

## Infrared studies of spinels—IV Normal spinels with a high-valency tetrahedral cation

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**Abstract**—The investigation of normal II–IV germanates, I–II–V vanadates and normal I–VI molybdate and tungstate spinels show that the high-frequency band of their i.r. spectrum must be assigned to a vibration of the tetrahedral group. A comparison is made with the assignment previously proposed for the normal II–III spinels, and it is suggested that the high-frequency absorption band of a spinel must be assigned to a vibration between the oxygen and the highest-valency cation, irrespective of the co-ordination of this cation. The medium- and low-frequency bands are often related to complex vibrations, as evidenced from the study of isotopic species. The Raman spectrum of the molybdates has also been investigated and the fundamentals have been assigned to the different symmetry species with the help of  $^{92}\text{Mo}$ – $^{100}\text{Mo}$  isotopic shifts. The i.r. spectrum of the I–II–V vanadates exhibits several abnormal features: the stretching vibration of the  $\text{VO}_4$  tetrahedron is represented by a broad, complex absorption, and the low-frequency band is missing.

### INTRODUCTION

IN THE preceding paper [1], we have shown that, for the cubic, normal II–III spinels, the high-frequency band  $\nu_1$  should be assigned to a vibration of the octahedral lattice. It has been pointed out, however, that this assignment is necessarily restricted to the spinels under consideration, and cannot be generalized to the whole spinel family. In fact, the published data on the normal germanate spinels  $\text{X}_2^{\text{II}}\text{GeO}_4$  [2] and on the sodium tungstate and molybdate spinels [3, 4] strongly support the assignment of the high-frequency band to a vibration of the tetrahedral group  $\text{GeO}_4$ ,  $\text{MoO}_4$  or  $\text{WO}_4$ . We present in this paper further experimental data which show that the high-frequency band must be assigned to a vibration of the tetrahedral group when this group is occupied by the highest-valency cation of the compound. In the course of this investigation, further examples of vibrational interactions have been evidenced by the study of isotopic species.

### EXPERIMENTAL

#### *Synthesis of the compounds*

Most of the compounds investigated have been synthesized by conventional solid state reactions (Table 1). The spinel form of  $\text{Mg}_2\text{GeO}_4$  has been prepared by precipitation of a solution of  $\text{Mg}_2\text{SO}_4 + \text{GeO}_2$  by ammonia, and recrystallization of the precipitate at  $800^\circ\text{C}$  in the presence of  $\text{MgCl}_2$  [2]. Silver molybdate was also prepared by precipitation ( $\text{AgNO}_3 + \text{Na}_2\text{MoO}_4$ ), and recrystallized from 2N ammonia.

The procedure had to be somewhat modified for the synthesis of isotopic compounds. Isotopic nickel was obtained as the element itself. It was transformed

[1] J. PREUDHOMME and P. TARTE, *Spectrochim. Acta* **27A**, 1817 (1971).

[2] P. TARTE, *Spectrochim. Acta* **19**, 49 (1963).

[3] R. H. BUSEY and O. L. KELLER, *J. Chem. Phys.* **41**, 215 (1964).

[4] P. CAILLET and P. SAUMAGNE, *J. Mol. Struct.* **4**, 191 (1969).

Table 1. Synthesis conditions

Compound	Starting mixture	Method	Temperature	Duration	Reference
Mg <sub>2</sub> GeO <sub>4</sub>		See text			
Ni <sub>2</sub> GeO <sub>4</sub>	Basic NiCO <sub>3</sub> + GeO <sub>2</sub>	Solid state reaction	1000°	7 hr	(a)
Co <sub>2</sub> GeO <sub>4</sub>	Co oxalate + GeO <sub>2</sub>	Solid state reaction	950°	7 hr	(a)
Fe <sub>2</sub> GeO <sub>4</sub>	Fe oxalate + GeO <sub>2</sub>	Solid state reaction	1000°	5 hr	(a)
LiCoVO <sub>4</sub>	LiVO <sub>3</sub> + Co oxalate	Solid state reaction	500°	7 days	(b)
LiNiVO <sub>4</sub>	LiVO <sub>3</sub> + basic NiCO <sub>3</sub>	Solid state reaction	500°	7 days	(b)
Na <sub>2</sub> MoO <sub>4</sub>	NaHCO <sub>3</sub> + MoO <sub>3</sub>	Solid state reaction	600°	1 day	(c)
Na <sub>2</sub> WO <sub>4</sub>	NaHCO <sub>3</sub> + WO <sub>3</sub>	Solid state reaction	600°	1 day	(c)
Ag <sub>2</sub> MoO <sub>4</sub>		See text			

(a) A. DURIF, E. BERTAUT and R. PAUTHENET, *Ann. Chim.* **13**, 525 (1956).

