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Theoretical Calculation of Structural Parameters of *C*-Type Sesquioxides

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The lattice energies of *C*-type sesquioxides are assumed to be represented by the Born–Lande expression,

$$E=\tfrac{1}{2}e^2\sum_{i\neq j} q_iq_j/r_{ij}+c\sum_{i\neq j} 1/r_{ij}^n\ .$$

Minimization of the energy yields values of the four positional parameters. Calculations are carried out for a number of values of *c* and *n*. Experimental (Born–Haber cycle) lattice energies are used to select the range of *c*. Agreement between calculated and experimental atomic coordinates is encouraging. For Y_2O_3, for example, the single-crystal and theoretical ($n=9$) data are, respectively, $u=-0{\cdot}0328$ (2), $x=0{\cdot}389$ (1), $y=0{\cdot}154$ (1), $z=0{\cdot}378$ (1) and $u=-0{\cdot}0330$, $x=0{\cdot}390$, $y=0{\cdot}152$, $z=0{\cdot}381$. Results are presented for a series of rare-earth oxides and re-examination of the experimental data is suggested in some cases.

Introduction

Calculation of the geometries of crystals from first principles is one of the major unsolved problems of structural chemistry. It is conceptually an easy task, merely involving minimization of the energy with respect to arbitrary displacements of all the atoms in the crystal. In practice, two complications must immediately be faced. The first of these is the more serious one: without the assumption of a space group for the crystal, the coordinates of all the atoms considered must be treated as independent variables. If the interatomic forces are long-range, many atoms contribute, and the minimum energy must be found in a space of many dimensions. It is well known that searching for minima in multidimensional spaces is a formidable mathematical problem (Wilde, 1964). The second complication is the inadequacy of our present knowledge of interionic potentials.

Previous theoretical calculations of this nature have tended to fall into two classes. In the first, *ab initio* calculations, including description of valence electrons, are carried out to calculate the structures of very simple crystals (Löwdin, 1947). In the second class of calculations, slightly more complicated crystals are considered, but the description of interionic forces is less adequate. Additional constraints are sometimes introduced which limit the range of possible motions of the atoms, and the results may be quite dependent on particular details of the constraints (v. Mertens & Zemann, 1966; Hase, Kleinstück & Schulze, 1967).

Even relatively unsophisticated calculations are known to yield lattice energies that are in good agreement with experiment; however, an unresolved question is whether crystal geometries can be obtained to the same level of accuracy.

The objective of the present investigation was to determine whether the simple Born model (Born & Lande, 1918) is capable of yielding reasonable atomic positional parameters for moderately complicated, essentially ionic crystal structures. No constraints on interatomic distances are introduced, but the experimentally known space group is assumed.

Calculation of structural parameters

For our study we selected sesquioxides of the *C*-type (bixbyite) structure, which represents a structure of moderate complexity, being defined by four positional parameters. In this structure, which belongs to the $\underline{I}a3(T_R^7)$ space group, there are 8 metal ions in site $\bar{3}(S_6)$: ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$), *etc*., 24 metal ions in $2(C_2)$: (u, 0, $\frac{1}{4}$), *etc.* and 48 oxygen atoms in the general positions (x, y, z), *etc.* Although positional parameters have been reported for many *C*-type oxides, most structure determinations have been made on polycrystalline samples, and to date single-crystal results are available for only three oxides: those of Y, In and Sc.

We assume that the lattice energy is represented by

$$E=\tfrac{1}{2}e^2\sum_{i\neq j} q_iq_j/r_{ij}+c'\sum_{i} 1/r_i^n\ , \qquad (1)$$

and obtain the positional parameters u, x, y and z which minimize the lattice energy. The first sum of equation (1) represents the attractive (Madelung) energy and the summation extends over all pairs of charges, q_i and q_j, separated by the interionic distance r_{ij}. The repulsive energy given by the second sum represents interaction only between unlike charges. Thus, in the case of M_2O_3, the expression $\Phi_j=b\sum_i 1/r_{ij}^n$ is taken to represent the repulsive energy between the jth oxygen ion and all metal ions. Since in the *C*-type M_2O_3 lattice all the oxygen ions occupy equivalent positions, the total repulsive energy is, under our assumption, $N\Phi_j$, where N is the number of oxygen ions. Some justification for this assumption may be found in the well-known strong distance dependence of interatomic repulsive forces. Consequently, the nearest, *i.e.* unlike, charges make the major contribution to the repulsive energy. A more adequate description of the repulsive energy would require consideration of the repulsive interaction between ions of like charge with the introduction of different hardness parameters, n and b, for different ionic species. This would complicate the calculations considerably. It was felt that models of such a degree of sophistication were not warranted in this exploratory investigation. Expressions similar to equation (1) reproduce the experimental lattice energies to within a few per cent for typically ionic solids (Tosi, 1965). As will be shown later, the calculated energies for C-type sesquioxides agree quite well with the corresponding experimental values, which may be taken to imply an essentially ionic bonding in these compounds.

