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The Arsenates $NaCa_2M_2^{2+}(AsO_4)_3$ (M^{2+} = Mg, Ni, Co): Influence of Cationic Substitutions on the Garnet–Alluaudite Polymorphism

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Cationic replacements in the arsenates $NaCa_2M_2^{2+}(AsO_4)_3$ (M^{2+} = Mg, Ni, Co) have a strong influence on their garnet–alluaudite polymorphism. The preferential formation of an alluaudite phase (at the expense of the garnet phase) is induced by the following cationic modifications: (i) The replacement of Na^+ by larger cations such as Ag^+, K^+, or Tl^+. The cation distribution is partly disordered in the Na and Ag compounds and ordered in the K and Tl compounds. (ii) The formation of vacancies through the (Na^+ or Li^+)–Ca^{2+} replacement, namely (Na or Li)$_{1-x}\square_{x/2}Ca_{2+x/2}Mg_2(AsO_4)_3$. The formation of a pure defect garnet phase is limited to small x values ($x = 0.1$ or 0.2) whereas a full series of defect alluaudite phases (terminating at $Ca_{2.5}Mg_2(AsO_4)_3$, $x = 1$) can be obtained. (iii) The replacement of Ca^{2+} by Mg^{2+} or Co^{2+}, leading to the new alluaudite-like compounds $NaCaMg_3(AsO_4)_3$, $NaCaCo_3(AsO_4)_3$, and $NaCo_4(AsO_4)_3$. Most of these results can be explained by the existence, in the alluaudite structure, of three crystallographic sites $X(2)$, $X(1)$, and $M(1)$, which are respectively larger, approximately equal to, or smaller than the dodecahedral sites of the garnet structure. A garnet–alluaudite transformation has not been observed in the corresponding vanadates, in which the garnet structure appears very stable. © 1997 Academic Press

INTRODUCTION

In a preceding paper (1), we have evidenced the garnet–alluaudite polymorphism of the arsenates $NaCa_2M_2^{2+}(AsO_4)_3$ (M^{2+} = Mg, Ni, Co, Mn), and this polymorphism has been discussed on the basis of the analogies and differences existing between these two types of structures. The most important differences appear in the structural role of the relatively large cations (Na + 2Ca) which occupy the three equivalent dodecahedral sites in the garnet structure whereas they are distributed over three rather different sites (labeled $X(2)$, $X(1)$, and $M(1)$) in the alluaudite structure. On the basis of these structural differences, it can be assumed that suitable cationic substitutions should promote the formation of either the garnet or the alluaudite structure. We have accordingly investigated the influence of the replacement of either Na^+ or Ca^{2+} by cations with either a smaller or a larger ionic radius. On the other hand, we are now engaged in the structural study of some alluaudite compounds by the Rietveld method. This investigation is still going on, and the detailed results will be published in due time, but we shall quote in this paper some results relevant to the specific case of $NaCa_2Mg_2(AsO_4)_3$.

EXPERIMENTAL

All experimental conditions are similar to those already given in (1).

The X-ray powder diagrams were recorded with a Siemens D-5000 diffractometer (Cu$K\alpha$ radiation; silicon as an external standard).

RESULTS

Cation–Oxygen Distances in $NaCa_2Mg_2(AsO_4)_3$; Preliminary Results of a Rietveld Analysis

The cation–oxygen distances for the different cationic sites of $NaCa_2Mg_2(AsO_4)_3$ are given in Table 1. It should be pointed out that, for the alluaudite structure, a final refinement is not easy because of the disordered distribution of the Na and Ca cations over the $X(2)$ and $X(1)$ sites. Nevertheless, the actual distances should not be grossly in error and can be used for a comparison with the corresponding distances in the garnet structure; in this latter case, the distances deduced from the Rietveld analysis are in good agreement with the distances deduced from a single crystal study of the mineral berzeliite $NaCa_2(Mg_{0.85}Mn_{0.15})_2(AsO_4)_3$ (2).

Two points should be considered in the results quoted in Table 1: the individual cation–oxygen distances and their mean value for each type of site.

