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Infrared studies of spinels—V. Lithium spinels of the type LiXY_4O_8

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Abstract—The i.r. spectrum of ordered spinels Li$X^{III}Y_4^{III}O_8$ (X^{III} = Ga, Fe, In; Y^{III} = Cr, Rh) are discussed and assigned with the help of ^{6}Li–^{7}Li isotopic shifts. Two bands only may be assigned to definite motions of specific cations or coordinated groups: one band in the 450–350 cm^{-1} region exhibits an important ^{6}Li–^{7}Li isotopic shift and is assigned to a displacement of the lithium cation. The lowest-lying frequency strongly depends on the mass of the X^{III} tetrahedral cation and thus is assigned to a translation of this cation. All the remaining bands, in the 700–500 cm^{-1} region, are related to mixed vibrations involving the simultaneous participation of X^{III} and Y^{III} cations. These assignments completely disagree with those of DEANGELIS *et al.*, which are shown to rely upon erroneous considerations. The disordered phase of $LiGaCr_4O_8$ (statistical distribution of Li and Ga cations on tetrahedral sites) has also been investigated and the main features of its i.r. spectrum are briefly discussed.

INTRODUCTION

SPINELS of the type Li$X^{III}Y_4^{III}O_8$ (X^{III} = Ga, Fe, In; Y^{III} = Cr, Rh) are characterized by a 1:1 ordering of the Li and X^{III} cations on the tetrahedral sites [1].

Some aspects of their i.r. spectrum were first investigated in this laboratory, in connection with the tetrahedral co-ordination of Li [2, 3]; but later on, a systematic investigation [4] led to more comprehensive and more refined assignments, which will be presented in this paper. A rather detailed discussion of our results is justified by the disagreement between our own interpretations and those recently proposed by DE ANGELIS *et al.* [5].

EXPERIMENTAL

Synthesis of the compounds

The synthesis may be carried out by solid state reaction between the stoichiometric quantities of lithium carbonate and the trivalent metal oxides. However, more reactive mixtures are obtained by first transforming the starting mixtures into nitrates, which are progressively heated up to 1000°C [1]. Nevertheless, some difficulties were experienced with the rhodium compounds, and repeated grinding and heating cycles were necessary to obtain compounds free from uncombined rhodium oxide. The purity of all compounds was checked by X-ray diffractometry.

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[1] J. C. JOUBERT, Doctorate Thesis, Grenoble (1965); J. C. JOUBERT and A. DURIF, *Bull. Soc. Franç. Mineral. Crist.* **89**, 26 (1966).

[2] P. TARTE, *Spectrochim. Acta* **21**, 313 (1965).

[3] P. TARTE, *Acad. Roy. Belg., Classe Sci., Mem.* **35**, 4a and 4b (1965).

[4] J. PREUDHOMME, Doctorate Thesis, University of Liège (1970).

[5] B. A. DE ANGELIS, V. G. KERAMIDAS and W. B. WHITE, *J. Solid State Chem.* **3**, 358 (1971).

All attempts to synthesize the corresponding aluminium compound $LiAlCr_4O_8$ were unsuccessful.

For all compounds obtained at 1000°C, the X-ray powder diagram exhibits the 200 peak which reveals the 1:1 ordering on tetrahedral sites (space group T_d^2–$F\bar{4}3m$). $LiGaCr_4O_8$ is the only compound of this family which has been obtained in the disordered state (space group O_h^7–$Fd3m$, with a statistical distribution of Li and Ga on tetrahedral sites). This phase has been obtained according to JOUBERT [1] by heating the ordered compound for a few minutes at 1350°C in a platinum boat, and dropping the boat into water. For the samples prepared in this way, the 200 peak is missing in the X-ray powder diagram, but the strongest peaks of free Cr_2O_3 are weakly, but definitely present, suggesting that some decomposition is beginning at this temperature.

Infrared spectra

The spectra were registered as mentioned in a previous paper [6].

THEORETICAL ANALYSIS

A theoretical analysis of the spinels presenting a 1:1 order on the tetrahedral sites has been carried out by WHITE and DE ANGELIS in 1967 [7]. A more detailed analysis which relies upon the determination of the number of atoms remaining invariant under the different symmetry operations of the group T_d^2–$F\bar{4}3m$ has been published more recently [5]. All the seven predicted i.r. active modes belong to the same T_2 representation. Thirteen modes are Raman active, 3 belonging to the A_1 representation, 3 to the E, and 7 to the T_2 representation. Because of the lack of a center of symmetry, these latest 7 modes should be observed in the i.r. and Raman spectra as well.

