Influence of M^{2+} Ions Substitution on the Structure of Lanthanum Hexaaluminates with Magnetoplumbite Structure

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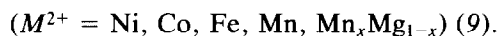*11, rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*

A series of compounds with the initial composition $LaM_xAl_{11}O_{18+x}$ has been studied with x ranging from 0 to 1, and M = Mn, Co, Cu. They exhibit a more or less distorted and defective magnetoplumbite arrangement. Their effective compositions have been determined by X-ray structure refinement. The smaller the content of M^{2+}, the higher the disorder in the crystal lattice, the worse the crystal growth, and more intense the diffuse scattering in (001) planes. The role of M^{2+} is compared to that of M^{2+} stabilizing γ-Al_2O_3 to give MAl_2O_4 spinels.

I. Introduction

First evidence of n-Al_2O_3–La_2O_3 alumina-rich phases was reported by Roth and Hasko in 1958 (*1*) but with no details on the true composition of these phases of the La_2O_3–Al_2O_3 system. Later investigations of these phases resulted in highly inconsistent conclusions concerning their thermal behavior, composition, and crystal structures (*2–4*). The more generally accepted formula was $LaAl_{11}O_{18}$ (La_2O_3, 11 Al_2O_3) and the existence range was quite narrow (1600–1850°C) (*5*). However, these phases can be obtained from room temperature to the melting point by introduction of divalent ions in the crystal lattice and then they have the general formula $LnMAl_{11}O_{19}$

where Ln = La to Gd (*7*), M^{2+} = Mg (*6–8*), Mn (*8*), Fe, Co, Ni, Cu (*9*). To understand the role played by M^{2+} ions in the formation of such compounds, we were interested in knowing their position in the lattice, which may vary with the nature or the total amount of inserted divalent ion.

The following compounds were obtained as single crystals from the melt, mainly by the Verneuil process (temperature of fusion $\cong$ 1850°C):

$LnMgAl_{11}O_{19}$

$\quad (Ln^{3+}$ = La, Pr, Nd, Sm, Eu, Gd) (*7*)

$LaMAl_{11}O_{19}$

$\quad (M^{2+}$ = Ni, Co, Fe, Mn, Mn_xMg_{1-x}) (*9*).

The first attempt at a structural determination was done on $LaMgAl_{11}O_{19}$ (*10*) and it confirmed that the structure was close to

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that of magnetoplumbite ($PbFe_{12}O_{19}$)(MP) (11), as previously assumed from powder diffraction studies (8). But owing to the neighboring atomic numbers of Al and Mg and possibly also to an inherent disorder in the structure, no clear conclusion was drawn on the divalent ion positions. The present work deals with single crystals of lanthanum aluminates containing Cu^{2+}, Co^{2+}, or Mn^{2+}. A whole series of single crystals with $LaMn_xAl_{11}O_{18+x}$ as a starting composition has been obtained where $0 < x < 1$. This enabled us to study single crystals with a variable content of Mn^{2+} ions, as well as compounds containing Co^{2+} and Cu^{2+}.

II. Preparation and Characterization

Single crystals of all compounds previously mentioned were prepared by the Verneuil method.

The apparatus and operating process have been reported elsewhere (12, 9). The starting powder is the intimate mixture of oxides La_2O_3, Al_2O_3, and Co_3O_4, MnO_2, or CuO. For the first two cases, the oxyhydrogen flame was kept quite reducing to insure Co and Mn in a divalent state. Reversely, for compounds containing Cu^{2+}, the crystal growth was attempted with a more oxidizing flame. Rather large rod-shaped crystalline boules are obtained by this technique, their growth axis is the a crystallographic direction and there is always a cleavage plane along (001). The various phases existing in the samples are identified by X-ray powder diffraction.

Several compositions were studied in order to establish the influence of M^{2+} ions in materials with the initial composition LaM_x $Al_{11}O_{18+x}$.

The following description concerns all types of samples (with various divalent ions) but it is more particularly devoted to Mn^{2+}-substituted compounds for which 10 different compositions between $x = 0$ and $x = 1$ have been prepared.

— When $x = 0$ (which corresponds to the theoretical composition $LaAl_{11}O_{18}$) the as grown samples are largely polycrystalline blocks, containing some small hexagonal platelets (1×1 mm²) of a pure magnetoplumbite-like phase, together with α-Al_2O_3 and $LaAlO_3$ phases.

