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Infra-red spectrum and tetrahedral co-ordination of lithium in the spinel LiCrGeO_4 . By

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The compound LiCrGeO_4 has been recently synthesized and recognized as a spinel on the basis of its X-ray powder diagram (Strunz & Jacob, 1960), but no information about the cation distribution has so far been reported. Both lithium and germanium are known to have a marked preference for tetrahedral co-ordination in oxygenated compounds, and their actual distribution in the spinel LiCrGeO_4 can not be decided without further investigation. The possibilities offered by infra-red spectroscopy (Tarte & Preudhomme; see also Tarte, 1962a) have been applied to this problem.

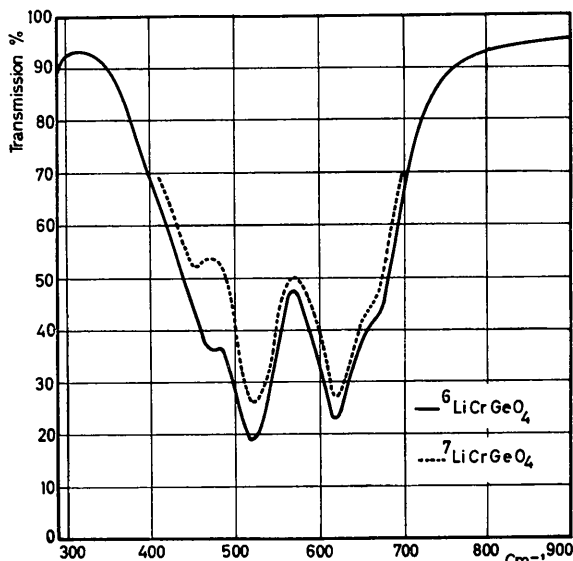


Fig. 1.

The observed infra-red spectrum is given in Fig. 1. Three strong bands only are observed in the 1000–300 cm^{-1} range, and one of these bands is moderately shifted towards higher frequencies when natural lithium (predominantly ${}^7\text{Li}$) is replaced by ${}^6\text{Li}$ (Table 1). Now, comparison of these results with previous infra-red investigations enables certain conclusions to be drawn.

(1) GeO_4 tetrahedra have been found to absorb in the 830–680 cm^{-1} range in a large series of orthogermanates

Table 1. *Isotopic shifts in the infra-red spectrum of LiCrGeO_4*

Observed frequencies		
${}^7\text{LiCrGeO}_4$	${}^6\text{LiCrGeO}_4$	$\Delta\nu$
623 cm^{-1}	623 cm^{-1}	0 cm^{-1}
526	523	-3
447	473	+26

(Tarte, 1962a). LiCrGeO_4 has no band in this spectral range; this is a first reason for believing that no GeO_4 tetrahedra are present in this structure.

(2) An infra-red investigation of lithium compounds with LiO_4 tetrahedra or LiO_6 octahedra (Tarte, 1962b) has revealed the occurrence, in the 500–400 cm^{-1} region, of infra-red bands related to LiO_4 tetrahedra; these bands are identified without doubt by the isotopic shift (20–30 cm^{-1}) related to the ${}^7\text{Li}$ - ${}^6\text{Li}$ replacement. No such bands are observed for LiO_6 octahedra and they are expected to lie below 300 cm^{-1} , the actual limit of our infra-red equipment. The conclusion is a straightforward assignment of the 447 cm^{-1} band in ${}^7\text{LiCrGeO}_4$ (473 cm^{-1} in ${}^6\text{LiCrGeO}_4$) to LiO_4 tetrahedra.

All the available infra-red data are thus consistent with the four-fold co-ordination of lithium, and six-fold co-ordination of germanium, the formula of the spinel being $\text{Li}^{\text{IV}}[\text{GeCr}]^{\text{VI}}\text{O}_4$. The infra-red spectrum, however, does not preclude the occurrence of a slight amount of germanium on tetrahedral sites.

There is great similarity between the infra-red spectra of LiCrGeO_4 and LiCrTiO_4 : from this similarity, it may be inferred that LiCrTiO_4 is also a spinel, with essentially the same cation distribution as LiCrGeO_4 , namely $\text{Li}^{\text{IV}}[\text{CrTi}]^{\text{VI}}\text{O}_4$.

A study of the ${}^7\text{Li}$ - ${}^6\text{Li}$ isotopic shift has been made in a series of lithium compounds (including the spinels LiAl_5O_8 and LiFe_5O_8) in order to determine the lithium co-ordination in these compounds; the results will be published in due course.

References

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Nb_3Si , a superconductor with the ordered Cu_3Au structure. By FRANCIS GALASSO and JANE PYLE, *United Aircraft Corporation, Research Laboratories, East Hartford, Connecticut*

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Many papers have been published characterizing one or more phases in the niobium-silicon system. Knapton consolidated much of the data when he presented the entire niobium-silicon phase diagram in which three compounds, Nb_4Si , Nb_5Si_3 , and NbSi_2 were shown and described (Knapton, 1955). In a later study by Samsonov

et al., further evidence was given for the existence of these compounds found by Knapton, along with a complete summary of their structural characteristics (Samsonov, Neshpor & Yermakova, 1958) (see Table 1). The purpose of this paper is to report the preparation and structure of another niobium silicide with the formula