

Vibrational studies of olivine-type compounds—II Orthophosphates, -arsenates and -vanadates $A^I B^{II} X^V O_4$

M. TH. PAQUES-LEDENT and P. TARTE

University of Liège, Department of General Chemistry, 4000-Sart Tilman,
Liège, Belgium

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Abstract—The i.r. and Raman spectra of $A B^{II} X O_4$ phosphates, arsenates and vanadates of olivine structure have been investigated, and their interpretation is discussed on both theoretical and experimental bases. Assignments have been deduced from the systematic investigation of pure compounds, solid solutions and isotopic species.

For all the compounds investigated, the stretching frequencies of the tetrahedral XO_4 anion may be considered as internal modes, but the corresponding bending frequencies can be considered as "internal" only for the phosphates and for the sodium compounds. For the arsenates and vanadates where A is lithium, the ^6Li - ^7Li isotopic shifts reveal important interactions between the Li translations and the AsO_4 or VO_4 bending vibrations.

It has also been possible to evidence a number of vibrational interactions in the case of the external vibrations.

Finally, we have further investigated to what extent the internal stretching vibrations of the complex anion are modified by the chemical nature of the bivalent cation B^{II} and an original correlation with the second ionization potential of the B^{II} cation is proposed.

INTRODUCTION

IN A PREVIOUS paper devoted to the vibrational spectrum of Mg_2SiO_4 [1], we have shown to what extent the investigation of isotopic species may lead to a realistic interpretation of the vibrational spectrum, despite the fairly low symmetry of the olivine structure. This type of structure is not limited to some orthosilicates and -germanates of the types $X_2^{II}SiO_4$, but is also represented in a fairly large number of compounds, which may be derived from the Mg_2SiO_4 formula, either by the double substitution $2 Mg^{II} \rightarrow 1A^I + 1B^{III}$, viz. $A^I B^{III} SiO_4$ or $A^I B^{III} GeO_4$, or by the double substitution $Mg^{II} Si^{IV} \rightarrow A^I X^V$, viz. $A^I B^{II} X^V O_4$ ($X^V = P, As$ or V).

The vibrational spectra of these compounds have not been reported so far. The interpretation of such spectra is difficult, as expected from the fairly low symmetry of these compounds and can be attempted only if a sufficient number of data are available.

This paper is devoted to the compounds $A^I B^{II} X^V O_4$ (orthophosphates, -arsenates, -vanadates) characterized by the olivine (or an olivine-like) structure. The silicates and germanates $A^I B^{III} X^{IV} O_4$ will be discussed in a next paper.

EXPERIMENTAL

Synthesis of the compounds

The compounds have been synthesized by solid state reaction between the lithium or sodium carbonate, the oxalates or carbonates of bivalent cations and the ammonium monohydrogenophosphate (or -arsenate) or the ammonium metavanadate. The mixture of reactives is submitted to a very slow heating; in

[1] M. TH. PAQUES-LEDENT and P. TARTE, *Spectrochim. Acta* 29A, 1007 (1973).

Table 1. Synthesis conditions

Compounds	Initial products	T°	Duration Colour
Orthophosphates			
LiMgPO ₄	Li ₂ CO ₃ + MgO + (NH ₄) ₂ HPO ₄	800°C	4 days white
LiNiPO ₄	Li ₂ CO ₃ + basic carbonate of Ni + (NH ₄) ₂ HPO	800°C	4 days {canary yellow}
LiCoPO ₄	Li ₂ CO ₃ + CoC ₂ O ₄ ·2H ₂ O + (NH ₄) ₂ HPO ₄	750°C	4 days violet
LiMnPO ₄	Li ₂ CO ₃ + MnC ₂ O ₄ ·2H ₂ O + (NH ₄) ₂ HPO ₄ (N ₂)	800°C	4 days light brown
	NH ₄ MnPO ₄ ·H ₂ O + Li ₂ CO ₃ (N ₂)	800°C	4 days light brown
LiFePO ₄	Li ₂ CO ₃ + FeC ₂ O ₄ ·2H ₂ O + (NH ₄) ₂ HPO ₄ (N ₂)	800°C	6 days green
	NH ₄ FePO ₄ ·H ₂ O + Li ₂ CO ₃ (N ₂)	800°C	6 days green
LiCdPO ₄	Li ₂ CO ₃ + CdCO ₃ + (NH ₄) ₂ HPO ₄	750°C	4 days white
Orthoarsenates			
LiMgAsO ₄	Li ₂ CO ₃ + MgO + (NH ₄) ₂ HAsO ₄	750°C	4 days white
LiNiAsO ₄	Li ₂ CO ₃ + basic carbonate of Ni + (NH ₄) ₂ HAsO ₄	750°C	4 days {canary yellow}
LiCoAsO ₄	Li ₂ CO ₃ + CoC ₂ O ₄ ·2H ₂ O + (NH ₄) ₂ HAsO ₄	750°C	4 days violet
LiMnAsO ₄	Li ₂ CO ₃ + MnC ₂ O ₄ ·2H ₂ O + (NH ₄) ₂ HAsO ₄	700°C	4 days {brownish pink}
LiCdAsO ₄	Li ₂ CO ₃ + CdCO ₃ + (NH ₄) ₂ HAsO ₄	700°C	4 days white
NaMnAsO ₄	NaHCO ₃ + MnC ₂ O ₄ ·2H ₂ O + (NH ₄) ₂ HAsO ₄	700°C	6 days beige
NaCdAsO ₄	NaHCO ₃ + CdCO ₃ + (NH ₄) ₂ HAsO ₄	700°C	5 days white
NaCaAsO ₄ bt°	NaHCO ₃ + CaCO ₃ + (NH ₄) ₂ HAsO ₄	650°C	6 days white
Orthovanadates			
LiMgVO ₄	Li ₂ CO ₃ + MgO + NH ₄ VO ₃	650°C	4 days white
LiMnVO ₄	Li ₂ CO ₃ + MnC ₂ O ₄ ·2H ₂ O + NH ₄ VO ₃	600°C	2 months brown
LiCdVO ₄	Li ₂ CO ₃ + CdCO ₃ + NH ₄ VO ₃	600°C	8 days white
NaCdVO ₄	NaHCO ₃ + CdCO ₃ + NH ₄ VO ₃	600°C	8 days ochre
NaCaVO ₄	NaHCO ₃ + CaCO ₃ + NH ₄ VO ₃	600°C	8 days white

any case, intermediate mixing and grinding are necessary before a pure phase is obtained.