The individual values reveal a broad distribution of the cation–oxygen distances, particularly for the $X(2)$ and $X(1)$

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TABLE 1
Cation–Oxygen Distances in $NaCa_2Mg_2(AsO_4)_3$

Alluaudite structure	Garnet structure	Berzeliite (2)
$X(2)$–O_1 2.97 (×2)		
–O_3 3.12 (×2)		
–O_6 2.36 (×2)		
–O_6 2.45 (×2)		
Mean 2.75		
$X(1)$–O_2 2.44 (×2)		
–O_4 2.38 (×2)	Dodecahedral site	
–O_4 2.61 (×2)	2.41 (×4)	2.420(5) (×4)
[–O_2 3.31 (×2)]	2.55 (×4)	2.521(5) (×4)
Mean 2.48	Mean 2.48	Mean 2.471
$M(1)$–O_1 2.04 (×2)		
–O_3 2.34 (×2)		
–O_4 2.27 (×2)		
Mean 2.22		
$M(2)$–O_1 2.23		
–O_2 1.99		
–O_3 1.91	Octahedral site	
–O_5 2.05	2.10 (×6)	2.098(4) (×6)
–O_5 2.35		
–O_6 2.14		
Mean 2.11		

sites. This is in agreement with previous structural determinations on either the mineral alluaudite itself (3) or compounds with an alluaudite structure (4, 5).

The mean values show that, for the same chemical composition, the $X(2)$, $X(1)$ and $M(1)$ sites of the alluaudite structure are much larger, approximately equal, or significantly smaller, respectively, than the dodecahedral site of the garnet structure.

Influence of Cationic Replacements on the Garnet–Alluaudite Polymorphism

Replacement of Na^+ by Another Monovalent Cation

Na–Li. As indicated previously (1), the $LiCa_2M_2^{2+}(AsO_4)_3$ compounds exhibit the garnet structure only, and no garnet–alluaudite polymorphism.

Na–Ag. This replacement has been attempted for the Mg^{2+} compound only. No garnet phase has been obtained, but the compound $AgCa_2Mg_2(AsO_4)_3$ does exist and has an alluaudite structure. It is probable that this preference for an alluaudite structure is determined by the larger size of the Ag^+ cation (ionic radius 1.28 Å, against 1.18 Å for the Na^+ cation in eightfold coordination (6)).

It is tempting to locate the largest cation (Ag^+) on $X(2)$, the largest site of the alluaudite structure. However, the infrared spectrum (Fig. 1) exhibits some diffuseness (more or less similar to that of the Na compound), suggesting some disorder in the distribution of the Ag^+ and Ca^{2+} cations over the $X(2)$ and $X(1)$ sites.

Na–K. This replacement leads to the pure alluaudite phases $KCa_2M_2^{2+}(AsO_4)_3$ (M^{2+} = Mg, Ni, Co), without the intermediate formation of a garnet phase. The large size of the K^+ cation (ionic radius 1.51 Å for an eightfold coordination) is clearly responsible for this behavior, but it has also another consequence on the cation distribution: the K^+ cation should have a strong preference for the large $X(2)$ site, and it should be essentially (if not totally) located on this site, thus leading to the suppression of the disorder existing in the Na and Ag compounds.

This hypothesis cannot be checked by X-ray diffraction (K^+ and Ca^{2+} have the same number of electrons), but the IR spectra shows that the diffuseness previously observed in the IR spectrum of $NaCa_2Mg_2(AsO_4)_3$ is greatly reduced in the IR spectrum of $KCa_2Mg_2(AsO_4)_3$ (Fig. 1): this can be immediately explained by an essentially ordered cation distribution (K^+ on $X(2)$; $2Ca^{2+}$ on $X(1)$ and $M(1)$).

The same vibrational behavior is observed for the Ni compound $KCa_2Ni_2(AsO_4)_3$, but, unexpectedly enough, *not* for the Co compounds: both $NaCa_2Co_2(AsO_4)_3$ and $KCa_2Co_2(AsO_4)_3$ compounds exhibit a more or less diffuse IR spectrum.

Since there is no reason to consider a K^+–Ca^{2+} disorder in this specific case, we must assume that some Ca^{2+}–Co^{2+} disorder is responsible for the observed diffuseness (the

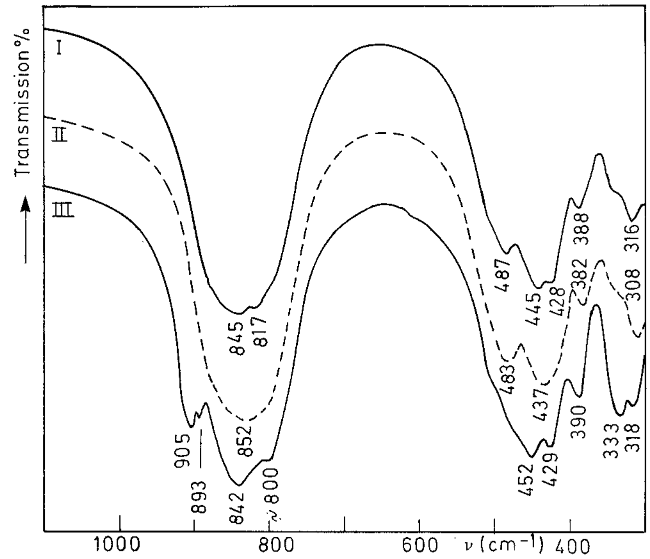

FIG. 1. IR spectra of $NaCa_2Mg_2(AsO_4)_3$ (I), $AgCa_2Mg_2(AsO_4)_3$ (II), and $KCa_2Mg_2(AsO_4)_3$ (III).