RESULTS AND INTERPRETATIONS

The general i.r. pattern appears as fairly homogeneous for the 3 chromium compounds, with 4 bands of strong or medium intensity in the 700–500 cm^{-1} region, one weak, sharp band in the 450 cm^{-1} region, and one band in the low-frequency (220–150 cm^{-1}) region. This pattern is exemplified here by the spectrum of $LiFeCr_4O_8$ (Fig. 1), a compound not obtained by DE ANGELIS *et al.* [5].

In view of the homogeneous appearance of the spectra, there is little point about the band to band correspondence which appears in Table 1. The situation is more complicated for the rhodites, since there are large variations in the relative intensities and in the shapes of the bands. Only for $LiInRh_4O_8$ is the i.r. pattern similar to that of the corresponding chromite. But for $LiGaRh_4O_8$ (Fig. 2) and $LiFeRh_4O_8$, the relative intensities of the bands between 700 and 500 cm^{-1} are so widely different from one compound to another that the band correspondences suggested by Table 1 are by no means evident, and in fact not certain. Likewise, the shape of the band assigned to a Li–O vibration (strong ^6Li–^7Li isotopic shift; see discussion below) is

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

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

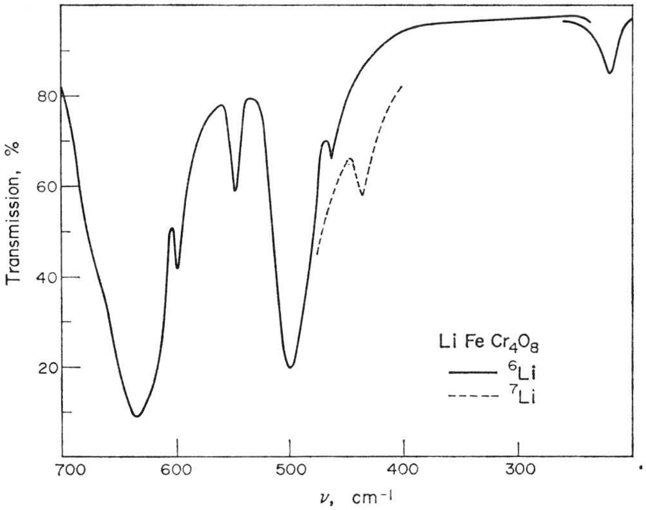

Fig. 1. I.R. spectrum of $\text{LiFeCr}_4\text{O}_8$.

Table 1

$\text{LiGaCr}_4\text{O}_8$			$\text{LiFeCr}_4\text{O}_8$			$\text{LiInCr}_4\text{O}_8$		
^{6}Li	^{7}Li	$\Delta\nu$	^{6}Li	^{7}Li	$\Delta\nu$	^{6}Li	^{7}Li	$\Delta\nu$
652	652	0	635	635	0	657	656	(−1)
612	611	(−1)	598	597	(−1)	582	582	0
565	564	(−1)	547	545	(−2)	543	543	0
515	515	0	498	495	(−3)	498	500	(+2)
470	445	−25	461	435	−26	430	411	−19
220	220	0	219	?		166	166	0
$\text{LiGaRh}_4\text{O}_8$			$\text{LiFeRh}_4\text{O}_8$			$\text{LiInRh}_4\text{O}_8$		
^{6}Li	^{7}Li	$\Delta\nu$	^{6}Li	^{7}Li	$\Delta\nu$	^{6}Li	^{7}Li	$\Delta\nu$
∼640	∼640	0	645	645	0	633	632	(−1)
∼610	∼610	0	594	595	(+1)	565	564	(−1)
∼560	∼560	0	540	540	0	538	537	(−1)
∼520	∼520	0	493	493	0	495	495	0
∼407	∼385	−22	402	376	−26	∼379	∼356	−23
						367	342	−25
	203			?		159	157·5	(−1·5)

very different for the chromites (where it is sharp) and for the rhodites (where it is rather broad, and split into 2 distinct components in the case of $\text{LiInRh}_4\text{O}_8$*).

