The Crystal Chemistry of Complex Niobium and Tantalum Oxides: V. Electrostatic Energy Calculations

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Abstract

Madelung energies and site potentials are used to show that ordered forms of columbite and wodginite are much more stable than the disordered forms, but that a mixture of the component oxides has an intermediate electrostatic energy. An ordering scheme for wodginite in which metal sites X_1 and X_2 are disordered is marginally unfavorable. Madelung energy of fergusonites is not sensitive to the niobium coordination. Site potentials in $M-Nb_2O_5$ show that edge-shared octahedra at the corners of ReO_3 blocks are not ideal sites for Nb^{5+} and Ta^{5+}, so that in many structures the corners are joined by tetrahedra.

Introduction

Certain problems noted in Part I prompted the calculation of Madelung energies for several of the phases described there. The main problems are: 1. the ubiquitous occurrence of disordered phases, even in situations where radioactivity could not reasonably be invoked; 2. the non-centrosymmetric ordering scheme in wodginite and the resolution of the two "disordered sites" indicated by X-ray analysis; 3. the existence of the three fergusonite structures at room temperature, and especially the tetrahedral coordination of tantalum and niobium in two of them.

The ionic model has been successfully applied in solid state chemistry, despite the fact that in almost all compounds a degree of covalency is present (Sanderson, 1967; Levin, Syrkin, Dyatkina, 1969). The calculation of cohesion energies using the purely ionic model gives reliable results even for compounds that are not purely ionic, for reasons discussed by Nieuwpoort and Blasse (1968). Two studies of particular interest to the mineralogist are the prediction, later verified (Fleet, 1971; Tokonami, Nishiguchi, and Morimoto, 1972), of the cation vacancy ordering arrangement in pyrrhotite (Bertaut, 1953), and the calculation of structural parameters for the C-type sesquioxide, Y_2O_3 (Gashurov and Sovers, 1970). The familiar rules of Pauling (1960), which are still widely used by mineralogists and crystallographers, are approximations to the Madelung energy approach. Limitations of the concept of "lattice energy" in relation to geochemical systems have been reviewed (Urusov, 1965).

Most previous studies of lattice energies report only the Madelung constants; however, the stability of ions in individual sites must also be considered (Van Gool and Piken, 1969). In a point-charge crystal, the electrostatic potential at a charged point is defined as the potential for that site after the corresponding charge has been removed. The site potential must have the correct sign relative to a particular ion, and its absolute value is also important. For an oxygen ion, for example, the anion must "see" a minimum stabilizing potential of about 9eV/mole (Adler, 1970) in order to stay in the site. In terms of the units given in Table 1, this corresponds to an absolute value of at least 0.7. In practice, each ion seems to have a preferred range of site potentials.

When comparing the relative stability of structures, it must be remembered that the Madelung energies are usually aproximately 90 percent of the total energy. The next largest term is the repulsion energy term. For the oxides discussed in these papers the differences between the repulsion forces will be negligible when the cation coordination numbers are the same in both arrangements, but the difference may become significant when structures containing cations with different coordination numbers are compared and contrasted. It should be remembered that a higher value of lattice energy corresponds to a more stable structure; the lattice energy of the dis-