— For increasing values of x, i.e., $0 < x < 0.3$ the Verneuil boules still are polycrystalline samples but some larger single crystal wafers (5×5 mm²) of a magnetoplumbite phase are available. Even a very small amount of Mn^{2+} ($x = 0.02$) is sufficient to improve noticeably the quality and size of these platelets; the higher the x value, the easier is the crystal growth.

— For $x > 0.3$, the samples are built of some large single crystals (10×10 mm²) of quasipure magnetoplumbite phase. The green color due to Mn^{2+} ions increases, of course, with the value of x.

— For $x \cong 1$, the crystal growth becomes much easier and resulting crystals have a good crystallinity. This holds for $LaCoAl_{11}$ O_{19} as well.

The "$LaCuAl_{11}O_{19}$" compound behaves differently. Large single crystals are obtained with this starting composition. The resulting crystals have a MP-like structure identified by X-rays, with some α-Al_2O_3 and $LaAlO_3$ between the wafers or spread over them. However, these crystals are colorless although they were expected to be blue. Volatilization and/or reduction of Cu^{II} into Cu^I or Cu^0 and loss of this copper must occur during the crystal growth process despite the oxidizing conditions we used. This assumption is confirmed by an EPR study: X-ray irradiation, which generally results in creation of some Cu^{2+} ions in crystals containing Cu^+ ions, gave no such defects in our crystals. Let us recall that EPR is sensitive to a very small amount of paramagnetic Cu^{2+} ions. Therefore, the as-prepared crystals, free of Cu^{2+}, apparently have a compo-

sition close to $LaAl_{11}O_{18}$ and this could result in a useful technique for growing good crystals of pure lanthanide aluminate.

III. Structural Determinations

1. Experimental

Single crystals of five different samples with various compositions have been used for this structural investigation. All crystallographic data and procedure are given in Table I. Except for the cobalt-containing compound, the diffraction intensities for all samples were collected with an Philips PW1100 diffractometer, equipped with a graphite monochromator to select the $MoK\alpha$ radiation, and using a $\theta/2\theta$ scanning with a speed 0.025°/sec. Measurements of the Co-substituted sample were performed with a semiautomatic Nonius diffractometer in approximately the same operating conditions. For each case, the crystal size, number of measured intensities, final value of the R factor, and the refined composition (13) are given in Table I. Absorption corrections have been neglected since the μr values are lower than 1.

Atomic parameters of $LaMgAl_{11}O_{19}$ (10) were taken as starting values for the refinement of these structures. Fourier and difference Fourier maps show noticeable atomic shifts in the more disordered phases and some residual electron density (see Table I).

The refined atomic coordinates and isotropic temperature factors are gathered in Tables II and III with emphasis on the shifted and/or partially occupied positions for which the corresponding ideal value is also given. Anisotropic thermal factors would be irrelevant in such disordered phases.

2. Discussion of the Structures

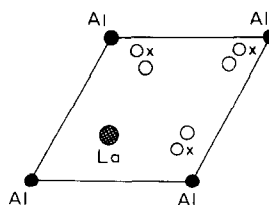These results show several fundamental features.

FIG. 1. Organization of ions in the mirror planes of MP structure ($z = 0.75$).

(a) Manganese-Substituted Compounds

$LaMnAl_{11}O_{19}$, $x = 1$. This "stoichiometric" phase is the only one having a true magnetoplumbite-like structure in which $La^{3+} + Mn^{2+}$ substitute $A^{2+} + B^{3+}$ in the $AB_{12}O_{19}$ network. It comes out of the refined parameters that some atoms are delocalized on several equivalent positions: La^{3+}, for instance, is slightly shifted from the theoretical position (0.667, 0.333, 0.25) and moreover, some La^{3+} has to be introduced in another crystallographic site to account for the rather large volume in which La can be moved (Fig. 1). In the same way, the Al(5) atom is on two equivalent positions split from the position in the mirror plane at $z = 0.25$, so as to have a tetrahedral environment rather than the fivefold coordination (expected on the theoretical position at (0, 0, 0.25)) (Fig. 2).
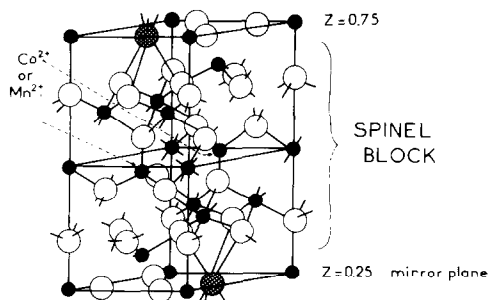

FIG. 2. Localization of M^{2+} ions in the spinel blocks of a magnetoplumbite structure. Black circles are Al atoms. White circles are O atoms. Dashed circles are La atoms.