TABLE 2
Unit Cell Parameters of the Na-Substituted Alluaudites

$M^+Ca_2Mg_2(AsO_4)_3$	*a*	*b*	*c*	*β*	*V*
Na(r_i = 1.18 Å)	12.290	13.077	6.791	113.74	999.1
Ag(r_i = 1.28 Å)	12.346	13.086	6.789	113.77	1003.8
K(r_i = 1.51 Å)	12.534	13.066	6.797	113.64	1019.8
Tl(r_i = 1.59 Å)	12.775	13.112	6.777	113.98	1037.2
$NaCa_2Ni_2(AsO_4)_3$	12.304	13.033	6.781	113.84	994.6
$KCa_2Ni_2(AsO_4)_3$[a]	12.458	12.974	6.767	113.45	1003.4
$NaCa_2Co_2(AsO_4)_3$	12.264	13.103	6.790	114.00	996.8
$KCa_2Co_2(AsO_4)_3$[a]	12.499	13.084	6.815	114.06	1017.6

[a] Slightly impure.

difference between the ionic radii of Ca^{2+} and Co^{2+} is smaller than for the Ca^{2+}–Mg^{2+} or Ca^{2+}–Ni^{2+} pairs). Additional work will be necessary to settle this point.

Na–Tl (*Mg^{2+} compound only*). The Tl^+ cation is still larger than the K^+ cation (r_i = 1.59 Å), but the results are qualitatively the same: no garnet is formed, but instead an alluaudite phase $TlCa_2Mg_2(AsO_4)_3$ is. The sharpness of the IR spectrum (very similar to that of the corresponding K^+ compound) points to an essentially ordered cation distribution.

Na–Rb or Na–Cs (*Mg compounds only*). Neither a garnet nor an alluaudite phase was obtained. These cations are probably too large to be accepted in these structures. The matter was not investigated further, and we don't know whether a single phase or a mixture of phases was obtained. The unit cell parameters of these new alluaudite phases are given in Table 2.

The variations of the unit cell volume are very roughly proportional to the increase in the ionic radius of M^+ (values for an eightfold coordination (3)) and are essentially determined by the increase in the *a* parameter. In contrast, the variations of the *b* and *c* parameters are small and somewhat erratic.

Replacement of Na^+ by Ca^{2+}

Such a replacement leads necessarily to the formation of vacancies: $2\,Na^+ \rightarrow Ca^{2+} + \square$. The existence of vacancies is very common in natural phosphates with an alluaudite structure (7). In contrast, little information is available about the existence of vacancies in the garnet structure (apart from the very peculiar case of the so-called hydrogarnets, where some Si atoms are replaced by four protons), but a series of vanadates with a defect garnet structure has been synthesized by Ronniger and Mill′ (8). We have thus attempted the synthesis of solid solutions $Na_{1-x}\square_{x/2}Ca_{2+x/2}Mg_2(AsO_4)_3$ to investigate the influence of the substitution rate *x* on the garnet–alluaudite transformation.

The results are briefly summarized in Table 3. At a moderate synthesis temperature (800–850°C), a pure garnet phase is obtained only for $x = 0$ and $x = 0.1$. Alluaudite is present in a very small amount for $x = 0.2$ and becomes the largely predominant phase for $x = 0.5$. At higher temperature, garnet is irreversibly transformed into the alluaudite phase. According to these results, the limiting composition for a pure garnet phase of this type lies somewhere between $x = 0.1$ and $x = 0.2$, corresponding to a small fraction (roughly 2–3%) of the dodecahedral sites of the garnet structure. In contrast, a continuous series of solid solutions (terminating at the end-member $x = 1$) is observed for the

