Infrared studies of spinels—I
A critical discussion of the actual interpretations

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Abstract—As a general introduction to an extensive investigation of the infrared spectrum of spinels, the authors present a critical discussion of the data and interpretations actually published in the literature. It is shown that the generally accepted interpretation relies on an oversimplified vibrational scheme, and also on too fragmentary experimental data. Moreover, this interpretation may be questioned on both theoretical and experimental bases. It is thus suggested that the assignment problem is more complicated than previously expected and should be reinvestigated on a systematic experimental basis.

INTRODUCTION

THE CRYSTAL chemistry of spinels has been, and is still, widely investigated by classical methods (X-ray and neutron diffraction, magnetic properties, Moessbauer effect) but, surprisingly enough, much less attention has been paid to their vibrational spectrum: if the really important publications only are taken into account, it may be said that no more than 3 or 4 papers have been devoted to this topic since the investigation of several ferrite spinels by WALDRON [1].

An infrared study of the germanate spinels was initiated in 1960 in this laboratory and the results [2] were encouraging enough to extend the work to the whole spinel family. However, rather serious difficulties in the interpretation of the spectra delayed the publication of the results until a set of coherent assignments has eventually been found and checked by appropriate experiments.

In view of the complexity of the problem, and since our assignments are at variance with the generally accepted interpretations, it is worth while to present first a general survey of the subject. We do *not* intend to present here an exhaustive review of the existing data, and most of the papers dealing with particular problems will not appear in the bibliography. Instead, this introductory paper is devoted to a critical discussion of the *essential* existing data and interpretations. Our own results and assignments will be presented and discussed in a series of forthcoming papers.

THE EXISTING DATA AND INTERPRETATIONS

The actual situation may be described by referring to 3 essential papers: (1) The first important paper on the infrared spectrum of spinels was published in 1955 by WALDRON [1], who gave experimental data on 7 ferrite spinels, and proposed tentative assignments based on a theoretical, although simplified, treatment of the vibrational problem. (2) The amount of available experimental data was considerably

[1] R. D. WALDRON, *Phys. Rev.* **99**, 1727 (1955).
[2] P. TARTE, *Spectrochim. Acta* **19**, 49 (1963).

increased by HAFNER [3], but no important progress was made as far as the interpretation problem is concerned. (3) More recently, WHITE and DE ANGELIS derived from the group theory the number of active fundamental modes for different types of spinel structure [4]. But here again, the problem of the band assignment relies on a simplified reasoning which remains open to discussion.

We shall now discuss the essential points of these papers.

R. D. WALDRON: *Infrared spectra of ferrites* [1]

Two essential points will be summarized and discussed: (a) the determination and description of the i.r. active modes, and (b) the assignment of the observed frequencies.

(a) *Determination and description of the i.r. active modes.* The determination has been made by WALDRON by referring to a rhombohedral primitive cell which, for a normal ferrite spinel $M^{II}Fe_2O_4$, contains $2M^{II}O_4$ tetrahedra and one Fe_4 tetrahedron. This primitive cell contains only 14 ions (against 56 ions in the full cubic crystallographic cell) and tetrahedral groups of T_d symmetry (against tetrahedral and octahedral groups in the cubic cell).

The application of group theory to this rhombohedral cell leads to the conclusion that four modes only are i.r. active. The description of these modes depends of course on symmetry considerations, but is somewhat predetermined by the particular geometry of the rhombohedral primitive cell.

After WALDRON, these 4 modes may be classified into 2 groups:

The 2 modes having the highest frequencies, ν_1 and ν_2 are due to the motion of oxygen with respect to the cations.

The 2 low-frequency modes ν_3 and ν_4 must be related to displacements of the metallic cations. Since, however, the corresponding absorption bands were not observed by WALDRON, no description of these modes is presented, and the detailed study is restricted to the ν_1 and ν_2 modes.