TABLE I

GENERAL FEATURES AND STRUCTURAL DATA FOR LANTHANUM HEXAALUMINATES COMPOUNDS

Starting composition	$LaMnAl_{11}O_{19}$	$LaCo_{0.75}Al_{11}O_{18.75}$	$LaMn_{0.02}Al_{11}O_{18.02}$	$LaAl_{11}O_{18}$	$LaCuAl_{11}O_{19}$
Crystallographic data			$P6_3/mmc$, $Z = 2$		
Lattice constants (Å)	$a = b = 5.574$ $c = 22.008$	$a = b = 5.577$ $c = 22.003$	$a = b = 5.550$ $c = 22.021$	$a = b = 5.550$ $c = 22.031$	$a = b = 5.546$ $c = 22.008$
Crystal size	$300 \times 300 \times 100$ μm	$300 \times 500 \times 100$ μm	$320 \times 480 \times 100$ μm		
Absorption coeff. (λMo)	$\mu = 5.7$ mm⁻¹ No absorpt. corrections	5.42 mm⁻¹ No	4.2 mm⁻¹ No	4.2 mm⁻¹ No	4.2 mm⁻¹ No
No. of independent reflections	939	650	885	790	860
R final value with isotropic B	0.062 with 625 refl.	Semiautomatic diffr. 0.06 with 400	0.068 with 741	0.062 with 787	0.082 with 857
Final Composition of the crystal	$LaMnAl_{11}O_{19}$	$La_{0.9}Co_{0.75}Al_{11.2}O_{18.9}$	$La_{0.85}Al_{11.5}O_{18.525}$	$La_{0.85}Al_{11.55}O_{18.60}$	$La_{0.85}Al_{11.6}O_{18.675}$
Residual density on difference maps	6 e⁻ on (0.667, 0.333, 0.24)		1 e⁻ on (0.85, 0.7, 0.19)	1 e⁻ on (0.75, 0.5, 0.25)	1 e⁻ on (0.667, 0.33, 0.22)
Substituting Ion	Mn^{2+} mainly in Al(2) tetrahedral site, no Mn^{2+} on Al (5)	Co^{2+} mainly tetrahedral site, no Co^{2+} in Al (5)	ε Mn^{2+} undetectable		No Cu^{2+} detected
Diffuse scattering (00.1) planes	Weak diffuse stripes in (00.1) planes	Strong diffuse scattering not totally resolved into spots	Intensely spotted diffuse scattering patterns		

TABLE II

STRUCTURAL PARAMETERS OF THE REFINED STRUCTURES OF SUBSTITUTED LANTHANUM ALUMINATES

Atom	Wyckoff position	Occupancy factor	x	y ($\times 10^4$)	z	B	Wyckoff position	Occupancy factor	x	y ($\times 10^4$)	z	B
			Starting compositions: LaMnAl$_{11}$O$_{19}$						LaCo$_{0.75}$Al$_{11}$O$_{18.75}$			
La(1)	6h	0.28	6676(2)	3552	2500	0.2	6h	0.3	6770(10)	3230	2500	0.1
	2d	1	6667	3333	2500							
La(2)	6h	0.05	7373(10)	4746	2500	0.2						
Al(1)	2a	1	0	0	0	0.4	2a	1 (εCo)	0	0	0	0
Al(2)	4f	1 (Mn)	3333	6667	0275(1)	0.1	4f	1 (Co)	3333	6667	0265(2)	0.1
Al(3)	4f	1	3333	6667	1899(1)	0.4	4f	1	3333	6667	1894(3)	0.2
Al(4)	12k	1	8328	6656	1083(1)	0.5	12k	1	8325(10)	6650	1079(1)	0.2
Al(5)	4e	0.5	0	0	2399(2)	0.4	4e	0.44	0	0	2382(5)	0.5
	2b	1	0	0	2500							
O(1)	6h	1	1811(6)	3622	2500	0.5	6h	1	1853(30)	3706	2500	0.5
O(2)	12k	1	1539(5)	3078	0526	0.3	12k	1	1530(20)	3060	0536(3)	0.2
O(3)	12k	1	5056(5)	0112	1501(1)	0.1	12k	1	5034(20)	0068	1505(3)	0.3
O(4)	4e	1	0	0	1492(2)	0.2	4e	1	0	0	1500(6)	0.1
O(5)	4f	1	6667	3333	0568(2)	0.3	4f	1	6667	3333	0571(6)	0.2
Final compositions:			LaMnAl$_{11}$O$_{19}$						La$_{0.9}$Co$_{0.75}$Al$_{11.2}$O$_{18.9}$			

Note. Characters in italic are the positions or occupation actors different from the theoretical ones (in boldface).