TABLE 3
Garnet versus Alluaudite Formation in the Compositions $Na_{1-x}Ca_{2+x/2}Mg_2(AsO_4)_3$

x	Cationic composition	Synthesis temperature (°C)	Duration (days)	Result
0	$NaCa_2Mg_2$	850	3	Garnet *a* = 12.346 Å
		950	1	Alluaudite
0.1	$Na_{0.9}\square_{0.05}Ca_{2.05}Mg_2$	800	3	Garnet *a* = 12.345 Å
		950	1	Alluaudite
0.2	$Na_{0.8}\square_{0.1}Ca_{2.10}Mg_2$	800	3	Garnet *a* = 12.346 Å + trace Alluaudite
		950	1	Alluaudite
0.3	$Na_{0.7}\square_{0.15}Ca_{2.15}Mg_2$	750	6	Impure garnet *a* = 12.346 Å + Alluaudite
		950	4	Alluaudite
0.5	$Na_{0.5}\square_{0.25}Ca_{2.25}Mg_2$	750	6	Alluaudite (predominant + ill-crystallized garnet *a* = 12.34 Å
		950	4	Alluaudite
0.75	$Na_{0.25}\square_{0.375}Ca_{2.375}Mg_2$	950	4	Alluaudite
1	$\square_{0.5}Ca_{2.5}Mg_2$	950	4	Alluaudite

alluaudite structure. In this last composition $Ca_{2.5}Mg_2(AsO_4)_3$, half of the $X(2)$ sites are empty, but this is not surprising, since *all* the $X(2)$ sites may be empty in the alluaudite structure (e.g., in some minerals and in the synthetic phosphate $NaCdIn_2(PO_4)_3$ (4)). In fact, this composition is somewhat unexpected, not because of the number of vacancies, but because it is, to the best of our knowledge, the first reported example of an alluaudite structure completely free from monovalent cations.

The variations of the unit cell parameters are negligible for the garnet phase, and small to very small for the alluaudite phase (Table 4). There are small irregularities in these variations, but the general trend is a small decrease in the unit cell volume for increasing values of x. These small irregularities are possibly related to variations in the disorder affecting the distribution of the cations and of the vacancies in the $X(2)$ ($\square$ + Na + Ca) and $X(1)$ (Na + Ca) sites.

Additional (although less systematic) experiments were also carried out with the corresponding Ni or Co compositions. The results are essentially the same: a pure garnet phase is obtained only for a low rate of substitution ($x = 0.1$), whereas a mixture containing a small quantity of the alluaudite phase is obtained for $x = 0.2$. Thus, the limiting composition for the formation of a pure garnet phase is practically the same as that for the Mg compound.

Replacement of Li^+ by Ca^{2+}

This is an interesting case since, as stated previously, the pure Li compounds $LiCa_2M_2^{2+}(AsO_4)_3$ do *not* exhibit a garnet to alluaudite transformation.

The study of a series of $Li_{1-x}Ca_{2+x/2}Mg_2(AsO_4)_3$ compositions ($0.1 \leq x \leq 0.5$) leads to the following results:

– The synthesis at 800°C leads to a garnet phase but, as in the case of the Na–Ca replacement, the formation of pure garnet is limited to small values of the substitution rate ($x = 0.1$–0.2). A mixture of phases is obtained for $x > 0.2$.

– DTA curves of the garnet phase ($x = 0.1$ or 0.2) exhibit an ill-defined endothermic signal near 1000°C which is not due to melting. For $x = 0.5$, the DTA experiments are inconclusive. But for all compositions ($0.1 \leq x \leq 0.5$), heating at 1000°C (20 min) followed by air-quenching leads to a pure alluaudite phase, whose a, b, and c parameters increase with the substitution rate x (as expected from the respective ionic radii of the Li^+ and Ca^{2+} cations). Thus, even a small amount of vacancies (0.05 corresponding to $x = 0.1$) is sufficient to restore the garnet–alluaudite transformation.

– The transformation is reversible: tempering the alluaudite phase at 800°C for 1 day induces the return to a garnet phase, which is pure only for $x = 0.1$ or 0.2 (in agreement with the results of the synthesis at 800°C).

Replacement of Ca^{2+} by Another Divalent Cation

Ca–Cd. We have already considered the replacement of Ca^{2+} by Cd^{2+} in the solid solutions $NaCa_{2-x}Cd_xMg_2(AsO_4)_3$ ($0 \leq x \leq 1$) (1): the alluaudite structure is formed at the expense of the garnet structure, even for relatively small x values ($x = 0.25$).

Ca–Sr. Attempts to replace one Ca^{2+} by one Sr^{2+} cation (nominal compositions $LiCaSrMg_2(AsO_4)_3$ and $NaCaSrMg_2(AsO_4)_3$) remained unsuccessful. After 15 days at 750°C, the Na composition led to an impure garnet, whose unit cell parameter was not significantly different from that of $NaCa_2Mg_2(AsO_4)_3$; at 850°C, the same composition gave a rather impure alluaudite phase, whose unit cell parameters were slightly smaller than those of $NaCa_2Mg_2(AsO_4)_3$. It is clear that no significant amount of Ca–Sr substitution occurred in these compositions.