As far as these modes are concerned, the basis of WALDRON's description is as follows: (1) In the spinel lattice, every oxygen anion is bonded to 3 octahedral and 1 tetrahedral cation (Fig. 1). (2) The 3 octahedral bonds are perpendicular to each other and thus provide, at least in a normal spinel, an isotropic force field in which the oxygen would be free to oscillate in the 3 directions if the tetrahedral bond was absent. (3) The tetrahedral cation C_T (Fig. 1) introduces a supplementary restoring force in a preferential direction along the C_T—O bond. This is responsible for the ν_1 mode in which the oxygen is forced to oscillate along the C_T—O bond, and thus appears as a stretching vibration of the tetrahedral group. (4) If we now consider an oxygen vibration at right angle with the preceding one, the restoring force due to the tetrahedral cation C_T will be negligible (if it is admitted that the bending force constant of the tetrahedron is small): this leads to the ν_2 mode, which may be considered as a stretching frequency of the octahedral group.

(b) *Assignment of the observed frequencies.* Two strong bands are generally observed in Waldron's spectra, and their assignment may be immediately derived

[3] St. HAFNER, *Z. Krist.* **115**, 331 (1961).
[4] W. B. WHITE and B. A. DE ANGELIS, *Spectrochim. Acta* **23A**, 985 (1967).
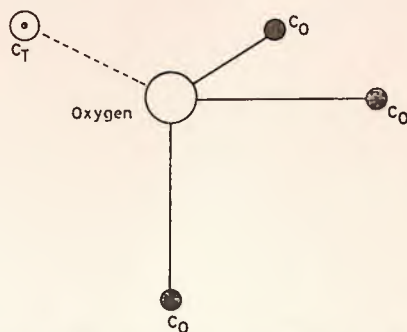
Fig. 1. The nearest cationic neighbours of the oxygen anion in the spinel lattice.
C_O: octahedral cation C_T: tetrahedral cation.

from the preceding description. The ν_1 mode, which is a stretching vibration of the tetrahedral group, corresponds to the highest restoring force and thus should be assigned to the high frequency band. The ν_2 mode (stretching vibration of the octahedral groups) is assigned to the low frequency band.

Discussion. Two points are open to discussion: the description of the normal modes of vibration; and the attribution of the higher restoring force to the tetrahedral cation–oxygen bond.

As mentioned previously, the primitive rhombohedral cell is more simple (and thus more easily amenable to a group theoretical treatment) than the full cubic crystallographic cell. But this choice implies a somewhat arbitrary description of the normal modes of vibrations: these are described as arising, in part from the vibration of the tetrahedral group, and in part from the oscillations of the octahedral cations.

Such a description is similar in all respects to the vibrational treatment of a true salt, with the separation of the vibrations into 2 types, namely the internal vibrations of the anion, and the so-called external vibrations of the cations.

It is well known, however, that apart from a few cases, the spinels must be considered as double oxides and not as salts.

But the most important point open to criticism is the systematic assignment of the high-frequency band to the stretching vibration of the tetrahedral group.

This assignment derives from the peculiar description of the vibrations chosen by WALDRON, in which the 3 octahedral bonds provide an isotropic force field, whereas the tetrahedral cation introduces a supplementary restoring force in a preferential direction along the C_T—O bond.

As a consequence, the highest restoring force is directed along the tetrahedral cation–oxygen bond, and the corresponding vibration, which is a stretching vibration of the tetrahedral group, must be assigned to the high-frequency absorption band.

Now, this statement neglects 2 important points:

First of all, the 4 i.r. active fundamentals belong to the same representation T_{1u}, with as a consequence the possibility of more or less strong vibrational interactions between these 4 modes.

Second, even if such interactions are weak, the proposed assignment will be true if, and only if the tetrahedral cation–oxygen bond is *stronger* (or at least of the same order of magnitude) than the octahedral cation–oxygen bond. Although this condition is fulfilled in some cases, this is certainly not true for all spinels, and it is necessary to discuss this point in some detail.

