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$Li_{21}Si_5$, a Zintl Phase as Well as a Hume-Rothery Phase*

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$Li_{21}Si_5$ is the most lithium-rich phase in the binary Li/Si system and substitutes the so-called $Li_{22}Si_5$. This was proved by a careful X-ray structure analysis ($F\bar{4}3m$-T_d^2; a = 1871.0 pm; Z = 16; R = 0.052; 397 *hkl*). The reduced Li content is due to ordered vacancies in the huge 6 × 6 × 6 superstructure of bcc (*cF*416). This gives rise to the formation of M_{26} clusters typical for γ-brass structures. Two different cluster types, namely $Li_{22}Si_4$ and $Li_{20}Si_6$, set up a complex linkage of diamond, zinc blende, and NaCl type partial structures, in which short Si–Si distances are avoided. $Li_{21}Si_5$ is on one hand a representative consistent only of main group elements of the Hume-Rothery phases for structural and electronic reasons (VEC = 20.5/13 = 1.58). On the other hand the two M_{26} clusters fulfill electronically an extended Zintl phase formalism, according to $[Li_{22}Si_4]^{4+}$ and $[Li_{20}Si_6]^{4-}$. The latter anion follows classical valence rules (Si^{4-} formation), while the former one carries a cage orbital in addition to the filled Si states, which is delocalized over the Li sites. The two quantum mechanically stable units act as donor–acceptor pairs, which is also reflected in the experimental valence electron density. In a new topological description the whole structure can be understood as being built of M_{14} cluster nuclei and a continuous periodic curved surface formed by the network of all remaining Li atoms.

Introduction

A few years ago we showed that there are only four stable phases in the binary lithium/silicon system (*1*). The structure and bonding of these compounds have been the subject of intensive investigations (*2–8*), because simple application of the valence rules valid for higher alkali metals fails in this case (*8–10*). A quantitative description of structure and bonding for the semiconductor $Li_{12}Si_7$ (*2–5*) was given by means of INDO calculations, especially with respect to the planar Si_5 ring being a 26-electron pentasila-cyclopentadienyl system and with respect to the planar Si_4 stars being 28-electron systems stabilized by a cage orbital of the enveloping Li atoms. In the same way the structure of $Li_{14}Si_6$ (*1*) is obviously stabilized by a cage orbital (*4, 6*) which is due mainly to the Li environment of the Si_2 dumbbells. $Li_{13}Si_4$ and $Li_{14}Ge_4$ (*9*) contain the same amount of isolated Si atoms and Si_2 dumbbells despite their different stoichiometry. The crystal structure and the two phases are similar but proved to be different. Still there might be a vacancy in the structure of $Li_{14}Ge_4$ (*10*). However, the cage orbital description is valid in both cases (*4*).

Another open question concerns the relationships between structure and bonding in

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the huge cubic arrangement of "$Li_{22}Si_5$" (*11*). "$Li_{22}Si_5$" belongs to the $Li_{22}Pb_5$-type family (*12*) which contains only compounds of Li with Si, Ge, Sn, Pb, and Tl (*13*). The structure of $Li_{22}Pb_5$, having one of the largest unit cells in the regime of intermetallic phases, was determined in 1958 by Zalkin and Ramsey, mainly on the basis of geometric arguments (*12*). They described the complex $cF432$ structure as an ordered derivative of a sixfold superstructure of bcc [$cI2$ (*14*)], overlooking the possibility of defect formation which is typical for γ-brass and related structures. In the present investigation, we show that the correct composition of this silicide is $Li_{21}Si_5$ and that the formation of ordered defects generates a direct link between this huge $cF416$ structure and the γ-brass arrangements (*15*).

Preparation and Properties

$Li_{21}Si_5$ is prepared from a stoichiometric melt of the pure elements [3 *N* lithium (Ventron), 5 *N* silicon (Wacker)] in sealed niobium ampoules at 1000 K. After a slow cool down (1 K/min) crystals of silvery metallic luster are obtained. $Li_{21}Si_5$ is brittle and decomposes peritectically at 890 K. The compound is very sensitive to air.

