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

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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, 1962*a*) have been applied to this problem.

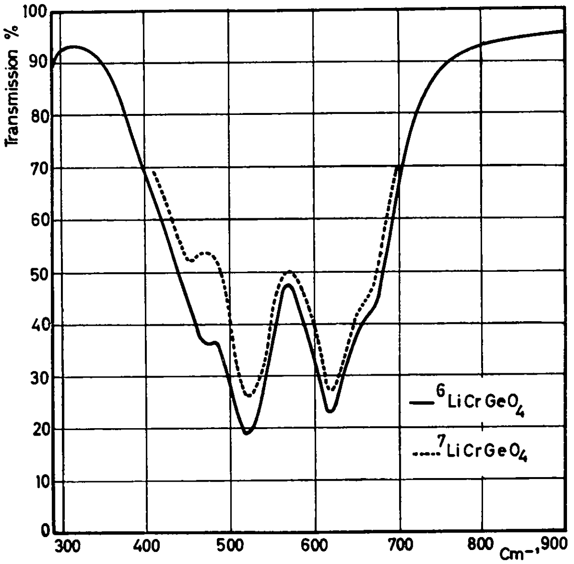

Fig. 1.

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 ^7Li) is replaced by ^6Li (Table 1). Now, comparison of these results with previous infra-red investigations enables certain conclusions to be drawn.

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

Observed frequencies		
$^7LiCrGeO_4$	$^6LiCrGeO_4$	$\Delta\nu$
623 cm.$^{-1}$	623 cm.$^{-1}$	0 cm.$^{-1}$
526	523	−3
447	473	+26

(1) GeO_4 tetrahedra have been found to absorb in the 830–680 cm.$^{-1}$ range in a large series of orthogermanates (Tarte, 1962*a*). $LiCrGeO_4$ 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, 1962*b*) 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 ^7Li–^6Li 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 $^7LiCrGeO_4$ (473 cm.$^{-1}$ in $^6LiCrGeO_4$) 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 $Li^{IV}[GeCr]^{VI}O_4$. 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 $Li^{IV}[CrTi]^{VI}O_4$.

A study of the ^7Li–^6Li 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.

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Nb_3Si, a superconductor with the ordered Cu_3Au structure.

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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

Nb_3Si which was prepared at the United Aircraft Corporation Research Laboratories.

Table 1. *Structural characteristics of phases in the system* Nb–Si
(Results of Samsonov)

Phase	Crystal system	Structural type	Lattice constants
Nb_4Si	Hexagonal	ε-Fe_3N	$a = 3{\cdot}59$ Å $c = 4{\cdot}46$
αNb_5Si_3	Tetragonal	Cr_5B_3	$a = 6{\cdot}56$ $c = 11{\cdot}86$
βNb_5Si_3	Tetragonal	Ni_3P	$a = 10{\cdot}00$ $c = 5{\cdot}07$
γNb_5Si_3	Hexagonal	Mn_5Si_3	$a = 7{\cdot}52$ $c = 5{\cdot}24$
$NbSi_2$	Hexagonal	$CrSi_2$	$a = 4{\cdot}78$ $c = 6{\cdot}56$

The samples were made from niobium and silicon powders (99% purity) which were mixed dry in stoichiometric quantities in a ball mill for approximately 1 hr. These mixtures were then made into pellets, sealed in evacuated silica capsules, and heated at 1100 °C. for 140 hr.

