Vibrational studies of olivine-type compounds—I. The i.r. and Raman spectra of the isotopic species of Mg_2SiO_4

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Abstract—A group theoretical analysis has been carried out for the olivine structure, and the isotopic species of the type compound Mg_2SiO_4 have been investigated by Raman and i.r. spectroscopy. New assignments have been deduced from ^{24}Mg–^{26}Mg and ^{28}Si–^{30}Si isotopic shifts. The 1000–475 cm^{-1} region of the i.r. spectrum is essentially related to internal (stretching and bending) modes of the SiO_4 tetrahedron whereas most of the lower frequency bands must be assigned to external modes. The SiO_4 totally symmetric, stretching frequency (ν_1) is observed at 842 cm^{-1} in the i.r. spectrum where it is unequivocally identified through the nearly complete lack of a ^{28}Si–^{30}Si mass effect, whereas this mass effect appears in the ν_3 components by a 10–15 cm^{-1} shift. It has also been possible to evidence a number of vibrational interactions, such as the mixing of the symmetric and antisymmetric stretching, Raman-active, modes, the simultaneous participation of both Mg and Si atoms to some translational modes, and the mixing of some translational and rotational modes. The significance of force constant calculations is also briefly discussed.

INTRODUCTION

THE VIBRATIONAL spectrum of silicates and germanates of the olivine type has not been exhaustively investigated, despite the relative simplicity of their chemical composition. This situation is most probably related to the fairly low symmetry of the crystal structure, with as a consequence the practical impossibility to propose a detailed and unique interpretation of the spectrum.

Previous attempts in this field include (1) the extensive experimental study by TARTE [1] of the i.r. spectra of pure compounds and solid solutions, which lead to interpret the spectra in terms of vibrations of tetrahedral SiO_4 (or GeO_4) groups, and octahedral XO_6 groups (X being a divalent cation such as Mg, Ni, Co, Mn . . .); (2) the work of DUKE and STEPHENS [2], essentially restricted to a study of the influence of the divalent cation on the vibrational frequencies of the SiO_4 tetrahedron; and (3) a more theoretical investigation of OEHLER and GÜNTHARD [3] essentially dealing with a normal coordinate analysis of Mg_2SiO_4 and the evaluation of a set of force constants. We have reinvestigated this whole family of compounds from both experimental and theoretical points of view [4], since it is expected that the combined use of isotopic studies and group theoretical considerations, together with the existing data on pure compounds and solid solutions, should lead to a more comprehensive interpretation of the spectra. We present and discuss here the spectra of

[1] P. TARTE, *Spectrochim. Acta* **19**, 25 (1963).
[2] D. A. DUKE and J. D. STEPHENS, *Am. Mineral.* **49**, 1388 (1964).
[3] O. OEHLER and Hs. H. GÜNTHARD, *J. Chem. Phys.* **51**, 4719 (1969).
[4] M. TH. PAQUES-LEDENT, Doctorate Thesis, University of Liège (1972).

the isotopic species of Mg_2SiO_4, which is particularly well suited for such an investigation, since stable isotopes are available for both Mg and Si atoms. Other series of olivine-type compounds will be discussed in forthcoming papers.

EXPERIMENTAL

Synthesis of the compounds

The compounds have been synthesized by solid state reaction at 1200°C between the oxides SiO_2 and MgO. The phase obtained with natural MgO and SiO_2 (essentially ^{24}Mg and ^{28}Si) was checked by X-ray diffractometry; this check was omitted for the other isotopic species (with either ^{26}Mg or ^{30}Si), which were prepared in very small quantities. The isotopic purities are given in Table 1.

Table 1. Isotopic purity data*

Element	Isotopic composition (%)		Element	Isotopic composition (%)	
Mg (Natural)	^{24}Mg	78·60	Si (Natural)	^{28}Si	92·28
	^{25}Mg	10·11		^{29}Si	4·67
	^{26}Mg	11·29		^{30}Si	3·05
^{26}Mg	^{26}Mg	99·70	^{30}Si	^{28}Si	3·78
				^{29}Si	0·67
				^{30}Si	95·55

* We have neglected the isotopic species whose abundance is less than 0·5 per cent.

Some crystal fragments of natural olivine $(Mg, Fe)_2SiO_4$ were also investigated by Raman spectroscopy. Since the Raman spectra were found to be very weak and thus of limited interest, these natural olivines were not chemically analyzed for their Mg:Fe ratio.

