

${}^6\text{Li}$ - ${}^7\text{Li}$ isotopic shifts in the infrared spectrum of inorganic lithium compounds—II. Rhombohedral LiXO_2 compounds

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Abstract—The infrared spectrum of some $\text{LiX}^{\text{III}}\text{O}_2$ compounds ($\text{X}^{\text{III}} = \text{Al, Ga, Co, Cr, Rh, Sc}$) with an ordered distribution of Li and X^{III} cations on octahedral sites has been investigated with the help of ${}^6\text{Li}$ - ${}^7\text{Li}$ isotopic replacement. The spectrum is essentially characterized by the occurrence of distinct, well individualized, $\text{X}^{\text{III}}\text{O}_6$ (in the 650–400 cm^{-1} region) and LiO_6 (in the 300–200 cm^{-1} region) frequencies. However, this vibrational behaviour seems to be restricted to the compounds with the rhombohedral $R\bar{3}m$ structure and cannot be generalized to all LiXO_2 compounds. Some specific features of the individual spectra have also been discussed.

INTRODUCTION

THE stretching vibrations of LiO_4 tetrahedra have already been investigated in a series of appropriate inorganic lithium compounds: the corresponding absorption bands are generally observed in the 400–550 cm^{-1} region of the infrared spectrum and are easily identified by a ${}^6\text{Li}$ - ${}^7\text{Li}$ isotopic shift of 20–25 cm^{-1} [1, 2]. The same identification technique has now been applied to inorganic solids of the $\text{LiX}^{\text{III}}\text{O}_2$ type, the structure of which contains LiO_6 octahedra. In view of the diversity of structures which are represented among these compounds, this paper is essentially restricted to the case of compounds with the rhombohedral ($R\bar{3}m$) structure ($\text{X}^{\text{III}} = \text{Al, Ga, Co, Cr, Rh}$).

EXPERIMENTAL

The compounds have been synthesized by solid state reaction in covered platinum or silver crucibles. In most cases, the synthesis temperature must not be too high in order to avoid, either Li losses by volatilization, or undesired polymorphic transformations. All attempts to synthesize α - LiGaO_2 at atmospheric pressure failed. This phase was very kindly put at our disposal by Dr. Remeika (Bell Telephone Laboratories) who synthesized it at 35 kbar and 1000°C.

The experimental conditions are collected in Table 1.

The i.r. spectra were registered with the following spectrometers: Unicam SP 100 (NaCl and KBr prisms, 1500–400 cm^{-1}), Perkin-Elmer 112 (CsI prism, 400–240 cm^{-1}), Cameca SI 36 (240–50 cm^{-1}). The conventional disc method has been used throughout, KI (1500–240 cm^{-1}) and polythene (240–50 cm^{-1}) being used as disc material.

RESULTS

Spectra showing the ${}^6\text{Li}$ - ${}^7\text{Li}$ isotopic shifts are shown in Figs. 1 and 2. It is evident that these spectra may be divided into 2 parts:

(1) a region of strong absorption between 400 and 700 cm^{-1} , which is not or only

[1] P. TARTE, *Spectrochim. Acta* **20**, 238 (1964); **21**, 313 (1965).

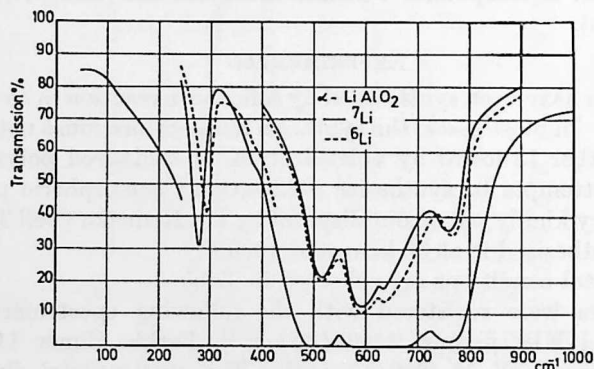
[2] P. TARTE, *J. Inorg. Nucl. Chem.* **29**, 915 (1967).