Structure Determination

The most lithium rich cubic phase in the Li/Si binary system has been studied twice up to now (*11, 16*). In both studies, the composition $Li_{22}Si_5$ was stated, obviously in analogy to the isotypic $Li_{22}Pb_5$, which is the prototype of the famous $cF432$ structure (*12*). The proposed space group is $F32$ (No. 196), but analysis of the given positional parameters shows that (1) the structure can be described in the space group $F\bar{4}3m$ (No. 216) without difficulties, and (2) Li atoms at the special positions $4a$, $4b$, $4c$, and $4d$ are involved in unreasonable short interatomic distances. Furthermore, it should be pointed out that Schäfer and co-workers (*11*) have found the composition $Li_{20.9}Si_5$ by chemical analysis.

TABLE I

CRYSTALLOGRAPHIC DATA AND DETAILS OF THE STRUCTURE DETERMINATION

Composition	$Li_{21}Si_5$; mole mass, 286.15 amu
Unit cell	a = 18.710(2) pm, $F\bar{4}3m$-T_d^2 (No. 216), Z = 16, V = 6449(1), 10^6 pm^3, μ = 4.05 cm^{-1}
Density	d_x = 0.7099(1) g cm^{-1}
X-ray experiment	0.1 × 0.1 × 0.1-mm single crystal $P\bar{1}$ four-circle diffractometer $\lambda(MoK\alpha)$ = 71.069 pm, graphite monochromator, 434 unique reflections
Absorption correction	Ψ scan, μR = 0.020
Structure determination	Structure suggestion of Schäfer *et al.* (*11*), refinement [least squares, 67 variables, 356 reflections *hkl* with $I > 3\sigma(I)$]
Residuals	R(aniso) = 0.071, $R\omega$(aniso) = 0.052

For our investigation a well-shaped single crystal was used—selected and prepared carefully under inert conditions, sealed and fixed in a glass capillary (*17*). The crystallographic data and the resulting atomic parameters are listed in Tables I and II. Table II also contains the earlier data for comparison. Interatomic distances of interest are compiled in Table III. The most important result is that the special positions $4a$, $4b$, $4c$, and $4d$ are unambiguously not occupied; therefore, the true composition is $Li_{21}Si_5$! The unit cell contains 16 M_{26} clusters which belong to four crystallographically independent clusters (A, A', D, D') of two different types—C_A and C_B (see below). We tried to unify these clusters pairwise ($A + A'$, $D + D'$) in a $Fd3m$ structure, omitting numerous weak observed reflections, but failed (R = 0.21). One important reason for this is the relative turn of 90° of the two C_D-type clusters with respect to each other (see below). This is

TABLE II

Positional and Thermal Parameters U_{eq} and U_{ij} (pm^2)

$Li_{21}Si_5$ (present work)				$Li_{22}Si_5$ Ref. (*11*)		$Li_{22}Pb_5$ Ref. (*12*)	
Atom	Site	*xyz*	U_{eq}	Atom	*xyz*	Atom	*xyz*
Si1	16(*e*)	$x = 0.9095(2)$	132(8)	Si1	0.911	Pb1	0.9141
Si2	16(*e*)	$x = 0.6675(2)$	85(6)	Si2	0.665	Pb2	0.6641
Si3	24(*f*)	$x = 0.3191(3)$	104(10)	Si3	0.322	Pb3	0.3211
Si4	24(*g*)	$x = 0.0720(3)$	150(11)	Si4	0.072	Pb4	0.0711
Li1	16(*e*)	$x = 0.054(1)$	137(71)	Li5	0.080	Li5	1/12
Li2	16(*e*)	$x = 0.167(1)$	141(73)	Li6	0.167	Li6	2/12
Li3	16(*e*)	$x = 0.309(2)$	347(105)	Li7	0.330	Li7	4/12
Li4	16(*e*)	$x = 0.438(2)$	340(116)	Li8	0.420	Li8	5/12
Li5	16(*e*)	$x = 0.579(1)$	155(85)	Li9	0.583	Li9	7/12
Li6	16(*e*)	$x = 0.821(2)$	480(142)	Li10	0.833	Li10	10/12
Li7	24(*f*)	$x = 0.177(2)$	118(71)	Li11	0.167	Li11	2/12
Li8	24(*g*)	$x = 0.576(2)$	259(91)	Li12	0.583	Li12	7/12
Li9	48(*h*)	$x = 0.842(1)$	297(67)	Li13	0.839	Li13	10/12
		$z = 0.012(1)$			−0.005		0
Li10	48(*h*)	$x = 0.662(1)$	227(53)	Li14	0.658	Li14	8/12
		$z = 0.511(1)$			0.493		6/12
Li11	48(*h*)	$x = 0.097(1)$	315(57)	Li15	0.087	Li15	1/12
		$z = 0.271(1)$			0.250		3/12
Li12	48(*h*)	$x = 0.086(1)$	165(51)	Li16	0.083	Li16	1/12
		$z = 0.750(1)$			0.750		9/12
				(special positions *a*, *b*, *c*, *d* omitted)			

