ted for by a root-mean-square amplitude of rotation of about 15°. This agrees well with the fact that the distance of O(2) to the mirror plane $y = 2x$ can be changed from 0 to 0·25 Å without significantly changing the value of $(R/R_{min})^{1/2}$, as the plot of x for O(2) in Fig. 2 shows.

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The Crystal Structure of Li₂Cu₅(Si₂O₇)₂ and the Proposal of New Values for the Effective Ionic Radii of Cu²⁺

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Synthetic copper lithium silicate, Li₂Cu₅(Si₂O₇)₂, is triclinic, $P\bar{1}$, with $a = 7·404$ (3), $b = 7·754$ (2), $c = 5·455$ (1) Å, $\alpha = 90·52$ (2), $\beta = 106·27$ (2), $\gamma = 114·64$ (3)°, $Z = 1$. The structure was deduced from Patterson syntheses and refined to $R = 0·040$ for 1203 observed reflexions. The structure contains Si₂O₇ pyrosilicate groups, three kinds of Cu²⁺ coordination polyhedra and one kind of trigonal bipyramidal coordinated Li⁺ ions. Cu(1) is in a square coplanar site, Cu(2) in an intermediate site between tetrahedral and square coplanar and Cu(3) in a distorted square pyramidal site. Based on the interionic distances between Cu²⁺ and O²⁻ in the recently determined structures, the following new values for the effective ionic radii are proposed: Cu²⁺(IV), 0·65 Å; (IV in IV + I or IV + II), 0·67 Å; (I or II in IV + I or IV + II), >0·9 Å.

Introduction

It is important, from the viewpoint of the coordination of divalent Cu ions, to investigate the crystal structure of copper silicates. Since natural specimens are frequently polycrystalline and very small, it is difficult to study them by X-ray single-crystal methods. Accordingly, the syntheses of these crystals are of substantial importance. Kawamura, Kawahara & Henmi (1976) first succeeded in synthesizing plancheite and shattuckite, and also obtained two new phases of anhydrous sodium copper silicates. These new phases have been found neither as natural minerals nor as synthetic products. The structure of the one of the phases (Na₂Cu₃Si₄O₁₂) was reported as a chain silicate (Kawamura & Kawahara, 1976), and that of the other

phase ($Na_2CuSi_4O_{10}$) as a Si—O pipe-like channel structure (Kawamura & Kawahara, 1977).

The present paper reports the crystal structure of another new phase, lithium copper silicate [Li_2Cu_5-($Si_2O_7)_2$], which has been obtained by hydrothermal syntheses. New values of the ionic radii for Cu^{2+}, based on these three and other recently investigated structural data, are also proposed.

Throughout the investigation, calculations were carried out at the Computer Center of Okayama University.

Experimental

Synthesis of the title compound was carried out with test-tube-type apparatus (400–600°C, 1000 kg cm^{-2}) with reagent mixtures of $CuSO_4.5H_2O$, SiO_2(gel) and Li_2CO_3 or CuO, SiO_2(gel) and $LiCO_3$. The chemical composition of this substance was determined by X-ray microprobe analyses.

The crystal of $Li_2Cu_5(Si_2O_7)_2$ was bluish, about 0·1 mm in diameter with no apparent euhedral forms.

The powder diffraction data are listed in Table 1 (Cu $K\alpha$: $\lambda = 1·54178$ Å). The diffraction peak positions were corrected with reference to the α-Al_2O_3 peaks used as internal standards.

The lattice dimensions and diffraction symmetry were estimated from precession photographs. Three-dimensional intensity data were collected from an approximately spherical crystal with a diameter of 0·05 mm, on an automated four-circle diffractometer with the 2θ–θ scan technique, Mo $K\alpha$ radiation ($\lambda = 0·70926$ Å) and a graphite monochromator. Intensities of 1315 reflections were collected up to $2\theta = 56°$, among which 110 reflections have zero intensities because of $I < 3\sigma$.

The intensities were converted to the structure factors by applying the Lorentz–polarization correc-

tions. No absorption corrections were made because of the small spherical crystal form.

The crystal data are shown in Table 2.

