Infrared studies of spinels—III
The normal II–III spinels

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Abstract—In accordance with theoretical expectations, 4 bands are generally observed in the i.r. spectrum of a number of cubic normal II–III spinels. The systematic investigation of pure compounds, solid solutions and isotopic species leads to a realistic and consistent set of assignments: the 2 high-frequency bands ν_1 and ν_2 essentially depend (in shape and position) on the chemical nature of the octahedral, trivalent cation and thus are essentially related to vibrations of the lattice of octahedral groups. The 2 low-frequency bands ν_3 and ν_4 must be assigned to complex vibrations involving the simultaneous participation of both cations, tetrahedral and octahedral. This complex origin is definitely demonstrated by the study of isotopic species. These assignments, which are in accordance with all the experimental data collected on normal II–III spinels, cannot be extended to other types of spinels (inverse II–III, normal II–IV, . . .)

INTRODUCTION

IN THE preceding paper [1], we have outlined and discussed the basic principles of the experimental methods which would eventually lead to a realistic interpretation of the i.r. spectrum of spinels. We present here the application of these principles to the most classical family of these compounds, namely the II–III spinels. The discussion will be restricted, however, to the cubic *normal* II–III spinels. From the vibrational point of view and for several reasons which will not be developed here, the case of the inverse spinels is considerably more complicated and will be discussed in another paper. In accordance with the general principles already outlined [1], we shall report here the i.r. spectra of pure compounds, of solid solutions and of isotopic species.

EXPERIMENTAL

Spectroscopic techniques

All the spectra were registered with a Beckman IR-12 (1000–200 cm^{-1} region) and a Cameca SI-36 spectrometer (200–50 cm^{-1}), KI and polythene discs being used in turn. Special care has been paid to the investigation of isotopic species, since the frequency shifts are expected to be rather small. Through the use of low scanning speeds and frequency scale expansion, it has been possible to measure the position of very sharp bands with a reproducibility of ± 0.2 cm^{-1} [2].

In routine conditions, the estimated error is ± 1 cm^{-1} for the low-frequency bands, which are usually sharp. The error may be larger for the high-frequency bands, which are more or less broad; for these bands, the situation may be further complicated by some non-reproducibility of the spectrum. This point will be discussed in another part of this paper.

[1] J. Preudhomme and P. Tarte, *Spectrochim. Acta* **27A**, 845 (1971).
[2] P. Tarte and J. Preudhomme, *Spectrochim. Acta* **26A**, 2207 (1970).

Synthesis techniques

All the phases investigated (pure compounds, solid solutions, isotopic species) have been synthesized by solid state reaction between the appropriate oxides, carbonates or oxalates.

The necessary quantities are weighed out, ground and mixed under petroleum ether in an agate mortar and progressively heated to the convenient temperature in covered platinum crucibles. In some cases, intermediate mixing and grinding are necessary before a single, pure spinel phase is obtained. The purity is checked by X-ray diffractometry. The initial mixture may also be transformed into nitrates by chemical attack with an excess of nitric acid. The resulting solution is evapo-

Table 1. Isotopic purity data*

Element	Isotopic Composition		Element	Isotopic Composition	
	isotope	atom %		isotope	atom %
Mg (natural)	24	78·6	^{64}Zn	64	99·66
	25	10·1	^{68}Zn	64	0·8
	26	11·3		68	98·5
^{26}Mg	26	99·70	^{106}Cd	106	88·40
^{50}Cr	50	90·40		110	2·02
	52	8·59		111	1·61
	53	0·83		112	2·49
^{54}Cr	52	6·96		113	1·14
	53	2·18		114	2·50
	54	90·60		116	1·36
^{58}Ni	58	99·89	^{116}Cd	112	0·53
^{62}Ni	60	0·51		114	1·44
	62	99·02		116	97·2

* We have neglected the isotopic species whose abundance is less than 0·5 per cent.

rated to dryness and the dry residue is progressively heated to the necessary temperature. For some compounds, several synthesis procedures have been used in connection with the non-reproducibility of their spectrum. More detailed information on the synthesis conditions may be found in J. Preudhomme's Doctorate Thesis [3].

These syntheses are generally carried out on a decigram scale. The quantities must be reduced to the milligram scale for the isotopic species, which are generally rather costly. These isotopic species have been purchased from the Oak Ridge National Laboratory. The relevant isotopic purities are collected in Table 1.

INVESTIGATION OF PURE COMPOUNDS

Experimental results

General features of the spectra. Nearly all the spectra of the investigated normal II–III spinels exhibit four bands corresponding to the four i.r. active fundamentals expected from group theoretical considerations. The three examples selected for Fig. 1 may be considered as representative of the general aspect of the spectra. The two high-frequency bands are strong or very strong, and more or less broad, whereas the two low-frequency bands are generally weak and sharp.

The observed frequencies are collected in Table 2, where they have been labeled ν_1, ν_2, ν_3 and ν_4 in the succession of decreasing wavenumbers.

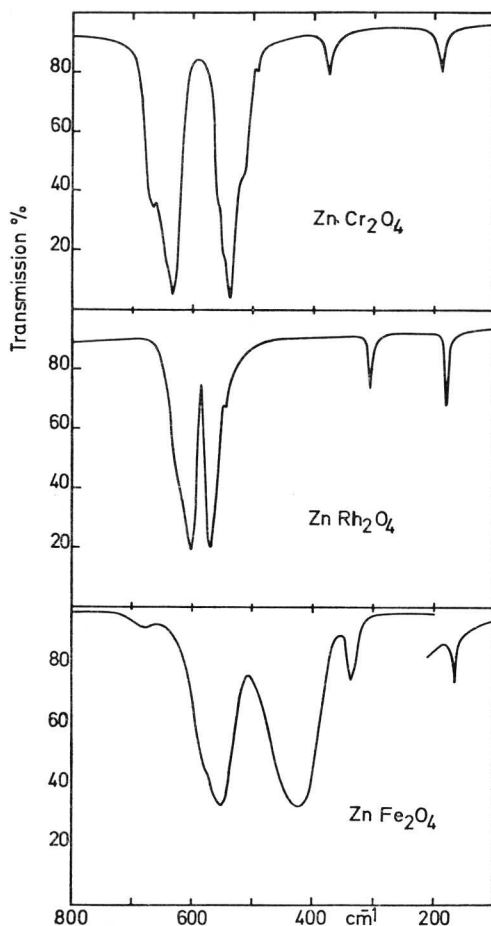[3] J. Preudhomme, Doctorate Thesis, University of Liege (1970).

Fig. 1. Typical infrared pattern for three normal II–III spinels.

Before discussing these results, the following remarks should be taken into account:

(1) The broadness of the two high-frequency bands essentially depends on the nature of the trivalent cation: these bands are broad or very broad for the aluminates, gallates and ferrites; the broadness is reduced for the chromites, and much reduced for the rhodites. But this broadness may also depend, for a given compound, on the synthesis conditions (see points 2 and 3 which follow).

