



Infra-red spectra of inorganic aluminates and characteristic vibrational frequencies of AlO_4 tetrahedra and AlO_6 octahedra

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Abstract—Some aspects of the interpretation of IR spectra of inorganic solids are discussed, with emphasis on the factors influencing the vibrational frequencies of cation-oxygen co-ordinated groups, namely the value of the co-ordination number, "isolated" or "condensed" state of the co-ordinated groups and vibrational interactions with neighbouring groups. These considerations are applied to the study of Al—O stretching frequencies in a series of aluminates.

Characteristic frequency ranges are as follows:

"Condensed" AlO_4 tetrahedra 900–700 cm^{-1} , "Isolated" AlO_4 tetrahedra 800–650 cm^{-1} , "Condensed" AlO_6 octahedra 680–500 cm^{-1} , "Isolated" AlO_6 octahedra 530–400 cm^{-1} .

Several cases of mixed vibrations (Al—O + Li—O) are found in the particular case of lithium aluminates from abnormal or erratic ^6Li - ^7Li isotopic shifts.

INTRODUCTION

A GOOD deal of controversy has arisen about the vibrational frequencies of AlO_4 tetrahedra and AlO_6 octahedra. The ranges ~ 1200 , 1000 or 900–700 cm^{-1} have been in turn assigned to AlO_4 tetrahedra, whereas the proposed characteristic frequencies of AlO_6 octahedra range from ~ 750 –400 cm^{-1} . SCHROEDER and LYONS [1] recently published a further paper on this matter, where they reached the conclusion that "the AlO_4 tetrahedra can be identified by the presence of an intense absorption in 900–775 cm^{-1} region, medium to strong absorption in 675–575 region, and no strong absorption around 740 cm^{-1} . The AlO_6 octahedra can be identified by strong absorption maxima around 760 and 670 cm^{-1} ...".

Some of their results and conclusions are at variance with our own data, and, moreover, some important spectroscopic aspects of the problem have been neglected in Schroeder and Lyons' paper. It is thus worth while to present a synthesis and a discussion of our own results in this field. Some particular aspects of this problem have already been discussed in previous papers [2–4].

EXPERIMENTAL

Most compounds were synthesized by solid state reaction between $\text{Al}(\text{OH})_3$ and the appropriate oxide or carbonate, at temperatures ranging from 600°C (for the low temperature form of LiAlO_2) to 1340°C (NiAl_2O_4 , $5\text{Al}_2\text{O}_3 \cdot 3\text{Y}_2\text{O}_3$). $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{SrO} \cdot \text{Al}_2\text{O}_3$ were obtained by dehydration of $3\text{CaO}(3\text{SrO}) \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ at 1200°C. Since the results collected in this paper have been obtained over a fairly long period of time (about 7 years), different types of spectroscopic equipment have been used,

[1] R. A. SCHROEDER and L. L. LYONS, *J. Inorg. Nucl. Chem.* **28**, 1155 (1966).

[2] P. TARTE, *Silicates Ind.* **28**, 345 (1963).

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

[4] P. TARTE and R. COLLONGUES, *Ann. Chim.* (13) **9**, 135 (1964).

but most spectra were obtained with the following spectrometers: 1500–400 cm^{-1} region: Unicam SP 100 spectrometer with NaCl and KBr prisms; 420–300 or 420–240 cm^{-1} : Perkin-Elmer 112 spectrometer with either a CsBr or a CsI prism. Samples were run as KBr or KI disks.

SOME SPECTROSCOPIC PROBLEMS INHERENT TO THE STUDY OF INORGANIC SOLIDS

1. *Simplification of the vibrational treatment*

Apart from rather simple cases, a rigorous vibrational treatment of inorganic solids is generally intractable. Strictly speaking, the different vibrational modes are those of the whole unit cell of the crystal; this implies that, in most cases, the number of fundamental frequencies is fairly high and, as a consequence, a detailed assignment of the observed frequencies to the different vibrational modes is nearly impossible.

In such cases, simplified methods must be used. For simple salts (sulphates, phosphates, nitrates, . . .), it is generally admitted, explicitly or implicitly, that the anion (SO_4^{2-} , PO_4^{3-} , NO_3^- . . .) is vibrating independently from the other co-ordinated groups present in the structure. This simplification has been discussed and extended by the author to double oxides and intermediate cases. A detailed discussion has been presented elsewhere [3, 5] and the conclusions may be summarized as follows: if a solid $\text{A}_x\text{B}_y\text{O}_z$ is constituted of AO_p and BO_q co-ordinated groups, two extreme cases must be considered:

- (1) AO_p and BO_q groups have rather different vibrational frequencies: in this case, vibrational interactions between these groups are weak or negligible, and the groups may be considered as vibrating independently. This concept of "separate" or "independent" vibrations has been put forward and discussed by the author a few years ago [3]. From the vibrational point of view, such compounds may be treated as salts. This is the case for a large series of *ortho*-silicates and *ortho*-germanates [5].
- (2) AO_p and BO_q groups have similar vibrational frequencies; in this case, the vibrational interactions between the groups may be so large that the concept of "separate" vibrations is meaningless: the vibrations are those of several groups, or of the unit cell, taken as a whole. Good examples of such interactions are found in II–III spinels with normal structure (bivalent cation on tetrahedral sites [6]).

Between these extremes, a number of intermediate cases are characterized by weak or moderate interactions. Such cases are easily observed in the i.r. spectra of some lithium compounds, where they appear as abnormally low or erratic ^6Li – ^7Li isotopic shifts [5].

