

INFRARED SPECTRA OF SOME SYNTHETIC TALCS¹

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ABSTRACT

The spectra of some synthetic talcs in which Mg^{2+} is wholly or partly replaced by another divalent ion have been investigated in some detail in the hydroxyl stretching region. Intensity relationships between the four bands observed in each case are consistent with a random distribution of the magnesium and substituting ion between the two crystallographically distinct octahedral sites. Bandwidths, which are exceptionally narrow, depend on the ionic radius and the concentration of the substituting ion. Both these factors, when superimposed on the characteristic splitting parameters of any ion, are also shown to have an appreciable effect on the frequency separation between the four observed bands. Spectra of the synthetic Mg-Ni talc series and their bearing on the assignments of the lattice vibrations is also discussed.

INTRODUCTION

Magnesium talc, $Mg_3Si_4O_{10}(OH)_2$, is the simplest trioctahedral 2:1 layer silicate and all others are related to it by one or more theoretical substitutions. It was subjected to a careful infrared study (Farmer, 1958) before similar detailed studies had been made on micas and its other more reactive clay mineral derivatives all of which have more complex spectral properties. Apart from an important study (Vedder, 1964) relating to the hydroxyl ions of talc, subsequent work (Saksena, 1961; Stubican and Roy, 1961 a, b; Farmer and Russell 1964) has been largely concerned with assignments of the lattice vibrations since talc provides ideal material for both theoretical and synthetic studies in this region.

Despite the fact that it would be of great practical interest to know the effects of substitutions in the octahedral layer on the infrared spectrum of talc, the only studies reported are those of Stubican and Roy (1961 a, b) on the lattice vibrations in the Mg-Ni talc series. The following investigation was undertaken to study the detailed effects of substitutions in the octahedral layer on the hydroxyl stretching vibrations of talc since it is clear that such information would be of assistance in the elucidation of the spectra, not only of the other trioctahedral layer silicates but also of other minerals such as tourmaline and many amphiboles which have talc like units in their structure. The significance of the hydroxyl ion vibrations for the determination of cation ordering in simple amphiboles has been clearly discussed by Burns and Strens (1966) and Strens (1966). The

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work recorded in the present paper has already been used in a study of part of the hydroxyl stretching region of the infrared spectrum of biotite mica (Wilkins, 1967).

Unfortunately at the time of writing no detailed X-ray structural examination of talc has been reported, due to difficulties associated with the complex layer stacking sequence. The significance of much of the infrared data recorded herein must therefore remain obscure until such time as refined structural information becomes available on at least one of the end members.

SYNTHESIS

Slightly acid solutions, approximately 0.01–0.02 N, containing 4 mM of sodium silicate were neutralized with concentrated ammonium hydroxide to pH 8 at boiling point. Immediately after the precipitation of hydrated silica, a total of 3 mM of Mg, Ni, Co, Zn, Fe, Mn and Cu in the form of fine powder of $\text{Mg}(\text{OH})_2$, NiCO_3 , ZnCO_3 , CoCO_3 , FeCO_3 , MnCO_3 , and basic copper carbonate was added to the beaker and the mixture kept boiling for 3 minutes. After complete precipitation magnetic stirring was applied for 10 minutes, then the precipitates were washed twice by means of a centrifuge using a total of 300 ml distilled water and air dried at 120°C. In order to avoid segregation of crystalline $\text{Mg}(\text{OH})_2$ and carbonates in the precipitates, the dried gels were pulverized and mixed manually.

Approximately 30 mg of starting gels were placed in silver liners made of 0.03 mm silver foil, shielded at both ends with multiple foldings and pressings. Syntheses were carried out hydrothermally in steel cold seal bombs under 2–3 kilobars pressure for periods of from 15–72 hours. Except for the $\text{Mg}_{84}\text{Zn}_{14}$, $\text{Mg}_{52}\text{Fe}_{48}$, and $\text{Mg}_{52}\text{Mn}_{48}$ talcs which were synthesized at 500–550°C, all others were produced at 680–700°C. The bombs were quenched by compressed air flow, the contents washed out by a jet of distilled water after cutting both ends of the liners and then dried at 120°C. Small amounts of ascorbic acid powder were added to the liner to maintain Fe and Mn in the divalent state during the heatings.