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	[3, 4]
α -LiGaO ₂		see text		[5]
LiScO ₂	Sc ₂ O ₃ + Li ₂ CO ₃	6 days at 600°C	Repeated grindings	[6, 7]
LiCrO ₂	Cr ₂ O ₃ + Li ₂ CO ₃	+2 days at 800°C 2 days at 740°C	Nitrogen atmosphere	[8]
LiRhO ₂	Rh ₂ O ₃ + Li ₂ CO ₃	5 days at 650°C		[9]
LiCoO ₂	Co ₃ O ₄ + Li ₂ CO ₃	2 days at 800°C	Oxygen atmosphere	[8]
LiInO ₂	In ₂ O ₃ + Li ₂ CO ₃	6 days at 600°C	Repeated grindings	[10]

weakly affected by the ⁶Li-⁷Li isotopic replacement; and

(2) an isolated, moderately sharp band in the 200-300 cm⁻¹ region, which is displaced towards higher frequencies when natural (essentially ⁷Li) is replaced by ⁶Li. As far as this latter band is concerned, the isotopic frequency ratio is very near 1.06-1.07 (Table 2); now, a rather rough calculation leads to a frequency ratio of 1.08 for an isolated LiO₆ octahedron. Since, in the actual case, the LiO₆ octahedra are interlinked by common oxygen atoms, and in view of the approximate character of the calculation, the discrepancy between the observed and calculated frequency ratio is not surprising, and the band under consideration may be assigned with confidence to an antisymmetric stretching motion of the LiO₆ octahedra. Conversely, the strong absorption of the 400-700 cm⁻¹ region (which is nearly insensitive to the isotopic

Fig. 1. Infrared spectrum of LiAlO₂.

- [3] H. A. LEHMANN and H. HESSELBARTH, *Z. Anorg. Allgem. Chem.* **313**, 117 (1961).
 [4] A. M. LEJUS and R. COLLONGUES, *Compt. Rend.* **254**, 2005 (1962).
 [5] M. MAREZIO and J. P. REMEIKI, *J. Phys. Chem. Solids* **26**, 1277 (1965).
 [6] C. J. M. ROOYMANS, *Z. Anorg. Allgem. Chem.* **313**, 234 (1965).
 [7] R. HOPPE, B. SCHEPERS, H. J. ROEHRBORN and E. VIELHABER, *Z. Anorg. Allgem. Chem.* **339**, 130 (1965).
 [8] P. F. BONGERS, Thesis, Leiden (1957).
 [9] E. F. BERTAUT and J. DULAC, *J. Phys. Chem. Solids* **21**, 118 (1961).
 [10] R. HOPPE and B. SCHEPERS, *Z. Anorg. Allgem. Chem.* **295**, 233 (1958).

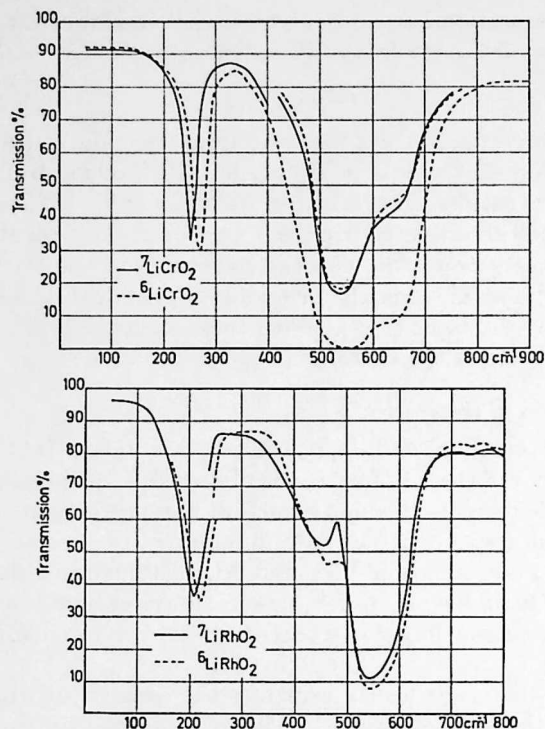


Fig. 2. Infrared spectrum of LiCrO_2 and LiRhO_2 .

Table 2

Compound LiXO_2		Observed frequencies (cm^{-1})				Frequency ratio for the low- frequency band	Ionic radius of X (\AA)
α LiAlO_2	${}^6\text{Li}$	767	~ 640	~ 595	519	295	1.065
	${}^7\text{Li}$	760	~ 640	~ 595	520	277	
α LiGaO_2	${}^7\text{Li}$	~ 600		~ 520	~ 405	225	0.62
LiCrO_2	${}^6\text{Li}$		~ 650		540	270	1.067
	${}^7\text{Li}$		~ 650		540	253	
LiRhO_2	${}^6\text{Li}$		~ 545		~ 465	223	1.062
	${}^7\text{Li}$		~ 543		~ 460	210	
LiCoO_2	${}^6\text{Li}$	~ 600				293	1.065
	${}^7\text{Li}$	~ 600				275	
LiScO_2	${}^6\text{Li}$	~ 650	~ 580	~ 550	~ 510	390 250	1.055
	${}^7\text{Li}$	~ 650	~ 580	~ 550	~ 510	400 380 237	
LiInO_2	${}^6\text{Li}$	~ 555	~ 435	378	309	?	1.053*
	${}^7\text{Li}$	~ 555	~ 437	359	308	226	

* For the 378 - 359 cm^{-1} band.

effect) is assigned to vibrational frequencies of the $X^{III}O_6$ octahedra. This assignment is consistent with previous data on the vibrational frequencies of $X^{III}O_6$ groups.