First adjustments of atomic parameters were achieved with a statistical distribution of Mn^{2+} over all Al sites, by using an average diffusion factor:

$$f = \frac{f(\text{Mn}^{2+}) + 11f(\text{Al}^{3+})}{12}.$$

Then it appeared that the Al(5) site was free of Mn^{2+}, while the Al(2) tetrahedral position had a higher Mn^{2+} content; this was simultaneously established by EPR and UV–V spectroscopy which indicate the local symmetry of Mn^{2+} (*14*).

The Al–O distances around the Al(2) atom range from 1.82 to 1.855, somewhat greater than classical Al–O values in tetrahedral coordination, which is also rather conclusive for Mn^{2+} located in the tetrahedral site within the spinel block of the structure (see Table IV) (Fig. 2).

LaMn$_{0.02}$Al$_{11}$O$_{18}$ and LaAl$_{11}$O$_{18}$ starting compositions. For a crystallographic approach, of course, 0.02 Mn were quite negligible, undetectable. But as their presence had a distinctive effect on the crystal growth, it was reasonable to expect some difference between compounds with $x = 0.02$ and $x = 0$.

In fact, no real difference can be pointed out in the final description of both structures (Table III). The main common feature is an important disorder shown by

(1) Splitting of several atoms, La, Al(5), O(1), O(2) among partially occupied positions (mainly atoms of the mirror planes as shown on Fig. 1).

(2) Vacancies on such positions as La, O(1), Al(4), Al(5), leading to a final composition around La$_{0.85}$Al$_{11.5}$O$_{18.52}$.

This corresponds to a Al/La ratio of about 13.5. The structure of "LaAl$_{11}$O$_{18}$" thus appears to have an AB_{12}O$_{19}$ framework with vacancies. This would lead to a formula of La$_{0.66}$Al$_{12}$O$_{19}$ as compared to the true magnetoplumbite structure (cf. PbFe$_{12}$O$_{19}$). However, we never succeeded in preparing such a phase, and the AB_{12}O$_{19}$ framework apparently cannot accommodate that many vacancies upon the A sites.

For these nonsubstituted phases, the average structure was determined by X-ray diffraction and did not account for the

TABLE III

Structural Parameters of the Refined Structures of Lanthanum Aluminates with Low M^{2+} Content

Atom	Starting compositions $LaMn_{0.02}Al_{11}O_{18.02}$						$LaAl_{11}O_{18}$						$LaCuAl_{11}O_{19}$					
	W	Occ.	x	y	z	B	W	Occ.	x	y	z	B	W	Occ.	x	y	z	B
La(1)	2d	0.56	6667	3333	2500	0.5	2d	0.55	6667	3333	2500	0.6	2d	0.56	6667	3333	2500	0.6
La(2)	6h	0.09	7208(6)	4416	2500	0.3	6h	0.1	7170(5)	4340	2500	0.4	12j	0.048	7256(19)	4399(19)	2500	0.2
Al(1)	2a	1	0	0	0	0.2	2a	1	0	0	0	0.3	2a	1	0	0	0	0.3
Al(2)	4f	1	3333	6667	0270(1)	0.3	4f	1	3333	6667	0269(1)	0.4	4f	1	3333	6667	0269(1)	0.4
Al(3)	4f	1	3333	6667	1899(1)	0.4	4f	1	3333	6667	1899(1)	0.5	4f	1	3333	6667	1898(1)	0.4
Al(4)	12k	0.95	8308(2)	6616	1077(0)	0.4	12k	0.952	8324(2)	6648	1076(0)	0.4	12k	0.96	8325(2)	6650	1076(0)	0.4
Al(5)	4e	0.42	0	0	2388(2)	0.5	4e	0.41	0	0	2386(2)	0.5	4e	0.42	0	0	2384(2)	0.5
O(1)	12j	0.42	2017(10)	3631(10)	2500	0.2	12j	0.437	2009(7)	3623(10)	2500	0.2	12j	0.44	2013(10)	3224(10)	2500	0.2
O(2)	24l	0.5	1621(20)	3115(20)	519(1)	0.4	24l	0.5	1634(13)	3121(13)	0518(1)	0.4	24l	0.5	1619(15)	3115(15)	0518(1)	0.4
O(3)	12k	1	5047(4)	0094(4)	1502(1)	0.3	12k	1	5034(5)	0068	1501(1)	0.4	12k	1	5030(5)	0060	1502(1)	0.3
O(4)	4e	1	0	0	1481(2)	0.4	4e	1	0	0	1481(2)	0.4	4e	1	0	0	1480(2)	0.3
O(5)	4f	1	6667	3333	0552(2)	0.3	4f	1	6667	3333	0554(2)	0.4	4f	1	6667	3333	554(2)	0.3
Final compositions		$La_{0.85}Al_{11.5}O_{18.5}$						$La_{0.85}Al_{11.5}O_{18.5}$						$La_{0.85}Al_{11.0}O_{18.7}$				