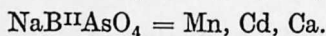
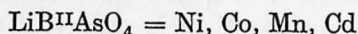
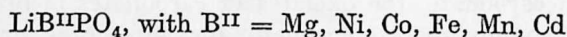
The temperatures of synthesis are listed in Table 1. All the phases obtained are checked by X-ray diffractometry but this check was omitted for some isotopic species (with ²⁶Mg, ⁵⁸Ni and ⁶²Ni) which were prepared in small quantities.

Spectra

The i.r. spectra were registered by the conventional pressed disc technique with a Beckman IR 12 (2000–200 cm⁻¹; KI discs) and a CAMECA-SI 36(200–50 cm⁻¹; polythene discs) spectrometer. The Raman spectra were obtained with a CODERG PHO double monochromator, equipped with a 50 mW He-Ne laser (Spectra Physics). The powdered sample is introduced into a glass capillary and formed into a cone which is illuminated along its axis by the laser beam. The scattered light is collected at a 90° angle.

CHEMICAL COMPOSITION AND STRUCTURE

The following synthetic compounds are characterised by a true olivine structure (space group $D_{2h}^{16} - P_{nma}$)



The naturally occurring mineral natrophylite NaMnPO_4 also has the olivine structure after BYSTRÖM [2] and MOORE [3]. But it should be pointed out that the corresponding synthetic compound prepared by conventional solid state reaction techniques does *not* have the olivine structure [4, 5].

In addition, a few other compounds are also characterized by an olivine-like X-ray powder diagram; but the occurrence of some reproducible extra-lines (not allowed in the olivine space group) strongly suggests that, despite some structural analogies, the space group of these compounds is different from that of olivines. This is the case for LiMgAsO_4 , $\text{LiB}^{\text{II}}\text{VO}_4$ with $B^{\text{II}} = \text{Mg, Mn, Cd}$ and $\text{NaB}^{\text{II}}\text{VO}_4$ with $B^{\text{II}} = \text{Cd, Ca}$ [4, 5].

CRYSTAL STRUCTURE AND VIBRATIONAL ANALYSIS

The primitive unit cell, space group $P_{nma} - D_{2h}^{16}$, is centrosymmetric, with 4 formula units in the cell.

There are 2 types of octahedral sites; the divalent cations B^{II} are located on the largest one with C_s symmetry, the monovalent cations A^{I} being located on the smaller one with C_i symmetry. To the best of our knowledge, there is no reported example of an olivine characterized by a statistical distribution of the cations on the C_s and C_i octahedral sites. Finally, the pentavalent cations X^{V} (P, As, V) are located in "isolated" tetrahedra XO_4 with site symmetry C_s . The arrangement of the different co-ordinated groups is given by GELLER and DURAND [6].

The vibrational analysis related to the olivine structure has been given elsewhere [1] and will not be repeated here. We shall just give the results of this analysis (Table 2) which relies on the hypothesis that the separation of the vibrations into internal (XO_4 groups) and external modes is a satisfactory approximation. The validity of this approximation will be discussed later on.

RESULTS

General considerations

Before presenting and discussing the results, some general remarks should be made:

(1) The number of predicted active fundamentals is rather large: 36 for the Raman spectrum and 35 for the i.r. spectrum.

(2) Most of the i.r. spectra are accordingly very complex (although the number of observed bands is smaller than the number of active fundamentals) with a large number of bands, most of them being observed in the $700\text{--}50\text{ cm}^{-1}$ region.

(3) The Raman spectra are more simple, but this is due, in most cases at least, to the low specific intensities of the spectra. This low intensity is related to the low polarisability of the constitutive atoms (for the phosphates) and to the fact that

[2] A. BYSTRÖM, *Ark. Kemi. Min. och. Geol.* **17B**, 1 (1944).

[3] P. MOORE, *Am. Min.* **57**, 1333 (1972).

[4] M. TH. PAQUES-LEDENT, Doctorate Thesis, Liège, Belgium (1972).

[5] M. TH. PAQUES-LEDENT, *Compt. Rend.* **274**, 1998 (1972).

[6] S. GELLER and J. L. DURAND, *Acta. Crystallogr.* **13**, 325 (1960).

Table 2. Types and activities of the normal modes of $ABXO_4$ compounds

Atome and site symmetry		Normal modes
Translations		
A^I	C_i	$\Gamma_A = 3A_u + 3B_{1u} + 3B_{2u} + 3B_{3u}$
B^{II} X^V	C_s	$\Gamma_B = \Gamma_X = 2A_g + B_{1g} + 2B_{2g} + 1B_{3g} + 1A_u + 2B_{1u}$ $+ 1B_{2u} + 2B_{3u}$
Rotations		
$X^V O_4$	C_s	$\Gamma_{rot} = 1A_g + 2B_{1g} + 1B_{2g} + 2B_{3g} + 2A_u + 1B_{1u}$ $+ 2B_{2u} + 1B_{3u}$
Internal modes		
XO_4	C_s	$\Gamma_{int} = \Gamma_{v_1} + \Gamma_{v_2} + \Gamma_{v_3} + \Gamma_{v_4}$ $\Gamma_{v_1} = A_g + B_{2g} + B_{1u} + B_{3u}$ $\Gamma_{v_2} = A_g + B_{1g} + B_{2g} + B_{3g} + A_u + B_{1u} + B_{2u} + B_{3u}$ $\Gamma_{v_3} = \Gamma_{v_4} = 2A_g + B_{1g} + 2B_{2g} + B_{3g} + A_u + 2B_{1u} + B_{2u}$ $+ 2B_{3u}$

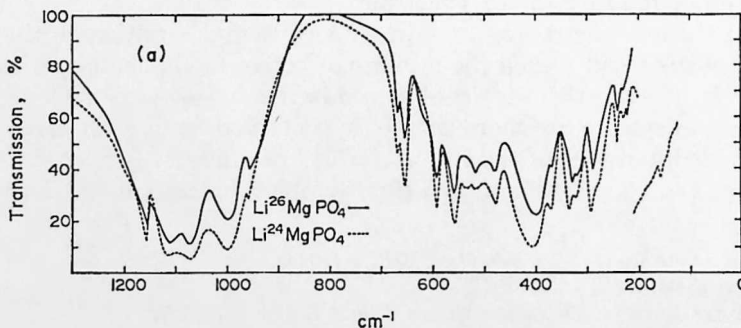
The A_u modes are Raman and i.r. inactive. Since the unit cell is centrosymmetric, the remaining u modes are i.r. active and the g modes are Raman active.