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si1	132(13)	U_{11}	U_{11}	−17(13)	U_{12}	U_{12}
Si2	85(11)	U_{11}	U_{11}	−29(11)	U_{12}	U_{12}
Si3	73(20)	146(15)	U_{22}	0	0	16(19)
Si4	158(25)	146(15)	U_{22}	0	0	−80(22)

Note. Standard deviations in parentheses; the components of the anisotropic temperature factors are defined for $\exp(2\pi^2 U_{11} h^2 a^{*2} + \ldots + 2U_{23} klb^* c^*)$. The older parameters for $Li_{22}Si_5$ and $Li_{22}Pb_5$ are also given.

necessary for bonding and packing reasons. There are some differences in the temperature factors of Li which might be due to frequent mobility of Li in theses phases.[1]

Results and Discussion

cF416 vs cF432

$Li_{21}Si_5$ crystallizes cubically in the space group $F\bar{4}3m$ (No. 216) with a = 1871.0 pm and Z = 16 formula units per unit cell. The structure represents a novel *cF*416 type, which is similar to the $Cu_{41}Sn_{11}$ structure (*18*), although the distribution of 4B atoms differs considerably. There is no

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[1] Additional material of the structure determination is deposited at the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG, and can be obtained by quoting the reference No. CSD 52297, the names of the authors, and the title of the paper.

TABLE III

Interatomic Distances below 350 pm

Si1	–Li9	262(2) 3x	Li1	–Li7	271(4) 3x	Li8	–Li10	262(2) 2x
	–Li6	287(4)		–Li1	286(4) 3x		–Li6	269(5) 2x
	–Li1	287(2) 3x		–Li9	286(3) 3x		–Si4	277(4)
	–Li7	289(2) 3x		–Si1	287(2) 3x		–Si2	277(2) 2x
	–Li12	299(2) 3x					–Li9	294(3) 2x
							–Li12	308(2) 4x
			Li2	–Li11	269(3) 3x			
Si2	–Li12	265(2) 3x		–Li3	273(4) 3x			
	–Li8	277(2) 3x		–Si4	283(2) 3x	Li9	–Si1	262(2)
	–Li5	287(2)		–Li9	291(3) 3x		–Si4	268(2)
	–Li6	289(4) 3x					–Li12	285(2) 2x
	–Li10	293(2) 3x					–Li1	286(3)
			Li3	–Li11	259(4) 3x		–Li11	288(3) 2x
				–Si4	272(4) 3x		–Li2	291(3)
Si3	–Li12	262(2) 2x		–Li2	273(4) 3x		–Li8	294(3)
	–Li7	266(4)		–Li3	312(8) 3x		–Li7	299(2) 2x
	–Li11	272(2) 2x					–Li10	339(2) 2x
	–Li4	276(4) 2x						
	–Li5	283(2) 2x	Li4	–Li5	268(4) 3x			
	–Li10	306(1) 4x		–Si3	276(4) 3x	Li10	–Li5	255(2)
				–Li10	299(4) 3x		–Li12	259(2) 2x
				–Li11	326(4) 3x		–Li8	262(2)
Si4	–Li9	268(2) 2x		–Li4	328(8) 3x		–Li11	267(3)
	–Li3	272(2) 2x					–Si4	279(2)
	–Li8	277(4)					–Si2	293(2)
	–Li10	279(2) 2x	Li5	–Li10	255(2) 3x		–Li4	299(4)
	–Li2	283(2) 2x		–Li4	268(4) 3x		–Si3	303(2) 2x
	–Li11	293(2) 4x		–Si3	283(2) 3x		–Li9	339(2) 2x
				–Si2	287(2)			
				–Li12	321(3) 3x			
						Li11	–Li3	259(4)
							–Li10	267(3)
			Li6	–Li8	269(5) 3x		–Li2	269(3)
				–Li12	280(4) 3x		–Si3	272(2)
				–Si1	287(4)		–Li9	288(3) 2x
				–Si2	289(4) 3x		–Si4	293(2) 2x
							–Li7	312(3)
							–Li4	326(4)
			Li7	–Li12	265(2) 2x		–Li12	345(2) 2x
				–Si3	266(4)		–Li11	349(3) 2x
				–Li1	271(4) 2x			
				–Si1	289(2) 2x			
				–Li9	299(2) 4x	Li12	–Li10	259(2) 2x
				–Li11	311(3) 2x		–Si3	262(2)
							–Li7	265(2)
							–Si2	265(2)
							–Li6	280(4)
							–Li9	285(2)
							–Si1	299(2)
							–Li8	308(2) 2x
							–Li5	321(3)
							–Li11	345(2) 2x