It is quite evident that the assignment of an absorption band to a vibrational mode of a given co-ordinated group is meaningful only if the concept of "separate" vibrations is a good approximation for the group under consideration.

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

[6] P. TARTE and J. PREUD HOMME, *Acta Cryst.* **18**, 227 (1963).

2. Factors influencing the vibrational frequencies of a co-ordinated group AO_n .

It is actually well known that, apart from the chemical nature and the valency state of the cation A, the value of the co-ordination number n is the principal factor determining the vibrational frequencies of a co-ordinated group AO_n : the smaller the co-ordination number, the shorter the bond length and hence the higher the vibrational frequencies.

The relation between vibrational frequencies and co-ordination number is only an approximate one, first because there is always a more or less important influence of the neighbouring groups (in other words, the concept of "separate" vibrations is always an approximation), second because the vibrational frequencies are affected by any distortion or deformation of the co-ordinated groups (these deformations are frequent in solids), and third because of an additional effect, namely the "isolated" or "condensed" state of the co-ordinated groups under consideration.

This effect is well known for some series of compounds, such as borates, phosphates or silicates: the stretching frequencies of "condensed" groups (co-ordinated groups interlinked by common oxygen atoms to form chains, or sheets or tridimensional networks) are significantly higher than the stretching frequencies of "isolated" groups (as in *ortho*-borates, phosphates or silicates). This is explained qualitatively by important vibrational interactions between neighbouring (identical) groups and is confirmed by a semi-quantitative mathematical treatment by MATROSSI [7]: the observed frequencies are those, not of a AO_n group, but of a chain, of a sheet or of a tridimensional network of such groups.

As a consequence, the stretching frequencies of *condensed* AO_6 (octahedral) groups may be as high as the stretching frequencies of *isolated* AO_4 (tetrahedral) groups, a situation which may lead to serious errors of interpretation if the above-mentioned effects are neglected.

When stating vibrational frequencies of co-ordinated groups AO_n , it is thus of utmost importance to clearly specify if the groups under consideration are "isolated" or "condensed".

Tables showing the importance of these effects have already been published by the author [3, 5].

APPLICATION TO THE VIBRATIONAL BEHAVIOUR OF Al—O BONDS

(a) General considerations

The characteristic frequencies of AlO_n co-ordinated groups proposed by different authors are collected in Table 1. The agreement is fairly good for tetrahedral AlO_4 groups, but significant discrepancies arise in the case of octahedral AlO_6 groups.

No discussion will be given here of the higher figures of 1000 and even 1200 cm^{-1} proposed in some earlier works for AlO_4 tetrahedra. These results were obtained with aluminosilicates, and such high frequencies are clearly related, not to AlO_4 tetrahedra, but to Si—O—Al mixed vibrations.

[7] F. MATROSSI, *J. Chem. Phys.* **17**, 679 (1949).

"Condensed" AlO_4 tetrahedra. This type of arrangement is found in numerous aluminates, and in some transition aluminas. Three examples only will be quoted here, namely $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ and $8\text{Al}_2\text{O}_3$ (Fig. 1).

The individual patterns are quite different, but are characterized by a common feature, namely the strong, more or less complex, absorption in the region $900\text{--}750\text{ cm}^{-1}$. This absorption must be assigned to AlO_4 tetrahedra or, more precisely, to some stretching vibrations of a lattice of interlinked AlO_4 tetrahedra. In the author's opinion, a more detailed discussion of the spectra, or of individual bands, is actually useless, in view of the complexity of the structure and of the spectra of these compounds. It could be just suggested that the fairly strong absorption observed

Table 1

	AlO_4 Tetrahedra	AlO_6 Octahedra	References
Al—O vibrational frequencies (cm^{-1})	900–800	near 750	KOLESOVA [8–10]
	900–775 and 675–575	760 and 670	SCHROEDER and LYONS [1]
	Condensed: 900–700	Condensed: 680–500	TARTE [3, 11] and this work
	Isolated: 800–650	Isolated: 530–400	

in the $400\text{--}500\text{ cm}^{-1}$ region may be due, at least in part, to some bending motion of the AlO_4 lattice.

"Isolated" AlO_4 tetrahedra. "Isolated" AlO_4 tetrahedra are found in some spinel aluminates and in the 3–5 rare earth aluminates ($3\text{R}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$) with garnet structure. In addition, structures containing "isolated" AlO_4 tetrahedra may be obtained with some convenient ferrites, where a low amount of tetrahedrally co-ordinated iron is replaced by aluminum (dilute solid solution). One example of each of these cases will be given here.

The spectrum of the garnet aluminate $5\text{Al}_2\text{O}_3 \cdot 3\text{Y}_2\text{O}_3$ is represented in Fig. 2. The pattern in the high-frequency region ($700\text{--}800\text{ cm}^{-1}$) is similar to the pattern given by garnet germanates [5], and the assignment of the three bands observed at 790, 730 and 697 cm^{-1} to the stretching vibrations of AlO_4 tetrahedra in the garnet structure is quite evident. The multiplicity of the bands is the result of two combined effects, namely vibrational couplings and deformation splitting. These effects have been discussed at length in previous papers [3, 5].

The spinel aluminate $\text{LiAl}_5\text{O}_8(\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3)$ gives an extremely complicated spectrum (Fig. 3), the detailed assignment of which is impossible (this point will be briefly discussed in the next section); but here again, the very strong bands in the

[8] V. A. KOLESOVA, *Opt. i Spektroskopia* **6**, 38 (1959).

[9] V. A. KOLESOVA, *Opt. i Spektroskopia* **10**, 414 (1961).

