

Vibrational spectrum of $A^I B^{III} O_2$ and $A^I B^{III} S_2$ compounds with the rhombohedral α - NaFeO_2 structure

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Abstract—The Raman and i.r. spectra of $A^I B^{III} X_2$ ($X = \text{O}$ or S) compounds with the α - NaFeO_2 rhombohedral structure are reported and discussed on the basis of a group theoretical analysis. Most of the sulfur compounds exhibit the two predicted Raman-active frequencies; they are shown to be independent of the mass of both A^I and B^{III} cations and correspond to motions of the anionic lattice. The origin of the 4 i.r. active fundamentals is more complex. The relative influence of A^I , B^{III} and X on these frequencies is discussed on the basis of appropriate experimental data.

INTRODUCTION

A FAIRLY large number of compounds $A_x B_y O_z$ are characterized by an octahedral co-ordination of both A and B cations. If, in addition, $x + y = z$, their structure may be, either identical to the NaCl structure (this situation corresponding to a statistical distribution of A and B cations), or derived from this structure through a suitable ordering of the cation distribution. NaCrO_2 (rhombohedral), LiFeO_2 (disordered cubic or ordered tetragonal), Li_2TiO_3 (monoclinic), Li_3NbO_4 (ordered cubic), are well-known examples of such compounds. A number of similar sulfur compounds have also been synthesized.

We shall report here on the vibrational (Raman and i.r.) spectrum of $A^I B^{III} O_2$ and $A^I B^{III} S_2$ compounds of the rhombohedral type, for which preliminary results from this laboratory have already been published [1]. Our experimental results and their interpretation will be discussed in connection with a recent paper of MOORE and WHITE on the same subject [2]. Further spectral data on other structural types [3] will be reported in due time.

EXPERIMENTAL

Spectroscopic techniques

The i.r. spectra were investigated in the 1000 – 50 cm^{-1} region with a Beckman IR 12 (1000 – 200 cm^{-1} ; KI discs) and a Cameca SI 36 (200 – 50 cm^{-1} ; polythene discs) spectrometer. Some samples were also run as nujol mull as a check of the reproducibility of the spectra.

The Raman spectra were registered with a Coderg PHO double monochromator equipped with a Spectra Physics 50 mW He–Ne laser. The sulfur compounds gave Raman spectra of good quality, whereas most of the oxygen compounds gave deceiving results; this must be related, in some cases at least, either to the low

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

[2] R. K. MOORE and W. B. WHITE, *J. Am. Ceram. Soc.* **53**, 679 (1970).

[3] M. TROMME, Doctorate Thesis—in preparation.

polarizability of the constitutive atoms (α -LiAlO₂), or to the very dark colour of the compounds (if the trivalent cation is Cr, Rh, Co, Ni).

Synthesis of the compounds

The syntheses were carried out in accordance with published literature data. The experimental conditions are collected in Table 1. All compounds were checked by X-ray diffractometry.

Table 1

Compound	Initial mixture	Experimental conditions	Remarks	References
α -LiAlO ₂	α -Al ₂ O ₃ + Li ₂ CO ₃	6 days at 600°C	Repeated grindings	[4, 5]
LiCoO ₂	Co ₂ O ₄ + Li ₂ CO ₃	2 days at 800°C	Oxygen atmosphere	[6]
LiCrO ₂	Cr ₂ O ₃ + Li ₂ CO ₃	2 days at 740°C	Nitrogen atmosphere	[6]
LiRhO ₂	Rh ₂ O ₃ + Li ₂ CO ₃	5 days at 650°C		[7]
NaCrO ₂	Cr ₂ O ₃ + NaHCO ₃	1 day at 850°C	Nitrogen atmosphere	[8]
NaRhO ₂	Rh ₂ O ₃ + NaHCO ₃	20 hr at 800°C	Nitrogen atmosphere	[9]
NaInO ₂	In ₂ O ₃ + NaNO ₃ (1:4)	2 hr at 900°C	Nitrogen atmosphere	This work
NaScO ₂	Sc ₂ O ₃ + NaNO ₃ (1:4)	2 hr at 900°C	Nitrogen atmosphere	This work
NaLuO ₂	Lu ₂ O ₃ + NaNO ₃ (1:4)	2 hr at 900°C	Nitrogen atmosphere	[10]
LiXS ₂	X ₂ O ₃ + Li ₂ CO ₃ (1:1, 2)	2 hr at 900°C	H ₂ S atmosphere	[11]
NaXS ₂	X ₂ O ₃ + NaHCO ₃ (1:2, 4)	2 hr at 900°C	H ₂ S atmosphere	[12]
KXS ₂	X ₂ O ₃ + KHCO ₃ (1:2, 4)	2 hr at 900°C	H ₂ S atmosphere	[11]