TABLE 4
Unit Cell Parameters of Defect Alluaudites $Na_{1-x}\square_{x/2}Ca_{2+x/2}Mg_2(AsO_4)_3$

Formulas	a (Å)	b (Å)	c (Å)	β (°)	v (Å^3)
$NaCa_2Mg_2(AsO_4)_3$ AL	12.2897(10)	13.0770(10)	6.7913(5)	113.74(40)	999.09(10)
$Na_{0.9}Ca_{2.05}Mg_2(AsO_4)_3$ AL	12.2797(8)	13.0701(6)	6.7850(4)	113.72(33)	997.013
$Na_{0.8}Ca_{2.1}Mg_2(AsO_4)_3$ AL	12.2941	13.0821	6.7813	113.776	998.085
$Na_{0.75}Ca_{2.125}Mg_2(AsO_4)_3$ AL	12.2893	13.0768	6.7816	113.794	997.195
$Na_{0.5}Ca_{2.25}Mg_2(AsO_4)_3$ AL	12.2912	13.0685	6.7801	113.821	996.285
$Na_{0.25}Ca_{2.375}Mg_2(AsO_4)_3$ AL	12.2880	13.0627	6.7672	113.747	994.267
$Ca_{2.5}Mg_2(AsO_4)_3$ AL	12.3169	13.0736	6.7623	113.873	995.747

Ca–M^{2+}(M^{2+} = *Mg, Ni, Co*). We shall consider here the formation of solid solutions in the systems $NaCa_{2-x}M^{2+}_{2+x}(AsO_4)_3$ (M^{2+} = Mg, Ni, Co). First of all, it must be pointed out that no pure garnet phase can be obtained, even for rather small substitution rates ($x = 0.05$). Clearly, these M^{2+} cations are too small to be accepted on the dodecahedral sites of the garnet structure, at least under normal pressure conditions (it is well known that garnets such as $Mg_3Al_2(SiO_4)_3$ can be formed only under very high pressures, e.g., 20–30 kbars).

In contrast, these cations are easily located on the $M(1)$ sites of the alluaudite structure. This leads, e.g., for the Mg compound, to a continuous series of solid solutions $NaCa_{2-x}Mg_{2+x}(AsO_4)_3$ terminating approximately near $x = 1.1$. This is just beyond the composition $NaCaMg_3(AsO_4)_3$, corresponding to the filling of the $M(1)$ sites of the alluaudite structure. A comparison with the garnet structure (Table 1) shows that this $M(1)$ site is larger than the octahedral site but smaller than the dodecahedral site of the garnet structure.

The limiting composition $x = 1.1$ implies that a small quantity of Mg^{2+} is accepted on the $X(1)$ site of the alluaudite structure. Independently from its strong distortion, this site is clearly too large for the relatively small Mg^{2+} cation.

A further increase in the substitution rate (nominal composition $NaCa_{0.75}Mg_{3.25}(AsO_4)_3$) leads to a mixture of an alluaudite phase and of one or several unidentified phase(s). The same additional peaks (but without the alluaudite phase) are present in the X-ray powder diagram of the final nominal composition $NaMg_4(AsO_4)_3$. An interpretation of this last result will be attempted later on.

The relationships between the composition and the unit cell parameters are regular, although not linear (Fig. 2).

Similar results were obtained with the Ni compound, although the study was restricted to the specific compositions $NaCa_2Ni_2(AsO_4)_3$ (garnet–alluaudite), $NaCaNi_3(AsO_4)_3$ (alluaudite only), and $NaNi_4(AsO_4)_3$ (unknown).

In contrast, unexpected results were obtained with the $NaCa_{2-x}Co_{2+x}(AsO_4)_3$ system, the behavior of which is characterized by two essential features:

(i) *All* compositions, including the end-member $NaCo_4(AsO_4)_3$, give an X-ray powder diagram which is easily accounted for by an alluaudite-like crystal cell.

(ii) For increasing values of x, the crystal cell parameters decrease regularly in the composition range $0 \leq x \leq 1$ (as already noticed for the Mg and Ni compounds, and as expected from the difference between the ionic radii of Ca^{2+} and either Mg^{2+}, Ni^{2+}, or Co^{2+} cations). But the crystal cell parameters *increase* in the composition range $1.25 \leq x \leq 2$ (Fig. 3). At first sight, the extension of the solid solutions to the $1.25 \leq x \leq 2$ composition range would suggest that the large $X(1)$ sites could be completely occupied by the relatively small Co^{2+} cation, a hardly acceptable hypothesis; moreover, this type of replacement could not explain the increase (instead of an expected decrease) of the crystal cell parameters in this same composition range.

