in thorium dioxide is not confined to its use as a nuclear material. It is a solid-state electrolyte and is traditionally used in fluorescent tubes. It is the simplest of the actinide dioxides to study since it does not show significant non-stoichiometry. The defect structure has been calculated by Colbourn and Mackrodt (1983) using pair potentials obtained from electron-gas calculations and modified to reproduce the lattice parameter. These calculations support the idea that the dominant defects in thoria are Frenkel pairs. However, the energies they obtain for the defect processes are much larger than those obtained from experimental diffusion or creep studies. This is particularly true for the cation processes where the discrepancy is approximately a factor of two. This problem occurs in the other fluorite oxides that have been studied (see, for example, Jackson *et al* (1986)). These problems suggest that it is worth studying the cohesive energy of thoria in some detail to see whether the pair potential approximation used in all the simulations to date is valid.

### 2. Method

The details of the calculation may be found in the papers of Wood and Pyper (1986) and Pyper (1986). An extensive review has also been given by Pyper (1991) and updated in some respects by a later paper (Pyper 1994a). It is therefore necessary only to give a brief review of the method here. The object is to calculate the cohesive energy of the oxide using relativistic Hartree–Fock methods (together with corrections for correlation and dispersion) but within the spirit of the ionic model.

We first require a definition of ionicity suitable for calculation. A general discussion of the meaning of ionicity has been given by Catlow and Stoneham (1983), who point out the

difficulties and contradictions in the literature. For the present purposes, we define an ionic crystal as composed of ions which have electronic charge distributions that are optimal for the crystal subject to two constraints. First, the ions are spherically symmetric and second, they contain a fixed, integral number of electrons. In particular, the oxide ion is  $O^{2-}$ , containing ten electrons.

The above definition of ionicity allows us to regard the crystal as being assembled in two stages. In the first stage, each ion is modified to a state which is optimal for the crystal environment such that, when in the second stage the ions are assembled to form the crystal, the total crystal energy with respect to the original *free* ions is minimized. The energy required to convert free ions to in-crystal ions is called the rearrangement energy,  $E_{re}(R_i)$  where  $R_i$  are the parameters defining the local environment. For a simple structure like the fluorite structure of thoria, this parameter list reduces to one, the lattice parameter  $R$  (here taken to be the cation-anion separation). The rearrangement energy for one ion of type  $X$  may therefore be written as

$$E_{re}^X(R) = E_X(R) - E_X \quad (1)$$

where  $E_X(R)$  is the energy of the optimized in-crystal ion wavefunction evaluated using the free-ion Hamiltonian and  $E_X$  is the energy of the free ion. In the case of the oxide ion, matters are somewhat more complex because the free  $O^{2-}$  ion is unstable. In this case,  $E_X$  is interpreted as the energy of an  $O^-$  ion plus a stationary, isolated electron. We only consider the anion rearrangement energy; the electrons of the  $Th^{4+}$  ion are tightly bound and are not significantly affected by the environment. The second stage of the calculation consists of computing the total energy of interaction between all the ions in their optimal in-crystal states when these are assembled to form the crystal with cation-anion spacing  $R$ . Thus the crystal cohesive energy  $U_L(R)$  measured with respect to the original free ions is given by adding this total interaction energy to the total rearrangement energy. Both the rearrangement and interaction energy components of  $U_L(R)$  can be written as the sum of a Hartree-Fock part, to be denoted by the superscript zero, plus corrections arising from electron correlation.

## 2.1. The Hartree-Fock calculation

**2.1.1. Basic theory.** The wavefunctions for both the free  $Th^{4+}$  ion and the in-crystal  $O^{2-}$  ions were computed in the relativistic Dirac-Fock orbital approximation by using the Oxford Dirac-Fock program (Grant *et al* 1980). The computation of the  $O^{2-}$  wavefunctions for one anion ( $a$ ) requires that a term  $F(r_a, R)$  describing the interaction between an anion electron and all the other ions ( $b \neq a$ ) in the crystal is added to the Dirac-Fock Hamiltonian of anion  $a$ . This term depends both on  $R$  and on the distance  $r_a$  of the electron from the nucleus of  $a$ . This environmental potential  $F(r_a, R)$  contains two terms, the Madelung well and one describing the effect of orthogonalizing the anion wavefunctions to the rest of the lattice. We discuss this in more detail later.

