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The Dimorphism of $LiMnFeF_6$: A New Kind of Cationic Order in the Structural Type Na_2SiF_6

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$LiMnFeF_6$ shows a dimorphism; the transition temperature $\alpha \rightarrow \beta$ occurs at 560°C. The symmetry of the two phases is trigonal (space group $P321$, $Z = 3$) and the unit cell data are very close to each other: $a_\alpha = 8.684(2), c_\alpha = 4.657(1), a_\beta = 8.723(2), c_\beta = 4.745(1)$ Å. The absolute structure of α-$LiMnFeF_6$ was determined from single-crystal X-ray data ($R = 0.020$). This crystalline form exhibits a new kind of cationic order in the structural type Na_2SiF_6. The cationic distribution of β-$LiMnFeF_6$ was specified from X-ray and neutron powder diffraction data; this compound is isotypical with the $LiMnGaF_6$ structure. The different kinds of cationic distribution related to the Na_2SiF_6 type are discussed and a classification of the compounds $Li(Na)M^{II}M^{III}F_6$ is given.

Introduction

Fluorinated compounds with formulation $AM^{II}M^{III}F_6$, in which A is an alkali metal, e.g., Li or Na, and M^{II} and M^{III} are cations of the first row transition, were extensively studied. Two structural types are well known: (i) trirutile type with quadratic symmetry for $LiNiCrF_6$ and many other compounds (*1*, *2*), and (ii) Na_2SiF_6 type with trigonal symmetry for $LiMnGaF_6$ (*3*) and $NaMnCrF_6$ (*4*).

The compounds $AM^{II}M^{III}F_6$ with trigonal symmetry are derived from Na_2SiF_6 type (*5*) by the substitution $Na^+ + Si^{4+} \rightarrow M^{II} + M^{III}$. Three different kinds of cationic order are now known for the phases $LiMnGaF_6$ (*3*), $NaMnCrF_6$ (*4*), and $LiMnInF_6$ (*6*). For the latter compound, the cationic order claimed by J. Gaile is the result of refinements on powder data.

Taking into account all the possibilities offered by the cationic network of Na_2SiF_6, other cation distributions may exist. For this reason $LiMnFeF_6$ was studied and the dimorphism of $LiMnFeF_6$ is presented with a description of both structures and discussion on the classification of the compounds $Li(Na)M^{II}M^{III}F_6$ which are related to Na_2SiF_6 type.

Experimental and Characterization

The compound $LiMnFeF_6$ was first synthetized by Viebahn (*3*). In the present study, $LiMnFeF_6$ was prepared by mixing stoichiometric amounts of LiF, MnF_2, and FeF_3 in gold tubes which were then sealed under argon. Starting from a temperature of 650°C, two phases, showing different X-ray patterns, can be obtained:

—air or water quenching gives a light beige powder (β form) whose X-ray powder diffraction is very close to those of $NaMnCrF_6$ or $LiMnGaF_6$.

—slow cooling (about 100°C/hr) leads to

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a pale green powder (α form) now showing an X-ray pattern very similar to that of $LiMnInF_6$. The two phases can be indexed on an hexagonal cell with very close parameters (Table I).

In order to obtain more details about the thermal behavior of these phases, analyses, using a Netzsch Model 404 differential thermal analyser, were performed on α-$LiMnFeF_6$. With a heating and cooling rate of 120°C/hr, the typical phase-transition peaks were seen at 560 ± 4°C for the $\alpha \rightarrow \beta$ conversion and at 495 ± 4°C for the $\beta \rightarrow \alpha$ conversion. The transition enthalpy (cal/g) for this reversible conversion is about eight times greater than that of $\alpha \rightarrow \beta$ SiO_2. If one considers the description of the α and β structures, reported below, this high transition enthalpy must be attributed to ion migration. The observed hysteresis for the reversible transition $\alpha \rightleftarrows \beta$ (ΔT = 65°C) does not seem to be a classical phenomenon for a phase transition, but such an important ΔT value has already been found in the first-order transition of $KAlF_4$: ΔT = 103°C (*11*). The preparation method previously described for α- and β-$LiMnFeF_6$ is then consistent with the thermal stability of each phase.

