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Studies of Spinels. VI. Antimonates $M_4^{II}M^{III}Sb^VO_8$, a New, Large Family of Spinels Presenting Order–Disorder Transitions

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A new family of complex antimonates $M_4^{II}M^{III}Sb^VO_8$ has been synthesized and investigated by X-ray diffractometry and ir and Mössbauer spectroscopy. Many of these compounds possess a spinel structure, with a cation distribution which depends on the nature of M^{II} and M^{III}. When all the tetrahedral sites are occupied by bivalent cations, these spinels $M_2^{II}[M_2^{II}M^{III}Sb]O_8$ are cubic, with either a disordered or a 3 : 1 ordered distribution of the octahedral cations. When the trivalent cation is able to go on the tetrahedral sites, the X-ray powder diagram may be either simple cubic (disordered cation distribution) or more complex, with a number of superstructure lines which can be indexed by considering an orthorhombic cell with $a \simeq a_{0_{spinel}}/2^{1/2}$; $b \simeq 3a$; $c \simeq a_{0_{spinel}}$, possible space group *Imma*. The cation distribution of this type of phase has not been fully elucidated, but the combined X-ray, ir, and Mössbauer evidence suggests the presence of the trivalent cation on both tetrahedral and octahedral sites, and a 2 : 1 order on both tetrahedral and octahedral sites, namely, $(M_4^{II} : M_2^{III})[M_8^{II} : M^{III}Sb_3]O_{24}$.

Introduction

Very few antimonates with spinel structure have been reported so far: $Zn_7Sb_2O_{12}$ (*1–4*) and $Co_7Sb_2O_{12}$ (*1, 2*), $Li_2Cr_3SbO_8$ and $Li_2Rh_3SbO_8$ (*5*), $Li_3Ti_2SbO_8$ (*5*), all with a simple spinel structure; $LiCoSbO_4$ and $LiZnSbO_4$ (*5, 6*), whose X-ray powder diagram exhibits superstructure lines corresponding to some type of cation ordering.

From the existence of some spinel tellurates $M_5^{II}TeO_8$ (e.g., Co_5TeO_8, Zn_4NiTeO_8, etc.) (*7, 8*), it was suspected that similar antimonates could also have the spinel structure. These may be deduced from the tellurate family by the coupled replacement $M^{II}Te^{VI} \rightarrow M^{III}Sb^V$, leading to the general formula $M_4^{II}M^{III}Sb^VO_8$. This eventually lead us to the synthesis of a large family of spinels, whose composition limits have not been fully investigated so far. We report here on some essential features of these compounds.

Experimental

Two slightly different synthesis procedures may be used.

(i) A carefully ground mixture of the appropriate oxides (or carbonates) is heated up to 600°C and maintained for 1 day at this temperature. The mixture is then reground and heated up to 700°C, and these cycles of grinding and heating are repeated until the temperature has been increased up to 1100–1300°C (1300–1350°C if M^{III} = Al; 1000–1100°C for copper-containing phases). The very progressive heating scheme is necessary to ensure Sb_2O_3 oxidation and to avoid Sb_2O_3 losses by volatilization.

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(ii) The mixture of oxides and elemental antimony is submitted to a chemical attack by nitric acid, followed by evaporation to dryness and thermal treatment. This last procedure has two advantages: The resulting mixture is more reactive; and the antimony is first oxidized to hydrated Sb_2O_5, and antimony losses by volatilization will not occur below 1000°C. So the heating scheme may be shortened.

All samples were air quenched from the synthesis temperature and later submitted to progressive cooling (50°C per day) down to 800°C. In addition, a much slower cooling scheme (1100°C down to 400°C in 4 months) was applied to some compounds.

All samples were investigated by X-ray powder diffractometry [C.G.R. diffractometer, Co$K\alpha$ radiation, no internal standard; in order to determine the crystallinity of the sample, the precise unit-cell parameters, and the departure from the ideal axial ratio in the orthorhombic phases, lines at high angles (50–70°θ for Co$K\alpha_1$ radiation) were taken], ir spectroscopy (Beckman IR 12, KBr disks for the 1000–250 cm^{-1} region; Polytec FIR 30 interferometer, polythene disks for the 350–30 cm^{-1} region), and, in some cases, Raman spectroscopy (Coderg PHO double monochromator, equipped with a 50-mW Spectra Physics He–Ne laser). Some Fe compounds were also investigated by Mössbauer spectroscopy in the Atomic and Molecular Physics Department at the University of Liège.

Results

Compositions Giving a Spinel Phase

As stated in the Introduction, the number of compositions leading to a spinel phase is unexpectedly large, and only a part of them have been investigated, especially for "mixed-cation" phases (phases containing different cations of the same valency).

