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Vibrational Spectra of Spinels with 1:1 Ordering on Tetrahedral Sites

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Infrared and Raman spectra have been measured on the compounds Cr_4GaLiO_8, Cr_4InLiO_8, and Rh_4InLiO_8. These have the structure of spinel with 1:1 order on the tetrahedral sites. Predicted and measured spectra agree well and additional features due to ordering can be clearly seen. The two tetrahedra are crystallographically equivalent in the disordered spinel structure and nonequivalent in the ordered structure. It is shown that ordering only partially decouples the motions of the tetrahedra.

Introduction

Cation ordering schemes that produce a change in space group or in unit cell population are expected to also produce predictable changes in the infrared spectrum (*1*). However, the magnitude and reliability of such changes have not been tested extensively. The spinels provide a convenient structural family for such study because of the large number of ordering schemes possible. Theoretical analyses of the vibrational behavior of some of these have been published (*2*). The present paper reports on spinels with 1:1 ordering on the tetrahedral sites.

There is evidence for peculiar behavior in Tarte and Ringwood's (*3*) spectra of Ni_2SiO_4–Ni_2GeO_4 solid solutions. They showed two different types of composition dependence in the infrared bands of intermediate compositions. One band shifted continuously with composition between the end-member values. The other two bands remained at nearly fixed frequency. At intermediate compositions, each band doubled so that the frequencies of both end members were represented. These results were explained by assuming "free" vibrations of the SiO_4 and GeO_4 tetrahedra. It was noted in the theoretical analysis (*2*) that this behavior could be equally well explained by an ordering of the silicon and germanium on the tetrahedral sites.

To further examine this question, we have measured the infrared and Raman spectra of Cr_4GaLiO_8, Cr_4InLiO_8, and Rh_4InLiO_8. X-Ray evidence shows that the tetrahedral cations in these structures are ordered. Our objectives are to show that the spectra can be interpreted on the ordering model although the relative intensities of the bands are surprising.

Theoretical Analysis

Spinel belongs to space group O_h^7, *Fd*3*m* with 8 A_2BX_4 formula units per unit cell. A factor group analysis was given previously (*2*). If the tetrahedral cations order, the equivalence of the 8 tetrahedra is lost and the center of symmetry is destroyed. The space group of the 1:1 tetrahedrally ordered spinels is T_d^2, $F\bar{4}3m$ with the same size of unit cell.

The compounds have the following site population (*4*) in $F\bar{4}3m$.

4 In^{3+} (or Ga^{3+})	in 4(a)	$\bar{4}3m$, *Td*	
4 Li	in 4(c)	$\bar{4}3m$, *Td*	
16 Cr^{3+} (or Rh^{3+})	in 16(e)	3*m*	C_{3v}
16 O(I)	in 16(e)	3*m*	C_{3v}
16 O(II)	In 16(e)	3*m*	C_{3v}

These positions lead to the invariance conditions and reducible representation shown in Table I. Analysis of the reducible representation of the primitive cell by standard factor group methods (*5*) leads to the modes and selection rules shown in

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TABLE I

INVARIANCE CONDITIONS FOR ORDERED SPINELS

Td	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Td	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
4 In^{3+}	4	4	4	4	4
4 Li^+	4	4	4	4	4
C_{3v}	E	$2C_3$	—	—	$3\sigma_v$
16 Cr^{3+}	16	4	0	0	8
16 O(I)	16	4	0	0	8
16 O(II)	16	4	0	0	8
ω_ρ	56	20	8	8	32
χ_ρ (fcc)	168	0	−8	−8	32
χ_ρ (Prim)	42	0	−2	−2	8

Table II. Since the site group of the tetrahedron is the same as the factor group, the spectra of the two tetrahedra will not exhibit any site group splitting. One will be the spectrum of the LiO_4 tetrahedron and the other the GaO_4 tetrahedron. However, the two sets of frequencies may be strongly mixed.

In a crystal it makes little sense to speak of "stretching" or "bending" vibrations, although the motions of the tetrahedron can be treated this way to a rough approximation.

One can get some insight into the unit cell motions by writing the symmetry coordinates. These were constructed from the symmetry coordinates of spinel as previously studied (*6*). The coordinates are referred to the primitive unit cell illustrated in Fig. 1. We concern ourselves mainly with the infrared-active species T_2.