Note. Standard deviations in parentheses.

doubt that $Li_{21}Si_5$ is identical with the former published compound "$Li_{22}Si_5$" (lattice constant, X-ray data, properties). With one exception ($Li_{22}Tl_5$) all members of the *cF*432 structure type are lithium compounds of the 4B elements. In all these cases the lithium positions have been established very poorly. Therefore, we are sure that the *cF*432 structure does not really exist and should be changed into *cF*416 according to the now proved $Li_{21}Si_5$ structure. In addition, the $Li_{22}Tl_5$ phase has to be investigated more precisely (*16*).

Structure-Type Relationships

The *cF*416 structure of $Li_{21}Si_5$ is a complex 6 × 6 × 6 superstructure of the simple bcc structure with a characteristic defect distribution similar to that of the famous γ-brasses (Fig. 1a). The defects are the centers of M_{26} clusters around the special positions 4*a*, 4*b*, 4*c*, and 4*d*. According to classical Hume-Rothery valence rules (*19, 20*) the γ-brass structure (e.g., Cu_5Zn_8) is favored with the valence electron concentration VEC = 21/13 = 1.615. More recent results show that the range $1.59 \leqq \mathrm{VEC} \leqq 1.77$ is allowed (*21*). $Li_{21}Si_5$ is very close to the lower limit (VEC = 20.5/13 = 1.577); therefore, $Li_{21}Si_5$ (and analogs) can be classified as Hume-Rothery phases of the main group elements. It is important to note in this context that *d* electrons are not taken into account in the Hume-Rothery rule, even if elements with unfilled *d* shells are involved. Although ranges of homogeneity are typical of Hume-Rothery phases the knowledge about variations of the structural details with respect to the composition is very limited. On the contrary, $Li_{21}Si_5$ is characterized by a constant atomic ratio Li : Si, which indicates the presence of a normal valence compound. The ratio Li : Si > 4, however, is not explainable by classical valence models. Such "hypervalencies" (here with Si) are also not included in the Zintl—Klemm concept (*22*). In addition to the isolated Si atoms, which can be described as Si^{4-} according to Zintl, direct Li-to-Li interactions may form $Li_2^{\pm 0}$, Li_4^{2+} or other units at the best to fulfill the valence rules for semiconductors.