(2) We have mentioned the occurrence of four "bands", but this should be taken in a broad sense, and it would be more appropriate to speak about "regions of absorption". For most of the compounds investigated, the two high-frequency bands ν_1 and ν_2 are more or less asymmetric. In some instances, this asymmetry depends (as the broadness) on the synthesis conditions and may eventually lead, either to the occurrence of distinct shoulders, or even to the splitting of the bands into two distinct components of similar intensity. It should be remarked that these variations *do not* affect the two low-frequency bands ν_3 and ν_4, which are essentially sharp,

Table 2. Frequency (in cm^{-1}) of the observed absorption bands

Compound	ν_1	ν_2	ν_3	ν_4
Zinc spinels				
$ZnAl_2O_4$	690	575	518	227 (+218)
$ZnCo_2O_4$	670	582	392	215
$ZnGa_2O_4$	593	455	333	175
$ZnCr_2O_4$	635	537	375	188
$ZnFe_2O_4$	552	425	336	166
$ZnRh_2O_4$	600	567	305	180
Chromites				
$MgCr_2O_4$	647	525	430	253
$ZnCr_2O_4$	635	537	375	188
$CoCr_2O_4$	630	530	380	199
$NiCr_2O_4$	625	512	374	182
$MnCr_2O_4$	620	512	380	194
$CdCr_2O_4$	624	510	369	153
Rhodites				
$MgRh_2O_4$	605	540	353	242
$ZnRh_2O_4$	600	567	305	180
$CoRh_2O_4$	603	560	320 + 308	197
$NiRh_2O_4$	597	543	304	?
$CdRh_2O_4$	618	548	300	143
Miscellaneous				
$MgAl_2O_4$	688	522	580	309
$CoAl_2O_4$	684	563	523	237
Co_3O_4	672	590	392	220
$CdFe_2O_4$	548	412	319	*

* Searched for, but not found.

and whose position remains essentially constant, even for samples (of a given compound) which show fairly significant differences in the contour of ν_1 and ν_2.

(3) We are thus facing a problem of non-reproducibility of experimental results, whose significance may thus be considered as questionable. This problem will be discussed at the end of this paper, but we just want to point here that this non-reproducibility is possibly related to the granulometry of the samples.

The values quoted in Table 2 refer to the samples which gave spectra characterized by a minimum broadness and simultaneously a minimum asymmetry of the bands; these features correspond to the best reproducibility, and the corresponding spectra are considered to be the most reliable.

It is now convenient to consider successively the vibrational behaviour of several families of pure compounds, namely the zinc spinels, the chromites and the rhodites.

Zinc spinels. Since the tetrahedral cation (Zn) remains the same, this family of spinels allows to investigate to what extent the vibrational frequencies depend on the nature of the octahedral (trivalent) cation. Now, before discussing any definite relationship, it is worth while to point out that:

(1) In a crystal, the cation–oxygen vibrational frequencies depend on the mass of the cation, the cation—oxygen bonding force and distance (which in turn are related to the cation electronic structure and ionic radius, and may be altered to some extent by the chemical nature of the neighbouring cations), and on the unit cell parameter a_0.

(2) When a cation is replaced by another, these four parameters are simultaneously modified. In most cases, it is thus impossible to find out a smooth relationship

between one of these parameters, and the vibrational frequencies. With these difficulties in view, we may now discuss the possible relationships between the above-mentioned parameters and the vibrational frequencies.

ν_1 and ν_2: the frequency of these two bands clearly depends on the nature of the trivalent cation (Table 2), with extreme values of 690 and 552 cm^{-1} for ν_1, 582 and 425 cm^{-1} for ν_2. There is, however, no significant relationship between these frequencies and either the ionic radius of the trivalent cation or the unit cell parameter a_0 [3]. Likewise, there is no relationship between these frequencies and the mass of the trivalent cation (Fig. 2).
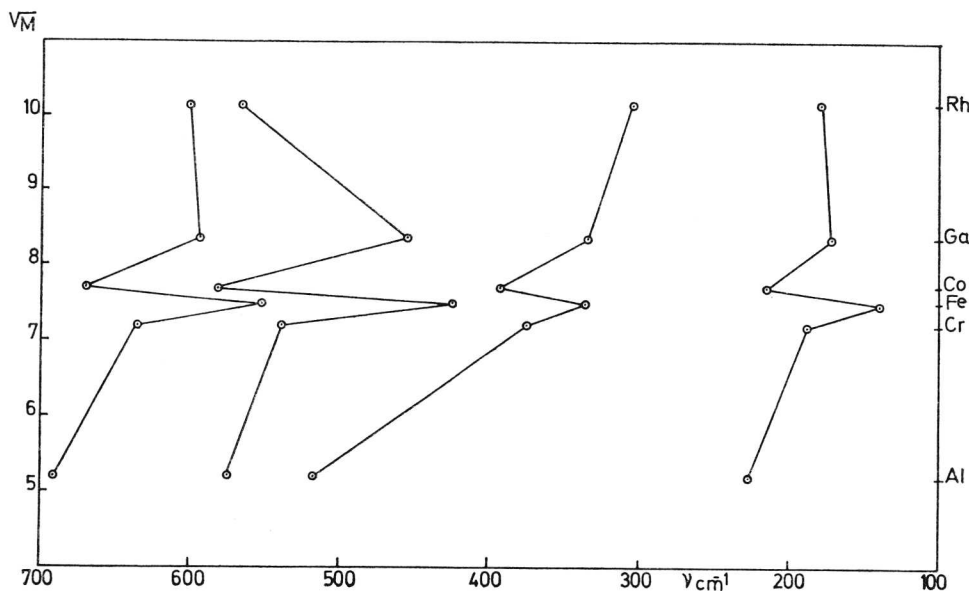

Fig. 2. Relationship between the vibrational frequencies and the square root of the mass of the trivalent cation for the zinc II–III spinels.

Since, however, these frequencies are rather sensitive to the chemical nature of the trivalent cation, the factor responsible for these variations must be the *bonding force between the trivalent cation and the oxygen anion*.

ν_3 seems to depend, although not very regularly, on the mass of the trivalent cation. But more or less similar relationships may be observed between this frequency and either the ionic radius of the trivalent cation, or the unit cell parameter a_0 [3]. Finally, as far as ν_4 is concerned, there is no conclusive evidence about a relation between its position and either the mass or the ionic radius of the trivalent cation, or the unit cell parameter a_0 [3].

The significance of these results will be discussed after a survey of the chromite and rhodite spinels.

Chromites. The systematic investigation of chromites is the necessary complement to the study of zinc spinels. The latter has shown how the vibrational frequencies depend on the nature of the octahedral (trivalent) cation. The study of chromites will show how these frequencies depend on the nature of the tetrahedral

(bivalent) cation. ν_1 and ν_2: it is clear from the data collected in Table 2 that the influence of the bivalent tetrahedral cation on these frequencies is much reduced. There is no significant relationship between these frequencies and the mass of the bivalent cation.

On the contrary, both ν_3 and ν_4 depend on the mass of the bivalent cation. The frequency variation is only moderate for ν_3, but more important for ν_4 (Fig. 3).