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

[11] P. TARTE, *Proc. Int. Conf. on Non-Crystalline Solids*, p. 549, Delft (1964).

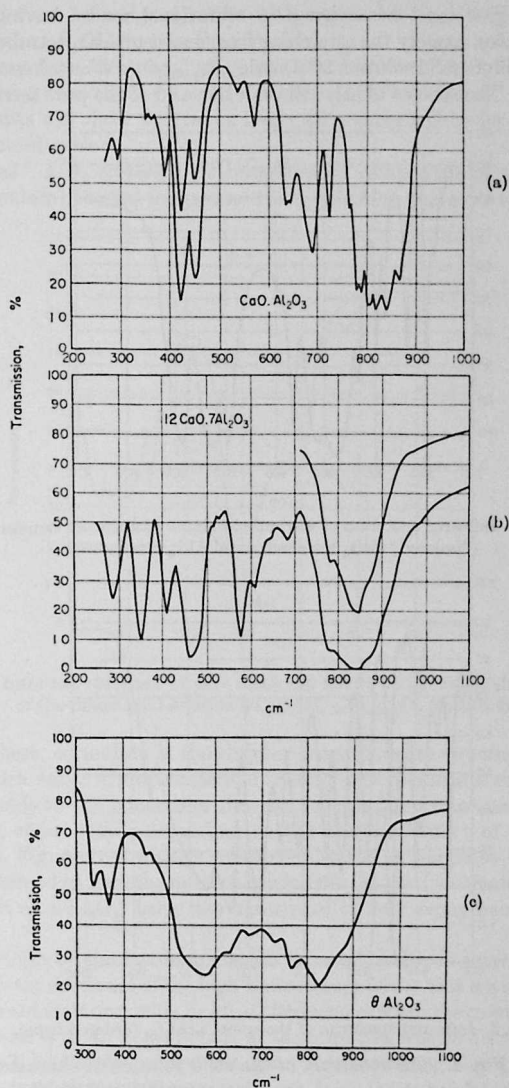


Fig. 1(a, b and c). Infra-red spectra of compounds with "condensed" AlO_4 tetrahedra: $\text{CaO} \cdot \text{Al}_2\text{O}_3$; $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$; $\theta\text{-Al}_2\text{O}_3$.

700–800 cm^{-1} region must be assigned to vibrational modes having the highest possible frequencies, namely the stretching frequencies of AlO_4 tetrahedra.

Finally, the dilute solid solution $2\text{CaO} \cdot (\text{Al}_{0.02}\text{Fe}_{0.98})_2\text{O}_3$ will be taken as an example of the last type. The spectra of this solid solution and of the pure ferrite compound

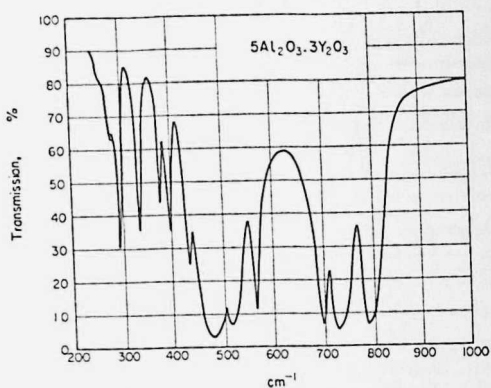


Fig. 2. Infra-red spectrum of yttrium aluminate with garnet structure ("isolated" AlO_4 tetrahedra and AlO_6 octahedra).

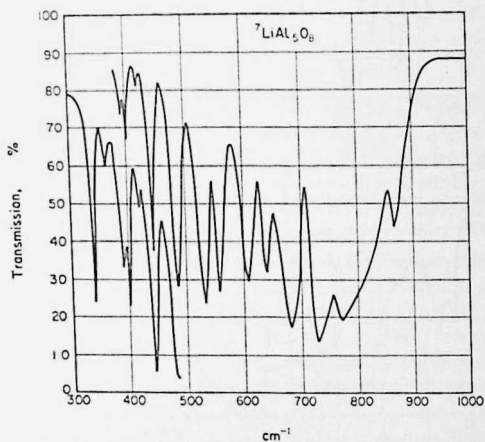


Fig. 3. Infra-red spectrum of the spinel LiAl_5O_8 (ordered type).

are compared in Fig. 4. The spectrum of the solid solution is characterized by the occurrence of a weak band at 784 cm^{-1} , the relative intensity of which depends on the amount of Al-Fe isomorphic replacement, as has been shown by a detailed infra-red study of the whole series of solid solutions $2\text{CaO} \cdot (\text{Fe}_{1-x}\text{Al}_x)_2\text{O}_3$ with x up to 0.70 [12].

[12] P. TARTE, *Rev. Chim. Minérale* **1**, 425 (1964).

This band must be assigned to the AlO_4 tetrahedra "isolated" (as far as dilute solid solutions are considered) in the structure.

It is evident from the preceding results that "isolated" AlO_4 tetrahedra absorb at slightly, but systematically lower frequencies than "condensed" AlO_4 tetrahedra. The next results will show that much larger differences will be found in the case of octahedral co-ordination.

"Condensed" AlO_6 octahedra. Representative compounds of this category are $\alpha\text{-Al}_2\text{O}_3$ (corundum), the low temperature form of LiAlO_2 , and some spinel aluminates.