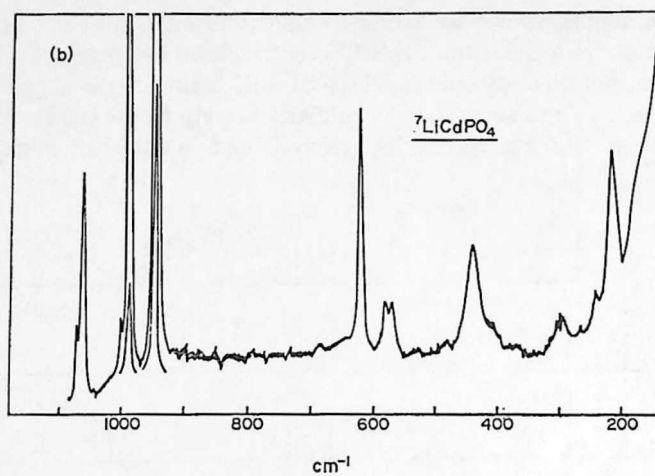
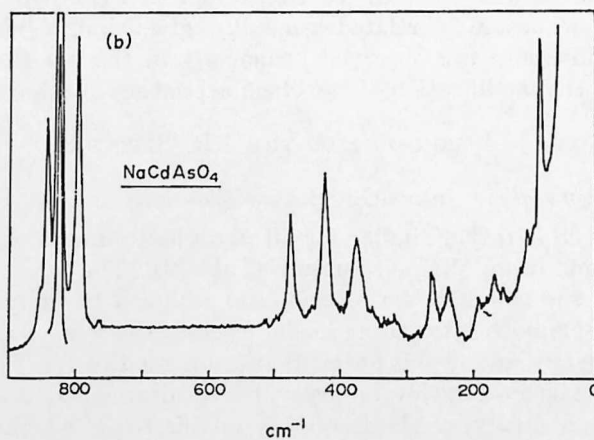
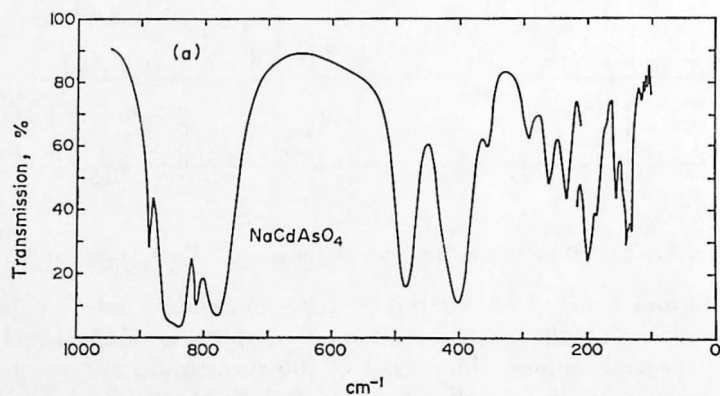
powders only were available. Some of the compounds were also more or less strongly coloured.

The i.r. spectra of $LiMgPO_4$ and $NaCdAsO_4$ and the Raman spectra of $LiCdPO_4$ and $NaCdAsO_4$ have been selected as fairly representative of the general pattern given by this family of compounds. They are represented in Fig. 1(a, b) and Fig. 2(a, b). These spectra may be divided into 2 regions:

(1) A series of high-frequency bands which are observed either in the 1200–900 or in the 950–700 cm^{-1} region, depending on the chemical nature of the tetrahedral anion (phosphate or arsenate): these are clearly related to the stretching vibrations of the tetrahedral anion.

(2) A rather complex pattern of bands in the 700–50 cm^{-1} region for the phosphates and in the 600–50 cm^{-1} region for the arsenates. These bands are expected to be due to the bending vibrations of the tetrahedral group and to the external modes. In view of the complexity of the spectra and since powder data only are

Fig. 1a. I.R. spectra of $Li^{24}MgPO_4$ and $Li^{26}MgPO_4$.

Fig. 1b. Raman spectrum of LiCdPO_4 .Fig. 2 (a, b). I.R. and Raman spectrum of NaCdAsO_4 .

available, the assignment of the bands to the different symmetry classes is ruled out. Nevertheless, with the help of the different techniques (namely the comparative study of pure compounds, isotopic species and solid solutions) it is possible to investigate some aspects of the assignment problem, namely to determine to what extent a given cation or co-ordinated group is participating to a vibration of given frequency.

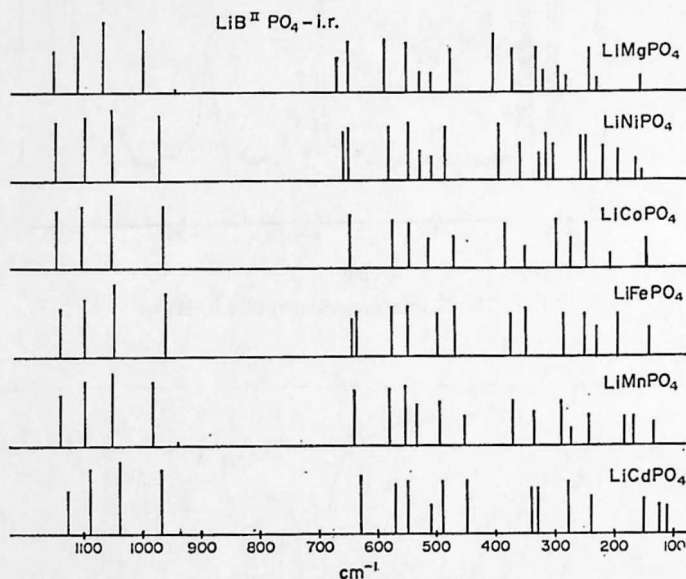


Fig. 3. General pattern of i.r. spectra for the $\text{LiB}^{\text{II}}\text{PO}_4$ compounds.