Note. Characters in italic are the positions or occupation factors different from the theoretical ones. W = Wyckoff position. Occ. = Occupancy factor.

TABLE IV

CATIONIC ENVIRONMENTS IN $LaMnAl_{11}O_{19}$

La(1)	O(3) × 4	2.658(3) Å
	O(1) × 2	2.702(3)
	O(3) × 2	2.750(3)
	O(1) × 2	2.767(3)
	O(1) × 2	2.885(3)
La(2)	O(1) × 2	2.248(3)
	O(3) × 4	2.574(3)
	O(1) × 2	2.839(3)
Al(1)	O(2) × 6	1.883(0)
Al(2)	O(2) × 3	1.818(0)
	O(5)	1.855(5)
Al(3)	O(3) × 3	1.877(3)
	O(1) × 3	1.977(3)
Al(4)	O(3) × 2	1.832(3)
	O(4)	1.848(3)
	O(5)	1.964(3)
	O(2) × 2	1.979(2)
Al(5)	O(1) × 3	1.763(5)
	O(4)	1.996(6)
	O(4)	2.491(6)

strong and well-organized diffuse scattering observed on all these deficient compounds ($x \ll 1$). It is mainly observable in the cleavage planes (Fig. 3). This diffuse scattering implies a local organization limited to a few adjacent unit cells (coherence domain). This local order, although not well explained up to now, could arise from coherent shifts of the lanthanum ion, in combination with a local order of the vacancies (0.85 La^{3+} instead of 1). However, it should be noticed that intensity measurements on a single crystal normally are performed on the diffraction peaks only; this could lead to a systematic error, since the diffuse intensity is neglected. This could result in an incorrect final composition.

These compounds are quite inert toward chemical agents and the results of chemical analysis by classical means are highly inconsistent. Therefore, the electron microprobe analysis of these crystals is in progress to provide a more accurate composition of the samples.

(b) Copper-Substituted Compound

Let us recall that no trace of copper was found in the crystals. Although the refinement of the structure, using the same conditions as before, leads to a worse value of R and a higher degree of disorder, the final composition obtained is quite similar to the former ones for nonsubstituted ($x \cong 0$) compounds; some of the theoretical atomic positions have to be split into more delocalized ones (atoms La(2) O(1) O(2)). This strong disorder is also accompanied by a well-defined diffuse scattering showing a local organization extending over a few unit cells.

(c) Cobalt-Substituted Compound

The adjustment of atomic parameters and occupation factors of a compound with initial composition $LaCo_xAl_{11}O_{18+x}$ ($x \cong 0.75$, Table III) gives a final formula close to $La_{0.925}Co_{0.75}Al_{11.1}O_{18.9}$. The cobalt is found mainly on the tetrahedral sites within the spinel block, as for Mn^{2+}, and once more the structure is of $AB_{12}O_{19}$ type with vacancies on La and Al sites. This disorder also manifests itself in the diffuse scattering pattern showing diffuse spots in intense streaks in the (001) plane.