(b) J. C. BERNIER, P. POIX and A. MICHEL, *Compt. Rend.* **253**, 1578 (1961); *Bull. Soc. Chim. France* 1661 (1963).

(c) J. LINDQUIST, *Acta Chem. Scand.* **4**, 1066 (1950).

into chloride by chemical attack with dilute HCl, and the NiCl<sub>2</sub> solution was precipitated by dimethylglyoxime, according to conventional analytical procedure. The Ni-dimethylglyoxime complex was used for the synthesis of Ni<sub>2</sub>GeO<sub>4</sub>.

Isotopic molybdenum element was transformed into MoO<sub>3</sub> by reaction with HNO<sub>3</sub>. Finally, owing to the very small quantity available, isotopic Ag<sub>2</sub>MoO<sub>4</sub> was recrystallized by fusion.

The isotopic purity data are collected in Table 2.

#### *Infrared and Raman spectra*

The i.r. spectra have been registered as described in the preceding paper [1]. AgI and/or polythene discs were used for the study of Na<sub>2</sub>MoO<sub>4</sub>, Na<sub>2</sub>WO<sub>4</sub> and Ag<sub>2</sub>MoO<sub>4</sub> in order to avoid any chemical reaction between the compound and the disc material. For the sodium salts, the grinding and mixing operations were carried out in a dry atmosphere (glove-box), since these compounds are liable to take up atmospheric moisture, thus leading to the di-hydrated salt.

The Raman spectra of the molybdates and tungstate have been obtained with a CODERG PHO double monochromator equipped with a 50 mW Spectra-Physics He-Ne laser.

## RESULTS

### *Germanates X<sub>2</sub><sup>II</sup>GeO<sub>4</sub> (X<sup>II</sup> = Ni, Co, Fe, Mg)*

A previous investigation of these compounds [2] did not include the low-frequency region, and was restricted to the study of pure compounds and solid solutions. We have now extended this study to the whole spectral range, and the existing assignments have been completed and refined by the study of some isotopic species.

Table 2. Isotopic purity data

Element	Isotopic composition*	
	Isotope	Atom %
<sup>58</sup> Ni	58	99.89
<sup>62</sup> Ni	60	0.51
	62	99.02
	92	98.27
<sup>92</sup> Mo	92	98.27
	100	0.6
	96	0.81
	98	1.69
<sup>70</sup> Ge	100	95.9
	70	91.38
	72	3.73
	73	1.01
	74	2.70
<sup>76</sup> Ge	76	1.18
	70	7.69
	72	6.65
	73	1.69
	74	10.68
	76	73.89

\* We have neglected the isotopic species whose abundance is less than 0.5 per cent.

The general i.r. pattern is rather similar to that already observed for the normal II–III spinels, with 2 strong, moderately broad high-frequency bands, and 2 weaker, sharp, low-frequency bands (Fig. 1). This analogy with the II–III spinels is, however, restricted to the general appearance of the spectrum, since the *assignment* of the bands is completely different: the high frequency band of the normal II–IV germanates has been assigned to the stretching vibration of the *tetrahedral* GeO<sub>4</sub> group [2], whereas the high-frequency band of the normal II–III spinels must be assigned to a vibration of the *octahedral* lattice [1].

The observed frequencies are collected in Table 3\*. Their assignment had already been deduced from the vibrational behaviour of solid solutions [2], but it is now possible to present a more elaborate interpretation on the basis of isotopic shifts (Tables 4 and 5).