Once we have obtained the ion wavefunctions, we use the formalism developed by Abarenkov and Antonova (1970) to calculate the crystal energy. They wrote the wavefunction of an ionic crystal containing  $N$  ions and  $N_T$  electrons as an antisymmetrized product of the wavefunctions of the individual ions thus:

$$|\Psi(r_1 \dots r_{N_T})\rangle = S\mathcal{A} \prod_{a=1}^N |\Phi(r_{N_a}, \dots, r_{N_a+N_a-1})\rangle \quad (2)$$

where the label  $a$  distinguishes different ions.  $N_{as}$  is the label of the electron appearing first in the wavefunction of ion  $a$ , which has  $N_a$  electrons.  $S$  is the normalisation constant and  $\mathcal{A}$  the antisymmetrizer. When this wavefunction is used to calculate the energy using the standard Hamiltonian, Abarenkov and Antonova showed that it is possible to write the crystal energy as

$$E_{\text{cr}}^0(R) = \sum_{a=1}^N E_a^0(R) + \sum_{a<b}^N V_{ab}^0(x_{ab}R) + \sum_{a<b<c}^N V_{abc}^0(x_{ab}R, x_{bc}R, x_{ac}R) + \dots \quad (3)$$

Here  $E_a^0(R)$  is the energy that a single ion  $a$  would have when isolated if it still retained its optimal in-crystal wavefunction and is thus the Dirac-Fock part of  $E_{\text{O}^{2-}}(R)$  in equation (1).  $V_{ab}^0(x_{ab}R)$  and  $V_{abc}^0(x_{ab}R, x_{bc}R, x_{ac}R)$  are the usual pair and three-body inter-ionic potentials and  $x_{ab}$  is the geometrical factor expressing the distance between ions  $a$  and  $b$  in terms of the cation-anion distance  $R$ . From here on we ignore all terms in the expansion beyond the pair potentials. It is useful to decompose the pair interaction between the ions  $a$  and  $b$  into the purely coulombic form it would have if the overlap between the wavefunctions of the two ions were negligible plus a remainder  $V_{sab}^0(x_{ab}R)$  which is of short range as denoted by the  $s$  subscript. Thus

$$V_{ab}^0(x_{ab}R) = V_{sab}^0(x_{ab}R) + Z_a Z_b / (x_{ab}R) \quad (4)$$

where  $Z_a$  is the net charge of ion  $a$ . The purely coulombic terms resulting from the use of (4) in (3) constitute a standard Madelung sum whilst the only non-negligible short-range terms are those  $V_{sCA}^0(R)$  between a cation and its eight nearest anions, those  $V_{sAA}^0(x_{AA}R)$  between an anion and its six closest anion neighbours and those  $V_{sCC}^0(x_{CC}R)$  between a cation and its twelve closest cation neighbours. After using these results the uncorrelated contribution  $U_L^0(R)$  to the crystal cohesion derived by subtracting from (3) the energy of free  $\text{O}^-$  ions becomes

$$U_L^0(R) = -M/R + 2E_{\text{re}}^0(R) + 8V_{sCA}^0(R) + 6V_{sAA}^0(x_{AA}R) + 6V_{sCC}^0(x_{CC}R). \quad (5)$$

Here  $M$  is the appropriate Madelung constant whilst  $E_{\text{re}}^0(R)$  is the prediction of the Dirac-Fock atomic orbital model for the rearrangement energy of one ion.

Given suitable wavefunctions, all the terms in (5) can be evaluated. The rearrangement energy is computed using the energy-analysis package associated with the Oxford Dirac-Fock program. The pair potentials can be calculated using RIP (relativistic integrals program), a computer program developed by Wood and Pyper (1986). This takes the Dirac-Fock orbitals computed for the individual ions and calculates the interaction using the full Dirac equation thereby accounting for the overwhelming majority of all the relativistic contributions to  $U_L^0(R)$ . This procedure neglects only purely quantum electrodynamic effects (Bethe and Salpeter 1957) and the inter-electronic Breit interaction (Breit 1929, 1930, 1932, Mittleman 1971, 1972) originating from the exchange of virtual transverse photons. Although both the Breit interaction and quantum electrodynamic effects make significant contributions to the binding energies of the innermost core electrons (Grant 1970), these contributions cancel in the evaluation of the interaction energy because the ion core orbitals remain essentially unchanged on entering the crystal. This then shows that the Breit and quantum electrodynamic contributions to  $U_L^0(R)$  can be safely neglected because these terms make only very small contributions to the energies of valence electrons (Pyper and Marketos 1981). However, the relativistic effects described by Dirac-Fock theory have been shown

(Rose *et al* 1978) to influence greatly the behaviour of even the valence electrons in atoms heavier than those of the third transition series. The mean radii and binding energies of valence orbitals in such heavy atoms can be changed by relativity by as much as 30%. For ThO<sub>2</sub> therefore it is essential to consider such effects by using relativistic Dirac–Fock rather than standard non-relativistic Hartree–Fock theory. The role played by relativity in the cohesion of a solid containing heavy ions has been studied explicitly (Pyper *et al* 1987) for the case of cubic PbF<sub>2</sub>. Full details of the RIP program are given in Wood and Pyper (1986).