CRYSTAL STRUCTURE AND ACTIVITY OF THE VIBRATIONAL MODES

Crystal structure and symmetry elements

All the compounds $A^I B^{III} X_2$ ($X = O$ or S) discussed in this paper are hexagonal and may be conveniently described by a rhombohedral primitive cell, space group $D_{3d}^5 - R\bar{3}m$, $Z = 1$. The structure may be considered as consisting of alternate layers of A^I , X and B^{III} (Fig. 1).

The co-ordinates of the atoms in the primitive rhombohedral cell are as follows:

	x	y	z
A^I	0	0	1/2
B^{III}	0	0	0
X	0	0	$\pm x$

- [4] H. A. LEHMANN and H. HESSELBARTH, *Z. Anorg. Allgem. Chem.* **313**, 117 (1961).
 [5] A. M. LEJUS and R. COLLONGUES, *Compt. Rend.* **254**, 2005 (1962).
 [6] P. F. BONGERS, Thesis, Leiden (1957).
 [7] E. F. BERTAUT and J. DULAC, *J. Phys. Chem. Solids* **21**, 118 (1961).
 [8] W. RÜDORFF and H. BECKER, *Z. Naturforsch. B* **9B**, 614 (1954).
 [9] J. J. SCHEER, A. E. VAN ARKEL and R. D. HEYDING, *Can. J. Chem.* **33**, 683 (1955).
 [10] V. I. SPITSYN, I. A. MURAV'eva, L. M. KORBA, and I. I. KORCHAK, *Russ. J. Inorg. Chem.* **14** (6) 759 (1969).
 [11] R. BALLESTRACCI, *Bull. Soc. Franc. Minéral. Crist.* **88**, 207 (1965).
 [12] R. BALLESTRACCI and E. F. BERTAUT, *Bull. Soc. Franc. Minéral. Crist.* **87**, 512 (1964).

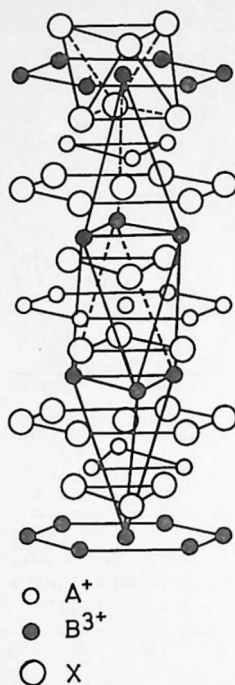


Fig. 1. Structure of the rhombohedral ABX_2 compounds.

This structure is rather favourable to a detailed vibrational analysis, in view of the occurrence of one formula unit only in the primitive cell, and of the fairly high symmetry of the structure (all the atoms are located on the trigonal axis).

Factor group analysis

The application of the symmetry operations of the D_{3d} group to the different atoms in the primitive rhombohedral cell leads to the irreducible representation:

$$\Gamma_i = 1A_{1g}(\text{R}) + 1E_g(\text{R}) + 3A_{2u}(\text{i.r.}) + 3E_u(\text{i.r.})$$

Two of these modes (one A_{2u} and one E_u) correspond to translations and should be subtracted. We finally expect 2 Raman and 4 i.r. bands. These conclusions are in agreement with those recently published by MOORE and WHITE [2].

RESULTS AND INTERPRETATIONS

Raman spectra

We shall first consider the Raman spectra of the sulfur compounds.

Most of the investigated compounds exhibit the 2 Raman-active vibrations predicted by the group theory (Fig. 2). The corresponding frequencies are collected in Table 2, from which the following points are evident:

(1) The frequencies of the corresponding Li, Na and K compounds are nearly the same, the frequency differences being very small and, in most cases, hardly significant.