The results and conclusions arrived at for some compounds can be extended without too much difficulty to the remaining compounds of the same family, at least in some spectral regions, since most of the spectra are very similar (Fig. 3). This is in accordance with the well-recognized fact that compounds which are both chemically and structurally related generally give similar vibrational spectra. Significant modifications are observed principally in the low-frequency region, in connection with the modification of the chemical nature of the cation.

ASSIGNMENT OF THE I.R. SPECTRA

The high-frequency region: internal stretching vibrations

The i.r. pattern is rather similar for all phosphates and is characteristic of the PO_4 anion engaged in an olivine structure (Table 3). The four strong, moderately broad, bands of the $960\text{--}1200\text{ cm}^{-1}$ region are assigned to components originating from the ν_3 antisymmetric stretching mode, whereas the weak, sharp band observed on the low-frequency side of this absorption is assigned to ν_1 . This last assignment is proposed on the basis of the low intensity, the results of $(\text{PO}_4, \text{AsO}_4)$ solid solutions, the sharpness and, finally, of the frequency of this band, which is very similar to the frequency of the strongest Raman peak (see below) and to the ν_1 frequency of

Table 3. $\text{LiB}^{\text{II}}\text{PO}_4$ compounds: i.r. stretching frequencies of the PO_4 anion (cm^{-1})

Compound	$\nu_1(\text{PO}_4)$	$\nu_3(\text{PO}_4)$
LiMgPO_4	958	1000–1070–1113–1157
LiNiPO_4	944	972–1058–1102–1148
LiCoPO_4		967–1057–1104–1148
LiFePO_4		964–1049–1096–1138
LiMnPO_4	947	984–1051–1096–1140
LiCdPO_4	941.5	967–1042–1091–1128

the PO_4 anion in solution. However it must be pointed out that the labelling “ ν_1 ” and “ ν_3 ” has no strict significance since both ν_1 and ν_3 of the free tetrahedral ion are split under the influence of both site and factor groups into a series of modes, some of which belong to the same representations and thus are liable to interact: the reality and importance of such a mixing between the split components of ν_1 and ν_3 modes has been demonstrated in the case of Mg_2SiO_4 on the basis of ^{28}Si — ^{30}Si isotopic shifts [1]. This kind of experimental proof is *impossible* in the actual case, since there is only 1 stable isotope of *phosphorus*.

In dilute solid solutions such as $\text{LiB}^{\text{II}}(\text{P}_{0.02}, \text{As}_{0.98})\text{O}_4$, the factor group effect disappears but the site group splitting is maintained: the ν_3 mode of the PO_4 anion is represented by 3 bands (Table 4) in accordance with the site symmetry of the tetrahedral group in the olivine structure (C_s). The assignment problem is more complicated for the arsenates since both symmetric and antisymmetric modes

Table 4. $\text{LiB}^{\text{II}}(\text{P}_{0.02}, \text{As}_{0.98})\text{O}_4$ dilute solid solutions: i.r. frequencies.

Compound	$\nu_3(\text{PO}_4)$ —(cm^{-1})	$\Delta\nu_3(\text{PO}_4)$ —(cm^{-1})
$\text{LiMg}(\text{P}, \text{As})\text{O}_4$	1008.5–1047–1097.5	89
$\text{LiNi}(\text{P}, \text{As})\text{O}_4$	977.5–1026.5–1085.5	108
$\text{LiCo}(\text{P}, \text{As})\text{O}_4$	976–1029–1088	112
$\text{LiMn}(\text{P}, \text{As})\text{O}_4$	987–1026–1085	98
$\text{LiCd}(\text{P}, \text{As})\text{O}_4$	975–1014–1082	107

have very similar frequencies. Since, in addition, isotopic frequencies are not available (there is only one stable isotope of arsenic), the discrimination between symmetric and antisymmetric modes is impossible and the group of bands of the 750–900 cm^{-1} region is simply assigned to the stretching motions (ν_1 and ν_3) without any further specification. The spectrum of dilute solid solutions $\text{LiB}^{\text{II}}(\text{P}_{1-x}, \text{As}_x)\text{O}_4$ ($X = 0.03$ et 0.05) exhibits 4 bands in this spectral region. These bands may be assigned to ν_1 plus the 3 split components of ν_3 .

The medium- and low-frequency regions

This part of the spectrum is expected to correspond to the internal bending modes of the anion and to the external modes (rotations and translations). The main point here will be to decide whether or not the distinction between internal and external modes is a satisfactory approximation; and if this is the case, to propose the right type of assignment for the numerous bands which are observed in this

region. Following a procedure of general use in this laboratory, these problems will be handled through the investigation of isotopic species.

Investigation of isotopic species

The ${}^6\text{Li}$ and ${}^7\text{Li}$ isotopic species have been synthesized and investigated for all lithium compounds. For practical reasons, isotopic studies on the bivalent cations B^{II} have been restricted to $\text{Mg}({}^{24}\text{Mg}-{}^{26}\text{Mg})$, $\text{Ni}({}^{58}\text{Ni}-{}^{62}\text{Ni})$ and $\text{Ca}({}^{40}\text{Ca}-{}^{44}\text{Ca})$.

According to the isotopic frequencies of LiMgPO_4 (Table 5), the bands may be classified into 3 types:

(1) The medium-frequency bands for which the isotopic shifts are small or negligible ($550-700\text{ cm}^{-1}$). Since in addition the i.r. pattern in this region is hardly modified by the nature of the bivalent cation B^{II} , these bands are assigned to the bending motions of the PO_4 tetrahedra (essentially ν_4 , with a possible contribution of ν_2).

(2) A few bands in the low-frequency region are also nearly insensitive to the masses of both cations, the most characteristic one being the 372 cm^{-1} band. Since their frequency is too low for their assignment to a bending motion of the PO_4 group, they are tentatively assigned to a rotation.

(3) The remaining bands which exhibit strong or moderate isotopic shifts are necessarily assigned to external translational modes. Some of them essentially depend on the mass of a given cation (either Li or Mg) and thus may be assigned to a translation of this specific cation. But for others, the frequency clearly depends on the masses of both Li and Mg cations.

Table 5. Isotopic shifts: LiMgPO_4 —i.r. spectra.