Simple phases (one type only of each M^{II} and M^{III} cations). Results related to simple phases are collected in Table I. For all (or nearly all) the trivalent cations investigated (except Lu, which is most probably too large), a pure spinel phase is formed with Zn or Co, namely, the bivalent cations whose tendency to occupy tetrahedral sites is strong or fairly strong. Mg also gives a spinel phase (ordered or not: see below) with many (but not all) of the investigated trivalent cations. The compounds with Ni or Cd were not systematically investigated, but a pure spinel phase was never obtained. Cd is probably too large to be the predominantly cationic species in a spinel phase. And if a pure spinel Ni_4FeSbO_8 did exist, it would imply the localization, on the tetrahedral sites, of a significant fraction of the Ni cations. Although not quite impossible, this is somewhat improbable.

Complex phases. We shall restrict ourselves to complex phases which may be written $M^{II}_{4-x}M'^{II}_{x}M^{III}SbO_8$, where x is an integer (1, 2, or 3). Even with these limitations, the number of possible compositions remains rather large, and only some of them have been investigated so far. At first sight, such compositions could be considered as presenting no particular interest, since they are mainly solid solutions between the above-mentioned simple phases. In fact, some of them are rather important, because the cation distribution, which in turn determines the possibility of order–disorder transitions, may be quite different in the solid solutions and in the parent compounds. On the other hand, it is possible to synthesize mixed phases for which at least one of the parent compounds is unknown (or, more precisely, has not been obtained so far). For example, Ni_4FeSbO_8 has not been obtained; but $Ni_3ZnFeSbO_8$ can be synthesized, with an ordered cation distribution which is quite different from that existing in the other parent compound Zn_4FeSbO_8.

TABLE I

SPINEL PHASES CORRESPONDING TO THE FORMULA $M_4^{II}M^{III}SbO_8$[a]

M^{II}		M^{III} Al	Ga	In	Fe	Cr	Rh	Sc
Zn_4	d[b]	8.464 (1100)	8.524(>800)	—	8.552 (1300)	8.521 (1200)	8.570 (1200)	—
	o	8.464 (1000)	8.524 (600)	8.669 (800)	8.552 (1000)	8.523 (700)		8.624 (1200)
Zn_3Co	d				8.545 (1200)			
	o			8.663	8.545 (800)			8.613
Zn_3Mg	d	8.450 (1300)			8.533 (1200)			
	o			8.654	8.533 (850)			8.610
Zn_3Ni	d			8.640	8.518 (1200)			
	o				8.518 (800)			8.590
Zn_3Cu	d			8.650	8.536 (1070)			8.608
	o							
Zn_2Co_2	d				8.533 (1200)	8.501		
	o							
Zn_2Mg_2	d				8.521 (1200)	8.499 (1300)		
	o							
Zn_2Ni_2	d			8.607	8.487 (1200)			8.561
	o							
Co_4	d	8.439 (1350)	8.508	8.651 (1350)	8.536 (1200)	8.499		(8.566)
	o		*		*			
Co_3Zn	d	8.446 (1350)	8.501 (1300)		8.538 (1300)			
	o							
Co_3Mg	d	8.438 (1350)	—		8.535 (1300)			
	o		*					
Co_3Ni	d	8.420 (1350)	8.477 (1350)		8.509 (1300)			
	o		*					
Co_2Ni_2	d	8.403 (1350)	—					
	o		*		*			
Mg_4	d	—	—		—	8.493 (1300)		
	o	*	*		*			
Mg_3Co	d	8.426 (1350)	—		—			
	o		*		*			
Mg_3Zn	d	8.424 (1350)	—		8.512	8.494 (1300)		
	o		*		*			
Mg_3Ni	d	—	—		—			
	o	*	*		*			
Mg_2Ni_2	d	—	—		—			
	o	*	*		*			
Mg_2Co_2	d		—					
	o		*					
Ni_3Zn	d	8.389	—					
	o	*	*					
Ni_3Mg	d	—	—		—			
	o	*	*					
Ni_3Co	d	—	—					
	o	*	*		*			

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[a] Cubic phases: unit-cell parameter (to 0.001 Å) and synthesis or tempering temperature (°C).

[b] (d) Disordered, (o) ordered, (—) disordered phase not obtained by air quenching from 1300°C, (*) orthorhombic phase.

Structural Types and Cation Distributions

On the basis of their X-ray powder diagrams, the antimonate spinels may be distributed into three structural types: face-centered cubic, space group $Fd3m\text{-}O_h^7$; primitive cubic, space group $P4_332\text{-}O^6$ or $P4_132\text{-}O^7$; orthorhombic, possible space group $Imma\text{-}D_{2h}^{28}$. A general view of the results is given in Table I.

Cubic Phases

Only cubic phases are *always* obtained for the compositions Zn_4, Zn_3M^{II}, and $Zn_2M_2^{II}M^{III}SbO_8$, when at least two Zn cations are present in the compound. In view of the strong preference of Zn for tetrahedral sites, the cation distribution is expected to be $Zn_2[M_2^{II}M^{III}Sb]O_8$, even if, by its very nature, the trivalent cation M^{III} is able to enter the tetrahedral sites. This type of distribution is supported by Mössbauer and vibrational spectra: Mössbauer spectra of such iron compounds (e.g., Zn_4FeSbO_8) exhibit one doublet whose isomer shift is within the range already observed for octahedral, trivalent iron (*9, 10*). And the ir spectrum of Al compounds (Zn_4AlSbO_8) has no band above 700 cm^{-1}, thus suggesting the absence of AlO_4 tetrahedra (*11*) (Fig. 1). A similar cation distribution (namely, bivalent cations only on tetrahedral sites) is also observed when M^{III} has a strong preference for octahedral sites and, in fact, is unable to enter tetrahedral sites (Cr, Rh, Sc). Here again, and as far as a pure spinel phase does really exist (Mg_4CrSbO_8 is a pure spinel but Mg_4ScSbO_8 has not been obtained), only cubic phases are observed. In fact, these cubic phases are obtained when no trivalent cations are on tetrahedral sites.