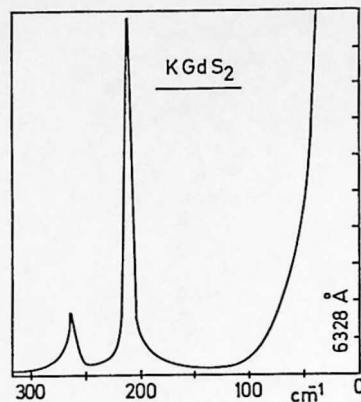


Fig. 2. Typical powder Raman spectrum of a sulfur compound.

Table 2. Raman frequencies of sulfur compounds

X	LiXS ₂	NaXS ₂	KXS ₂
La		disordered structure	
Pr		(NaCl)	
Nd		203	258
Sm	disordered structure	208	262
Eu	(NaCl)	brown compound	
Gd		212	268
Tb		211	269
Dy		216	274
Ho	211	?	216
Er	219	285	219
Yb	spectrum not obtained		(?)
Lu	217	290	282
		greenish compound	
Y	disordered structure	217	278
	(NaCl)		
In		162	278
Cr	other structures	black compound	
			other structure
			black compound

It is quite clear that the nature of the monovalent cation has practically no influence on the corresponding vibrational modes.

(2) The frequencies *do* depend on the *nature* of the trivalent cation, but *not* on their *mass*. This last point is evident from the consideration of the nearly equal vibrational frequencies of the corresponding yttrium and holmium compounds, despite the large mass ratio of these elements (89/165). Moreover, there is a small but systematic increase of the frequencies with increasing mass of the trivalent lanthanide cation. In view of the well-known lanthanide contraction, this result strongly suggests that the frequency trend in this family is essentially determined by the variation of the lanthanide ionic radius, and thus by the lanthanide-sulfur distances. This

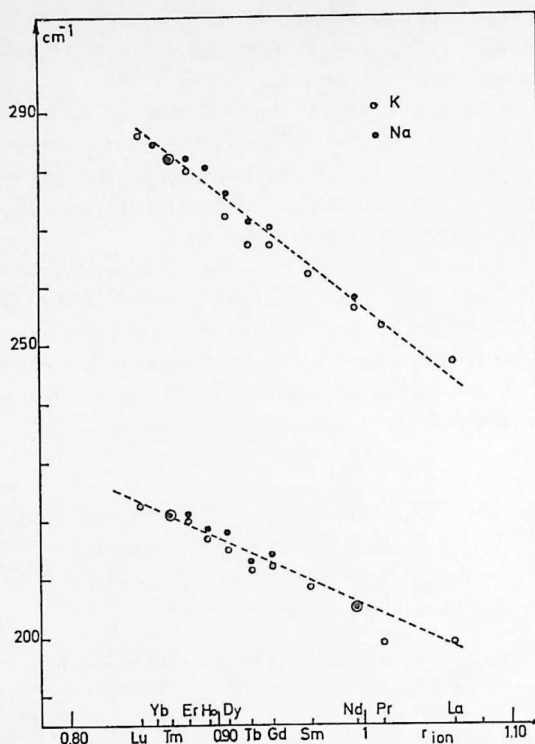


Fig. 3. Relationship between the Raman frequencies and the ionic radius of the rare earth for the sulfur compounds.

conclusion is supported by the rather regular variation exhibited in Fig. 3. From these experimental data, the following conclusions may be drawn concerning the Raman-active vibrations:

1. The Raman-active frequencies are essentially determined by the bonding force between the anion and the trivalent cation. The monovalent cation does not play any significant role and should be practically at rest during these vibrations.
2. The role of the trivalent cation is essentially restricted to providing the restoring force: the lack of a mass effect is a good indication that, here also, there is no significant displacement of the trivalent cation.
3. It may thus be concluded that the anions only are moving during the Raman-active vibrations.

To support these conclusions, we can use the correlation chart showing the reduction of the space group representation into those of the particle site symmetries, since the site group is necessarily a subgroup of that of the unit cell. The correlation chart shows that when an atom lies on a site having the same symmetry as the unit cell, it is always at rest during the symmetrical vibrations. For the compounds discussed in this paper, this is effectively the case for the 2 cations A^I and B^{III} . The A_{1g} ,

totally symmetric, mode could be described as a collective motion of the anionic sheet against the cationic sheet, along the trigonal axis: this type of motion does not alter the symmetry elements of the crystal.