M_{26} Cluster

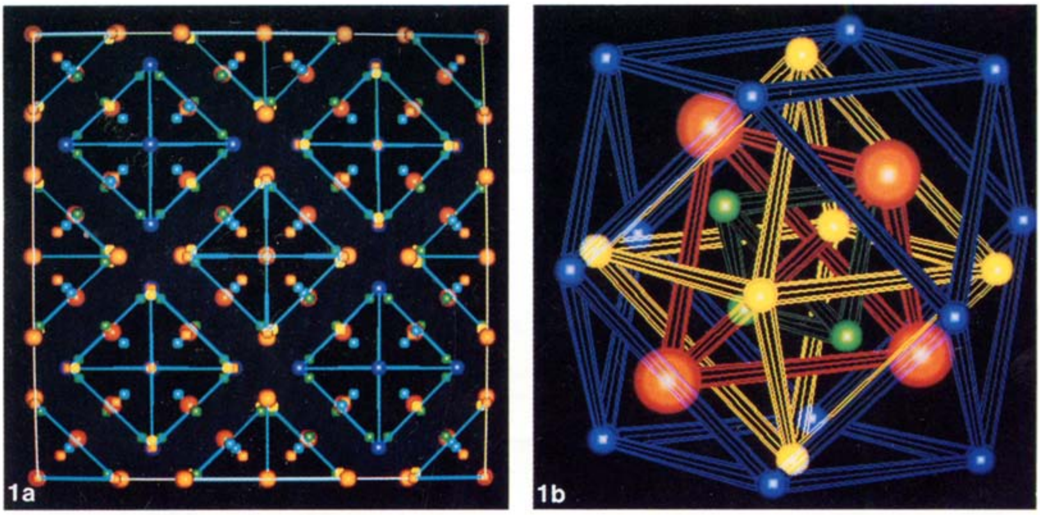
The 416 atoms of the $Li_{21}Si_5$ structure form 16 M_{26} (Fig. 1b) clusters which are assembled by shells of a smaller inner tetrahedron (IT), a larger outer tetrahedron (OT), an octahedron (OH), and a cuboctahedron (CO), namely by 4 + 4 + 6 + 12 atoms. The point symmetry is $\bar{4}3m$. Figure 2 shows the relation between the structures of $Li_{21}Si_5$ (*cF*416) and Cu_5Zn_8 (*cI*52). The 16 M_{26} clusters belong to *four* crystallographically independent classes which differ by their composition, namely,

$$A, A' = Li_{22}Si_4 = Li_4Si_4Li_6Li_{12}$$
$$D, D' = Li_{20}Si_6 = Li_4Li_4Si_6Li_{12}$$

and which act electronically as acceptor (*A*) and donor (*D*) units.

Coordination

The coordination of all atoms still reflects characteristics of the bcc arrangement with about 8 + 6 near neighbors. According to deformations that result from the defects and cluster formation there is some variation in the individual surroundings. In general, the coordination (*m*Si + *n*Li) dependent on the actual site in the 26-atom cluster is about (3 + 10) for Li(IT), (3 + 10) and (4 + 9) for Li(OT), (0 + 13) for Si(OT), (3 + 10) for Li(OH), (0 + 13) for Si(OH), and (2 + 13) to (4 + 11) for Li(CO). The intracluster and intercluster distances cannot be selected by magnitude, but all atoms at IT, OT, and OH sites yield two-thirds of their coordination sphere from their own clusters, while the CO sites get two-thirds of their coordination sphere from neighboring clusters. The Li–Li and Li–Si contacts range from about 2.5 to 3.5 Å while Si–Si



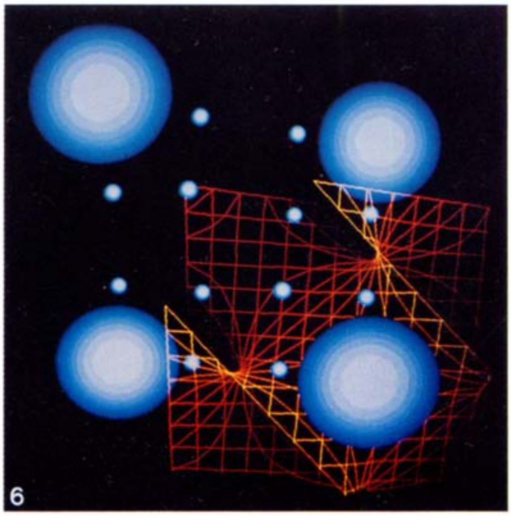


FIG. 1. (a) The structure of $Li_{21}Si_5$ along [100] (Si, large spheres; Li, small spheres). The 6 × 6 × 6 superstructure of bcc is clearly to be seen. The octahedra (OH) of the M_{26} clusters have been outlined in blue. (b) The M_{26} cluster composed of inner tetrahedron (IT, gray) outer tetrahedron (OT, red), octahedron (OH, yellow), and cuboctahedron (CO, blue), which occurs 16 times in the unit cell.