TABLE II

NORMAL MODES AND SELECTION RULES FOR ORDERED SPINELS

Td	Total modes	Acoustic modes	Tetrahedral modes	Lattice modes	Selection rules
A_1	3	0	$2(\nu_1)^a$	1	Raman
A_2	0	0	0	0	—
E	3	0	$2(\nu_2)$	1	Raman
T_1	3	0	0	3	Inactive
T_2	8	1	$4(\nu_3,\nu_4)$	3	IR + Raman

[a] Usual notation: ν_1 = symmetric stretch, ν_2 = symmetric bend, ν_3 = antisymmetric stretch, and ν_4 = antisymmetric bend.

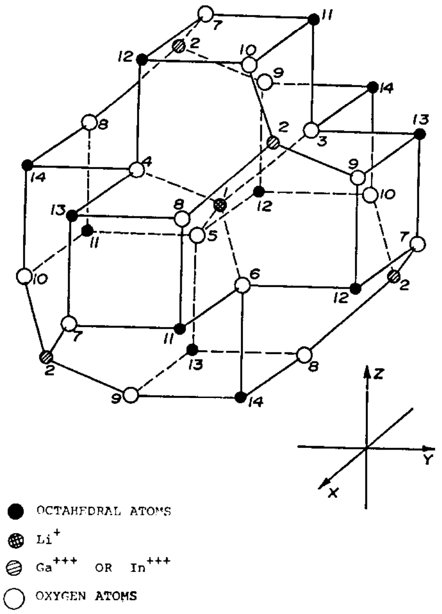

FIG. 1. Wigner–Seitz cell for spinel with 1:1 ordering on tetrahedral sites. The numbering on the atoms is also the labeling used for the normal coordinates.

Since all species appear several times in the reduction of the representation, in some cases linear combinations of symmetry coordinates must be used to form normal coordinates. The symmetry coordinates will be assumed to be normal coordinates, except for some of the T_2 modes.

In what follows, "tetrahedron 1" shall be the one formed by atoms 1, 3, 4, 5, 6, and "tetrahedron 2" of the one formed by atoms 2, 7, 8, 9, 10. There are eight T_2 modes, of which one is a translation, the other seven are both ir and Raman active. Five normal coordinates ($T_2{}^1$, $T_2{}^2$, $T_2{}^3$, $T_2{}^4$, $T_2{}^5$ [Table III]) must be obtained by forming linear combinations of the following five symmetry coordinates (only one component of the triply degenerate species is indicated). x_i stands for the displacement of atom i from its equilibrium position.

x_1	Li^+
x_2	Ga^{3+}
$x_3 + x_4 + x_5 + x_6$	Oxygens of tet. 1
$x_7 + x_8 + x_9 + x_{10}$	Oxygens of tet. 2
$x_{11} + x_{12} + x_{13} + x_{14}$	Octahedral cations

The translation $T_2{}^1$ is the sum of the five symmetry coordinates (the normalization factor is $1/\sqrt{14}$). The superscript is merely a notation to distinguish between the various T_2 modes.

TABLE III

NORMAL COORDINATES FOR T_2 MODES OF ORDERED SPINEL[a]

Acoustic

$$T_2{}^1 = \frac{1}{\sqrt{14}}[x_1 + x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8 + x_9 + x_{10} + x_{11} + x_{12} + x_{13} + x_{14}]$$

Octahedral stretch

$$T_2{}^2 = \frac{1}{\sqrt{35}}[x_1 + x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8 + x_9 + x_{10}] - \frac{5}{2\sqrt{35}}[x_{11} + x_{12} + x_{13} + x_{14}]$$

Translatory between tetrahedra

$$T_2{}^3 = \tfrac{1}{2}[x_1 - x_2] + \tfrac{1}{4}[x_3 + x_4 + x_5 + x_6 - x_7 - x_8 - x_9 - x_{10}]$$

Tetrahedral antisymmetric stretch

$$T_2{}^4 = \frac{3}{\sqrt{21}}[-x_1 + x_2] + \frac{1}{2\sqrt{21}}[x_3 + x_4 + x_5 + x_6 + x_7 + x_8 + x_9 + x_{10} + x_{11} + x_{12} + x_{13} + x_{14}]$$

$$T_2{}^5 = \frac{3}{\sqrt{21}}[x_1 - x_2] + \frac{1}{2\sqrt{21}}[x_3 + x_4 + x_5 + x_6 + x_7 + x_8 + x_9 + x_{10} + x_{11} + x_{12} + x_{13} + x_{14}]$$

Octahedral deformation

$$T_2{}^6 = \frac{1}{2\sqrt{2}}[y_{11} + y_{12} - y_{13} - y_{14} - z_{11} + z_{12} + z_{13} - z_{14}]$$

Tetrahedral deformation

$$T_2{}^7 = \frac{1}{2\sqrt{2}}[y_3 + y_4 - y_5 - y_6 + z_3 - z_4 - z_5 + z_6]$$

$$T_2{}^8 = \frac{1}{2\sqrt{2}}[-y_7 + y_8 + y_9 - y_{10} - z_7 + z_8 - z_9 + z_{10}]$$

[a] Only one component of the triply degenerate species is given.