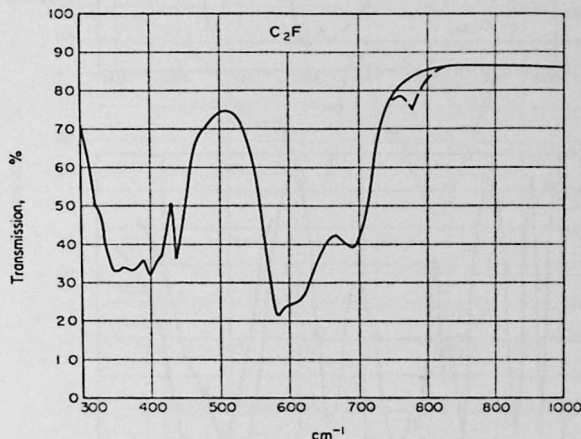


Fig. 4. Infra-red spectrum of pure dicalcium ferrite $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ (full line) and of the dilute solid solution $2\text{CaO}\cdot(\text{Al}_{0.92}\text{Fe}_{0.08})_2\text{O}_3$ (dashed line).

Among these, corundum is the simplest case, since its structure is built up by AlO_6 octahedra only. Unfortunately, a number of experiments carried out in this laboratory leads to the conclusion that the i.r. spectrum of corundum is not fully reproducible, some details depending on the thermal history of the sample [13]. Nevertheless, Fig. 5 gives what is considered by the author to be the most reliable spectrum obtained so far: the most characteristic feature (which anyway is common to all spectra of $\alpha\text{-Al}_2\text{O}_3$) being the occurrence of two strong bands near 650 and 600 cm^{-1} .

The spectrum of the low-temperature form of LiAlO_2 is reproduced in Fig. 6, together with the spectrum of the high-temperature form: this is a clear-cut example of the downward shift occurring in Al—O frequencies when the co-ordination number is changed from 4 to 6. Some details of these spectra will be discussed in the next section: it will be simply pointed out, here, that the strong absorption due to AlO_6 octahedra is centred near 600 cm^{-1} .

Finally, the spectrum of natural MgAl_2O_4 (Fig. 7) will be taken as an example of a normal II—III spinel, with 6-fold co-ordinated aluminum.

[13] P. TARTE, Unpublished results.

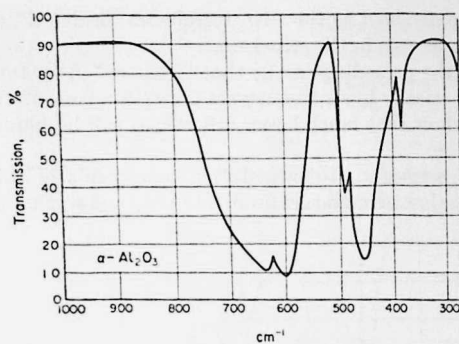


Fig. 5. Infra-red spectrum of $\alpha\text{-Al}_2\text{O}_3$.

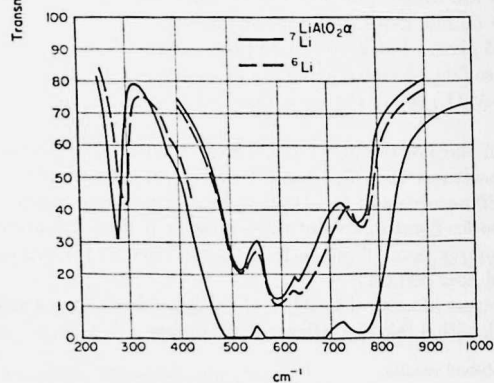
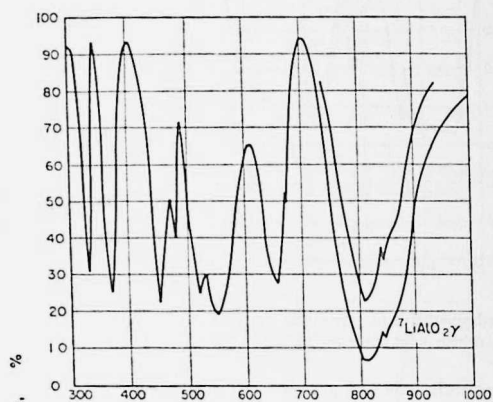


Fig. 6. Compared infra-red spectra of the high- (γ) and of the low- (α) temperature forms of LiAlO_2 .

Considerable caution must be exercised here in the assignment of the bands, since it has been shown in a previous paper [6] that the vibrational frequencies of the different co-ordinated groups are frequently mixed up in normal II-III spinels.

Since, however, all normal II-III aluminate spinels investigated so far exhibit a strong band in the 670 cm^{-1} region, irrespective of the chemical nature of the bivalent cation (in a normal XAl_2O_4 spinel, this band is observed in the region $650\text{--}680\text{ cm}^{-1}$, for $\text{X} = \text{Mg, Co, Mn, Zn or Fe}$), it may be assumed that this band is essentially (but not purely) an Al—O stretching vibration of the AlO_6 lattice.

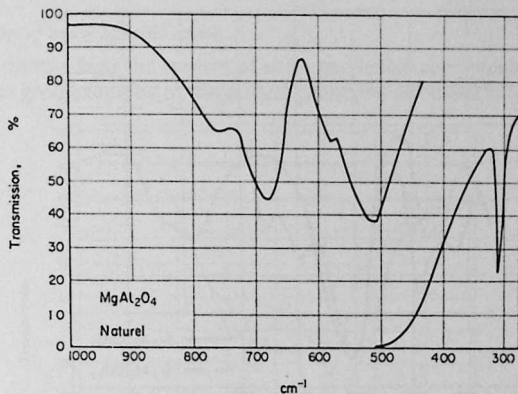


Fig. 7. Infra-red spectrum of the natural spinel MgAl_2O_4 .