Before the infrared spectrum of the product was taken it was first examined by X-ray diffractometer and checked for general purity and specifically for absence of possible hydroxyl containing species, mainly amphiboles. Spectra were obtained from samples dispersed in KBr using a Cary-White 90 infrared spectrophotometer with slits uniformly set at 1.4 cm^{-1} with a scanning speed of $0.03\text{ cm}^{-1}/\text{sec}$. The instrument was carefully calibrated at the time the spectra were run using the water vapour spectrum.

STRUCTURE

The structure of magnesium talc was determined by Gruner (1934) and Hendricks (1938). It consists of two sheets of linked silicate tetrahedra forming an hexagonal network of indefinite extent and joined through the apices of the tetrahedra to the adjoining silicate layer by magnesium ions. Two hydroxyl ions complete the octahedral co-ordination of each magnesium ion. The silicate layers are therefore joined by a brucite-like layer. Bonding is largely ionic and charges are satisfied mainly within each sandwich layer. Between the sheets then, attractive forces are small as are the forces controlling the stacking of the talc layers leading to complex stacking sequences.

Since the b axis of magnesium talc (Stemple and Brindley, 1960) is larger than that of an unsubstituted silicate layer (Radoslovich and Norrish, 1962) it seems likely that the silicate layers are stretched at least into their limiting form of hexagonal symmetry but perhaps also with additional distortions.

The hydroxyl ions are located below the centre of each hexagonal hole in the silicate sheet. On the opposite side each hydroxyl ion is adjacent to three magnesium ions, two of which are symmetry related and the third is situated on a centre of symmetry. The immediate environment of the OH ions is close to trigonal.

OH STRETCHING VIBRATIONS

The vibrational spectrum of talc in the OH stretching region is particularly simple. On the basis of the pseudo-symmetry of the site and the position of positive and negative ions in the first co-ordination sphere, the orientation of the OH dipole is expected to be approximately normal to the layer and the study of single crystals proves this to be so (Serratosa and Bradley, 1958). Vibrational coupling between hydroxyl ions is expected to be small for the same reasons as Vedder and MacDonald (1963) have discussed for muscovite.

The spectrum of any talc in which magnesium is partially replaced by another divalent cation shows a splitting of the hydroxyl stretching fundamental into as many as four peaks depending on the degree of substitution. Vedder (1964) showed that the relative intensities of these absorptions could be expressed by $1:3x/1-x:3(x/1-x)^2:(x/1-x)^3$ where $1-x$ and x are the concentrations of the substituting ion and magnesium respectively. This corresponds to a random distribution of the two species over M(1) and M(3) sites in the octahedral layer. From high to low frequency the four bands are related to OH ions vibrating close to 3Mg^{2+} , $2\text{Mg}^{2+}+\text{R}^{2+}$, $\text{Mg}^{2+}+2\text{R}^{2+}$ and 3R^{2+} ions.

The spectra of the synthetic Mg-Ni talcs illustrated in Figure 1 confirm that the distribution is close to random in the series. The bands are the sharpest of any purely vibrational bands in known silicates and very nearly uniform in shape. In each case, measured band width at half height, $\Delta\nu_{\frac{1}{2}}$, is close to 3 cm^{-1} . Allowing for slight instrumental broadening the true bandwidth may be nearer 2.5 cm^{-1} at room temperature. This is a reflection of the extremely regular environment of the hydroxyl ions.

