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Infra-red spectrum and cation distribution in spinels.

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The determination of cation distribution is one of the major problems in the crystal chemistry of spinels. A classical approach is given by the study of the relative intensities in the X-ray powder diagram; but a recent collection of infra-red data (Tarte, 1962*a*, Table 2) shows that, for a series of cations X, the infra-red frequency of a co-ordination group XO_n depends upon the co-ordination number n; however, this is true only if the vibrations of the XO_n group are essentially independent (*i.e.* not strongly coupled with other vibrational modes). There are two possibilities: (1) The vibrations of a given group—say $(XO_4)^{p-}$—may be considered as independent (or nearly so)*; if X is isomorphously replaced by increasing amounts of another cation Y, so as to give solid solutions $[(X, Y)O_4]^{p-}$, the infra-red bands related to the XO_4 groups progressively disappear and are replaced by new bands due to the YO_4 groups (Tarte, 1962*a*). (2) The vibrations are coupled in such a manner that they cannot be related to definite co-ordination groups; they are representative of the unit cell as a whole. In this case, no particular effect is noticed in the infra-red spectra of solid solutions; all the bands are simply shifted towards higher or lower frequencies.

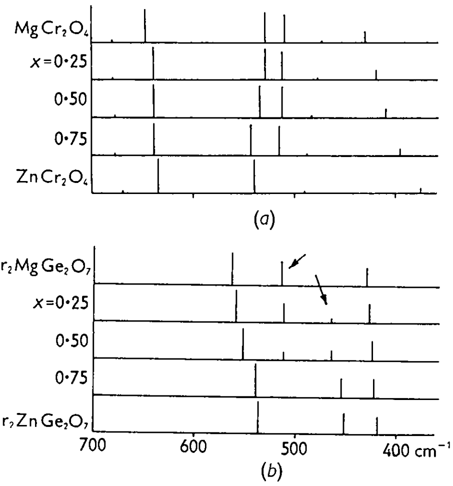

Fig. 1. (*a*) Infra-red spectra of $(Mg_{1-x}Zn_x)Cr_2O_4$ solid solutions. (*b*) Part of the infra-red spectra of $Sr_2(Mg_{1-x}Zn_x)Ge_2O_7$ solid solutions. Arrows point to the bands related to MgO_4 and ZnO_4 tetrahedra. The relative intensities of the other bands (related to the Ge_2O_7 group) are not affected by the Mg–Zn substitution.

We have applied these considerations to a large series of spinels, where it turns out that these two possibilities are both represented.

(*a*) The infra-red spectra of the spinel solid solutions $Ni_2(Si,Ge)O_4$ (Tarte & Ringwood, 1962) are representative of the first, as far as the high-frequency vibrational mode is concerned (ν_3 stretching mode of SiO_4 and GeO_4 tetrahedra). However, the low-frequency modes are more or less mixed up with the vibrations of neighbouring groups, and thus are not really independent. This is true also for the other spinel germanates X_2GeO_4 (X^{II} =Co, Fe, Mg) (Tarte, 1962*b*); in such cases, it can be inferred from the infra-red spectrum whether the spinel is normal or inverse.

(*b*) A number of published spectra (Hafner, 1961) and our own results show that the II–III spinels are representative of the second case. One example will be quoted here ($MgCr_2O_4$–$ZnCr_2O_4$). The infra-red spectra of $(Mg, Zn)Cr_2O_4$ solid solutions are given as line diagrams in Fig. 1(*a*); apart from an unexplained doubling of the vibration near 530–540 cm.$^{-1}$ in all compounds containing magnesium, the replacement of MgO_4 by ZnO_4 tetrahedra has no important effect on the spectrum. This may be contrasted with the spectra of $Sr_2(Mg, Zn)Ge_2O_7$ solid solutions (Fig. 1(*b*)), where the replacement of MgO_4 by ZnO_4 tetrahedra is characterized by the correlative replacement of the 514 cm.$^{-1}$ by the 452 cm.$^{-1}$ band. Hence, we have good reasons to believe that, in most II–III spinels, the infra-red bands should be related, not to specific co-ordination groups, but to complex vibrations of larger groups such as the whole spinel unit cell.

This conclusion is in disagreement with the statement of Waldron (1955), followed by Hafner (1961), that the high-frequency infra-red band of spinels is chiefly related to a vibration of tetrahedral groups, the other band corresponding to octahedral groups. Even in the more favourable case of independent vibrations, the band related to the tetrahedral groups is not necessarily the high-frequency band (as in the above-mentioned spinel germanates) but may well be a low-frequency band (see following paper on $LiCrGeO_4$, Tarte, 1962*b*).

The large difference in the spectroscopic behaviour of normal II–IV (germanates) spinels, and normal II–III spinels may be explained in a very simple manner. In the first case, one of the vibrational modes (ν_3 stretching mode of SiO_4 or GeO_4 tetrahedra) has a much higher frequency (800–700 cm.$^{-1}$) than the others (ν_4 bending mode of SiO_4 or GeO_4 tetrahedra, and stretching mode of XO_6 octahedra, all below 500 cm.$^{-1}$) and is therefore an independent vibrational mode. In II–III spinels, the vibrational modes of both tetrahedral and octahedral groups have similar frequencies (generally in the 650–400 cm.$^{-1}$ range), and it is highly probable that severe interactions between these vibrations preclude the occurrence of frequencies specifically related to a given co-ordination group. Further work is in progress in order to check these considerations.

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* This is *always* an approximation.