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* A more or less similar splitting, with 2 components at 411 and 403 cm^{-1}, is *sometimes* observed in the spectrum of $^7\text{LiInCr}_4\text{O}_8$, but this splitting is *not* reproducible: the low-frequency component is of variable intensity and is definitely absent in some spectra of the ^{7}Li compound. Moreover, there is always *one* component only in the spectrum of the ^{6}Li compound. The 403 cm^{-1} band is thus considered as being of spurious origin, although we have been unable to trace any possible impurity which would be responsible for it.

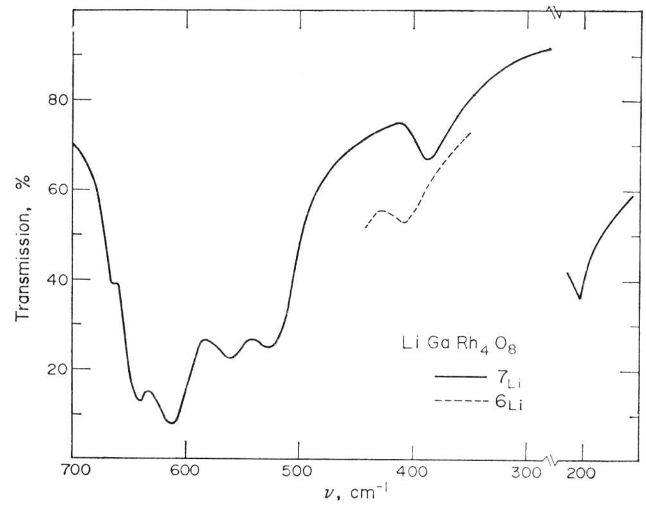

Fig. 2. I.R. spectrum of $LiGaRh_4O_8$.

Assignments

A detailed assignment of all the observed frequencies is actually impossible for several evident reasons:

(1) All the i.r. active modes belong to the same representation T_2 and thus may interact.

(2) All atoms are allowed to move during these vibrations; but the relative amplitudes of motion are unknown, and thus, the actual importance of the vibrational interactions cannot be evaluated. But some of them may be very large since the compounds under consideration are of the double oxide type.

(3) It is thus imperative that definite assignments be restricted to these frequencies for which there is sufficient experimental evidence about the participation of the various atoms. The assignment problems related to spinels and the appropriate experimental methods for solving them, have been outlined in preceding papers [8, 9]. They lead to a coherent interpretation scheme for the normal II–III [6], II–IV and I–VI [10] spinels. In the actual case of $LiX^{III}Y_4^{III}O_8$ spinels, we have collected 2 types of important experimental information, namely ^6Li–^7Li isotopic shifts, and the vibrational behaviour of some solid solutions. The significance of these data, and their contribution to the assignment problem will now be discussed.

^6Li–^7Li *isotopic shifts*

It is evident from the isotopic data (Table 1) that *one band only* is strongly shifted in the spectrum of the corresponding ^6Li–^7Li isotopic compounds, and thus must be assigned to some translation of the lithium cation. This mode has been previously described as an antisymmetric stretch of the LiO_4 tetrahedron [2]; and indeed, the isotopic shift is of the right order of magnitude for this type of vibration [11].

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[8] J. PREUDHOMME and P. TARTE, *Spectrochim. Acta* **27A,** 961 (1971).

[9] J. PREUDHOMME and P. TARTE, *Spectrochim. Acta* **27A,** 845 (1971).

[10] J. PREUDHOMME and P. TARTE, *Spectrochim. Acta* **28A,** 69 (1972).

[11] P. TARTE, *Spectrochim. Acta* **20,** 238 (1964).

Nevertheless, and in view of the double oxide nature of the compounds under discussion, it may be considered as more appropriate to speak about a lithium translation. Any query about this point may be a fruitless one, since we have no information about the displacements of the oxygen atoms. And whatever the final description, the main point of interest is the important contribution of the lithium cation (and of the Li—O bonds) to this vibration.

We may now discuss the possible contribution of the other cations to this frequency. Of interest is the fact that we find 2 nearly linear relationships (one for the chromites, the other for the rhodites) between this frequency and the unit cell parameter a_0 (Fig. 3).