Single crystals of α-$LiMnFeF_6$ were grown in a chloride flux of zinc chloride. For this growth, a mixture of ($LiF + MnF_2 + FeF_3$) and $ZnCl_2$ (molar ratio 1/12) was heated at 580°C for 12 hr under 1 atm argon pressure. After slow cooling of this flux (4°C/hr) down to 300°C, pale green crystals (<1 mm^3) with hexagonal or trigonal prism habits were isolated. X-Ray analysis gave evidence that only the α form is present.

TABLE I

EXPERIMENTAL DATA FOR $LiMnFeF_6$. SYMMETRY: TRIGONAL Z = 3. TRANSITION TEMPERATURE: α-$LiMnFeF_6$ $\underset{495 \pm 4°C}{\overset{560 \pm 4°C}{\rightleftarrows}}$ β-$LiMnFeF_6$

	α-$LiMnFeF_6$	β-$LiMnFeF_6$[a]
Color	Pale green	Light beige
a (Å)	8.684(2)	8.723(2)
c (Å)	4.657(1)	4.745(1)
V (Å)	304.14	312.68
ρ_{calc} (g/cm^3)	3.795	3.691
ρ_{expt} (g/cm^3)	3.70 ± 0.05	3.59 ± 0.05

[a] Our cell data agree with those of W. Viebahn (*3*).

The results of the crystallographic study—(i) no conditions limiting possible reflections and (ii) Laüe-symmetry $\bar{3}m$ with two-fold rotation axis in the a direction—are consistent with the space groups $P\bar{3}m1$, $P3m1$, and $P321$ and not with $P\bar{3}1m$, $P31m$, and $P312$. The nonlinear optical measurements, made on α- and β-$LiMnFeF_6$ powder specimens (frequency doubling level twice as high as quartz), are consistent with a noncentrosymmetric structure. So, only the space groups $P3m1$ and $P321$ are possible.

Structure Determination

α-$LiMnFeF_6$. A crystal with a hexagonal prism habit limited by ±{001}, ±{010}, ±{$\bar{1}$10}, ±{100} faces (base edges 0.12 mm and height 0.06 mm) was mounted on an automatic four-circle Nonius CAD4 diffractometer. The radiation used (Mo$K\alpha$ filtered by a graphite monochromator) allowed 3748 reflections to collect in the half-space with the following conditions: $-15 \leq h \leq +15$, $0 \leq k \leq 15$, $-8 \leq l \leq +8$ and $3° < \theta < 40°$. After Lorentz polarization corrections, only 3700 reflections are in agreement with the $I > 3\sigma$ test. All the calculations needed for structure determination have been made with the SHELX programm (*7*). So, after analytical absorption corrections (μ = 66.3 cm^{-1}) and intensities averaging in Laüe group 32, 1213 independent reflections remain for structure refinement. Among the space groups allowed, only $P321$ was able to explain the three-dimensional Patterson map when using the 1*a*, 2*d*, 3*e*, and 3*f* sites for heavy atoms and 6*g* sites for fluorine atoms. Different cationic distributions between the available positions were tried and the best results were obtained for Li^+ in $1a$–$2d$, Mn^{2+} in $3e$, and Fe^{3+} in $3f$. Taking into account the anomalous dispersion, the refinement of positional parameters and isotropic thermal parameters for all the atoms leads to the conventional R factors, R = 0.035 and R_w = 0.035. The introduction of secondary extinction parameter and anisotropic thermal parameters for all atoms, except the lithium ones, lowers the discrepancy factors to $R_1 = 0.027$ and $R_{w1} = 0.030$.

Then considering that there is no symmetry plane perpendicular to the trigonal axis, it was interesting to search whether the former proposition was representative of the absolute crystal configuration. So, the enantiomeric configuration was tested with the same refinement conditions. The results are $R_2 = 0.020$ and $R_{w2} = 0.020$ (secondary extinction parameter $x = 19.8(9) \times 10^{-3}$, weighting scheme $w = 1.000/(\sigma^2(F) + 0.001548 F^2)$. The Hamilton test (*8*) applied to the weighting factors R_w—R_{w1}/R_{w2} = $1.48 > \mathcal{R}_{1.1171,\,0.005} = 1.00$—indicates that the last refinement represents the absolute configuration of the studied crystal with a 99.5% significance level.[1] The positional parameters and the anisotropic thermal parameters of this absolute structure are listed in Table II.