With increasing ionic radius of the substituting ion, two effects become apparent. All bands become slightly broader, including the one of highest frequency which represents hydroxyl ions vibrating close to three magnesium ions, and all bands develop low frequency tails: Figure 2 shows

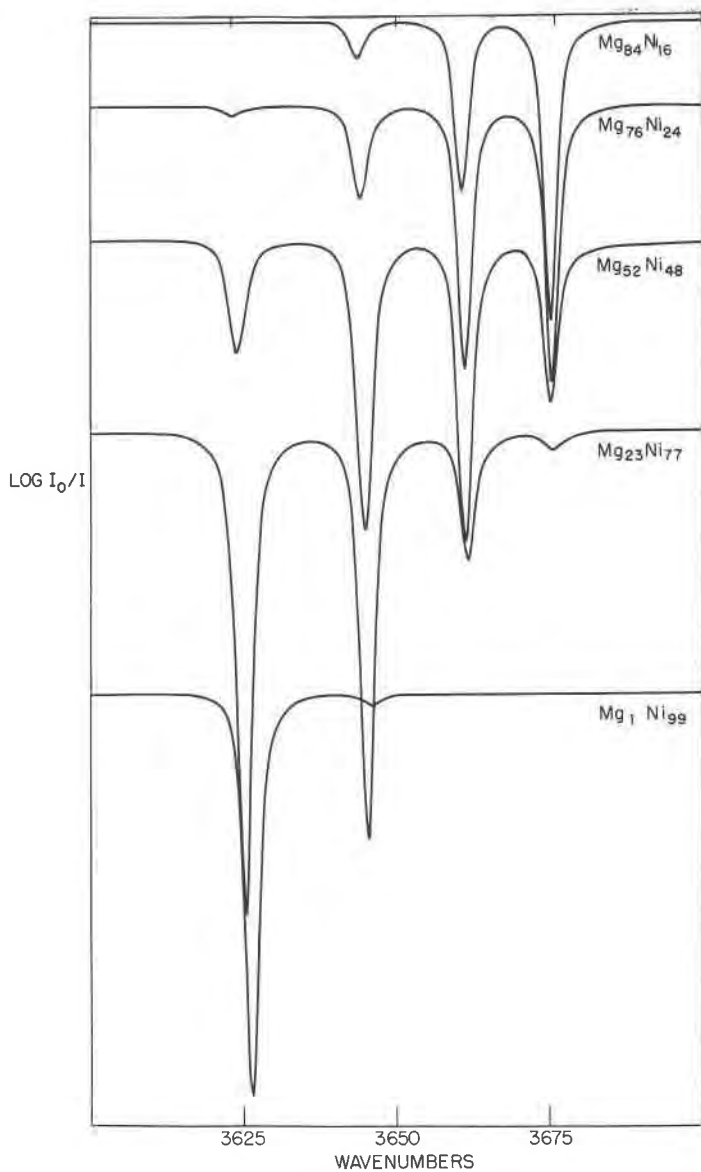


FIG. 1. OH stretching vibrations of synthetic Mg-Ni talcs. Compositions determined from the spectra assuming random distribution of cations in the octahedral layer. 5-7.5 mg samples in KBr disks.

