

Influence of Cationic Substitutions in $\text{Na}_3\text{Fe}_2(\text{AsO}_4)_3$: Transition from the Garnet to the Alluaudite Structure

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Received May 2, 1997; in revised form December 1, 1997; accepted December 2, 1997

The substitution in $\text{Na}_3\text{Fe}_2(\text{AsO}_4)_3$ of Na^+ by either Li^+ or Ca^{2+} and a vacancy, is able to stabilize an alluaudite structure at the expense of either the garnet or the rhombohedral structure of the parent compound. In the system $(\text{Na}_{1-x}\text{Li}_x)_3\text{Fe}_2(\text{AsO}_4)_3$, pure garnet phases are obtained at 700°C in the $0 \leq x \leq 0.333$ composition range, whereas pure (or nearly so) alluaudite phases are obtained at 870°C in the $0.333 \leq x \leq 0.666$ composition range (namely, from $\text{Na}_2\text{LiFe}_2(\text{AsO}_4)_3$ to $\text{NaLi}_2\text{Fe}_2(\text{AsO}_4)_3$). In contrast, vacancies (as in $(\text{Na}_{1-x}\square_{x/2})_3\text{Fe}_2(\text{AsO}_4)_3$) are hardly accepted in the garnet structure, whereas the range of formation of a pure alluaudite (at 870°C) is more extended ($0.166 \leq x \leq 0.666$), the last composition corresponding to $\text{Na}\square\text{CaFe}_2(\text{AsO}_4)_3$. The stabilization of an alluaudite structure at the expense of a garnet structure has already been observed in previous work and is discussed in relation with the structural role of lithium and vacancies. © 1998 Academic Press

INTRODUCTION

In previous papers, we have shown that some arsenates $\text{NaCa}_2M_2^{2+}(\text{AsO}_4)_3$ ($M^{2+} = \text{Mg, Ni, Co, Mn}$) exhibit a garnet-alluaudite polymorphism (1), and that it is possible to stabilize the alluaudite at the expense of the garnet phase through suitable cation substitutions (2). We show here to what extent the application of such substitutions to the garnet arsenate $\text{Na}_3\text{Fe}_2(\text{AsO}_4)_3$ is able to induce a garnet-to-alluaudite transformation. The possible existence of such an alluaudite phase is suggested by the alluaudite structure of the similar arsenate $\text{Na}_3\text{In}_2(\text{AsO}_4)_3$ (3).

EXPERIMENTAL

All experimental procedures (synthesis, X-ray diffraction, vibrational spectroscopy, differential thermal analysis) have already been described (1). In view of the polymorphism of $\text{Na}_3\text{Fe}_2(\text{AsO}_4)_3$ (4–8), two temperatures were successively selected for the final thermal treatment, namely 700°C (garnet phase) and 870°C (rhombohedral phase).

RESULTS

Two types of cationic substitutions have been attempted, namely $\text{Na}^+ \rightarrow \text{Li}^+$ (system $(\text{Na}_{1-x}\text{Li}_x)_3\text{Fe}_2(\text{AsO}_4)_3$) and $\text{Na}^+ \rightarrow \text{Ca}^{2+}$ (system $(\text{Na}_{1-x}\square_{x/2}\text{Ca}_{x/2})_3\text{Fe}_2(\text{AsO}_4)_3$).

Na⁺-Li⁺ Replacement: $(\text{Na}_{1-x}\text{Li}_x)_3\text{Fe}_2(\text{AsO}_4)_3$ ($0 \leq x \leq 1$)

The results are quoted in Table 1. Briefly, these results show the existence of three compositional domains: a first one ($0 \leq x \leq 0.333$) essentially characterized by the formation at 700°C of a pure garnet phase whose a_0 parameter decreases from 12.222 to 12.170 Å; a second one ($0.417 \leq x \leq 0.666$) in which pure alluaudite phase is obtained at 870°C ; and the final one ($0.833 \leq x \leq 1$), mainly characterized by the formation of mixtures.

The variations of the unit cell parameters of the pure alluaudite phases ($0.417 \leq x \leq 0.666$) are plotted in Fig. 1. As expected from the small ionic radius of Li (9), we find a decrease of the cell volume when x increases; but quite unexpectedly, there is a very significant increase of the a parameter. A possible explanation of this behavior will be proposed in the discussion.

Infrared spectra. For several reasons which have been discussed previously, it is practically impossible to propose a detailed interpretation of the vibrational spectrum of compounds with the alluaudite structure. Nevertheless, and even though a detailed structural analysis is lacking, such spectra are useful to decide whether the distribution of the cations is ordered (1–3).

