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Some General Aspects of Solid Oxides*

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In the application of solid oxides to actual materials, problems selections modifications, and sometimes molecular engineering are necessary. Some semiquantitative tools are reviewed with attention to broad applicability rather than to a detailed knowledge of special materials. The electrostatic model is very useful for many oxides. If applicable, computer techniques permit the rapid calculation of lattice self-potentials, potentials at interstitial sites and field strengths at ionic sites. Complicated irregular structures are equally assessible as highly symmetric structures. Some recent calculations in V_2O_5 and MoO_3 are quoted as examples. Another tool is the full use of crystallographic data, which are available for many oxides. Small deviations from the real positions of the ions can lead to useful idealizations. The electrostatic energies of the real and the ideal structure give a first order estimate of the usefulness of the idealizations. The concept of krypto-modifications is very helpful in this context, be it more in a qualitative than in a quantitative interpretation. The solid solubility of MoO_3 in V_2O_5 is used as an example.

Introduction

Since 1968 the research program of the Inorganic Chemistry Department of the State University, Utrecht, has been directed to fundamental problems of energy storage and energy conversion. From this very broad interdisciplinary field subjects are selected which can be studied by using techniques and theories of solid state chemistry (mainly oxides), catalysis, electrochemistry, and coordination chemistry. This explains why solid oxides are just a part of the present activities. It will be obvious that the use of the available knowledge of oxides is more relevant for the present program than to try to extend the knowledge of one special material in detail, although sometimes this may be necessary (V_2O_5, In_2O_3). The broad application of the available knowledge of oxides to specified problems requires generalization and simplification rather than specialization. The present contribution is based upon a selection of the methods which we try to develop to that end.

One of the most difficult aspects of the exploration and modification of solid oxides is the perplexing variety of structures (*1*) and phase diagrams (*2*). Many of the sophisticated approaches in chemical bonding and in the relationships between structures and properties fail when the structures of the materials become irregular. One has introduced many concepts to explain irregular properties, for example covalent bonding vs ionic bonding, crystal field and ligand field corrections, polarization, Jahn–Teller effect, cation interaction, etc. Their quantitative application, however, is very cumbersome when the structures of the materials are irregular. Sometimes the reasons for irregularity do not apply, although the materials are irregular. Examples at V_2O_5 and In_2O_3 in which we became interested in connection with a special set up of fuel cells (*3*) and with the related oxidation of CO to CO_2 (*4*). In these materials, crystal fields, etc. do not seem to be the major cause for irregularity of the structure. Another example is β-Al_2O_3 which plays an important role in rechargeable

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batteries (*5*). Whenever a compound fulfills the condition of being "ionic," it is β-Al_2O_3 and still its structure is very particular (*6*).

In relation to another subject (*7*) we were confronted with the stability of cubic and hexagonal perovskites: Do the hexagonal perovskites qualify for one-dimensional metallic or superconduction? Polarization has been suggested as an important factor for the stability of hexagonal perovskites (*8*). Especially the problems concerning β-Al_2O_3, the perovskites, the irregularities of structures and phase diagrams induced the approach outlined in the forthcoming sections.

Ionic Model

The history of the ionic model is long and well known. A few aspects are of importance for the present discussion. Obviously, there are many materials for which the ionic model is not an acceptable description, but when it applies the electrostatic contributions can be calculated completely. The present computer facilities permit precise calculations, whereas earlier use of the theory was sometimes vague or very approximative. Large numbers of atoms per unit cell and the lack of symmetry are no longer prohibitive for complete calculations.

For the calculation of the electrostatic energy the potential at the lattice sites must be known. For other calculations, for example in the case of diffusion, the potential at interstitial sites is relevant. Both types of potential can be calculated with the formula developed by Ewald (*9*). The computerized form (*10*) requires the position of the ions and their charges as input data, together with the dimensions of the unit cell. When the potentials at the symmetrically different ion positions have been calculated, the Madelung constant and the electrostatic energy are known at once.

When using the ionic model in specific problems, polarization is often suggested to apologize for the fact that the structure with the lowest electrostatic energy is not prevailing. The concept polarization has been used in many different interpretations, some of them being rather vague. However, when it occurs in an ionic approach exact field strengths should be used. Weenk and Harwig recently went through the details of the methods to calculate the field strength in a general ionic lattice (*11*). Convergence and computation time were studied using the Ewald formulas and the Bertaut method (*12*). The field strength and its direction is obtained with reasonable computer time for any point in any crystal.

Some Applications

Calculations of potentials and field strengths are useful in situations where a first order approximation to the involved energies is important.