*2.1.2. The environmental potential.* We require the wavefunctions of the anions in the crystal environment. To get these, we require a method of estimating the effect of the environment on the anion. We assume that this can be described by a local potential. Possible forms of this potential have recently been discussed in detail by Pyper (1994a). The electrostatic term is, in principle, straightforward. Here the only refinement is to note that we do not require a detailed description of its behaviour beyond the nearest neighbours and it is therefore convenient to multiply it by a smoothing function. The difficulty lies in obtaining a local potential that describes the orthogonalization term. Pyper has compared the various functions suggested in the literature. Here we use a function having the general form

$$F(r_a, R) = -(\phi/R)\{1 + \exp[g(r_a - r_0)]\}^{-1} + A \sum_b \sum_i \{[\rho_{ib}(r_b)]^k\}^0. \quad (6)$$

This is very similar to the ODMFS (optimized with density Madelung Fermi smoothed model) discussed by Pyper (1994a). The first term represents the electrostatic term;  $\phi/R$  being the Madelung potential at the anion site. The smoothing part contains two parameters,  $r_0$  and  $g$ .  $r_0$  is fixed by requiring that the smoothed electrostatic term reproduces the exact Madelung result at the distance where the latter has the value  $-\phi/2R$ .  $g$  is fixed by requiring that the smoothed expression also reproduces the exact result half-way between  $r_0$  and  $R$ . The second term represents the orthogonalization to the nearest-neighbour ions. The  $b$  sum is over the four cations adjacent to anion  $a$  whilst the  $i$  sum is over all the occupied orbitals of cation  $b$ . The quantity  $\rho_{ib}(r)$  is the density at position  $r$  generated by an electron occupying orbital  $i$  of ion  $b$ . For each ion  $b$ , this term is then expanded as a series of spherical harmonics centred on nucleus  $a$ . We take only the zero-order (spherically symmetric) term of this expansion. This is denoted by the superscript zero. Only this term needs to be considered if one makes the usual demand that the atomic orbitals have the standard angular symmetries of atomic orbitals. The quantities  $A$  and  $k$  are variational parameters to be determined by minimizing the cohesive energy with respect to them for a given lattice parameter  $R$ .

## 2.2. The correlation and dispersion terms

The Hartree–Fock calculation discussed above omits the effects of electron correlation. Here we estimate these terms and add them to the crystal binding energy. There are two sources of correlation to consider: the intra-ionic correlation and the inter-ionic correlation. The assumption that the cations are unaffected by the crystal environment causes any intra-ionic correlation in the cations to cancel out of the cohesive energy. However, this is not the case for the anions, which are profoundly modified by their environment. We must therefore calculate the difference in the correlation energy between the free O<sup>-</sup> ion and the O<sup>2-</sup> in various environments. The only practical way to estimate correlation effects for this problem

is to use density-functional theory. A common approximation is to assume that the electron density varies sufficiently slowly that at each point the functional may be assumed to be that of a non-relativistic uniform electron gas with the same density. We use the standard expression for the correlation term in the electron-gas approximation and incorporate the Cowan correction (Cowan 1967) to remove electron self-correlation. The correlation energy  $E_a^{\text{corr}}$  of species  $a$  ( $a = \text{free O}^-$  or  $\text{O}^{2-}$  in crystal) is

$$E_a^{\text{corr}} = \sum_i \int \rho_{ia}(\mathbf{r}) F^{\text{corr}}[\rho_{Ta}(\mathbf{r}) - \rho_{ia}(\mathbf{r})] d\mathbf{r} \quad (7)$$

where  $\rho_{Ta}(\mathbf{r})$  is the Dirac-Fock prediction for the total electron density of species  $a$  and the  $i$  summation is over all orbitals occupied in species  $a$  generating electron densities  $\rho_{ia}(\mathbf{r})$ . The functional chosen is

$$F^{\text{corr}}[\rho(\mathbf{r})] = \begin{cases} -0.438\beta^{-1} + 1.325\beta^{-3/2} - 1.47\beta^{-2} - 0.4\beta^{-5/2} & \beta \geq 10 & (8) \\ -0.06156 + 0.01898 \ln \beta & 0.7 \leq \beta \leq 10 & (9) \\ 0.0311 \ln \beta - 0.048 + 0.009\beta \ln \beta - 0.01\beta & \beta \leq 0.7 & (10) \end{cases}$$

where  $\beta^3 = 3/[4\pi\rho(\mathbf{r})]$ . This is the Gordon-Kim functional (Gordon and Kim 1972). There are many others, but the differences between them are not great.

The use of densities  $\rho_{ia}(\mathbf{r})$  derived from relativistic orbitals with functionals such as (8)–(10) based on non-relativistic theory might at first sight seem to be slightly inconsistent. However, it has been shown (Pyper *et al* 1977) for the interaction of two mercury atoms that the density-functional predictions of the kinetic-energy contribution to the interatomic potential remain essentially unchanged on replacing the non-relativistic kinetic-energy functional by the corresponding relativistic one. Since relativity would be expected to modify the kinetic energy more than the correlation energy, it follows, for the electron densities relevant to the interaction of ions in solids, that the correlation energies predicted using the relation (7) would remain essentially unchanged on replacing (8)–(10) by the corresponding functional derived from relativistic theory. However, it was also found (Pyper *et al* 1977) that the density functional predictions of the interaction energy were greatly changed on replacing the non-relativistic mercury-atom electron density by the relativistic one. This strongly suggests that most of the relativistic modifications of the correlation energy have been included in the present calculations simply by using the relativistic rather than the non-relativistic densities in (7).