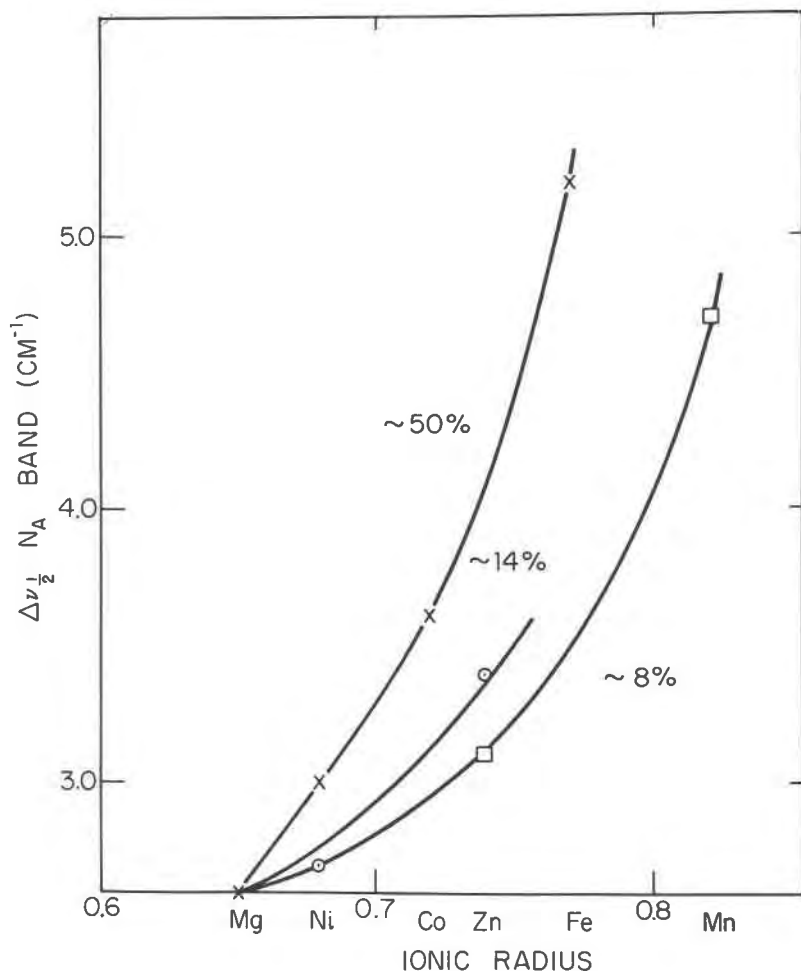


FIG. 2. Effect of ionic radius and concentration of substituting ion on band widths in some synthetic talcs. X, O and □ represent material with approximately 50%, 14% and 8% of Mg replaced by another ion.

the effect of both ionic radius and concentration of substituting ion on the width of the N_A band¹ in several of the synthetic talcs. It is apparent that if sufficient data were available, a series of lines could be drawn for the variation of N_A band width with ionic radius for various constant concentrations of substituting ion.

The band broadening is apparently a second order effect resulting from

¹ The terminology is that used by Wilkins (1967).

the presence of a substituting ion in the octahedral layer immediately outside the first co-ordination sphere of the hydroxyl ion. It should be noted that instrumental broadening is largest with the narrowest bands so that the true line shape is not that given on the diagram but is something quite close to it.

SPLITTING PARAMETERS

The origin of the observed splitting of the OH stretching fundamental is in the change in the force field in the vicinity of the proton when one two or three other cations replace magnesium ions. Burns and Strens

TABLE 1. BAND FREQUENCIES (cm^{-1}) IN THE HYDROXYL STRETCHING REGION OF THE INFRARED SPECTRUM OF SOME SYNTHETIC TALCS

Talc composition	OH ion vibration frequency close to—								
	Mg	Mg	Mg	Mg	Mg	R	Mg	R	R
Mg ₁₀₀	3676.6			—			—		
Mg ₈₄ Ni ₁₆	3676.5			3661.9			3644.8		
Mg ₇₆ Ni ₂₄	3676.6			3662.3			3645.2		
Mg ₅₂ Ni ₄₈	3676.5			3662.5			3645.9		
Mg ₂₈ Ni ₇₇	3676.7			3662.9			3646.2		
Mg ₁ Ni ₉₉	—			—			3646.9		
Mg ₅₄ Co ₄₆	3677.4			3661.4			3643.3		
Mg ₉₂ Zn ₈	3676.6			3664.4			3649.7		
Mg ₈₆ Zn ₁₄	3676.8			3665.2			3651.6		
Mg ₅₂ Fe ₄₈	3678.3			3663.5			3646.0		
Mg ₉₂ Mn ₈	3677.1			3663.6			3650.0		
Mg ₅₅ Cu ₄₅	3676.0			3669.9			3663.7		