Structure determination and refinement

Three-dimensional Patterson syntheses were carried out, and the structure determination was attempted in the $P\bar{1}$ space group. Positions of three kinds of Cu atoms were easily found from the maps. The positions of the Si and O atoms were found from $D_{(F_o-F_c)}$ maps with the phases given by these Cu atoms. The position of the Li atom was obtained by further $D_{(F_o-F_c)}$ maps calculated with three Cu, two Si and seven O positional parameters.

The parameters of all the atoms were refined to $R = 0·054$ with a full-matrix least-squares program (Sakurai, 1971) and isotropic temperature factors. The anisotropic temperature factors of the Li atom did not converge in the course of the refinement. The procedure was continued with anisotropic temperature factors for Cu, Si and O atoms and isotropic ones for Li. The R factor was finally reduced to 0·040. Scattering factors corresponding to neutral atoms were used throughout the calculations (International Tables for X-ray Crystallography, 1974). The final atomic parameters are listed in Table 3.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33680 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Crystal data of* $Li_2Cu_5(Si_2O_7)$

Space group: $P\bar{1}$

$a = 7·404(3)$ Å	$\alpha = 90·52(2)°$
$b = 7·754(2)$	$\beta = 106·27(2)$
$c = 5·455(1)$	$\gamma = 114·64(3)$
$D_x = 4·10$ g cm^{-3}	μ(Mo $K\alpha$) = 105·5 cm^{-1}

Table 1. *The X-ray powder data of* $Li_2Cu_5(Si_2O_7)_2$

d_{obs}	I_{obs}	h k l	d_{calc}
6·44 Å	22	1 0 0	6·394 Å
4·41	30	$\bar{1}$ 1 1	4·395
3·71	24	1 $\bar{1}$ 1	3·687
		$\bar{1}$ $\bar{1}$ 1	3·651
3·41	54	$\bar{2}$ 1 1	3·396
3·062	24	1 $\bar{2}$ 1	3·048
2·931	100	$\bar{2}$ 2 1	2·921
2·626	67	1 2 0	2·618
		2 $\bar{1}$ 1	2·615
2·507	19	$\bar{1}$ $\bar{1}$ 2	2·501
2·395	17	2 0 1	2·406
2·348	26	$\bar{3}$ 2 1	2·348
		$\bar{3}$ 1 0	2·344
2·245	15	0 $\bar{3}$ 1	2·245
		0 $\bar{2}$ 2	2·240

Table 3. *Atomic positional parameters* ($\times 10^4$) *with their standard deviations in parentheses*

	x	y	z
Cu(1)	0000(–)	0000(–)	0000(–)
Cu(2)	6126(1)	1832(1)	9184(1)
Cu(3)	4212(1)	2877(1)	3383(1)
Si(1)	7723(2)	1388(2)	5021(3)
Si(2)	2148(2)	4011(2)	7991(3)
Li	1143(12)	4513(11)	2448(14)
O(1)	2251(6)	0175(5)	3053(7)
O(2)	6523(6)	0387(5)	2078(7)
O(3)	6606(6)	2615(5)	5886(7)
O(4)	1876(6)	2638(5)	0273(7)
O(5)	0160(5)	2834(5)	5353(7)
O(6)	8200(6)	4215(5)	1041(7)
O(7)	4146(4)	4527(5)	7047(7)

Description of the structure

The crystal structure of $Li_2Cu_5(Si_2O_7)_2$ contains (Si_2O_7) pyrosilicate groups, three types of Cu^{2+} coordination polyhedra and one type of Li^+.

The surroundings of the Cu^{2+} ions are illustrated in Fig. 1. Cu(1) is in an approximately square coplanar site, Cu(2) in a four-coordinated intermediate site between square coplanar and tetrahedral and Cu(3) in the 4 + 1 distorted and elongated square pyramidal site. The distortion of the Cu(3) coordination polyhedra is considered to be due to the relatively short Cu—O distance of an additional more weakly bonded O atom [Cu(3)—O(7) = 2·387 Å]. The coordination polyhedra of Cu(1) and Cu(3) share their edges forming infinite chains along the direction [111]. The coordination polyhedra of Cu(2) also share edges. These shared edges are shorter than other unshared edges (Fig. 1).