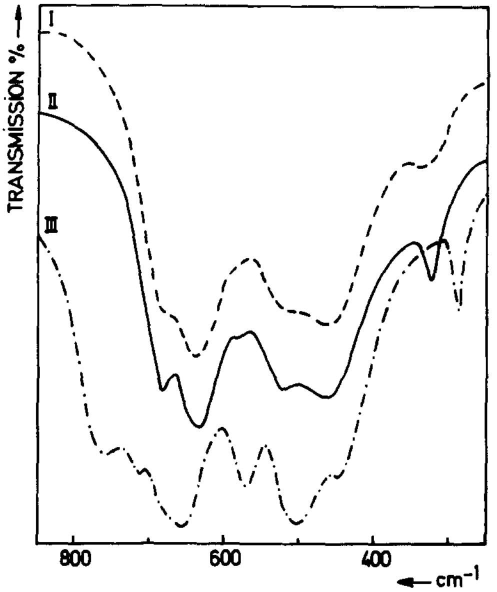

FIG. 1. Infrared spectra of cubic Zn_4AlSbO_8 (I, disordered; II, ordered) and of orthorhombic Mg_4AlSbO_8 (III). For the latter compound, bands in the 800–700 cm^{-1} region point to the existence of AlO_4 tetrahedra; these bands are missing in the spectra of Zn_4AlSbO_8, where all Al^{3+} cations should be octahedrally coordinated.

Order–Disorder Transitions in the Cubic Phases

The cation distribution $M_2^{II}[M_2^{II}M^{III}Sb]$ suggests the possibility of two ordering schemes: either a 3:1 octahedral order obtained by putting together $2M^{II}+M^{III}$ against Sb^V, or a 1:1 octahedral order of the type $2M^{II}/M^{III}+Sb^V$, the latter being less probable than the former in view of the cation valencies. Both types of order are well known in spinels, leading to either a primitive cubic cell (3:1 order) or a diagonal, tetragonal cell (1:1 order). Most of the $Zn_4M^{III}SbO_8$ compounds (some of them only after tempering at an appropriate temperature) exhibit a number of superstructure lines which are easily indexed by considering a primitive cubic cell with $a = a_{0_{\text{spinel}}}$ (Table I), thus revealing a 3:1 ordering of the octahedral cations. No 1:1 ordering has been detected so far in the X-ray powder diagrams.

Generally, an ordered phase is slightly denser than the corresponding disordered one, and the unit-cell parameter is accordingly smaller. No such variation has been observed here; it is within the precision limits of our a_0 determinations (± 0.001 Å). It is perhaps worthwhile to point out that, even in the 3:1 ordered phases, some disorder must remain, since two types of cations ($2M^{II} + 1M^{III}$) must be located on the three available octahedral sites. The ability of ordering strongly depends on the nature of the bivalent cation: Nearly all the phases $Zn_4M^{III}SbO_8$ have been obtained in the ordered state (one exception only: Zn_4RhSbO_8), and some of them are still ordered after air quenching from 1300°C.

This is also true if one of the four Zn cations is replaced, leading to $Zn_3M^{II}M^{III}SbO_8$ phases. But no 3:1 ordering has been obtained so far if the number of Zn cations is reduced to 2 ($Zn_2M_2^{II}M^{III}SbO_8$), or if Zn is absent (e.g., Co_4Cr, Co_4Sc, Mg_4CrSbO_8).

Copper has a marked deleterious influence on the ordering process: No ordering has been observed for the compounds $Zn_3CuM^{III}SbO_8$ investigated so far (M^{III} = In, Fe, Sc). This influence is also evident from the study of the phases $Zn_{4-x}Cu_xInSbO_8$: Ordering is immediately obtained by air quenching from 1100°C for $x = 0.05$, 0.10, 0.20, and 0.30; for $x = 0.50$ and 0.70, ordering is achieved only after slow cooling (from 1100 to 700°C in several weeks); and for $x = 1.0$ and 2.0, no ordering has been observed so far.

Likewise, the ordering process is influenced by the nature of the trivalent cation (ordering is obtained very easily for Zn_4FeSbO_8; with much difficulty for Zn_4CrSbO_8; and not at all for Zn_4RhSbO_8), but the matter has not been investigated systematically.