(1966) have observed the same effect in cummingtonite-grunerite and tremolite-actinolite amphiboles, where Fe and Mg are distributed over sites directly analogous to those of talc. They have suggested the splitting is related to the electronegativity difference between Fe and Mg. The magnitude of the splittings in some synthetic Mg-Ni, Mg-Co, Mg-Zn, Mg-Fe, Mg-Mn and Mg-Cu talcs can be obtained from the data listed in Table 1. The frequencies recorded are peak frequencies. Although they have been measured to 0.1 cm^{-1} , the absolute accuracy is probably not better than $\pm 0.5 \text{ cm}^{-1}$, though relative accuracy is better except where frequencies have been measured on bands in which absorption intensity is low.

The Pauling electronegativities of Mg, Ni, Co, Zn, Fe, Mn, and Cu, all in the divalent state, are 1.2, 1.8, 1.7, 1.5, 1.7, 1.4, and 2.0 respectively

(Gordy and Thomas, 1956). It is apparent that although in general the ions with higher electronegativity do have larger splitting parameters, it is not invariably so, nor is the electronegativity difference between magnesium and its substituting ion related in a simple quantitative manner with the splitting parameter.

It was apparently on the assumption that the splitting caused by Mn^{2+} would be considerably less than that caused by Fe^{2+} that Burns and Strens (1966) recorded the absence of Mn^{2+} in the M(1), M(3) posi-

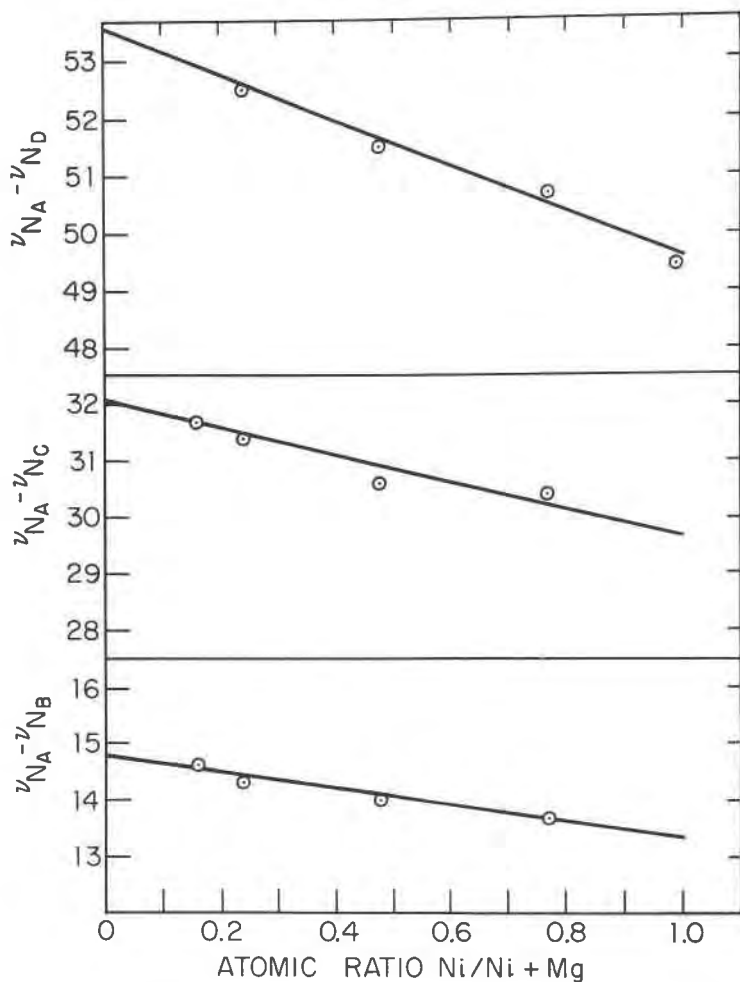


FIG. 3. Frequency separation between bands in the synthetic Mg-Ni talc series. Compositions determined from the spectra assuming random distribution of Mg and Ni in the octahedral layer.

tions of a manganoan cummingtonite. The data of Table 1 show that frequencies of Mg-Fe and Mg-Mn associations are so close that no resolution is possible and Mn^{2+} in sites adjacent to hydroxyl ions will be measured as Fe^{2+} unless extremely detailed work is undertaken.