The investigation of the 2 possible isotopic species of Ni<sub>2</sub>GeO<sub>4</sub> shows that the high-frequency band  $\nu_1$  is the *only* mode which seems to be related to an essentially *localized* vibration, namely the antisymmetric stretch of the GeO<sub>4</sub> tetrahedron. The 3 remaining modes correspond to complex vibrations involving a simultaneous and significant displacement of both tetrahedral and octahedral cations. We may notice, however, a predominant influence of germanium on  $\nu_2$ , and a predominant influence of nickel on  $\nu_3$  and  $\nu_4$ . This is in agreement with the purely qualitative assignments already deduced from the investigation of solid solutions [2]. Thus,  $\nu_2$  could be roughly assigned to a bending vibration of the tetrahedral GeO<sub>4</sub> group, whereas  $\nu_3$  and  $\nu_4$  are essentially related to vibrations of the octahedral lattice.

\* In this table, the frequencies have been labeled  $\nu_1, \nu_2 \dots$  in the succession of decreasing wavenumbers. There seems to be, however, a crossing over of  $\nu_2$  and  $\nu_3$  for Mg<sub>2</sub>GeO<sub>4</sub> [2].

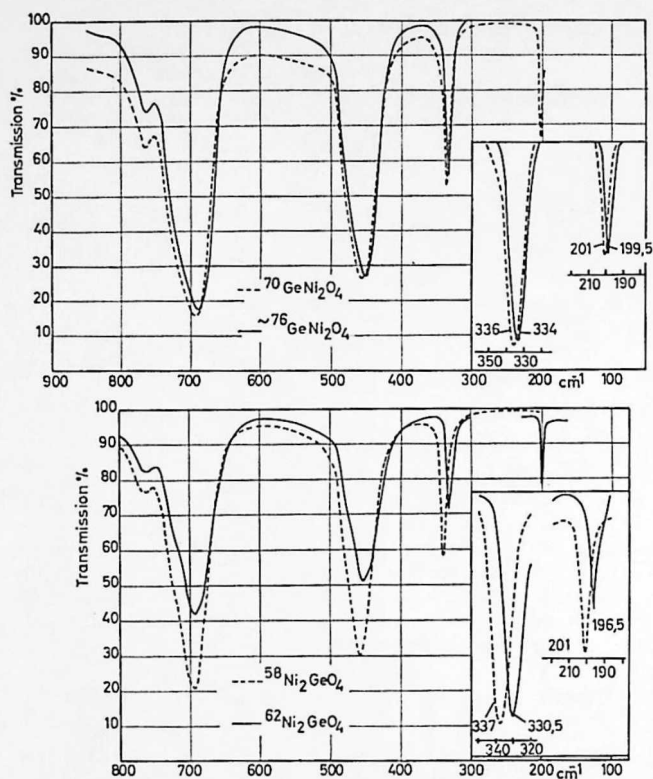


Fig. 1. Infrared spectrum of  $\text{Ni}_2\text{GeO}_4$ , showing the frequency shifts related to the isotopic replacement of the tetrahedral (Ge) and octahedral (Ni) cations.

Table 3. Fundamental frequencies of the normal II-IV germanate spinels

	$\text{Ni}_2\text{GeO}_4$	$\text{Co}_2\text{GeO}_4$	$\text{Fe}_2\text{GeO}_4$	$\text{Mg}_2\text{GeO}_4$
$\nu_1$	690	679	688	694
$\nu_2$	453	427	402	450
$\nu_3$	335	321	319	485
$\nu_4$	199	186	178	274

Table 4. Isotopic shifts in the i.r. spectrum of  $\text{Ni}_2\text{GeO}_4$  and  $\text{Co}_2\text{GeO}_4$

	$\text{Ni}_2\text{GeO}_4$				$\text{Ni}_2\text{GeO}_4$				$\text{Co}_2\text{GeO}_4$			
	$^{70}\text{Ge}$	$^{76}\text{Ge}$	$\text{cm}^{-1}$	$\Delta\nu$ %	$^{58}\text{Ni}$	$^{62}\text{Ni}$	$\text{cm}^{-1}$	$\Delta\nu$ %	$^{70}\text{Ge}$	$^{76}\text{Ge}$	$\text{cm}^{-1}$	$\Delta\nu$ %
$\nu_1$	694	688	-6	0.87	692	692	0	0.00	688	679	-9	1.31
$\nu_2$	456	451	-5	1.1	455	453	-2	0.44	434	427.5	-6.5	1.51
$\nu_3$	336	334	-2	0.60	337	330.5	-6.5	1.9	325	321	-4	1.25
$\nu_4$	201	199.5	-1.5	0.75	201	196.5	-4.5	2.2	not investigated			

