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The Cation Array of the Oxyhydroxides of Trivalent Metals

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The structures of the oxyhydroxides of trivalent metals, *M*OOH, are analyzed in terms of their cation arrays. For *M* = Al, Ga, In, Sc, Mn, Y, and *Ln*, the cations form aggregates which can be derived from the structures of their parent metal. However, the compounds of the 3*d* transition metals, V, Cr, and Fe, show *M–M* distances which are expanded with respect to those of their metallic nets. These distances are on the order of 3.00 Å and coincide with the *M–M* distance of the next *p* element, in this case Ga. This could be interpreted in terms of the charge transfer from the *d* orbitals to the metal *p* orbitals via the O atoms. In the case of Yb, a tetragonal YbOOH phase is stabilized whose cation array is a distortion of fcc Yb in which the O^{2-} and the OH^- anions are inserted into the metallic net without any volume increase. © 1997 Academic Press

INTRODUCTION

In previous papers (1–6) we have reported examples of how the cations, in inorganic solids, are not situated at random but they reproduce topology and distances of the parent metal. Thus, the structures of oxides are regarded as the metal structure, sometimes deformed and sometimes opened up by the inclusion of anions. This feature, which is to be expected in compounds with unsaturated valences in which electrons nontransferred to the anions can be used in the formation of metal–metal bonds (as, for example, in alkali metal suboxides or in subhalides of both transition metals and lanthanides), is also observed in compounds with saturated valences such as TiO_2 (1), Mg_2SiO_4 (2), $Mg(OH)_2$ (3) MgB_4 (4), the M_2O_3 sesquioxides (M = Sc, In, Y, Tl, *Ln*) (5), and the aluminum oxides, hydroxides, and oxyhydroxides (6). The fact that Al aggregates are observed in the two phases of AlOOH (diaspore and boehmite) has led us to investigate systemetically all the oxyhydroxides *M*OOH of trivalent metals (M = Sc, Y, Ga, In, V, Cr, Mn, Fe, *Ln*) to see if metal aggregates also appear in these compounds some of which are considered as ionic in nature.

DESCRIPTION OF THE STRUCTURES

The Oxyhydroxides of the Elements of the Group 13 (Al, Ga, In) and of the 3d Metals

All these compounds are summarized in Table 1 with the structure type and the aggregates present in the structure. Also the *Me–Me* distances in the aggregates are compared with the corresponding values in the pure metals. The synthesis and structure of TlOOH has not been reported.

Two of the most common structure types are diaspore and böhmite, the two phases of AlOOH which were previously described (6) on the basis of their cation arrays. Nevertheless, a clear view of the folded planes present in böhmite are represented in Fig. 1.

A clear difference exists between the two groups of compounds. All the oxyhydroxides of the Group 13 elements present phases in which the *Me–Me* distances of the pure metals are maintained in the compounds. Thus, the linear chains appearing in GaOOH (diaspore-like) are the same as those that appear along [111] of the In-type structure of elemental Ga, and the linear chains running parallel to the *c* axis of InOOH are the same as those that exist along [100] of the structure of bct In. In the other phase of GaOOH, the cation array of which is related to that of Ga_2O_3 (corundum-type) (9), no metal aggregate can be defined in terms of the Ga–Ga distances which are 10% longer than in the pure metal.

In the oxyhydroxides of the 3*d* metals, the behavior is not uniform. Whereas in ScOOH the two phases reproduce Sc–Sc distances of the metallic structures (fcc and hcp) and in MnOOH dimers can be identified with a Mn–Mn distance the same as that of fcc Mn, the other compounds (M = V, Cr, Fe) show *Me–Me* distances which are expanded with respect to the distances in the pure metals (see Table 1).