TABLE 1. Lattice Energies and Site Potentials

	Electrostatic Lattice Energy kcal/mole MO_2	Anion Site Potentials esu charge/Å	Cation Site Potentials esu charge/Å					
			2+	3+	3½+	4+	4½+	5+
a. Ordered and disordered columbites								
Ixiolite (disordered)	3069	1.67				-3.49		
Columbite $MnNb_2O_6$	3519	1.46 1.63 2.06	-2.13					-3.40
$MnO + Nb_2O_5$	3314*							
b. Centrosymmetric wodginites								
Graham & Thornber	3219	1.60 1.63 1.93 1.99	-1.74			-2.85		-3.41
Grice	3284	1.36 1.62 1.79 2.59	-2.25			-2.69		-3.45
Electrostatically balanced (Grice)	3196	1.57 1.69 1.82 2.17			-2.61 -2.74		-3.25	
$SnO_2 + MnO + Nb_2O_5$	3263*							
c. Non-centrosymmetric wodginites								
$Ta\ Mn\ X^{4+}\ X^{5+}\ O_8$	3673	1.06; 2.17(21)	-2.11			-3.43		-3.85 -3.80
$Ta\ Mn\ X_1^{4.5+}\ X_2^{4.5+}\ O_8$	3651	1.13; 2.14(25)	-2.10				-3.69 -3.60	-3.68
$Ta\ Mn\ X^{4.8+}\ X^{4.2+}\ O_8$	3624	1.21; 2.05(31)	-2.10			-3.47		-3.68 -3.95
d. Fergusonites								
T (tetrahedral) Wyckoff	3130	1.66		-2.23				-3.54
Komkov	3159	1.60		-2.08				-3.79
M (tetrahedral)	3143	1.53 1.61 1.74 1.85	-2.33 -2.32					-3.51 -3.50
M' (octahedral)	3125	1.54 1.75		-2.30				-3.51
$Nb_2O_5 + Y_2O_3$	3011*							
e. Oxides								
$M-Nb_2O_5$	4448* ($MO_{2.5}$)	1.19 1.20 1.38 1.39 1.94 2.52 3.23						-2.65 -3.59 -4.13
MnO**	1047 (MO)	1.58	-1.58					
Y_2O_3†	1573 ($MO_{1.5}$)							
SnO_2††	3109							

*   The tetragonal form of Nb_2O_5 was used in the calculations as it is much easier to compute. The stable room temperature form will have a higher lattice energy, so these are minimum values.
** Calculated from NaCl.   † Calculated from Mertens & Zemann (1966).   †† Van Gool and Piken (1969).

ordered form of a structure may gain an entropy contribution of the order of 100 kcal/mole.

Energy Calculations

Electrostatic energies and site potentials were calculated using a modified Ewald method (Slater and Decicco, 1963; Ewald, 1921) assuming a fully ionic structure.

1. *Disordered Phases*

The frequent occurrence of disordered or partly disordered columbites and ixiolites poses a problem in view of the abundant evidence of the last few decades that in oxides the ordered state is inherently the most stable (Wadsley, 1955). These minerals have normally had every advantage in their approach to their present state; having crystallized as large single crystals in a pegmatite, they have often cooled without interruption to ambient temperatures.

A calculation of the electrostatic energy of the ordered and disordered forms confirms that the former is far more stable from this point of view (Table 1, a).

We have also calculated Madelung energies for Nb_2O_5 and for MnO (see section 4, below, and Table 1, e), and it is evident (Table 1, a) that the compound $MnNb_2O_6$ is not much more stable than a physical mixture of the oxides. In addition, the disordered form is far less stable than a mixture of the component oxides, even allowing a reasonable entropy contribution. This strongly supports our idea that the disorder is introduced through attempted disproportionation of the ordered phase. However, all the site potentials for the ordered and disordered forms are reasonable and typical for ions of the various types.

2. Ordering of Wodginite

Although X-ray structure determination has shown (Part II) that the non-centrosymmetric space group Cc is preferred for the wodginite structures, it has not indicated the reason for this preference, nor has it fully resolved the ordering scheme.

The electrostatic energy calculation (Table 1, b and c), even assuming sites X_1 and X_2 to be completely disordered, clearly shows the superiority of the non-centrosymmetric structure over any of the centrosymmetric schemes proposed (Part II). The improved lattice energy, however, has been attained at the expense of a rather unfavorable anion site potential for oxygen O_3, which is listed first in Table 1, c. The mean value of the remaining seven anion site potentials is also given.

We cannot be dogmatic about the ordering on cation sites X_1 and X_2 because of the small differences involved. The greatest electrostatic lattice energy is attained if X_2 is filled with Nb^{5+} and Ta^{5+}, and all the vacancies are present on site X_1, giving it a net charge of $4+$. This assignment is consistent with the site potentials, but does not seem to accord with the size difference between X_1 and X_2. It is perhaps worth noticing that in the structure with the highest lattice energy, most of the anion site potentials are closely similar.

The prerequisites for the formation of the wodginite structure are still not very clear, but in view of its lattice stability (greater than columbite) it is not surprising that wodginite is more widespread in nature than has been supposed.