FIG. 5. Experimental valence electron density contours around the cluster A' in a three-dimensional plot (contour 0.1 $e/\text{Å}^3$, orange; Si, large green spheres; Li, small blue spheres). Along the red arrow the diamond-like interaction expands, and along the white arrow the ZnS-type link occurs. Note that only for the interstice of the latter link does significant density exist.

FIG. 6. Partition of M_{26} clusters into central M_{14} nuclei (large blue spheres) and one set of CO sites (small blue spheres) for one-eighth of the unit cell (the M_{14} representative at $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}$ has been omitted for clarification). All CO site sets follow, with only small deviations, the topology of periodic zero-potential surface (POPS) calculated for the supergroup of $F\bar{4}3m$, namely, $Fd\bar{3}m$. This surface is nearly identical to the so-called Schwarz D surface, an intersection free periodic minimal surface (IPMS).

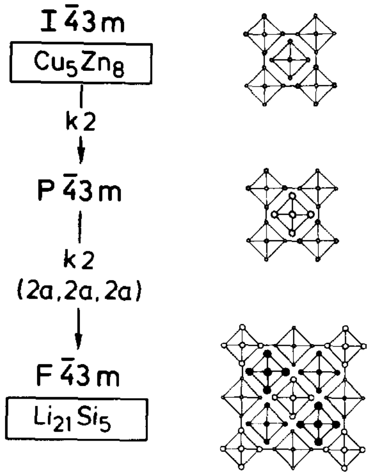


FIG. 2. Symmetry group–subgroup relationship between Cu_5Zn_8 (γ-brass) and $Li_{21}Si_5$. This correlation shows the reduction of the I lattice of γ-brass to the F lattice of $Li_{21}Si_5$. Left: Symmetry relationships between the two structures. Right: The different numbers of symmetry-inequivalent units.

distances are larger than 4.3 Å (Table III) and thus of the Van der Waals type.

Arrangement

The present structure is a complex and heterogeneous bcc arrangement in two respects: (1) There is a distorted and heterogeneous arrangement of single atoms. (2) There is an undistorted but heterogeneous arrangement of clusters A, A', D, D' which act as pseudoatoms of type C_A and C_B, respectively (*23, 24*). In the latter arrangement each cluster (C_A, C_B) is surrounded tetrahedrally by four clusters of the same and four clusters of the other type. The second coordination sphere is an octahedron formed by six clusters of the other type (Fig. 3a). Therefore the two general cluster types $C_A = A, A'$ and $C_D = D, D'$ form diamond networks (Fig. 3b), while the heterogeneous set $C_A + C_D$ forms ZnS-type arrangements (Fig. 3c) and NaCl-type arrangements (Fig. 3d) as well. In this way, all the M_{26} cluster set up a huge Zintl phase of the classical type, namely the arrangement of NaTl, replacing Na by $C_D(D, D')$ and Tl by $C_A(A, A')$. Within the C_A substructure the main interaction is provided by the atoms Si1(OT) of A, and within the C_D substructure it is provided by the atoms of Si3(OH) of D' (Table IV). The cluster pairs ($A + D$) and ($A' + D'$), on the other hand, set up two interpenetrating zinc blende arrangements (Fig. 3c) which are coupled in the first case via Si4(OH) of D and in the latter case via Si2(OT) of A' and Si3(OH), respectively. Finally the two cluster sets ($A + D'$) and ($A' + D$) form two interpenetrating substructures of the NaCl type coupled by Si3(OH) of D' and Si4(OH) of D, respectively (Fig. 3d). The Si atoms at the OT positions of the C_A clusters are involved only in one type of linkage, either of the diamond type (Si2 of $A' \rightarrow A'$) or the ZnS type (Si2 in A'–D'). To avoid closed-shell repulsions between Si atoms of neighboring C_A clusters, it is necessary that all these clusters have the same orientation with respect to the outer tetrahedra (Fig. 4).