In this group of compounds three phases have not been taken into account. First is δ-FeOOH, because the Fe subnet present vacants (18). Second is CoOOH, isostructural with delafossite which has been formulated as $HCoO_2$ due to the existence of a symmetrical $O \cdots H \cdots O$ bond (22). It should be outlined that in CrOOH, however, the H atom is forming a true O–H bond (15). Finally NiOOH has not

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TABLE 1
The Oxyhydroxides of Group 13 and of the 3*d* Metals

Compound	Structure type	Metal aggregates	*Me–Me* distances	Parent metals	Ref.
AlOOH	Diaspore	Linear chains	2.84 × 2	2.86	(6)
AlOOH	Böhmite	Folded planes	2.87 × 2; 2.85 × 4	2.86	(6)
GaOOH	Diaspore	Linear chains	2.97 × 2	2.81, 2.99	(7)
GaOOH	GaOOH	None	3.33 × 2; 3.34 × 1	2.81, 2.99	(8)
InOOH	InOOH	Linear chains	3.27 × 2	3.27, 3.38	(10)
α-ScOOH	Diaspore	Linear chains	3.21 × 2	3.21, 3.30	(11)
γ-ScOOH	Böhmite	Folded planes	3.24 × 2; 3.38 × 4	3.21, 3.30	(12)
VOOH	Diaspore	Linear chains	3.03 × 2	2.62, 3.04	(13)
α-CrOOH	Delafossite	3^6 nets	2.98 × 6	2.50, 2.88	(14)
β-CrOOH	InOOH	Linear chains	2.96 × 2	2.50, 2.88	(16)
MnOOH	MnOOH	Dimers	2.75	2.73	(17)
β-FeOOH	β-FeOOH	Linear chains	3.02 × 2; 3.09 × 2	2.48, 2.87	(19)
FeOOH	Diaspore	Linear chains	3.02 × 2	2.48, 2.87	(20)
γ-FeOOH	Böhmite	Folded planes	3.06 × 2; 3.08 × 4	2.48, 2.87	(21)

been considered because of the lack of accuracy in the reported values for the unit cell parameters.

The Oxyhydroxides of the Lanthanides

*M*OOH (*M* = Y, *Ln*) are all isostructural (23–29). The compounds for *Ln* = La, Tb, Ho, Er, Yb, and Lu have been reported. They are monoclinic and their unit cell parameters are collected in Table 2. The seven monoclinic phases can be related to the structure of their respective parent metal and will be discussed below. YbOOH presents an additional tetragonal phase which will be discussed later.

Their cation array is represented in Fig. 2a. It is formed by linear chains, parallel to **b**, which are interconnected, forming a set of folded planes like those appearing in AlOOH (boehmite) and γ-ScOOH. Within the chains, the *M–M* distances range from 3.55 Å in LuOOH to 3.93 Å in LaOOH and are relatively close (except Yb) to the *M–M* distances in the hcp phases of the respective metals (see Table 3). However, the interchain distances (denoted as *d* in Fig. 2b) are somewhat shorter and agree better with the shortest *M–M* distances of the respective bcc metallic phases (see Table 3). Topologically, the fragments observed in Fig. 2 can be derived from a bcc arrangement. Thus, the rectangles of dimensions $b \times c$ (b and c being the unit cell parameters collected in Table 2) could be considered as a rectangular distortion of (100) planes of the bcc metallic structure (see Fig. 2b). In fact, the mean values (*m* in Table 3) of b and c are almost coincident with the unit cell parameters of the bcc phases of the metals (see Table 3). The maximum deviation is of 3.8% for YOOH. These rectangles