Li^+ is surrounded by a trigonal bipyramidal arrangement of O atoms. The mean Li—O distance is 2·145 Å, which corresponds to the octahedral Li—O distance.

In the Si_2O_7 group (Fig. 2), the bridging angle [Si(1)—O(5)—Si(2)] is 130·2°. This value is relatively small compared with that of other pyrosilicates. The

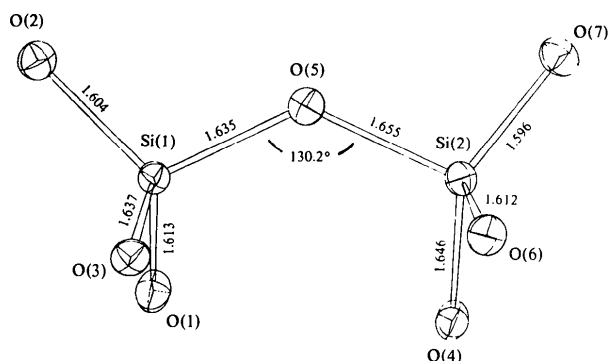Fig. 2. The coordination of oxygen atoms around the two silicon atoms, Si(1) and Si(2), in the Si_2O_7 group (distances in Å).

Si—O bridging bonds are significantly longer than those of the non-bridging bonds (Table 4), except for Si(1)—O(3) (1·637 Å) and Si(2)—O(4) (1·646 Å), which are longer than the bridging Si(1)—O(5) (1·635 Å). This fact may be due to the strong covalent character of the Cu—O bonds.

Discussion on the ionic radii for Cu^{2+}

According to the table of effective ionic radii by Whittaker & Muntus (1970) [corrected values of Shannon & Prewitt (1969)] the value of Cu^{2+} (IV) (0·70 Å) is almost the same as those of Fe^{2+} (IV) (0·71

Fig. 1. The surroundings of Cu(1), Cu(2) and Cu(3).

Table 4. *Interatomic distances (Å) and angles (°) with their standard deviations in parentheses*

Cu(1)—O(1) (×2)	1·955(4)	O(1)—O(4)	2·507(6)	80·9(2)
—O(4) (×2)	1·909(3)	—O(4)	2·942(4)	99·1(2)
Cu(2)—O(1)	2·776(5)	O(1)—O(3)	2·646(6)	65·1(2)
· O(2)	1·970(4)	O(2)—O(2')	2·563(5)	82·4(1)
—O(2')	1·921(3)	—O(6)	2·832(5)	94·8(2)
—O(3)	1·982(4)	O(2')—O(3)	3·002(5)	100·5(1)
—O(6)	1·878(3)	O(3)—O(6)	2·775(5)	91·9(2)
Cu(3)—O(1)	1·960(3)	O(1)—O(3)	2·904(5)	94·4(2)
—O(3)	1·999(4)	—O(4)	2·507(6)	78·6(2)
—O(4)	1·997(4)	O(3)—O(7)	2·894(6)	94·9(2)
· O(7)	1·927(4)	—O(7')	2·966(7)	84·6(2)
—O(7')	2·387(4)	O(4)—O(7)	2·788(4)	90·6(2)
		O(7)—O(7')	2·823(6)	81·0(2)
Si(1)—O(1)	1·613(4)	O(1)—O(2)	2·659(5)	111·4(2)
—O(2)	1·604(4)	—O(3)	2·646(6)	109·0(2)
—O(3)	1·637(5)	—O(5)	2·611(5)	107·0(2)
—O(5)	1·635(4)	O(2)—O(3)	2·661(6)	110·4(2)
		—O(5)	2·651(4)	109·9(2)
		O(3)—O(5)	2·664(6)	109·0(2)
Si(2)—O(4)	1·646(4)	O(4)—O(5)	2·664(5)	107·6(2)
—O(5)	1·655(3)	—O(6)	2·568(6)	104·1(2)
—O(6)	1·612(5)	—O(7)	2·777(6)	117·9(2)
—O(7)	1·596(5)	O(5)—O(6)	2·616(5)	106·4(2)
		—O(7)	2·550(5)	103·3(2)
		O(6)—O(7)	2·732(7)	116·8(2)
Li—O(3)	2·141(7)			
—O(3)	2·192(11)			
—O(5)	2·151(9)	Si(1)—O(5)—Si(2)		130·2(3)
—O(6)	2·008(9)			
—O(6')	2·233(9)			