One of the first applications was with respect to the major causes for the occurrence of *p*-type or *n*-type conductivity in oxides (*13*). This question is in the literature often related to the question whether a cation vacancy or an anion vacancy is most favorable. Although simple approaches, such as the larger volatility of oxygen than of metals, were disapproved long ago, another generalization is still sometimes used. This generalization originates from the studies of simple compounds, such as NaCl, ZnO, etc., where the positions of the anion and cation are symmetrically equivalent. In an electrostatic approach the major energy contribution to remove an ion will be the same for anion and cation. However, in less symmetric compounds this contribution will be different for anions and cations, as is immediately obvious from the lattice self-potentials (see Table I).

A second application is with respect to crystal field correction. Analytical formulas have been developed to calculate the potential

TABLE I

	Potential (V)		Ratio
	Cation site	Anion site	Cation:anion
Cu_2O	−12.91	11.04	0.856
ZnO	−12.15	12.15	1.000
Cr_2O_3	−11.79	12.85	1.090
SnO_2	−10.84	12.44	1.148

at some distances from the center of a tetrahedron, octahedra, etc. (*14*).

These potentials are used in the calculation of the crystal field. However, it is unnecessary to limit the calculations to the surrounding four or six ions—the potentials can be calculated taking the complete lattice into account. Recently, these calculations have been applied in connection with photon electron spectroscopy.

In another application, precise values of lattice potentials, Madelung energies, and field strengths at anion sites in spinels were required. A fairly complete survey of the relevant data of spinels is now available (*15*).

Field strengths have been calculated at certain sites in a large number of compounds (*11*). A good agreement between the Bertaut series and the Ewald approach was obtained. Interesting is the large difference in field strengths for the different sets of oxygen ions in, for example, MoO_3 and $PbTiO_3$ (Table II).

A more extensive investigation of the influence of the field strength on the stability of hexagonal and cubic perovskites is in preparation (*16*).

It will be obvious that the availability of programs for calculating the aforementioned properties is very stimulating for answering the many questions about stability which arise regularly in materials research.

The broadness of the field in which it can be used is in our approach more important than the accuracy which can be obtained with sophisticated calculations for special materials. Much of the philosophy behind our approach to materials research coincides with the ideas formulated by Phillips (*17*).

Structural Approach

Another important approach to material problems is the qualitative use of available structural information. Generally, two concepts are frequently applied in the description of oxides, viz the filling of tetrahedral and octahedral holes in close-packed oxygen layers and the use of tetrahedral and octahedral units in building the total structure. In spite of their very usefulness both concepts have their limitations:

(1) A realistic look into the interstitial space of a close-packed structure shows a voidal, somewhat continuous space. Although we can recognize points with a tetrahedron or octahedron next neighbor surrounding, the relevance of the continuity of that voidal space is the major aspect when diffusion phenomena are involved.

(2) The close-packed oxygen-ion lattice is rather surprising as a building theme,

TABLE II

FIELD STRENGTHS AT ANION SITES

Compound	Ion site[a]	Position[a]			Field[b] strength	Field direction[c]		
MoO_3	$O^{2-}(1)$	0.015	0.23	0.25	17.3	−0.145	1	0
	$O^{2-}(2)$	0.56	0.1	0.25	8.7	0.76	1	0
	$O^{2-}(3)$	0.525	0.435	0.25	4.2	−0.9	1	0
$PbTiO_3$	Pb^{2+}	0.0	0	0	1.9	0	0	−1.0
	Ti^{4+}	0.5	0.5	0.541	1.49	0	0	−1.0
	$O^{2-}(1)$	0.5	0.5	0.112	7.48	0	0	−1.0
	$O^{2-}(2)$	0.5	0	0.612	1.29	0	0	+1.0

[a] Data according to Wyckoff (*1*).
[b] In V Å^{-1}.
[c] Proportional to the value V. Å^{-1} along the axes.

since ionic charges of one sign try to stay away from each other. Thus, the inclusion of, for example, Ba^{2+} ions in the close-packed oxygen layers in hexagonal perovskites can be considered normal rather than surprising.

(3) The use of tetrahedra and octahedra as building units is a very powerful method in the description of structures. Coupling of octahedra, for example, is a necessary tool in the description of the ordered disorder in shear structures (*18*). However, it remains important to remember that along the lines used to picture the tetrahedra or octahedra, repulsive forces are acting. Although the coherence of the used units originates from the cations, "empty" units do occur in the description on an equal footing as "filled" units. Here again the repulsive forces seem to be a better aid to describe structures than the attracting forces.

These remarks are not to disapprove the use of these concepts for situations in which they are useful, but rather to point out limitations of their use in *all* situations. This becomes obvious when more irregular structures are considered.

