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Infrared studies of spinels—II
The experimental bases for solving the assignment problem

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Abstract—The problem of interpreting the i.r. spectrum of spinels is discussed. Since the four i.r. active fundamentals belong to the same representation T_{1u}, vibrational interactions must be expected and any assignment of the observed frequencies to localized vibrations is necessarily an approximation. The validity of this approximation is discussed for different types (weak or strong) of vibrational interactions, and emphasis is put on the identification of the cations which are involved in either "localized" or "complex" vibrations. These assignment problems may be solved by appropriate experimental methods, namely the systematic investigation of the vibrational behaviour of: (i) homogeneous families of pure compounds; (ii) isotopic species, including isotopes of medium-weight cations; (iii) solid solutions.

INTRODUCTION

IN THE preceding paper, we have shown that no satisfactory solution has been proposed so far to the problem of interpreting the i.r. spectrum of spinels.

The failure to solve this problem is related to:

(1) The lack of systematic experimental data.

(2) In some cases, an arbitrarily simplified description of the vibrations.

(3) A premature generalization to all spinels of a very limited number of results and interpretations which were deduced from the study of rather specific cases.

We shall present in this paper the basic principles of our own approach to this problem.

Two main topics will be discussed:

(1) The occurrence of "characteristic" (or "localized") vibrations (vibrations which may be considered as restricted to one type of cation or co-ordinated group only), in contrast with "complex" (or "mixed") vibrations (involving the simultaneous participation of two types of cations or co-ordinated groups).

(2) As far as characteristic vibrations may be taken into account, the assignment of the observed frequencies to vibrations of a definite co-ordinated group.

"LOCALIZED" VS. "COMPLEX" VIBRATIONS

It should be first recalled that the 4 i.r. active fundamentals of a spinel lattice belong to the same representation T_{1u} [1] and thus are liable to interact one with another. As a consequence, any assignment to the localized vibration of a definite co-ordinated group is *necessarily an approximation*. The point is to know to what extent this approximation may be accepted.

Generally speaking, the possibility of significant vibrational interactions depends

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

on the actual vibrational frequencies of the different co-ordinated groups; if the vibrational frequencies are quite different, the possibility of vibrational interactions is very remote. This is well illustrated by the spinel molybdate Na_2MoO_4, where the high-frequency band may be immediately assigned to the antisymmetric stretch of the MoO_4 tetrahedron. On the contrary, strong coupling may occur between co-ordinated groups, the frequencies of which are of the same order of magnitude; in this case, the assignment of a frequency to the vibration of a definite group is clearly meaningless. Now, since the spinel lattice is constituted of "isolated" tetrahedra (no common oxygen between tetrahedra) and "condensed" octahedra (interlinked by an edge, Fig. 1), we must consider the following possibilities of vibrational interactions:

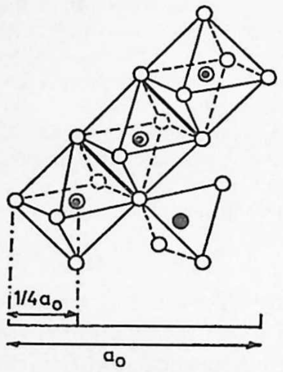

Fig. 1. Occurrence of "isolated" tetrahedra and of "condensed" octahedra in the spinel lattice.

Interactions between (1) identical tetrahedra, (2) different tetrahedra, (3) identical octahedra, (4) different octahedra, and (5) tetrahedra and octahedra.

(1) *Interactions between identical tetrahedra*

These interactions are in fact vibrational couplings between identical tetrahedra which are present in the same unit cell. They may be evidenced by the study of appropriate dilute solid solutions [2–4]. Although not negligible, these interactions are not very important in view of the "isolated" character of the tetrahedra. They are not sufficient to modify the absorption range of the tetrahedra under consideration, and they do not preclude the assignment of a given frequency to the vibration of a definite co-ordinated group.