The energy calculations on the two structures proposed by Grice (1972) and by Grice and Ferguson (1974) are of very great interest, since the partly disordered model was derived from a consideration of Pauling's electrostatic valency rule (Pauling, 1960) and yet gave an inferior electrostatic lattice energy. A glance at the site potentials (Table 1, b) shows that the electrostatic balancing procedure has given a much more even distribution, but this is not favored by the overall energy. The individual coordination polyhedron is evidently too small a unit on which to base electrostatic valency considerations, especially where highly charged ions are involved. Wadsley (1967) has already taken issue with Pauling's third rule (face- and edge-sharing of polyhedra), and has proposed that in lattice compounds such as those described in these papers, the group should replace the single polyhedron as the basic unit of structure. With this idea we agree. Wadsley supposed that the stability of the group was an indication of a strong covalent bonding system extending from each metal atom well beyond the immediate ligands to include other members of the group. Our results indicate that the formation of a strong covalent bonding network is not a necessary condition for the stabilization of structural units larger than the coordination polyhedron. We also believe—and the following results on fergusonite are further evidence of this—that unusual or distorted coordination does not necessarily imply covalent bonding as opposed to ionic bonding, since the electrostatic energy alone is of sufficient magnitude to stabilize structures in which they occur. This has been discussed recently by Baur (1970).

The electrostatic valency rule has also been shown not to hold for water molecules in crystalline hydrates (Ferraris and Franchini-Angela, 1972).

Again the electrostatic energy associated with the component oxides is greater than that of the disordered structure. It is of the same magnitude as the energy calculated for the centrosymmetric structure, but the non-centrosymmetric structure has a considerable advantage.

3. The Fergusonite Structures

Structures have been determined for three forms of fergusonite as discussed in sections 4a and 4b of Part I. In view of the uncertainty as to the oxygen parameter of the tetragonal form, the coordination of the (Ta,Nb) atoms, and which structure is stable at room temperature, we have calculated lattice energies and site potentials for each structure (Table 1, d).

The lattice energies for the tetrahedral and octahedral phases are quite similar, and the cation and anion site potentials are remarkably consistent for all structures. Evidently there is no fundamental change in bonding between the structures, and the four second-nearest anions to (Ta,Nb) must be considered part of the coordination polyhedron. It appears from the lattice energies that Komkov's (1959) oxygen parameters for the tetragonal structure are more likely to be correct than those of Wyckoff (1965). Only second-nearest bonds are affected. In Komkov's structure, the niobium is more closely 8-coordinated and the yttrium has a somewhat better average Y-O distance of 1.10 Å as compared to 0.93 Å in the Wyckoff structure. There is no clear-cut indication whether M or M' is the thermodynamically stable phase at room temperature, although the figures favor the M form. The overall lattice energy for the fergusonites is somewhat less

than that of the columbites and wodginites because of the larger size of the A cation, which increases the average inter-atomic distances. It is of the same magnitude as the sum of the component oxides, which is consistent with the metamict nature of many fergusonites.

4. *The Pure Oxides*

In order to compare the lattice energies of the compounds with those of the component oxides, it was necessary to obtain figures for the latter.

SnO_2 has been tabulated by W. Van Gool and A. G. Picken (1969).

MnO is easily calculated from the results for NaCl.

Y_2O_3 can be derived from the Madelung constant determined by Mertens and Zemann (1966).

Nb_2O_5 had to be calculated *ab initio*. Of the two complete structures available, by far the easiest to calculate was the tetragonal structure of M-Nb_2O_5 (Mertin, Andersson, and Gruehn, 1970). This is not the most stable form, and its electrostatic energy might be expected to be somewhat lower than that of the room-temperature form. The site potentials calculated for this structure are very informative (see Table 1, e). Of the cation sites, the very high potential of -4.13 is found for the octahedra in the center of the ReO_3-type block. This is a site normally occupied by a 6-valent ion. These are understandably linked along c by oxygens with low site potentials. The low cation potential of -2.65 occurs in octahedra sharing edges at the corners of the ReO_3-type blocks, and the high oxygen-site potentials link these octahedra along c. The other anomalously low oxygen-site potential links pairs of edge-sharing octahedra in the edges of the ReO_3 blocks.

Our calculations thus show up the "weakness" in the structure and indicate why the corners of ReO_3 blocks in the niobate block structures are more often linked by means of a tetrahedral niobium atom than by edge-shared octahedra.

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