Rhodites. There is a full analogy in the vibrational behaviour of rhodites and chromites. Here again, ν_1 and ν_2 are nearly insensitive to a modification of the
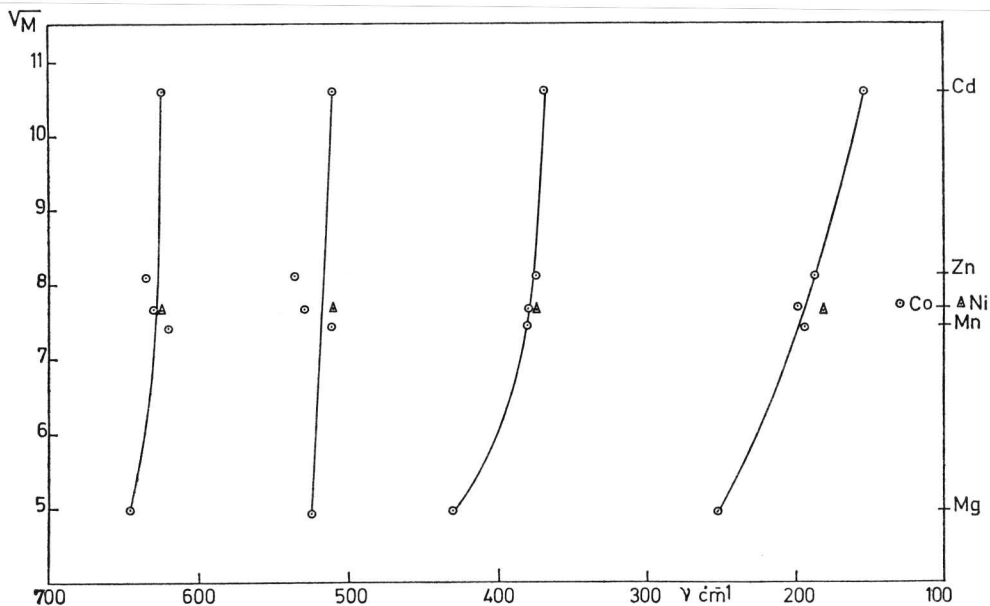

Fig. 3. Relationship between the vibrational frequencies and the square root of the mass of the bivalent cation for the chromites.

bivalent cation, whereas ν_3 and ν_4 depend, the first moderately, the second more strongly, on the mass of the bivalent cation. This parallelism is illustrated in Fig. 4.

General survey of the results on pure compounds and preliminary interpretations

Vibrational behaviour and origin of ν_1 and ν_2. It is evident from the preceding results that ν_1 and ν_2 are nearly independent from the nature of the bivalent, tetrahedral cation, the small frequency differences (which are observed, for example, between the different chromites) being most probably related to second-order effects.

On the other hand, these frequencies clearly depend on the very nature of the trivalent, octahedral cation. As stated previously, there is, however, no significant mass effect, and the influence of the trivalent cation should be related to the cation—oxygen bonding force. *Thus, the bulk of the existing experimental evidence leads to assign ν_1 and ν_2 to vibrations of the lattice of condensed octahedra.*

The vibrational behaviour of ν_3 is much more complicated: after the above-mentioned results, the frequency seems to depend on the nature of the trivalent cation
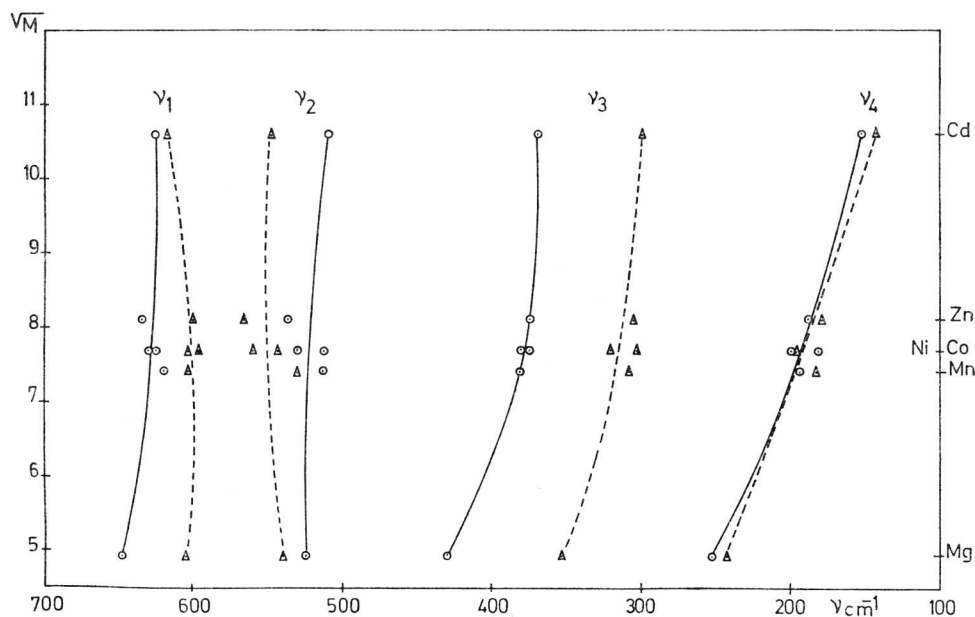
Fig. 4. Vibrational analogies between chromites and rhodites. ———— chromites;
– – – – rhodites.

(mass or ionic radius), but also (although to a less extent) on the mass of the bivalent cation. *Thus, v_3 seems to be related to a complex vibration involving the participation of both types of cations, tetrahedral and octahedral.*

Finally, we have found that v_4 clearly depends on the mass of the bivalent, tetrahedral cation. *Thus, v_4 must be assigned to some type of vibration involving a displacement of the tetrahedral cation.*

It should be made quite clear, however, that these assignments are provisional, and *must* be checked by further appropriate experiments. The necessary information will be gained through the investigation of solid solutions and of isotopic species.

INVESTIGATION OF SOLID SOLUTIONS

The usefulness of solid solutions for interpreting the i.r. spectrum of inorganic solids has been discussed several years ago [4].

Numerous papers dealing with the vibrational behaviour of much simpler systems (solid solutions of binary compounds with cubic symmetry) have appeared since: they show that the situation is much more complex than previously expected, and that the interpretation of the vibrational spectrum of solid solutions is by no means a simple task, even for binary compounds.

Since we are dealing here with ternary compounds of the double oxide type, which are likely to give rise to complex vibrational modes, there is very little hope to find out a satisfactory theoretical explanation of the experimental results. As a matter of

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[4] P. TARTE, *Spectrochim. Acta* **18,** 467 (1962).

fact, we have found a somewhat unexpected diversity in the vibrational behaviour of various solid solutions. Thus, there will be no claim about the generality of the results which are discussed hereafter; nor is it possible to present a sufficiently detailed interpretation of them. Nevertheless, these results as such bring complementary information about the origin of the bands. We have investigated the two possible types of solid solutions, resulting from the isomorphous replacement of either the tetrahedral cation, or the octahedral cation.

Isomorphic replacement of the tetrahedral cation

Three solid solutions of this type have been investigated, namely $(Mg, Co)Cr_2O_4$, $(Mg, Zn)Cr_2O_4$ and $(Mg, Cd)Cr_2O_4$.