Variations in peak frequency, like those in bandwidth, are related both to ionic radius and the extent of substitution of the ion replacing magnesium in the octahedral layer. The splitting parameters N_A-N_B , N_A-N_C , N_A-N_D for the Mg-Ni talc series are plotted against composition determined from intensity distribution amongst the four bands in Figure 3.

TABLE 2. TALC COMPOSITIONS DETERMINED FROM THE RATIO OF INTEGRATED INTENSITIES OF OH STRETCHING BANDS ASSUMING RANDOM DISTRIBUTION OF CATIONS

Intensity comparison made between bands—			Mean composition
$N_A N_B$	$N_B N_C$	$N_C N_D$	
Mg _{0.767} Ni _{0.233}	Mg _{0.746} Ni _{0.254}	—	Mg _{0.76} Ni _{0.24}
Mg _{0.615} Ni _{0.385}	Mg _{0.502} Ni _{0.498}	Mg _{0.450} Ni _{0.550}	Mg _{0.52} Ni _{0.48}
—	Mg _{0.248} Ni _{0.752}	Mg _{0.212} Ni _{0.788}	Mg _{0.23} Ni _{0.77}
Mg _{0.579} Co _{0.421}	Mg _{0.533} Co _{0.467}	Mg _{0.516} Co _{0.484}	Mg _{0.54} Co _{0.46}

The magnitude of the effect is different for each type of association and increases in the order N_A , N_B , N_C , N_D . These variations are superimposed on the splitting parameters which are characteristic for each substituting cation at infinite dilution. Since the low frequency bands increase in frequency faster than the high frequency bands upon increasing substitution of a larger cation, the general result is that the band system becomes compressed. The compression amounts to about 8% for the Mg-Ni talc series and will be greater for larger ions such as Fe^{2+} .

HYDROGEN BONDING CONTRIBUTION

In silicate studies, a lowering of the stretching frequency of an OH ion in a structurally related group of species has usually been correlated with shortening of the O-H—O distance in the structure and the resulting increased strength of hydrogen bonding. Another feature of the hydrogen bond and just as important, is the relationship between absorption coefficient and the strength of hydrogen bonding (Huggins and Pimentel, 1956). This may increase by an order magnitude while the vibration frequency decreases 200 cm^{-1} . It is caused by movement of the charge distribution in the hydrogen bond during vibration (Coulson, 1957).

Although it seems unlikely that hydrogen bonding contributes to the

lower vibration frequencies of hydroxyl ions close to octahedral associations with few magnesium ions in talc, it is one of the few situations where even a slight increase in absorption coefficient with decrease in vibration frequency could be easily detected.

Table 2 gives the composition of four substituted talcs determined from the ratio of integrated intensities of different pairs of hydroxyl bands assuming random distribution of the cations. Determinations are not very accurate because the bands are slightly instrumentally broadened, but it is significant that in each case the apparent $Mg^{2+}/(Mg^{2+}+R^{2+})$, ratio decreases with the mean frequency of the pair of bands from which the determination was made. This is in accord with what would be expected if there was random distribution of the two cations over the non-equivalent octahedral sites together with a small hydrogen bonding contribution to the band intensity.