The IR spectra presented here are limited to two peculiar compositions for which an ordered distribution of the cations would be possible, namely $\text{Na}_2\text{LiFe}_2(\text{AsO}_4)_3$ (2 Na in X(2) and X(1), Li in M(1)) and $\text{NaLi}_2\text{Fe}_2(\text{AsO}_4)_3$ (Na in X(2), 2 Li in X(1) and M(1)). The spectra (Fig. 2) are more or less diffuse, indicating some disorder in the distribution of the Na and Li cations over the X(2), X(1), and M(1) sites.

TABLE 1
Phase Compositions in the System $(\text{Na}_{1-x}\text{Li}_x)_3\text{Fe}_2(\text{AsO}_4)_3$

Composition	Synthesis T and results			Transition T(°C)
	700°C	870°C		
$x = 0$	$\text{Na}_3\text{Fe}_2(\text{AsO}_4)_3$	G(12.222 Å)	R	860
$x = 0.166$	$\text{Na}_{2.5}\text{Li}_{0.5}$	G(12.196 Å)	R > AL (+tr.G)	
$x = 0.25$	$\text{Na}_{2.25}\text{Li}_{0.75}$	G(12.185 Å)	AL > R	840
$x = 0.333$	Na_2Li	G(12.170 Å)	AL(+tr.R)	818
$x = 0.417$	$\text{Na}_{1.75}\text{Li}_{1.25}$	G(12.152 Å) (+tr.AL)	AL	
$x = 0.5$	$\text{Na}_{1.5}\text{Li}_{1.5}$	AL	AL	
$x = 0.583$	$\text{Na}_{1.25}\text{Li}_{1.75}$	AL(+tr.G)	AL	
$x = 0.666$	NaLi_2	AL(+tr.X)	AL	
$x = 0.833$	$\text{Na}_{0.5}\text{Li}_{2.5}$	AL + X	AL + M	
$x = 1$	$\text{Li}_3\text{Fe}_2(\text{AsO}_4)_3$	X	M	

Notes: G: garnet phase (4), R: rhombohedral phase (5), AL: alluaudite phase, X: unidentified phase (s), M: monoclinic phase, $\text{Fe}_2(\text{SO}_4)_3$ type (6), tr.: trace.

Another peculiar feature is the occurrence in the 950–900 cm^{-1} region of a band characterized by an unusually high frequency. A similar band is observed in the IR spectrum of $\text{Na}_3\text{In}_2(\text{AsO}_4)_3$ (3) and related compounds (10, 11); it is assigned to an unusually short As–O bond (3).

Na–Ca Replacement: $(\text{Na}_{1-x}\square_{x/2}\text{Ca}_{x/2})_3\text{Fe}_2(\text{AsO}_4)_3$
($0 \leq x \leq 1$)

The results are collected in Table 2. Very roughly, there are some analogies with the results quoted in Table 1, but a pure garnet phase is obtained only for a very small substitution rate x ; correlatively, a pure alluaudite phase is obtained in a much extended composition range. Clearly, the garnet structure does not accept a significant amount of vacancies (see discussion).

For the pure alluaudite phases, there is a regular increase of the unit cell parameters with the substitution rate x , (Fig. 3). Since the ionic radii of Na^+ and Ca^{2+} are nearly the same (in fact, the ionic radius is slightly smaller for Ca^{2+} than Na^+ (9)), this increase should be related to the replacement of Na^+ by vacancies on the X(2) site.

DISCUSSION

The Respective Structural Roles of Li and Na in the Alluaudite Structure

We shall first discuss an apparent contradiction between the behavior reported here in the $(\text{Na}, \text{Li})_3\text{Fe}_2(\text{AsO}_4)_3$ system (stabilization by Li^+ of the alluaudite at the expense of the garnet structure) and that observed in the $(\text{Na}$ or $\text{Li})\text{Ca}_2\text{M}_2^+(\text{AsO}_4)_3$ compounds, in which the Na compounds exhibit a garnet-alluaudite polymorphism (1), whereas the garnet structure only is observed for the Li compounds.