Å), Pd^{2+} (0.72 Å) or Pt^{2+} (IV) (0.68 Å). But in comparison of the cell dimensions and interatomic distances of the following two isostructural pairs: $BaCuSi_4O_{10}$ (Pabst, 1959)–$BaFeSi_4O_{10}$ (Hazen & Burnham, 1975) and $KNaCuSi_4O_{10}$ (Pozas, Rossi & Tazzoli, 1975)–$KNaFeSi_4O_{10}$ (Golovachev, Drozdov, Kuz'min & Belov, 1971), it is evident that the effective ionic radii of Cu^{2+} (IV) are significantly smaller than those of Fe^{2+} (IV). There is further evidence that CuO has a more distorted structure than PdO and PtO. The mean interatomic distance of Cu–O (1.95 Å) is smaller than those of Pd–O (2.01 Å) or Pt–O (2.02 Å) (Moore & Pauling, 1941; Åsbrink & Norrby, 1970). This fact also suggests that the value for Cu^{2+} (IV) is smaller than those of Pd^{2+} or Pt^{2+}.

Expected Cu–O distances deduced from the ionic radii of Whittaker & Muntus (1970) have the following

values (coordination numbers in parentheses): Cu^{2+}–O^{2-} (IV_{sq}) 1.99, (V) 2.02, (VI) 2.10 Å, where the ionic radius of O^{2-} for '3.5' coordination (1.29 Å) was adopted, because in the structures of the compounds in Table 5, the average coordination number of O^{2-} is approximately 3.5. However, the following mean distances of Cu–O can be obtained from recently determined precise structural data (Table 5): Cu^{2+}–O^{2-} (IV) 1.94 ± 0.01, (IV in IV + I or IV + II) 1.96 ± 0.01, (I or II in IV + I or IV + II) > 2.2 Å. Because the Cu^{2+} ion is hardly ever coordinated by regular or nearly regular octahedrally arranged O atoms, such a coordination state is not considered. Considering cation coordination around O^{2-} in individual Cu–O bonds, the new effective ionic radii were calculated. The following ionic radii for Cu^{2+}, therefore, are more suitable in the table of Whittaker & Muntus