A quite different situation occurs for the two Si atoms at OH positions of C_D. D' is rotated 90° with respect to D. This lowers

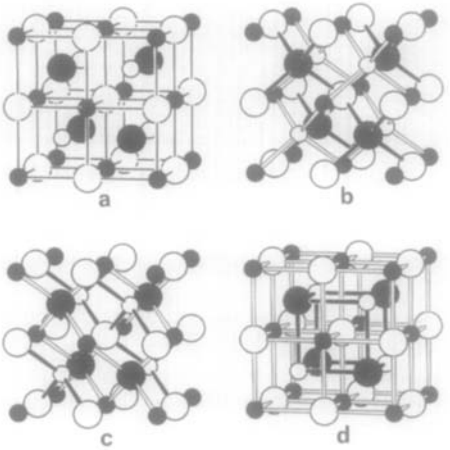


FIG. 3. (a) Arrangement of clusters A (small bold circle), A' (small open circle), D (large bold circle), and D' (large open circle) in the unit cell of $Li_{21}Si_5$. (*b–d*) Interpenetrating substructures: (b) diamond, (c) ZnS, (d) NaCl.

the C_D repulsions between their Li(OT) tetrahedra which are expanded to get into contact with the C_A clusters in the ZnS substructures. The main interactions between the tetrahedra (IT, OT) along [111] are displayed in Fig. 4. It is obvious that only the 90° rotation of D' allows for the short contact Li5(OT, D') to Si2(OT, A') supplying a backbond between A' and D'. This does not affect the OH(Si) sites which provide for ZnS type, NaCl-type, and diamond-type interactions as well. Obviously this is one reason for the $F\bar{4}3m$ symmetry of the structure instead of $Fd3m$ symmetry. Pearson *et al.* (*23*) have given geometrical arguments for structural details and for the special stoichiometry of γ-brasses by means of the ratio of radii and packing considerations. For a binary M_xN_y phase with a ratio $r_x/r_y > 1.1$ and a tendency to avoid M–M contacts two optimal compositions have been proposed for a $cF416$ structure, namely, $M_{11}N_{41}$ and M_5N_{21}. The composition $Li_{21}X_5$ (X = Si, Ge, Sn, Pb) fulfills by far best the geometrical requirements (*23*) of the Hume-Rothery rules and the Zintl concept.

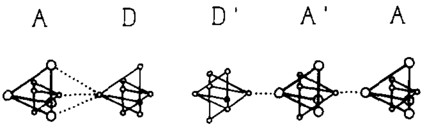


FIG. 4. Arrangement of IT and OT tetrahedra of the four cluster types along [111] (Si, large circles; Li, small circles). The relative turn of 90° of D' with respect to D inverses the orientation of the IT and OT of D'. Attractive interactions are indicated by broken lines.

TABLE IV

IMPORTANT LINKS BETWEEN M_{26} CLUSTERS ACCORDING TO THREE DIFFERENT TYPES OF INTERACTIONS: DIAMOND, ZINC BLENDE AND ROCK SALT

	Type of connectivity		
Cluster	Diamond	ZnS	NaCl
A	*A′*	*D*	*D′*
OT,Si1	IT,Li6 CO,Li12	—	—
IT,Li1	—	—	—
OH,Li7	CO,Li12	OT,Li2	OH,Si3
CO,Li9	OH,Li8 CO,Li12	OH,Si4 CO,Li11	
A′	*A*	*D′*	*D*
OT,Si2	—	OT,Li5 CO,Li10	—
IT,Li6	OT,Si1	—	—
OH,Li8	CO,Li9	CO,Li10	OH,Si4
CO,Li12	OH,Li7 CO,Li9 OT,Si1	CO,Li10 OH,Si3	—
D	*D′*	*A*	*A′*
OH,Si4	CO,Li10	CO,Li9	OH,Li8
IT,Li3	—	—	—
OT,Li2	—	CO,Li9	—
CO,Li11	OH,Si3 CO,Li10	CO,Li9	—
D′	*D*	*A′*	*A*
OH,Si3	CO,Li11	CO,Li12	OH,Li7
IT,Li4	—	—	—
OT,Li5	—	OT,Si2	—
CO,Li10	CO,Li11 OH,Si4	CO,Li12 OH,Li8 OT,Si2	—