β-LiMnFeF$_6$. The structure determination of this phase, in the $P321$ space group, was made by fitting powder intensity data collected from both X rays and neutron diffraction. Taking into account Mössbauer experiment results (*12*)—evidence for two

TABLE II

POSITIONAL PARAMETERS AND ANISOTROPIC TEMPERATURE FACTORS IN α-$LiMnFeF_6$[a,b]

Atom	Site	x	y	z	B_{eq} (Å^2)	$U_{11} \times 10^4$	$U_{22} \times 10^4$	$U_{33} \times 10^4$	$U_{23} \times 10^4$	$U_{13} \times 10^4$	$U_{12} \times 10^4$
Li1	$1a$	0	0	0	1.22(10)	154(13)	—	—	—	—	—
Li2	$2d$	$\frac{1}{3}$	$\frac{2}{3}$	0.5055(8)	1.22(7)	155(9)	—	—	—	—	—
Mn	$3e$	0.3545(0)	0	0	0.48(1)	74(1)	83(1)	68(1)	4(1)	2(0)	41(1)
Fe	$3f$	0.6875(0)	0	$\frac{1}{2}$	0.41(1)	61(1)	56(1)	67(1)	2(1)	1(0)	28(0)
F1	$6g$	0.5311(1)	0.4235(1)	0.2709(1)	0.70(1)	93(3)	115(3)	110(2)	41(2)	35(2)	50(3)
F2	$6g$	0.2214(1)	0.4374(1)	0.2769(1)	0.70(1)	115(3)	98(3)	112(2)	−5(2)	−39(2)	60(3)
F3	$6g$	0.2215(1)	0.1130(1)	0.2435(1)	0.69(1)	111(3)	100(3)	106(2)	−41(2)	−13(2)	55(3)

[a] Estimated standard deviations are given in parentheses.

[b] The vibrational coefficients relate to the expression $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

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[1] See NAPS document No. 03959 for 6 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 for up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

different sites for the Fe^{3+} ions—the structural refinements were done in order to specify if β-$LiMnFeF_6$ was isostructural to $LiMnGaF_6$ or to $NaMnCrF_6$. In these structures the trivalent ion is located in the 1*a* and 2*d* sites and the main structural difference comes from the inversion of alkaline (Li, Na) and manganese ions between the 3*e* and 3*f* positions.

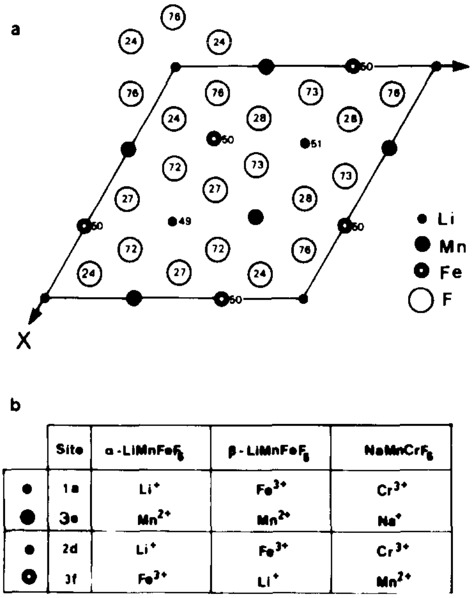
Neutron diffraction recordings were performed at the H.F.R. of Grenoble (I.L.L.) using the D1A instrument ($\lambda = 2.988$ Å); 27 independent intensities were collected at 135K (part of diffraction work for magnetic structure determination). X-Ray intensities were recorded on a semiautomatic Philips goniometer with Cu*K*α radiation (back graphite monochromator); 44 intensities corresponding to 68 *hkl* triplets were collected at room temperature. Because of the relative vicinity of the neutronic scattering constants for Li and Mn ($b_{Li} = -0.214$ and $b_{Mn} = -0.387$), the refinements with neutron data should be less sensitive to cationic distribution than the refinements with X-ray data. From least-squares refinements, it can be concluded that β-$LiMnFeF_6$ has the cationic distribution of $LiMnGaF_6$ ($R_{R.X.} = 0.085$, $R_{neutron} = 0.027$) rather than that of $NaMnCrF_6$ ($R_{R.X.} = 0.25$, $R_{neutron} = 0.050$). For these results the positional parameters are listed in Table III.

