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LATTICE ENERGY CALCULATIONS FOR VACANCY STRUCTURES

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Abstract Madelung energy calculations were carried out for a number of rare earth oxides including some with vacancy-containing structures. The calculated enthalpies of formation for PrO_2, Pr_2O_3, and Pr_9O_{16} (but not for Pr_7O_{12}) fall on a straight line when plotted as a function of the oxygen/metal atom ratio.

INTRODUCTION

For stoichiometric ionic structures, Madelung energy calculations are relatively straightforward. Difficulty is encountered when species are present that are nonspherical, ions having more than one charge of the same sign, or vacancies. In the first case, some type of multipolar expansion must be employed, but in the case of multiple charges combined with vacancies the situation is more difficult. In fact Madelung calculations of the latter type do not seem to have been reported heretofore.

Recently Blake[1] has devised a program for Madelung energy calculations that can be applied to all of the situations described above. It is based on Bertaut's use of spherical charge clouds in place of point charges in the lattice.[2] No overlap of charge clouds is permitted and the ionic radii are adjusted for this requirement. Prof. Blake has made his program available to us, and we have used it for the calculation of the Madelung energy E_M of both stoichiometric and vacancy-containing rare earth oxides, with particular emphasis on those of praseodymium.

OXIDE STRUCTURES

The structures and thermodynamic properties of the rare earth oxides have been intensively studied, especially by Eyring and his coworkers[3], for more than thirty years, and are reasonably well known. For oxides of the formula, M_nO_{2n-2}, with n varying from 7 to 11, the structures are based on the MO_2 fluorite lattice structure shown in Figure 1. Oxygen vacancies are formed along certain directions in the lattice. In the M_7O_{12} structure, the vacancies □ are formed along the $[111]_F$ direction as shown in Figure 2. Comparing this structure with that of the basic fluorite structure in Figure 1, it can be seen that metal-centered vacancy pairs are formed. In M_9O_{16} structures, planes of vacancy-centered pairs parallel to the a and c axes are formed with differing arrangements for other oxides. Below n = 7 it is postulated that oxygen intact $(2\bar{3}1)_F$ planes are

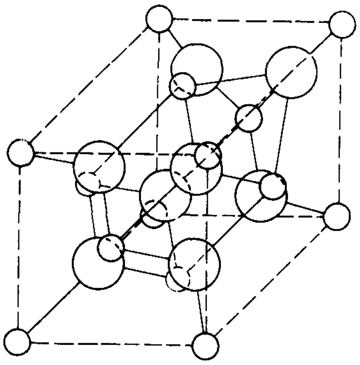
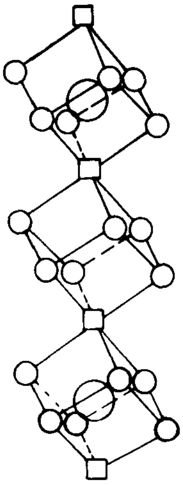


FIGURE 1. Fluorite unit cell.



M_7O_{12} STRUCTURE

FIGURE 2.

deleted progressively and the lattice is restored by a crystallographic shear mechanism. Martin and Hoskins[4-6] have attempted to provide a theory for the structures on the basis that coordination defects are formed consisting of the missing oxide anion, the six surrounding oxide anions, and the praseodymium ions, to form a $Pr_{7/2}\square O_6$ unit. This is sited in the lattice as described above for the various oxides. They argue that there is little interaction between neighboring coordination defects.

MADELUNG CALCULATIONS

In Table 1 are shown the results of our Madelung energy calculations for a series of oxides. The only comparisons available are for Pr_2O_3, Eu_2O_3, and TbO_2 from the work of Angelov[7,8]; the present values are 1-2% higher. Angelov compared the Madelung energies with experimental lattice

TABLE 1. Madelung energies (E_M) oxygen-to-metal atom ratio (n) number of metal atoms per formula unit (M) and ratio E_M/M

Structure	n	M	$-E_M$(kJ/mol)	$-E_M/M$(kJ/mol)
PrO_2	2	1	12127	12127
TbO_2	2	1	12681	12681
Pr_2O_3 (cubic)	1.5	2	14944	7472
Eu_2O_3 (nonoclinic)	1.5	2	15064	7532
UY_6O_{12}	1.71	7	71912	10273
$Zr_3Sc_4O_{12}$	1.71	7	69771	9967
Pr_7O_{12}	1.71	7	64637	9234
Pr_9O_{16}	1.78	9	94743	10527
$Tb_{11}O_{20}$	1.818	11	121582	11053

energies calculated using a Born-Haber cycle and found the former to be larger by a factor of about 1.16. This is due to the neglect of repulsion, van der Waals forces, and vibrational terms. In the calculations below we have estimated the lattice energies to be 0.86 times our calculated Madelung energies.