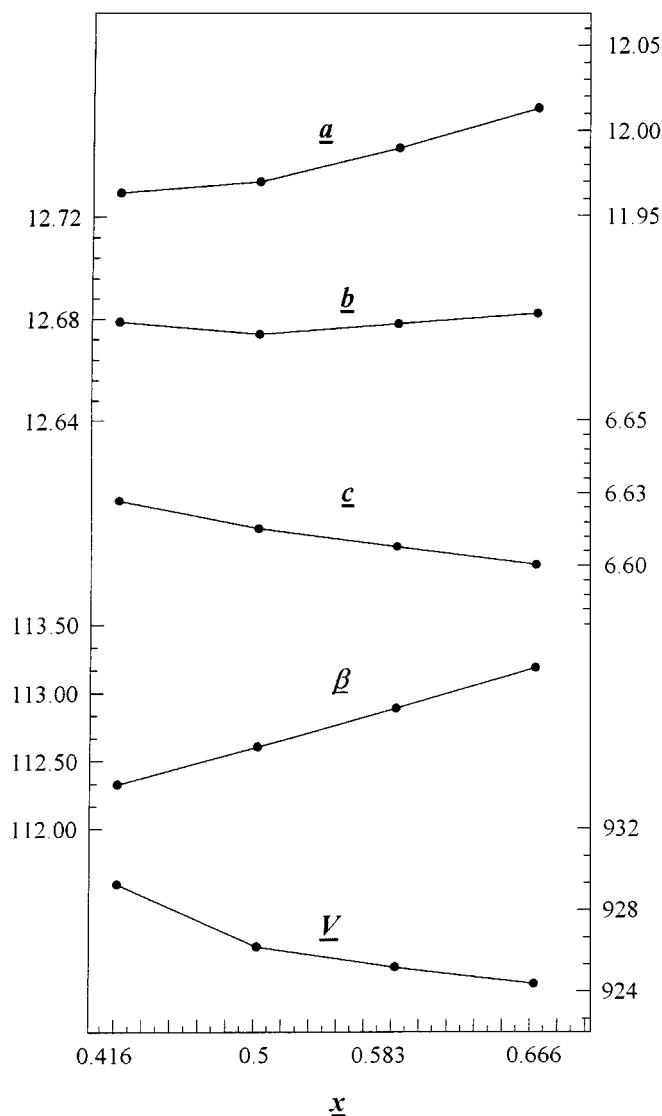


FIG. 1. Variations of the unit cell parameters with the substitution rate x for the pure alluaudite phases in the system $(\text{Na}_{1-x}\text{Li}_x)_3\text{Fe}_2(\text{AsO}_4)_3$.

The $\text{NaCa}_2\text{M}_2^+(\text{AsO}_4)_3$ compounds contain only one Na^+ cation which, in the alluaudite phase, is located (at least in part) on the large X(2) site. This site is too large to accommodate the much smaller Li^+ cation, which prefers the somewhat smaller dodecahedral site of the garnet structure. This latter structure is accordingly more stable than the alluaudite structure for the $\text{LiCa}_2\text{M}_2^+(\text{AsO}_4)_3$ compounds.

If, on the contrary, several Na^+ cations are present in the compound under consideration (e.g., $\text{Na}_3\text{Fe}_2(\text{AsO}_4)_3$), a Na–Li replacement becomes possible in an alluaudite structure, since these Li^+ cations can be accommodated on the smaller M(1) and X(1) sites. More precisely, since the octahedral M(1) site of the alluaudite structure is significantly smaller than the dodecahedral c site of the garnet