(2) *Interactions between different tetrahedra*

If a spinel structure contains 2 types of tetrahedra, XO_4 and YO_4, their vibrational behaviour will depend on the specific values of their vibrational frequencies. If these frequencies are rather different, the vibrational interactions will be weak

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[2] K. Wickersheim, R. Lefever and B. Hanking, *J. Chem. Phys.* **32**, 271, (1960).
[3] P. Tarte, *Bull. Acad. Roy. Sci. Belg.* **46,** 169 (1960).
[4] P. Tarte, *Mém. Acad. Roy. Belg.* **35,** 4a and 4b (1965).

and each type of group will contribute to the spectrum by its own characteristic frequency. This behaviour is illustrated by the spinel $LiFeCr_4O_8$, the structure of which contains LiO_4 and FeO_4 tetrahedra: its spectrum exhibits at 435 cm^{-1} a band which is essentially related to a vibration of the LiO_4 tetrahedra [4]. On the contrary, if the vibrational frequencies of the XO_4 and YO_4 groups are similar, the interactions will be sufficient to lead to an unique, average frequency which can be assigned neither to XO_4 nor to YO_4 group.

(3) *Interactions between identical octahedra*

Since the octahedral groups have edges in common, much more important vibrational interactions are expected in this case. This leads to a very significant upwards shift for the absorption range of a lattice of "condensed" octahedra, with respect to the absorption range characteristic of the corresponding isolated octahedra [4]. On the other hand, it is no longer appropriate to speak about a "localized" vibration, since all the octahedral lattice is moving. This vibration, however, may still be considered as characteristic of the octahedral groups taken as a lattice.

(4) *Interactions between different octahedra*

The occurrence of different octahedral groups possessing similar frequencies will of course lead to strong interactions and consequently to an averaging of the frequencies. This is the case for the spinel $LiCrGeO_4$, where the high-frequency band must be assigned to a mixed vibration of the CrO_6–GeO_6 lattice [5]. The situation is much more complicated if the octahedral lattice is constituted of octahedra possessing different frequencies. We may expect, either the averaging phenomenon mentioned above, or a complex behaviour such as the splitting of a frequency into several bands, none of which, however, may be related to a definite co-ordinated group [6]; or finally the occurrence of distinct vibrational frequencies, but this last case is expected to occur only if the vibrational frequencies of the octahedral groups are very different.

(5) *Interactions between octahedral and tetrahedral groups*

The above-mentioned considerations are still valid here. Vibrational interactions are expected to be found when the vibrational frequencies of these groups are not sufficiently different. Such complex vibrations should be related to the whole spinel unit cell.

EXPERIMENTAL SEARCH FOR EITHER LOCALIZED OR COMPLEX VIBRATIONS

Owing to its purely qualitative character, the preceding discussion can just give some insight about the *possibility* of significant vibrational interactions. But the real occurrence of such interactions in a specific case should be determined by appropriate experimental methods. Such methods rely on a modification of the cations, and a study of the corresponding modifications in the spectrum. Two possibilities must be considered: the replacement of a cation by one of its isotopes; or its replacement by another cation without change of the crystal structure (isomorphic replacement leading to solid solutions).

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[5] P. TARTE, *Acta Cryst.* **16**, 228 (1963).

[6] P. TARTE, *Spectrochim. Acta* **19**, 49 (1963).

(1) *Isomorphic substitution* (*study of solid solutions*)

Various possibilities of isomorphic substitutions have been investigated in this laboratory. Since the results have already been published [4, 6], we just need to give a brief summary of them. When a cation Y is substituting for a cation X, the following types of vibrational behaviour have been observed:

(I) The progressive replacement of a co-ordinated group XO_n by its equivalent YO_n brings out the progressive replacement of some bands (which are thus assigned to XO_n) by new bands (which are assigned to YO_n). Such a behaviour (Fig. 2a) is characteristic of the occurrence of localized vibrations of XO_n or YO_n groups. It has been found, for example, in the spectrum of phenacites solid solutions $Zn_2(Si_{1-x}Ge_x)O_4$; where the SiO_4 bands are progressively replaced by the GeO_4 bands with increasing values of x [4].