IV. Conclusion

We may summarize the preceding results as follows: a series of compounds with the initial composition $LaM_xAl_{11}O_{18+x}$ has been studied for x values ranging from 0 to 1. For $x = 1$ (Mn^{2+} ion) the $LaMnAl_{11}O_{19}$ sample has a well-defined slightly distorted MP structure, where the Mn^{2+} ion is essentially found in the tetrahedral sites of the spinel block. When lowering x to 0 (0.7, 0.02, 0), the corresponding crystals show a deficient MP structure: partial occupancy and displacements of La, Al, and O sites of the mirror plane are accompanied by strong diffuse scattering in these planes. In all these
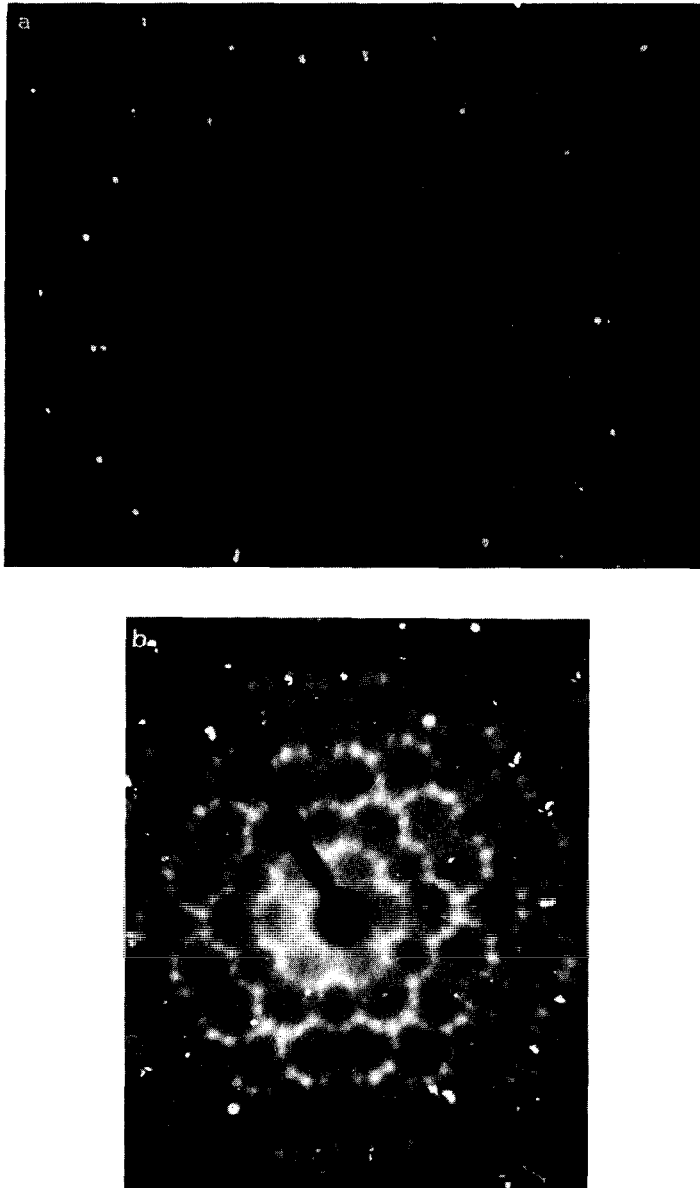
FIG. 3. X-Ray diffuse scattering patterns of deficient lanthanum hexaaluminates in (001) planes. (a) $LaMnAl_{11}O_{19}$, (b) with initial composition $LaMn_{0.02}Al_{11}O_{18.02}$.

nonstoichiometric phases, the charge com-
pensation mechanism probably is very
complicated, since in most of them the va-
cancies and interstitial atoms can be found
simultaneously.

As can be seen, the M^{2+}-substituted ions
are those which give with Al_2O_3 the corre-
sponding MAl_2O_4 spinel compounds. But
we have been dealing with M^{2+} in tetrahe-
dral sites mainly and one would expect a

different behavior for Ni^{2+}, for instance, which is known to give a mixed spinel structure, with Ni^{2+} mainly in an octahedral environment. Therefore the study of La $NiAl_{11}O_{19}$ is now on progress.

In conclusion, the role of M^{2+} ions in these magnetoplumbite-like compounds can be compared to the one they play in forming spinels with γ alumina. This alumina is a well-known unstable phase, with a deficient spinel structure, the formula of which may be written as $Al_{2.67}\square_{0.33}O_4$. The corresponding nonstoichiometric $M_xAl_{2.67-0.67x}$ $\square_{0.33(1-x)}O_4$ spinels, or MAl_2O_4 stoichiometric ones can then be considered as γ-alumina stabilized by reduction of the number of vacancies (*14*). The same mechanism might occur in magnetoplumbite hexaaluminates where M^{2+} could stabilize the spinel blocks of these phases by reducing the amount of vacancies in the unit cell. This could explain the easier preparation of a magnetoplumbite phase when M^{2+} ions are present.

Acknowledgments

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