TABLE III

ATOMIC COORDINATES FOR β-$LiMnFeF_6$ (NEUTRON DIFFRACTION RESULTS ARE PRINTED IN ITALICS)

Atom	Site	*x*	*y*	*z*	B^a (Å^2)
Fe1	1*a*	0	0	0	0.65
		0	*0*	*0*	*0.60*
Fe2	2*d*	$\frac{1}{3}$	$\frac{2}{3}$	0.493(17)	0.65
		$\frac{1}{3}$	$\frac{2}{3}$	*0.506(4)*	*0.60*
Mn	3*e*	0.360(2)	0	0	0.80
		0.352(4)	*0*	*0*	*0.6*
Li	3*f*	0.69(2)	0	$\frac{1}{2}$	1.00
		0.714(4)	*0*	$\frac{1}{2}$	*0.6*
F1	6*g*	0.537(6)	0.418(6)	0.273(9)	1.20
		0.541(1)	*0.420(2)*	*0.268(4)*	*0.8*
F2	6*g*	0.223(6)	0.458(10)	0.280(8)	1.20
		0.226(4)	*0.462(6)*	*0.270(5)*	*0.8*
F3	6*g*	0.217(9)	0.099(11)	0.238(10)	1.20
		0.221(4)	*0.098(6)*	*0.226(5)*	*0.8*

[a] Isotropic thermal parameters not refined.



	Site	α-$LiMnFeF_6$	β-$LiMnFeF_6$	$NaMnCrF_6$
●	1a	Li^+	Fe^{3+}	Cr^{3+}
●	3e	Mn^{2+}	Mn^{2+}	Na^+
●	2d	Li^+	Fe^{3+}	Cr^{3+}
●	3f	Fe^{3+}	Li^+	Mn^{2+}

FIG. 1. (a) (001) projection of α-$LiMnFeF_6$ absolute configuration and (b) cationic distribution of β-$LiMnFeF_6$ and $NaMnCrF_6$ related to the fluorine framework of α-$LiMnFeF_6$.

Discussion of the Structures

α-$LiMnFeF_6$

The structure of α-$LiMnFeF_6$ is a new example of cationic distribution in the Na_2SiF_6 structural type. It can be described as a slightly distorted hexagonally close-packed fluorine framework with cations placed in half of the octahedral sites. In other words, this structure can be viewed as built up from octahedra-sharing edges and (or) corners to give a three-dimensional network. This can be seen in Fig. 1a, which represents the projection of the studied enantiomeric form on the (001) plane. The octahedra of lithium are quite regular, while those of manganese and iron are distorted, as shown in Table IV, where most of the bond angles and edge lengths are collected.

β-$LiMnFeF_6$

This phase is not a new structural type but is isotypic with the $LiMnGaF_6$ structure. In this structure, the average distances in octahedra—$\overline{\text{Li–F}}$ = 2.04, $\overline{\text{Mn–F}}$ = 2.14, $\overline{\text{Fe–F}}$ = 1.92 Å—are in good agreement with those observed for α-$LiMnFeF_6$ (Table IV). The fluorine framework of α-$LiMnFeF_6$ can be used to describe the structure of the β form. In Fig. 1b, the cationic distribution in β-$LiMnFeF_6$ and $NaMnCrF_6$ is compared to that of α-$LiMnFeF_6$ (for $NaMnCrF_6$ one should consider the reflection of the structure, presented in Ref. (*4*), through the (001) plane). The only major difference between α and β forms is an inversion between the alkaline and trivalent ions.