It may be concluded from these data that "condensed" AlO_6 octahedra are characterized by strong absorption bands in the $680\text{--}500\text{ cm}^{-1}$ region.

The higher figure of 760 cm^{-1} proposed by KOLESOVA [8], followed by SCHROEDER and LYONS [1], refers to bands of weak or even negligible intensity, which could well be combination frequencies (see next section for the case of LiAlO_2), or to bands which (in aluminum silicates) could well be assigned to mixed Si—O—Al vibrations.

"Isolated" AlO_6 octahedra. Such structural units are present in the rare earth garnet aluminates $3\text{R}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ already mentioned above, in the more classical garnets such as $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, and in the so-called hydrogarnets $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ or $3\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ (the formula of these compounds being more correctly written $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$).

The spectrum of the hydrogarnet $\text{Sr}_3\text{Al}_2(\text{OH})_{12}$ will be first discussed as being the most clear-cut example for "isolated" AlO_6 octahedra: all the aluminum is six-fold co-ordinated, the OH bands are immediately identified by the OH—OD isotopic replacement, and the Sr—O vibrational frequencies are so low (near 200 cm^{-1} in a number of Sr compounds) that they cannot interfere with Al—O vibrations. The spectrum Fig. 8 immediately proves that the strong band at 510 cm^{-1} is an essentially "pure" AlO_6 vibration, and that no other AlO_6 band appears at higher frequencies; the corresponding calcium compound exhibits a similar strong band at 530 cm^{-1} . The medium-intensity absorption in the $400\text{--}300\text{ cm}^{-1}$ region is

probably related to other AlO_6 vibrations more or less affected by OH (OD) bending or torsional motions.

In the yttrium-aluminum garnet $5\text{Al}_2\text{O}_3 \cdot 3\text{Y}_2\text{O}_3$, 6Al atoms (out of 10) are four-fold co-ordinated, the remaining 4 being six-fold co-ordinated. The spectrum of this compound (Fig. 2) has already been discussed from the point of view of AlO_4 vibrations, which were assigned to the three strong bands of the $700\text{--}800\text{ cm}^{-1}$ region. The strong bands near 500 cm^{-1} are in turn assigned to stretching vibrations of isolated AlO_6 octahedra. Other *a priori* possible assignments would be bending vibrations

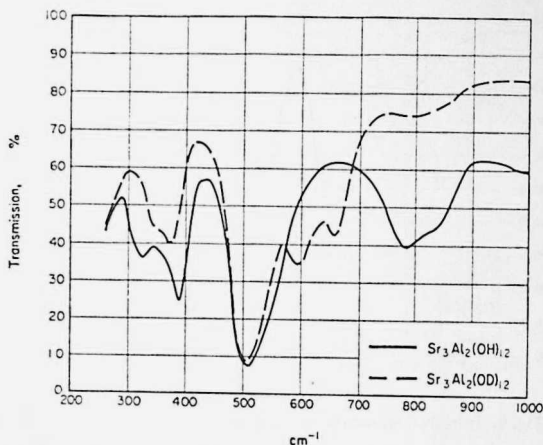


Fig. 8. Infra-red spectrum of the hydrogarnet $\text{Sr}_3\text{Al}_2(\text{OH})_{12}$ and of the deuterated compound.

of AlO_4 tetrahedra, and stretching vibrations of YO_8 dodecahedra. Experimental data on the bending frequencies of isolated AlO_4 tetrahedra are completely missing; but from the $700\text{--}800\text{ cm}^{-1}$ value corresponding to the stretching motions, the bending frequencies may be estimated to lie in the $300\text{--}400\text{ cm}^{-1}$ region. Now, as far as Y—O frequencies are concerned, it must be noticed that the corresponding isotypic iron compound $5\text{Fe}_2\text{O}_3 \cdot 3\text{Y}_2\text{O}_3$ has no absorption band in the 500 cm^{-1} region, and that Y—O stretching frequencies corresponding to 8-fold co-ordination of yttrium have been found in the $300\text{--}400\text{ cm}^{-1}$ region in the spectrum of yttrium *ortho*-borate YBO_3 [14].

It is thus very highly probable that at least some of the strong bands near 500 cm^{-1} in the spectrum of $5\text{Al}_2\text{O}_3 \cdot 3\text{Y}_2\text{O}_3$ must be assigned to the stretching vibrations of AlO_6 octahedra. This is in full agreement with the unequivocal assignment already discussed for $\text{Sr}_3\text{Al}_2(\text{OH})_{12}$.

Finally, the case of natural garnets $\text{X}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, with $\text{X}^{\text{II}} = \text{Mg, Fe, Mn and Ca}$, will be briefly reported. A detailed assignment of the spectra of these compounds is not easy, because of the occurrence of both SiO_4 bending and AlO_6 stretching

[14] J. P. LAPERCHES and P. TARTE, *Spectrochim. Acta* 22, 1201 (1966).

frequencies in the same spectral region; however, a systematic discussion, which has been reported elsewhere [5] leads to the conclusion that, in these compounds, the AlO_6 stretching frequencies are represented by two bands located, the first one in the region $500\text{--}460\text{ cm}^{-1}$, and the second one near 390 cm^{-1} .

In conclusion, "isolated" AlO_6 octahedra are characterized by strong bands in the $530\text{--}400\text{ cm}^{-1}$ region. It may be objected that one type of structure only (the garnet type) has been investigated here; the chemical compositions, however, are so widely different, that the proposed frequency range may be considered as representative of AlO_6 isolated octahedra.