Spectra

The i.r. spectra were registered by the conventional pressed disc technique, with a Beckman IR 12 (2000–200 cm^{-1}; KI discs) and a CAMECA SI 36 (200–50 cm^{-1}; polythene discs) spectrometer.

The Raman spectra were obtained with a CODERG PHO double monochromator, equipped with a 50 mW He–Ne laser (Spectra Physics).

The powdered sample is introduced into a glass capillary and formed into a cone which is illuminated along its axis by the laser beam. The scattered light is collected at a 90° angle.

CRYSTAL STRUCTURE AND NORMAL MODES OF VIBRATION

The olivine belongs to the space group D_{16}^{2h}–Pbnm; the primitive unit cell is centrosymmetric, with 4 formula units in the cell.

The essential symmetry elements of the Si and Mg atoms are given in Table 2. It will be noticed that the Mg atoms are distributed into 2 sets of non-equivalent MgO_6 octahedra, depending on their site symmetry (C_i or C_s) and available

Table 2. Symmetry properties of Si and Mg atoms in the olivine structure

Atom	Coordination number	Position (Wyckoff notation)	Site symmetry
Si	tetrahedral	c type	C_s
Mg	octahedral	c type	C_s
Mg	octahedral	a type	C_i

space (the MgO_6 octahedra with C_s symmetry being larger than those with C_i symmetry).

The irreducible representation related to the Mg_2SiO_4 crystal has been obtained in 2 ways, namely (i) the method of BAGHAVANTAM and VENKATARAYUDU [5], which relies on the determination of the number of atoms which remain invariant under the various symmetry operations of the D_{2h} group; and (ii) the correlation method which relies on the transformation of the irreducible representation when passing from the site group of a given atom to the factor group (D_{2h} in the actual case) [6].

This treatment has been carried out by assuming the separation of the vibrations into internal (SiO_4) and external (lattice) modes, the validity of this approximation being supported by the previous results of TARTE [1] on pure compounds and solid solutions.

The essential steps of the correlation method are given in Tables 3 and 4 for the

Table 3. Application of the correlation method to the external modes

Atom and site symmetry		$t_{y'}$	$f_{y'} = n.t_{y'}$	Representation corresponding to the site symmetry	Correlation	Representation corresponding to the factor group D_{2h}
		Translations				
Mg(a)	C_i	3	12	A_u	$\xrightarrow{C_{2h}(y)}$	$3A_u + 3B_{1u} + 3B_{2u} + 3B_{3u}$
Mg(c)	C_s	1	4	$(T_x)A'$	$\xrightarrow{\sigma_{xz}}$	$A_g + B_{2g} + B_{1u} + B_{3u}\ (\times 2)$
		1	4	$(T_y)A'$	$\nearrow$	
		1	4	$(T_z)A''$	$\longrightarrow$	$B_{1g} + B_{3g} + A_u + B_{2u}$
Si(c)	C_s			identical to Mg(c)		
		Rotations				
Si(c)	C_s	1	4	$(R_x)A''$	$\xrightarrow{\sigma_{xz}}$	$B_{1g} + B_{3g} + A_u + B_{2u}\ (\times 2)$
		1	4	$(R_y)A''$	$\nearrow$	
		1	4	$(R_z)A'$	$\longrightarrow$	$A_g + B_{2g} + B_{1u} + B_{3u}$

external and the internal modes respectively. One interesting point is evidenced by this treatment: there is no Raman-active species in the irreducible representation related to the Mg atoms located on a sites (C_i symmetry). Or, in other words, the Mg atoms on the a sites are not allowed to move during the Raman-active vibrations.

[5] S. BAGHAVANTAM and T. VENKATARAYUDU, *Theory of groups*, Andhra University (1948).
[6] R. S. HALFORD, *J. Chem. Phys.* **14**, 8 (1946).

Table 4. Application of the correlation method to the internal modes

Point T_d	Site group C_s	Factor group D_{2h}
$A_1(\nu_1) \longrightarrow$	$A'(\times 4) \longrightarrow$	$A_g + B_{2g} + B_{1u} + B_{3u}$
$E(\nu_2) \longrightarrow$	$A' + A''(\times 4) \longrightarrow$	$\begin{cases} A_g + B_{2g} + B_{1g} + B_{3g} \\ + A_u + B_{1u} + B_{2u} + B_{3u} \end{cases}$
$F_2(\nu_3) \longrightarrow$	$2A' + A''(\times 4) \longrightarrow$	$\begin{cases} 2A_g + B_{1g} + 2B_{2g} + B_{3g} \\ + A_u + 2B_{1u} + B_{2u} + 2B_{3u}(\times 2) \end{cases}$
$F_2(\nu_4) \longrightarrow$	$2A' + A''(\times 4)$	

This is in relation with the fact that these atoms are located on inversion centers of the crystal cell.