For a given coordination number, the bonding force between oxygen and a cation depends on the nature of the cation and, for a given cation, depends on its valency. This clearly appears in Table 1, which gives after experimental data obtained in our laboratory the absorption region of isolated MnO_4 tetrahedra as a function of the Mn valency. These data clearly demonstrate that, for a given cation in a given coordination state, the stretching frequency, and the bonding force,

Table 1. Absorption region corresponding to the stretching vibrations of MnO_4 tetrahedra as a function of manganese valency

Mn valency	Corresponding compound	Absorption region (cm^{-1})
VII	$KMnO_4$	930–900
V	$Ba_3(MnO_4)_2$	830–750
III	$Sr_2Mn_2^{III}GeO_7$ — solid	
	$Sr_2Mn_2^{II}Ge_2O_7$ solution	600–550
II	$Sr_2MnSi_2O_7$	450

strongly depends on the valency of the cation. In fact, the importance of this factor is so great that the influence of the valency state is still evident, even if one compares the absorption ranges of *different* cations. Here again, the absorption ranges collected in Table 2 have been obtained in our laboratory by the investigation of appropriate compounds or families of compounds. The quoted absorption ranges refer to the stretching frequency of condensed octahedral groups.

Table 2. Influence of the valency on the stretching frequency of various condensed octahedral groups

Valency	Cation	Absorption range of the corresponding condensed octahedra (cm^{-1})	Absorption range for a given valency (cm^{-1})
V	Nb	850–700	850–700
	Ta	850–700	
IV	Ge	650–550	
	Sn	650–550	650–550
	Ti	650–550	
III	Al	650–500	
	Ga	600–500	650–400
	Fe	550–400	
	Cr	650–550	
II	Mg	450–350	
	Ni	400–300	
	Co	350–300	450–300
	Mn	<320	
	Fe	<320	

The conclusion which may be drawn from these results is quite clear: as far as one is concerned with cations whose masses and electronic structures are not too widely different the valency state is generally the most important factor determining the cation–oxygen bonding force, and the corresponding vibrational frequency.

With these results in view, we may now turn back to the spinel case. If the tetrahedral cation C_T is characterized by a higher valency than the octahedral cation C_0, the bonding force C_T–O will be larger than the bonding force C_0–O, and WALDRON's assignment of the high-frequency band to the tetrahedral stretching vibration must be essentially correct. The I–VI (Na_2MoO_4, Na_2WO_4, ...) and the normal II–IV (Ni_2GeO_4, ...) spinels are typical examples of this possibility. A considerably less clear-cut situation, however, is offered by the II–III spinels (normal or inverse) and by the inverse II–IV spinels, the tetrahedral sites of which are occupied by a relatively low valency cation. In such cases, the origin of the high-frequency band is by no means evident and, in a preliminary paper [5], the present authors have expressed the opinion that the vibrational frequencies could possibly be related to complex motions of the lattice, involving a contribution of both tetrahedral and octahedral groups.

Table 3. Absorption ranges

Condensed octahedral groups		Isolated tetrahedral groups	
AlO_6	650–500	MgO_4	550–500
GaO_6	600–500	ZnO_4	500–400
FeO_6	550–400	CoO_4	450–400
CrO_6	650–550	LiO_4	500–400
GeO_6	650–550		
SnO_6	650–550		
TiO_6	650–550		

We may now go further by considering the absorption ranges for different coordinated groups which are actually found in numerous spinels, namely "isolated" tetrahedra and "condensed" octahedra. Here again, the values collected in Table 3 have been obtained in our laboratory through the study of appropriate non-spinel compounds, for which unequivocal assignments could be made. The absorption ranges corresponding to bivalent or monovalent cations in "isolated" tetrahedra are consistently and significantly lower than the absorption ranges corresponding to tri- or tetra-valent cations forming a lattice of condensed octahedra. These examples clearly demonstrate that Waldron's assignment of the high-frequency band to the tetrahedral group is rather questionable, at least for the inverse II–IV and normal II–III spinels. Indeed, the actual data would suggest that the high-frequency band should be assigned to the stretching vibration of the *octahedral* groups. This has been already verified in one case at least, namely the spinel LiCrGeO$_4$, where the study of the ^6Li-^7Li isotopic shifts leads to the unequivocal identification of the LiO$_4$ vibration: this must be assigned to the *low-frequency* band near 450 cm^{-1}, whereas the high-frequency band near 630 cm^{-1}, which exhibits no ^6Li-^7Li shift, is

[5] P. TARTE and J. PREUDHOMME, *Acta Cryst.* **16**, 227 (1963).

necessarily assigned to the stretching vibration of the lattice of $GeO_6 + CrO_6$ octahedra [6]. Moreover, it is worth while to point out the very satisfactory agreement between the frequency of this band, and the absorption ranges corresponding to GeO_6 and CrO_6 octahedra (Table 2): this suggests that the absorption ranges quoted for octahedral groups in Table 2 may be applied to the spinel compounds without significant corrections.