(b) *Discussion of some specific cases*

We shall discuss here the spectra of some particular compounds, either because they represent good examples of the general principles discussed in previous sections,

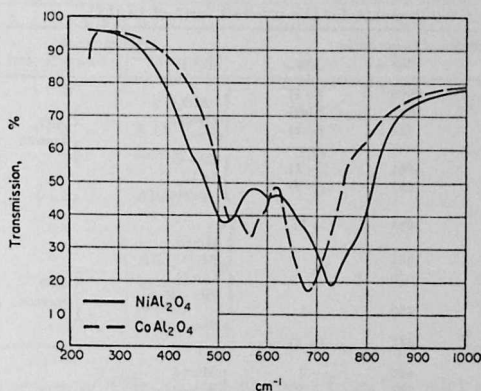


Fig. 9. Infra-red spectra of the spinels CoAl_2O_4 (normal) and NiAl_2O_4 (essentially inverse).

or because our results or interpretations are at variance with those presented by SCHROEDER and LYONS [1].

(1) *II-III Aluminate spinels.* The spectra of CoAl_2O_4 and NiAl_2O_4 (Fig. 9) are taken as an example of a normal (CoAl_2O_4) and an essentially inverse (NiAl_2O_4) spinel. Although the co-ordination of Al is octahedral in the first compound and in part tetrahedral in the second, the difference in position of the high-frequency band is rather small (683 and 728 cm^{-1} for Co and NiAl_2O_4 respectively). This is due, in part, to the fact that we are dealing here with *condensed* octahedra in the first compound, and *isolated* tetrahedra in the second: here is a good example of a point discussed previously, namely the stretching frequencies of condensed AO_6 octahedra may be as high as the stretching frequencies of isolated AO_4 tetrahedra. Moreover, it should be remembered that the vibrational modes of II-III spinels are not really "independent" vibrations, this leading to some "averaging" of the vibrational frequencies.

In conclusion, we are dealing here with a most unfavourable case, and it would

be quite uncautious to conclude, from infra-red data alone, the normal or inverse structure of CoAl_2O_4 and NiAl_2O_4 spinels.

(2) LiAl_5O_8 spinel. The spectrum of this compound is extremely complicated and the author has shown that this complexity, which is highly abnormal for a spinel, may be explained—at least in part—by two factors, namely important vibrational interactions, and the occurrence of both cations (Li and Al) on both types of crystallographic sites (tetrahedral and octahedral) [4]. However, the distribution of the cations on tetrahedral and octahedral sites is not random, as admitted by SCHROEDER and LYONS [1] after DEBRAY and HARDY [15], but on the contrary ordered as far as the sample has been obtained at 1250°C or below. An order-disorder transition takes place near 1270° only; this transition brings out important changes in the i.r. spectrum, but these changes have already been discussed elsewhere [4].

Table 2. Vibrational frequencies, ^6Li - ^7Li isotopic shifts and band assignments for the ordered form of LiAl_5O_8

^6Li	Vibrational frequencies ^7Li	$\Delta\nu$	This paper	Assignments Schroeder and Lyons
870	869	(-1)	} AlO_4 stretch	} AlO_6 stretch
770	772	(+2)		
728	729	(+1)		
682	681	(-1)	} Al—O (AlO_6 ?) stretch	
649	647	(-2)		
625	614	-11	} Mixed Al—O Li—O vibrations	} LiO_4 stretch
588				
567	561			
541	536			
532				
494	490	-4		
447	446	(-1)	} Mixed Al—O Li—O vibrations	
423	420	-3		
	401			
400	390			
365 (?)	361	-4 ?		
338	337	(-1)		

We shall here limit ourselves to the discussion of some band assignments which do not agree with those of SCHROEDER and LYONS [1]. Our observed frequencies for the ^6Li and the ^7Li compound are collected in Table 2*, together with the controversial assignments. If Schroeder and Lyons' assignment is accepted, only the weak band at 869 cm^{-1} is left for AlO_4 tetrahedra, an untenable position if it is remarked that this band disappears in the disordered form, the structure of which still contains AlO_4 tetrahedra. Moreover, this assignment is in disagreement with the results discussed in the previous section. Thus, the assignment of the two strong high-frequency bands to AlO_4 stretch is much more reliable. The two next bands (681 and 647 cm^{-1}) exhibit no significant ^6Li - ^7Li isotopic shift and thus are essentially Al—O

* There is nearly a systematic difference between our frequencies and those of Schroeder and Lyons. The reason for this discrepancy is not evident but, since our spectrometer was carefully calibrated against frequency standards, we assume our values to be essentially correct.

[15] L. DEBRAY and A. HARDY, *Compt. Rend. Acad. Sci. Paris* 251, 725 (1960).

vibrations, possibly AlO_6 stretch. Most of the remaining bands are more or less affected by a significant ^6Li - ^7Li isotopic shift, but either this shift is much inferior to the theoretical value for a "pure" LiO_4 vibration, or the general patterns for ^6Li and ^7Li compounds are sufficiently different so as to prevent any correlation between individual bands: nearly all these bands must be assigned to mixed AlO_6 - LiO_4 vibrations. This is a very clear-cut example of important vibrational interactions between different groups having similar vibrational frequencies.

(3) LiAlO_2 , *high and low temperature forms*. The spectra of both forms have

Table 3

H— LiAlO_2				L— LiAlO_2			
^6Li	^7Li	$\Delta\nu$	Assignment	^6Li	^7Li	$\Delta\nu$	Assignment
844	843	(-1)	} AlO_4 stretch	767	760	-7	} Combination band
812	812	0					
676	674	(-2)		~640	~640	0	} AlO_6 stretch
656	654	(-2)		~595	~595	0	
				519	520	(+1)	
561	553	-8	AlO_4 - LiO_4 lattice	295	277	-18	LiO_6 stretch
520	522	(+2)	AlO_4				
496	481		} AlO_4 - LiO_4 lattice Mixed frequencies				
481							
461	453	-8					
373	370	-3					
343	330	-13					

already been presented (Fig. 6) and discussed from the point of view of the Al—O frequency versus co-ordination change.