This structural difference is also observed when calculating the coulombian energy part, *W*, of the network by the Bertaut method (*9*, *10*): $W_\alpha = -2695$ and $W_\beta = -2682$ kcal/mole. The small difference between the network energies is in good agreement with the reversible character of the transition and is not far from the transition enthalpy energy ($\Delta Ht \simeq 4.5$ kcal/mole)

TABLE IV

POLYHEDRAL EDGE LENGTHS AND MAIN DIFFERENT BOND ANGLES IN α-$LiMnFeF_6$[a,b]

Octahedron of manganese: Symmetry 2	
2 × Mn11–F1 = 2.090 Å	F12–Mn11–F15 = 91°5
	F15–Mn11–F23 = 98°2
2 × Mn11–F2 = 2.118	F12–Mn11–F31 = 93°6
	F12–Mn11–F36 = 174°2
2 × Mn11–F3 = 2.170	F24–Mn11–F36 = 84°4
	F24–Mn11–F31 = 85°6
F12–F23 = F15–F24 = 3.000	F31–Mn11–F36 = 81°4
F12–F24 = F15–F23 = 3.180	
F12–F31 = F15–F36 = 3.106	
F24–F31 = F23–F36 = 2.914	
F23–F31 = F24–F36 = 2.883	
F12–F15 = 2.994	Average distances: $\overline{\text{F–F}}$ = 2.999 Å
F31–F36 = 2.831	$\overline{\text{Mn–F}}$ = 2.126
Octahedron of iron: Symmetry 2	
2 × Fe11–F1 = 1.958 Å	F12–Fe11–F15 = 86°2
	F12–Fe11–F22 = 89°9
2 × Fe11–F2 = 1.932	F12–Fe11–F25 = 83°7
	F12–Fe11–F32 = 88°0
2 × Fe11–F3 = 1.917	F12–Fe11–F35 = 173°8
	F22–Fe11–F32 = 94°2
F12–F22 = F15–F25 = 2.749 Å	F22–Fe11–F35 = 91°5
F12–F25 = F15–F22 = 2.595	F32–Fe11–F35 = 97°8
F12–F32 = F15–F35 = 2.693	
F22–F32 = F25–F35 = 2.819	
F22–F35 = F25–F32 = 2.758	
F12–F15′ = 2.675	Average distances: $\overline{\text{F–F}}$ = 2.733 Å
F32–F35 = 2.890	$\overline{\text{Fe–F}}$ = 1.935

TABLE IV—*Continued*

Octahedron of lithium 1: Symmetry 32

6 × Li11-F3 = 2.013 Å

F33-F32 = F31-F32 = F31-F33 = 2.883
F35-F36 = F34-F35 = F34-F36 = 2.883
F33-F35 = F31-F36 = F32-F34 = 2.831
F32-F35 = F31-F34 = F33-F36 = 2.791

F31-Li11-F32 = 91°4
F31-Li11-F34 = 87°8
F31-Li11-F35 = 178°9
F31-Li11-F36 = 89°3

Average distances: $\overline{\text{F-F}}$ = 2.847 Å
$\overline{\text{Li-F}}$ = 2.013

Octahedron of lithium 2: Symmetry 3

3 × Li21-F1 = 1.999 Å

3 × Li21-F2 = 2.024

F16-F15 = F14-F15 = F14-F16 = 2.957
F16-F23 = F14-F21 = F15-F22 = 2.595
F15-F23 = F14-F22 = F16-F21 = 2.837
F22-F23 = F21-F22 = F21-F23 = 2.984

F14-Li21-F15 = 95°4
F14-Li21-F21 = 80°3
F14-Li21-F22 = 89°6
F14-Li21-F23 = 173°7
F21-Li21-F22 = 94°9

Average distances: $\overline{\text{F-F}}$ = 2.843 Å
$\overline{\text{Li-F}}$ = 2.012

Interatomic distances and angles

Fe11-Mn12 = Fe11-Mn13 = 3.726 Å
Fe11-Li21 = Fe13-Li22 = 2.987
Fe11-Mn11 = 3.708
Mn11-Li11 = 3.076
Mn11-Li21 = 3.655
Mn13-Li21 = 3.627
Li11-Li21 = 5.533

Mn13-F21-Fe13 = 132°7
Mn12-F21-Fe13 = 133°8
Li11-F31-Mn11 = 94°6
Li11-F31-Fe13 = 130°7
Li21-F21-Fe13 = 98°0
Li21-F21-Mn12 = 124°1
Li21-F11-Mn13 = 125°0

[a] Standard deviations are all <0.002 Å and <0°1.