After summing up, the irreducible representation corresponding to the olivine crystal is as follows:

$$\Gamma_i = 11A_g + 7B_{1g} + 11B_{2g} + 7B_{3g} + 10A_u + 14B_{1u} + 10B_{2u} + 14B_{3u}.$$

After taking into account that the A_u modes are Raman and i.r. inactive, and subtracting the 3 acoustical modes ($1B_{1u} + 1B_{2u} + 1B_{3u}$), we obtain the number and types of vibrations which are either Raman, or i.r. active (Table 5).

Table 5. Types and activities of the normal modes of Mg_2SiO_4

Type	Raman active		i.r. active	
Internal modes (SiO_4)	$\left.\begin{matrix} 6A_g \\ 3B_{1g} \\ 6B_{2g} \\ 3B_{3g} \end{matrix}\right\}$	8 stretching 10 bending	$\left.\begin{matrix} 6B_{1u} \\ 3B_{2u} \\ 6B_{3u} \end{matrix}\right\}$	7 stretching 8 bending
Rotations	$\begin{matrix} 1A_g \\ 2B_{1g} \\ 1B_{2g} \\ 2B_{3g} \end{matrix}$		$\begin{matrix} 1B_{1u} \\ 2B_{2u} \\ 1B_{3u} \end{matrix}$	
Translations	$\begin{matrix} 4A_g \\ 2B_{1g} \\ 4B_{2g} \\ 2B_{3g} \end{matrix}$		$\begin{matrix} 6B_{1u} \\ 4B_{2u} \\ 6B_{3u} \end{matrix}$	
Total	$11A_g + 7B_{1g} + 11B_{2g} + 7B_{3g}$		$13B_{1u} + 9B_{2u} + 13B_{3u}$	

EXPERIMENTAL RESULTS AND ASSIGNMENTS

Infrared spectrum

After the previous assignments proposed by Tarte [1], the i.r. spectrum of Mg_2SiO_4 may be divided into 3 regions.

(1) The 1050–800 cm^{-1} region, corresponding to the various stretching vibrations of the SiO_4 tetrahedron.

(2) The 650–475 cm^{-1} region, corresponding to the bending vibrations of SiO_4.

(3) Below 475 cm^{-1}, the bands corresponding to external modes, which are essentially described as vibrations of the MgO_6 octahedra.

Some comments should be made about these assignments: (1) the distinction between stretching and bending vibrations of the SiO_4 group is in agreement with the general vibrational behaviour of XO_4 tetrahedral groups, and is experimentally justified by the lack of absorption bands in the intermediate 800–650 cm^{-1} region; (2) the 475 cm^{-1} limit between the internal bending, and the external modes is less clear-cut; likewise, no attempt was made to discriminate between translational and rotational modes.

Since this interpretation was deduced from the study of solid solutions, and since in such crystals the vibrational behaviour of solid solutions is too complicated to be completely understood, it is worthwhile to re-investigate the existing assignments by an independent method, namely the study of isotopic species [7].

Isotopic data

The spectra of the isotopic species are shown in Figs. 1 and 2. The observed frequencies and the isotopic shifts are collected in Table 6.
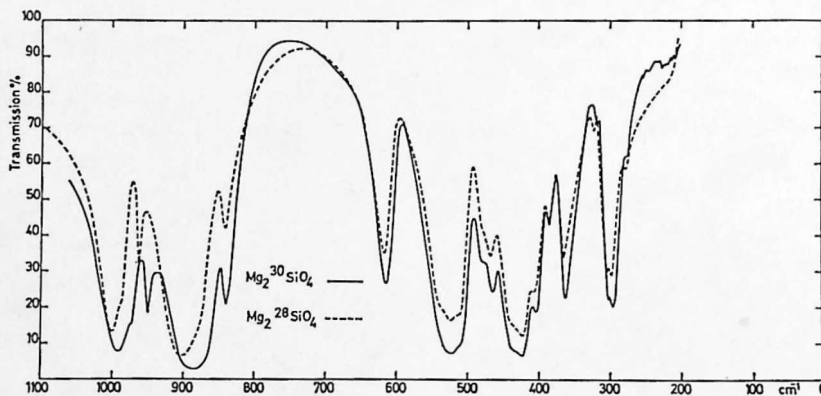