Pyper (1994a) has shown that the use of (7)–(10) gives poor results for intra-ionic correlation. However, he has shown that it is possible to construct a systematic scheme to correct the poor density-functional predictions of electron correlation contributions to ionization potentials by introducing correction functions  $A_{\text{corr}}(\xi)$  derived from experimental data and dependent on a parameter  $\xi$  characterizing the electronic structure of the species whose ionization is being considered. The correlation correction to the rearrangement energy is thus evaluated from

$$E_{\text{re}}^{\text{corr}}(R) = A_{\text{corr}}(\xi)[E_{\text{O}^{2-}}^{\text{corr}}(R) - E_{\text{O}^-}^{\text{corr}}] \quad (11)$$

where  $E_{\text{O}^-}^{\text{corr}}$  and  $E_{\text{O}^{2-}}^{\text{corr}}$  are the predictions of (7) for respectively the correlation energy of a free  $\text{O}^-$  ion and that of an  $\text{O}^{2-}$  ion in the crystal with closest cation-anion separation  $R$ . For the neon iso-electronic sequence  $A_{\text{corr}}(\xi)$  was shown to be given by

$$A_{\text{corr}}(\xi) = 1.055 + 0.292\xi + 0.127|\xi|^{3.241}. \quad (12)$$

Application of this relation requires the  $\xi$  value for an in-crystal  $O^{2-}$  ion. For such an ion it was shown that  $\xi$  could be deduced from the polarizability  $\alpha$  of such an ion through

$$\alpha^{-1} = 0.092754 - 0.005797\xi^4. \quad (13)$$

A recent re-examination (Fowler *et al* 1994) of experimental and theoretical data for refractive indices and ionic polarizabilities of solid quadrivalent oxides showed the polarizability of an  $O^{2-}$  ion in  $ThO_2$  to be 15.349 au from which  $\xi$  is found to be 1.477 corresponding to an  $A_{\text{corr}}(\xi)$  value of 1.936. The required correlation contribution  $E_{\text{re}}^{\text{corr}}(R)$  to the  $O^{2-}$  ion rearrangement energy can now be computed from (11). The total rearrangement energy  $E_{\text{re}}(R)$  of one in-crystal  $O^{2-}$  ion is given as the sum of the Dirac-Fock and correlation contributions by

$$E_{\text{re}}(R) = E_{\text{re}}^0(R) + E_{\text{re}}^{\text{corr}}(R). \quad (14)$$

The inter-ionic electron correlation consists of two contributions, the first not involving the exchange of electrons between the ions whilst the second originates from such exchange. The first contribution is traditionally called the dispersion energy and is of long range in that it does not depend on the overlap between the wavefunctions of the interacting ions and does not therefore vanish when this overlap is negligible. The second contribution being of short range and vanishing for negligible ion wavefunction overlap is conventionally regarded as a correlation correction to the uncorrelated short-range interaction  $V_{\text{sab}}^0(x_{\text{ab}}R)$ . The total short-range interaction between the ions  $a$  and  $b$  is thus given as the sum

$$V_{\text{sab}}(x_{\text{ab}}R) = V_{\text{sab}}^0(x_{\text{ab}}R) + V_{\text{sab}}^{\text{corr}}(x_{\text{ab}}R) \quad (15)$$

where  $V_{\text{sab}}^{\text{corr}}(x_{\text{ab}}R)$  is the exchange-dependent correlation term. Density-functional theory provides the only currently feasible way of evaluating the  $V_{\text{sab}}^{\text{corr}}(x_{\text{ab}}R)$ . Here we use the functionals (8–10) so that the method becomes identical to that used by Gordon and Kim (1972). Since the functionals (8–10) yield the entire correlation energy of a uniform electron gas and not just the exchange-dependent contribution, there would be a problem of double counting if the total correlation energy of such a gas were to be calculated by adding an independently evaluated dispersion contribution to the prediction derived from the functionals (8)–(10). The major portion of the density dependence of the correlation energy of a uniform electron gas arises from the electron–electron interactions occurring over short distances since the long-range correlation effects are very nearly independent of the density (Raimes 1972, Rae 1975). Hence if the difference between the correlation energy of a pair of interacting ions and the sum of the correlation energies of the non-interacting ions is evaluated using the local density approximation (7) in conjunction with the functionals (8)–(10), the contribution from the long-range correlations will cancel almost exactly. Hence the dispersive attraction between a pair of ions is almost completely missed by such a calculation of the correlation energy because these attractions originate almost entirely from electron correlations of long range. Since it is only the short-range correlations in a uniform electron gas which are significantly density dependent, correlation contributions to interaction energies evaluated using (7)–(10) will arise almost entirely from short-range-correlation effects which play almost no role in the dispersive interactions. This shows that the local-density approximation (7)–(10) yields only the short-range-correlation terms  $V_{\text{sab}}^{\text{corr}}(x_{\text{ab}}R)$  and hence that the total correlation energy is obtained only after adding separately evaluated dispersive attractions. The studies of both the inert gas dimers (Clugston and Pyper 1979) and the cohesion of ionic crystals (Pyper 1986) provide

strong confirmatory numerical evidence that the dispersive attractions are physically quite distinct from the local-density approximation (7)–(10) for the correlation energy so that any double counting introduced by including both these correlation terms is minimal. Since the dispersion energy is often 5% of the total cohesion it cannot be omitted whilst the short-range correlation energy is also too large to be dismissed.