Bonding

The electronic structure of $Li_{21}Si_5$ can be rationalized by means of a recent SCF CNDO/INDO cluster calculation (*25*). Omitting 16 atoms per unit cell from the central positions of the 16 clusters, there is a gain in energy by the accompanied distortion and contraction with respect to bcc. Thus clusters, local stability islands, are formed out of the uniform bcc matrix (*25*). The major part of the cluster orbitals is occupied according to the Zintl rule. That means that all Si atoms exhibit a filled octet state (closed shell) and are formally Si^{4-}. The donor clusters $C_D(D, D') = Li_{20}Si_6$ are stable as 48-electron systems, gaining 4 electrons from $C_A(A, A') = Li_{22}Si_4$. According to $\{Li^+_{20}[Si^{4-}]_6\}^{4-}$ and $\{Li^+_{22}[Si^{4-}]_4\}^{4+}$ only the clusters C_D obey the Zintl concept but not the units C_A. These 34-electron systems have 2 electrons per cluster in excess in a low-lying Li state (HOMO) which is delocalized over the CO sites and stabilized by the central cluster field. We term this new type of localized state a *cage orbital* (*4*). After the transfer of four electrons the C_D moieties act as donor with respect to C_A. This gives rise to different systems of back bonding (donor–acceptor interactions).

In Fig. 5 are displayed three-dimensional contour plots of valence electron densities, calculated from the X-ray data for a region around cluster *A*. First, it is quite obvious that the Si atoms are enveloped in a huge density sack which links with small tails to the neighboring Li atoms.

In the direction marked by the red arrow, the diamondlike interaction $A \rightarrow A'$ expands without significant electron density in the interstice. We would expect this because backbonds should preferably occur between clusters of different types ($C_D \rightarrow C_A$). Along the white arrow the ZnS-type interaction occurs. This gives rise to an electron density tail between the CO site (Li) of *A* and the OH site (Si) of *D*. These findings are in complete agreement with the theoretical analysis (*25*). In the ZnS-type arrangement of $A' \rightarrow D'$, even stronger backbonding occurs because of the special orientation of *A*′. Two instead of one Si atom (Si2, Si3) supply this intercluster linkage simultaneously.

General Topology and Curved Surfaces

The whole structure of $Li_{21}Si_5$ and of course of all fcc γ-brasses can be divided into two equivalent parts by an intersection free periodic mimimal surface (IPMS), namely the *D* surface of the mathematician H. Schwarz (*26–28*).

We have recently shown that periodic zero-potential surfaces (POPS) generated by point charges at proper point configurations of the corresponding symmetry groups display a very similar if not identical shape (*29–31*). They appear to have the same (topological) genus as the minimal surfaces and the structures in question (*32, 33*). The present surface separates two interpenetrating partial structures either of the diamondlike or the ZnS-like linkage according to choice of origin. In any case, the CO sites of all clusters are situated approximately on this space dividing *D* surface (Fig. 6). In this way they set up a network that follows very closely the curved POPS and IPMS, respectively, separating the spatial regions of the central M_{14} cluster nuclei. It is interesting to note that the latter carry all the occupied electronic states, e.g., the silicon states, except the cage orbitals. According to this novel interpretation of the γ-brass structure one might think about favorable and maximal electron numbers in terms of separated central M_{14} cluster nuclei and an interstitial N_{12} surface formed by the CO positions (*34*). The leading importance of an extended partial structure set up by these CO positions is supported by a large number of related but quite different intermetallic phases, e.g., Tl_7Sb_2, α-Mn, Cu_5Zn_8, $Li_{21}Si_5$, Cu_{41}, Sn_{11}, $Cd_{45}Sn_{11}$, Mg_6Tl, and Na_6Tl. In all these phases the CO and the OT sites are fully occupied without exception, while the other positions exhibit quite varying occupancy (*24*). If there is a significant difference in electronegativity the CO sites carry the less electronegative, and the OT or OH sites the more electronegative, species.

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