The octahedral stretching $T_2{}^2$ is exactly the same as the equivalent T_{1u} mode of spinel. There is also a translatory mode $T_2{}^3$, corresponding to one tetrahedron moving against the other, which has the same form in the ordered and disordered structures.

$T_2{}^4$ and $T_2{}^5$ are the tetrahedral antisymmetric stretching modes:

$$T_2{}^4{:}\ -\frac{3x_1}{\sqrt{21}} + \frac{3x_2}{\sqrt{21}} + \frac{x_3}{2\sqrt{21}} + \cdots + \frac{x_{14}}{2\sqrt{21}}$$

$$T_2{}^5{:}\ \frac{3x_1}{\sqrt{21}} - \frac{3x_2}{\sqrt{21}} + \frac{x_3}{2\sqrt{21}} + \cdots + \frac{x_{14}}{2\sqrt{21}}$$

$T_2{}^6$ is the same mode as T_{1u}^5 of spinel and can be approximately described as a deformation of the octahedra. The two remaining modes, $T_2{}^7$ and $T_2{}^8$, are the deformation modes of the two tetrahedra. $T_2{}^7$ involves mainly tetrahedron 1. $T_2{}^8$ involves mainly tetrahedron 2. Although each antisymmetric stretch now has an independent symmetry coordinate and thus a separate frequency, the motions are still coupled since both modes involve all 14 atomic displacement coordinates.

Experimental Methods and Results

Three spinels with 1:1 ordering on tetrahedral sites were studied: Cr_4GaLiO_8, Cr_4InLiO_8, and Rh_4InLiO_8. They were all prepared by solid-state reactions. The corresponding high purity oxides and carbonates were mixed in the correct stoichiometric ratios. The components were ground in an agate mortar, were prefired for 4–6 hr at 600°C for the decomposition of the carbonates and were then sintered at 1000°C in air atmosphere. The details are tabulated below. Attempts to prepare two other compounds, Cr_4FeLiO_8 and Rh_4GaLiO_8 by the same methods were unsuccessful.

Composition	Raw materials	Sintering conditions
Cr_4GaLiO_8	Cr_2O_3, Ga_2O_3, Li_2CO_3	30 hr at 1000°C in air
Cr_4InLiO_8	Cr_2O_3, In_2O_3, Li_2CO_3	60 hr at 1000°C in air
Rh_4InLiO_8	Rh_2O_3, In_2O_3, Li_2CO_3	60 hr at 1000°C in air

The X-ray diffraction patterns are in agreement with the diffraction pattern generated by using the

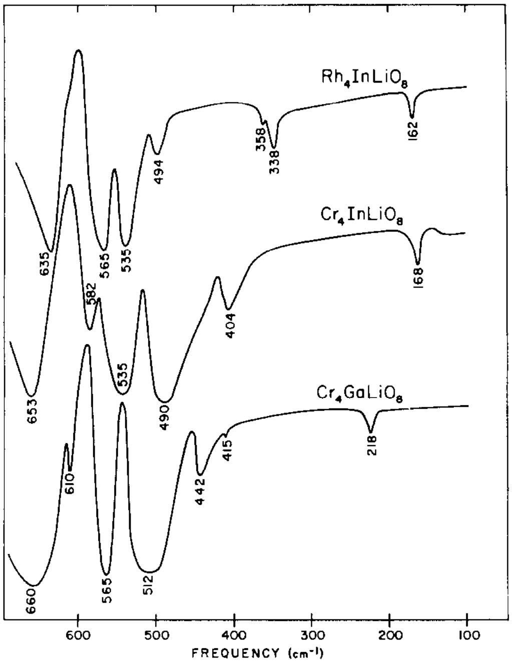

FIG. 2. Infrared spectra for ordered spinels.