${}^6\text{Li}-{}^7\text{Li}$ $\Delta\nu$	${}^6\text{Li}{}^{24}\text{MgPO}_4$ (cm^{-1})	${}^7\text{Li}{}^{24}\text{MgPO}_4$ (cm^{-1})	${}^7\text{Li}{}^{26}\text{MgPO}_4$ (cm^{-1})	${}^{24}\text{g}-{}^{26}\text{Mg}$ $\Delta\nu$	Assignments
0.5	158	157.5			
1	230	229	226	3	essentially trans- lations of Mg cations
3.5	245	241.5	240.5	1	
10	290	280			
2	296	294	289	5	essentially trans- lations of Li cations
3	325	322	318	4	
6	341	335	330	5	
2	374	372	371	1	translations of both Li and Mg cations
9	416	407	399	8	
16	495	479	479		
1	518	517	515	2	essentially $\nu_4(\text{PO}_4)$
~24		535	534	1	
1	559	558	558		essentially $\nu_4(\text{PO}_4)$
1	594	593	592	1	
4	659	655	655	1	
4	673	669	668.5	0.5	

A similar behaviour is observed for the isotopic species of LiNiPO_4 ; but as expected, the frequency shifts related to the ^{58}Ni – ^{62}Ni isotopic replacement are small and, for some bands at least there remains some uncertainty about the participation of the Ni cation (Table 6).

Table 6. Isotopic shifts: LiNiPO_4 —i.r. spectra

^7Li – ^6Li $\Delta\nu(\text{cm}^{-1})$	$^7\text{LiNiPO}_4$ (cm^{-1})	$^6\text{LiNiPO}_5$ (cm^{-1})	$^7\text{Li}^{62}\text{NiPO}_4$ (cm^{-1})	$^7\text{Li}^{58}\text{NiPO}_4$ (cm^{-1})	^{62}Ni – ^{58}Ni $\Delta\nu(\text{cm}^{-1})$	Assignments
	163	163	163	163		--- rotation
-11	192	192	187	~192	-5	} translations of both Li and Ni cations
	226	226	224	226	+2	
- 3.5	246.5	250	246	246	-2	
- 1	256	257	254.5	256	-1.5	
- 2	304	306	303	304	-1	
	313	313	312.5	313	-0.5	} essentially translations of Ni cations
-12	327	339	326	328	-2	
+ 3	360	357	359	361		
-16	396	412	395	395		
-32	477	509	477.5	477	+0.5	} essentially translations of Li cations
~24	~510		~528	~528		
- 3	550	553	551	551		
- 3.5	582.5	586	583	582.5	+0.5	} essentially $\nu_4(\text{PO}_4)$
	650	650	650	650		
	661	661	660.5	661	-0.5	

For the remaining phosphates $\text{LiB}^{\text{II}}\text{PO}_4$ ($B^{\text{II}} = \text{Co}, \text{Mn}, \text{Fe}, \text{Cd}$), ^6Li – ^7Li isotopic species only have been investigated. The results are consistent with the preceding ones, namely the lack of significant shifts for the bands in the 550–660 cm^{-1} region, these bands being assigned to PO_4 bending vibrations, and strong ^6Li – ^7Li frequency shifts in the 350–550 cm^{-1} region.*

Arsenates $\text{LiB}^{\text{II}}\text{AsO}_4$

The bending modes of the AsO_4 anion are expected in the 400–500 cm^{-1} region; but in fact, all the bands of the 200–550 cm^{-1} region are more or less strongly shifted by the ^6Li – ^7Li isotopic replacement (Table 7). It is thus clear that the AsO_4 bending modes are strongly mixed up with translational modes of the Li cation and that no more precise assignments can be given on the basis of powder spectra alone.

Sodium arsenates $\text{NaB}^{\text{II}}\text{AsO}_4$ ($B^{\text{II}} = \text{Mn}, \text{Cd}, \text{Ca}$)

For these compounds, partial assignments have been deduced from the study of ^{40}Ca – ^{44}Ca isotopic species and from $\text{Na}(\text{Cd}, \text{Ca})\text{AsO}_4$ solid solutions (Table 8). Both isotopic and isomorphous replacements lead to essentially similar conclusions: some

* Tables giving the isotopic frequencies are available on request to the authors.

Table 7. $\text{LiB}^{\text{II}}\text{AsO}_4$ compounds: i.r. frequencies —
 ${}^7\text{Li}$ - ${}^6\text{Li}$ shift

${}^7\text{LiCdAsO}_4$	${}^6\text{LiCdAsO}_4$	$\Delta\nu^7\text{Li}-{}^6\text{Li}$
209	213	- 4
242	254	-12
324(sh)	337(sh)	-13
338	357	-19
397	402	-5
420(sh)		
457	479	-22
508	525(sh)	-17
780	780	
836	838	- 2
862(sh)	862(sh)	
888	888	

Table 8. I.r. frequencies: $\text{Na}(\text{Cd}, \text{Ca})\text{AsO}_4$ solid solutions and NaCaAsO_4 isotopic shifts

NaCdAsO_4	$\text{Na}(\text{Cd}, \text{Ca})\text{AsO}_4$ 0.75 0.25	$\text{Na}(\text{Cd}, \text{Ca})\text{AsO}_4$ 0.5 0.5	$\text{Na}(\text{Cd}, \text{Ca})\text{AsO}_4$ 0.25 0.75	$\text{Na}^{40}\text{CaAsO}_4$	$\text{Na}^{44}\text{CaAsO}_4$	$\Delta\nu^{40}\text{Ca}-{}^{44}\text{Ca}$
131						
139	135.5	135.5	136	138	138	
154	152	153.5	157.5	162.5	162.5	
	178.5	176.5	167			
185			180	183	180	3
199	199	197	196.5	194	192	2
	227	223(sh)				
234		245	240	236	232	4
259	257	254	252	252	252	
290	290	292	289	284.5	284.5	
		302	308	313	306	7
356	360(sh)	360(sh)				
402	402	402	400	400	400	
		425(sh)	428	430	430	
483	482	480	478	475	477	2
782	{ 776 789	{ 785 800	798	797	797	
814	813	816	819	820	820	
840	~844	844	845	845	845	
855(sh)	855(sh)	855	855	855	855	
887	889	892	894	894	894	

bands are sensitive to the mass of Ca and are also modified in the $\text{Na}(\text{Cd}, \text{Ca})\text{AsO}_4$ solid solutions. These bands must be assigned to modes involving at least a translation of the bivalent cation. For the remaining bands which are neither sensitive to the mass of Ca nor strongly modified in the solid solutions, two types of assignments are possible:

(1) The medium-frequency bands of the $350\text{--}500\text{ cm}^{-1}$ region must be assigned to the bending motions of the AsO_4 anion; these modes are now essentially free from interactions with the external modes in connection with the higher mass of the monovalent cation;

(2) The low-frequency bands will be assigned to external modes which do not involve a significant displacement of the bivalent cation: either a translation of the other cations or a rotation of the AsO_4 group.