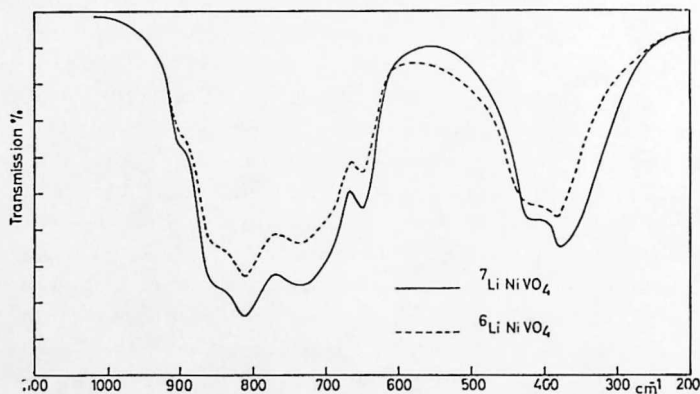
Table 5. Assignment of the bands for the normal II–IV germanate spinels

Assignment deduced from		
	Solid solutions	Isotopic shifts
$\nu_1$	GeO <sub>4</sub> stretch	GeO <sub>4</sub> stretch
$\nu_2$	Essentially, but not purely GeO <sub>4</sub> bend	Mixed vibration with predominant influence of the tetrahedral cation
$\nu_3$ $\nu_4$	Vibrations of the octahedral groups	Mixed vibrations with predominant influence of the octahedral cation

It is quite clear, however, that this type of assignment gives only an extremely rough picture of what really happens in the spinel lattice.

*Vanadates* LiX<sup>II</sup>VO<sub>4</sub> (X<sup>II</sup> = Ni, Co, Cu)

The synthesis and structure of these compounds have been reported by J. C. BERNIER *et al.* [5] and by J. C. JOUBERT [6]. The pentavalent vanadium is located on the tetrahedral sites, whereas Li and X<sup>II</sup> are distributed on the octahedral sites, the distribution being disordered if X<sup>II</sup> = Ni or Co (simple cubic spinel structure), or ordered if X<sup>II</sup> = Cu (distorted orthorhombic spinel structure). We shall neglect here the copper compound, for which the ordered distribution of the cations introduces additional i.r. active frequencies. The i.r. spectrum of LiNiVO<sub>4</sub> is represented in Fig. 2; the observed frequencies are collected in Table 6.

Fig. 2. Infrared spectrum of LiNiVO<sub>4</sub>.

The LiNiVO<sub>4</sub> spectrum exhibits several unusual features, the most evident one being the complex pattern of broad bands in the 850–650 cm<sup>-1</sup> region. One vibrational mode only (namely the antisymmetric stretching frequency of the VO<sub>4</sub> tetrahedron) and thus one absorption band is expected to be observed in this region.\*

\* The restoring force corresponding to the bivalent or monovalent cation–oxygen bond is too low to account for high-frequency bands. In the case of octahedral co-ordination of the cation, the corresponding absorption bands are generally observed below 400 cm<sup>-1</sup> [7].

[5] J. C. BERNIER, P. POIX and A. MICHEL, *Compt. Rend.* **253**, 1578 (1961); *Bull. Soc. Chim. France*, 1661 (1963).

[6] J. C. JOUBERT, Thèse de Doctorat, Grenoble (1965).

[7] P. TARTE, *Mém. Acad. Roy. Belges* **35**, 4a and 4b (1965).

Table 6. Frequencies of the disordered I-II-V vanadate spinels

LiNiVO <sub>4</sub>	LiCoVO <sub>4</sub>
~ 855	
~ 815	~ 815
~ 735	~ 755
~ 654	
~ 437	
~ 375	~ 370

Qualitatively, the splitting (which is very large for LiNiVO, and moderate for LiCoVO<sub>4</sub>) could be tentatively explained in the following manner: each oxygen of the VO<sub>4</sub> tetrahedron may be bonded to two types of cations (namely Li and X<sup>II</sup>), and this may introduce some asymmetry in the VO<sub>4</sub> tetrahedron (without disturbing the overall cubic symmetry of the whole unit cell). It is also worth while to mention that all the vanadate spinels investigated so far exhibit in this region a more or less complex pattern of bands, all of which must be assigned to stretching vibrations of the VO<sub>4</sub> tetrahedron. Whatever the final explanation of the observed complexity, the important point is that the high-frequency absorption must be assigned to vibrations of the tetrahedral group.