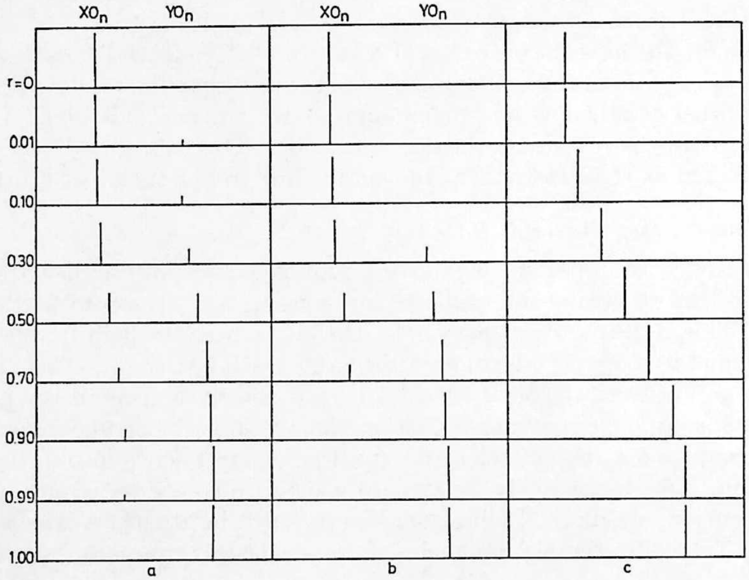

Fig. 2. Schematic vibrational behaviour of solid solutions involving the progressive replacement of XO_n by YO_n co-ordinated groups. r = replacement percentage. a: nearly ideal "localized" vibration; b: intermediate case; c: "complex" vibration.

(II) In other cases, the only modification of the spectrum is simply a progressive frequency shift of all the existing bands (Fig. 2c). These bands are not characteristic of either XO_n or YO_n frequencies and should be assigned to mixed vibrations.

(III) Intermediate cases have also been observed, for which the new bands are observed only for medium concentrations of the substituting cations (Fig. 1b) [6]. In this case, the approximation of localized vibrations is only a rough one.

(IV) Finally, we must mention the rather complex, and still unexplained vibrational behaviour of the spinel solid solutions $(Ni, Mg)_2GeO_4$ and $(Co, Mg)_2GeO_4$ [6].

We may conclude that, apart from some specific unexplained cases, the vibrational behaviour of solid solutions may give information about the localized or complex character of vibrations.

However, the drawbacks of this method should also be considered:

(1) It is not always possible to find out a convenient cation Y which is able to substitute for X, and for which the YO_n vibrational frequencies are sufficiently different from the corresponding XO_n frequencies.

(2) There is no theoretical support to the experimental results (our theoretical knowledge of the vibrational behaviour of solid solutions is still unsatisfactory, even in the simple case of binary compounds), and their interpretation is not always evident. From this point of view, the case of condensed octahedra is rather difficult in view of the important vibrational interactions which already exist in the pure compound.

(3) The isomorphic replacement of a cation by another involves a simultaneous change of *four* parameters which are able to modify the vibrational frequencies, namely the cationic mass, the cation-oxygen distance and bonding force, and the unit cell dimensions. And there is little hope to distinguish between the relative contributions of these different factors.

(2) *Isotopic substitution*

The method of isotopic substitution has been used for a long time in vibrational spectroscopy, but it has generally been restricted to very light elements. It was recently extended to medium-weight cations, by NAKAMOTO *et al.* in the case of metal complexes [7], and by the authors in the case of various inorganic compounds [8]. This method is able to give unequivocal evidence of mixed vibrations involving the simultaneous participation of 2 cations; but it also has its own limitations, such as the availability of convenient isotopic species, and the smallness of the isotopic shifts. Difficulties of a more fundamental nature have also been encountered, such as the lack of isotopic shifts for some vibrations of a lattice of condensed octahedra. [8]. It is clear that both methods—isotopic and isomorphic replacement—offer complementary possibilities and thus should be used simultaneously whenever possible.