Orthorhombic Phases

The X-ray powder diagram of some compounds exhibits, in addition to prominent spinel reflections, a fairly large number of peaks which are generally weak or very weak and cannot be accounted for by the above-mentioned 3:1 or 1:1 octahedral order (Fig. 2). These peaks were first assigned to some unknown impurities; but it was rapidly realized that, in some cases at least, they may *reversibly* disappear or reappear as a function of temperature: They disappear (thus leaving a simple spinel diagram) by quenching from a sufficiently high temperature and come back by slow cooling, or tempering, at a lower temperature. This suggests that these extra peaks are due to some cation ordering, a hypothesis which is definitely confirmed by the strong analogy existing between these X-ray diagrams and that of ordered $LiGaTiO_4$ (*12*). In this latter case, Bertaut and Patrat have interpreted the X-ray diagram on the basis of an orthorhombic cell derived from the spinel lattice with $a = a_{0_{sp}}/2^{1/2}$; $b = 3a$; $c = a_{0_{sp}}$.

This interpretation may be extended without modification to the antimonates under consideration and leads to the indexing of all observed reflections. Examples (Co_4GaSbO_8 and Mg_4FeSbO_8) of indexed powder diagrams are given in Table II. Indexed powder diagrams of other phases are available on request from the authors. Information on the orthorhombic phases obtained so far is collected in Table III.

Unit-Cell Parameters and Volumes of the Orthorhombic Phases

For the unit-cell parameters, the "ideal" ratio would be $b = 3a$ and $c = a2^{1/2}$. A look at Table III shows that this is generally not the case. There is no really clear-cut trend for the b/a ratio, which is either greater or smaller than 3; it may be noticed, however, that it is generally smaller than 3 for Al compounds. On the contrary, the $a2^{1/2}/c$ ratio is *always* greater than unity, with a general increase with decreasing ionic radius of the trivalent cation: The average values of $a2^{1/2}/c$ are 1.002 for Fe; 1.005 for Ga; and 1.007 for Al compounds. For Fe compounds,

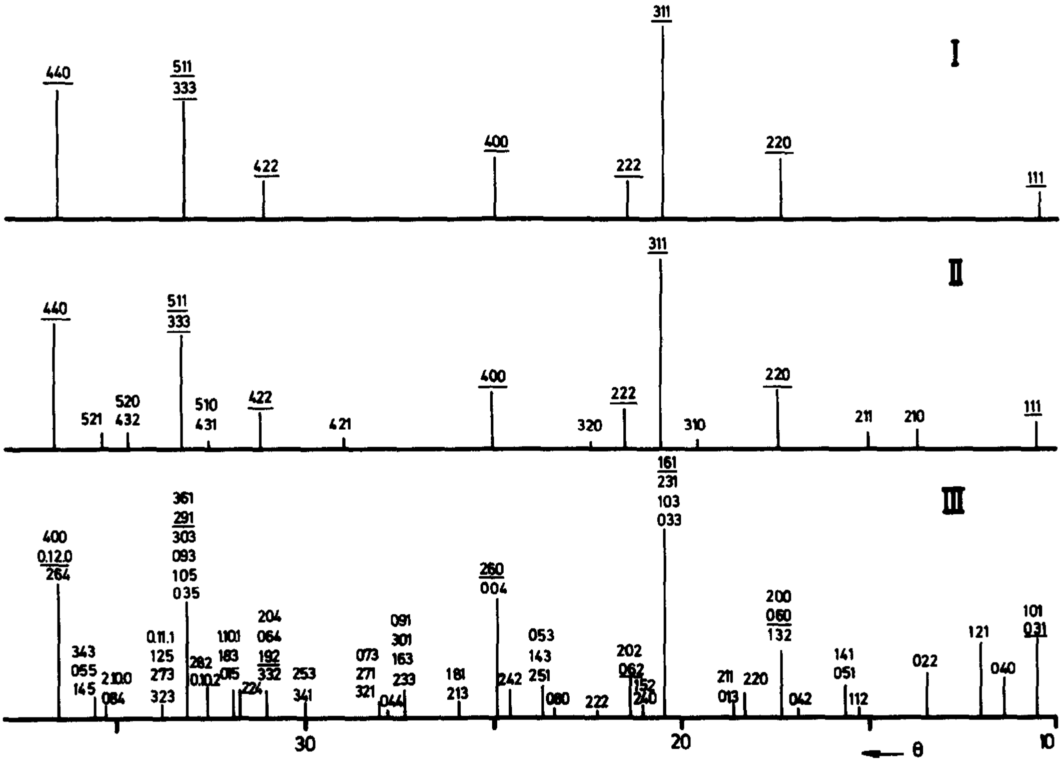

FIG. 2. Examples of the three types of X-ray powder diagrams (Co*Kα* radiation). (I) Zn_4AlSbO_8, quenched from 1100°C (disordered, face-centered cubic *Fd*3*m*); (II) Zn_4AlSbO_8, quenched from 1000°C (3:1 octahedral order; primitive cubic $P4_332$ or $P4_132$); (III) Mg_4FeSbO_8 (complex order, orthorhombic). The relative intensities of the most intense spinel reflections (311, 400, 511–333, 440) are greater than indicated in these diagrams. The underlined *h k l* are the spinel ones or the indices deduced from the spinel ones in the new orthorhombic cell.

the departure from unity is rather small and does not appear in a standard powder diagram; but the phenomenon is easily evidenced by investigating the doublet 4.12.0–008, which lies in the 55–60°θ range for Co*Kα* radiation. In the case of an $a/b/c$ ideal ratio, there would be perfect overlap and one peak only should be present; but in fact, we always observe a doublet, whose separation gives immediately an idea of the departure from the ideal case.