For computational purposes we introduce dimensionless distances $\varrho = r/a_0$, where a_0 is the lattice parameter, and rewrite equation (1) as

$$Ea_0 = (1/2)e^2 \sum_{i \neq j} q_i q_j/\varrho_{ij} + c \sum_i 1/\varrho_i^n . \qquad (2)$$

The first sum converges slowly and conditionally. We compute it by the method of Bertaut (1952) in which the point charges are replaced by non-overlapping spherically symmetric charge distributions. The Madelung energy can then be expressed as an absolutely convergent infinite series

$$\begin{aligned} M &= \tfrac{1}{2}e^2 \sum_{i \neq j} q_i q_j/\varrho_{ij} \\ &= (18\pi R^2/Z) \sum_t (\mathrm{Mu})_t |F_t|^2 (\sin\alpha - \alpha\cos\alpha)^2/ \\ &\qquad \alpha^8 - (3/5RZ) \sum_i q_i^2 , \end{aligned} \qquad (3)$$

where

$$\alpha = 2\pi t R , \qquad (4)$$

and

$$F_t = \sum_i q_j \exp[2\pi i(hx_j + ky_j + lz_j)] . \qquad (5)$$

One half the shortest interionic dimensionless distance is denoted by R; Z is the number of molecules in the unit cell, q_i is the charge of the ith ion, which we take as $+3$ for metal and -2 for oxygen, $(\mathrm{Mu})_t$ is the multiplicity factor, and t is the dimensionless magnitude of the reciprocal lattice vector, $t_{hkl} = (h^2 + k^2 + l^2)^{1/2}$ in a cubic lattice. In all our calculations the summation in equation (3) was terminated at $t_{hkl} = 12$ and corrected for the error introduced by neglecting the contribution from values of t greater than 12 (Templeton, 1955). Under these conditions the calculated Madelung energy was within 0·02% of the convergent value. The derivatives of M with respect to the positional parameters are evaluated in a straightforward manner by expressing the structure factors in terms of u, x, y and z (*International Tables for X-ray Crystallography*, 1952).

Although several mathematical treatments exist which improve the convergence of the repulsion term (Tosi, 1965), it was found more convenient to compute this term by direct summation. If we select the origin at one of the oxygen atoms, the position vector of the jth metal ion in the λth unit-cell may be written as

$$\boldsymbol{\varrho}_{j\lambda} = \boldsymbol{\varrho}_\lambda + \boldsymbol{\varrho}_j , \qquad (6)$$

where

$$\boldsymbol{\varrho}_\lambda = (\lambda_1 \mathbf{a}_1 + \lambda_2 \mathbf{a}_2 + \lambda_3 \mathbf{a}_3)/a_0, \lambda_1(\lambda_2, \lambda_3) = 0, \pm 1, \pm 2, etc., \qquad (7)$$

and

$$\boldsymbol{\varrho}_j = (j_1 \mathbf{a}_1 + j_2 \mathbf{a}_2 + j_3 \mathbf{a}_3)/a_0,\ 0 \le j_1, j_2, j_3 < 1 . \qquad (8)$$

The repulsion term then becomes

$$\begin{aligned} R &= c \sum_i 1/\varrho_i^n \\ &= c \sum_{j=1}^{32} \sum_\lambda 1/|\boldsymbol{\varrho}_\lambda + \boldsymbol{\varrho}_j|^n , \end{aligned} \qquad (9)$$

which is in a convenient form for evaluating derivatives with respect to the positional coordinates u, x, y and z. It may be shown that

$$\partial R/\partial x = nc \sum_{j=1}^{32} \sum_\lambda (j_1 + \lambda_1)/|\boldsymbol{\varrho}_\lambda + \boldsymbol{\varrho}_j|^{n+2} , \qquad (10)$$

with similar expressions for y and z, except that the subscripts of j and λ are 2 and 3 in the expressions for $\partial R/\partial y$ and $\partial R/\partial z$ respectively. It may also be shown that

$$\partial R/\partial u = -nc \sum_{j=1}^{24} \sum_\lambda (q_{ij} + \lambda_i)\,(\partial q_{ij}/\partial u)/|\boldsymbol{\varrho}_\lambda + \boldsymbol{\varrho}_j|^{n+2} \qquad (11)$$

where

$$q_{ij} = j_i , \qquad (12)$$

and

$$\partial q_{ij}/\partial u = \pm 1 , \qquad (13)$$

the sign of the last derivative and the value of i being functions of j. In this case the sum extends over the twenty-four metal ions in C_2 sites, those in S_6 being independent of u.