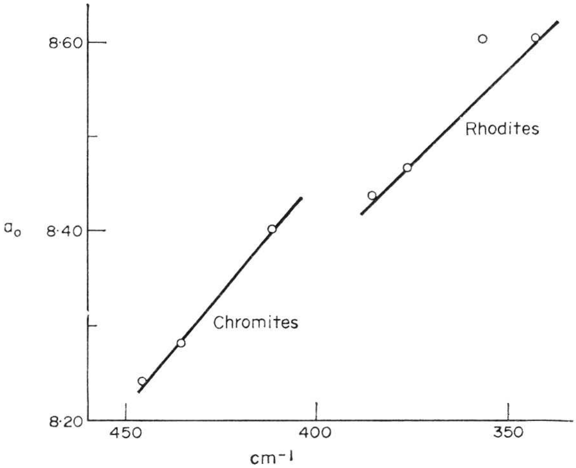

Fig. 3. Relationship between the Li–O frequency and the unit cell parameter a_0.

This would suggest that there is no *important* specific influence of the trivalent octahedral cations, and that the frequency under discussion is *predominantly* related to a lithium translation. But this does not preclude a secondary influence of the octahedral cation (which in fact is suggested by the occurrence of 2 different relationships for the chromites and for the rhodites) and even of the trivalent, tetrahedral cation. For all the remaining bands, the ^{6}Li–^{7}Li isotopic shifts are either non-existent, or non-significant.

Assignment of the remaining frequencies

High-frequency bands. Before discussing the relevant experimental data, it is worth while to come back to some general rules which were derived from our previous studies on normal spinels.

(i) First of all, it has been shown that the highest-frequency strong band must be assigned to a vibration of the coordinated group(s) containing the highest-valency cation. This is in accordance with a large number of consistent experimental data [6, 10], and with the statement that the highest frequency is related to the highest cation–oxygen bonding force, which in turn is strongly correlated with the cation valency [9].

(ii) Of interest is also the mass effect of the cation responsible for this high-frequency vibration. It has been shown through the study of suitable isotopic species that 2 widely different types of behaviour have been observed, depending on the co-ordination of the highest-valency cation. If the high-frequency mode is related to a vibration of the tetrahedral group, we find an isotopic mass effect of the tetrahedral cation [10], and this mode may be conveniently described as the antisymmetric stretch of the tetrahedral group. If, on the contrary, the high-frequency mode is related to a vibration of the octahedral groups, we find no measurable isotopic mass effect of the octahedral cation [6]; thus, this mode may be described as a vibration of the whole oxygen lattice, the restoring force being essentially provided by the octahedral, high-valency cation.

Thus, the presence or the lack of a cationic mass effect may be helpful in determining the nature (tetrahedral or octahedral) of the co-ordinated groups responsible for the high-frequency bands of a spinel.

If we apply these considerations to the actual case of the $LiX^{III}Y_4^{III}O_8$ spinels, the situation is as follows: The octahedral and half of the tetrahedral sites are occupied by cations of the *same* valency (Y^{III} and X^{III}); since, for similar cations, the vibrational frequencies of "isolated" tetrahedral groups and those of "condensed" octahedral groups are of the same order of magnitude (See Table 3 in Ref. [8]), it is evident that, in the actual case, the assignment of the observed frequencies to vibrations of definite coordinated groups will be very difficult. Moreover, since all the i.r. active vibrations belong to the same representation, the probability of vibrational interactions is very high, and an assignment to specific vibrations of either XO_4 or YO_6 groups may be meaningless.

This last statement is strongly supported by the frequency values quoted in Table 1 for the pure compounds, and also by the vibrational behaviour of $Li(Ga_{1-x}In_x)Cr_4O_8$ solid solutions.

Let us first consider the 2 chromites $LiFeCr_4O_8$ and $LiGaCr_4O_8$. Their unit cell parameters a_0 are not very different (8·280 Å for the former, and 8·242 Å for the latter), and thus the influence of this factor on the vibrational frequencies must be small. On the other hand, it has been shown previously that, if isomorphic compounds are considered, and in the absence of important vibrational interactions, the frequencies corresponding to the antisymmetric stretching motion are significantly higher for GaO_4 than for FeO_4 tetrahedra [3].