Table 5. *Recent* Cu–O *data*

Chemical formula		$Cu-O_{IV}$ (Å)	Additional Cu–O (Å)	Coordination state	References
$Li_2Cu_5(Si_2O_7)_2$	(1)	1.932		IV_{sq}	Present work
	(2)	1.938	(2.776)	$IV_{sq}IV_{tet}$	
	(3)	1.971	2.387	IV + I	
$Na_2Cu_3Si_4O_{12}$	(1)	1.928		IV_{sq}	Kawamura & Kawahara (1976)
	(2)	1.940		IV_{sq}	
	(3)	1.954		IV_{sq}	
$Na_2CuSi_4O_{10}$		1.967	2.511	IV + I	Kawamura & Kawahara (1977)
$KNaCuSi_4O_{10}$		1.978	2.549	IV + I	Pozas *et al.* (1975)
$Cu_6(Si_6O_{18}).6H_2O$		1.962	2.502, 2.648	IV + I + I	Ribbe, Gibbs & Hamil (1977)
$Cu_5(SiO_3)_4(OH)_2$	(1)	1.967	2.587	IV + II	Evans & Mrose (1977)
	(2)	1.995	2.310, 2.617	IV + I + I	
	(3)	1.919	2.692, (2.781)	IV + I	
$Ca_2Cu_2Si_3O_{10}.2H_2O$	(1)	1.943	2.453	IV + I	Laughon (1971)
	(2)	1.964	2.240	IV + I	
$CuSiF_6.6H_2O$	(1)	2.074	2.074	VI_{oct}	Ray, Zalkin & Templeton (1973)
	(2)	1.970	2.367	IV + II	
$Li_2Cu_2P_6O_{18}$	(1)	1.960	2.352, 2.452	IV + I + I	Laügt & Durif (1974)
	(2)	1.958	2.323, 2.427	IV + I + I	
$K_2Cu(PO_3)_4$		1.971	2.432, 2.527	IV + II	Laügt, Tordjman, Bassi & Guitel (1974)
$Cu_5(PO_4)_2(OH)_4$	(1)	1.946	(2.757)	IV_{sq}	Shoemaker, Anderson & Kostiner (1977)
	(2)	1.964	2.395, (2.757)	IV + I	
	(3)	1.980	2.346, 2.493	IV + I + I	
$Cu_5(PO_4)_2(OH)_4$-II	(1)	1.949	(2.723)	IV_{sq}	Anderson, Shoemaker, Kostiner & Ruszala
	(2)	1.962	2.296	IV + I	(1977)
	(3)	1.972	2.379, 2.466	IV + II	
$Cu_5V_2O_{10}$	(1)	1.961	2.501, (2.852)	IV + I	Shannon & Calvo (1973)
	(2)	1.957	2.481, (2.702)	IV + I	
	(3)	1.965	2.287	IV + I	
	(4)	2.007	2.388, 2.492	IV + I + I	
	(5)	1.948	2.230	IV + I	
CuV_2O_5		1.977	2.438	IV + II	Calvo & Manolescu (1973)
$Cu_3(OH)_2(CO_3)_2$	(1)	1.938		IV_{sq}	Zigan & Schuster (1972)
	(2)	1.959	2.358, (2.761)	IV + I	
$Na_2Cu(CO_3)_2.3H_2O$		1.970	2.362, 2.600	IV + I + I	Harlow & Simonsen (1975)
$K_2Cu(C_2O_4)_2.2H_2O$	(1)	1.947	2.462	IV + II	Weichert & Löhn (1974)
	(2)	1.943	2.631	IV + II	
$CuSe_2O_5$		1.932	(2.725)	IV_{sq}	Meunier, Svensson & Carpy (1976)
$CuTe_2O_5$		1.957	2.305, (2.780)	IV + I	Hanke & Kupčik (1973)
$Cu_3(IO_3)_6.2H_2O$	(1)	1.952	2.528	IV + II	Ghose & Wan (1974)
	(2)	1.953	2.456, 2.483	IV + II	
$Ba_2[Cu(OH)_6]$		1.965	(2.805)	IV_{sq}	Dubler, Korber & Oswald (1973)

(1970): Cu^{2+} (IV) 0.65 ± 0.01, (IV in IV + I or IV + II) 0.67 ± 0.01, (I or II in IV + I or IV + II) > 0.9 Å. In Shannon & Prewitt's (1969) table, these values are 0.08 Å higher.

The Cu^{2+} can substitute for some kinds of ions in regular octahedral and tetrahedral sites, and in such a case, the structures are frequently distorted. The spinel type compounds, with structural formula $(Fe_{1-x}^{3+}, Cu_x^{2+})_{tet}(Fe_{1+x-y}^{3+}, Cr_y^{3+}, Cu_{1-x}^{2+})_{oct}O_4$, permit continuous substitution between Fe^{3+} and Cu^{2+} in tetrahedral sites and Fe^{3+}, Cr^{3+} and Cu^{2+} in octahedral sites, and have tetragonally distorted structures about the two end compositions respectively, because of the distortion of the coordination polyhedra of Cu^{2+} (Delorme, 1958).

In general the Cu^{2+} ion can substitute for the regular octahedral and tetrahedral cations when structural tolerance is obtained, and the following ions are listed as such cations: Li^+ (IV), Mg^{2+} (IV), Fe^{2+} (IV), Co^{2+} (IV), Zn^{2+} (IV), Al^{3+} (VI), Cr^{3+} (VI), Fe^{3+} (IV, VI), Co^{3+} (VI) and Ni^{3+} (VI). The above group of ions consists principally of some of the four-coordinated divalent and six-coordinated trivalent metal ions of the first transition series.

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