Table 3. i.r. frequencies (in cm^{-1}) of the $(Mg, Co)Cr_2O_4$ solid solutions

Composition	ν_1	ν_2	ν_3	ν_4	
$MgCr_2O_4$	647	525	430	253	
$Mg_{0.75}Co_{0.25}$	643	527	421	253	
$Mg_{0.50}Co_{0.50}$	640	530	414	257	196
$Mg_{0.25}Co_{0.75}$	637	530	402		197
$CoCr_2O_4$	630	530	380		199
Maximum frequency shift (in % of the average frequency)	-2.6%	$+1\%$	-12.6%	-25.3%	

The first one, $(Mg, Co)Cr_2O_4$, is most interesting because the pure end members have the same unit cell dimension ($a_0 = 8.333$ and 8.332 Å for $MgCr_2O_4$ and $CoCr_2O_4$ respectively). This eliminates one of the factors which may alter the vibrational frequencies.

The observed frequencies are collected in Table 3, and the general features of the spectra are represented in Fig. 5.

The influence of the (Mg, Co) isomorphic replacement on the ν_1 and ν_2 frequencies is very small (and indeed, this must be the case if our previous assignment of these bands to vibrations of the octahedral groups is essentially correct).

On the contrary, ν_3 and ν_4 are significantly modified, although in a widely different manner.

For ν_3, the change is of the continuous type, the band being very significantly, but progressively shifted towards the lower frequencies when Co replaces Mg. The importance of the shift (12.6 per cent of the average frequency) points to a significant role of the tetrahedral cation in the vibration under discussion. But the continuous nature of the phenomenon strongly suggests that we are dealing here with a complex vibrational motion, and not with a localized vibration of the tetrahedral groups [1].

On the contrary, ν_4 is split into two components (at least for the 50/50 composition), the position of which is very similar to the frequency of the corresponding band in either $MgCr_2O_4$ or $CoCr_2O_4$. Moreover, the relative intensity and the broadness of the bands depend on the percentage of isomorphic replacement. It is thus evident that the ν_4 mode is strongly related to a vibration of the tetrahedral cation. It is not, however, a purely localized vibration, since the splitting does not appear in the
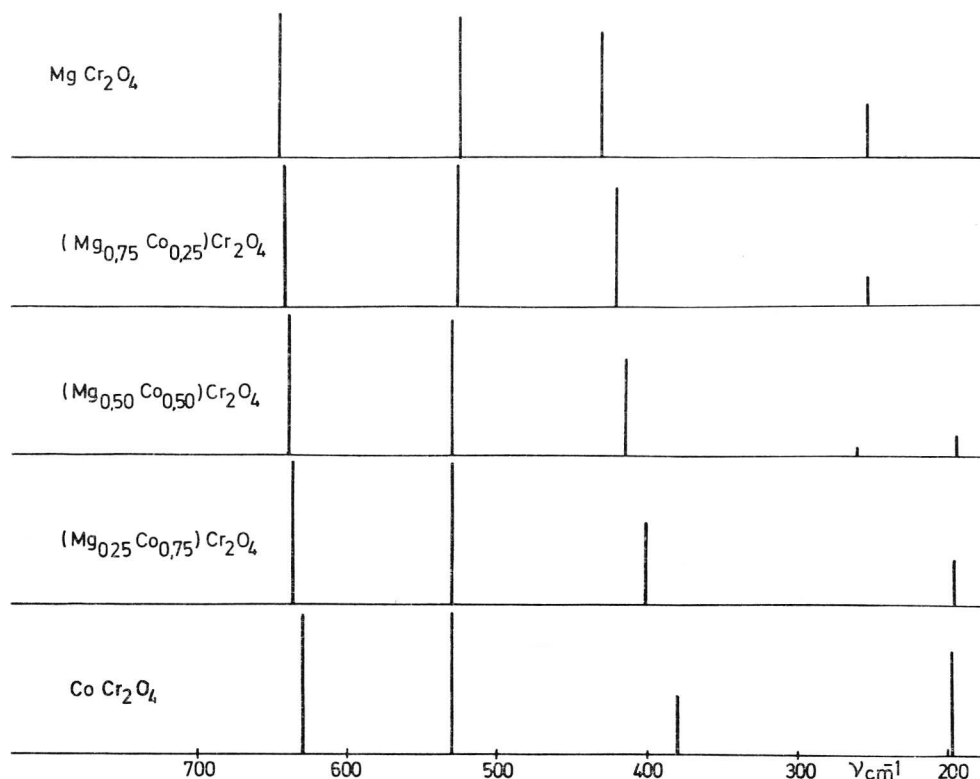
Fig. 5. Vibrational behaviour of the $(Mg, Co)Cr_2O_4$ solid solutions.

whole range of compositions of the solid solutions [1]. The two other solid solutions $(Mg, Zn)Cr_2O_4$ and $(Mg, Cd)Cr_2O_4$ exhibit the same type of vibrational behaviour (a rather small frequency shift for ν_1 and ν_2; a continuous and significant shift for ν_3; the splitting of ν_4, at least for the 50/50 solid solution). There is no need to discuss them at length, and the conclusions are identical to those already deduced from the investigation of the $(Mg, Co)Cr_2O_4$ solid solutions.

Isomorphic replacement of the octahedral cation

From the vibrational point of view, this case is considerably more complicated than the preceding one, since the octahedral groups are interlinked by an edge. As a consequence, the concept of "localized" vibration is meaningless here, and the probability of important vibrational interactions is much higher than in the case of the "isolated" tetrahedral groups.

Solid solutions $ZnCr_2O_4$–$ZnRh_2O_4$. The behaviour of these solid solutions is the most simple one, namely a more or less important shift of all the vibrational frequencies. Apart from the fact that this shift is rather large for ν_3 (Table 4), thus suggesting a participation of the trivalent cation to this vibrational mode, it is hard to draw firm conclusions from this type of results.

Solid solutions $ZnCr_2O_4$–$ZnAl_2O_4$. Here also, there is a continuous frequency shift for ν_1, ν_2 and ν_4. But ν_3 exhibits a fairly complex behaviour, at least in the

Table 4. i.r. frequencies (in cm^{-1}) of the $Zn(Cr, Rh)_2O_4$ solid solutions

Composition	ν_1	ν_2	ν_3	ν_4
$ZnCr_2O_4$	635	537	375	188
$Cr_{0.75}Rh_{0.25}$	630	546	362	184
$Cr_{0.50}Rh_{0.50}$	627	555	343	180
$Cr_{0.25}Rh_{0.75}$	615	557	323	178
$ZnRh_2O_4$	600	567	305	180
Maximum frequency shift (in % of the average frequency)	-5.5%	$+5.5\%$	-20.6%	-5.5%

5–40% Al composition range, where the single frequency is replaced by a multiplet (Fig. 6). Although not explained, this experimental fact may be considered as a good evidence for the participation of the octahedral cation to the ν_3 vibrational mode.