A detailed interpretation of the medium-frequency region is practically impossible: the bands near 400 cm<sup>-1</sup> may be assigned, either to a VO<sub>4</sub> bending vibration (which is expected to lie in this region), or to vibrations involving the participation of the octahedral cations, or, most probably, to complex vibrational modes; this last interpretation is supported by the occurrence of a significant (although ill-defined in view of the broadness of the bands) <sup>6</sup>Li-<sup>7</sup>Li isotopic shift.

We may finally notice the lack of any definite absorption band in the low-frequency region (350-100 cm<sup>-1</sup>), in opposition with the vibrational behaviour of practically all the spinels discussed so far. This is most probably related to the disordered distribution of the Li and X<sup>II</sup> cations on the octahedral sites. By analogy with the germanate spinels discussed above, it is expected that the low-frequency band must be assigned to some complex vibration with a predominant contribution of the octahedral cations. In view, however, of the statistical distribution of Li and X<sup>II</sup> on the octahedral sites, there is no well-defined vibrational motion, and the related frequency is spread over a more or less broad range; thus, the corresponding absorption band (which is intrinsically weak in other spinels) is too broad and too weak to be observed.

#### *Tungstate and molybdates* Na<sub>2</sub>WO<sub>4</sub>, Na<sub>2</sub>MoO<sub>4</sub> and Ag<sub>2</sub>MoO<sub>4</sub>

From the vibrational point of view, these compounds have been considered as the most favourable case in the spinel family, since they are true salts with a well-individualized anion [8]. Nevertheless, the assignment of the observed frequencies to either internal or external vibrational modes is only an approximation, since all the four i.r. active modes (two internal, two external) belong to the same representation  $T_{1u}$ , whereas 3 (out of a total of 5) Raman active modes belong to the

[8] W. B. WHITE and B. A. DE ANGELIS, *Spectrochim. Acta* **23A**, 985 (1967).

same representation  $T_{2g}$ . The Raman and i.r. spectra of  $\text{Na}_2\text{WO}_4$  and  $\text{Na}_2\text{MoO}_4$  have already been reported and discussed in the literature [3, 4], but the assignment of the observed frequencies to the different classes of Raman-active modes ( $A_{1g}$ ,  $E_g$  and  $T_{2g}$ ) is essentially empirical and has been made by analogy, since powder spectra only were available.

We have synthesized and investigated the isotopic molybdates with  $^{92}\text{Mo}$  and  $^{100}\text{Mo}$  in order to check the previous assignments, and to search for some information about the vibrational behaviour of the so-called external (lattice) frequencies. The results are collected in Tables 7 (for  $\text{Na}_2\text{MoO}_4$ ) and 8 (for  $\text{Ag}_2\text{MoO}_4$ ).

Table 7. Isotopic shifts and band assignments for  $\text{Na}_2\text{MoO}_4$  and  $\text{Na}_2\text{WO}_4$ 

Na <sub>2</sub> MoO <sub>4</sub>											
Raman					I.r. (All T <sub>1u</sub> )						
<sup>92</sup> Mo	<sup>100</sup> Mo	Δν		Assign- ment	<sup>92</sup> Mo	<sup>100</sup> Mo	Δν		Free ion	Na <sub>2</sub> WO <sub>4</sub>	
		cm <sup>-1</sup>	%				cm <sup>-1</sup>	%		R	I.r.
892.5	892	(0.5)	(0.05)	A <sub>1g</sub>					ν <sub>1</sub>	930	
814	806	8	0.99	T <sub>2g</sub>	840	832	8	0.95	ν <sub>3</sub>	814	840
383	380.5	2.5	0.66	T <sub>2g</sub>	319	317	2	0.63	ν <sub>4</sub>	377	309
304	304	0	0	E <sub>g</sub>					ν <sub>2</sub>	313.5	
					231	230.5	(0.5)	(0.2)			229
					178.5	176	2.5	1.4			169
119	114.5	4.5	3.8	T <sub>2g</sub>						94.5	