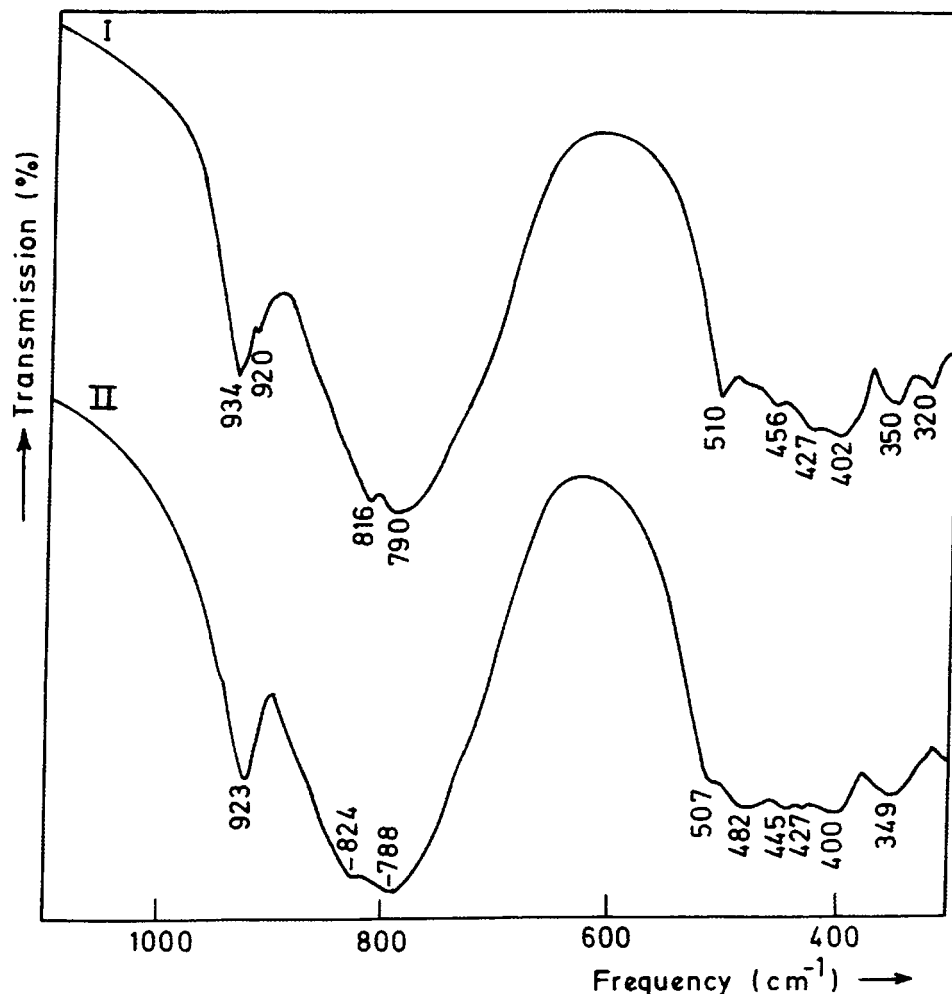


FIG. 2. Infrared spectra of the alluaudite phase of (I) $\text{Na}_2\text{LiFe}_2(\text{AsO}_4)_3$ and (II) $\text{NaLi}_2\text{Fe}_2(\text{AsO}_4)_3$.

structure, it is a better site for the small Li cation, with as a consequence some stabilization of the alluaudite with respect to the garnet structure.

TABLE 2
Phase Compositions in the System $(\text{Na}_{1-x}\square_{x/2}\text{Ca}_{x/2})_3\text{Fe}_2(\text{AsO}_4)_3$

Composition	Synthesis temperature and results	
	700°C	870°C
$x = 0$ $\text{Na}_3\text{Fe}_2(\text{AsO}_4)_3$	G	R
$x = 0.083$ $\text{Na}_{2.75}\square_{0.125}\text{Ca}_{0.125}$	G + AL	R + AL
$x = 0.166$ $\text{Na}_{2.50}\square_{0.25}\text{Ca}_{0.25}$	AL > G	AL
$x = 0.333$ $\text{Na}_2\square_{0.5}\text{Ca}_{0.5}$	AL (impure)	AL
$x = 0.666$ $\text{Na}\square\text{Ca}$	AL (impure)	AL
$x = 0.833$ $\text{Na}_{0.5}\square_{1.25}\text{Ca}_{1.25}$	AL + ?	AL + Y
$x = 1$ $\square_{1.5}\text{Ca}_{1.5}\text{Fe}_2(\text{AsO}_4)_3$	AL + ?	Y

Notes: G: garnet phase (4), R: rhombohedral phase (5), AL: alluaudite phase, Y: unidentified phase (s).

It is also significant to recall that, in the system $(\text{Na}_{1-x}\text{Li}_x)_3\text{Fe}_2(\text{AsO}_4)_3$, the limiting composition for the formation of a pure alluaudite phase is near $\text{NaLi}_2\text{Fe}_2(\text{AsO}_4)_3$ (Table 1). The same limit $\text{NaLi}_2\text{In}_2(\text{AsO}_4)_3$ was already found for the $(\text{Na}_{1-x}\text{Li}_x)_3\text{In}_2(\text{AsO}_4)_3$ solid solutions (10). Such a limiting composition supports the hypothesis that the small Li^+ cation is not accepted (at least in significant quantities) on the large X(2) site of the alluaudite structure.