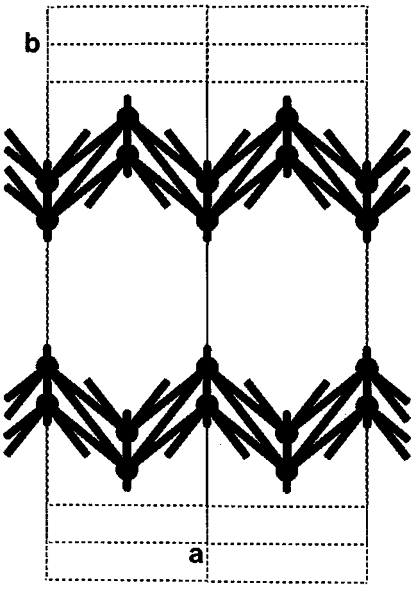

FIG. 1. View of the cation array in γ-ScOOH (böhmite-like) showing the Sc aggregates. All atoms forming the accordion-like folded planes are separated by distances of 3.24 (chains) and 3.38 Å (interchains).

TABLE 2
Unit Cell Parameters for *M*OOH (*M* = Y, La, Tb, Ho, Er, Yb, Lu)

	a (Å)	*b* (Å)	*c* (Å)	β (Å)	Reference
Y	6.05	3.63	4.28	112.5	(23)
La	6.572	3.929	4.417	112.5	(24)
Tb	6.04	3.69	4.33	109.0	(25)
Ho	5.96	3.64	4.31	109.1	(26)
Er	5.95	3.65	4.30	109.1	(27)
Yb	5.87	3.58	4.27	109.3	(28)
Lu	5.836	3.552	4.247	109.33	(29)

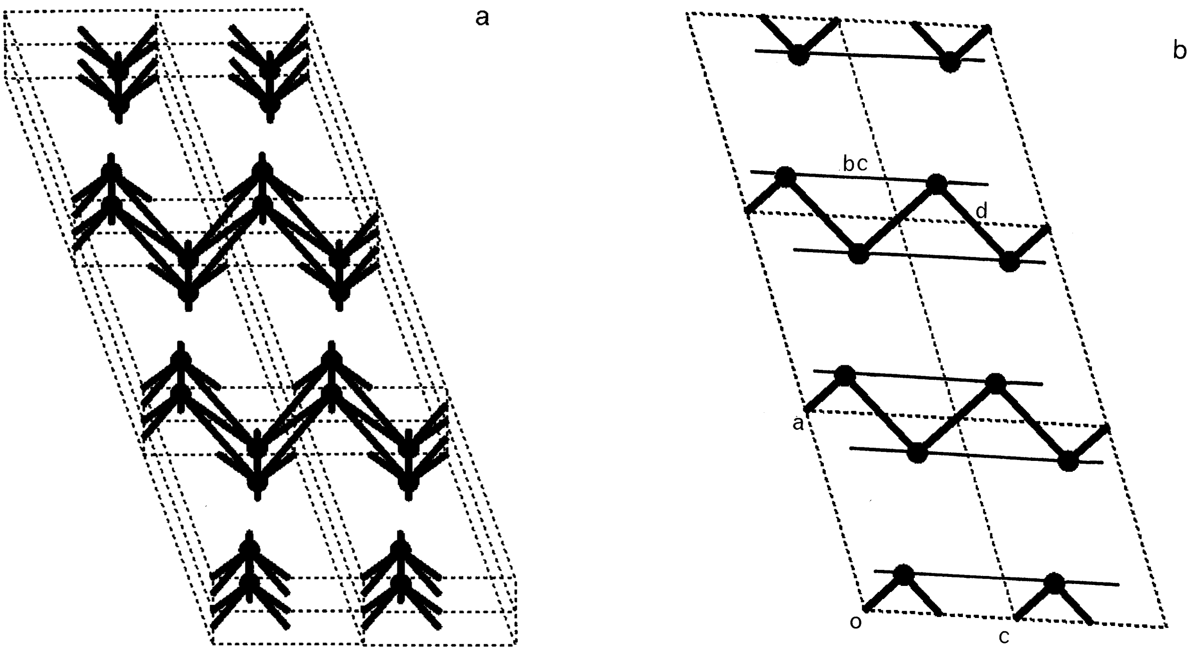

FIG. 2. (a) A 3D view of the cation array in *Ln*OOH, showing the accordion-like folded planes. (b) A projection on the *ac* plane, showing the fragments of a bcc structure. The line denoted as bc represents the $(100)_{\mathrm{bcc}}$ planes, formed by rectangles of dimensions $b \times c$ in the real structure. *d* denotes the distances from the capping atom to the four atoms forming the $(100)_{\mathrm{bcc}}$ face (interchain distances in Table 2).