$\text{Na}_2\text{MoO}_4$ . The lack of a significant isotopic shift, together with the high intensity, support the assignment of the 892 and 304 cm<sup>-1</sup> Raman bands to the  $A_{1g}$  and  $E_g$  modes, which correspond to the  $\nu_1$  and  $\nu_2$  modes of the free ion. The two Raman bands near 810 and 380 cm<sup>-1</sup> are necessarily assigned to the  $T_{2g}$  modes and have their counterpart in the i.r. spectrum near 840 and 319 cm<sup>-1</sup> respectively. It may be noticed that, for these bands, the isotopic shift is practically the same for the corresponding Raman and i.r. bands (8 cm<sup>-1</sup> for the vibration corresponding to the antisymmetric stretch of the  $\text{MoO}_4$  ion— $\nu_3$  for the free ion; and 2 cm<sup>-1</sup> for the vibration corresponding to the antisymmetric bend— $\nu_4$  for the free ion); but the absolute values may be fairly different: about 380 (Raman) and 320 cm<sup>-1</sup> (i.r.) for the  $\nu_4$  frequency.

The three lattice frequencies (two i.r., one Raman active) correspond to translations, since the rotational modes are inactive in both Raman and i.r. spectra. In a somewhat naive description of a lattice mode, they may be represented as a translation of the  $\text{Na}^+$  cation against the  $(\text{MoO}_4)^{2-}$  anion, which, being much heavier, could be considered at rest with respect to the light  $\text{Na}^+$  cation. A critical, detailed examination of this description would imply the investigation of isotopic compounds of sodium and molybdenum. Since there is only one stable isotope of sodium, we must restrict this investigation to the isotopic species of molybdenum. Indeed, the  $^{92}\text{Mo}$ – $^{100}\text{Mo}$  isotopic shift is very small (and in fact non-significant) for the 231 cm<sup>-1</sup> i.r. band and this suggests that this band is essentially related to a translational motion of the octahedral  $\text{Na}^+$  cation. The lack of influence of the tetrahedral cation is also supported by the fact that the corresponding frequency is nearly the same in  $\text{Na}_2\text{MoO}_4$  and  $\text{Na}_2\text{WO}_4$  (Table 7).

Table 8. Isotopic shifts and band assignments for  $\text{Ag}_2\text{MoO}_4$ 

		Raman		Assign- ment	Infrared (All $T_{1u}$ )				Free ion
$^{92}\text{Mo}$	$^{100}\text{Mo}$	$\Delta\nu$			$^{92}\text{Mo}$	$^{100}\text{Mo}$	$\Delta\nu$		
		$\text{cm}^{-1}$	%			$\text{cm}^{-1}$	%		
873	873	0	0	$A_{1g}$				$\nu_1$	
765	758	7	0.92	$T_{2g}$	802	794	8	1.0	$\nu_3$
354	351	3	0.85	$T_{2g}$	288	286	2	0.7	$\nu_4$
277.5	277	(0.5)	(0.18)	$E_g$					$\nu_2$
	91 (see text)				136	134	2	1.5	

This is no longer true, however, for the lowest-frequency i.r. and Raman bands observed near 176 and 115  $\text{cm}^{-1}$  respectively: for both bands, the  $^{92}\text{Mo}$ - $^{100}\text{Mo}$  isotopic shifts are quite significant in view of the sharpness of the bands; this mass effect of the tetrahedral cation is also in agreement with the frequency lowering which is observed when passing from  $\text{Na}_2\text{MoO}_4$  to  $\text{Na}_2\text{WO}_4$ . Thus, even in the simple case of true salts, the so-called external frequencies cannot be simply described as a cation displacement against the complex anion, but most probably correspond to a simultaneous displacement of the cation and of the atom which is at the centre of the complex anion. In the actual case, where this atom (Mo) is fairly heavy with respect to the cation ( $\text{Na}^+$ ), the participation of this atom to the vibration is the most important for the lowest lying frequency.

$\text{Ag}_2\text{MoO}_4$ . As far as the internal frequencies are concerned, the results given by this compound do not differ markedly from those already discussed in the case of  $\text{Na}_2\text{MoO}_4$ . We found a general decrease of all the internal frequencies, but this is not unexpected in view of the significant increase of the unit cell parameter ( $a_0 = 8.99\text{Å}$  for  $\text{Na}_2\text{MoO}_4$ , and  $9.26\text{Å}$  for  $\text{Ag}_2\text{MoO}_4$ ).