Although the $LiCrGeO_4$ case may be considered as a fairly peculiar one, the above-mentioned results are sufficient to show that Waldron's assignments are open to discussion for all spinels in which the tetrahedral sites are occupied by a low valency cation.

S. Hafner: Die Absorption einiger Metalloxyde mit Spinellstruktur [3]

Most of the compounds investigated are II–III spinels, for which Hafner's experimental results may be very briefly summarized as follows: (1) Two strong bands are generally observed in the 1000–400 cm $^{-1}$ region. (2) The position of these bands depends essentially on the nature of the *octahedral* cation, and to a reduced extent on the nature of the tetrahedral cation.

But, as far as the interpretations are concerned, Hafner entirely follows Waldron's description of the vibrations and assignments. Thus, the high-frequency band is assigned without discussion to the stretching vibration of the tetrahedral group, a rather unexpected conclusion in view of Hafner's own observation that the position of this band depends more strongly on the nature of the octahedral cation. Anyway, a further discussion of Hafner's interpretations is not necessary, since they are identical to those of Waldron: the criticism developed in the preceding section may thus be applied without any change.

W. B. White and B. A. De Angelis. Interpretation of the vibrational spectra of spinels [4]

Three important points of this paper will be summarized or discussed here: (1) The application of the group theory to the classification of the vibrational modes; (2) The interpretation of the spectra; (3) The vibrational behaviour of solid solutions. (1) The principal, and very important, contribution of this paper is the application of the group theory to the classification of the vibrational modes of the spinels. This leads to the knowledge of the i.r. and Raman active fundamentals for different types of spinel structures and of cation ordering. For a simple spinel such as $MgAl_2O_4$, there are only 4 i.r. (in agreement with Waldron's findings) and 5 Raman active fundamentals. But this number may be as high as 31 (i.r.) and 50 (Raman) for the spinel $LiZnNbO_4$, the structure of which is tetragonal with a 1:1 ordering of the Li and Nb cations on the octahedral sites. (2) The group theory does *not* allow, however, the assignment of the observed frequencies to the normal modes. *For this assignment, White and De Angelis go back to Waldron's approximation,** where the frequencies

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* Although they admit themselves that "for most ionic spinels listed in Table 1, this is not a very accurate approximation."

[6] P. Tarte, *Acta Cryst.* **16**, 228 (1963).

are assigned, in part to the vibrations of tetrahedral groups, and in part to the translation of the octahedral cations. *Here again, the high frequency band is assigned without discussion to the stretching vibration of the tetrahedral group.* Of course, this assignment is the right one for the first examples (Na_2WO_4 and Na_2MoO_4) quoted by the authors; but we know from the preceding discussions that it is highly questionable for all spinels where the tetrahedral site is occupied by a low valency cation. No definite assignment is proposed for the 3 remaining fundamentals. (3) Finally, the authors discuss the vibrational behaviour of solid solutions, in connection with a possible ordering of the cations. It is well known that an order-disorder transition may bring out important changes in the number of active vibrational modes: the ordering of the cations lowers the overall symmetry and thus increases the number of active fundamentals. Now, as far as solid solutions are concerned, WHITE and DE ANGELIS express the opinion that, if the spectrum of solid solutions exhibits supplementary bands with respect to the spectrum of the corresponding pure compound, there must be some kind of ordering of the cations present in the solid solution. A theoretical treatment of the vibrational behaviour of solid solutions is still needed (this point will be briefly discussed in the next paper) but nevertheless, we may show that this conclusion is erroneous.

