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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.

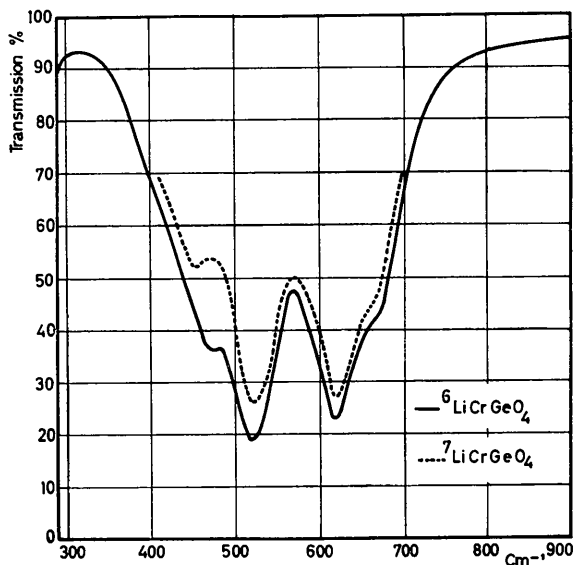


Fig. 1.

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_3O_8 and LiFe_3O_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