Variations of the Unit Cell Parameters and the Structural Role of Li in the Solid Solutions $(\text{Na}_{1-x}\text{Li}_x)_3\text{Fe}_2(\text{AsO}_4)_3$

We have already pointed out the unexpected increase of the a parameter (against a volume decrease) when Li replaces Na in the solid solutions $(\text{Na}_{1-x}\text{Li}_x)_3\text{Fe}_2(\text{AsO}_4)_3$ ($0.417 \leq x \leq 0.666$). Such variations in opposite directions had never been observed for a number of solid solutions

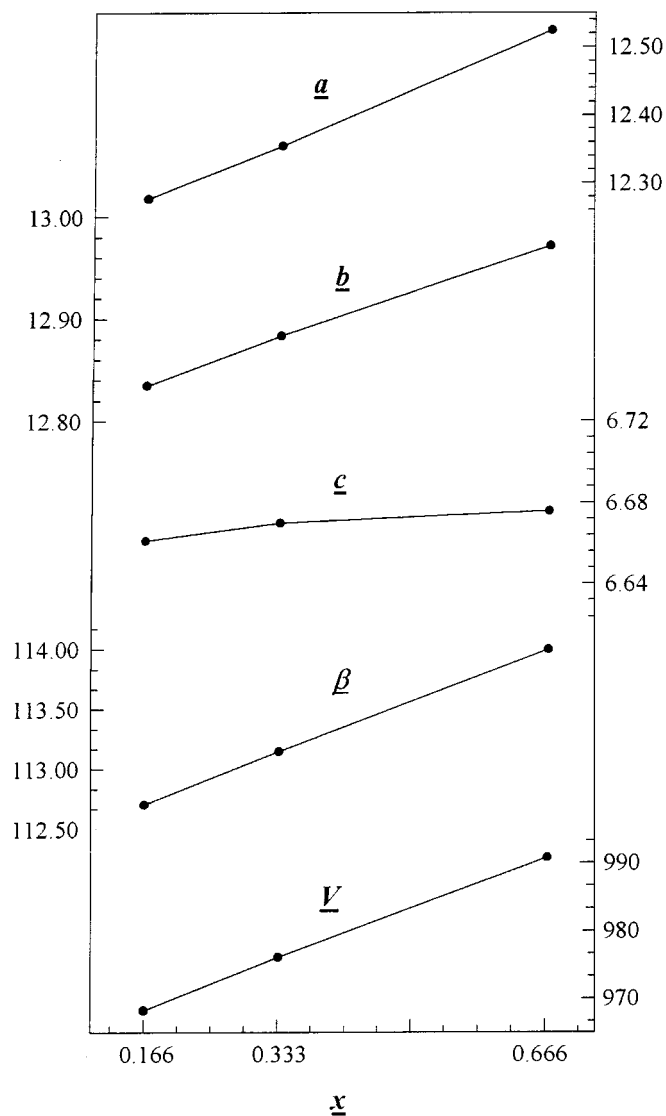


FIG. 3. Variations of the unit cell parameters with the substitution rate x for the pure alluaudite phases in the system $(\text{Na}_{1-x}\text{Ca}_{x/2})_3\text{Fe}_2(\text{AsO}_4)_3$.

with the alluaudite structure (10), and we have accordingly investigated the behavior of the other alluaudite phases existing in that system ($0.160 \leq x \leq 0.417$ and $x = 0.833$). The results are plotted in Fig. 4.

We shall not consider here the results corresponding to $x = 0.833$. There is practically no variation of the unit cell parameters with respect to those corresponding to $x = 0.666$: this latter composition ($\text{NaLi}_2\text{Fe}_2(\text{AsO}_4)_3$) is thus the Li-rich end-member of these solid solutions.

The most interesting result observed for the $0.166 \leq x \leq 0.416$ range is the very significant decrease of the a parameter (together with a similar decrease of the cell volume). Of course, these data must be considered with caution: these alluaudite phases are not pure, and their true chemical