Irregular structures occur in V_2O_5 and In_2O_3, which are relevant materials in our approach. More detailed studies have been published (*19–21*) and are in progress (*22, 23*).

Limiting the discussion to V_2O_5, one might wonder why its structure is irregular. It has been described with irregular octahedra (*24*) (6-coordination), with distorted trigonal bipyramidal coordination polyhedra of oxygen around vanadium (*25*) (5-coordination) and with tetrahedra in a two-dimensional network (*26*) (4-coordination). Octahedron coupling leads to zigzag shaped rows. The more accurate determination of lattice position is from Backmann et al. (*27*). All these descriptions might give the impression that V_2O_5 is a particular material very different from, for example, spinels.

In our approach we don't wonder about the fact that V_2O_5 exists, we assume that the ionic model is an acceptable first order approximation, and we conclude that its structure must be irregular. The following data illustrates these statements.

Assume for a moment that we try to build V_2O_5 from a close-packed oxygen-ion structure. The cubic unit cell in that structure contains four O^{2-} and thus 12 O^{2-} per three unit cells. We have to add four V^{5+} and to remove two O^{2-} in order to come to the composition V_4O_{10} per three unit cells. Comparison with the real structure shows that the tetragonal unit cell with $a = 11.733$ Å, $b = c = 3.911$ Å, $V = 179.5$ Å^3 and with the ion positions indicated in Fig. 2A can be considered as a twice idealized structure.

The field strengths have been calculated for all ion positions in this idealized structure. They are indicated in Fig. 1 after multiplication with +5 for the cations and −2 for the anions. Readjustion of the structure cannot occur exactly according to the acting forces, since V^{5+} and O^{2-} will be on a collision course. The V^{5+} shifts farthest away from its original

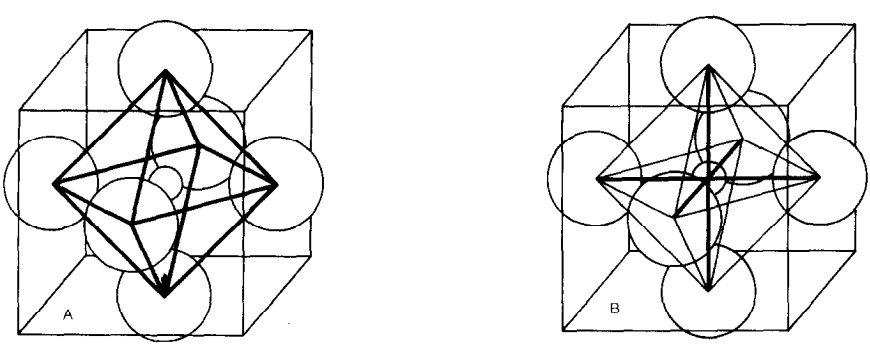

FIG. 1. Repulsive forces (A) rather than attractive (B) forces are used in schematic representations of structures.

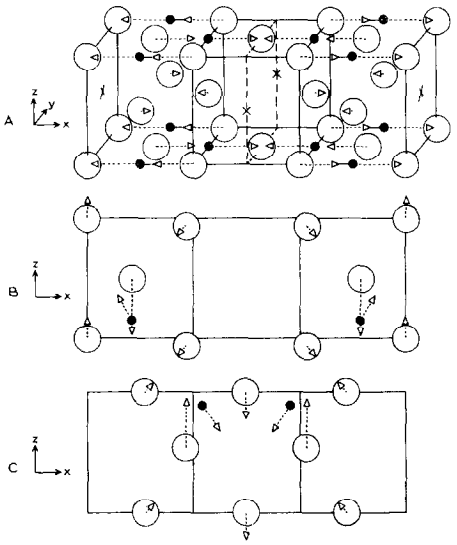

FIG. 2. Structure of V_2O_5 and electrostatic forces acting upon the ions. A. Position of ions and lattice dimensions idealized. B. and C. Actual positions and dimensions. B: $y = 0$, C: $y = 0.5$.

position together with smaller shifts of the O^{2-} ions and a readjustment of the lattice parameters to $a = 11.519$ (−1.82%), $b = 3.564$ Å (−8.9%), $c = 4.373$ Å (= +11.8%), $V = 179.5$ Å^3. All shifts occur perpendicular to the b-axis. The final positions and the remaining forces are indicated in Figs. 1B and 1C. Full details of the calculations will be published (*28*).

In this view the structure of V_2O_5 is described as a closepacked oxygen lattice with distortions following from the stoichiometric composition. This is important when doping of V_2O_5 with MoO_3 is studied.

Lattice self potentials and field strengths on lattice points were calculated for MoO_3 using the crystal data of Kihlborg (*29*). For the idealized structure the cell dimensions and the ion positions were adapted. Again a close-packed oxygen lattice can be used for the basic description. Fig. 3A shows the forces acting on the ions in an idealized lattice on idealized positions, whereas Figs. 3B and 3C show the actual positions in the real lattice.