Thus, it may be predicted that, as far as "localized" GaO_4, FeO_4 and CrO_6 vibrations could be considered, the frequencies related to CrO_6 groups should be nearly the same for $LiFeCr_4O_8$ and $LiGaCr_4O_8$, whereas the band related to the vibration of the tetrahedral group should be observed at a significantly lower frequency for $LiFeCr_4O_8$ than for $LiGaCr_4O_8$. If we now consider the frequency differences between the corresponding bands of these compounds (Table 2), we do not

Table 2

$LiGaCr_4O_8$	652	611	564	515
$LiFeCr_4O_8$	635	597	545	495
Difference	17	14	19	20
$LiInCr_4O_8$	656	582	543	500

find any characteristic behaviour, all the frequencies being more or less lowered when passing from the gallium to the iron compound. The greatest frequency differences are found for the bands located near 550 and 500 cm^{-1}, which are thus the best possible candidates for the assignment to the tetrahedral group. But, besides the fact that these frequencies are rather low for such an assignment (frequencies related to $\mathrm{GaO_4}$ or $\mathrm{FeO_4}$ groups are generally observed in the 750–650 cm^{-1} region), it may be noticed that the corresponding frequencies are nearly the same for the indium and for the iron compound: this is definitely against the suggested assignment, since the indium atom is about 2 times as heavy as the iron atom, and the corresponding frequency should be significantly lower (this type of mass effect is easily observed in the lowest frequency band: see below). It is thus impossible to assign any of the considered frequencies to a specific vibration of the $X^{\mathrm{III}}\mathrm{O}_4$ tetrahedral group. This conclusion is fully substantiated by the vibrational behaviour of the $\mathrm{Li(Ga}_{1-x}\mathrm{In}_x)\mathrm{Cr_4O_8}$ solid solutions (Fig. 4). Apart from the high-frequency band near 650 cm^{-1}, which is hardly displaced and thus is certainly *not* related to a vibration of the $X^{\mathrm{III}}\mathrm{O}_4$ tetrahedral group, the 3 bands in the 600–500 cm^{-1} region are progressively shifted by an amount which is of the same order of magnitude for the 3 bands: thus, none of them can be specifically assigned to a vibration of the tetrahedral $\mathrm{GaO_4}$ or $\mathrm{InO_4}$ group.

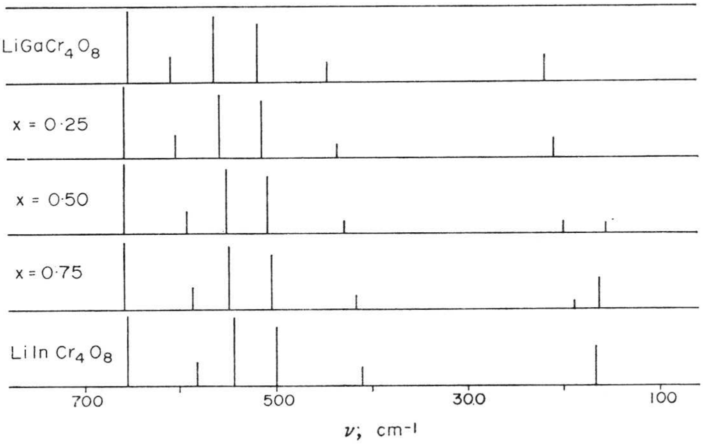

Fig. 4. Schematic i.r. spectra of $\mathrm{Li(Ga}_{1-x}\mathrm{In}_x)\mathrm{Cr_4O_8}$ solid solutions, showing (1), the practical lack of influence on the highest-frequency band, (2) the continuous shift of the medium-frequency bands, and (3) the 2-modes behaviour of the low-frequency band.

It may thus be concluded, from both experimental evidence and very simple theoretical expectations, that the 4 high-frequency bands are not related to vibrations of specific co-ordinated groups, but must be assigned to complex motions of the whole spinel lattice, involving the simultaneous participation of both tetrahedral X^{III} and octahedral Y^{III} cations.

Low-frequency band

It is clear from the experimental data (Table 1) that the lowest-lying frequency essentially depends on the nature of the tetrahedral trivalent cation. This is also demonstrated by the 2-modes behaviour of this band in the spectra of Li $(Ga_{1-x}In_x)$ Cr_4O_8 solid solutions (Fig. 4), in contrast with the one-mode behaviour of the corresponding band in $LiFe(Cr_{1-x}Rh_x)_4O_8$ solid solutions. Thus, this band is essentially related to a translation of the trivalent, tetrahedral cation. A small participation of the octahedral cation is not excluded; but it is impossible to decide whether the frequency difference between the corresponding chromium and rhodium compounds is due to a Cr–Rh mass effect, or to the increase of the unit cell parameter a_0, or both.