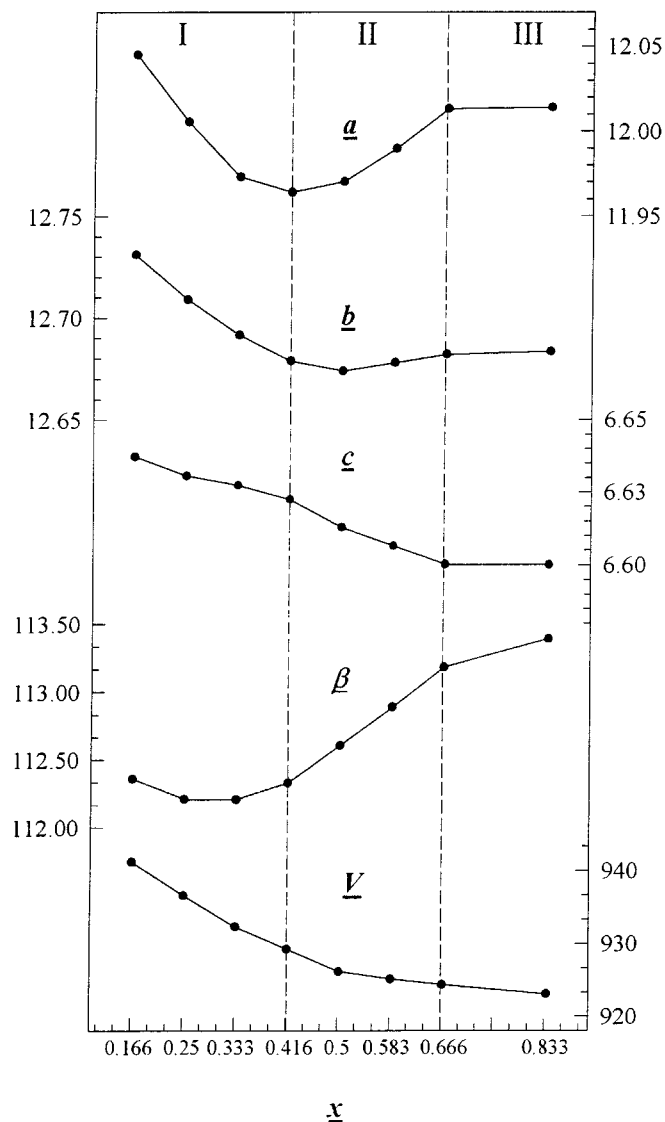


FIG. 4. Variations of the unit cell parameters with the substitution rate x for all the alluaudite phases in the system $(\text{Na}_{1-x}\text{Li}_x)_3\text{Fe}_2(\text{AsO}_4)_3$. I and III: impure phases; II: pure alluaudite phases. The point corresponding to the nominal composition 0.833 in the range III is to be shifted toward a smaller unknown value, as the product is rather impure; it is only given as information.

composition can be somewhat different from the nominal composition used in Fig. 4. Nevertheless, the following remarks suggest that these results are significant, and that the true and the nominal compositions should not be too different.

(i) The regular decrease of the cell volume when x increases from 0.166 to 0.416 indicates that increasing quantities of Li are really substituting for Na; since the a , b , and c parameters also decrease, we find in this composition range a "classical" behavior of the system.

(ii) We can compare the variations of the molar volume V_M to those of pure phases (for which the true composition is the nominal one), namely the equivalent garnet phases obtained at 700°C (Table 1), and the similar alluaudite phases where Fe is replaced by In (10, 11). These variations are very similar (Fig. 5), thus indicating that the compositions of the Fe-alluaudite phases are not grossly in error.

(iii) It is also possible to compare the values of the molar volume of an hypothetical $\text{Na}_3\text{Fe}_2(\text{AsO}_4)_3$ alluaudite deduced from the extrapolation of the data given by different solid solutions, namely $(\text{Na}_{1-x}\text{Li}_x)_3\text{Fe}_2(\text{AsO}_4)_3$ (approximate composition), $\text{Na}_3(\text{In, Fe})_2(\text{AsO}_4)_3$, and $(\text{Na, Ca, } \square)_3\text{Fe}_2(\text{AsO}_4)_3$ (pure phases with a well known composition) (10, 11) (Fig. 6).

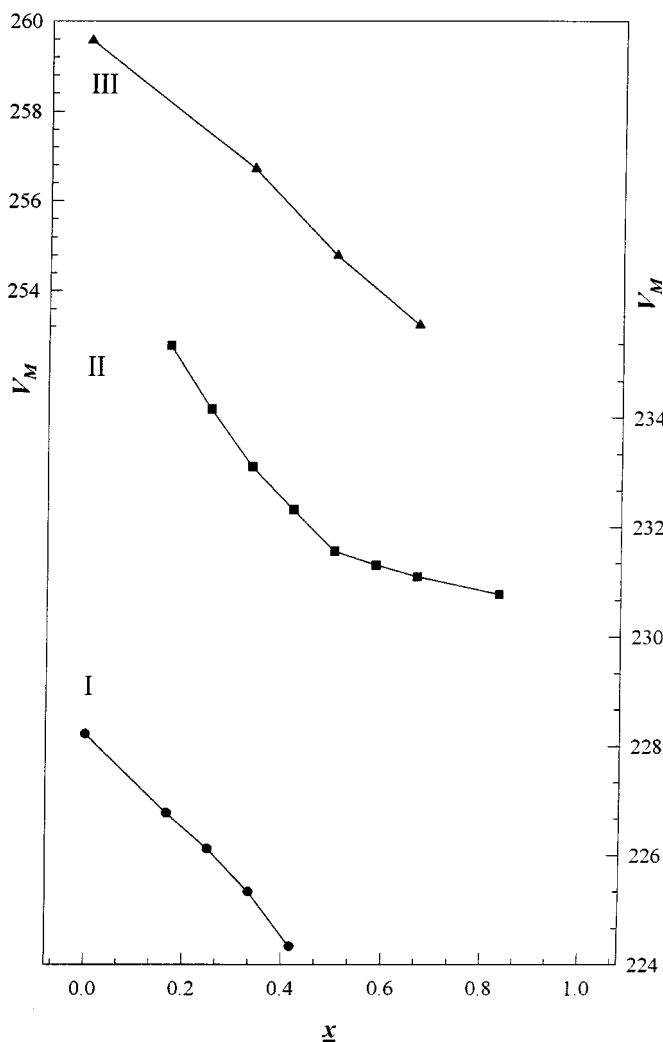
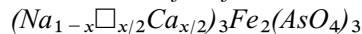