Here again, some assignments will be discussed and revised with the help of ^6Li - ^7Li isotopic shifts (Table 3). All the high-frequency part of the spectrum of H— LiAlO_2 is clearly related to Al—O vibrations (stretching motions of the AlO_4 lattice), but the 522 cm^{-1} band, assigned by Schroeder and Lyons to a Li—O stretch, is also an Al—O vibration (probably some bending motion of the AlO_4 lattice, although the hypothesis of a fairly low frequency stretch cannot be completely rejected). All remaining bands exhibit significant, although abnormally low, ^6Li - ^7Li shifts, and hence must be assigned to complex mixed vibrations of the LiO_4 - AlO_4 lattice.

The spectrum of L— LiAlO_2 is more simple: the low frequency band (below 300 cm^{-1}) exhibits a ^6Li - ^7Li isotopic shift which is of the right order of magnitude for a pure (or nearly so) LiO_6 stretching vibration, and the three strong bands in the 650–500 cm^{-1} are clearly AlO_6 vibrations. There just remains the medium-intensity band near 760 cm^{-1} , which has been assigned by KOLESOVA [10], followed by SCHROEDER and LYONS [1] to an AlO_6 stretch; but this assignment must be revised in view of the significant ^6Li - ^7Li isotopic shift. This band cannot be a pure LiO_6 vibration for two reasons: first, because the shift is much inferior to the theoretical

value, and second, because the frequency itself is much too high for a LiO_6 vibration (which in fact is observed below 300 cm^{-1}).

On the other hand, the occurrence of mixed $\text{LiO}-\text{AlO}$ vibrations is fairly improbable here, since the vibrational frequencies of LiO_6 and AlO_6 octahedra are so different (<300 and $500\text{--}650\text{ cm}^{-1}$ respectively) that the possibility of mutual vibrational perturbations is very remote. There remains the possibility of a combination (summation) frequency $\text{LiO}_6 + \text{AlO}_6$, which actually seems to be the most reasonable hypothesis.

(4) *Calcium aluminates* $\text{CaO}\cdot\text{Al}_2\text{O}_3$, $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$, $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ and $3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$. Our spectra (Fig. 1 for the 1.1 and 12.7 compounds) are somewhat or very different from those of SCHROEDER and LYONS [1]. A final explanation of these discrepancies is actually impossible in most cases, since a clear-cut comparison of the results seems to be very difficult indeed.

As far as the 3.5 compound is concerned, it is actually well known that the 3.5 molecular ratio has been discredited, the true ratio being 1.2.

The case of the 1.1, 12.7 and 5.3 compounds is much more complicated, the relevant points being as follows:

- (a) Our spectra of the 1.1, 12.7 and 5.3 compounds are different from those of Schroeder and Lyons.
- (b) Polymorphism may be invoked in the case of the 5.3 compound, which exists, either as a metastable, orthorhombic phase [16], or as a cubic phase which is in fact the 12.7 compound [17]. However, most of the frequency values given by Schroeder and Lyons for the 5.3 compound are in fact those of the 1.1 compound; moreover, it has been found in our laboratory that initial mixtures corresponding to the 5.3 composition essentially lead to the 1.1 compound if the firing temperature is not sufficiently high.
- (c) There is some apparent inconsistency in Schroeder and Lyons' data for the 1.1 compound since it is impossible to find out in their published spectrum the frequency values collected in their Table 3. Hence, a detailed comparison with our own data is impossible.
- (d) Schroeder and Lyons state in their paper that powdered X-ray diffraction patterns were obtained on all preparations, but they do not precise whether or not these data have been compared with published standard patterns. Their schematic diagram (Fig. 4 of their paper) only gives "the more intense lines".
- (e) Schroeder and Lyons' synthesis temperature ($\sim 1000^\circ\text{C}$) is rather low for calcium aluminates: it appears from the very abundant literature on calcium aluminates that reactions between Al_2O_3 and CaCO_3 are not complete until temperatures of $1200\text{--}1300^\circ\text{C}$ are reached.

As a conclusion, it is suggested that Schroeder and Lyons' samples under discussion were, either not well crystallized, or uncompletely reacted, in view of their rather low synthesis temperature.

Their data on Sr and Ba luminates, however are in good agreement with the spectra obtained in our laboratory.

[16] E. ARUJA, *Acta Cryst.* **10**, 337 (1957).

[17] J. JEEVARATNAM, L. S. DENT-GLASSER and F. P. GLASSER, *Nature* **194**, 764 (1962).

(5) *Tricalcium aluminate* $3\text{CaO}\cdot\text{Al}_2\text{O}_3$. The spectrum of Schroeder and Lyons is in essential agreement with ours (which has been published elsewhere [18]).