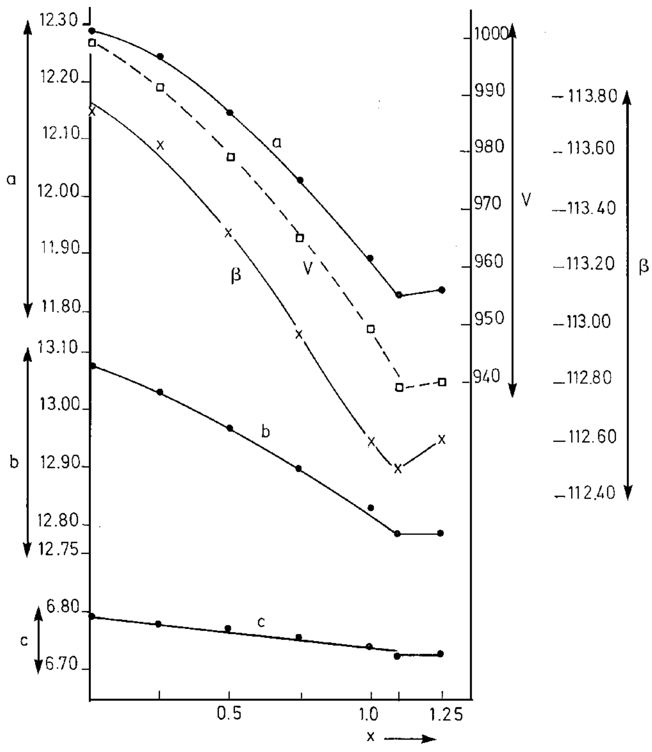

FIG. 2. Relationships between the unit cell parameters and the substitution rate x for the alluaudites $NaCa_{2-x}Mg_{2+x}(AsO_4)_3$, $0 \leq x \leq 1.25$.

Both anomalies could be accounted for if we assume that the additional Co^{2+} ions corresponding to the composition range $NaCaCo_3(AsO_4)_3$–$NaCo_4(AsO_4)_3$ are located not on the $X(1)$ site, but on another site which is normally unoccupied in the alluaudite structure (or, alternatively, in a very similar, alluaudite-like structure).

This is supported by the existence of several compounds whose structure is clearly very similar to that of alluaudite, and in which Cu^{2+} ions (or some of them) are characterized by a fourfold, square planar coordination which does not correspond to the classical sites of the alluaudite structure: $AgCu_4(AsO_4)_3$ (9), $Cu_{1.35}Fe_3(PO_4)_3$ (10), and the mineral johillerite $Na(Mg, Zn)_3Cu(AsO_4)_3$ (11).

Moreover, according to our own results, there are strong, very significant analogies between the IR spectra of synthetic $NaMg_3Cu(AsO_4)_3$ (structurally equivalent to johillerite) and of $NaCo_4(AsO_4)_3$: such analogies are evident, not only at the level of the overall IR pattern in the 1100–400 cm^{-1} region, but also in the presence, in the 650–600 cm^{-1} region, of a relatively strong band which cannot be assigned to a vibration of the ortho-arsenate ion, and is probably due to a characteristic vibration of the