There is also a general increase of unit-cell parameters and volumes with increasing values of the ionic radii of the cations; but no quantitative relationship could be derived, because of the complexity of both chemical composition and cation distribution (see below).

Until now, we have obtained only five compounds as both orthorhombic and cubic (disordered) structures. In this case, the ordering brings out a very significant volume decrease (Table IV; the volume of the cubic phase has been multiplied by $\frac{3}{2}$, so as to allow a direct comparison with that of the orthorhombic phase). To better realize the importance of this contraction, it is useful to consider, for a given compound such as Co_4FeSbO_8, what reduction of the cell edge a_0 would be necessary to obtain the observed volume contraction if the crystal cell remained cubic: it is found

TABLE II

INDEXED POWDER DIAGRAMS OF ORTHORHOMBIC Co_4GaSbO_8 AND Mg_4FeSbO_8

	Co_4GaSbO_8		Mg_4FeSbO_8	
h k l	*d*	*I*	*d*	*I*
101–031	4.912	12	4.912	17
040	4.519	4	4.512	11
121	4.318	5	4.309	16
022	3.837	4	3.843	11
112			3.403	2
141–051	3.325	3	3.320	6
042			3.088	2
200–060–132	3.007	22	3.003	13
220	2.858	2	2.851	5
211–013	2.789	0.8	2.796	4
161–231–103–033	2.566	100	2.561	100
152–240			2.501	2
202–062	2.454	20	2.453	8
222			2.367	1
080	2.257	1	2.257	3
053–143–251	2.225	1.6	2.225	8
242	2.156	2	2.155	7
260	2.129	25	2.124	42
004	2.117	(11)		
181–213			2.049	2
091–301–163–233	1.9490	2.5	1.9490	4
044			1.9192	2
073–271–321			1.9060	4
253–341	1.7932	1	1.7897	2
204–064–192–332	1.7374	9	1.7349	7
224	1.6991	2.5	1.7015	6
1.10.1–183–015	1.6953	2.5	1.6939	6
282–0.10.2	1.6627	2.5	1.6605	7
361–291–303–093	1.6386	33	1.6351	36
105–035	1.6306	(14)		
0.11.1–125–273–323			1.6069	3
2.10.0–084			1.5463	3
343–055–145	1.5339	1	1.5361	5
400–0.12.0	1.5052	(23)	1.5023	66
264	1.5016	42		
4.12.0	1.0649	6	1.0633	7
008	1.0586	3	1.0609	4

that the cell edge should drop from 8.536 to 8.526 Å.

Cation Distribution in the Orthorhombic Phases

It must first be pointed out that the cation distribution responsible for the orthorhombic spinel antimonates has not been fully elucidated so far. So we must restrict ourselves to the discussion of some experimental facts and of the various cation distributions which are compatible with them.

The first point is of a chemical nature: Orthorhombic spinel antimonates are *never* obtained when all the tetrahedral sites are occupied by bivalent cations, either because there is a sufficient number of bivalent cations with a strong tetrahedral preference (Zn in $Zn_2M^{II}_2$, Zn_3M^{II}, or $Zn_4M^{III}SbO_8$), or because the trivalent cation is necessarily located on the octahedral sites (Cr, Rh, Sc). On the contrary, orthorhombic phases may be obtained when the chemical nature of the cations is such that the trivalent cation may be located on the tetrahedral sites; this is the case for M^{II} = Mg, Co, Ni and M^{III} = Al, Ga, Fe. Indeed, the ir spectrum of orthorhombic Mg_4AlSbO_8 shows in the 800–700 cm^{-1} region strong bands which point to the presence of AlO_4 tetrahedra (*11*). These bands are missing in the ir spectrum of Zn_4AlSbO_8, where the coordination of Al is octahedral (Fig. 1). The most simple cation distribution corresponding to this situation would be $(M^{II}:M^{III})[M^{II}_3:Sb^{V}]$, leading to the possibility of a simultaneous 1 : 1 (tetrahedral) and 3 : 1 (octahedral) cation ordering. Although fairly attractive, this hypothesis is not supported by the following facts:

(i) One case of simultaneous 1 : 1 tetrahedral and 3 : 1 octahedral order in (LiZn)-$[LiMn_3]O_8$ slowly cooled to 350°C is already known; it leads, not to an orthorhombic, but to a primitive cubic phase, space group $P2_13$-T^4 (*13, 14*).