FIG. 5. Variations of the molar volume V_M with the substitution rate x for (I) the pure garnets $(\text{Na}_{1-x}\text{Li}_x)_3\text{Fe}_2(\text{AsO}_4)_3$, (II) the corresponding (impure) alluaudite phases, and (III) the pure alluaudite phases $(\text{Na}_{1-x}\text{Li}_x)_3\text{In}_2(\text{AsO}_4)_3$.

The results of this extrapolation cannot be very rigorous, since, according to our results on the behavior of solid solutions with the alluaudite structure (10), the relationship between the composition and the cell parameters is generally not linear. Nevertheless, the two extrapolations deduced from the $\text{Na}_3(\text{In, Fe})_2(\text{AsO}_4)_3$ and $(\text{Na, Ca, } \square)_3\text{Fe}_2(\text{AsO}_4)_3$ solid solutions converge very well towards a 240 Å³ figure for the molar volume of $\text{Na}_3\text{Fe}_2(\text{AsO}_4)_3$. For the solid solutions $(\text{Na, Li})_3\text{Fe}_2(\text{AsO}_4)_3$, a somewhat lower figure of about 238 Å³ is obtained. But these last results can be corrected considering the following points. For the $x = 0.5, 0.416,$ and 0.333 values, the alluaudite phase is pure or nearly so, and the corresponding points are reliable. For the lower x values, the alluaudite phase is more and more mixed with the rhombohedral phase, and this involves an accordingly increased uncertainty about its true chemical composition. It is possible to estimate the direction in which the actual values should be corrected. According to J. M. Winand (12), Na^+ is more easily accepted than Li^+ in the rhombohedral phase; thus in a mixture of rhombohedral and alluaudite phases ($x = 0.25$ and 0.166 Table 1), the rhombohedral phase will be enriched in Na^+ and the alluaudite enriched in Li^+ with respect to the nominal composition. This implies that the points corresponding to $x = 0.166$ and 0.25 in Fig. 6 should be slightly shifted toward higher x values. The extrapolation curve would then be displaced toward about 240 Å³.

The main conclusion of this discussion is that, for the alluaudite phases of the $(\text{Na}_{1-x}\text{Li}_x)_3\text{Fe}_2(\text{AsO}_4)_3$ solid solutions, the variations of the unit cell parameters are "classical" in the $0 \leq x \leq 0.416$ composition range (decrease of the $a, b, c,$ and V parameters with an increasing percentage of Li) and "abnormal" in the $0.416 \leq x \leq 0.666$ composition range (an increase of the a parameter against a decrease of the volume). This can be tentatively explained as follows. In the $0 \leq x \leq 0.333$ composition range, the Na-Li replacement occurs predominantly on the M(1) site, a pseudo-octahedral site characterized by a good matching between the available volume and the ionic radius of Li^+ ; this leads to "classical" changes in the unit cell parameters. In the $0.333 \leq x \leq 0.666$ composition range, the additional Li cations must go into the X(1) site, a very distorted pseudocube which is too large for the small Li^+ cation. It is reasonable to assume that this cation will occupy an off-center position more or less similar to that existing in the johillerite structure (13); this would be responsible for the "abnormal" variations observed in this composition range. This hypothesis is supported by the strong analogy with the behavior of the $\text{NaCa}_{2-x}\text{Co}_{2+x}(\text{AsO}_4)_3$ solid solutions (2, 10).