The minimum lattice energy was found by a combination of steepest-descent and Newton–Raphson methods (Margenau & Murphy, 1956). At the minimum, the four derivatives of the energy with respect to the positional parameters p_i,

$$\partial E/\partial p_i = \partial M/\partial p_i + \partial R/\partial p_i,\ i = 1, 2, 3, 4 , \qquad (14)$$

should vanish. Starting with a reasonable choice of u, x, y and z, the four derivatives as well as the average of their absolute values,

$$D = \sum_{i=1}^{4} |\partial E/\partial p_i|/4 , \qquad (15)$$

are calculated. The parameter corresponding to the derivative having largest absolute value is then changed by a fixed increment, Δp_i, the sign of which is determined by the sign of its derivative. The four derivatives and their average, D, are computed for the new set of positional parameters. If the new D is smaller than the old D, the above process is repeated; otherwise, one selects the second largest derivative, changes the corresponding parameter and proceeds as before. In this way a set of positional parameters yielding a minimum value of D is determined. Finally, the parameters are refined by obtaining corrections to them as

$$\Delta p_i = -(\partial E/\partial p_i)/(\partial^2 E/\partial p_i^2)\,, \qquad (16)$$

employing the linear terms of the Taylor expansion of $\partial E/\partial p_i$. The second derivatives are calculated numerically. This process is repeated until the corrections Δp_i become smaller than some preset convergence criterion, ε. The value of ε was such as to yield positional parameters correct to four significant figures.

Calculations have been carried out for a series of integral values of the exponent n ranging from 6 to 10. The range of the constant c was chosen to give lattice energies ranging from 3000 to 3500 kcal.mole^{-1}. All calculations have been made for a maximum ϱ_λ [see equation (6)] of 2·0, which corresponds to inclusion of all ions within a sphere of radius approximately 20 Å surrounding the central ion. Checks with a maximum ϱ_λ of 4·0 ($\sim$40 Å sphere) indicate that the equilibrium positional parameters are correct to within 0·0001 for $\varrho_\lambda = 2$.

Results and discussion

The results of minimization of the lattice energy are shown in Figs. 1–4. There are two ways in which these results can be compared with experiment. The first one requires a reliable value of the hardness parameter n and an equally reliable estimate of the cohesive forces not explicitly considered in equation (1), *i.e.* van der Waals forces, zero-point vibration energies and covalent contributions. In this case the extra cohesive energy is subtracted from the experimental Born–Haber-cycle value and the resulting net energy, together with the exponent n, may be used to determine the structural parameters from Figs. 1–4.

An estimate of the covalent contribution to the cohesive energy is difficult to make. In fact, it is customary to obtain semi-quantitative indications of covalent bonding in nearly ionic crystals through a comparison of the theoretical and the experimental cohesive energy. For a cubic lattice, the repulsive parameter n is usually obtained from measurement of the compressibility of the crystal. For a static solid,

$$V(\mathrm{d}^2E/\mathrm{d}V^2) = 1/K\,, \qquad (18)$$

where K is the isothermal compressibility. Consideration of the vibrational energy of the solid leads to somewhat more complicated expressions (Tosi, 1965). The thermodynamic data necessary to obtain repulsive parameters are not available for *C*-type oxides. These data, however, would be of little value for our purposes since the evaluation of the theoretical lattice energy requires knowledge of the structural parameters.

The van der Waals forces represent only a minor fraction of the cohesive energy in ionic solids (a few per cent), and their evaluation is subject to considerable uncertainty. The study of interionic forces in calcium fluoride by Reitz, Seitz & Genberg (1961), yields a van der Waals contribution of approximately 3% of the total lattice energy; the vibrational energy at room temperature amounts to 1% of the total energy. Although these contributions to the total lattice energy are relatively small, their effects on the structural parameters may not be negligible. It was felt, however, that inclusion of the van der Waals and vibrational contributions, with the consequent introduction of more parameters, would complicate the calculation unnecessarily. We have also not considered the effect of crystal field stabilization. This probably amounts to a few kcal.mole^{-1} for the $4f^n$ configuration (George & McClure, 1959) which is an order of magnitude smaller

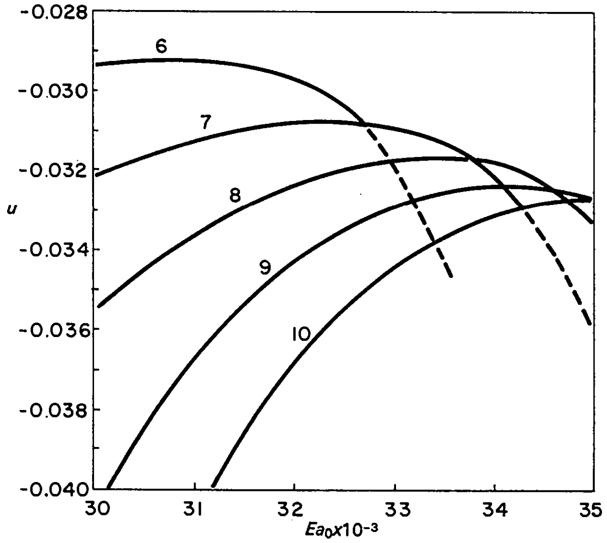

Fig. 1. Metal positional parameter, u, for cubic sesquioxide *vs.* lattice energy times lattice parameter, Ea_0 (kcal Å.mole^{-1}). The repulsive exponent n is shown next to the appropriate curve.