are capped by the atoms forming the intermediate chains. The distances from the capping atom to the four atoms of the *bc* rectangle are the interchain distances collected in Table 2 (*d* in Fig. 2b) and, as said above, are close to the *d* values of the bcc metallic phases. Thus, the *Ln* subarray could be seen as the result of an opening of the bcc metallic net by elongating four of the eight shortest *M–M* distances. These elongated distances are the interblock distances which range from 4.279 Å in LaOOH to 3.875 Å in LuOOH. A further displacement along $[010]_{\mathrm{bcc}}$ would lead to the cation subarray in the *Ln*OOH compounds.

TABLE 3

***Me–Me* Distances in *Ln*OOH and in the *Ln* Metallic Phases to See the Equivalence between the Interchain *Me–Me* Distances and the Values in the Metallic Phases (d_{bcc} and a_{hcp})**

	Me–Me chains	a_{hcp}	d_{bcc}	*Me–Me* interchains	$m(b, c)$	a_{bcc}
Y	3.63	3.65	3.56	3.48 × 2; 3.53 × 2	3.96	4.11
La	3.93	3.77	3.69	3.735 × 4	4.17	4.26
Tb	3.69	3.60	3.48	3.56 × 2; 3.60 × 2	4.01	4.02
Ho	3.64	3.58	3.43	3.53 × 2; 3.55 × 2	3.98	3.96
Er	3.65	3.56	3.41	3.39 × 2; 3.65 × 2	4.00	3.94
Yb	3.58	—	3.48	3.47 × 2; 3.54 × 2	3.93	4.02
Lu	3.55	3.50	3.38	3.44 × 2; 3.47 × 2	3.90	3.90

Note. Compare also the mean values (*m*) of *b* and *c* (see Table 1) with the corresponding values of a_{bcc}. All values are given in Å.

The Tetragonal Phase of YbOOH

YbOOH is the only compound for which this tetragonal phase has been reported (30). Its unit cell parameters are $a = 5.465$, $c = 5.327$ Å, $P\bar{4}2_1m$, and $Z = 4$. The Yb array is represented in Fig. 3 and consists of irregular $\mathbf{6}^3$ planar nets, perpendicular to *c*, which are situated at $z = 0.2000$ and $z = 0.8000$. Within a unit cell the two nets are spaced 3.197 Å apart and are rotated 90° with respect to each other. Each $\mathbf{6}^3$ net has another one at 2.131 Å in the contiguous unit cell. Within each hexagon, the *M–M* distances are 2 × 3.39 and 4 × 3.89 Å.

The irregular $\mathbf{6}^3$ nets just described are in fact the result of a distortion of the $\mathbf{4}^4$ planar nets forming the (200) planes of a fcc structure. The distorted $\mathbf{4}^4$ planar net has dimensions of 3.39, 2 × 3.89, and 4.34 Å (*d* distance in Fig. 3). The resulting trapeze has been shaded in the bottom right side of Fig. 3 and the mean value of its four edges (3.88 Å) is just the value of the *M–M* distance in fcc Yb ($a = 5.48$, $d = 3.87$ Å). The distortion can clearly be seen in the upper left side of Fig. 2 where a fcc unit cell has been depicted to show how the face-centering atom is shifted toward one of the corners, giving rise to the trapeze defined above (the largest distance is not drawn in this part of the figure). It is also noteworthy how the atoms centering the faces perpendicular to the drawing plane are also shifted from their ideal positions. Because the mean Yb–Yb distance, in the distorted $\mathbf{4}^4$ net of YbOOH, is coincident with the *M–M* distance in fcc Yb,