The isotopic shifts are of the same order of magnitude (Table 8). The results on external frequencies are incomplete. The low-frequency Raman band is extremely weak, and it was observed only on crystals of millimeter size obtained by recrystallization from ammoniacal solution. We were unable to observe this band in the spectrum of the isotopic species, since these compounds were prepared in very small quantity. The value quoted in Table 8 is thus related to the natural mixture of Mo isotopes (average atomic weight: 96). In the i.r. spectrum, one external frequency only has been observed (instead of two), although the spectrum has been scanned down to 50  $\text{cm}^{-1}$ . We have no definite explanation of this result. Here again, we find a significant  $^{92}\text{Mo}$ - $^{100}\text{Mo}$  isotopic shift.

#### THE TELLER-REDLICH PRODUCT RULE AND THE APPROXIMATION OF THE "ISOLATED" TETRAHEDRAL GROUP

Since the isotopic replacement of the tetrahedral cation was investigated for the molybdates and the germanates, the Teller-Redlich product rule has been applied to the antisymmetrical stretching and bending vibrations of the tetrahedral group considered as an independent vibrating unit.

It is expected that any significant departure from this approximation will be revealed by an inequality in the product rule. For a free  $\text{XO}_4$  ion or molecule where



the isotopic replacement is applied to the central atom X only (and not to oxygen), the Teller-Redlich product rule reduces to:

$$\frac{\nu_{\sigma}}{\nu_{\sigma}^z} \frac{\nu_{\delta}}{\nu_{\delta}^z} = \frac{m_X^z}{m_X} \cdot \frac{m_X + 64}{m_X^z + 64}$$

where  $\nu_{\sigma}$  and  $\nu_{\delta}$  refer to the antisymmetric stretching and bending frequencies respectively,  $m_X$  being the mass of the central atom X. The superscript  $z$  refers to the heavy isotope of X. This equation has been applied to the two high-frequency bands of the i.r. spectrum (which are more or less representative of the internal vibrations of the tetrahedral group), and to the two  $T_{2g}$  Raman internal frequencies of the molybdates. The results are collected in Table 9.

Table 9. Application of the product rule to the isotopic tetrahedral groups

Compound and type of spectrum	Numerical value of:	
	Left-hand side of equation	Right-hand side of equation
Na <sub>2</sub> MoO <sub>4</sub> I.r.	1.032	1.034
Na <sub>2</sub> MoO <sub>4</sub> Raman	1.033	
Ag <sub>2</sub> MoO <sub>4</sub> I.r.	1.034	
Ag <sub>2</sub> MoO <sub>4</sub> Raman	1.036	
Ni <sub>2</sub> GeO <sub>4</sub> I.r.	1.040	1.064
Co <sub>2</sub> GeO <sub>4</sub> I.r.	1.058	

The product rule is satisfactorily verified for the molybdates, and this is not too unexpected: the bonding force between the oxygen and the monovalent, octahedral cation (Na or Ag) should be small with respect to the "internal" bonding force of the molybdate ion. It may be concluded that the vibrational interactions between the internal and the external frequencies are small. This is no longer true for the germanates, but the situation is fairly different here. By comparison with the molybdates, there is a reduction of the valency and hence of the bonding force of the tetrahedral cation, and an increase of the valency and of the bonding force of the octahedral cation. Thus, the separation between the internal and the external frequencies is significantly reduced, a situation which is favourable to the occurrence of mixed vibrations. Indeed, the investigation of solid solutions [2] and of the appropriate isotopic species (Tables 4 and 5) has shown that the assignment of the 450 cm<sup>-1</sup> band of Ni<sub>2</sub>GeO<sub>4</sub> to a bending motion of the GeO<sub>4</sub> tetrahedron is only a rather rough approximation, since there is a significant participation of the nickel cation to this vibration.

It should be emphasized, however, that not too much *quantitative* value should be assigned to the figures quoted in Table 9. Since the isotopic shifts are small, the experimental error on the frequency measurements is never negligible, thus involving some uncertainty on the numerical value of the left-hand side of the product rule equation.

Nevertheless, the results quoted in Table 9 suggest that, even for medium-weight isotopes, the Teller-Redlich product rule may be helpful for the *qualitative* detection of vibrational interactions. This point should be further investigated.