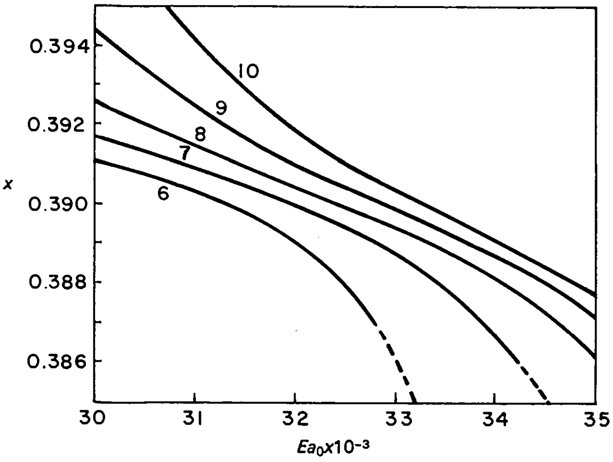

Fig. 2. Same as Fig. 1 for oxygen positional parameter x.

than the estimated error in M_2O_3 lattice energy. Of course, no crystal field stabilization is expected for Sc^{3+}, Y^{3+}, and In^{3+}.

Because of these difficulties with small corrections to the energy, comparison of theoretical and experimental structural parameters based on the *theoretical* lattice energies is hardly possible at present. It was decided, therefore, to use a different approach. The accuracy in the structural parameters of *C*-type oxides determined by X-ray techniques is highest in the case of the metal-ion parameter *u*. In typical single-crystal X-ray analyses the estimated error in *u* is of the order of 0·0001, while the errors in the oxygen parameters *x*, *y*, *z* are of the order of 0·001. For oxides for which single-crystal X-ray data are available (Y_2O_3, In_2O_3 and Sc_2O_3), we propose then to determine from Figs. 1–4 the lattice energy which corresponds to the experimental *u*-parameter (to within the estimated error) and then to use the energy so obtained to determine the corresponding oxygen parameters *x*, *y* and *z*. Furthermore, we require that the structural parameters correspond to energies not exceeding the experimental Born–Haber-cycle values, *i.e.* $|E_{\text{theo}}| \leq |E_{\text{exp}}|$, and that the theoretical energies be reasonably close to the experimental values.

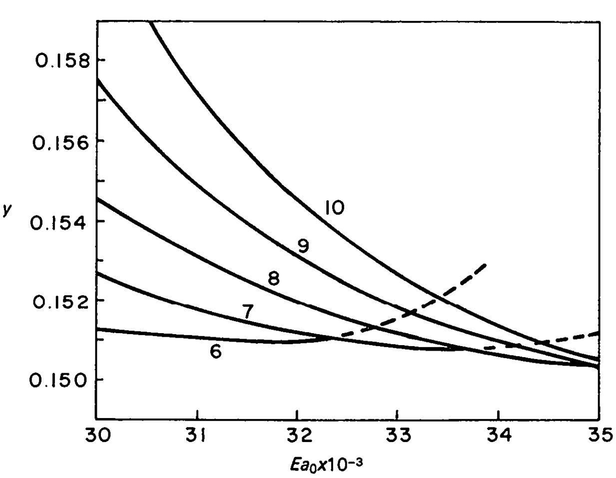

Fig. 3. Same as Fig. 1 for oxygen positional parameter *y*.

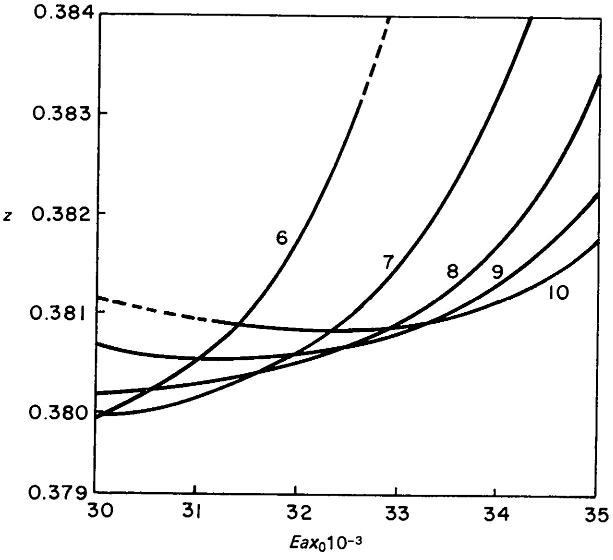

Fig. 4. Same as Fig. 1 for oxygen positional parameter *z*.

