

Conte P.

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Infra-Red Spectrum of the Spinel Ni_2SiO_4 , Ni_2GeO_4 and their Solid Solutions

ONE of us (A. E. R.)¹ has recently succeeded in synthesizing the spinel form of Ni_2SiO_4 and of the solid solutions $\text{Ni}_2(\text{Si,Ge})\text{O}_4$. An infra-red examination of these new phases has been carried out, as it is expected to throw some light on the interpretation of the infra-red spectra of the spinel germanates.

A schematic representation of the observed infra-red patterns is given in Fig. 1. The spectra of Ni_2SiO_4 and Ni_2GeO_4 spinels are characterized by their great simplicity (3 strong bands only in the spectral range 1,000-280 cm^{-1}), which may be contrasted with the complex spectrum given by the olivine form of Ni_2SiO_4 . This increase in complexity is related to both the lower symmetry of the olivine structure, and a fairly large deformation of the SiO_4 tetrahedra². This particular problem will not be discussed here.

Now, so far as the assignment of the spectra is concerned, the experimental results may be treated in two different ways³: the rigorous one is to consider the possible vibrational modes of the whole unit cell and to deduce from the symmetry properties which of the vibrations are infra-red active: Waldron⁴ has carried out such a treatment in the case of spinel ferrites and found that 4 fundamental modes only are infra-red active. It is possible, however, to consider separately the vibrations of the different co-ordinated groups present in the structure (SiO_4 tetrahedra, NiO_6 octahedra, etc.); such a treatment is only an approximate one and should be used with caution, but its reliability has been verified by one of the authors in a number of cases³. Despite its approximate character, this method may be very useful because of its ability to give information about the co-ordination around a given ion.

The successive spectra of the solid solutions $\text{Ni}_2(\text{Si}_{1-x}\text{Ge}_x)\text{O}_4$ are characterized by the following changes when x is varying from 0 to 1 (the prominent features only will be discussed here):

(1) A decrease of intensity and a small downward shift of the band centred near 820 cm^{-1} ; this band eventually disappears in pure Ni_2GeO_4 .

(2) The appearance and increase of intensity of a band centred near 700 cm^{-1} .

(3) The bands centred near 510 and 470 cm^{-1} exhibit a similar, but not so clear-cut, behaviour; the former band disappears abruptly for $0.40 < x < 0.60$, while the appearance of the latter is masked by the existence of a low-intensity band in this region,

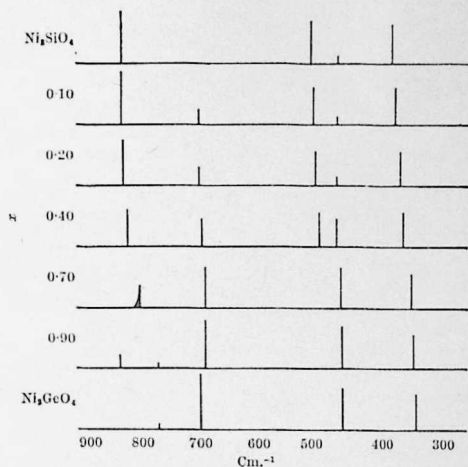


Fig. 1. Block diagram of the successive infra-red spectra in the series $\text{Ni}_2(\text{Si}_{1-x}\text{Ge}_x)\text{O}_4$

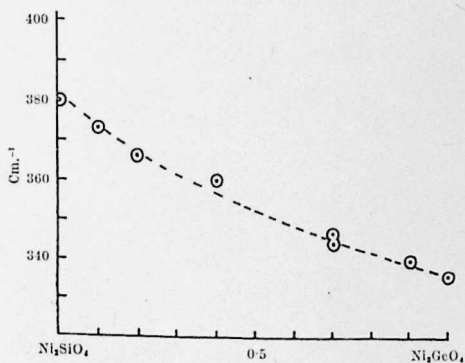


Fig. 2. Position of the low-frequency band versus composition

even in Ni_2SiO_4 (this weak band may well be due to either Ni_2SiO_4 itself, or to an accompanying impurity, namely, NiO or Ni-talc).