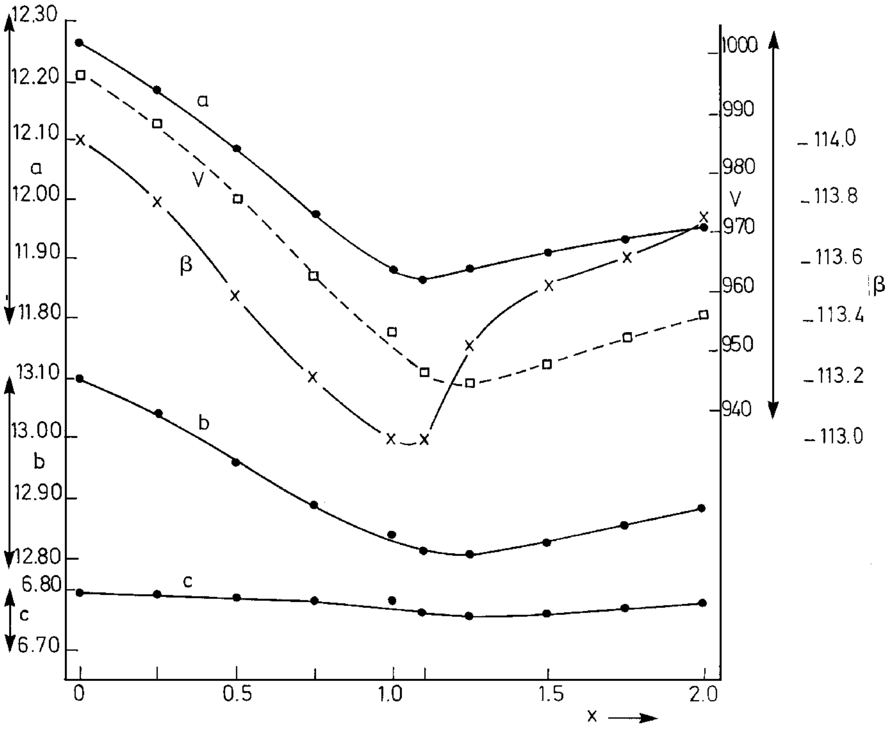

FIG. 3. Relationships between the unit cell parameters and the composition for the alluaudite-like phases $NaCa_{2-x}Co_{2+x}(AsO_4)_3$ ($0 \leqslant x \leqslant 2$).

CuO_4 square group. The existence of an equivalent band of the IR spectrum of $NaCo_4(AsO_4)_3$ suggests the existence of similar CoO_4 groups.

We are now investigating the possible existence of further compounds presenting this behavior, and a more detailed study of this peculiar problem will be presented in due time.

DISCUSSION

Since the $X(2)$ site of the alluaudite structure is significantly larger than the dodecahedral site of the garnet structure (Table 1), we may expect that the replacement of Na^+ by a larger cation should promote the formation of an alluaudite at the expense of the garnet phase. Our results show that this is indeed the case when Na is replaced by either Ag, K, or Tl cations. Since no garnet is formed under these conditions, this raises the more general question: is it possible to introduce significant quantities of these large cations in a garnet structure?

According to literature data and to experiments carried out in this laboratory, this does not seem possible in the case of the arsenates; moreover, these cations are not considered in the review paper by Geller (12), discussing the structural role of a number of the cations in the garnet structure. Nevertheless, according to Ronniger and Mill' (13), the vanadates offer an exceptional opportunity to introduce fairly large cations in the garnet structure, e.g., Ag(Ca or $Pb)_2M_2^{2+}(VO_4)_3$ with M^{2+} = Co, Mg, Zn, Mn, ..., KPb_2 (Mn or $Cd)_2(VO_4)_3$, and $TlPb_2Cd_2(VO_4)_3$. Likewise, the vanadate $KCa_2Mg_2(VO_4)_3$ has a garnet structure (JCPDS card No. 24-1044).

Thus, it does not seem possible to discuss this problem on an absolute basis, and actually, there is no general way to predict the formation of either a garnet or an alluaudite structure.

Likewise, no general rule can be found if we consider the replacement of Ca^{2+} by the larger Sr^{2+} cation (r_i = 1.26 Å). Sr^{2+} is able to occupy the dodecahedral sites of the garnet structure, either totally, as in some germanates $Sr_3M_2^{3+}(GeO_4)_3$ (M^{3+} = Sc, In, Y, Lu → Ho) (12), or partially, as in the vanadates $NaSr_2$ (Mn or $Cd)_2(VO_4)_3$ (13). But according to the results presented in this paper, this possibility cannot be extended to the arsenate $NaCa_2Mg_2(AsO_4)_3$, where it was found impossible to replace Ca by Sr, even on a very small scale. As far as the alluaudite structure is concerned, our results are in agreement with the fact that there is no reported occurrence of significant amounts of Sr^{2+} cations in an alluaudite structure. This cannot be related to the size of the Sr^{2+} cation, the ionic radius of which (1.28 Å) is between the ionic radii of Na^+(1.18 Å) and K^+(1.51 Å) cations, which are known to occupy the $X(2)$ sites of the alluaudite structure. Additional attempts at

Ca–Sr substitutions in various alluaudite-like compounds should be carried out to complete these results.

The opposite case, namely the introduction of a smaller cation in the garnet structure, is apparently not amenable to a simple reasoning.

– The replacement of Ca^{2+} by the slightly smaller cation Cd^{2+} (as in $NaCaCdMg_2(AsO_4)_3$) leads to a stabilization of the alluaudite structure. This can be tentatively explained by a better matching between the size of the Cd^{2+} cation and the size of the $M(1)$ site of the alluaudite structure, which is somewhat smaller than the dodecahedral site of the garnet structure (Table 1).