Solid solutions $CdCr_2O_4$–$CdFe_2O_4$. The behaviour of these solid solutions is very similar in many respects to that already found for the preceding system. We found a very important, although continuous, shift for ν_1 and ν_2. But ν_3 is split into two components, at least in the 5–50% Fe composition range. The vibrational behaviour of ν_4 has not been investigated so far.
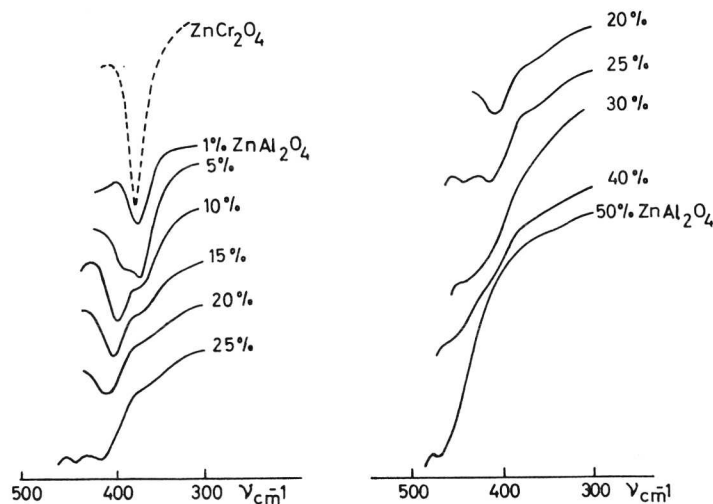

Fig. 6. Splitting of the ν_3 frequency in a given compositional range of the $Zn(Al, Cr)_2O_4$ solid solutions.

We may now summarize and discuss the information gained through the investigation of solid solutions:

(1) The vibrational modes ν_1 and ν_2 are *never* split, whatever the type of solid solution (isomorphic replacement of either the tetrahedral or the octahedral cation). Now, if one of these modes were related to a vibration of the isolated tetrahedral group, we should observe a splitting of this mode in the solid solutions involving the isomorphic replacement of the tetrahedral cation (such as $(Mg, Co)Cr_2O_4$). Since

no splitting is observed, we must assign ν_1 and ν_2 to vibrations of the condensed octahedral groups. The lack of splitting of these bands in solid solutions involving the replacement of the octahedral cation is qualitatively justified by the condensed arrangement of the octahedra, this type of arrangement leading to some averaging of the vibrational frequencies (1). This assignment is also supported by the fact that, for these bands, the frequency shifts are the least if the tetrahedral cation is modified, and the largest if the octahedral cation is modified.

(2) The splitting of ν_3 in some solid solutions such as $Zn(Cr, Al)_2O_4$ points to an important participation of the octahedral cation to this vibrational mode. But the significant shift of ν_3 in solid solutions such as $(Mg, Co)Cr_2O_4$ shows that the role of the tetrahedral cation is by no means negligible. ν_3 is thus a complex vibration involving the participation of both tetrahedral and octahedral cations.

(3) ν_4 clearly depends on the nature of the tetrahedral cation. The influence of the octahedral cation is small or negligible.

INVESTIGATION OF ISOTOPIC SPECIES

The most evident advantages and drawbacks of this method have been discussed in a recent paper [2]. The number of investigated isotopic species has been restricted, either by the non-availability of convenient stable isotopes, or by the cost of the available ones. The results are collected in Tables 5 and 6. We shall first discuss the vibrational behaviour of ν_3 and ν_4.

Table 5. Isotopic frequencies and isotopic shifts for $MgCr_2O_4$

	^{24}Mg	^{26}Mg	$\Delta\nu$		^{50}Cr	^{54}Cr	$\Delta\nu$	
ν_1	646	646	(0)		650	649	(-1)	
ν_2	523	524	$(+1)$		527	526	(-1)	
ν_3	431	425	-6	1.4%	435	427·5	-7.5	1.7%
ν_4	253·5	250	-3.5	1.4%	254	251·5	-2.5	1.0%

$MgCr_2O_4$. The results given by this compound are the most significant, because we were able to investigate the two possible types of isotopic species. Two points are evident from the data collected in Table 5 and Fig. 7:

(1) We now have the *definite proof of the complex origin of* ν_3, since this frequency is shifted by the isotopic replacement of either Mg or Cr. This complex origin had already been suspected from the vibrational behaviour of pure compounds and of solid solutions.

(2) ν_4 *is also related to a complex vibration*. This is a new aspect of the assignment of this band: the experimental data on pure compounds and solid solutions pointed to a predominant influence of the tetrahedral cation, but gave no really significant information about the participation of the octahedral cation. It will be noticed, however, that the *relative* influence of the octahedral cation is more important on ν_3 than on ν_4.

These conclusions are supported by further experimental data (Table 6); both ν_3 and ν_4 are shifted, whatever the kind of isotopic replacement (tetrahedral or octahedral cation). On the other hand, the *relative* values of these shifts (expressed

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Table 6. Isotopic frequencies and isotopic shifts for some normal II–III spinels

| | ZnAl$_2$O$_4$ | | | | ZnCr$_2$O$_4$ | | | |
	^{64}Zn	^{68}Zn	$\Delta\nu$		^{64}Zn	^{68}Zn	$\Delta\nu$	
ν_1	688	688	(0)		635	634	(−1)	
ν_2	572	572	(0)		537	536	(−1)	
ν_3	518	518	(0)		375	374	−1	0·27%
ν_4	228·5	225·5	−3	1·3%	190	186	−4	2·1%
	219·5	216	−3·5	1·6%				

| | ZnRh$_2$O$_4$ | | | | MgRh$_2$O$_4$ | | | |
	^{64}Zn	^{68}Zn	$\Delta\nu$		^{24}Mg	^{26}Mg	$\Delta\nu$	
ν_1	602	602	(0)		610	609	(−1)	
ν_2	568	568	(0)		548	548	(0)	
ν_3	305	304	−1	0·33%	354·5	348·5	−6	1·7%
ν_4	181·5	178	−3·5	1·9%	244	241·5	−2·5	1·0%

| | CdCr$_2$O$_4$ | | | | CdRh$_2$O$_4$ | | | |
	^{106}Cd	^{116}Cd	$\Delta\nu$		^{106}Cd	^{116}Cd	$\Delta\nu$	
ν_1	623	623	(0)		619	619	(0)	
ν_2	513	513	(0)		547	548	(+1)	
ν_3	369·5	368	−1·5	0·40%	301	299·5	−1·5	0·50%
ν_4	154·5	151·5	−3	2·0%	145	141·5	−3·5	2·4%

| | CoCr$_2$O$_4$ | | |
	^{50}Cr	^{54}Cr	$\Delta\nu$
ν_1	631	628	(−3)	
ν_2	530	527	(−3)	
ν_3	383	375	−8	2·1%
ν_4	200	196·5	−3·5	1·7%

in percent of the average frequency) show that: (1) ν_3 is more strongly affected than ν_4 by the isotopic replacement of the octahedral cation. (2) On the contrary, ν_4 is more sensitive than ν_3 to the isotopic replacement of the tetrahedral cation. This is not true, however, if the tetrahedral cation is fairly light (Mg).

We have now to discuss the vibrational behaviour of ν_1 and ν_2. We are facing here a somewhat unfavourable situation in view of the relative broadness and of the non-reproducibility of the bands. Nevertheless, it is evident that the isotopic replacement of the tetrahedral cation has no significant influence on the vibrational frequencies of ν_1 and ν_2 (Tables 5 and 6). This is in agreement with the previous assignment of these bands to vibrations of the octahedral groups.