The following sources of thermodynamic data were used: Samsonov (1968) for the ionization potentials and heats of sublimation; Gibson & Harvey (1966) for the heats of formation of the lanthanide oxides and Y_2O_3; and Wyckoff (1964) for the lattice parameters. The heats of formation of In_2O_3 and Sc_2O_3 were those reported by Holley, Huber & Meierkord (1952) and by Mah (1962) respectively. The standard heat of formation of gaseous O^{2-} was taken to be 197 kcal.mole^{-1} (Gaffney & Ahrens, 1969).

Assuming that the accuracy of an ionization potential is roughly indicated by the number of significant figures quoted by investigators, we estimate that for most metals considered in this paper the probable error for the total ionization energy is of the order of a few kcal.mole^{-1}, with the exception of Gd, for which it may be as high as 30–40 kcal.mole^{-1}. The errors in sublimation energies are usually estimated to be 1–2 kcal.mole^{-1}, although in some cases discrepancies between the values obtained by different investigators are about 20 kcal. Accuracies of heats of formation are better than 1 kcal.mole^{-1}. According to a recent investigation (Gaffney & Ahrens, 1969) the heat of formation of O^{2-} is 197 ± 5 kcal. The uncertainty, however, represents merely the spread in the values obtained for a series of oxides and the actual error may be higher than 5 kcal. Apart from the uncertainty associated with $\Delta H_f(O^{2-})$, which is the same for all sesquioxides, the errors for the lattice energies are estimated to range between 10 and 50 kcal.mole^{-1}, probably being closer to 10 kcal.mole^{-1} for most oxides. The uncertainty in $\Delta H_f(O^{2-})$ will raise the latter value to approximately 25 kcal.mole^{-1}.

Yttrium, indium and scandium oxides

Table 1 lists the Born–Haber cycle lattice energies and experimental structural parameters for Y_2O_3, In_2O_3 and Sc_2O_3. The theoretically calculated structural parameters are also given in Table 1 for a number of repulsive parameters. Starting with Y_2O_3, we notice that the theoretical oxygen parameters obtained for three different values of *n* all agree with the experimental values to within better than 2%. In fact, the agreement is almost to within the estimated experimental error. On the basis of this agreement it is difficult to decide between the three choices of *n*. On the basis of lattice energies, however, it is seen that $n = 7$ is unlikely since the corresponding energy is 250 kcal.mole^{-1} below the experimental value. By analogy with CaF_2, we estimate the combined van der Waals and vibrational contributions in Y_2O_3 not to exceed 100 kcal.mole^{-1}, which would imply that 150 kcal.mole^{-1} is contributed by covalent bonding.

Such a high degree of covalency can hardly be consistent with the observed atomic arrangement in solid Y_2O_3. A value of n lying between 8 and 9 is more acceptable from the energy viewpoint. It is interesting that this value is in good agreement with Pauling's estimate (Pauling, 1927) for the Y–O interaction ($n=8{\cdot}5$). The agreement between experimental and theoretical structural parameters is thus surprisingly good. In fact, it is no worse than the agreement between single-crystal X-ray values and polycrystalline neutron diffraction data, the latter being $u=-0{\cdot}0314$, $x=0{\cdot}389$, $y=0{\cdot}150$ and $z=0{\cdot}377$ (Fert, 1962).

We next turn to In_2O_3. As seen in Table 1 there are appreciable discrepancies between the two single-crystal determinations. In both cases the intensities were obtained with the stationary-crystal, stationary-counter technique using the same crystal. Absorption and secondary extinction corrections were made and separate isotropic thermal parameters were used for In(1), In(2) and oxygen; the R values for both refinements were about 3%. The investigator concluded that both sets of data are equially reliable, the Cu data probably suffering from a very high absorption correction and the Mo data having a very large extinction correction. The discrepancy between these two determinations suggests that the errors in Y_2O_3 and Sc_2O_3 parameters obtained from single-crystal data may exceed the reported standard deviations.

As Table 1 shows, it is not possible to match either the z-parameter obtained from the Cu data or the y-parameter determined from the Mo data. As in the case of Y_2O_3, it is difficult to select the appropriate repulsion parameters on the basis of the agreement between the experimental and theoretical structural parameters. On the basis of energy arguments similar to those employed for Y_2O_3, we tend to reject $n=8$ and are inclined to favor n lying closer to 10. In the case of Sc_2O_3 we present the results of two independent investigations. In both cases single crystals were used. The data of Norrestam (1968), however, should be somewhat more accurate than those of Geller, Romo & Remeika (1967). The former collected single-crystal diffractometer data and applied absorption corrections; in the latter case film techniques were used and absorption corrections were not applied. In both cases, however, good agreement is achieved in structural parameters and lattice energy for $n=9$.

We have seen that the structural parameters obtained on the basis of a fairly simple theoretical model agree quite well with the experimentally determined parameters for reasonable choices of lattice energy. The results are encouraging enough to justify a more stringent test of the model. It appears that such a test may be provided by very accurate structural parameters for a number of rare earth sesquioxides.