The dispersion energy  $U_{\text{disp}}(R)$  of the crystal is given by

$$U_{\text{disp}}(R) = - \sum_{a < b}^N \sum_{n=3}^{\infty} \chi_{2n}^{ab}(x_{ab}R) C_{2n}^{ab} / (x_{ab}R)^{2n} \quad (16)$$

where the  $C_{2n}^{ab}$  are the dispersion coefficients and the  $\chi_{2n}^{ab}(x_{ab}R)$  are dispersion damping functions. These functions are unity at longer interionic separations where ion-wavefunction overlap is negligible but are reduced at smaller  $x_{ab}R$  thus taking account of the effect of the overlap of the wavefunctions and suppressing the singularities in the undamped expression as  $x_{ab}R$  tends to zero. The complex expressions for the  $\chi_{2n}^{ab}(x_{ab}R)$  were derived by Jacobi and Czanak (1975) and by Pyper (1986). They are discussed in Pyper (1991, 1994a). For the closest cation–anion, anion–anion and cation–cation pairs it is essential to take account of the damping of the dispersion interactions (Pyper 1986) because  $U_{\text{disp}}(R)$  values derived neglecting this damping are very significantly too large leading to appreciable overestimation of the crystal cohesion. Only the first two terms of the  $n$  summation in (16) make a significant contribution to the cohesive energy. We obtain values for the  $C_6^{ab}$  coefficients using the Slater–Kirkwood (1931) approximation and the  $C_8^{ab}$  coefficients using the Starkschall–Gordon (1972) formulae. A discussion of how to obtain both these numbers (as well as the dispersion damping parameters on which the  $\chi_{2n}^{ab}(x_{ab}R)$  depend) is found in Fowler *et al* (1994). The final expression used to predict the total crystal cohesive energy  $U_L(R)$  is given by adding to the uncorrelated prediction  $U_L^0(R)$  of equation (5) the correlation contribution (11) to the rearrangement energy, the short-range two-body correlation terms entering (15) and the dispersion energy (16). The result is

$$U_L(R) = -M/R + 2E_{\text{re}}(R) + 8V_{\text{sCA}}(R) + 6V_{\text{sAA}}(x_{\text{AA}}R) + 6V_{\text{sCC}}(x_{\text{CC}}R) + U_{\text{disp}}(R). \quad (17)$$

### 3. Results

We begin with the results for the oxide rearrangement energy shown in table 1. There are a number of points to note. The most important is that the term is large and changes markedly as the lattice expands. This is the case for all the other oxides that have been studied (MgO and CaO by Pyper (1994a) and also UO<sub>2</sub> (Harding *et al* 1994; preliminary results derived using the methods of Pyper (1994a, b) are quoted in Lindan (1993)). Therefore the attempts that have been made in the older literature to define a unique value for the second ionization potential for the oxide ion are pointless. There is no such number. This observation is reinforced by the result that the rearrangement energy even varies between different crystals at their respective equilibrium geometries. Thus our value of 1242 kJ mol<sup>-1</sup> for  $R = 4.5$  bohr in ThO<sub>2</sub> is significantly larger than those of 1026 kJ mol<sup>-1</sup> and 1039 kJ mol<sup>-1</sup> found for  $E_{\text{re}}(3.981)$  and  $E_{\text{re}}(4.544)$  for MgO and CaO at their respective equilibrium geometries (Pyper 1994a). All three of these rearrangement energies are considerably larger than the values (between 751 kJ mol<sup>-1</sup> and 885 kJ mol<sup>-1</sup>) which have been deduced (Morris 1957, Huggins and Sakamoto 1957) by comparing semi-empirical calculations of oxide lattice



energies with experimental data. It is beyond the scope of this paper to discuss either the reasons for these differences or the significance of the semi-empirical values, topics to be addressed elsewhere. Also, table 1 shows that the variation in the correlation contribution to the rearrangement energy is large too; this quantity cannot be estimated accurately from a Hartree–Fock calculation alone. Finally, the rearrangement energy is intrinsically a many-body term. However, it is not an explicit term in the sense of the three-body terms in equation (3) and certainly not of the bond-bending type.

Pyper (1991) refers to this type of term as an ‘implicit’ many-body term. This point has been made, in effect, by previous authors. Boyer *et al* (1985) refer to this effect as their ‘potential-breathing’ model. It is worth, however, stressing that there is no analogy here with the terms used to model directional bonds; the analogy is, if anywhere, with the kinds of term found in embedded-atom or Finnis–Sinclair models (Finnis and Sinclair 1984).

**Table 1.** Values of the parameters  $A$  and  $k$  of the environmental potential (see equation (6)) and rearrangement energies for the oxide ion in thoria.