DISCUSSION

All the phases investigated are derived from the MgO (NaCl) structure by replacing 2 Mg^{2+} by one Li^+ plus one X^{3+} cation. But, owing to the ordered distribution of Li^+ and X^{3+} cations on octahedral sites, the cubic symmetry is destroyed and, for the compounds investigated here ($X^{3+} = Al, Ga, Co, Cr$ or Rh), the symmetry is rhombohedral, space group $R\bar{3}m$, and the structure may be represented by alternate layers of Li^+ , O^{2-} and X^{3+} ions, the LiO_6 and XO_6 octahedra being connected by a sheet of common oxygen atoms [5, 9]. With these structural data in view, we may now discuss some aspects of the vibrational spectrum.

1. *The general features of the spectra*

1.1 *Occurrence of characteristic LiO_6 and $X^{III}O_6$ vibrations.* It is well known that, in close-packed lattices of the NaCl type, the observed frequencies are nearly always related, not to a particular cation-anion bond, but to vibrational motions of the whole lattice. The situation appears to be quite different in the case of the $LiXO_2$ compounds investigated here, since the LiO_6 and XO_6 octahedra exhibit distinct vibrational frequencies. Qualitatively, differences in the vibrational behaviour of NaCl-type and $LiXO_2$, rhombohedral-type compounds may be explained by at least 3 factors:

(1) One of these factors is nearly certainly the ordered distribution of the Li^+ and X^{3+} cations on the octahedral sites. This is supported by the fact that only a single, very broad absorption band is present in the high-temperature form of $LiFeO_2$, the structure of which is disordered (true NaCl structure with a statistical distribution of Li and Fe cations).

(2) A second factor responsible for the occurrence of distinct LiO_6 and XO_6 vibrations is the large difference between the vibrational frequencies of these groups.

(3) Finally, the peculiar type of structure of the compounds under investigation must also play an important role in the actual vibrational behaviour.

From this point of view, one would be tempted to describe the spectrum of the rhombohedral phases as arising from the distinct vibrations of the LiO_6 and XO_6 octahedral layers.

This is supported by the investigation (which is still going on) of further $LiXO_2$ compounds with various structures; although perfect ordering of Li^+ and X^{3+} cations on octahedral sites is still present, the structure is more complicated than for rhombohedral phases, since both LiO_6 and XO_6 octahedra are always present in a given layer. In these cases, the vibrational behaviour is more complex and the observed 6Li - 7Li isotopic shifts strongly suggest that the XO_6 and LiO_6 vibrations are more or less mixed up.

Thus, the actual results suggest that the occurrence of distinct LiO_6 and XO_6 frequencies is related to the peculiar type of structure characterized by separate layers of LiO_6 and XO_6 octahedra.

Nevertheless, further experimental and theoretical work is needed to clear up the role of the structure and of the ordered character of the cation distribution.

This latter point will be studied in compounds which can be obtained with an ordered or disordered structure: this is the case of LiFeO_2 , already mentioned and to a less extent, of LiInO_2 : the disordered structure cannot be obtained in the case of the pure compound itself, but it is stabilized by the addition of 5 moles % of MgO in solid solution [11]. Likewise, NiO-LiNiO_2 solid solutions are characterized by a progressive ordering of Li^+ and Ni^{3+} cations when more and more Ni^{2+} is replaced by $\text{Li}^+ + \text{Ni}^{3+}$ [12].

1.2 *Influence of the unit cell dimensions on LiO_6 stretching frequency.* The LiO_6 stretching frequency is fairly sensitive to the ionic radius of the trivalent cation (Table 2). As expected, the LiO_6 frequency is higher for smaller ionic radii (and as a consequence for smaller unit cell volumes), but the correlation is purely qualitative, and no rigorous relationship has been found between the existing data.