Using such estimated lattice energies we can obtain the enthalpies of formation of the non-stoichiometric oxides using cycles of the type shown in Figure 3 for the reduction of PrO_2 to Pr_9O_{16}. A similar calculation for the reduction of Pr_9O_{16} to Pr_7O_{12} gave a positive enthalpy value of 36177 kJ (the reverse sign of what is expected). Since all of the other values in the cycle are used in other calculations that give reasonable values, the Madelung energy for Pr_7O_{12} was examined further. Values of the Madelung energies were calculated using the coordinates for Pr_7O_{12} obtained by Von Dreele, et al.[12] and from the

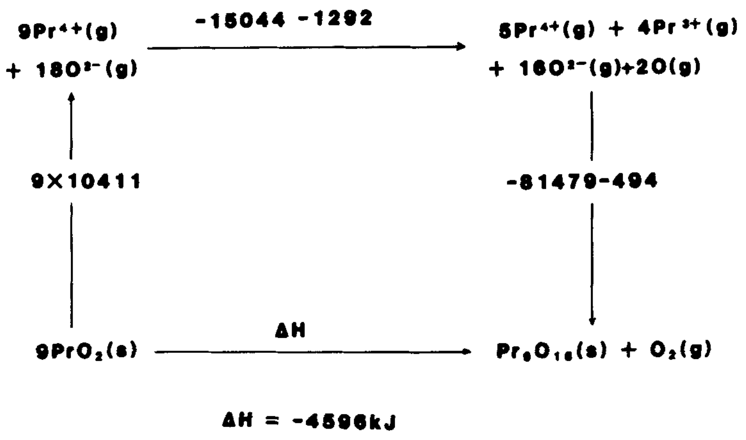


FIGURE 3.

Cycle for the reduction of PrO_2 to Pr_9O_{16}. The Madelung energies of Table 1 are multiplied by 0.86. The reference enthalpies for the processes $O_2 \rightarrow 2\,O$, $Pr^{+3} \rightarrow Pr^{+4} + e$, and $O + 2e \rightarrow O^{--}$ are taken from Refs. 9-11.

coordinates of UY_6O_{12} and $Zr_3Sc_4O_{12}$ as shown in Table II. Although the values differ by several thousand kJ, none are large enough to make the reduction of Pr_9O_{16} to Pr_7O_{12} have a negative enthalpy. At this point the reason for the discrepancy is not understood.

TABLE II Madelung energy values for Pr_7O_{12} using similar structures

Structure	$-E_M$(kJ)
Pr_7O_{12} Coordinates	64637
UY_6O_{12} "	66338
$Zr_3Sc_4O_{12}$ "	63139

The effect of moving the charges on the Pr ions in Pr_7O_{12} is shown in Table III. As is evident there is very little change, suggesting that migration of charges may be possible at higher temperatures. Nothing is known concerning the activation energy for migration, but it is probably considerably larger than the energy differences, since the oxides are not reported to be conducting.

TABLE III Effect of charge variation on Pr_7O_{12} Madelung energies (using $Zr_3Sc_4O_{12}$ coordinates)

Charge Shift	$-E_M$(kJ)
1-2	63139
1-3	63132
1-4	62932
1-5	63140
1-6	63129
2-6	63118
2-4	63138

The enthalpies of formation for the praseodymium oxides were calculated using a Born-Haber cycle and are plotted as a function of the O/Pr ratio in Figure 4. The value for Pr_9O_{16} (-1293 kJ/mol) falls nicely on a line connecting PrO_2 (-895) and Pr_2O_3 (-2104) but that for Pr_7O_{12} (-643)(not shown) is well below the line. If the straight line relation is valid, then the increase in lattice energy with increasing M^{4+} ions is offset by the large increase in the M^{3+}/M^{4+} ionization energy. It would also be in agreement with Martin's argument[4-6] of little interaction between coordination defects. However, it is

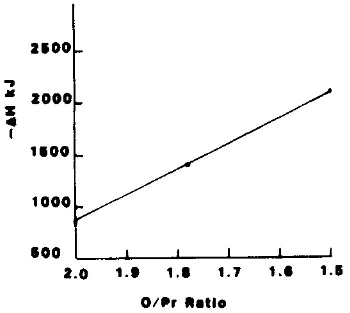


FIGURE 4. Plot of ΔH_f as a function of O/Pr ratio

in disagreement with the calculations of Parks and Barker[13] on the energetics of dispersal of defects in superlattices. In addition one is tempted to question the correctness of the M_nO_{2n-2} oxide formulae, but these are firmly established by known phase diagrams for these systems.[14]

Any experimental enthalpy of reaction values are going to depend on the nature of the structures between pure phases. If the transition from one lattice structure to another goes smoothly as oxygen is added or removed, the enthalpy will increase or decrease linearly. However, Inaba, et al.[15,16] find strong hysteresis effects in transitions between Pr_7O_{12} and Pr_9O_{16}.

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