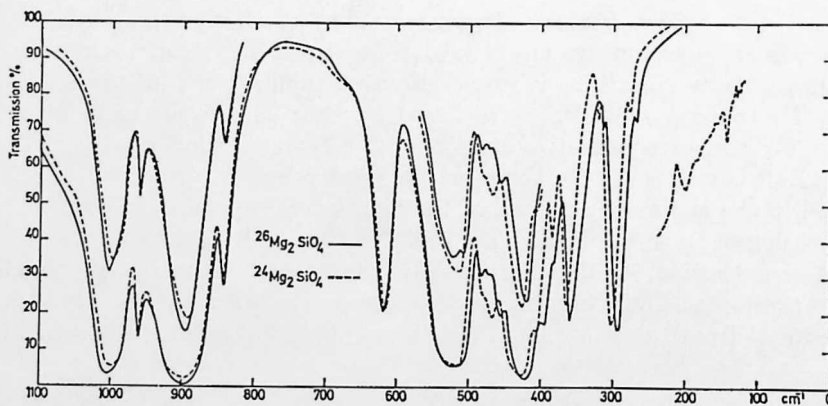Fig. 1. I.R. spectrum of ^{30}Si–^{28}Si isotopic species.

Fig. 2. I.R. spectrum of ^{26}Mg–^{24}Mg isotopic species.

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

Table 6.

$\Delta\nu$ $^{24}Mg-^{26}Mg$	$^{26}Mg_2$ $^{28}SiO_4$	$^{24}Mg_2$ $^{28}SiO_4$	$^{24}Mg_2$ $^{30}SiO_4$	$\Delta\nu$ $^{28}Si-^{30}Si$	Assignments
+3	~998*	~1001*	991*	+10	
+0·5	961	961·5	950·5	+11	Internal modes:
+1	899·5	900·5	885	+15·5	$\nu_3(SiO_4)$
+0·5	841·5	842	840·5	+1·5	$\nu_1(SiO_4)$
—		—	—		
+1·5	615	616·5	614·5	+2	Essentially
	515*	{522·5* / 509(sh)	522 / 509(sh)		Internal bending modes
+2	480	482(sh)	480(sh)	+2	
—		—	—		
+11	455·5	466·5	463·5 . . .	+3	. . . . Complex translations involving
	436	436	436 . . .		. . . /both Mg and Si cations but
+5·5	420	425·5	425·5 . . .		predominant contribution of the
					Mg cations
+10	405	415	412	+3	. . . / Either symmetric bending or
+2	382	384	384		. . . / rotation of the SiO_4 tetrahedron
+4·5	359·5	364	362·5 . . .	+1·5	. . . . complex vibrations involving trans-
+7	313·5	320·5	317·5 . . .	+3	. . . / lation of Mg cations and some
					motion of the SiO_4 tetrahedron
+8	292·5	300·5	300·5		
		295·5(sh)	295·5(sh)		Translational modes of the Mg
					cations
+9·5	268	277·5	277·5		
		199			
		142			

(sh): shoulder

* : broad bands

1000–800 cm⁻¹ *region*. The results are very simple: the isotopic shifts related to the $^{24}Mg-^{26}Mg$ replacement are either negligible or non-significant: the role of the magensium on these vibrations is practically negligible; but 3 of these bands are shifted by 10–15 cm⁻¹ when ^{28}Si is replaced by ^{30}Si: this is of the right order of magnitude for the antisymmetric stretch of the SiO_4 tetrahedron (ν_3 of the free ion). This shift is very small for the remaining sharp band at 842 cm⁻¹, which must be assigned to the symmetric stretch of the SiO_4 group (ν_1 of the free ion).

These assignments agree with those already given by Tarte [1].

650–475 cm⁻¹ *region*. Quite unexpectedly, the isotopic shifts are very small (and in fact non-significant since these bands are not very sharp)*: no definite assignment can be deduced from the isotopic data. Since this group of bands is only slightly

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* The apparently important change in the 522–509 cm⁻¹ doublet is also non-significant, since the 2 components of this doublet are broad, and a relatively small change in the shape of the bands (in connection with the granulometry of the sample) may bring out a non-negligible shift of the apparent absorption maximum.

modified by the replacement of the divalent cation (Mg, Ni, Co, Mn, Ca), it has been assigned to the antisymmetric bending motions of the SiO_4 group (ν_4 of the free ion) [1].