– In contrast, the replacement of Na^+ by the smaller Li^+ cation (in $LiCa_2Mg_2(AsO_4)_3$) leads to the stabilization of the *garnet* structure.

This apparent contradiction is probably related to the different structural roles of the cations involved in these substitutions.

In the Ca–Cd replacement, the occupancy of the $X(2)$ site by the $Na^+ + Ca^{2+}$ cations is probably not significantly modified, and the crystal-chemical modifications (replacement of Ca^{2+} by Cd^{2+}) are mainly limited to the $M(1)$ and, probably to a less extent, to the $X(1)$ sites.

The situation is different in the case of the Na–Li replacement. The structural role of Li in the alluaudite structure has not been investigated so far, but this cation is very probably too small to go into the large $X(2)$ site. If an alluaudite phase was formed, this would imply a complete redistribution of the cations over the $X(2)$, $X(1)$, and $M(1)$ sites with, in view of the relative ionic radii of the Li^+ and Ca^{2+} cations, a full (or nearly so) occupancy of the $X(2)$ site by the Ca^{2+} cation and a distribution of the second Ca^{2+} and Li^+ cations on the $X(1)$ and $M(1)$ sites. We have no reference compound which would allow an evaluation of the stability of such a cation distribution, and we may assume that the lack of formation of an alluaudite structure is perhaps determined by the *relative* stabilities of the two structures in the available temperature range (actually limited by the melting point).

The influence of vacancies can also be understood on the basis of the large size of the $X(2)$ site of the alluaudite structure. The cations located in this site are very weakly bound to the remainder of the structure, and their replacement by a vacancy does not seem to alter seriously the stability of the alluaudite structure. Indeed, this site is empty in a fairly large number of natural minerals (7) or in various synthetic arsenates (results to be published). There is no equivalent site in the garnet structure and, to the best of our knowledge, there is no reported occurrence of a significant amount of vacancies on the dodecahedral sites of most of the compounds with a garnet structure, namely silicates, germanates, or arsenates.

Thus, it would be tempting to consider that the introduction of vacancies in a compound with the garnet structure may induce its transformation into an alluaudite structure. Here again, this cannot be extended to the vanadates, because of the existence of a series of vanadates with a defect garnet structure (8), such as $(\square_{0.5}Ca_{2.5})M_2^{2+}(VO_4)_3$ (M^{2+} = Ni, Co, Mg, Zn, Mn) or $(\square_{0.25}Ca_{2.75})$ $(\square_{0.25}M_{1.75}^{2+})(VO_4)_3$. Their thermal behaviour has not been investigated, but most of them are synthesized at a relatively high temperature (950°C), indicating that their thermal stability is rather good.

TABLE 5
Compared Structures of Arsenates and Vanadates

Arsenates	Vanadates
$NaCa_2M_2^{2+}(AsO_4)_3$ garnet–alluaudite polymorphism (1)	$NaCa_2M_2^{2+}(VO_4)_3$ garnet (15, 16)
$NaCaCdM_2^{2+}(AsO_4)_3$ alluaudite (1)	$NaCaCdM_2^{2+}(VO_4)_3$ garnet[a]
$AgCa_2Mg_2(AsO_4)_3$ alluaudite[a]	$AgCa_2Mg_2(VO_4)_3$ garnet (13)
$KCa_2M_2^{2+}(AsO_4)_3$ alluaudite[a]	$KCa_2Mg_2(VO_4)_3$ garnet (JCPDS 24-1044)
$\square_{0.5}Ca_{2.5}Mg_2(AsO_4)_3$ alluaudite	$\square_{0.5}Ca_{2.5}Mg_2(VO_4)_3$ garnet (8)
$Na_2LnMg_2(AsO_4)_3$ alluaudite[b]	$Na_2LnMg_2(VO_4)_3$ garnet (14)

[a] This work.

[b] To be published.

One point is clearly evidenced by this discussion. Starting from arsenates with a garnet structure, suitable cationic modifications induce a transformation into an alluaudite structure, and this transformation can be justified by the matching between the sizes of the available sites in the two structures and the size of the substituting cations. But this correlation cannot be applied to the corresponding vanadates, which exhibit only the garnet structure. Up to now, we don't know *why* some vanadates have a garnet structure and the corresponding arsenates are of the alluaudite type, but the number of observed cases (Table 5) is such that this cannot be fortuitous. It should be added that, independently from the search for garnet–alluaudite transitions, some attempts to synthesize vanadates with an alluaudite structure met no success. The actual conclusion is that no vanadate with an alluaudite structure has been reported so far.

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