An appropriate description of the E_g mode is harder to find out in view of the lower symmetry and of the degenerate character of this vibration. It may be considered as a motion of the anions in a plane perpendicular to the trigonal axis. A definite assignment of the 2 Raman peaks to the A_{1g} and E_g modes is actually impossible, since powders only were investigated.

Raman spectra of oxygen compounds were obtained in 3 cases only, namely NaScO_2 (389 cm^{-1}) NaLuO_2 (387 and 511 cm^{-1}) and NaInO_2 (330 and 500 cm^{-1}). In this latter case, as for NaInS_2 , there is an inversion of the relative intensities of the 2 peaks as compared with those generally observed (the high-frequency peak being here the strongest). A discussion of this particular point would be premature in view of the lack of systematic data on oxygen compounds.

Infrared spectra

Oxygen compounds $A^I B^{III} O_2$. The results already published [1] have now been completed by the study of further appropriate compounds. The new data are collected in Table 3, together with some previous data (Table 2 in Ref. [1]) which are important for the discussion of the results.

Table 3. I.r. frequencies of oxygen compounds

	ν_1	ν_2	ν_3	ν_4
NaCrO_2	$\approx 615^*$	532	347	189
NaRhO_2	$\approx 570^*$	542	293	183
NaInO_2	500	385	294	150
${}^6\text{LiCrO}_2$	$\approx 650^*$	540		270
${}^7\text{LiCrO}_2$	$\approx 650^*$	540		253
${}^6\text{LiRhO}_2$		~ 545	~ 465	223
${}^7\text{LiRhO}_2$		~ 543	~ 460	210

* Shoulder

First of all, it should be noticed that, for the sodium compounds at least, we observe 4 bands (Fig. 4) in accordance with theoretical expectations; they have been labelled $\nu_1 \dots \nu_4$ (Table 3) in the order of decreasing frequencies. If we consider all the spectra obtained so far (including those of the lithium compounds already published [1]), two bands are very conspicuous and are immediately identified: ν_2 (very strong and broad), and the low-lying frequency ν_4 (weak but sharp). They also exhibit a very characteristic behaviour in connection with the nature of the monovalent A and of the trivalent B cation.

In view of the systematic and important ${}^6\text{Li}$ - ${}^7\text{Li}$ isotopic shift, it is evident that ν_4 depends on the mass of the monovalent cation [1]; this conclusion is also supported by the frequency decrease which is observed when passing from a lithium to the corresponding sodium compound. This frequency also depends to some extent on the nature of the trivalent B cation, but *not* on the *mass* of this cation: this lack of a significant mass effect of B is shown by the similarity of the ν_4 frequency for

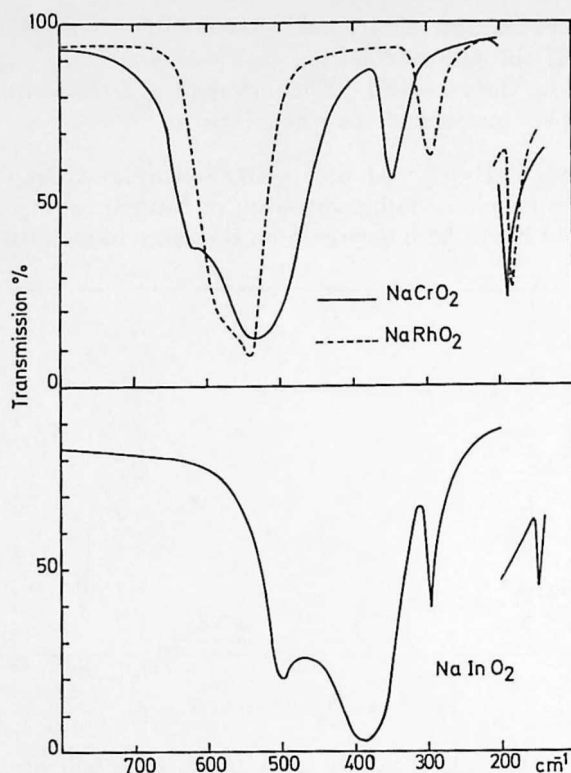


Fig. 4. I.r. spectrum of some oxygen compounds.