(ii) The very great similarity between the X-ray diagrams of $LiGaTiO_4$ and of the antimonates suggests an analogy in the cation distribution. For $LiGaTiO_4$, the proposed space group is *Imma*-D_{2h}^{28} and the cation distribution is $(Ga_2:Li)[(Ti_3Ga):Li_2]$ with a 2 : 1 ordering on both tetrahedral and octahedral sites (*12*). Two points should be considered separately in this information:

TABLE III

UNIT-CELL PARAMETERS, VOLUMES, AND AXIS RATIOS OF THE ORTHORHOMBIC PHASES[a]

	a	b	c	V	b/a	$a2^{1/2}/c$
Al compounds						
Mg_4	5.961	17.864	8.378	892.1	2.997	1.006
Mg_3Ni	5.967	17.809	8.355	887.8	2.985	1.010
Mg_2Ni_2	5.948	17.803	8.354	884.6	2.993	1.007
Ni_3Zn	~5.947	~17.766	~8.351	~882.3	~2.987	~1.007
Ni_3Mg	5.941	17.789	8.336	881.0	2.994	1.008
Ni_3Co	5.934	17.833	8.340	882.6	3.005	1.006
Mean					2.993	1.007
Ga compounds						
Mg_4	~5.987	~17.970	~8.446	~908.7	~3.001	~1.002
Mg_3Zn	5.987	17.993	8.441	909.3	3.005	1.003
Mg_3Co	6.004	18.000	8.450	913.2	2.998	1.005
Mg_3Ni	5.986	17.959	8.431	906.3	3.000	1.004
Mg_2Ni_2	5.978	17.935	8.414	902.1	3.000	1.005
Mg_2Co_2	6.010	18.030	8.453	916.0	3.000	1.006
Co_4	6.026	18.066	8.470	922.1	2.998	1.006
Co_3Mg	6.010	18.056	8.460	918.0	3.004	1.005
Co_3Ni	5.991	18.022	8.446	911.9	3.008	1.003
Co_2Ni_2	5.989	17.960	8.428	906.6	2.999	1.005
Ni_3Zn	5.972	17.909	8.408	899.3	2.999	1.004
Ni_3Mg	5.978	17.927	8.397	899.9	2.999	1.007
Ni_3Co	5.986	17.906	8.407	901.1	2.991	1.007
Mean					3.000	1.005
Fe compounds						
Mg_4	6.014	18.053	8.491	921.9	3.002	1.002
Mg_3Zn	6.012	18.028	8.502	921.5	2.999	1.000
Mg_3Co	6.022	18.067	8.498	924.6	3.000	1.002
Mg_3Ni	6.000	18.028	8.477	916.9	3.005	1.001
Mg_2Ni_2	5.997	17.994	8.463	913.2	3.000	1.002
Co_4	6.023	18.130	8.514	929.7	3.010	1.000
Co_2Ni_2	5.999	18.003	8.468	914.5	3.001	1.002
Ni_3Co	5.991	17.983	8.442	909.5	3.002	1.004
Mean					3.002	1.002

[a] The parameters have been refined by a least-squares program written in Fortran IV. Typical standard deviations are 0.002–0.005 Å for a, 0.005–0.015 for b and 0.001–0.003 for c. In a few cases, the superstructure lines were broad, thus leading to larger errors.

the space group, and the cation distribution. Space group: The extinction rules of the *Imma* space group (hkl present only if $h+k+l=2n$; $hk0$ if $h=2n$ ($k=2n$)] are verified in the X-ray powder diagram of the orthorhombic antimonates. Thus, *Imma* may be adopted as a *possible* space group. It must be immediately pointed out that the site multiplicities involved in this space group are not compatible with the (1 : 1) [3 : 1] ordering suggested above. Cation distribution: If we extend to antimonates the (2 : 1)(2 : 1) cation ordering proposed for $LiGaTiO_4$, we obtain the following distribution (after multiplying by 3 the original formula in order to have integer numbers of atoms on each site): $(M^{II}_4 : M^{III}_2)[M^{II}_8 : M^{III} + Sb^{V}_3]$. The most importance difference, with respect to the

TABLE IV

VOLUME CONTRACTION ASSOCIATED TO THE CUBIC → ORTHORHOMBIC TRANSITION

Compound	$V_{\text{cub}}\times\frac{3}{2}$	V_{ortho}	$V_{\text{cub}}/V_{\text{ortho}}$
$Mg_3ZnFeSbO_8$	925.1	921.5	1.0039
Co_4GaSbO_8	923.8	922.1	1.0018
Co_4FeSbO_8	932.9	929.7	1.0034
$Co_3NiGaSbO_8$	913.7	911.9	1.0019
$Ni_3ZnAlSbO_8$	885.6	882.3	1.0037

(1 : 1)[3 : 1] order suggested previously, is the presence of the trivalent cation M^{III} on both tetrahedral and octahedral sites, in the 2 : 1 abundance ratio. On the other hand, it is necessary to achieve the 2 : 1 octahedral order, to put together $M^{\text{III}}+3\text{Sb}^{\text{V}}$ against $8M^{\text{II}}$. This is quite possible, but, in view of the valencies of the cations participating in the ordering phenomenon, it would be more appealing to consider the distribution $8M^{\text{II}}+M^{\text{III}}:3\text{Sb}^{\text{V}}$, leading to a 3 : 1 octahedral order.