Lanthanide oxides

On the basis of the results presented above we expect that the hardness parameters for lanthanide oxides should be approximately 9 or 10 and that the Ea_0 values computed from equation (2) should be quite close to the corresponding experimental values. All six experimental structure determinations of lanthanide oxides have been carried out by neutron diffraction using polycrystalline samples, and therefore the posi-

Table 1. *Positional parameters of sesquioxides of* Y, In *and* Sc

Compound	$Ea_0 \times 10^{-3}$ (kcal Å.mole^{-1})	$-u$	x	y	z	Remarks
Y_2O_3	−32·200	0·0328 (2)	0·389 (1)	0·154 (1)	0·378 (1)	exp.[a]
	−32·860	0·0330	0·3900	0·1520	0·3808	theo., $n=9$
	−31·730	0·0326	0·3907	0·1522	0·3805	theo., $n=8$
	−29·720	0·0326	0·3920	0·1530	0·3798	theo., $n=7$
In_2O_3	−33·900	0·0332 (1)	0·3905 (13)	0·1529 (11)	0·3832 (13)	exp., Cu *Kα*[b]
	−33·750	0·0333	0·3894	0·1519	0·3810	theo., $n=10$
	−32·600	0·0334	0·3903	0·1523	0·3806	theo., $n=9$
	−31·300	0·0332	0·3912	0·1528	0·3803	theo., $n=8$
	−33·900	0·0337 (1)	0·3912 (12)	0·1558 (11)	0·3796 (13)	exp., Mo *Kα*[b]
	−33·360	0·0338	0·3899	0·1522	0·3808	theo., $n=10$
	−32·360	0·0337	0·3906	0·1526	0·3806	theo., $n=9$
	−30·960	0·0337	0·3915	0·1532	0·3802	theo., $n=8$
Sc_2O_3	−31·900	0·0351 (2)	0·3928 (7)	0·1528 (7)	0·3802 (7)	exp.[c]
	−31·730	0·0349	0·3913	0·1535	0·3806	theo., $n=9$
	−30·280	0·0349	0·3922	0·1541	0·3802	theo., $n=8$
	−31·900	0·03546 (4)	0·39137 (11)	0·15477 (11)	0·38137 (11)	exp.[d]
	−31·490	0·0355	0·3917	0·1539	0·3807	theo., $n=9$
	−30·030	0·0355	0·3927	0·1546	0·3802	theo., $n=8$

[a] Paton & Maslen (1965).
[b] Marezio (1966).
[c] Geller, Romo & Remeika (1967).
[d] Norrestam (1968).

tional parameters, especially u, are not of sufficiently high accuracy. For these compounds, then, we follow a different method of comparison with experiment. The repulsive parameter is fixed at $n=9$, and the data of Figs. 1–4 are used to obtain u, x, y and z, employing Ea_0 calculated from Born–Haber cycles. Under the assumption that the repulsive exponent n does not vary along the lanthanide series, the variation of positional parameters is due entirely to variation of the experimental Born–Haber lattice energies. It should be pointed out though that the range of the experimental lattice energies for rare-earth oxides is not much larger than the probable error in E. In view of this, the small variations in calculated positional parameters may not be significant. The results listed in Table 2 show that for all rare-earth oxides the positional parameters are $u=-0·0332(4)$, $x=0·3902(4)$, $y=0·1521(4)$ and $z=0·3807(1)$.

As may be seen from Fig. 5, the calculated parameters are in good agreement with experimental measure-

Table 2. *Lattice energies and positional parameters for lanthanide sesquioxides*[a,b]

Compound		$-Ea_0\times 10^{-2}$ (kcal Å.mole^{-1})	$-u$	x	y	z
Pr_2O_3	*T*	331	0·0328	0·3898	0·1517	0·3808
	E[c]	—	0·0290	0·385	0·155	0·382
Nd_2O_3	*T*	329	0·0330	0·3900	0·1519	0·3807
Sm_2O_3	*T*	330	0·0329	0·3899	0·1518	0·3807
Eu_2O_3	*T*	329	0·0330	0·3900	0·1519	0·3807
Gd_2O_3	*T*	327	0·0332	0·3902	0·1522	0·3807
Tb_2O_3	*T*	331	0·0328	0·3898	0·1517	0·3808
Dy_2O_3	*T*	324	0·0336	0·3905	0·1525	0·3806
	E[d]	—	0·028	0·387	0·148	0·378
Ho_2O_3	*T*	326	0·0334	0·3903	0·1523	0·3807
	E[e]	—	0·0270	0·388	0·152	0·382
Er_2O_3	*T*	328	0·0331	0·3901	0·1520	0·3807
	E[e]	—	0·0330	0·394	0·149	0·380
Tm_2O_3	*T*	327	0·0332	0·3902	0·1522	0·3807
	E[d]	—	0·033	0·392	0·153	0·377
Yb_2O_3	*T*	326	0·0334	0·3903	0·1523	0·3807
	E[e]	—	0·0336	0·391	0·151	0·380
Lu_2O_3	*T*	329	0·0330	0·3900	0·1519	0·3807

[a] Theoretical values are calculated with $n=9$ and $|Ea_0|=|Ea_0|$ (exp).
[b] Theoretical = *T*, experimental = *E*.
[c] Eyring & Baenziger (1963).
[d] Hase (1963).
[e] Fert (1962).