$R$ (bohr)	$A$	$k$	$E_{re}^0[\text{O}^{2-}]$ (Hartree)	$E_{re}[\text{O}^{2-}]$ (Hartree)
3.5	11.0	1.48	1.157 344	0.985 288
4.0	13.05	1.43	0.796 463	0.648 361
4.25	14.0	1.42	0.687 989	0.549 592
4.5	11.1	1.25	0.603 403	0.472 924
4.75	11.5	1.25	0.544 227	0.421 355
5.0	10.7	1.19	0.499 439	0.382 903
5.5	7.0	0.92	0.439 300	0.331 823

Table 2 shows both the uncorrelated  $V_{sXY}^0(x_{XY}R)$  and short-range-correlation  $V_{sXY}^{\text{corr}}(x_{XY}R)$  contributions to the short-range parts of the pair potentials. The contribution  $V_{XY}^{\text{disp}}(x_{XY}R)$  of dispersion to the interaction of one ion of type X with one of its nearest neighbours of type Y in the crystal with geometry defined by  $R$  is given by

$$V_{XY}^{\text{disp}}(x_{XY}R) = -\chi_6^{\text{XY}}(x_{XY}R)C_6^{\text{XY}}/(x_{XY}R)^6 - \chi_8^{\text{XY}}(x_{XY}R)C_8^{\text{XY}}/(x_{XY}R)^8 \quad (18)$$

These quantities are also reported in table 2. It is sometimes useful to work with the total non-point-coulombic interactions, that  $V_{XY}^{\text{npc}}(x_{XY}R)$  for the pair of ions X and Y being defined as

$$V_{XY}^{\text{npc}}(x_{XY}R) = V_{sXY}(x_{XY}R) + V_{XY}^{\text{disp}}(x_{XY}R). \quad (19)$$

It is seen that the correlation (and dispersion) terms make significant contributions to the final non-point-coulombic interactions. The total crystal cohesion  $U_L(R)$  is not just the Madelung term and twice the rearrangement energy plus the sum of non-point-coulombic interactions

$$8V_{\text{Th}^{4+}-\text{O}^{2-}}^{\text{npc}}(R) + 6V_{\text{O}^{2-}-\text{O}^{2-}}^{\text{npc}}(x_{\text{O}^{2-}-\text{O}^{2-}}R) + 6V_{\text{Th}^{4+}-\text{Th}^{4+}}^{\text{npc}}(x_{\text{Th}^{4+}-\text{Th}^{4+}}R)$$

because the contributions from the dispersive attractions between more distant pairs of ions cannot be neglected. The separations  $(x_{ab}R)$  entering these terms are, however, sufficiently large that all the functions  $\chi_{2n}^{ab}(x_{ab}R)$  damping these more distant attractions are unity. The full total crystal cohesions  $U_L(R)$  evaluated from (17) are reported in table 3. Predictions for the equilibrium lattice parameter,  $R_e$ , the lattice energy,  $-U_L(R_e)$ , and the

**Table 2.** Pair potentials for  $\text{ThO}_2$  (for function definitions see the text). Note that  $x_{\text{CC}} = 2\sqrt{2/3}$ ;  $x_{\text{AA}} = 2/\sqrt{3}$ .

$R$ (bohr)	$V_{\text{sTh}^{4+}-\text{O}^{2-}}^0(R)$ (Hartree)	$V_{\text{sTh}^{4+}-\text{O}^{2-}}^{\text{corr}}(R)$ (Hartree)	$V_{\text{Th}^{4+}-\text{O}^{2-}}^{\text{disp}}(R)$ (Hartree)
3.5	0.302 035	-0.006 826	-0.048 071
4.0	0.146 648	-0.004 582	-0.024 605
4.25	0.103 822	-0.003 620	-0.017 620
4.5	0.076 205	-0.002 950	-0.012 674
4.75	0.055 496	-0.002 422	-0.009 176
5.0	0.041 124	-0.001 993	-0.006 699
5.5	0.023 512	-0.001 340	-0.003 676
$R$ (bohr)	$V_{\text{sO}^{2-}-\text{O}^{2-}}^0(x_{\text{AA}}R)$ (Hartree)	$V_{\text{sO}^{2-}-\text{O}^{2-}}^{\text{corr}}(x_{\text{AA}}R)$ (Hartree)	$V_{\text{O}^{2-}-\text{O}^{2-}}^{\text{disp}}(x_{\text{AA}}R)$ (Hartree)
3.5	0.024 286	-0.001 233	-0.023 077
4.0	0.011 144	-0.001 066	-0.012 168
4.25	0.007 509	-0.000 999	-0.008 823
4.5	0.005 400	-0.000 949	-0.006 415
4.75	0.003 586	-0.000 900	-0.004 688
5.0	0.002 399	-0.000 853	-0.003 452
5.5	0.001 166	-0.000 739	-0.001 921
$R$ (bohr)	$V_{\text{sTh}^{4+}-\text{Th}^{4+}}^0(x_{\text{CC}}R)$ (Hartree)	$V_{\text{sTh}^{4+}-\text{Th}^{4+}}^{\text{corr}}(x_{\text{CC}}R)$ (Hartree)	$V_{\text{Th}^{4+}-\text{Th}^{4+}}^{\text{disp}}(x_{\text{CC}}R)$ (Hartree)
3.5	0.008 328	-0.000 619	-0.002 360
4.0	-0.000 167	-0.000 168	-0.000 980
4.25	-0.001 007	-0.000 084	-0.000 659
4.5	-0.001 363	-0.000 040	-0.000 456
4.75	-0.001 500	-0.000 018	-0.000 322
5.0	-0.001 493	-0.000 008	-0.000 232
5.5	-0.001 238	-0.000 002	-0.000 127