However, quite unexpectedly, we find an isotopic shift which is, either practically negligible (MgCr$_2$O$_4$), or small and probably non-significant (CoCr$_2$O$_4$) for the isotopic replacement of the octahedral cation (Cr). This lack of a significant ^{50}Cr–^{54}Cr isotopic shift seems to be in contradiction with the previous assignment of ν_1 and ν_2 to vibrations of the octahedral groups (CrO$_6$ groups in the chromites). However, before rejecting this assignment, it is worth while to call back to the following experimental facts:

(1) We have investigated the ^{50}Cr–^{54}Cr isotopic shift in the i.r. spectrum of Cr$_2$O$_3$, for which all the bands are necessarily related to vibrations of the the Cr–O
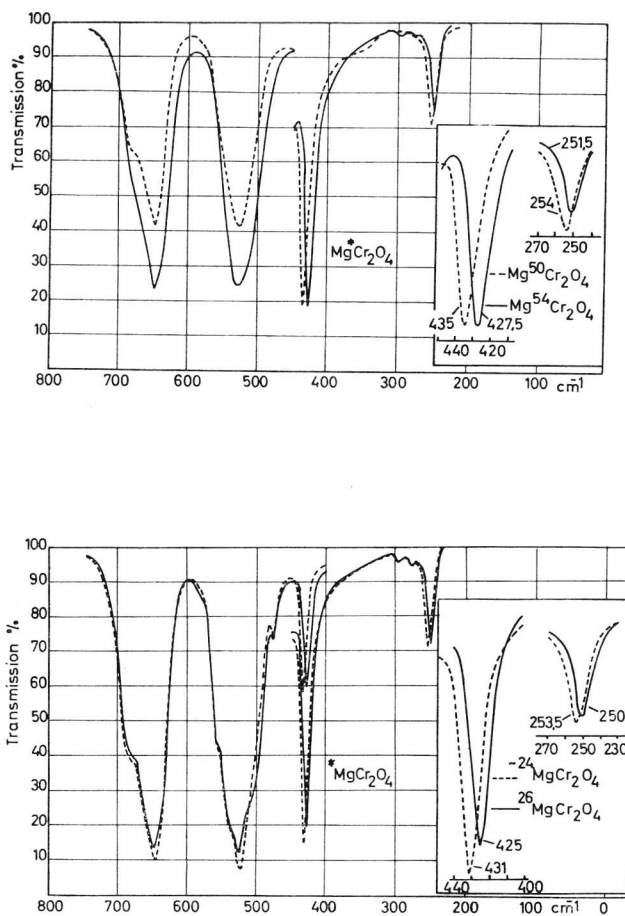
Fig. 7. Isotopic shifts in the i.r. spectrum of $MgCr_2O_4$.

bonds. Here again, the observed isotopic shifts are negligible (and non-significant) for the high-frequency bands [2].

(2) The investigation of the zinc spinels has shown that the two high-frequency bands depend on the bonding force, but *not* on the mass, of the octahedral cation.

(3) We have also investigated several non-spinel, but isomorphic chromium and rhodium compounds, the structure of which contains condensed CrO_6 or RhO_6 octahedra (Cr_2O_3 and Rh_2O_3 [2], $LiCrO_2$ and $LiRhO_2$ [5], $CaCr_2O_4$ and $CaRh_2O_4$ [3]).

For every pair of isomorphic Cr and Rh compounds, the high-frequency bands are observed in the same spectral region, or even at nearly the same frequency, despite the large difference in the masses of Cr (atomic weight 51·996) and Rh (atomic weight 102·91). Here again, there is no cationic mass effect on the high-frequency vibrations of a lattice of condensed octahedra. Thus, if we come back to

[5] P. TARTE and J. PREUDHOMME, *Spectrochim. Acta* **26A,** 747 (1970).

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the chromite spinels, we may conclude that the lack of a significant ^{50}Cr–^{54}Cr isotopic shift for the high-frequency bands ν_1 and ν_2 does not preclude their assignment to vibrational motions of the octahedral groups.

Discussion

There is little point about the complex origin of ν_3 and ν_4: the isotopic shifts definitely demonstrate the simultaneous participiation of both tetrahedral and octahedral cations to these vibrations. There is, however a predominant influence of the octahedral cation on ν_3, and of the tetrahedral cation on ν_4. This latter point results from the vibrational behaviour of pure compounds, solid solutions and isotopic species.

The assignment of ν_1 and ν_2 should be more carefully discussed for at least two reasons: (1) our assignments are in contradiction with those generally accepted [6–8], and (2) the interpretation of the experimental results is not as evident as for ν_3 and ν_4. Our arguments are as follows:

(1) *ν_1 and ν_2 do not significantly depend on the nature of the tetrahedral cation*

This is already suggested by the small frequency changes of ν_1 and ν_2 which are related to the change of the tetrahedral cation in chromites (Tables 2). But the most significant evidence comes from the lack of a frequency shift related to the isotopic replacement of the tetrahedral cation. Since the tetrahedral groups are "isolated", the vibrations which are essentially related to these groups *must* exhibit a significant isotopic shift: this has been experimentally verified with the germanate spinels Ni_2GeO_4 and Co_2GeO_4, where ν_1 and ν_2 must be assigned to vibrations of the tetrahedral GeO_4 groups [3, 9].

In the actual case of the normal II–III spinels, $MgRh_2O_4$ seems to be one of the most favourable compounds, because of the relative sharpness of ν_1 and ν_2, and of the relatively low mass of Mg, the tetrahedral cation. A rough calculation [3] leads to a frequency ratio of 1·01 for the antisymmetric stretching vibration of $^{24}MgO_4$ and $^{26}MgO_4$ tetrahedra. Hence, the frequency shift should be 6 or 5 cm^{-1} for ν_1 and ν_2 respectively, if one of these bands was related to the antisymmetric stretch of the MgO_4 group. Since the observed shifts are either non-existant, or non-significant (Table 6), it may be concluded that Mg does not play a significant role in the ν_1 and ν_2 vibrations.

This is true also for the various isotopic compounds investigated so far (Tables 5 and 6), and we may thus generalize to the normal II–III spinels the conclusion that there is no important participation of the tetrahedral cation to the ν_1 and ν_2 vibrations.

(2) *ν_1 and ν_2 clearly depend on the nature of the octahedral cation*

This appears from the investigation of the zinc spinels (Table 2, Fig. 2). There is, however, no relationship between the vibrational frequencies and the *mass* of the

[6] R. D. Waldron, *Phys. Rev.* **99,** 1727 (1955).

[7] S. Hafner, *Z. Krist.* **115,** 331 (1961).

[8] W. B. White and B. A. de Angelis, *Spectrochim. Acta* **23A,** 985 (1967).

[9] P. Tarte and J. Preudhomme, *Compt. Rend.* **270,** 474 (1970).

octahedral cation, and we came to the conclusion that the determinant factor was the bonding force between the oxygen and the octahedral cation.