$LiAlO_2$ and $LiCoO_2$ [1], and for $NaCrO_2$ and $NaRhO_2$ (Table 3). It may be concluded that ν_4 essentially corresponds to some motion of the monovalent cation, whose frequency is more or less influenced by the nature of the trivalent cation and by the dimensions of the crystal unit cell.

Although completely different, the vibrational behaviour of ν_2 is also a very clear-cut one. From the lack of any 6Li - 7Li isotopic shift [1] and since the frequencies of the corresponding Li and Na compounds are nearly the same (Table 3), it may be concluded that this vibration is practically not affected by the nature of the monovalent cation. If we now consider the influence of the trivalent cation, we already know from the study of $LiCrO_2$ and $LiRhO_2$ that the *mass* of the trivalent cation has no influence on this vibration [1]. This is now fully substantiated by the frequency values observed for $NaCrO_2$ and $NaRhO_2$ (Table 3). There is, however, a strong influence of the *nature* of the trivalent cation (as exemplified by $NaRhO_2$ and $NaInO_2$), acting through its ionic radius, or the cation-oxygen bonding force, or both.

We may conclude that ν_2 corresponds to a vibration of the oxygen lattice, without any significant displacement of the monovalent or trivalent cation, the restoring force being determined by the nature of the trivalent cation.

Finally, it appears that the vibrational behaviour of ν_1 and ν_3 is more complicated: the consideration of the values collected in Table 3 strongly suggests that these frequencies depend on the mass of both monovalent and trivalent cations, and thus correspond to complex motions of the whole lattice.

Sulfur compounds $A^I B^{III} S_2$. At first view, and apart from the expected shift towards the low frequencies, the i.r. spectrum of $NaCrS_2$ is very similar to that of $NaCrO_2$ (Fig. 5), and it can be interpreted on the same bases. But the extension of

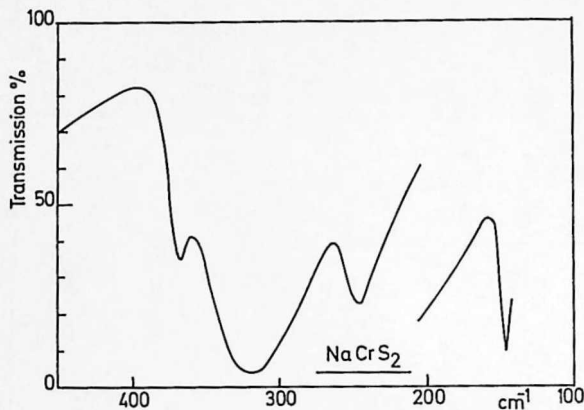


Fig. 5. I.r. spectrum of $NaCrS_2$.

these assignments to the whole family of $A^I B^{III} S_2$ rhombohedral compounds with B^{III} = rare earth is a matter of difficulty for several experimental reasons.

1. The low frequency band ν_4 has been observed in 2 cases only ($LiLuS_2$ and $LiYbS_2$), where it has been found to be extremely weak. We suspect that the failure to observe this band in other compounds is due to this weakness.

2. The bands corresponding to the 3 remaining modes ν_1 , ν_2 , ν_3 are observed in a fairly small frequency interval (generally about 100 cm^{-1} , or even less in some cases), and thus are likely to be partially or totally overlapped. In some cases ν_1 and/or ν_3 are so weak that their identification is doubtful.

With these difficulties in mind, we may now discuss the results collected in Table 4.

ν_1 is generally weak or very weak, and its unequivocal identification is possible only in a limited number of spectra. The existing data are however sufficient to show that its frequency depends on the mass of the trivalent cation (the ν_1 frequencies are higher for $NaYS_2$ and KYS_2 than for the corresponding rare earth compounds) and of the nature of the monovalent cation. No further correlation can be traced through the existing experimental data.

ν_2 is very strong (as in the case of oxygen compounds); it appears at slightly increasing frequencies when passing from the potassium to the sodium and lithium compounds; but within a given family (either the potassium or the sodium compounds), the frequency variations are small and erratic.