However, in view of the very small isotopic shifts, and since both ν_2 and ν_4 modes of the free ion are split into components which belong to the same representations (see the correlation table above), it seems to us more appropriate to assign these bands to bending motions of the SiO_4 tetrahedron, without attempting any discrimination between the symmetric (ν_2) and antisymmetric (ν_4) modes.

Low-frequency region (475–200 cm^{-1}). The results in this region may be classified as follows: (1) 2 bands (near 300 and 270 cm^{-1}) are very sensitive to the mass of the Mg cation, with no measurable influence of the mass of silicon. They are assigned to translational motions of the Mg cation. (2) 3 bands (near 460, 410 and 320 cm^{-1}) are also very sensitive to the mass of Mg, but in addition exhibit a small, although significant, ^{28}Si–^{30}Si isotopic shift. They must be assigned to complex translations involving both Mg and Si atoms, with however a predominant contribution of the Mg cations. (3) For 2 bands (near 420 and 360 cm^{-1}), the isotopic shifts are moderate for Mg, and very small or inexistant for Si. The participation of Mg to these vibrations was already deduced from the vibrational behaviour of $(Mg, Ni)_2SiO_4$ solid solutions [1]. However, since the ^{24}Mg–^{26}Mg isotopic shifts are rather moderate, these vibrations cannot be simply described as a translational motion of the Mg cation, and it seems more appropriate to assign these frequencies to complex vibrations involving simultaneously a translation of the Mg cation and some motion of the SiO_4 tetrahedron which does not imply a significant displacement of silicon: either a rotation or a bending vibration of the symmetric ν_2 type. Since these 2 bands are fairly strong, and since the vibrations associated to the ν_2 components are expected to appear only weakly in the i.r. spectrum, the contribution from this latter type of vibration is probably not very important. (4) Finally, the band near 380 cm^{-1} is nearly insensitive to both Mg and Si isotopic replacements. Thus, it should be essentially assigned to either a symmetric bending, or a rotation of the SiO_4 tetrahedron, or to a combination of these motions.

It is evident from this discussion that no more precise assignments or description can be given for the low-frequency modes. The number of i.r. active fundamentals is so large, and the possibilities of vibrational interactions are so numerous, that it is practically excluded to find out a "purely translational", or "purely rotational", or "purely bending" mode. Nevertheless, it is generally possible, with the help of the isotopic data, to determine which type of motion is *predominantly* responsible for a given frequency.

Raman spectra

Very few Raman data are available in the literature, but some assignments have been proposed by GRIFFITH [8]. Here again, isotopic data are essential to a realistic interpretation of the spectrum. Unfortunately, the Raman spectrum of Mg_2SiO_4 is intrinsically very weak (in connection with the low polarizability of its constituting atoms): 8 bands only (against a total of 36 predicted Raman-active

[8] W. P. GRIFFITH, *Nature* **224**, 264 (1969).

fundamentals) have been observed in the spectrum of natural olivine, and good measurements of the isotopic shifts have been possible only for the 4 high-frequency bands corresponding to stretching vibrations of the SiO_4 tetrahedron.

The available experimental data and the corresponding assignments are collected in Table 7. Owing to the lack of isotopic data, the assignments for the low-frequency

Table 7. Mg_2SiO_4 Raman frequencies and isotopic shifts

$\Delta \nu$ (cm^{-1}) $^{28}Si-^{30}Si$	$Mg_2{}^{30}SiO_4$ (cm^{-1})	$Mg_2{}^{28}SiO_4$ (cm^{-1})		Assignments
		330	w	External mode
		~425	w	bending vibrations
		543	w	
		586	w	
+ 5·5	817·5	823	m	complex stretching vibrations
+ 3·5	851·5	855	st	
+ 7	912	919	w	(see text)
+ 8	951	959	w	

Intensity: w = weak; m = medium; st = strong.

bands are only tentative. But it is worth while to discuss the behaviour of the stretching modes.

Griffith [8] has assigned the 855 cm^{-1} peak to the ν_1 mode on the basis of its high intensity (it is the strongest band of the spectrum), whereas the 823 cm^{-1} peak is assigned to ν_3. Our isotopic data show that the situation is not so simple. The isotopic shifts are practically the same for both 823 and 855 peaks; moreover, these shifts are too large for a totally symmetric vibration, and too small for an antisymmetric vibration. It is clear that both bands must be assigned to complex vibrations with simultaneous symmetric and antisymmetric character.