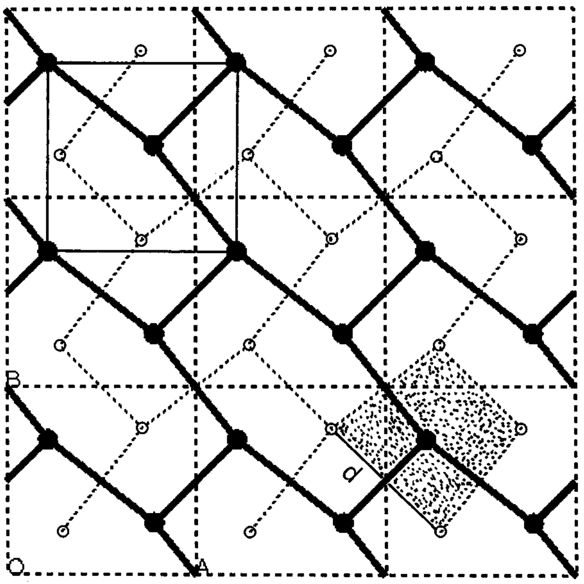

FIG. 3. The cation array of t-YbOOH, projected on the *ab* plane, showing the irregular $\mathbf{6}^3$ nets. The two planar nets are at $z = 0.20$ and $z = 0.80$. At the bottom right side we have shaded a trapeze derived, by distortion, from a $\mathbf{4}^4$ planar net of a fcc structure. At the top left, a cubic unit cell has been depicted to show how this cation array is a distortion of fcc Yb.

their unit cells must also be coincident, i.e., 5.465 Å in the compound and 5.48 Å in the metal. The *c* axis of YbOOH (5.327 Å) deviates only 3% from the value in the pure metal.

It can be concluded that the unit cell of YbOOH can be regarded as the unit cell of fcc Yb in which alternate, distorted $\mathbf{4}^4$ nets have been displaced, along *c*, up to produce alternate spacings of 2.131 and 3.197 Å, instead of the regular spacing of 2.74 Å in the pure metal. Distortion takes place, however, maintaining the unit cell volume almost constant. Thus, two oxygens and one hydrogen are inserted into the net of fcc Yb without a significant volume change (a contraction of 3% is produced). This distortion, however, does not take place at random since the shortest *M–M* distances between atoms of the closest adjacent nets (4×3.48 Å) reproduce exactly the values of the *M–M* distances in the high-pressure-phase bcc Yb ($a = 4.02$, $d = 3.48$ Å) (31). Again, high pressure and oxidation seem to be correlated as we have reported elsewhere (32).

DISCUSSION

The compounds just discussed represent additional examples of how cations, in inorganic solids, are not distributed at random but they maintain, in many instances, topology and distances of the pure metals. As in C–Ln_2O_3 (5) and in many other compounds, these structural features occur in compounds with saturated valences in which either cations are supossed to have a noble gas configuration, as in Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Y^{3+}, and La^{3+}, or the nonspherical configuration corresponds to noninteracting inner electrons as they are the 4*f* states in the Ln^{3+} cations.

However, in the compounds of the 3*d* series, the agreement is rather poor and only ScOOH and MnOOH show *M–M* distances as in the pure metals. Moreover, in MnOOH the aggregates are only dimers. This behavior of the 3*d* metals could be explained if we assume that the *M–M* bonding, in the bulk transition metals, has a marked *d–d* character with a very small contribution of the *s* and *p* states (33) and that these *d–d* interactions become greatly diminished, in the oxyhydroxides, by the presence of an octahedral O environment which makes the t_{2g} electrons adopt a marked nonbonding character.