**Table 3.** Cohesive energy  $U_L(R)$  computed from equation (17) as a function of lattice parameter.

$R$ (bohr)	$U_L(R)$ (Hartree)
3.5	-1.886 924
4.0	-2.868 452
4.25	-3.037 932
4.5	-3.092 930
4.75	-3.087 682
5.0	-3.038 700
5.5	-2.876 231

bulk compressibility were derived from these results by fitting them to a seven-term function of the type devised by Simons *et al* (1973). We thereby obtain the equilibrium lattice parameter as 4.593 bohr (compared with an experimental value of 4.582 bohr (Wyckoff 1963)).

Before we can compare our computed lattice energy with experiment, an experimental value must be derived from a Born-Haber cycle. The cohesive energies calculated in table 3 are with respect to  $\text{Th}^{4+}$ ,  $\text{O}^-$  and free, stationary electrons whereas the experimentally available quantity is the heat of formation of solid  $\text{ThO}_2$  from thorium metal and gaseous oxygen. All the quantities needed to derive the experimental lattice energy are available,

being reported in table 4, with the exception of the third and fourth ionization potentials of thorium. These latter had therefore to be derived from atomic relativistic Dirac-Fock calculations. The results of such calculations performed with the Oxford Dirac-Fock program (Grant *et al* 1980) for neutral thorium and its first four ions are reported in table 5 along with the ionization potentials predicted as the appropriate differences of the total Dirac-Fock energies. Comparison of the results with experimental ionization potentials (known only for neutral thorium and Th<sup>+</sup>) suggests that electron-correlation effects, which are not included in the Dirac-Fock calculations, increase each ionization potential by only about 0.5 eV. The best current estimates (table 4) of the third and fourth Th ionization potentials are therefore given by adding 0.5 eV to each of the Dirac-Fock predictions. The data of table 4 yield an experimental value of 8100 kJ mol<sup>-1</sup> for the lattice energy, compared with the calculated value of 8130 kJ mol<sup>-1</sup>. Considering the uncertainties in both experimental and calculated quantities, such agreement is remarkably good.

Table 4. The lattice energy of thoria.

Property	Value	Reference
Sublimation energy of thorium	598 kJ mol <sup>-1</sup>	Katz <i>et al</i> (1986)
Dissociation energy of oxygen	41 260 cm <sup>-1</sup>	Chase <i>et al</i> (1985)
Electron affinity oxygen atom	-1.461 121 5 eV	Chase <i>et al</i> (1985)
First ionization potential of thorium	6.08 eV	Hildebrand <i>et al</i> (1985)
Second ionization potential of thorium	11.5 eV	Hildebrand <i>et al</i> (1985)
Third ionization potential of thorium	18.11 eV	This work (calculation)
Fourth ionization potential of thorium	27.21 eV	This work (calculation)
Enthalpy of formation of thoria	-292.01 kcal mol <sup>-1</sup>	Wagman <i>et al</i> (1981)
Lattice energy (experiment)	8100 kJ mol <sup>-1</sup>	
Lattice energy (theory)	8130 kJ mol <sup>-1</sup>	

Table 5. Dirac-Fock predictions of thorium ionization potentials.

Species	Type of calc. <sup>a</sup>	$E_{\min}$ (Hartree)	Calculated IP (eV)	Experimental IP (eV)
Th	6d <sup>2</sup> 7s <sup>2</sup> (3 CSF) $J = 2$ (AL)	-26 524.811 974	5.714	6.08 ± 0.12 <sup>b</sup>
Th <sup>+</sup>	6d 7s <sup>2</sup> (1 CSF)	-26 524.601 977	11.083	11.9 ± 0.1 <sup>b</sup> 11.5 <sup>c</sup>
Th <sup>2+</sup>	5f 6d (4 CSF) $J = 4$ (AL)	-26 524.194 689	17.606	
Th <sup>3+</sup>	5f (1 CSF)	-26 523.547 681	26.710	
Th <sup>4+</sup>		-26 522.566 093		

<sup>a</sup> AL = single manifold average level calculation and CSF = relativistic configuration state function (see Grant *et al* 1976).

<sup>b</sup> From Hildebrand *et al* (1985).

<sup>c</sup> From Katz *et al* (1986).

Finally, we can compare the bulk moduli. Here we calculate a value of  $17.5 \times 10^{10}$  N m<sup>-2</sup> compared with the experimental value of  $19.3 \times 10^{10}$  N m<sup>-2</sup> (Macedo *et al* 1964). Again, this shows that the calculation performs well.