The same considerations may be applied to the 919 and 959 cm^{-1} bands: the isotopic shifts are larger, suggesting a more important contribution of the antisymmetric character, but they are still smaller than the expected value for a purely antisymmetric stretch (about 13 cm^{-1}).

In conclusion, none of the observed Raman-active, stretching frequencies of the SiO_4 group can be assigned to a vibration which would be specifically symmetric (ν_1) or antisymmetric (ν_3) with respect to the silicon atom. This result is not too unexpected, since under the influence of the site group (C_s) and factor group (D_{2h}), both ν_1 and ν_3 of the free tetrahedron are split into several components, some of which belong to the same representation (A_g and B_{2g} for the Raman-active vibrations; see Table 4) and thus are able to interact. But here again, the study of isotopic species is the only way to prove experimentally that such interactions do really occur.

DISCUSSION AND CONCLUSIONS

The preceding results and assignments may be considered as a good example of the possibilities offered by the isotopic substitution in the case of crystals of moderate

to fair complexity. In the high frequency region (1050–500 cm^{-1}), the lack of significant vibrational interactions between internal and external modes appears as a good approximation, in agreement with the vibrational behaviour of solid solutions [1]. In the lower frequency region essentially corresponding to the external modes, it is possible to distinguish between the various types of translational modes, either simple (translation of one cation only) or complex (simultaneous translation of different cations), rotational modes, or mixed modes (translation + rotation). Likewise, the isotopic data offer the unique possibility to show the more or less important mixing of symmetric and antisymmetric modes for the Raman-active stretching vibrations. Although such considerations about the mixing or non-mixing of vibrations remain qualitative in nature, they correspond to realistic, and not simply reasonable, assignments.

More detailed assignments could be deduced from the investigation of monocrystals. But even in this case, the probability of really observing the 35 i.r.-active and 36 Raman-active modes is very remote; moreover, this type of investigation is unable to give information about the mixing of normal modes which belong to the same representation. Thus, it appears practically impossible to arrive at a detailed, unequivocal correlation between the observed frequencies and the various vibrational modes.

A detailed interpretation of the i.r. spectrum of Mg_2SiO_4 was recently proposed by OEHLER and GÜNTHARD [3] on the basis of a normal coordinate treatment, followed by the computation of the fundamental frequencies deduced from a convenient set of force constants. Despite the interest of such a treatment, it should be noticed that the resulting assignments are not supported by our isotopic data. If we consider as an example the band located near 900 cm^{-1}, it is assigned by OEHLER and GÜNTHARD to a Mg—Mg vibration whereas our isotopic data bring the unequivocal proof that this band is essentially related to an antisymmetric stretch of the SiO_4 tetrahedron. Likewise, most of the assignments proposed for the 650–200 cm^{-1} region are in contradiction with our isotopic data.

The main reason for such large discrepancies must be searched in the rather arbitrary choice of the force constants, whose final values are in evident contradiction with simple experimental evidence (e.g. $F_{Mg-Mg} > F_{Mg-0}$). Moreover, a number of interactions have been neglected in this treatment. It may be argued that the final set of force constants leads to a good agreement between the calculated and observed frequencies. But this agreement is by no means a proof (over even an argument) that the force constants and the assignments are essentially correct. It has been shown by LEIGH, SZIGETI and TEWARY [9] that the vibrational frequencies of a solid may be accurately calculated, not from an unique set of force constants, but from a whole series of sets of conveniently (and more or less arbitrarily) chosen force constants. This comes from the fact that the vibrational spectrum of a solid is determined by a number of force constants which is much higher than the number of available frequencies. It is clear that such a situation precludes the assignment of vibrational frequencies on the basis of force constant calculations: the only realistic procedure is to make *first* assignments on the basis of appropriate experimental

[9] R. S. LEIGH, B. SZIGETI and V. K. TEWARY, *Proc. Roy. Soc. London* A320, 505 (1971).

data (such as the investigation of isotopic species), and then use these assignments to make force constant calculations which, although necessarily approximate, will lead to the right order of magnitude of these force constants.

The degree of approximation will of course depend on the chemical and crystallographic complexity of the investigated crystal. From this point of view, the olivine case appears as a fairly difficult one, and it is necessary to solve the assignment problem before attempting force constant calculations. The vibrational spectra of further olivine-type compounds and their interpretation will be discussed in forthcoming papers.