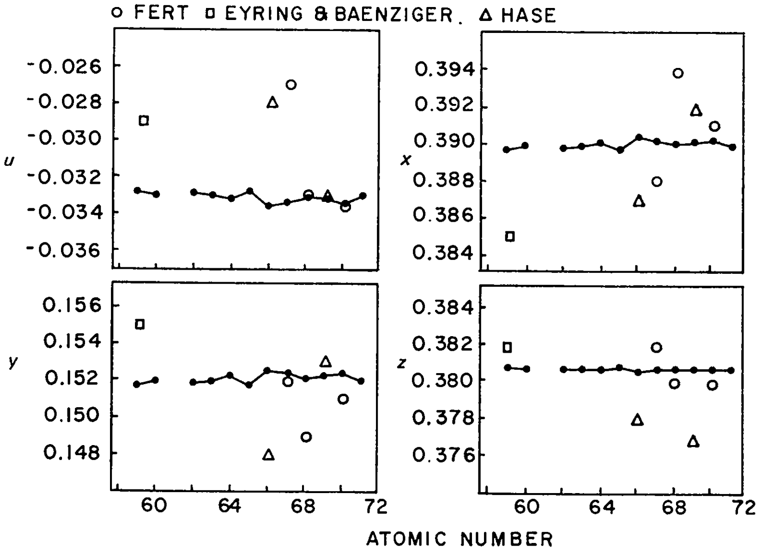

Fig. 5. Positional parameters u,x,y,z calculated from experimental lattice energies for lanthanide sesquioxides *vs.* atomic number of the metal. Experimental neutron diffraction data are represented by circles, squares and triangles.

ments for Yb_2O_3 and Tm_2O_3, and in fair agreement for Er_2O_3. Considerable discrepancies are found for Pr_2O_3, Dy_2O_3 and Ho_2O_3. The experimental Ea_0 value for Ho_2O_3 is the same as that for Yb_2O_3, and it is quite reasonable to assume the same value of n for both oxides. The structural parameters for Ho_2O_3 are then expected to be identical with those for Yb_2O_3. Although this appears to be nearly true for the experimental oxygen coordinates, the metal-ion parameter reported for Ho_2O_3 ($-0{\cdot}0270$) is completely inconsistent with the theoretical model for any reasonable choice of n and Ea_0. Similarly, the metal-ion parameters for Pr_2O_3 ($-0{\cdot}0290$) and Dy_2O_3 ($-0{\cdot}028$) disagree considerably with the theoretical predictions.

As mentioned earlier, the structural parameters available for the rare-earth oxides are not very accurate. This is especially true of the u parameters. Although it is rather unlikely that the holmium parameter determined by neutron diffraction could be off by 24%, a structure refinement based on single crystal data is obviously desirable for Ho_2O_3 as well as for other rare-earth oxides. Since the repulsive parameter is expected to remain virtually constant for this series, the cubic lanthanide oxides are ideally suited for further examination of the model. Initial results are encouraging and accurate structural parameters for this group of compounds are expected to suggest modifications to the model necessary to put it on a firmer basis.

Finally, we note an observation concerning the metal–oxygen bond lengths in the two M_2O_3 metal sites. Each S_6 metal ion is surrounded by six equidistant oxygen atoms, whereas six oxygen atoms surrounding the C_2 metal ion fall into three equidistant pairs. Marezio (1966) gave a qualitative explanation for this effect in terms of repulsive forces and noted that the average $M(C_2)$–O bond length is nearly equal to the value of the oxygen–metal distance for the S_6 site. Our calculations confirm this quantitatively: for all sets of theoretical parameters listed in both Tables 1 and 2, the reduced bond length in the S_6 site, as well as the average of the three C_2 bond lengths, is $0{\cdot}215$. This value is precisely the average M–O distance observed in many C-type sesquioxides (Geller, Romo & Remeika, 1967).

The arrangement of the six oxygen ions around the C_2 metal ion may be considered to represent a slightly distorted cube with two oxygen atoms missing from opposite corners of one face. From consideration of repulsive forces, Marezio (1966) suggested that the two oxygen atoms separated from both unoccupied corners by an edge of the imaginary cube should have the smallest M–O distance. The largest M–O distance should be found for the two oxygen atoms separated from either unoccupied corner by a face diagonal. This ordering of the three $M(C_2)$–O bond lengths is indeed observed for all single-crystal results and for all theoretical results listed in Tables 1 and 2. A different ordering is obtained with the experimental data for Pr_2O_3, Dy_2O_3, Er_2O_3 and Tm_2O_3. In addition, the average $M(C_2)$–O length differs substantially from the $M(S_6)$–O length for Pr_2O_3 and Er_2O_3. These results lend further support to the need for re-examination of the lanthanide sesquioxide experimental results.