Strens (1966) has reported "cation clustering" (more 3 Mg^{2+} and 3 R^{2+} associations than predicted by random mixing) in several amphiboles. It is apparent that this would produce a similar intensity effect as observed here in the talc series. It is not easily possible to distinguish between the two alternatives unless an independently determined $Mg^{2+}/(Mg^{2+}+R^{2+})$ value is known for the talc of interest.

Regardless of the cause, however, the $Mg^{2+}/(Mg^{2+}+R^{2+})$ determination from the spectrum assuming random distribution of the cations will be in error, the proportion of substituting ion being overestimated. The error appears to be only a few percent but requires evaluation by careful synthesis and infrared examination.

LATTICE VIBRATIONS

The lack of a refined X-ray structural analysis makes precise work on the lattice vibrations impossible at present. But since some inconsistencies exist between the theoretical approach (Farmer, 1958; Saksena, 1961, Farmer and Russell, 1964) and the synthetic approach of Stubican and Roy (1961 *a, b*), opportunity is taken here to support the synthetic work by presenting a more extensive series of Mg-Ni talcs with better resolved spectra (Fig. 4).

When synthesized the Mg-Ni talc series was only intended for use in the study of hydroxyl ion vibrations, but the purity, especially of the two Ni rich samples was sufficiently high for them to be useful in studying the lattice vibrations as well. Charge compositions were Mg_{100} , $Mg_{80}Ni_{20}$, $Mg_{60}Ni_{40}$, $Mg_{40}Ni_{60}$, $Mg_{20}Ni_{80}$, Mg_1Ni_{99} talc. Deviation of the synthetic material from the expected composition is matched by the appearance of some unidentified impurities. Residual uncertainties can usually be said to exist about the purity of any synthetic silicate material, especially