RAMAN SPECTRA

High-frequency region

Several Raman peaks are observed in the 900–1100 cm^{-1} region for the phosphates and 800–900 cm^{-1} region for the arsenates. One of these peaks is of much higher intensity than the others and is assigned to an essentially symmetric stretching mode (ν_1 of the free ion). For the phosphates, this peak is located near 950 cm^{-1} ; this is the right order of magnitude for the ν_1 mode of the PO_4 ion. The other peaks of lower intensity and higher frequency (1000–1100 cm^{-1}) are assigned to modes which, at first approximation, should have an antisymmetric character (ν_3 of the free ion) (Table 9).

Table 9. $\text{LiB}^{\text{II}}\text{PO}_4$: Raman frequencies and assignments

LiMnPO_4	LiCdPO_4	Intensity	Assignment	
148	94	w	Translations of B^{II} and rotations	External modes
203		w		
237	217	m		
305	297	w	} $\nu_2(\text{PO}_4)$	Internal modes essentially
410(sh)	410	w		
442	438	m	} $\nu_4(\text{PO}_4)$	
580	570	w		
590	580	w	} $\nu_1(\text{PO}_4)$	
626	622	m		
948.5	944	s		
999			} $\nu_3(\text{PO}_4)$	
1006	988	m		
1018	1005	w		
1067	1064	m		
1080	1073	w		

s: strong; m: medium; w: weak.

For the arsenates, the assignment must rely on intensity considerations alone, since both symmetric and antisymmetric modes have similar frequencies.

No coincidences are found between i.r. and Raman frequencies: this is in agreement with the fact that the unit cell is centrosymmetric.

Medium- and low-frequency regions

The most prominent feature is the lack of any significant ^6Li – ^7Li isotopic shift. This is in accordance with the theoretical expectation deduced from the correlation method: the Li atoms are located on C_i sites and these atoms are not allowed to move during the Raman-active vibrations.

As a consequence, the bending modes of the tetrahedral anion (which could not be observed in the i.r. spectra of $\text{LiB}^{\text{II}}\text{AsO}_4$ compounds because of their mixing with Li translations), are observed without difficulty in the Raman spectrum. They may be tentatively assigned to vibrations with symmetric (ν_2) or antisymmetric (ν_4) character on the basis of their relative intensities and by comparison with the

frequency values observed in solution. But no strict significance should be given to such an assignment for two reasons:

(1) Stable isotopes of P or As not available and thus direct experimental evidence is lacking;

(2) Under the influence of the site group and of the factor group, both ν_2 and ν_4 are split into components, some of which may be strongly mixed up.

The low-frequency peaks (below 350 cm^{-1}) are assigned to external modes, either rotations or translations of the cations which are located on sites of C_s symmetry. The assignments in this region are only very fragmentary, since we just have experimental data on isotopic ^{40}Ca - ^{44}Ca in NaCaAsO_4 (Table 10).

Table 10. Raman frequencies: $\text{LiB}^{\text{II}}\text{AsO}_4$ and $\text{NaB}^{\text{II}}\text{AsO}_4$ compounds

Intensity	LiCdAsO_4	NaCdAsO_4	$\text{Na}^{40}\text{CaAsO}_4$	$\text{Na}^{44}\text{CaAsO}_4$	$\Delta\nu^{40}\text{Ca}-^{44}\text{Ca}$
w			90	88.5	1.5
w	88	92	121	121	
vw	145	148			
vw			203	198	5
vw	241	235	234	233	1
w			260.5	252	8.5
w		261	270	267.5	2.5
w		325	~343	~340	~3
m	360	377	368	368	
w	429	426	432	432	
vw			444	444	
w	484	477	467	467	
w			782		
m		780	798		
s	794	794	813.5		
vs	822	823	829		
m	850	841.5	843		
w		851	873		
w			898		

vs: very strong; s: strong; m: medium; w: weak; vw: very weak.

Finally two comments should be made about the spectra of the arsenates. First the Raman spectra of the corresponding compounds $\text{LiB}^{\text{II}}\text{AsO}_4$ and $\text{NaB}^{\text{II}}\text{AsO}_4$ are very similar (in contrast with the i.r. spectra which are rather different): this should be related to the fact that the alkali cations do not participate to the Raman spectrum. Secondly, some of the external Raman active modes have a higher frequency for the Na than for the corresponding Li compound. This is opposite to the frequency change expected from the fact that the unit cell parameters are larger for the Na than for the Li compounds. A similar behaviour has been observed for olivine-type silicates and germanates $\text{AB}^{\text{III}}\text{XO}_4$, and will be discussed in a future paper.

Investigation of some related orthovanadates

The compounds $\text{LiB}^{\text{IV}}\text{VO}_4$ for which $B^{\text{II}} = \text{Co}, \text{Ni}, \text{Cu}$ have a spinel structure [7], whereas LiZnVO_4 has a phenakite structure [8]. On the other hand, BLASSE has proposed an olivine structure for LiMgVO_4 [9]. Our own X-ray powder data

[7] J. C. BERNIER, P. POIX, and A. MICHEL, *Compt. Rend.* **253**, 1578 (1961).

[8] G. BLASSE, *J. Inorg. Nucl. Chem.* **25**, 136 (1963).

[9] G. BLASSE, *J. Inorg. Nucl. Chem.* **25**, 230 (1963).

do not completely agree with this statement: besides a number of diffraction lines which may be accounted for by an olivine structure, we find some extra (but quite reproducible) lines which would be forbidden in the D_{2h}^{16} olivine space group. The same considerations may be applied to the compounds LiMnVO_4 and LiCdVO_4 which were not previously investigated. The parameters of the proposed orthorhombic unit cell are given in Table 11.