FURTHER DATA ON VIBRATIONAL INTERACTIONS

Experimental proof of vibrational interactions between identical, "isolated" tetrahedral groups

The fairly large ^6Li–^7Li isotopic shift of the medium-frequency band, together with its sharpness for the chromium compounds, offers a good opportunity to demonstrate the occurrence of vibrational interactions between the "isolated" LiO_4 groups. The principle of this experiment is very simple: the spectrum of an homogeneous compound containing equal quantities of Li isotopes will exhibit, either 2 distinct Li–O bands near the frequencies of the pure isotopic compounds, or one single band at an average frequency, depending on the absence or presence of significant vibrational interactions.

For a *mechanical mixture* consisting of 50 per cent of each of the isotopic species $^6LiGaCr_4O_8$ and $^7LiGaCr_4O_8$, the i.r. spectrum clearly exhibits the 2 Li–O bands corresponding to the 2 isotopic phases (Fig. 5). This experiment was simply intended to check that the 2 bands are effectively observed when they must appear. The mixture of isotopic species is then heated up to 1000°C so as to give a *single, homogeneous phase* of isotopic composition $^6Li_{0.5}{}^7Li_{0.5}GaCr_4O_8$. The spectrum of this phase exhibits a single absorption band at an average frequency (Fig. 5). This points to significant vibrational interactions between LiO_4 groups. Of course, this result does not imply that important interactions occur between vibrations of *different* groups, such as LiO_4 and GaO_4. In fact, the absence of significant interactions of this type is evidenced by the lack of ^6Li–^7Li isotopic shifts for all the other bands of the spectrum.

INFRARED SPECTRUM OF DISORDERED $LiGaCr_4O_8$

$LiGaCr_4O_8$ is the only compound of this family which can be obtained in the disordered state [1].

Surprisingly enough, there is no drastic modification of the spectrum when passing from the ordered to the disordered phase (Fig. 6 and Table 3). Out of the 6 bands observed in the spectrum of the ordered phase, 4 are only moderately broadened without significant change of their frequency (652, 564, 445 and 220 cm^{-1}) one is significantly displaced from 515 to 531 cm^{-1}, and the sharp band near 611 cm^{-1} disappears nearly completely. The weak shoulders near 613 and 515 cm^{-1}, although reproducible, are not necessarily related to the true disordered phase: they are possibly due to some small ordered regions resulting from imperfect quenching.

This hypothesis is justified by the difficulty of quenching the disordered phase [1]. Whatever the origin of these weak shoulders, the main point of interest is the small

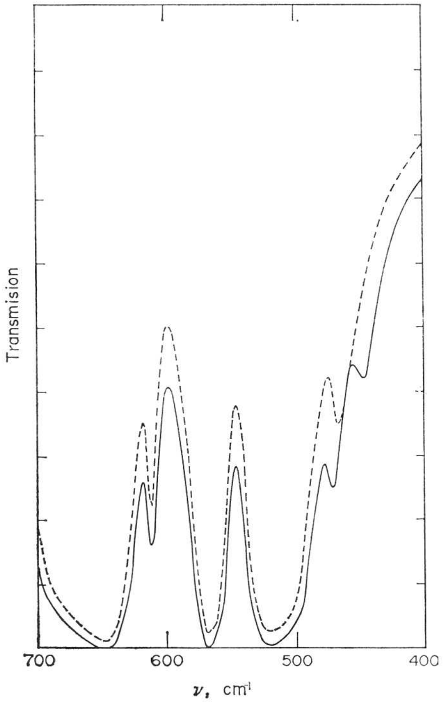

Fig. 5. Part of the i.r. spectrum of: (1) Full line: a mechanical mixture of $^6LiGaCr_4O_8$ + $^7LiGaCr_4O_8$ showing separate ^{6}Li–O and ^{7}Li–O frequencies. (2) Dashed line: the corresponding homogeneous phase $^6Li_{0\cdot5}{}^7Li_{0\cdot5}GaCr_4O_8$ showing an average Li–O frequency.

difference between the spectra of the ordered and disordered phases. This is in contrast with the drastic changes which are generally observed when the order–disorder transition is related to the cation distribution on the *octahedral* sites [4, 12]. This may be related to the fact that, in this latter case, the number of predicted infrared active fundamentals is very large (21 for 3:1 ordering on octahedral sites with space group O^7–$P4_132$, against 7 i.r. active modes in the actual case of 1:1 ordering on tetrahedral sites, space group $T_d{}^2$–$F\bar{4}3m$,) with as a consequence a more important change in the spectrum when passing from the ordered to the disordered phase. Finally two other points may be briefly mentioned.