This lack of a significant mass effect, which is supported by the investigation of isotopic species (isotopic replacement of the octahedral cation), has also been observed for a series of non-spinel compounds (see above).

This unexpected and somewhat puzzling phenomenon seems to be related to the high-frequency vibrations of some lattices of condensed octahedra. Qualitatively, it may be explained by the existence of antisymmetric, i.r. active modes characterized by the predominant displacement of the lattice of oxygen anions, with small or negligible displacements of the cations. Such an explanation does not hold in the
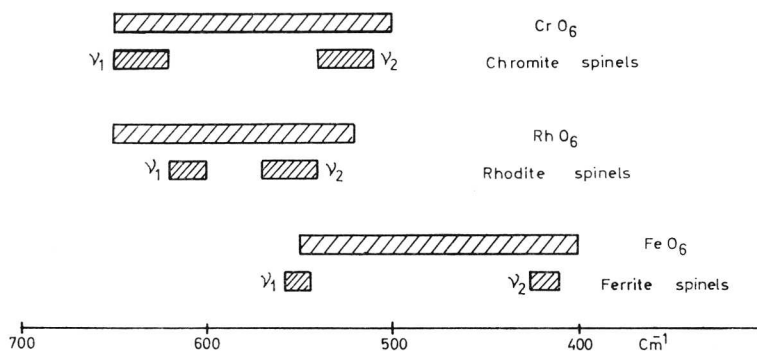

Fig. 8. Analogy between the absorption ranges of CrO_6, RhO_6 and FeO_6 "condensed" octahedra in non-spinel compounds, and the ν_1 and ν_2 frequencies for the chromite, rhodite and ferrite spinels.

case of "isolated" octahedra, for which the two i.r. active vibrations involve a significant displacement of the cation.

The assignment of ν_1 and ν_2 to vibrational motions of the octahedral lattice is also supported by the very good correspondence between the observed frequencies, and the absorption ranges of some condensed octahedral groups (Table 3 in Ref. [10]). This correspondence is well illustrated by Fig. 8, which allows an easy comparison of the absorption ranges of different $X^{III}O_6$ condensed octahedra in non-spinel compounds, and the absorption ranges of ν_1 and ν_2 in the corresponding spinel compounds. It is worth while to point out: (1) the very great similarity of the absorption ranges of CrO_6 and RhO_6 octahedra, illustrating the lack of a mass effect; (2) the very significant lowering of the absorption range of FeO_6 octahedra (in both non-spinel and spinel compounds), which is most probably due to a lowering of the cation—oxygen bonding force.

We may thus conclude that ν_1 and ν_2 essentially correspond to vibrations of the lattice of octahedral groups. Since the four i.r. active fundamentals belong to the same representation T_{1u} [8], some vibrational interactions must occur.

We can say, however, that the participation of the tetrahedral cation to these vibrations is too small to be evidenced by the actual experimental data.

[10] J. PREUDHOMME and P. TARTE, *Spectrochim. Acta* **27A**, 961 (1971).
[11] P. TARTE, *Spectrochim. Acta* **19**, 49 (1963).

Discussion of Some Specific Features

Non-reproducibility of some spectra

This point has already been mentioned. It should be noticed, first that this non-reproducibility is restricted to the high-frequency bands ν_1 and ν_2 (which are more or less broad), the low-frequency, sharp bands remaining at the same position; and second, that this non-reproducibility is exhibited by samples which are all pure and well-crystallized if one refers to their X-ray powder diagram.
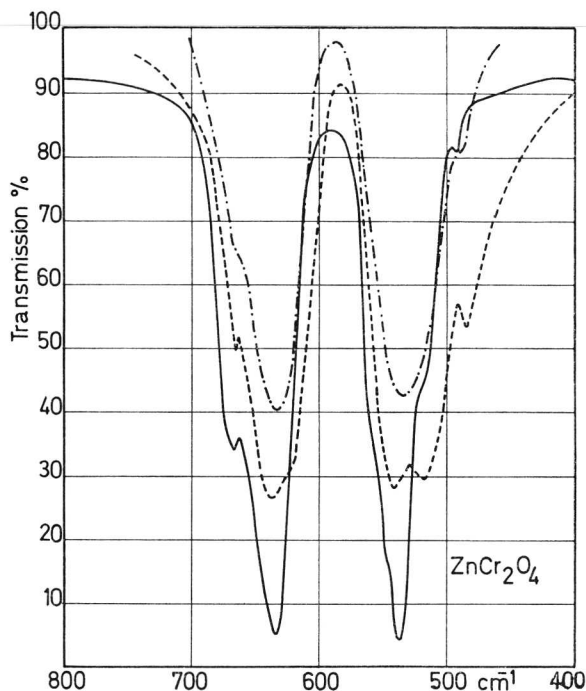
Fig. 9. Non-reproducibility of the two high-frequency bands in the case of $ZnCr_2O_4$.

The non-reproducibility essentially appears as variations in the position, broadness and shape of the ν_1 and ν_2 bands. In the most favourable case of maximum sharpness, these bands are already asymmetric; but for different samples of a given compound, the degree of asymmetry and the intensity of the shoulders may be greatly enhanced, even leading in a few cases to the splitting of the bands into two distinct components of similar intensity (Fig. 9).

Now, these spectral variations are clearly related to the synthesis conditions of the sample. A maximum of broadness (or asymmetry, or splitting) is generally observed for the samples synthesized at relatively low temperatures (this temperature being however sufficient to give a pure, well-crystallized compound); for these samples, the shape of the bands also depends on the chemical nature of the starting materials. If higher synthesis temperatures are used (but still within the limits of stability of the compound), the sharpness of the bands increases, and there is a

general modification towards what could be called a standard, reproducible spectrum.

We have thus good reasons to believe that the observed non-reproducibility is related to the granulometry of the sample, and this may be explained in the following manner: we have shown that the two high-frequency bands must be assigned to vibrations of the trivalent cation—oxygen bonds, for which the ionic character must be fairly important; this last point is supported by the large intensity of the bands. Thus, there must be a significant frequency difference between the longitudinal optic and the transversal optic modes. Since (as it is generally the case) our "absorption" curves are in fact the resulting effect of combined reflection and absorption phenomena, both longitudinal optic and transversal optic modes appear separately in the
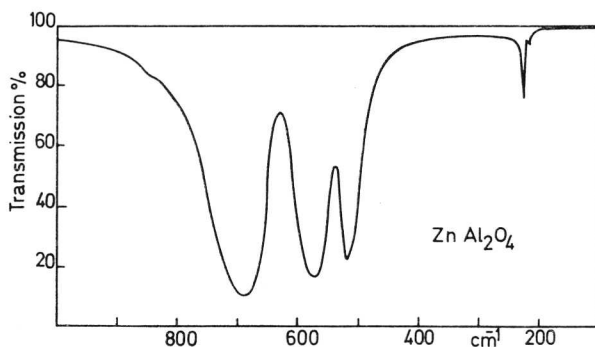

Fig. 10. Infrared spectrum of $ZnAl_2O_4$.

spectrum of very fine-grained samples, whereas relatively coarse-grained samples exhibit an unique, average frequency.