Table 11. Tentative unit cell parameter for vanadates

	$a_0(\text{\AA})$	$b_0(\text{\AA})$	$c_0(\text{\AA})$
LiMgVO_4	4.72	10.425	6.22
	4.80	10.31	6.00[9]
LiMnVO_4	4.88	10.64	6.34
LiCdVO_4	4.93	11.03	6.47

Strictly speaking, these compounds are not olivines, but they may be considered as having an olivine-like structure and their vibrational spectrum may be compared to that of true olivine-type compounds.

I.R. spectra (Fig. 4a)

The high-frequency region ($750\text{--}900\text{ cm}^{-1}$) corresponding to the stretching vibrations of the VO_4 ion is characterized by a very broad absorption with a few well-defined bands. This peculiar shape of the bands cannot be ascribed to the crystal structure, since a similar behaviour has been observed for the corresponding spinels LiCoVO_4 and LiNiVO_4 [10], and for some other orthovanadates. Thus, this seems to be related to some property of the V—O bonds in the VO_4 group.

The medium- and low-frequency regions exhibit a reduced number of bands for which precise assignments are impossible. The assignments proposed in Table 12 are deduced from the observed ^6Li — ^7Li isotopic shifts and from the known frequency range corresponding to the VO_4 bending vibrations.

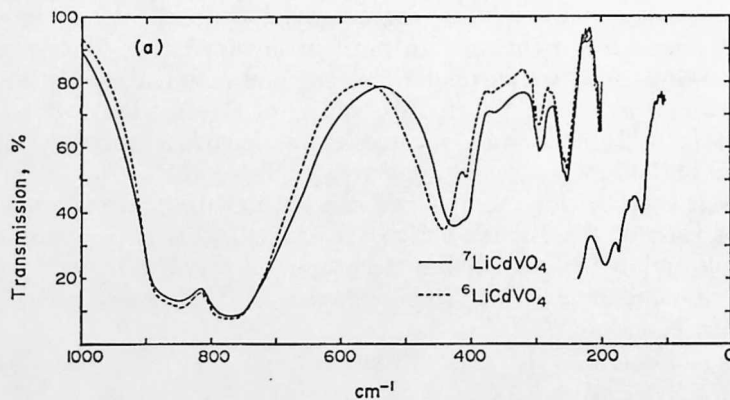


Fig. 4a. I.r. spectra of $^6\text{LiCdVO}_4$ and $^7\text{LiCdVO}_4$.

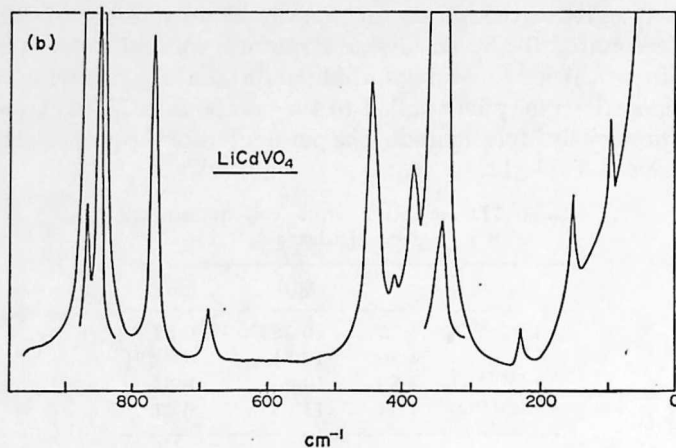
Fig. 4b. Raman spectrum of LiCdVO_4 .

Table 12. I.r. spectra: orthovanadates

$\Delta\nu^{6}\text{Li}-^{7}\text{Li}$	$^{6}\text{LiCdVO}_4$	$^{7}\text{LiCdVO}_4$	NaCdVO_4	NaCaVO_4	Assignments
1	203	202	212	250(sh)	} Essentially external frequencies
1	253	252	~252	275	
	294	294		290	
0.5	407	406.5	392	375(sh)	} Na compounds: $\nu_4(\text{VO}_4)$ Li compounds: "mixed frequencies"
22	442	420	413	407	
	770	770	770	780	} ν_1 and ν_3 modes: Internal frequencies
	845	845			
	875	875	880	875	

Raman spectra

The Raman spectra (Fig. 4b) are characterized by their strong intensity, a property which seems to be common to most orthovanadates. Two peaks (near 850–880 and 340–360 cm^{-1}) are particularly strong and may reasonably be assigned to symmetric vibrations of the VO_4 ion (ν_1 and ν_2 of the free ion). But the most interesting feature of these Raman spectra is the occurrence of very significant ^{6}Li – ^{7}Li isotopic shifts in the 350–500 cm^{-1} region (Table 13).

It is thus clear that for these compounds, the lithium atoms are allowed to move during some at least of the Raman-active vibrations. This is in opposition with the selection rules related to the olivine structure and this is a further proof that, despite the olivine-like structure of these compounds, their space group must be different from D_{2h}^{16} .

DISCUSSION

1. The approximations related to the assignment problem

A first point is evidenced by the actual results, namely the importance of isotopic studies for a realistic interpretation of the spectra of crystals of moderate to fair

Table 13. Raman spectra: Orthovanadates

Intensity	$\Delta\nu^{6\text{Li}-7\text{Li}}$	$^6\text{LiCdVO}_4$	$^7\text{LiCdVO}_4$	NaCaVO_4	Assignments
m		94	94	90	} Essentially external modes
m		152	152	153	
w				210	
m		228	228	228	
w				280	
vs		343	343	357	} $\nu_2(\text{VO}_4)$ essentially
		350(sh)	350(sh)		
m				407	} $\nu_4(\text{VO}_4)$ essentially
m	9	395	386		} mixed frequencies
w			~410		
s	11	456	445		
m	-1	686	687	731	} $\nu_3(\text{VO}_4)$ $\nu_1(\text{VO}_4)$
s	+1	766	765	781	
vs		849.5	849.5	870.5	
m		867	867	897	

vs: very strong; s: strong; m: medium; w: weak.

complexity. Although it has its own limitations, the isotopic replacement is certainly one of the best methods to evidence the simultaneous participation of several cations to a given vibrational mode and, as a consequence, to check to what extent the separation of the vibrations into internal and external modes may be considered as a satisfactory approximation.