(1) A rather small quantity of free Cr_2O_3 appears in the X-ray powder diagram of $LiGaCr_4O_8$ quenched from 1350°C. This Cr_2O_3 is responsible for the very weak band observed at about 417 cm^{-1} in the i.r. spectrum of the disordered phase. Among the other i.r. bands of Cr_2O_3 [13], the 444 and 307 cm^{-1} bands are too weak to appear at the impurity level considered here; the 2 remaining bands near 643 and 583 are stronger but rather broad, and are obscured by the strong spinel bands at 652 and 565 cm^{-1}.

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[12] J. Preudhomme, *Compt. Rend.* **267C,** 1632 (1968).

[13] P. Tarte and J. Preudhomme, *Spectrochim. Acta* **26A,** 2207 (1970).

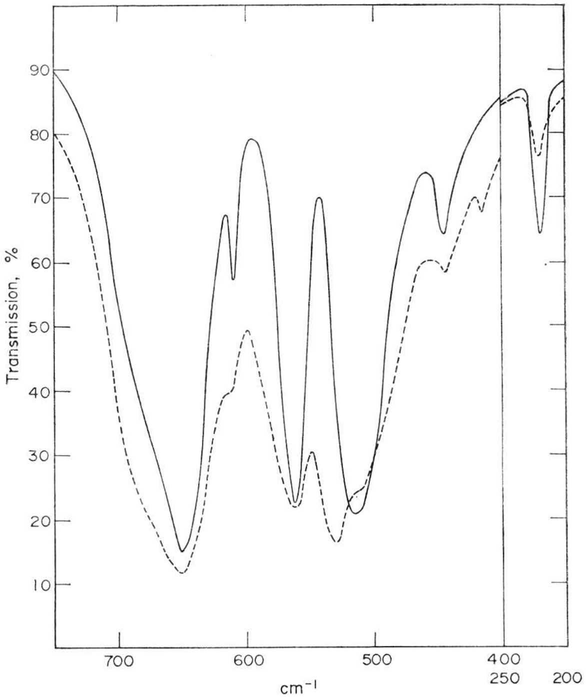

Fig. 6. I.R. spectra of the ordered (full line) and disordered (dashed line) phases of $^7LiGaCr_4O_8$.

Table 3

$^7LiGaCr_4O_8$		$^6LiGaCr_4O_8$	
Ordered	Disordered	Ordered	Disordered
652	651	652	652
611	613*	612	613*
564	564	565	565
	531		532
515	515*	515	515*
445	444	470	470*
	417†		417†
220	220	220	220

* Weak shoulders (see text).

† Cr_2O_3 impurity.

(2) The spectrum of disordered $^6LiGaCr_4O_8$ is practically identical to the spectrum of the corresponding ^7Li phase, except for the band related to the Li translation: this band is considerably broader for the ^6Li than for the ^7Li phase (Fig. 7). We have no definite explanation for this unexpected behaviour; but quite similar differences were already noticed in the i.r. spectrum of ^6Li and ^7Li spinels characterized by a disordered cationic distribution on the octahedral sites [4].

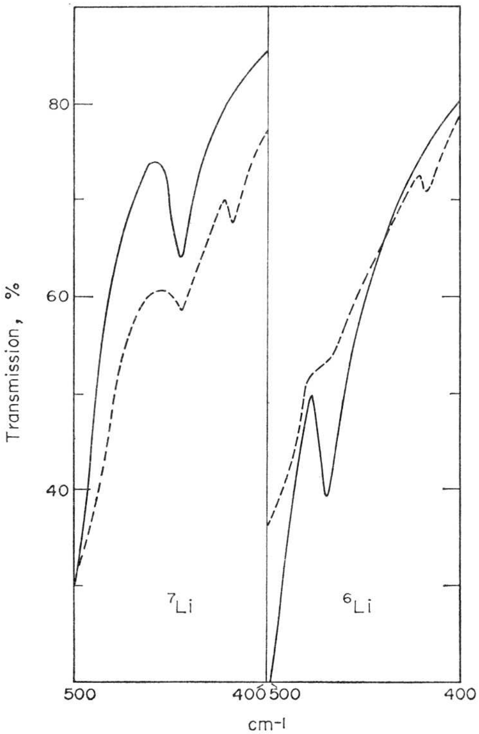

Fig. 7. Relation between the isotopic species (^{6}Li or ^{7}Li) and the broadening of the Li–O band in the disordered phase of $LiGaCr_4O_8$. Full line: ordered; dashed line: disordered phase.