The Formation of Defect Structures in the System



Two points must be emphasized here: the very limited range of formation of the garnet phase; and the early

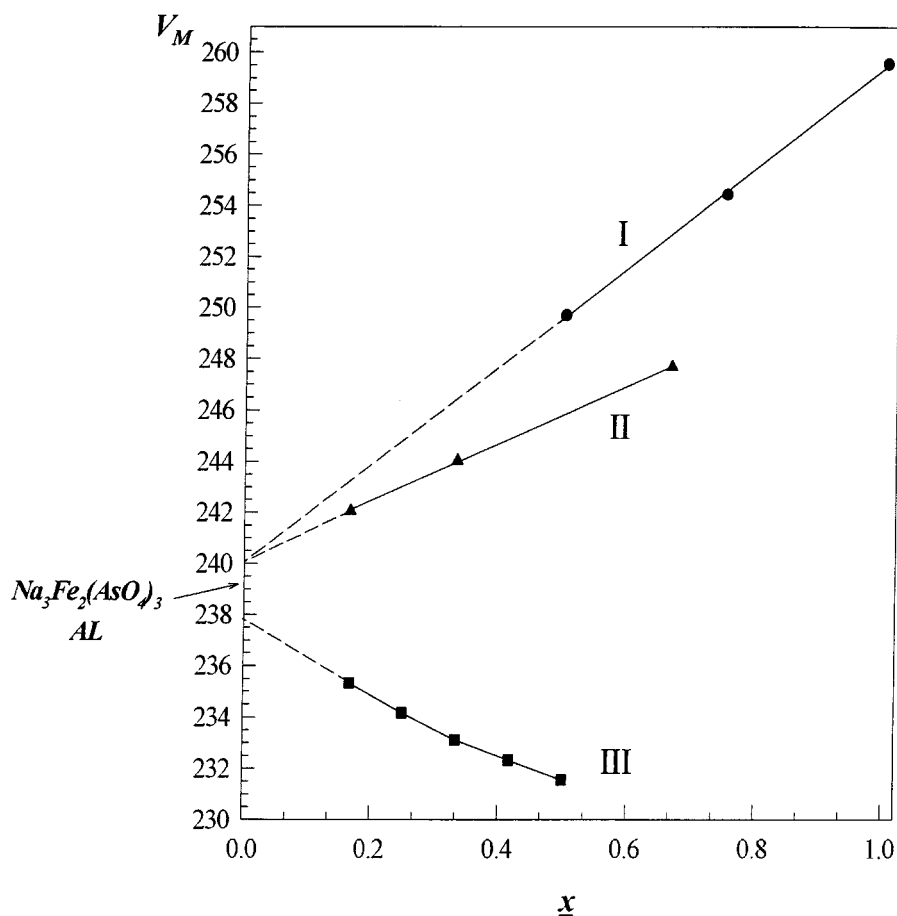


FIG. 6. Extrapolation of the molar volume V_M of some solid solutions to hypothetical $\text{Na}_3\text{Fe}_2(\text{AsO}_4)_3$ alluaudite: (I) $\text{Na}_3(\text{Fe}_{1-x}\text{In}_x)_2(\text{AsO}_4)_3$ (pure); (II) $(\text{Na}_{1-x}\square_{x/2}\text{Ca}_{x/2})_3\text{Fe}_2(\text{AsO}_4)_3$ (pure); and (III) $(\text{Na}_{1-x}\text{Li}_x)_3\text{Fe}_2(\text{AsO}_4)_3$ (impure).

appearance of the alluaudite phase. The unit cell parameter of the garnet phase is hardly modified by the $2\text{Na}^+ \rightarrow \square + \text{Ca}^{2+}$ substitution, and it is inferred that a very small number of vacancies is accepted in the garnet structure. This is in agreement with previous results on the $2\text{Na} \rightarrow \square + \text{Ca}$ substitution in the $\text{NaCa}_2\text{Mg}_2(\text{AsO}_4)_3$ garnets (2, 10) and with the fact that most of the compounds with a garnet structure don't contain a significant amount of vacancies on the dodecahedral or octahedral sites (one noticeable exception is presented by the vanadates $(\square_{0.5}\text{Ca}_{2.5})\text{M}_2^{2+}(\text{VO}_4)_3$ and $(\square_{0.25}\text{Ca}_{2.75})(\square_{0.25}\text{M}_{1.75}^{2+})(\text{VO}_4)_3$ (14). On the contrary, the existence of vacancies on the large X(2) site is a well known property of the alluaudites, either natural (15) or synthetic (2, 10, 11, 16). This site is normally occupied by relatively big monovalent cations (mainly Na^+ ; sometimes K^+ in synthetic compounds) which are very weakly bound to the remainder of the structure; their replacement by a vacancy does not alter seriously the stability of the alluaudites.

ACKNOWLEDGMENTS

The authors thank the FNRS and the scientific council of the University of Liège for financial support for the acquisition of the D 5000 Siemens diffractometer.

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