(4) The band lying in the low-frequency region (400–300 cm.^{-1}) does not suffer any important change in intensity, but it is smoothly shifted towards low

frequencies when x increases; this shift is a quite regular one, as illustrated by Fig. 2.

Now, the following reasoning seems to be rather attractive²: the bands which are disappearing when x increases should be assigned to co-ordinated groups around silicon; the bands the intensity of which increases should be assigned to co-ordinated groups around germanium; and the low-frequency band, the intensity of which remains nearly unchanged, should be assigned to co-ordinated groups which are maintained throughout the whole series, namely, co-ordinated groups around nickel. The precise nature of these co-ordinated groups depends on the normal or the inverse nature of the spinels, and we shall first discuss the spectrum of Ni_2SiO_4 in this respect.

The high-frequency band 825 cm.^{-1} may be assigned to the antisymmetric stretching frequency of either SiO_4 tetrahedra (normal spinel), or SiO_6 octahedra (inverse spinel). The antisymmetric stretching frequency of SiO_4 tetrahedra in orthosilicates has been reported to lie in the $1,000\text{--}850 \text{ cm.}^{-1}$ range (ref. 5); the assignment of the 825 cm.^{-1} band to SiO_4 tetrahedra is thus fairly reasonable. This is consistent with the fact that the occurrence of SiO_6 octahedra has never been proved in silicates; on the other hand, a comparison of the available characteristic frequencies for XO_4 (tetrahedral) and XO_6 (octahedral) groups^{3,6} allows a rough estimation of the absorption range which may be expected for SiO_6 octahedra: this turns out to be $700\text{--}600 \text{ cm.}^{-1}$.

Ni_2SiO_4 is thus a normal spinel, and the three strong bands may be assigned as follows: 825 cm.^{-1} , asymmetric stretching frequency of SiO_4 tetrahedra; 516 cm.^{-1} , asymmetric bending frequency of SiO_4 tetrahedra; 380 cm.^{-1} , asymmetric stretching frequency of NiO_6 octahedra.

The same reasoning may be applied to Ni_2GeO_4 , and will not be repeated; we just need to mention that the antisymmetric stretching frequency of GeO_4 tetrahedra has been observed in the $830\text{--}670 \text{ cm.}^{-1}$ range in a large series of orthogermanates (Tarte, P., to be published): the 689 cm.^{-1} band of Ni_2GeO_4 may thus be considered as good evidence for the occurrence of GeO_4 tetrahedra, and Ni_2GeO_4 is a normal spinel, a conclusion in accordance with the X-ray data of Durif-Varambon⁷ and Romeijn⁸.

The spectral changes in the whole series $\text{Ni}_2(\text{Si}_{1-x}\text{Ge}_x)\text{O}_4$ when x increases from 0 to 1 are now readily understood. The progressive replacement of the 825 by the 690 cm.^{-1} band is related to the replacement of SiO_4 by GeO_4 tetrahedra; the same is true for the bands 516 and 470 cm.^{-1} ; we have already noticed that the changes are not so regular for

this pair of bands: this may be explained by the fact that these bands are related, not to a pure bending mode of SiO_4 or GeO_4 tetrahedra, but to a composite motion where this bending mode is somewhat mixed up with a motion of the lattice as a whole. Finally, the low-frequency band may be assigned to a motion which can be roughly described as a stretching frequency of the NiO_6 octahedra with, however, a more-or-less important contribution of the whole lattice motion. The regular shift of this band towards the low frequencies when the germanium content increases is readily explained by the expansion of the lattice.

P. TARTE

Department of General Chemistry,
University of Liège.

A. E. RINGWOOD

Department of Geophysics,
Australian National University,
Canberra.

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