Discussion

Some of the compounds discussed in this paper have also been investigated by De Angelis *et al.* [5]. The agreement between the experimental data may be considered as satisfactory, but there is fundamental disagreement about the assignments, and this point must be discussed in some detail.

(1) First of all, we must point to an evident, and fundamental inconsistency in De Angelis paper: it is stated on p. 359 that "In a crystal it makes little sense to speak of "stretching" or "bending" vibrations . . . ." (and indeed this statement is essentially correct for the compounds under consideration, which are of the double oxide type). But in Table 2 of this paper, the normal modes are distributed into "tetrahedral" and "lattice" modes, as if one was dealing with a salt; furthermore, all the discussion and the resulting assignments are made in terms of stretching and bending motions of tetrahedral and octahedral groups.

(2) The highest-frequency bands are systematically assigned to vibrations of the tetrahedral groups. But we have shown [6, 10] that this is true only if the tetrahedral group is occupied by the highest-valency cation, a condition not fulfilled here. Indeed, the experimental facts discussed in the previous part of the present paper show that, for all the high-frequency bands, it is impossible to speak about characteristic vibrations of specific co-ordinated groups.

(3) Most of the assignments proposed by De Angelis *et al.* rely on intensity considerations whose details are too numerous to be discussed here, but which, by and large, are essentially meaningless.

We just shall quote here the starting considerations, which are as follows (on p. 361): "We use as the basis of our assignments the argument that the ordering is only a small perturbation on the underlying spinel structure. Intense bands of spinel should remain intense in the ordered structure, whereas bands that are forbidden in the spinel may appear weakly in the ordered structure". Such a statement is clearly untenable, since this is a rather oversimplified scheme with respect to the complex factors which determine the band intensities. And our own experimental data on various types of ordered spinels [4, 12] show it to be completely erroneous.

In view of this erroneous starting point, it would be a tedious and useless task to discuss point by point all the assignments proposed by De Angelis *et al.* We shall just consider, as an example, their assignment of the 2 high-frequency i.r. bands. Intensity considerations lead De Angelis *et al.* to assign these 2 bands, for $LiGaCr_4O_8$, to mixed vibrations of the GaO_4 and LiO_4 tetrahedral groups, the higher frequency near 660 cm^{-1} being essentially related to the antisymmetric stretching of GaO_4, with some contribution of LiO_4, whereas the reverse is true (essentially LiO_4, with some contribution from GaO_4) for the lower frequency near 610 cm^{-1}. Our own experimental data show these assignments to be completely wrong. The assignment of the 610 cm^{-1} band to the antisymmetric stretch of (essentially) the LiO_4 tetrahedra is in contradiction with the complete lack of ^6Li–^7Li mass effect on this frequency (Table 1). On the other hand, the high-frequency band near 660 cm^{-1} cannot be assigned to a GaO_4 antisymmetric stretch, since the frequencies are nearly the same for the Ga and for the In compound (see previous part of this paper). Moreover, a significant participation of the Li cation to this vibration (as stated by De Angelis *et al.*) would imply a non-negligible ^6Li–^7Li isotopic shift, a prevision which is in contradiction with the experimental evidence (Table 1). Thus, De Angelis *et al.* suggest, between GaO_4 and LiO_4, a strong vibrational coupling which is in fact inexistent, but completely miss the strong interaction between GaO_4 tetrahedra and CrO_6 octahedra.

In conclusion, and as far as the i.r. spectra are concerned, there is only one point of agreement between the 2 sets of assignments: the lowest-lying frequency is assigned, in both papers, to a translation of the tetrahedral, trivalent, cation. Finally, we have no Raman data on these compounds, and thus no experimental basis for discussing the assignments proposed by De Angelis *et al.* But most of these Raman assignments appear to be as arbitrary as the infrared ones and thus cannot be accepted without discussion. If, in addition, it may be considered that "some of these Raman bands may not be real" (p. 363 of Ref. [5]), it appears that the Raman spectrum of these compounds remains an open question.

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