Even though *d–d* interactions also exist in the compounds, it is also true that the population of the *s* and *p* states increases as a consequence of the mixing with *s* and *p* orbitals of the ligands, in such a way that a charge transfer from 3*d* to the 4*s* and 4*p* excited states takes place via the O atoms. The importance of this mixing between metal 4*s* and 4*p* orbitals with ligand 2*s* and 2*p* orbitals has been suggested on the basis of APW band calculations (34). It has also been clearly stated (35) that although the discussion of the effect of covalency on the magnetic properties of transition metal ions reveals charge and spin density to be transferred from the metal ion to the ligands, the net charge transfer is of course in the opposite direction.

It could be said therefore that, as a consequence of this charge transfer, the 3*d* elements (cations) behave structurally, in the oxides, as if they were the first *p* element after the transition series; i.e., they give *M–M* distances as if they were the Ga atom. This correlates well with *M–M* distances observed in the oxyhydroxides (around 3.00 Å) which are in good agreement with the Ga–Ga distances in GaOOH, in the In-type phase of metallic Ga (2.985 Å) and in most of the Ga oxides, as Ga_2O_3 and the Ga-containing spinels (around 3.00 Å). It should be added that the same occurs in the NaCl-type monoxides of the 3*d* metals, the *M–M* distances of which are about 3.00 Å, with extreme values of 2.900 Å for CrO and 3.144 Å for MnO, and in the ABO_2 delafossites containing one 3*d* metal and also in the AB_2O_4 spinels ($B = 3d$ metal), both showing *B–B* distances close to the value of 3.00 Å (36).

This could be an explanation of why the oxides of the 3*d* metals, as the corundum-type M_2O_3 (Ti_2O_3, Cr_2O_3, Fe_2O_3), adopt the structure of Al_2O_3 and Ga_2O_3 or why the C–Mn_2O_3 structure is related to that of In_2O_3 and Tl_2O_3. In connection with this, the anomalous behavior of ScOOH should be outlined, two phases of which are related to AlOOH (diaspore and boehmite), but preserving the Sc–Sc distances as in metallic Sc.

In the oxyhydroxides of the IIIb metals (Al, Ga, In) and of the lanthanides (including Y), the agreement is quite good as can be seen in Table 2. All these compounds present M–M distances and topologies derivable from the respective elemental structures. With respect to the lanthanide oxyhydroxides, this feature is consistent with the results obtained in a previous study on the C–M_2O_3 sesquioxides (M = Sc, Y, In Tl, *Ln*) of the bixbyite-type, the cationic arrays of which are also related to the structure of the parent metal (5) as if some kind of interaction would exist between cations.

It should be pointed out that recently an electron density study on Y_2O_3, Dy_2O_3, and Ho_2O_3 has been reported (37) in which the residual electron density around the M^{3+} cations, far from being spherical, presents a hexagonal structure, with maxima pointing toward the six M^{3+} neighbors; i.e., the electron density around $M(1)$ atoms does not seem to be influenced by the oxygen environment but by the other cations. In view of this, it should be of greatest interest to extend such studies to some of the compounds discussed here to see if residual electron density around cations also results, influenced by the presence of other cations which are situated at distances as in the pure metals. The study should be especially interesting in the case of YOOH or ScOOH, the cations of which are assumed to have spherical symmetry. The appearance of structure in the residual electron density around Y^{3+} in Y_2O_3 (37) is, in our opinion, a challenge difficult to understand.

We can conclude by saying that the distortion of a $\mathbf{4}^4$ net to give an irregular $\mathbf{6}^3$ net, as occurs in t-YbOOH, has previously been described (38) as a purely geometrical concept which serves to correlate planar nets of different compounds. We can add, however, that this process is physically meaningful when the cation subarray, in YbOOH, is compared with the structure of the parent metal. The process we have geometrically described could well be a real one when t-YbOOH is synthesized. Examples of such mechanisms have been given elsewhere (4).

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