ASSIGNMENT OF THE OBSERVED FREQUENCIES TO DEFINITE CO-ORDINATED GROUPS

The extensive use of the two above-discussed methods—isotopic and isomorphic replacements—allows the identification of the frequencies which may be considered as more or less localized, and simultaneously leads to the identification of the cation which is responsible for the vibration under consideration. These methods are, however, either costly (isotopic replacement), or time-consuming (synthesis of a number of solid solutions). On the other hand, difficulties may appear in the interpretation of the results, especially in the case of a lattice of condensed octahedra.

There remains a third method, namely the *systematic investigation of homogeneous families of pure compounds*. In most cases, this type of investigation *is not able to*

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[7] K. NAKAMOTO, K. SHOBATAKE and B. HUTCHINSON, *J. Chem. Soc., Lond.* 1451 (1969).

[8] P. TARTE and J. PREUDHOMME, *Spectrochim. Acta* **26A,** 2207 (1970).

give direct evidence about the localized or complex origin of the observed frequencies, and thus the interpretation of the results must be used with caution.

Nevertheless, the possibilities offered by this method are twofold:

(1) If we consider a normal spinel $A^{II}B_2^{III}O_4$ (A = tetrahedral; B = octahedral cation), there is no difficulty in studying how the spectrum is modified when, say the tetrahedral cation A is changed, B being kept the same (this is quite possible with a series of chromites $A^{II}Cr_2O_4$, with A^{II} = Mg, Zn, Co, Cd, Mn, Ni); and conversely, we may keep A constant and change B (zinc spinels $ZnB_2^{III}O_4$, with B^{III} = Al, Ga, Fe, Co, Cr, Rh). It is thus possible to investigate to what extent a given frequency depends on the nature of either the tetrahedral or the octahedral cation.

(2) The second possibility is the comparison of the frequencies related to a series of pure spinels with the absorption ranges which may be characteristic of a series of various co-ordinated groups (tetrahedral or octahedral). These absorption ranges have been determined in our laboratory through the i.r. study of selected families of non-spinel compounds, for which unequivocal assignments could be made [4].

It is evident, however, that this rather empirical procedure has many drawbacks and should be used with much caution:

(a) The study of various compounds leads to the knowledge of absorption *ranges*, the limits of which are necessarily more or less uncertain.

(b) These absorption ranges are significant only if the vibrations may be related to a definite type of cation or coordinated group. They are meaningless in the case of complex vibrations.

(c) In connection with the preceding point, it appears that, for most compounds of the double oxide type, the comparison is (or may be) significant for the high-frequency bands only: our experimental results have shown that, apart from some specific cases, most of the low-frequency bands are generally related to complex vibrations.

Thus, the comparison between known absorption ranges and actual observed frequencies is able to give rapidly *preliminary* information about the possible origin of the bands. But these provisional assignments *must* be checked by more rigorous techniques, such as the isomorphic and isotopic replacement.

CONCLUSIONS

A significant and realistic interpretation of the i.r. spectrum of the spinels requires a good knowledge of the correlations which may exist between the chemical nature of the cation (or of the co-ordinated groups) and the observed vibrational frequencies.

This knowledge may be gained through the use of 3 methods:

(1) The systematic study of homogeneous families of pure spinels. Such a study allows a comparison of the observed frequencies with the characteristic absorption ranges of definite co-ordinated groups; it also shows to what extent a given frequency depends on the nature of either the tetrahedral or the octahedral cation. The assignments which may be deduced from these data should be considered as

tentative only, since there is no definite proof that the observed frequencies may be related to vibrations of an unique type of co-ordinated group.

(2) The method of isomorphic replacement may give information about the validity of the "localized vibration" approximation. It *must* be used to check the preliminary assignments deduced from the first method.

(3) Finally, whenever applicable, the method of isotopic replacement seems to be more sensitive than the isomorphic replacement to the occurrence of mixed vibrations.

Since our assignments problem is by no means a simple one, and since our interpretations disagree with those generally accepted in the literature, we made (as far as possible) a simultaneous use of the three methods so as to gain the best available evidence for the proposed interpretations. The experimental data and the resulting assignments will be presented in a series of forthcoming papers.

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