Conclusions

It is shown that positional parameters of C-type sesquioxides may be calculated theoretically if the correct space group is assumed and experimentally determined lattice parameters and lattice energies are used. The results are in good agreement with X-ray structure determinations for Y_2O_3, Sc_2O_3, Yb_2O_3, Tm_2O_3 and Er_2O_3. Re-examination of the experimental results is suggested for In_2O_3, Ho_2O_3, Dy_2O_3 and Pr_2O_3. In the lanthanide series, the variation of calculated structural parameters is very small and mirrors that of lattice energies, with no smooth trend. With a probable error of 30 kcal.mole^{-1} in lattice energy the errors in structural parameters are estimated to be $(3\text{–}4)\times10^{-4}$ for u, x, and y and 1×10^{-4} for z. Since the range of the parameters calculated for rare earth oxides is of the same order of magnitude, the variations may not be significant. Our results show that for all rare-earth oxides the structural parameters are $u=-0{\cdot}0332(4)$, $x=0{\cdot}3902(4)$, $y=0{\cdot}1521(4)$ and $z=0{\cdot}3807(1)$.

Note added in proof: Recently very accurate structural parameters were obtained for Y_2O_3 from single-crystal neutron-diffraction data (O'Connor & Valentine, 1969). The parameters, $u=-0{\cdot}0327(3)$, $x=0{\cdot}3907(3)$, $y=0{\cdot}1520(3)$, $z=0{\cdot}3804(3)$, are in striking agreement with values predicted for $8<n<9$ (see Table 1).

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Structural Study of the Thorium Carbohydrides by X-rays and Proton Nuclear Magnetic Resonance: Evidence for Vacancy Induced Hydrogen Position Correlations

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The action of hydrogen on the hypo-stoichiometric monocarbides of thorium has been studied for various estimated carbon-vacancy contents in the homogeneity range of the carbide phase. The carbides can capture a considerable number of hydrogen atoms, and under saturation conditions, the ratio number of H_2 atoms/number of vacancies can be as high as 8. The structure of the carbohydrides remains f.c.c. during hydrogenation. The X-ray study of the variation of the cell parameter with hydrogen content showed it to behave very differently according to the initial carbon vacancy concentration. N.m.r. measurements likewise indicated, starting from certain hydrogen contents, a very rapid variation and exceptionally high values of the second moment calculated by integration of proton resonance spectra. These experimental results can be explained by the existence of strong correlations between the hydrogen atom positions in the carbohydride structure. These correlations would appear for sufficiently high hydrogen concentrations and are induced by the vacancies. They can be represented by configurations of pairs or triples of hydrogen atoms localized in the vicinity of the vacancy; the most probable configuration is that of pairs formed by one of the hydrogen atoms situated in the octahedral space left vacant by the missing carbon atom, the other being situated at one of the tetrahedral sites surrounding this vacancy.

The action of hydrogen on a certain number of the monocarbides of the transition metals Ti, Zr and Hf (Rexer & Peterson, 1964; Goretzki, Bittner & Nowotny, 1964; Goretzki, Ganglberger, Nowotny & Bittner, 1965; Yvon, Nowotny & Kieffer, 1967), and also on carbides of the lanthanide and actinide series, Y, Ho, Er, Th, U and Pu (Pascard, Lorenzelli & Dean, 1964) has already been observed. The hydrogenation of thorium carbides appears to be a complex process. Peterson & Rexer (1962) report the existence of two thorium carbohydrides ThC.ThH_2 (closed-packed hexagonal structure) and ThC.2ThH_2 (monoclinic) obtained by the action of hydrogen at 800°C on a low carbon-content ThC–Th mixture. However, Pascard *et al.* (1964) note that there is a reversible reaction of the single-phase thorium-rich monocarbide at medium temperatures (400°C), which gives rise to a face-centred cubic carbohydride structure by simple extension of the monocarbide unit cell. These structurally simple compounds form the subject of the present study. In particular, they offer favourable conditions for a study of the hydrogen atom positions in the lattice by nuclear magnetic resonance.

1. ACTION OF HYDROGEN ON THE THORIUM-RICH MONOCARBIDE

Experimental method

After having confirmed the absence of any reaction of hydrogen with the stoichiometric monocarbide ThC, we prepared a series of single-phased under-stoichiometric monocarbides. These compounds, which are obtained by direct reaction between the metal and a measured quantity of carbon, are prepared from a mixture of thorium hydride and graphite powder cold