This type of behaviour is very easily observed in the more simple case of the highly ionic oxide MgO, for which very fine-grained samples exhibit two bands near 550 and 400 cm^{-1} (corresponding to the longitudinal optic and transversal optic frequencies respectively), whereas *one* strong band is observed near 490 cm^{-1} for the *same* sample heated up to 1300°C.

Our hypothesis is also supported by the fact that the washing in water, followed by sedimentation and decantation, is sufficient to bring out significant changes in the band shape for fine-grained samples: this is immediately explained by the elimination of the finest grains during the decantation process.

Infrared spectrum of $ZnAl_2O_4$

The i.r. pattern of this compound has a somewhat peculiar appearance with three (and not two) strong bands in the high-frequency region, and one band (plus a very weak side-band) in the low-frequency region (Table 2 and Fig. 10). This last band is certainly ν_4, and the side-band is not an artifact, since it is found in all spectra, and it exhibits an isotopic ^{64}Zn–^{68}Zn shift (Table 6). But the origin of this supplementary band is still unknown. Now, as far as the 518 cm^{-1} band is concerned, two possible assignments should be taken into account: in view of its fairly high frequency and strong intensity, this band may be assigned to a splitting of ν_2 (the two components being the 575 and the 518 cm^{-1} bands); but in this case, there is no band

left for ν_3; or it may be assigned to ν_3. This must be the right assignment since, in the solid solutions $ZnAl_2O_4$–$ZnCr_2O_4$, this band is shifted down to lower frequencies (with a splitting in a limited compositional range: Fig. 6), and is finally represented in pure $ZnCr_2O_4$ by the band at 375 cm^{-1}, whose assignment to ν_3 is undisputable. The high value of 518 cm^{-1} for ν_3 in $ZnAl_2O_4$ is easily justified by the very moderate mass of Al, since ν_3 clearly depends on the mass of trivalent cation.

We have no definite explanation for its unusually strong intensity; but this could be possibly explained by some kind of interaction between ν_2 and ν_3, since these two bands belong to the same representation T_{1u}, and since their frequencies are not very different. A more or less similar situation occurs in the case of $CoAl_2O_4$, for which the ν_2 and ν_3 frequencies are not very different (563 and 523 cm^{-1} respectively): here again, the very moderate mass of the trivalent cation is certainly responsible for the high frequency value of ν_3.
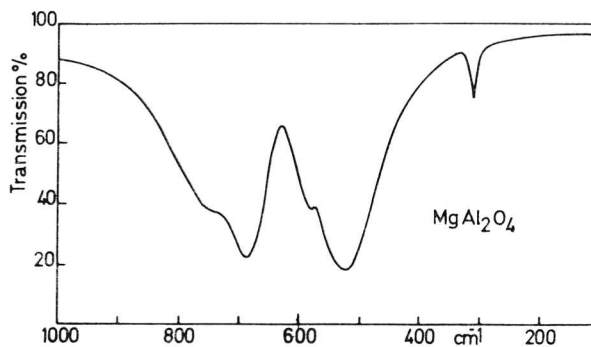

Fig. 11. Infrared spectrum of natural $MgAl_2O_4$.

Infrared spectrum of $MgAl_2O_4$

We consider here the spectrum of the natural compound since, in the synthetic material, the cationic distribution is slightly inversed. The i.r. pattern (Fig. 11) is somewhat different from the typical spectra of Fig. 1, with two strong bands at 688 and 522 cm^{-1} (which must correspond to ν_1 and ν_2), but only one sharp band at 309 cm^{-1}. This last band must be assigned to ν_4 (the corresponding frequency is 242 cm^{-1} for $MgRh_2O_4$, 253 cm^{-1} for $MgCr_2O_4$, and is expected to be significantly higher for $MgAl_2O_4$ in view of the mass effect of the trivalent cation). But there is no clear-cut evidence about the occurrence of ν_3. It is possible, however, to estimate a rough value for this frequency in the following manner.

We know from the bulk of our experimental data that ν_3 depends on the mass of both cations, tetrahedral and octahedral. Since ν_3 is observed at 518 cm^{-1} in $ZnAl_2O_4$ and 523 cm^{-1} in $CoAl_2O_4$, it is expected to lie at a still higher frequency in $MgAl_2O_4$. Now, when passing from a zinc spinel to the corresponding magnesium spinel, we find for ν_3 a frequency increase of about 50 cm^{-1} ($ZnRh_2O_4$: 305—$MgRh_2O_4$: 353 cm^{-1}; $ZnCr_2O_4$: 375—$MgCr_2O_4$: 430 cm^{-1}). Since ν_3 is observed at 518 cm^{-1} in $ZnAl_2O_4$, it is expected to be found somewhere near 570 cm^{-1} in $MgAl_2O_4$. The same reasoning holds for a change of the octahedral cation: when passing from a chromite

to an aluminate, we find a frequency increase of 143 cm^{-1} (ZnCr$_2$O$_4$: 375—ZnAl$_2$O$_4$: 518 cm^{-1}; CoCr$_2$O$_4$: 380—CoAl$_2$O$_4$: 523 cm^{-1}). If the same frequency increase is applied to the ν_3 frequency of MgCr$_2$O$_4$, namely 430 cm^{-1}, we find again a value of about 570 cm^{-1} for the ν_3 frequency of MgAl$_2$O$_4$. Now, the spectrum of this compound exhibits a weak, but distinct and quite reproducible shoulder near 580 cm^{-1}. We thus assign this shoulder to ν_3, which is now at a higher frequency than ν_2. This exceptional crossing-over of ν_2 and ν_3 may be correlated with the fairly light masses of Mg and Al cations, since ν_3 depends on the masses of both cations, whereas ν_2 does not depend on these masses.

Conclusions

The systematic investigation of the i.r. spectrum of cubic, normal II–III spinels by appropriate methods leads to a consistent set of assignments:

The two high-frequency bands ν_1 and ν_2 are essentially related to vibrations of the lattice of octahedral groups: their frequency is essentially determined by the nature (but not by the mass) of the octahedral, trivalent cation. For these vibrational modes, no definite influence of the tetrahedral, bivalent cation has been evidenced so far; however, we cannot completely reject a small contribution of this cation through vibrational interactions with ν_3 and ν_4: such interactions must occur, since the four i.r. active fundamentals belong to the same representation T_{1u}, but their real importance is still unknown.

The two low-frequency bands ν_3 and ν_4 correspond to complex vibrations involving the simultaneous participation of the tetrahedral and of the octahedral cations, with, however, a predominant influence of the octahedral cation on ν_3, of the tetrahedral cation on ν_4.

It must be pointed out that these assignments have been deduced in the case of the *normal, II–III* spinels. They do *not* apply, either to the *inverse, II–III* spinels (this case will be discussed in another paper), or to the *normal, II–IV* spinels: in this latter case, previous studies have shown that the two high-frequency bands are essentially related to vibrations of the *tetrahedral* groups, and this has been definitely confirmed by the investigation of isotopic species [3].

It is thus evident that the assignment of the four i.r. active fundamentals of a spinel to either tetrahedral or octahedral groups (or to complex vibrations) depends on the type of spinel under consideration.

This point, and the related experimental data, will be discussed in a forthcoming paper.