[b] Each atom is noted by two numbers (X *n* *m*). *n* refers to the independent positions as noted in Table II. *m* refers to the coordinates of an equivalent position as given in the order of International Tables. For example, F32 means fluorine F_3 in position $y, x - y, z$.

estimated by comparison with the $\alpha \rightarrow \beta$ SiO_2 transition in D.T.A. measurements. Taking into account that the repulsion terms are very similar in the α and β forms, the values of W_α and W_β are also consistent with the fact that the stable room temperature form is α-$LiMnFeF_6$.

Classification of Li(Na)$M^{II}M^{III}F_6$ Compounds

As previously stated, Na_2SiF_6 structure shows a fluorine framework related to the hexagonally close-packed framework with cations placed in half of the octahedral sites. In space group *P*321, four crystallographic sites are used (1*a*, 2*d*, 3*e*, and 3*f*) for only three kinds of cations (Li(Na), M^{II}, and M^{III}). When looking at all the cationic distribution possibilities that lead to an order, it is clear that only six different orders, collected in three groups, are possible (Table V). The main difference between two

TABLE V

CLASSIFICATION OF $AM^{II}M^{III}F_6$ COMPOUNDS RELATED TO Na_2SiF_6 STRUCTURE

		Group 1		Group 2		Group 3	
		a	b	a	b	a	b
	Site	α-$LiMnFeF_6$		β-$LiMnFeF_6$ $LiMnGaF_6$	$NaMnCrF_6$		
z = 0	1*a*	A^+	A^+	M^{III}	M^{III}	M^{II}	M^{II}
	3*e*	M^{II}	M^{III}	M^{II}	A^+	M^{III}	A^+
z = ½	2*d*	A^+	A^+	M^{III}	M^{III}	M^{II}	M^{II}
	3*f*	M^{III}	M^{II}	A^+	M^{II}	A^+	M^{III}

groups lies in the charge of the cation present in sites 1*a* and 2*d*. Inside each group, the difference comes only from a cation inversion between the 3*e* and 3*f* sites.

Group 2 is the only case for which the two distributions are known: $LiMnGaF_6$ (*3*) and $NaMnCrF_6$ (*4*). It seems that the size of cations has a strong influence on the cationic distribution and the following criteria can be derived:

—the smallest ion always fills the 1*a* and 2*d* sites;

—the biggest ion always fills the 3*e* site at level $z = 0$;

—the ion of medium size fills the 3*f* site at level $z = \frac{1}{2}$.

For group 1, only one example is known: α-$LiMnFeF_6$. However, the compounds of the family $LiM^{II}InF_6$ certainly have a distribution related to this group if we consider first the great similarity of the X-ray patterns and secondly the cationic distribution suggested by Gaile *et al.* (*6*). From our observations, the phases α-$LiMnTiF_6$ and α-$LiMnVF_6$ (*6*) should also belong to this group, but powder X-ray studies do not allow us to settle if the cationic distribution is *a* or *b*.

The compounds of group 3 differ from those of group 2 only by the inversion of M^{II} and M^{III} ions between the 1*a*, 2*d*, and 3*e* sites. Presently, no compound belonging to this group is known.

In Fig. 2, the three known cases of cationic order are presented. Though these structures are closely related to the Na_2SiF_6 structural type, it must be borne in mind that no solid solution is possible between these three compounds.

From this classification, it can be seen that compounds derived from Na_2SiF_6 structure are particularly interesting for the study of magnetic superexchange interactions. This will be the subject of a subsequent paper.

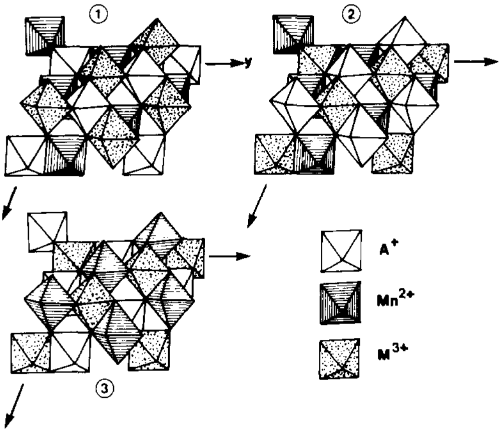


FIG. 2. Idealized representation ($z = 0, z = \frac{1}{2}$) of the three known cationic repartitions: ① α-$LiMnFeF_6$, ② β-$LiMnFeF_6$, ③ $NaMnCrF_6$.

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