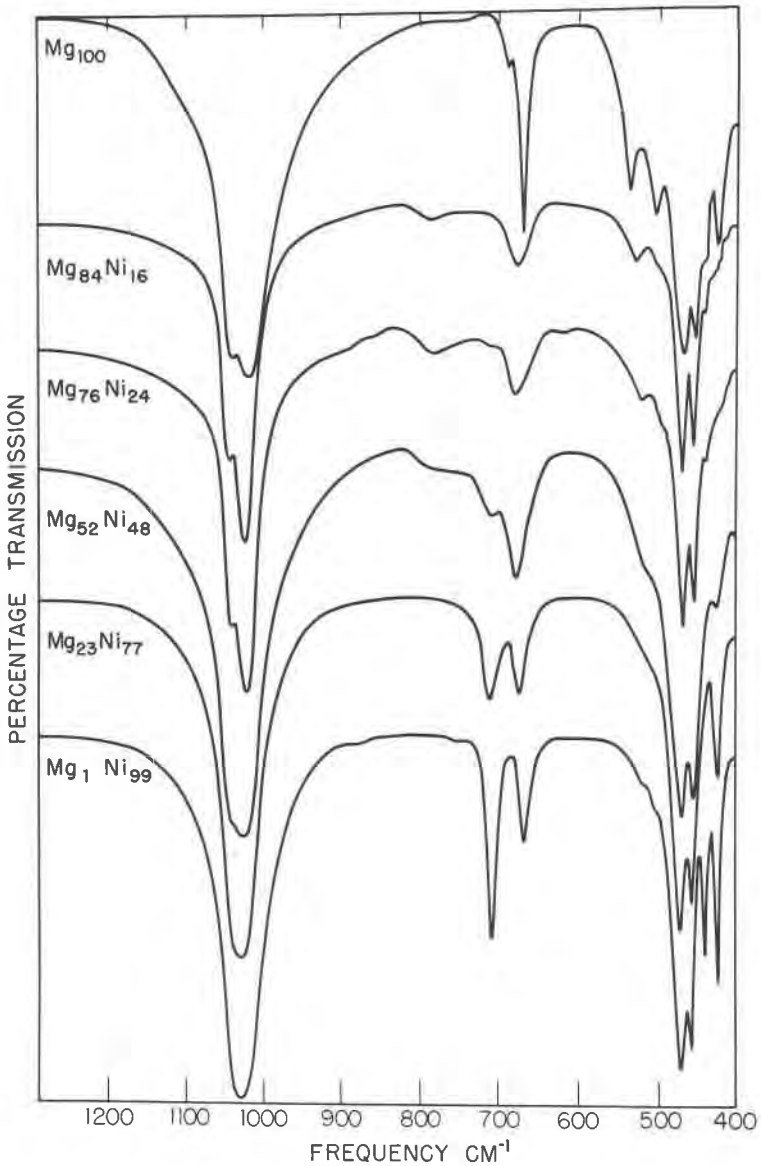


FIG. 4. Lattice vibrations in the Mg-Ni talc series. 1 mg samples in KBr disks.

those produced in short hydrothermal runs, because particles poorly crystalline to X-rays cause absorption in the infrared. For this reason, confirmation of spectra of synthetic silicates produced under different

conditions from different starting materials much increases the value of the results obtained. In the present series the broad weak absorptions at about 625 and 780 cm^{-1} are clearly spurious since they show no regular variation with talc composition.

The most striking characteristic of the 800-400 region is the strong doublet at 452 and 467 cm^{-1} which persists throughout the complete series as Stubican and Roy (1961 *a, b*) observed, absorption in the higher frequency band being somewhat greater. It seems clear that the two bands must not be assigned to Mg-O vibrations as originally favoured by Farmer, but to Si-O bending vibrations.

The 690 cm^{-1} band which, as Farmer has shown represents a dipole oscillation normal to the sheet, does not appear to persist even in the $\text{Mg}_{84}\text{Ni}_{16}$ talc. Its significance, as well as that of bands in the same region in the Ni rich talcs remains obscure.

Other calculations of vibration frequencies of an isolated silicon-oxygen sheet using a more complete set of force constants (Stepanov and Prima, 1958; Vedder, 1964) than those used by Saksena (1961) give values which are more consistent with the assignment of the 452-467 cm^{-1} doublet to Si-O bending vibrations as suggested by the synthetic Mg-Ni talc series.

DISCUSSION AND CONCLUSION

In the present state of our knowledge on the effect of substitutions in silicates on the vibrations of associated OH ions, the most useful approach is empirical, through study of the spectra of suitably substituted simple synthetic compounds. Talc has the simplest spectrum of all the trioctahedral layer silicates and its exceptionally sharp bands enable the effects of ionic size and concentration of the substituting ion on band shapes and frequencies to be easily studied.

With increasing tetrahedral Al for Si replacement as in the micas and other trioctahedral clay minerals, bandwidths become greater and overlap precludes complete resolution. Nevertheless, by analogy with talc, it should be possible at least in part, to derive some information from these minerals by consideration of the shape of the band envelope, such as has been attempted for biotite mica (Wilkins 1967). Tuddenham and Lyon (1959) have observed systematic changes in the hydroxyl stretching region of the spectra of chlorites and it may be possible in part to explain these variations in a similar manner.

Some analytical consequences of this investigation of talc may be noted. The intensity distribution between the four hydroxyl bands of the spectrum of a Mg talc- R^{2+} talc binary solution, where R^{2+} is any other divalent ion, gives a measure of the composition of the octahedral layer. The composition of a talc in a mixture of mineral species may

therefore be determined provided no other hydroxyl containing species is present which absorbs in the same region, especially amphiboles and in particular tremolite-actinolite (Burns and Sterns, 1966). Even when an amphibole is present it may still be possible to determine the composition of the talc by careful comparison of band widths and frequencies.

The cell dimensions of some substituted talcs (Pistorius, 1963) do not vary sufficiently for them to be very useful in determining compositional variation. Since only a few milligrams are needed, an infrared spectrum will therefore be a useful tool to examine material produced in experimental phase equilibria studies.

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