1.3 *Variability of the infrared pattern related to the XO_6 groups.* It has already been observed that some families of isomorphous compounds give rather similar infrared patterns. This is no longer true for the compounds investigated here: the infrared pattern related to the $\text{X}^{\text{III}}\text{O}_6$ vibrations is rather different for LiAlO_2 , LiGaO_2 and LiCrO_2 , although these compounds are isostructural. Likewise, simple isomorphous oxides such as $\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$, Cr_2O_3 and Rh_2O_3 exhibit quite different infrared patterns.

It does not seem that this behaviour may be explained by simple qualitative considerations; but it is worth while to mention that such differences in the spectra of isomorphous compounds are observed when these compounds are of the simple or double oxide type, whereas great similarities are generally observed in the spectra of isomorphous salt-type compounds, the structure of which contains well-individualized anions.

2. Discussion of some specific features of the spectra

2.1 *Non-reproducibility of the spectrum of LiAlO_2 .* The infrared spectrum of a sample prepared by LEJUS and COLLONGUES [4] is somewhat different from the spectrum of our own sample (Fig. 3), whereas the spectrum published by

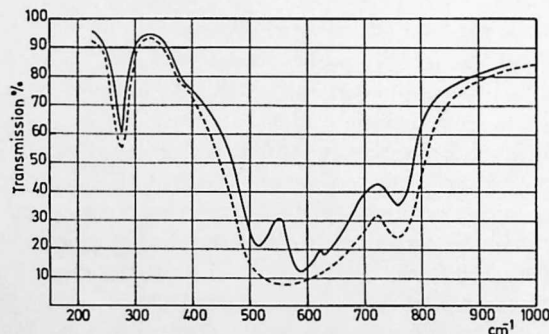


Fig. 3. Non-reproducibility of LiAlO_2 spectrum. Dashed line: Lejus and Colongue's sample; full line: our own sample.

[11] H. SCHWARZ and D. BOMMERT, *Z. Anorg. Allgem. Chem.* **345**, 246 (1965).

[12] W. BRONGER, H. BADE and W. KLEMM, *Z. Anorg. Allgem. Chem.* **333**, 188 (1964).

KOLESOVA [13] seems to represent an intermediate case. All three samples are, however, α -LiAlO₂ if one refers to their X-ray powder diagram; moreover, the discrepancies are observed in the bands related to the AlO₆ vibrations (500–650 cm⁻¹) only, whereas the fairly sharp band related to LiO₆ vibrations (277 cm⁻¹) appears with the same position, shape and relative intensity in the available spectra (the spectrum published by Kolesova does not extend to these low frequencies).

We are actually unable to present a reasonable explanation of these differences. Indeed, the rather broad absorption observed in the spectrum of Lejus and Collongue's sample seems to represent fairly well the envelope of the three distinct bands of our own sample. This behaviour could be explained by some kind of disorder affecting the AlO₆ layer; but it is hard to imagine how this disorder could be present without affecting more or less seriously the vibrational behaviour of the LiO₆ layer.

2.2 *Similarity of the vibrational frequencies of CrO₆ and RhO₆ octahedra.* In view of the higher mass and of the larger ionic radius of rhodium, the stretching frequency of RhO₆ octahedra is expected to be lower than the corresponding frequency of CrO₆ octahedra, at least in chemically and structurally similar compounds.

The actual results on LiCrO₂ and LiRhO₂ do not verify this expectation. In both compounds, the strong absorption related to the X^{III}O₆ stretching vibration (and identified as such by the lack of a ⁶Li-⁷Li isotopic shift) is centred near 540 cm⁻¹. (In fact, the frequency related to the rhodium compound is slightly *higher* (Table 2); but this difference is hardly significant in view of the broadness of the band.) On the contrary, the LiO₆ band is fairly strongly displaced towards lower frequencies in the rhodium compound, in connection with the general influence of the unit cell volume already mentioned.

This case is a good example of the difficulties which may be encountered in the interpretation of the infrared spectra of solids. As far as LiO₆ and X^{III}O₆ octahedra may be considered as vibrating independently, the assignment of the spectra of LiCrO₂ and LiRhO₂ could be proposed on the following basis, which seems quite reasonable: those bands which are significantly displaced towards lower frequencies when passing from LiCrO₂ to LiRhO₂ are related to the X^{III}O₆ vibrations (because of the influence of the mass and ionic radius of Rh), whereas the bands related to LiO₆ vibrations should not be seriously displaced. This would lead to assign the 540 cm⁻¹ absorption to LiO₆, and the low-frequency band to X^{III}O₆ vibrations. In fact, we know through the ⁶Li-⁷Li isotopic shifts that this assignment is completely wrong, and is the reverse of the correct assignment.