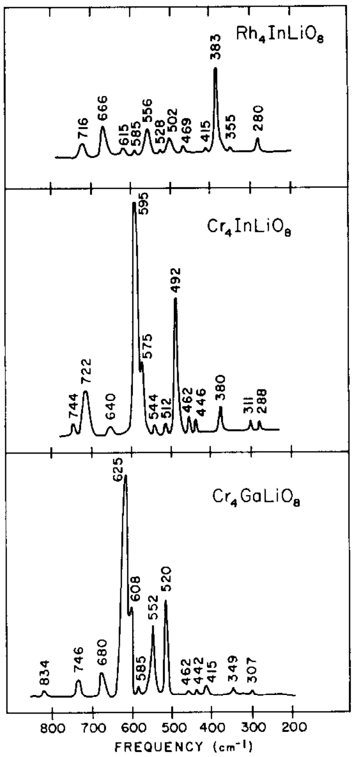

FIG. 3. Raman spectra for ordered spinels. These spectra are composites of various individual measurements and the strong background scattering has been removed. Because of the background, relative intensities are only approximate.

reported lattice parameters (*4*) and a computer program.

The infrared spectra of these spinels were obtained on a Beckman IR-11 spectrophotometer. The samples were ground to a very fine powder and spread uniformly over the surface of polyethylene plates. Raman spectra were obtained from pressed powders using the Spex Ramalog spectrometer with both 488 and 514 nm lines of a 200 mW ionized argon laser source.

The spectra of Cr$_4$GaLiO$_8$, Cr$_4$InLiO$_8$, and Rh$_4$InLiO$_8$ are given in Figs. 2 and 3. The frequencies are tabulated in Table IV.

Discussion and Assignments

If the tetrahedral cations were disordered so that the compounds had the spinel structure, 4 bands would be expected in the infrared and 5 in the Raman spectrum. In the ordered structures the number of ir bands should increase to 7 while the number of Raman bands increases to 13. Seven ir bands were observed in Cr$_4$GaLiO$_8$ and Rh$_4$InLiO$_8$ although only six were found in Cr$_4$InLiO$_8$. The predicted 13 Raman bands were found in Cr$_4$GaLiO$_8$ and Cr$_4$InLiO$_8$, with Rh$_4$InLiO$_8$ exhibiting only 12. Rh$_4$InLiO$_8$, however is a black compound, and the Raman spectra were very weak and should not be considered completely reliable. The band intensities in all spectra vary considerably and the shift in band frequency from one compound to another was more than was expected.

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. The assignments are listed in Table IV. All ir-active bands should also be Raman active, and the agreement between the two measurements is not as good as it should be. The maximum disagreement is on the order of 20 cm^{-1}.

The two highest frequency Raman bands have no equivalent ir bands. They are assigned to the two A_1 tetrahedral modes which correspond to the symmetric stretching frequencies of the GaO$_4$ and LiO$_4$ tetrahedra.

The strongest band in the infrared spectrum of Cr$_4$GaLiO$_8$ at 660 cm^{-1} corresponds to a very weak band in the Raman spectrum. Likewise, the weaker 610 cm^{-1} band in Cr$_4$GaLiO$_8$ corresponds to the

TABLE IV

BAND ASSIGNMENTS

	Cr_4GaLiO_8		Cr_4InLiO_8		Rh_4InLiO_8			
	ir	Raman	ir	Raman	ir	Raman		Assignments
A	—	834 cm^{-1}	—	744	—	716	$A_1(\nu_1)$	$(Ga,Li)O_4$ sym. stretch
	—	746	—	722	—	666	$A_1(\nu_1)$	$(Li,Ga)O_4$ sym. stretch
B	660	680	653	640	635	615	$T_2{}^4(\nu_3)$	$(Ga,Li)O_4$ antisym. stretch
	610	625	582	595	565	585	$T_2{}^5(\nu_3)$	$(Li,Ga)O_4$ antisym. stretch
	—	608	—	575	—	556	A_1	Octahedral sym. stretch
	565	585	535	544	535	528	$T_2{}^2$	Octahedral stretch
C	—	552	—	512	—	502	$E(\nu_2)$	Ga–O Symmetric bending
	512	520	490	492	494	—	$T_2{}^8(\nu_4)$	GaO_4 Deformation
	—	462	—	462	—	469	$E(\nu_2)$	Li–O Symmetric bending
	442	442	404	?	338	?	$T_2{}^7(\nu_4)$	LiO_4 Deformation
	415	415	(404)	380	358	355	$T_2{}^6$	Octahedral deformation
D	—	349	—	446	—	415		
	—	307	—	311	—	383		
	—			288	—	280		
E	218	—	169	—	162	—	$T_2{}^3$	