In relation to this point, it should be remembered that the validity of this approximation cannot be simply deduced by analogy. In the actual case, only the stretching frequencies of the tetrahedral anion may be considered as internal modes for all the compounds investigated. But the corresponding bending frequencies can be considered as "internal" only for the phosphates and for the sodium compounds; for the arsenates and the vanadates containing lithium, some at least of the bending vibrations of the anion are strongly mixed up with Li translational motions and thus are no longer internal modes. Thus, despite the isotopic character of these compounds, the separation of the vibrations into internal and external modes is not valid for the whole family and does depend on the nature of the constitutive atoms.

Likewise the real origin of the external modes (translations, rotations or a mixture of them) cannot be decided without the help of isotopic data. Nevertheless, owing to the complexity of the compounds investigated, these assignments remain essentially qualitative in nature.

The only way to go deeper into this problem would be the study of monocrystals.

2. Correlations between the splitting of the stretching degenerate modes, the deformation of the tetrahedral ion and the chemical nature of the bivalent cation

Besides the assignment problem, we also have investigated to what extent the internal stretching vibrations of the complex anion are modified by the chemical nature of the bivalent cation B^{II} .

It has been previously considered that the importance of the splitting of a degenerate mode in a dilute solid solution* was related to the importance of the geometrical deformation of the anion in the type of structure investigated. The actual results on $\text{LiB}^{\text{II}}\text{PO}_4$ compounds do not support this hypothesis. For all these compounds we find a rather large splitting for the ν_3 components of either the PO_4 ion in $\text{LiB}^{\text{II}}(\text{P}_{0.02}, \text{As}_{0.98})\text{O}_4$ or the AsO_4 ion in $\text{LiB}^{\text{II}}(\text{P}_{0.96}, \text{As}_{0.04})$ dilute solid solutions. On the other hand, a detailed investigation of the structure of LiMnPO_4 [6] leads for the PO_4 anion, to 4 P—O distances which are nearly equal: the differences are ranging about the limits of the experimental error ($\pm 0.007 \text{ \AA}$ and 0.01 \AA). The only significant deformation of the tetrahedron is related to the occurrence of different angles, namely about 106° and 112° . But this type of deformation does not seem to be sufficient to explain the large splitting of the ν_3 mode. A new tentative explanation of these results may be proposed on the basis of the following experimental facts:

(1) A large splitting of the ν_3 components corresponding to the tetrahedral group has been found for *all* compounds of the olivine type investigated so far: $\text{X}_2^{\text{II}}\text{SiO}_4$ and $\text{X}_2^{\text{II}}\text{GeO}_4$ [11] $\text{A}^{\text{I}}\text{B}^{\text{II}}\text{PO}_4$ and $\text{A}^{\text{I}}\text{B}^{\text{II}}\text{AsO}_4$ (this paper), $\text{A}^{\text{I}}\text{B}^{\text{III}}\text{SiO}_4$ and $\text{A}^{\text{I}}\text{B}^{\text{III}}\text{GeO}_4$ [4]. Thus the splitting should be qualitatively related to the type of structure, irrespective of the chemical nature of the tetrahedral anion or of the valency difference between the cations.

(2) Even if the 2 octahedral cations are chemically identical (as in $\text{X}_2^{\text{II}}\text{SiO}_4$), there are 2 rather different types of octahedral sites in the olivine structure and thus 2 types of cation—oxygen bonds. Every oxygen of the tetrahedral anion is bonded to 3 octahedral cations, either 2 cations on sites of C_i symmetry (viz. A^{I}) and 1 cation on sites of C_s symmetry (viz. B^{II}) or, conversely, 2 cations on sites of C_s symmetry and 1 cation on C_i sites: the 2 oxygen atoms which are simultaneously bonded to a given B^{II} cation and to a given tetrahedral cation correspond to this second type.

Now, the type of bonding (and the bonding force) between the oxygen and the octahedral cation has necessarily an influence on the type of bonding between the same oxygen and the tetrahedral cation. As a consequence, the 2 kinds of oxygen environments must lead to 2 types of bonds between the oxygen and the tetrahedral cation within a given tetrahedral group: this may be responsible for the splitting of the ν_3 mode. If this explanation is correct, the splitting is related, not to a geometrical deformation (as previously suggested) but to an unequal distribution of the bonding forces within the tetrahedral group.

Moreover, the value of the splitting must depend on the nature of the octahedral cation. Our results show that this is really the case (Table 4); in addition, it seems to be a qualitative correlation between the importance of the splitting and the second ionization potential of the bivalent cation [4]: the splitting is larger for higher values of the ionization potential (Fig. 5). This fact is also in agreement with the proposed origin of the splitting: a higher value of the second ionization potential

* The splitting observed for a pure compound is not significant since it is the result of the combined influences of the site group and the factor group. Only in dilute solid solutions is it possible to observe the influence of the site group (viz, the deformation) alone.

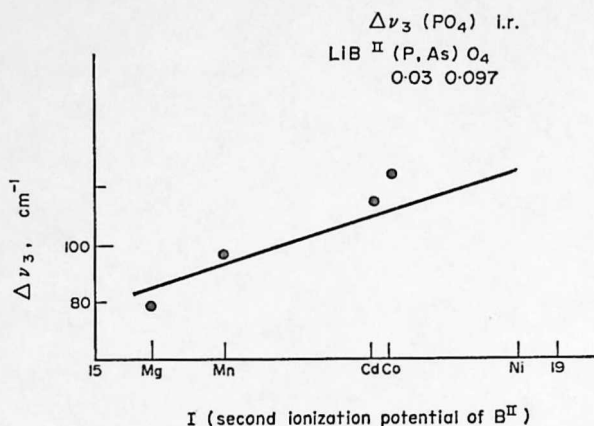


Fig. 5. Relation between the $\Delta\nu_3(\text{PO}_4)$ interval in $\text{LiB}^{\text{II}}(\text{P}_{0.03}\text{As}_{0.97})\text{O}_4$ solid solutions and the second ionization potential of B^{II} .

of the octahedral cation B^{II} implies a stronger interaction with the adjacent P—O (or As—O) bond and eventually a larger difference in the distribution of the bonding forces within the tetrahedral group.

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NOTE ADDED IN PRESS

Erratum to paper No. I. (*Spectrochim. Acta* **29A**, 1007–1016). In paper No. I of this series, the space group of olivine has been labeled Pbnm; but this setting of the axes is erroneous with respect to the site and factor group analysis as given in this paper. The correct labeling of the space group is Pnma, as in the present paper. We are indebted to Prof. E. FUNCK to have drawn our attention upon this error.