Table 4. I.r. frequencies of sulfur compounds

X	LiXS ₂				NaXS ₂				KXS ₂			
	ν_1	ν_2	ν_3	ν_4	ν_1	ν_2	ν_3	ν_4 not observed	ν_1	ν_2	ν_3	ν_4 not observed
La								Disordered	260	218	168	
Pr								structure (NaCl)	sh 270	220		
Nd					275	246	207		sh 260	230		
Sm					sh 277	239	203		sh 265	225		
Eu					sh 280	240	205		sh 270	223		
Gd					sh 280	245	210		276	227		
Tb					sh 280	254	206		279	235		
Dy						249	211		275	230		
Ho	sh 320	260	295			256	213		275	232	178	
Er		260	300			248	212		280	236		
Tm		261	302		288	245	213		282	231		
Yb	sh 330	259	309	165	sh 285	246	213		288	225	183	
Lu	sh 337	262	310	160		257	216		279	233		
Y						309	261	223	304	244	187	
								Disordered				
								structure (NaCl)				

Finally, the vibrational behaviour of ν_3 is not simple, but it may be interpreted (as for the oxygen compounds), by the simultaneous influence of both cations.

This band has been observed without difficulty in most sodium compounds, but only in a limited number of potassium compounds, where it is very weak. These results show a small, but significant mass effect of the trivalent cation (by the comparison of the corresponding yttrium and holmium compounds), a small influence of its ionic radius, but a very significant influence of the nature of the monovalent cation. It is actually premature to decide whether this influence is related to the mass of the cation, or to its ionic radius, or both. However, the importance of the shift suggests some contribution from a mass effect, and this would explain the peculiar i.r. pattern given by the lithium compounds. For Na and K compounds, ν_3 appears on the low-frequency side of ν_2 . Now, this absorption seems to be missing in the spectra of Li compounds. If however a significant mass effect is taken into account, ν_3 should be shifted enough to be, either at approximately the same frequency that, or even at a higher frequency than, ν_2 . This seems to be effectively the case for the few Li compounds available, but it is clear that the assignment problem is complicated by the occurrence of 3 vibrational modes (ν_1 , ν_2 , ν_3) in the same frequency range. A general scheme of this vibrational behaviour is given in Fig. 6.

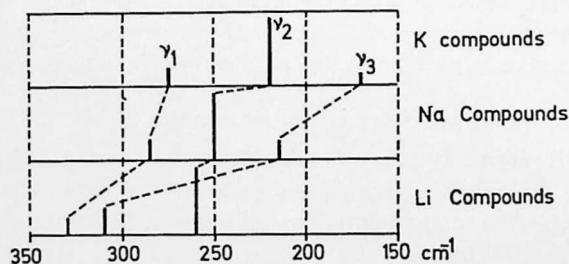


Fig. 6. Relative absorption regions for sulfur compounds.

DISCUSSION

The i.r. spectra of some of these compounds were recently published and discussed by MOORE and WHITE [2]. But unfortunately, their experimental results are so drastically different from ours that any comparison is impossible. They obtain, for the type of compounds discussed here, very flattened spectra with a fairly large number (7-9) of absorption maxima which seem to be merged in a continuous absorption.

We tried to reproduce their spectra by modifying our synthesis and sampling techniques, but this task appeared to be a hopeless one. In view of these unexplained (and so far unaccountable) discrepancies, we would not like to engage into a fruitless discussion. Nevertheless, some points in Moore and White's paper should be considered.

From a purely experimental point of view, it is stated by Moore and White that "... it seems clear that the spectra ... are intrinsically diffuse and that the lack of resolution cannot be blamed on sample preparation or experimental technique." If, however, we plot on the same scale their spectrum of disordered LiFeO_2 and a spectrum obtained in this laboratory (and nearly identical to that published in 1965 [13]), it is quite clear that their spectrum is characterized by an abnormally low transmission outside the band (Fig. 7). Likewise, their spectrum of $\gamma\text{-LiAlO}_2$ appears to be "smoothed out" with respect to the spectrum of the same compound published by one of the present authors in 1967 [14]. These 2 examples clearly show that Moore and White's sampling technique is not as good as it should be, and this may have some influence on the shape of their i.r. spectra.

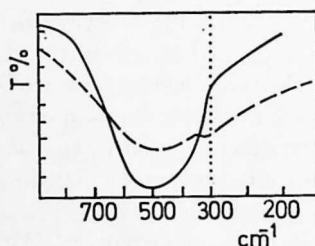


Fig. 7. I.r. absorption of disordered LiFeO_2 .
 ——— obtained in this laboratory.
 - - - - - after Moore and White.