But the interpretation proposed by Schroeder and Lyons remains open to discussion. This interpretation relies on a asserted peculiar structure of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, where AlO_6 groups are in the form of very elongated octahedra with two widely different Al—O distances, namely four Al—O short distances (1.9 Å) forming a square, and two others equal to 2.6 Å: the complex series of bands in the 900–800 cm^{-1} region

Table 4

Compound	Co-ordination number	Al—O distances	Ref.	Al—O frequencies
$\text{CaO}\cdot\text{Al}_2\text{O}_3$ $\gamma(\text{high})$	4	1.68 to 1.82	(1)	900–650
LiAlO_2 $\alpha(\text{low})$	4	1.755 and 1.766	(2)	850–650
LiAlO_2	6	1.90	(3)	640–520
$\alpha\text{-Al}_2\text{O}_3$	6	1.92	(4)	650–590
Pyrope	6	1.886	(5)	460–390
General data	4	1.77–1.80	(6)	900–650
	6	1.85–1.98		680–400

(1) M. W. DOUGILL, *Nature* **180**, 292 (1963); cited in H. F. W. TAYLOR: the *Chemistry of Cements*, Vol. 1, p. 153. Academic Press (1964).

(2) M. MAREZIO, *Acta Cryst.* **19**, 396 (1965).

(3) M. MAREZIO and J. P. REMEIK, *J. Chem. Phys.* **44**, 3143 (1966).

(4) R. E. NEWNHAM and Y. M. DE HAAN, *Z. Krist.* **117**, 235 (1962).

(5) G. V. GIBBS and J. V. SMITH, *Am. Mineralogist* **50**, 2023 (1965).

(6) Al—O distances from *International Tables for X-ray crystallography*, Vol. 3, p. 262. Kynoch Press (1962).

is assigned to the square AlO_4 group with short distances, whereas the strong band near 740 cm^{-1} is assigned to the long (2.6 Å) Al—O distances.

Now, it is worth while to point out that:

(1) There is no definite proof of the occurrence of elongated octahedra in the structure of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$. After JEFFERY [19], "the structure determination of tri-calcium aluminate has still to be completed, and at present the evidence for a postulated structure or pseudo-structure is too doubtful to make discussion worth while".

(2) Even if this type of structure is fundamentally correct, the assignment of the 740 cm^{-1} frequency to an Al—O bond with 2.6 Å distance seems to be untenable if one considers the actual correlations between co-ordination number, Al—O distances and Al—O stretching frequencies (Table 4): it is quite evident that the stretching frequency of an Al—O bond with 2.6 Å distance should be very low, even if due allowance is made for possible interactions or perturbations related to environmental influences. In the author's opinion, all the strong bands in the 700–900 cm^{-1} region

[18] P. TARTE, *Silicates Ind.* **31**, 343 (1966).

[19] J. W. JEFFERY, *The Chemistry of Cements* (Edited by H. F. W. TAYLOR), Vol. 1, p. 160. Academic Press (1964).

must be assigned to fairly short Al—O distances in either distorted AlO_6 octahedra or AlO_4 tetrahedra.

(6) *Glassy phases.* Infra-red spectroscopy has already been used for determining the co-ordination number of aluminum in a series of glasses. The infra-red spectrum of a series of aluminosilicate glasses is characterized by the occurrence, in the 700–800 cm^{-1} region, of a broad band whose intensity increases with the amount of aluminum, and which is assigned to AlO_4 tetrahedra.

This assignment is in agreement with the characteristic frequency ranges discussed

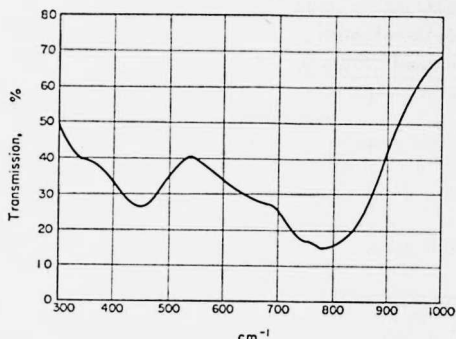


Fig. 10. Infra-red spectrum of a glassy phase $2\text{CaO} \cdot (\text{Al}_{0.8}\text{Fe}_{0.2})_2\text{O}_3$.

previously, and with other experimental data obtained by quite different methods such as molar refractivity [20] and X-ray fluorescence [21]. The infra-red spectra of these glasses have been discussed elsewhere [11] and need no further comment here; but it is worth while mentioning that an aluminate glass of entirely different composition, namely $2\text{CaO}(\text{Al}_{0.80}\text{Fe}_{0.20})_2\text{O}_3$, also has strong infra-red bands near 800 cm^{-1} which may be assigned with confidence to AlO_4 tetrahedra (Fig. 10): it is encouraging that the absorption bands related to AlO_4 tetrahedra are found in the same spectral region for glassy structures of so widely different compositions.

CONCLUSIONS

Through the different examples discussed in this paper, it appears that a more or less detailed assignment of the infra-red spectrum of inorganic solids is by no means an easy task when compounds of the so-called "double oxides" type are dealt with. Vibrational interactions are frequent, either between identical groups interlinked by common oxygen atoms (this is the case of "condensed" groups), or between different groups characterized by similar vibrational frequencies: such vibrational interactions preclude the assignment of the observed infra-red bands to the vibration modes of a specific co-ordinated group. However, if due care is exercised in the choice of the compounds investigated and in the interpretation of the spectra, it is possible to study how the cation-oxygen vibrational frequencies depend on the co-ordination

[20] D. E. DAY and G. E. RINDONE, *J. Am. Ceram. Soc.* **45**, 489 (1962).

[21] D. E. DAY and G. E. RINDONE, *J. Am. Ceram. Soc.* **45**, 579 (1962).

number *and also on environmental conditions*, an important factor which has been nearly completely neglected by most authors.

Only if these conditions are fulfilled is it possible to define spectral regions which may be considered as really characteristic of a given type of co-ordinated group.

Further examples of similar problems will be published in due course.

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