(iii) In contrast with cubic phases such as Zn_4FeSbO_8, which give one doublet corresponding to octahedral Fe, all orthorhombic phases $M_4^{\text{II}}FeSbO_8$ give a Mössbauer spectrum consisting of *two* doublets characterized by a 2 : 1 intensity ratio, and very different quadrupole splittings.[1] This gives the unquestionable proof that there are two types of Fe cations, characterized by rather different environments. Two interpretations of this result may be proposed: Iron may be located on tetrahedral sites only, like $(M_3^{2+}Fe_2^{3+}Fe^{3+})[M_9^{2+}Sb_3^{5+}]$; but there are two rather different types of FeO_4 tetrahedra. Although not impossible, this interpretation is not very probable. Or iron may be distributed over tetrahedral and octahedral sites in a 2/1 ratio like $(M_4^{2+}Fe_2^{3+})$-$[M_8^{2+}Fe^{3+}Sb_3^{5+}]$. This latter distribution is much more probable than the former one, and it is supported by the fact that the less intense doublet is characterized by an isomeric shift and a quadrupole splitting which are very similar to those observed in Zn_4FeSbO_8 (octahedral Fe^{3+}). To check this point, solid solutions $Mg_4Fe_{1-x}Cr_xSbO_8$ were synthesized and investigated by both X-ray diffractometry and Mössbauer spectroscopy. For such solid solutions, the following predictions can be made:

—If all Fe of the orthorhombic phase is located on tetrahedral sites, its replacement by significant amounts of Cr is impossible, and solid solutions will be necessarily of the cubic, disordered type.

—If, on the contrary, the orthorhombic phase is characterized by the distribution of $\frac{2}{3}$ Fe over tetrahedral and $\frac{1}{3}$ Fe over octahedral sites, it should be possible to replace this octahedral Fe by Cr without destroying the cationic order responsible for the orthorhombic symmetry. The limiting composition would be $Mg_4Fe_{0.67}Cr_{0.33}SbO_8$, corresponding to the cation distribution $(Mg_4;Fe_2)[Mg_8CrSb_3]$. Experiments were carried out for $x = 0.05$, 0.10, 0.20, and 0.30. Phases with $x = 0.05$ and 0.10 immediately gave an orthorhombic phase by air quenching from 1300°C; in the same conditions, cubic phases were obtained for $x = 0.20$ and 0.30, but they transformed into orthorhombic phases by progressive cooling from 1300 to 1050°C and tempering for 3 days at this temperature. X-Ray powder diagrams point to a small, although significant, decrease of unit-cell parameters with increasing x values, thus showing that Cr has really replaced some Fe. But the most interesting result is given by Mössbauer spectroscopy; the doublet characterized by the greater intensity and the larger quadrupole splitting (tetrahedral Fe) is not significantly modified; but the second doublet, characterized by a small intensity and a smaller quadrupole splitting, decreases in intensity with increasing values of x and nearly completely disappears for $x = 0.30$. This is a further indication that this second

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[1] A detailed discussion of the Mössbauer results will appear elsewhere.

doublet is due to octahedral Fe (and not to a second type of tetrahedral Fe). In the pure Fe compound, the cation distribution is thus $(Mg_4Fe_2)[Mg_8FeSb_3]$. Such a distribution gives strong support to a tetrahedral 2:1 order since, in view of the chemical formula $M_4^{II}M^{III}SbO_8$, this tetrahedral 2:1 order *necessarily* implies the localization of $\frac{2}{3}$ of M^{III} on tetrahedral, and the remaining $\frac{1}{3}$ on octahedral sites. This does not solve, however, the problem of the distribution over octahedral sites, namely, either $M_8^{II}:M^{III}+3Sb^{V}$ (2:1 order) or $8M^{II}+M^{III}:Sb_3^{V}$ (3:1 order).

(iv) Intensities of X-ray diffraction peaks. The cation distribution giving the lowest possible value of the reliability factor R was searched with the help of a FORTRAN crystallographic least-squares refinement program from the Argonne National Laboratory modified by P. Wolfers at the CNRS, Grenoble. However, this search was limited to the available crystallographic sites deriving from the spinel structure in the *Imma* space group, for the compound Mg_4FeSbO_8.

The lowest R values are obtained with the following cation distribution:

Tetrahedral sites

$$\left.\begin{array}{l} 8\ Mg^{2+} \text{ in } 8\ h \\ 4\ Fe^{3+} \text{ in } 4\ e \end{array}\right\} 2:1 \text{ order}$$

Octahedral sites

$$\left.\begin{array}{l} 8\ Mg^{2+} \text{ in } 8\ h \\ 8\ Mg^{2+} \text{ in } 8\ g \\ 4\ Sb^{5+} \text{ in } 4\ b \\ 2Sb^{5+} + 2\ Fe^{3+} \text{ in } 4\ c \end{array}\right\} 2:1 \text{ order}$$

It should be pointed out that: (i) Iron is distributed over tetrahedral and octahedral sites, in a 2:1 ratio, in perfect agreement with the interpretation of Mössbauer data; (ii) It was impossible to get R values smaller than 11%. This would suggest that atomic positions are not grossly in error, but also that some features of the proposed structure are possibly not correct. In connection with this point, it may be remembered that the *Imma* space group has been deduced from powder data, and that very faint peaks noncompatible with this group may escape detection. This matter must be further studied and the possibility of obtaining single crystals of these orthorhombic compounds is presently under investigation.