strongest band in the Raman spectrum. This is the result expected if these two modes are the tetrahedral antisymmetric stretching frequencies. If the structure were that of disordered spinel, one band would appear only in the ir while the other would appear only in the Raman. The frequencies of ir and Raman bands would be equal except for the small shift due to factor group splitting. On the contrary, if the two tetrahedra were not only ordered but completely de-coupled (as proposed by Tarte (*7*)) the frequencies would appear in both ir and Raman, with comparable intensities, and at frequencies expected for the free tetrahedra. The fact that we observe bands of similar frequency (too high for typical LiO_4 and too low for typical GaO_4) and with reversed intensities suggests that the change in selection rules predicted by the ordering does indeed occur but that the coupling between the two tetrahedra is still quite strong and that they vibrate with something approaching an average of the expected GaO_4 and LiO_4 tetrahedral stretching frequencies.

The band at 608 cm^{-1} in the Raman spectrum of Cr_4GaLiO_8 and corresponding bands in the other compounds has no ir equivalent. This band can be assigned to the A_1 lattice mode (Table II) which in the parent spinel structure is a symmetrical stretch around the octahedral cation. The frequency is in good agreement with other 6-coordinated chromium compounds.

The intense band at 565 cm^{-1} can then be assigned to the $T_2{}^2$ octahedral stretch which is both ir and Raman active. Both octahedral stretching frequencies decrease rather uniformly as the size of the cations is increased. This reflects the increasing length of the octahedral bond that occurs when larger ions are placed in either the octahedral or tetrahedral sites.

The C-group of bands are all assigned to deformation frequencies. There is considerable uncertainty in these since there are no clear-cut criteria for specific assignments. The E-symmetry deformations occur only in the Raman and so these can be picked out. The lowest frequency, 415 cm^{-1} band is assigned to the octahedral deformation. It has the lowest intensity in the ir and was so assigned because this mode does not appear at all in the disordered structure. The remaining two frequencies, occurring in both ir and Raman are assigned to the $T_2{}^7$ and $T_2{}^8$ tetrahedral deformation frequencies. Because of the coupling between the two tetrahedra, one cannot make a clear distinction between vibrations of the GaO_4 tetrahedron and the LiO_4 tetrahedron. We have simply stated that the higher of the two frequencies for each pair contains a larger contribution from the more strongly bonded GaO_4 tetrahedral bond. The weak octahedral deformation is not observed in Cr_4InLiO_8, presumably because it overlaps the 404 cm^{-1} deformation band. In Rh_4InLiO_8 it appears at a higher frequency than the deformation band. These assignments were made on the basis of the relative intensities of these two sets of bands.

The *D*-group of bands are a set of Raman lines for which no specific assignment can be made. Table II indicates that there is a single *E*-symmetry lattice mode, a deformation frequency, that has not already been assigned. Yet 2 to 3 Raman bands appear in this region and are of comparable intensity. It should be remarked that measurement of Raman spectra on these highly colored compounds is very difficult in this region and we do not exclude the possibility that some of these bands may not be real.

The *E*-group band occurs in the ir spectrum but the corresponding Raman line could not be observed. It seems quite clearly to be the $T_2{}^3$ lattice mode which corresponds to the motion of the two tetrahedra against each other. The shift in frequency with cation size bears this out.

Conclusions

The appearance of additional bands in the ir and Raman spectra of the ordered spinels predicted by the decrease in space group symmetry is indeed observed. The mere occurrence of ordering, however, does not insure complete decoupling of the tetrahedra. The coupling is reflected in the proximity of the pairs of tetrahedral vibrational frequencies and the relative intensity of the ir and Raman bands. The frequencies assigned to motions of the LiO_4 tetrahedron, in particular, are unusually high and can be explained only if their motion is strongly mixed with the motion of the GaO_4 tetrahedron.

Thus Tarte's hypothesis of "free" vibrations of individual tetrahedra can be seen as the limiting case of zero coupling. At the other limit is the spectrum of the spinel structure itself in which the motions of the two tetrahedra are so tightly coupled that the tetrahedral bands appear only as average values except for factor-group splitting. It seems possible that the separation of such pairs of modes will be useful as a measure of the degree of coupling within a particular crystal.

The infrared spectra are more clear-cut and were easier to interpret than the Raman spectra. This may be due to experimental difficulties in obtaining spectra from these highly colored compounds.

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