Small amounts of the products were ground for powder X-ray diffraction studies. The diffraction photographs were taken using a 57·3 mm. radius Philips camera and high-intensity Cu $K\alpha$ radiation with a setting of 50 kV. and 40 mA. for $3\frac{1}{2}$ hr. The powder photographs thus obtained contained an X-ray pattern which could be indexed on the basis of a small cubic unit cell of 4·211 Å, and weak extra lines which were all identified as belonging to tetragonal αNb_5Si_3. The 4·211 Å value for the cubic phase was determined by extrapolation of a_0 versus $\frac{1}{2}[(\cos^2\theta/\sin\theta)+(\cos^2\theta/\theta)]$ to $\theta=90°$ (Nelson & Riley, 1945). The λ, Cu $K\alpha_1$ and λ, Cu $K\alpha_2$ used to derive the lattice constant are 1·5405 Å and 1·5443 Å, respectively. No systematic absences were observed among the reflections. However, it was noted that the reflections whose indices were all odd or all even were much stronger than the others, indicating that the atoms were probably in a pseudo face-centered cubic arrangement. Since the volume of the unit cell could only contain one formula unit of Nb_3Si (calculated density 6·82 g.cm.$^{-3}$), a logical structure is one in which the silicon atoms occupy the corners of the cubic cell and niobium atoms are in the faces. Adopting these positions, one Si atom at 0, 0, 0 and Nb atoms at $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; and $0, \frac{1}{2}, \frac{1}{2}$, the relative intensities were calculated using the formula

$$I \propto P|F_{hkl}|^2(1+\cos^2 2\theta)/\sin^2\theta\cos\theta$$

where P is the multiplicity factor, F_{hkl} the structure amplitude, and the remaining term is the combined Lorentz and polarization factors. The structure amplitudes were calculated using atomic scattering factors for silicon from a paper by Berghuis *et al.* and those for niobium from a paper by Thomas & Umeda (Berghuis *et al.*, 1955; Thomas & Umeda, 1957).

The agreement between the observed and calculated intensities given in Table 2 indicates that the positions of the atoms selected were probably correct. In this structure each silicon atom is surrounded by 12 niobium atoms at a distance of 2·98 Å, while the niobium atoms are coordinated to 4 silicon atoms and 8 other niobium atoms at the same distance. After determining the atomic positions, it was found that this arrangement of atoms was the same as that adopted by ordered Cu_3Au and commonly referred to as the $L1_2$ type structure.

Table 2. *Comparison of observed and calculated intensities and d/n values*

hkl	*d/n* Observed	*d/n* Calculated	Observed intensity	Calculated intensity
100	4·20 Å	4·20 Å	*m*+	13
110	2·97	2·97	*m*+	11
111	2·424	2·427	*s*+	100
200	2·104	2·103	*s*	47
210	1·881	1·880	*m*−	6
211	1·717	1·717	*m*−	4
220	1·486	1·486	*s*	32
300, 221	1·401	1·402	*w*+	3
310	1·330	1·330	*w*	2
311	1·269	1·268	*s*	36
222	1·214	1·214	*m*	10
320	1·165	1·166	*w*−	1
321	1·125	1·124	*w*	2
400	1·052	1·052	*m*−	6
410, 322	1·022	1·021	*w*	2
411, 330	0·992	0·992	*w*−	1
331	0·966	0·965	*s*−	20
420	0·941	0·940	*s*−	20
421	0·919	0·918	*w*	2
332	0·897	0·897	*w*−	1
422	0·859	0·858	*s*−	21
500, 430	0·842	0·841	*w*−	1
510, 431	0·826	0·825	*m*−	4
511, 333	0·810	0·809	*s*	39
432, 520	0·782	0·781	*m*	8

In recent years A_3B-type compounds have been studied extensively because they often adopt the β-tungsten structure which seems to be a favorable arrangement of atoms for superconducting compounds. From an empirical rule derived from a study at this laboratory (Galasso, 1962), it was felt that Nb_3Si would be a superconductor with a high-transition temperature (> 18 °K.) if it had the β-tungsten structure. The small silicon atoms, however, probably would not fit well between the chains of niobium atoms which would run through the β-tungsten structure, and Nb_3Si therefore adopted the ordered Cu_3Au structure. As a consequence, instead of having a high-transition temperature, it was found to become superconducting at 1·5 °K.

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