#### DISCUSSION AND CONCLUSIONS

For all the spinels discussed in this paper, the high-frequency band (or absorption region) of the i.r. spectrum must be assigned to the antisymmetric stretch of the tetrahedral group. This is strongly supported by the very good correspondence between the actual frequencies observed for each type of compound, and the characteristic stretching frequency of the corresponding tetrahedral anion in non-spinel compounds (Table 10).

Table 10

Absorption region of the high frequency band in spinels	Antisymmetric stretching frequency of the tetrahedral group in corresponding non-spinel compounds
$X_2^{IV}GeO_4$ germanates: 700–680 $cm^{-1}$	$GeO_4$ : 800–650 $cm^{-1}$
$LiX^{IV}VO_4$ vanadates: 850–650 $cm^{-1}$	$VO_4$ : 900–800 $cm^{-1}$
Tungstate and molybdates: 840–800 $cm^{-1}$	$MoO_4$ and $WO_4$ : 900–800 $cm^{-1}$

For molybdates and germanates, this assignment is definitely proved by the frequency shifts related to the isotopic replacement of the tetrahedral cation. And in the case of  $Ni_2GeO_4$ , for which the isotopic replacement of both cations (tetrahedral and octahedral) has been investigated, the lack of influence of the octahedral cation on this frequency is a further confirmation of the proposed assignment.

These results are in agreement with the generally accepted assignment of the high-frequency band of spinels [8–10], and contradict the statement of LUTZ [11], that there is no vibrational frequency which is characteristic of the tetrahedral group. Two comments should be made about this statement:

- (1) *Strictly speaking*, this statement is correct as far as the i.r. spectrum is concerned since the four i.r. active fundamentals belong to the same representation  $T_{1u}$ ; as a consequence, vibrational interactions *must* occur. From a *practical* point of view however, no influence of the octahedral cation could be experimentally detected, and, for the spinels investigated here, the high-frequency band is *essentially* related to a vibration of the tetrahedral group.
- (2) The situation is somewhat different in the case of the Raman spectrum, since the five Raman-active fundamentals are distributed into three different symmetry classes: since there is only *one*  $A_{1g}$  and *one*  $E_g$  mode, each of them is unable to couple with another mode and, in some cases at least, may be really characteristic of the vibration of a given co-ordinated group. This seems to be the case in the Raman spectrum of the molybdate and tungstate spinels: there is no

[9] R. D. WALDRON, *Phys. Rev.* **99**, 1727 (1955).

[10] St. HAFNER, *Z. Krist.* **115**, 331 (1961).

[11] H. D. LUTZ, *Z. Naturforsch.* **24A**, 1417 (1969).

doubt that the  $A_{1g}$  mode, which has the highest frequency of the spectrum, correspond to the symmetric stretch of the  $\text{MoO}_4$  or  $\text{WO}_4$  tetrahedral group.

It is now convenient to discuss the actual results and assignments with respect to those already presented in our previous paper [1].

There seems to be a fundamental contradiction between the final conclusions of the two papers, since the high-frequency band of the spinels is assigned to a vibration of the tetrahedral group in the present paper, but to a vibration of the octahedral lattice in the preceding one.

There is in fact no inconsistency in these assignments: one of them is related to normal I–VI, I–II–V and normal II–IV spinels, where the highest-valency cation is located on the tetrahedral sites; the other is true for normal II–III spinels, where the highest-valency cation is located on the octahedral sites. *Our conclusions simply imply that the high-frequency band of the spinels should be assigned, not systematically to a vibration of the tetrahedral group (as it is generally accepted), but to a vibration between the oxygen and the highest-valency cation, irrespective of the co-ordination of this cation. Thus, the high-frequency absorption band of a spinel will be assigned to a vibration of either tetrahedral or octahedral groups, according to the location of the highest-valency cation.*

We shall present in a next paper further results which show that this conclusion is of general value and may be applied to *all* spinels, irrespective of the normal or inverse, ordered or disordered distribution of the cations.

Now, as far as the lower frequency bands are concerned, they are generally related to complex vibrations. The tungstate and molybdates seem to be the only spinels for which the separation of the vibrations into internal and external modes may be considered as a satisfactory approximation.

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