#### 4. Conclusions

We have shown that thorium dioxide may be described by an (appropriately defined) ionic model. The interionic potentials have been calculated using the RIP program and shown to give the cohesive energy, lattice parameter and bulk modulus in excellent agreement with experiment. The calculations have shown the importance of the self-energy of the oxygen ion, and in particular its strong variation with the local environment. This effect is stronger than in the oxides with the rock-salt structure where it had been reported before. This is a many-body term (although not of the bond-bending type). Future potential models should take this effect into account.

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#### References

- Abarenkov I V and Antonova I M 1970 *Phys. Status Solidi* **38** 783  
Bethe H A and Salpeter E F 1957 *The Quantum Mechanics of One and Two Electron Atoms* (Berlin: Springer)  
Breit G 1929 *Phys. Rev.* **34** 553  
—— 1930 *Phys. Rev.* **36** 383  
—— 1932 *Phys. Rev.* **39** 616  
Boyer L L, Mehl M J, Feldman J L, Hardy J R, Flocken J W and Wong Y 1985 *Phys. Rev. Lett.* **54** 1940  
Catlow C R A and Stoneham A M 1983 *J. Phys. C: Solid State Phys.* **16** 4321  
Chase M W, Davues C A, Downey J R, Frurip D J, McDonald R A and Syverud A N 1985 *JANAF Thermochemical Tables* 3rd edn; *J. Chem. Ref. Data* **14** Supplement 1  
Clugston M J and Pyper N C 1979 *Chem. Phys. Lett.* **63** 549  
Colbourn E A and Mackrodt W C 1983 *J. Nucl. Mater.* **118** 50  
Cowan R D 1967 *Phys. Rev.* **163** 54  
Finnis M W and Sinclair J E 1984 *Phil. Mag. A* **50** 45  
Fowler P W, Harding J H and Pyper N C 1994 in preparation  
Gordon R G and Kim Y S 1972 *J. Chem. Phys.* **56** 3122  
Grant I P 1970 *Adv. Phys.* **19** 747  
Grant I P, Mayers D F and Pyper N C 1976 *J. Phys. B: At. Mol. Phys.* **9** 2777  
Grant I P, McKenzie B J, Norrington P H, Mayers D F and Pyper N C 1980 *Comput. Phys. Commun.* **21** 207  
Harding J H, Lindan P J D and Pyper N C 1994 in preparation  
Hildebrand D L, Gunvich L V and Yungman V S 1985 *Chemical Thermodynamics of Actinide Elements and Compounds* part 13 (Vienna: IAEA)  
Huggins M L and Sakamoto 1957 *Proc. Phys. Soc. Japan* **12** 241  
Jackson R A, Murray A D, Harding J H and Catlow C R A 1986 *Phil. Mag. A* **53** 27  
Jacobi N and Czanak Gy 1975 *Chem. Phys. Lett.* **30** 367  
Katz J J, Seaborg G T and Morse L R 1986 *Chemistry of the Actinide Elements* (London: Chapman and Hall)  
Lindan P J D 1993 *PhD Thesis* Keele University  
Macedo P B, Capps W and Watchman J B 1964 *J. Am. Ceram. Soc.* **47** 651  
Mittleman M 1971 *Phys. Rev. A* **4** 893  
Mittleman M 1971 *Phys. Rev. A* **6** 2395  
Morris D F C 1957 *Proc. Phys. Soc. A* **242** 116  
Pyper N C 1986 *Phil. Trans. R. Soc. A* **320** 107  
Pyper N C 1991 *Adv. Solid State Chem.* **2** 223  
Pyper N C 1994a *Phil. Trans. R. Soc.* at press  
Pyper N C 1994b *Chem. Phys. Lett.* **220** 70

- Pyper N C, Grant I P and Gerber R B 1977 *Chem. Phys. Lett.* **49** 479
- Pyper N C and Marketos P 1981 *J. Phys. B: At. Mol. Phys.* **14** 1387
- Pyper N C, Marketos P and Malli G L 1987 *J. Phys. C: Solid State Phys.* **20** 4711
- Rae A I M 1975 *Mol. Phys.* **29** 467
- Raimes S 1972 *Many-Electron Theory* (Amsterdam: North-Holland)
- Rose S J, Pyper N C and Grant I P 1978 *J. Phys. B: At. Mol. Phys.* **11** 1171
- Simons G, Pam R G and Finlan J M 1973 *J. Chem. Phys.* **59** 3229
- Slater J C and Kirkwood J G 1931 *Phys. Rev.* **37** 682
- Starkschall G and Gordon R G 1972 *J. Chem. Phys.* **56** 2809
- Wagman D D, Evans W H, Parker V B, Schuman R H and Nutall R L 1981 *NBS Technical Note 270/8 (US Department of Commerce)*
- Wood C P and Pyper N C 1986 *Phil. Trans. R. Soc. A* **320** 71
- Wyckoff R W G 1963 *Crystal Structures* vol 1 (New York: Interscience) p 243