The electrostatic energies of the different configurations are summarized in Table III.

Solid solubility of MoO_3 in V_2O_5 is readily understood in terms of kryptomodifications. This concept was used earlier for a quantitative approach to the descriptions of grossly nonstoichiometric oxides (*26*). Presently, its application is directed to the qualitative understanding of the formation of solid

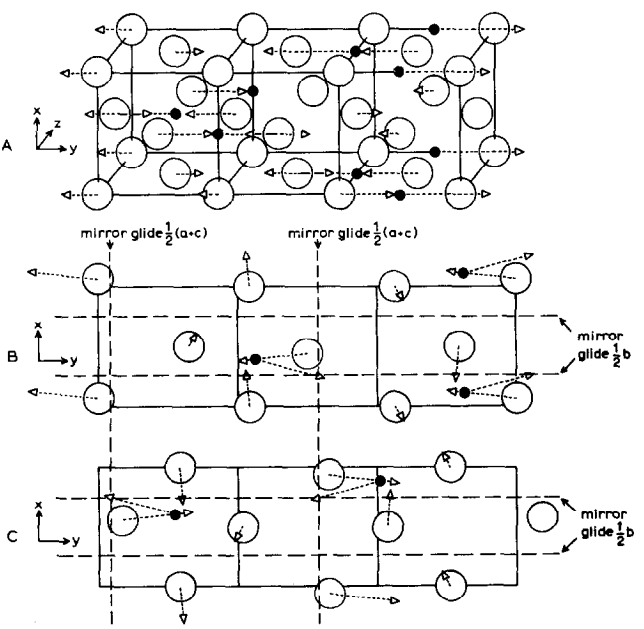

FIG. 3. Structure of MoO_3. Compare Fig. 2. B: $z = 0$; C: $z = 0.5$.

TABLE III

ELECTROSTATIC ENERGIES OF V_2O_5 AND MoO_3 (kcal mole^{-1})

Unit cell Position of ions	Ideal[a] Ideal[d]	Real[b] Ideal[e]	Real[b] Real[f]	Kryptomodification[c]	Volume unit cell (in all cases)
V_2O_5	8880.6	8772.1	9434.8	8879.1	179.5 Å^3
MoO_3	5411.3	5350.7	6057.7	6037.4	202.9 Å^3

[a] V_2O_5: $a = 11.733$ Å, $b = c = 3.9111$ Å. MoO_3: $a = c = 4.075$ Å, $b = 12.224$ Å.

[b] V_2O_5: $a = 11.519$ Å, $b = 3.564$ Å, $c = 4.373$ Å. MoO_3: $a = 3.963$ Å, $b = 13.855$ Å, $c = 3.696$ Å.

[c] V_2O_5 in the real MoO_3 structure, after removing two O^{2-} per unit cell. MoO_3 in the real V_2O_5 structure, after adding two O^{2-} per unit cell.

[d] Compare Fig. 2.

[e] Compare Fig. 3.

[f] V_2O_5: See Ref. (*1*) for positions. MoO_3: See Ref. (*29*) for positions.

solutions. In the present case the solid solution can be described as a more or less ideal solution of V_2O_5 and MoO_3 in a structure which fits into the V_2O_5 structure. This extrapolated MoO_3 structure is a nonexisting kryptomodification. The Gibbs free energy of the kryptomodification will be higher than that of the real MoO_3 structure.

According to the electrostatic calculations (Table III), this additional energy will not be very large and an extensive range of solid solution can be expected. The excess of oxygen originating from the composition difference between Mo_4O_{12} and V_4O_{10} can fill the empty sites in the close-packed oxygen lattice of V_2O_5. Other idealizations of the V_2O_5 structure, which were mentioned already, are not better than the close-packed layer approximation used above. However, doping with other oxides, might enforce one of these descriptions to become predominating or, as in the case of $V_{16}O_{23}$, might demonstrate which ions of the V_2O_5 structure will disappear first.

In conclusion, the major features of the irregular structure of V_2O_5 and some of its derivatives can be made plausible with the assumptions used to describe the more regular structures. This method of simplification is more fruitful in understanding and guiding the modifications of V_2O_5 by doping or reduction. The detailed study of the real structure and properties of V_2O_5 is less useful for this approach.

Finally, the approach outlined in this paper has contributed very much to the understanding of the major aspects in some other problems, for example fast ion conduction. Electrostatic calculations together with structural considerations have revealed the conditions for high ionic conduction in solids in such a way that the theory might guide the selection of new materials (*27*).

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