On the other hand, there are some errors or inconsistencies in their discussion and interpretation of the experimental results. If we restrict ourselves to the case of rhombohedral compounds, the following points may be considered:

1. Number of observed and predicted i.r. fundamentals

Moore and White find 7 to 9 bands which are more or less arbitrarily distributed into 2 groups of 4. This doubling with respect to the number of predicted i.r. active fundamentals is tentatively explained by "the possibility that the spectra of these

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

[14] P. TARTE, *Spectrochim. Acta* **23A**, 2127 (1967).

structures behave like the middle composition of a solid solution . . . and exhibit two-mode behaviour."

This explanation is clearly meaningless, since the phases under consideration are true compounds and have nothing to do with solid solutions. The two-mode behaviour of a solid solution is related to the occurrence of 2 different cations (or anions) on *equivalent* crystallographic sites in the structure; but in the present case, the occurrence of 2 cations (together with their *ordered* distribution) is already taken into account by the group theory, which leads to the prediction of 4 i.r. fundamentals. There is no reason to find a supplementary doubling of these modes, and in fact, we generally observe 3 or 4 i.r. bands in our own spectra.

2. Origin of the strong, high-frequency absorption

Moore and White find a downward frequency shift when passing from lithium ($LiAlO_2$, $LiCoO_2$, $LiCrO_2$) to sodium ($NaInO_2$) compounds and their paper expresses the following statement: "the shift to lower frequency when the heavier sodium is substituted for the light lithium can be clearly seen. This frequency shift contrasts with TARTE's statement [14] that vibrations resulting from lithium-oxygen bonds would of necessity occur at lower frequencies than vibrations of a trivalent cation-oxygen bond." It appears that this criticism is a quite unfortunate one indeed. First, because it relies on a meaningless basis: it will be evident to every spectroscopist that any frequency shift observed when passing from, say, $LiCrO_2$ to $NaInO_2$ cannot be assigned to the specific influence of the Na cation, since *both* cations are simultaneously modified.

Second, because our own experimental results (Table 3 of this paper) show it to be erroneous: the position of the strong band ν_2 is not or hardly affected by the nature of the monovalent cation, and clearly depends on the nature of the trivalent cation ($LiRhO_2$: 544; $NaRhO_2$: 542; $NaInO_2$: 385 cm^{-1}). This point has already been discussed in the preceding part of this paper.

3. Discrepancies between the experimental data

Moore and White wonder at the complexity of their spectra. But unexpectedly enough, they do not mention the fundamental differences between their spectrum of α - $LiAlO_2$ and our own spectrum of this compound; this latter spectrum was certainly known to them, since it is discussed in a paper [16] which is otherwise criticized by them (see the preceding point). Likewise, it is a bit surprising to see that their spectrum of α - $LiAlO_2$ does not extend above 650 cm^{-1} , despite the fact that this compound exhibits near 760 cm^{-1} a medium-intensity band which has already been observed by KOLESOVA [15] and by the present authors [14].

Finally, it may be mentioned that the discrepancies between our results and those of Moore and White are not restricted to the rhombohedral, but also extend to the tetragonal, $LiInO_2$ -type, compounds. These results and their interpretation [3] will be discussed in another paper.

[15] V. A. KOLESOVA, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 2082 (1962).

CONCLUSIONS

The Raman and i.r. investigation of a fairly large number of rhombohedral $A^I B^{III} X_2^{II}$ compounds gave results which are consistent with group theoretical considerations. No explanation can be offered so far about the drastic differences between these results and those recently published by MOORE and WHITE [2]. A discussion of these results, and the fact that our data are consistent with theoretical expectations lead us to consider that our results must be essentially reliable.

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ADDENDUM

During the completion of this manuscript, we came across the recent paper of BRÜESCH and SCHÜLER dealing with the same subject [16]. Very broadly speaking, this latter paper is characterized by a more physical treatment of a smaller number of compounds, and it may be considered that both papers complete each other. For the compounds whose investigation is reported in both papers, it is worth while to point out to the excellent agreement between the experimental data. This gives further support to the results discussed in our paper.

[16] P. BRÜESCH and C. SCHÜLER, *J. Phys. Chem. Solids* **32**, 1025 (1971).