Some Surprising Features of the Orthorhombic Phases

Whatever the final structure, it is worthwhile to point to some unexpected and surprising properties of the orthorhombic phases.

(i) Perhaps the most unexpected fact is the easy ordering between bivalent and trivalent cations on the tetrahedral sites, despite the fact that both valencies and ionic radii of these cations are not very different. Indeed, to the best of our knowledge, there is, for the spinel structure, no well-established case of ordering between bivalent and trivalent cations (Fe_3O_4 should not be considered here, since the order has an electronic origin).

(ii) With the preceding point in mind, it is still more unexpected that some of these phases are still ordered after air quenching from 1300°C (Table I). This does not imply that these phases are still ordered at 1300°C; but the ordering process must be very rapid. This suggests, for the ordered phases, a great stability with respect to the disordered ones.

(iii) The great stability is confirmed by the fact that ordered phases are still obtained with cations which otherwise have a deleterious effect on the ordering process. Copper and nickel are typical cases for this. For example, the inverse spinel germanate $Zn_{1.1}Ni_{0.9}GeO_4$ has been obtained in the ordered form (*15, 16*) but not the corresponding Cu phase $Zn_{1.1}Cu_{0.9}GeO_4$; in a similar phase like $Zn_{1.2}Co_{0.8}GeO_4$, the replacement of only 10% (on a molar basis) of the bivalent cations by copper completely stops the ordering process (*15, 16*); likewise, we have already mentioned in this paper the fact that Zn_4InSbO_8 is very easily ordered but not $Zn_3CuInSbO_8$; in contrast to this, the compounds $Mg_3CuFeSbO_8$ and $Mg_3CuGaSbO_8$ are very easily obtained as ordered, orthorhombic phases.[2] A similar trend is observed with the Ni cation. Generally, Ni-containing spinels are less easily ordered (in some cases, not ordered) than their Ni-free analogs (e.g., Zn_2TiO_4 and $ZnNiTiO_4$; $Zn_{0.9}Co_{1.1}GeO_4$ and $Zn_{1.1}Ni_{0.9}GeO_4$; Zn_4FeSbO_8 and $Zn_3NiFeSbO_8$; etc). The reverse is true for the orthorhombic phases: All compounds of the type $Ni_3M^{II}M^{III}SbO_8$ synthesized so far have been obtained as orthorhombic, ordered phase whereas, for most of them, the disordered phase could not be obtained even by air quenching from 1300°C.

(iv) The existence of ordered, orthorhombic $Ni_3M^{II}M^{III}SbO_8$ phases presents another puzzling feature. The 2:1 tetrahedral order implies for, say $Ni_3MgGaSbO_8$, a cation distribution $(Mg_3Ni{:}Ga_2)$-$[Ni_8GaSb_3]$: Some Ni is necessarily present on tetrahedral sites, whereas $\frac{1}{3}$ of Ga is located on octahedral sites. This is quite unexpected in view of the relative preferences of Ga and Ni for tetrahedral and octahedral sites, respectively.

Magnetic Properties

The magnetic properties of some compounds have been investigated by magnetic susceptibility measurements, neutron diffraction, and Mössbauer spectroscopy. The investigated compounds, which contain between one and five magnetic cations in the formula $M_4^{II}M^{III}SbO_8$, are paramagnetic at room temperature; but magnetic ordering and associated ferrimagnetism appear at more or less lower temperatures, depending on the nature, number, and distribution of the cations. This problem cannot be properly handled without a detailed knowledge of the cation distribution, and the discussion of these results will accordingly be delayed.

Spinel Phases Derived from $M_4^{II}M^{III}SbO_8$

A number of compounds may be theoretically derived from the formula $M_4^{II}M^{III}SbO_8$, but this matter has not been fully investigated so far. We shall only mention here the existence of spinel tellurates $LiM_3^{II}M^{III}Te^{VI}O_8$. These compositions may be derived either from the antimonates by the double replacement $M^{II}Sb^{V} \rightarrow LiTe^{VI}$, or from the known tellurates $M_5^{II}TeO_8$ (*7*, *8*) by the replacement $2\,M^{II} \rightarrow Li + M^{III}$. Progress on such compounds is hindered by their low thermal stability; but for some of them ($M^{II} = $ Ni or Co; $M^{III} = $ Al, Ga, or Fe), the X-ray powder diagram shows a spinel structure whereas weak extra lines point to an orthorhombic superstructure very similar to that observed in the $M_4^{II}M^{III}SbO_8$ antimonates. This analogy is strongly supported by Fe Mössbauer spectra of $LiFeCo_3TeO_8$, which are quite similar to those of $M_4^{II}FeSbO_8$ orthorhombic antimonates.

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