If we consider a solid solution where 2 cations, X and Y, replace each other in a statistical way, the X-ray diagram and the space group of this solid solution and of the corresponding pure compounds are the same: this results from the *geometrical* equivalence of the X and Y cations. For the same reason, these cations are equivalent for the group theory, which relies on geometrical considerations. *But this geometrical equivalence does not necessarily imply a vibrational equivalence.* If the masses, or if the cation–oxygen bonding forces, of the X and Y cations are sufficiently different, the X–O and Y–O vibrational frequencies may also be significantly different, and will appear as distinct absorption bands in the spectrum of solid solutions. Thus, *this spectrum will exhibit supplementary bands with respect to the spectrum of the pure compounds, irrespective of the ordered or disordered distribution of the cations.*

Experimentally, this is verified by the study of systems which are able to form a *continuous* series of solid solutions, and for which the possibility of cation ordering is thus excluded. Several systems of this type have already been investigated [7], and their i.r. spectrum exhibits absorption bands which may be unequivocally assigned to distinct X–O and Y–O vibrations. Thus, on both theoretical and experimental evidence, we may consider as erroneous the stating that the occurrence of supplementary bands in solid solutions is necessarily related to a cation ordering.

The same reasoning may be applied to the case of disordered *inverse* spinels. The space group is the same that for a normal spinel ($O_h^7 - Fd3m$) and thus simple group theoretical considerations lead to the prediction of 4 i.r. active fundamentals (as in a normal spinel). If, however, the above-mentioned criticism is taken into account, it appears that the i.r. spectra of disordered inverse spinels could possibly exhibit more than 4 i.r. fundamentals, since 2 different cations A and B are located on the octahedral sites. It does not seem that this possibility has been investigated so far, but we shall present experimental results which support this view.

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

Finally, we must mention a rather recent paper by Lutz, in which a completely different interpretation has been proposed [8]. On the basis of a normal coordinate analysis, the author concludes that there is no characteristic vibration of the tetrahedral groups, whereas such characteristic vibrations may exist, at least as a first approximation, for octahedral groups. No detailed justification is given by the author, but it should be pointed out that this conclusion is in contradiction with well-established interpretations, such as the assignment of the high frequency band to the antisymmetric stretch of the tetrahedral group in spinel germanates $X_2{}^{II}GeO_4$ [2], tungstate and molybdate Na_2WO_4 and Na_2MoO_4 [3, 4].

Conclusions

Although the authors agree about the number and symmetry species of the i.r. active vibrations of an ordinary AB_2O_4 spinel lattice, there is fundamental disagreement about the interpretation of the spectrum: (a) Most of the preceding authors have *systematically* assigned the high-frequency band to the stretching vibration of the tetrahedral group [1, 3, 4]. (b) The opposite opinion has been recently expressed, that localized vibrations could exist for octahedral groups only, but not for tetrahedral groups [8]. (c) It has also been suggested that, in some cases at least, the observed frequencies cannot be assigned to the vibrations of definite coordinated groups (either tetrahedral or octahedral), but instead are related to complex vibrations of the whole spinel lattice [5]. Now, if we consider the published experimental data, we found an unexpected scarcity of unequivocal assignments. The assignment of the high-frequency band to the stretching vibration of the tetrahedral group has been proved for 2 types of spinels only, namely the normal germanates $X^{II}GeO_4$ [2], and the normal molybdate and tungstate Na_2MoO_4 and Na_2WO_4 [3, 4]. This assignment supports the first type of interpretation; but the detailed discussion presented in this paper suggests that this interpretation is probably restricted to the spinels, the tetrahedral sites of which are occupied by the highest valency cation. The opposite interpretation, namely the assignment of the high-frequency band to a vibration of the octahedral lattice, must be considered in the case of the spinel $LiCrGeO_4$ [6].

Although very few in number, these data and interpretations prove that the high-frequency band cannot be systematically assigned to either the tetrahedral or the octahedral groups, and that this interpretation problem is more complicated than previously expected.

It is thus quite clear that the problem of the band assignment should be re-investigated on a new basis. This basis will be defined and discussed in the next paper.

[8] H. D. Lutz, *Z. Naturforsch.* **24a**, 1417 (1969).