We are now investigating a series of structurally related chromium and rhodium compounds: all the spectra collected so far confirm the very great similarity of CrO₆ and RhO₆ stretching frequencies, at least when these octahedral groups are interlinked by common oxygen atoms. On the other hand, we now have some reasons to believe that, in such lattices of condensed octahedra, the mass effect of the central cation on the highest vibrational frequencies may be small or even negligible. If this point is confirmed by further work, the great similarity between CrO₆ and RhO₆ stretching frequencies is no longer surprising and is explained if the restoring forces of the Cr—O and Rh—O bonds are of the same order of magnitude.

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

2.3 *Vibrational behaviour of LiScO_2 and LiInO_2 .* After the existing literature data, these compounds are isomorphous, with a tetragonal symmetry, space group $I4_1/amd$ [6, 7, 11, 14], and primarily, it was not intended to include their infrared study in this paper (devoted to the rhombohedral compounds). This discussion, however, is not out of place here for the following reason.

The infrared spectrum of LiScO_2 is somewhat more complicated than the spectra of the rhombohedral compounds (Fig. 4 and Table 2), *but the vibrational behaviour*

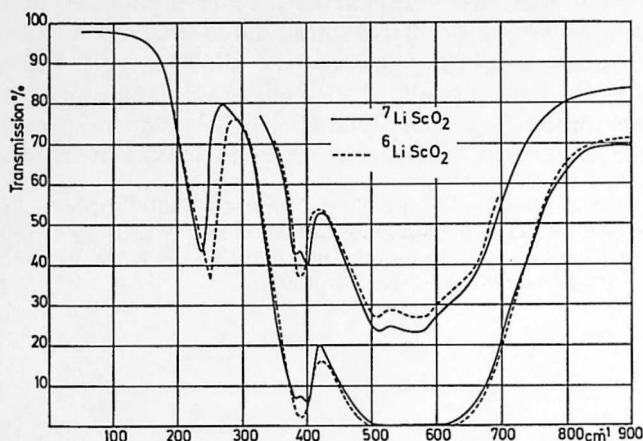


Fig. 4. Infrared spectrum of LiScO_2 .

of its Li—O bonds is essentially the same (one band near 250 cm^{-1} , with a ^6Li - ^7Li frequency ratio not very different from 1.06—Table 2). On the contrary, the infrared spectrum of LiInO_2 is different in every respect with a more complicated behaviour of the Li—O vibrations (Fig. 5 and Table 2). These results are unexpected: in view

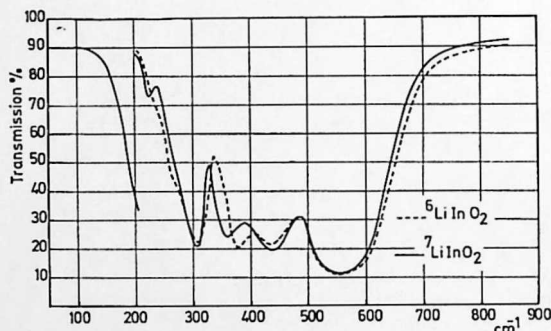


Fig. 5. Infrared spectrum of LiInO_2 .

of the admitted isomorphism of these compounds, their infrared spectra should be similar, and different from those of the rhombohedral phases. Now, it is worth while to mention that MAREZIO and REMEIKA [15] have recently expressed the opinion

[14] R. HOPPE and H. J. ROEHRBORN, *Naturwiss.* **48**, 452 (1961).

[15] M. MAREZIO and J. P. REMEIKA, *J. Chem. Phys.* **44**, 3348 (1966).

that the space group of these compounds may be in error. Our infrared results may be considered as supporting this view. We feel, however, that any detailed discussion of the possible relationships between the structure and the vibrational spectrum should be delayed until more structural and spectroscopic data have been collected.

CONCLUSIONS

For nearly all compounds discussed in this paper, the LiO_6 stretching vibration appears as a characteristic, well-individualized band in the $300\text{--}200\text{ cm}^{-1}$ region. But despite the apparent homogeneity of the actual results, it would be premature to extend these conclusions to all compounds of the $\text{LiX}^{\text{III}}\text{O}_2$ type. Studies on further LiXO_2 compounds, which are actually carried out in this laboratory, point to a more complex, but structurally dependent, vibrational behaviour and strongly suggest that, in some cases at least, the LiO_6 and $\text{X}^{\text{III}}\text{O}_6$ vibrations are more or less mixed up.

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