

Crystal and electronic structures of $\text{La}_2\text{LiGe}_{6-x}$ ($x = 0.21$) and $\text{La}_2\text{LiGe}_4\text{Si}_2$

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The synthesis and characterization of a new ternary dilanthanum lithium hexagermanide, $\text{La}_2\text{LiGe}_{6-x}$ ($x = 0.21$), belonging to the Pr_2LiGe_6 structure type, and a quaternary dilanthanum lithium tetragermanium disilicide, $\text{La}_2\text{LiGe}_4\text{Si}_2$, which crystallizes as an ordered variant of this type, are reported. In both structures, Li is on a site of mmm symmetry. All other atoms are on sites of $m2m$ symmetry. These structures are new representatives of a homologous linear structure series based on structural fragments of the AlB_2 , CaF_2 and ZrSi_2 structure types. The observed 17-vertex polyhedra are typical for La atoms and the environment of the Li atom is cubic. Two Ge atoms are enclosed in a tetragonal prism with one added atom (nine-vertex polyhedron). The trigonal prismatic coordination is typical for Ge or Si atoms. The metallic nature of the bonding is indicated by the interatomic distances and electronic structure calculations.

Comment

The reaction of rare earth metals (RE) with lithium and the p -elements of Group IV (Si, Ge and Sn) resulted in an isostructural series of compounds: RELiGe_2 (Pavlyuk *et al.*, 1986), $\text{RE}_2\text{Li}_2\text{Ge}_3$ (Pavlyuk, Pecharskii, Bodak & Bruskov, 1988; Pavlyuk, Pecharskii & Bodak, 1989), RELiSn_2 (Pavlyuk, Bodak *et al.*, 1989), RE_4LiGe_4 (Pavlyuk *et al.*, 1990), RELiGe (Pavlyuk *et al.*, 1991; Pavlyuk & Bodak, 1992*a*) and $\text{RE}_3\text{Li}_2\text{Ge}_3$ (Pavlyuk & Bodak, 1992*b*). A new ternary germanide, RE_2LiGe_6 (RE = Ce and Pr), which crystallizes in an orthorhombic structure with the space group $Cmmm$, was detected earlier during the systematic study of ternary germanium-rich alloys of the Ce–Li–Ge and Pr–Li–Ge systems (Pavlyuk, Pecharskii & Bodak, 1988).

During a systematic study of ternary La–Li–Ge alloys synthesized with a high Ge content, a new ternary phase was detected. The powder diffraction pattern of this compound

was similar to that of the RE_2LiGe_6 (RE = Ce and Pr) ternary phases, but had added reflections which belonged to another phase. Substitution of some of the Ge atoms by Si in $\text{La}_2\text{LiGe}_{6-x}\text{Si}_x$ quaternary alloys with $x = 2.0$ altered the unit-cell dimensions. Also at this composition, there was a significant decrease in the intensities of the 041, 151, 170 and 171 reflections and an increase in the intensities of the 001, 110 and other reflections. It appeared very likely that these changes were connected with an ordering process. It was decided to investigate these ternary and quaternary phases further using single-crystal methods.

The single-crystal data proved that both La_2LiGe_6 , (I), and $\text{La}_2\text{LiGe}_4\text{Si}_2$, (II), crystallize in the same orthorhombic crystal system in the space group $Cmmm$, with 18 atoms per unit cell.

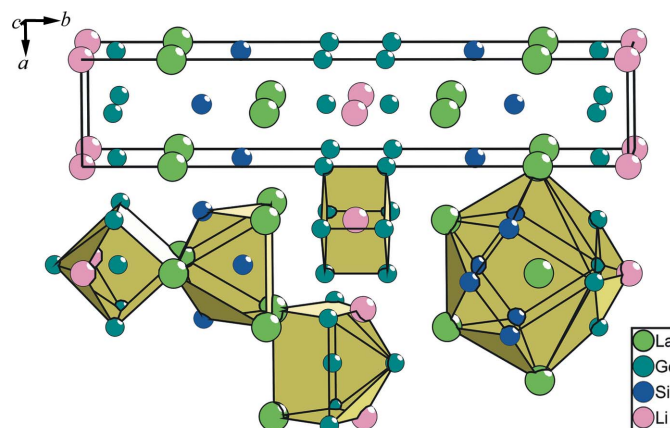


Figure 1
A projection of the unit cell and coordination polyhedra of the atoms for $\text{La}_2\text{LiGe}_4\text{Si}_2$, (II).

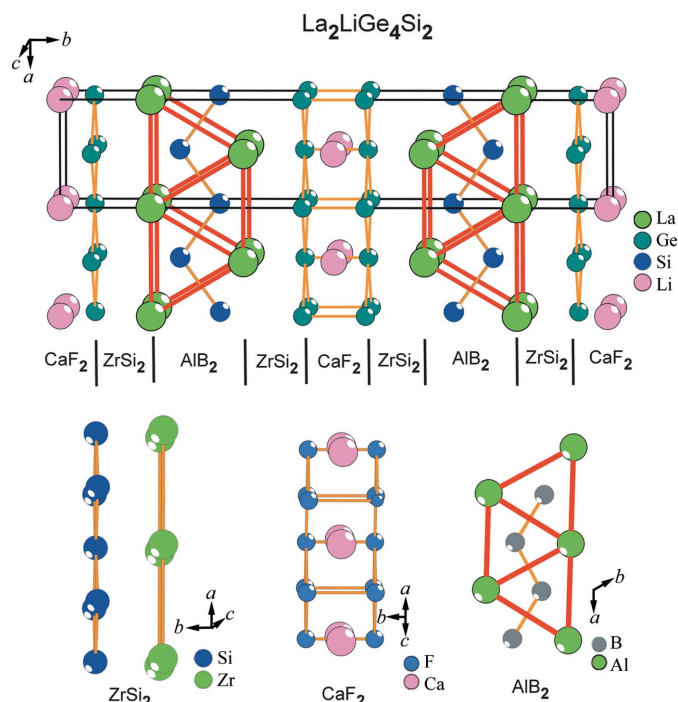
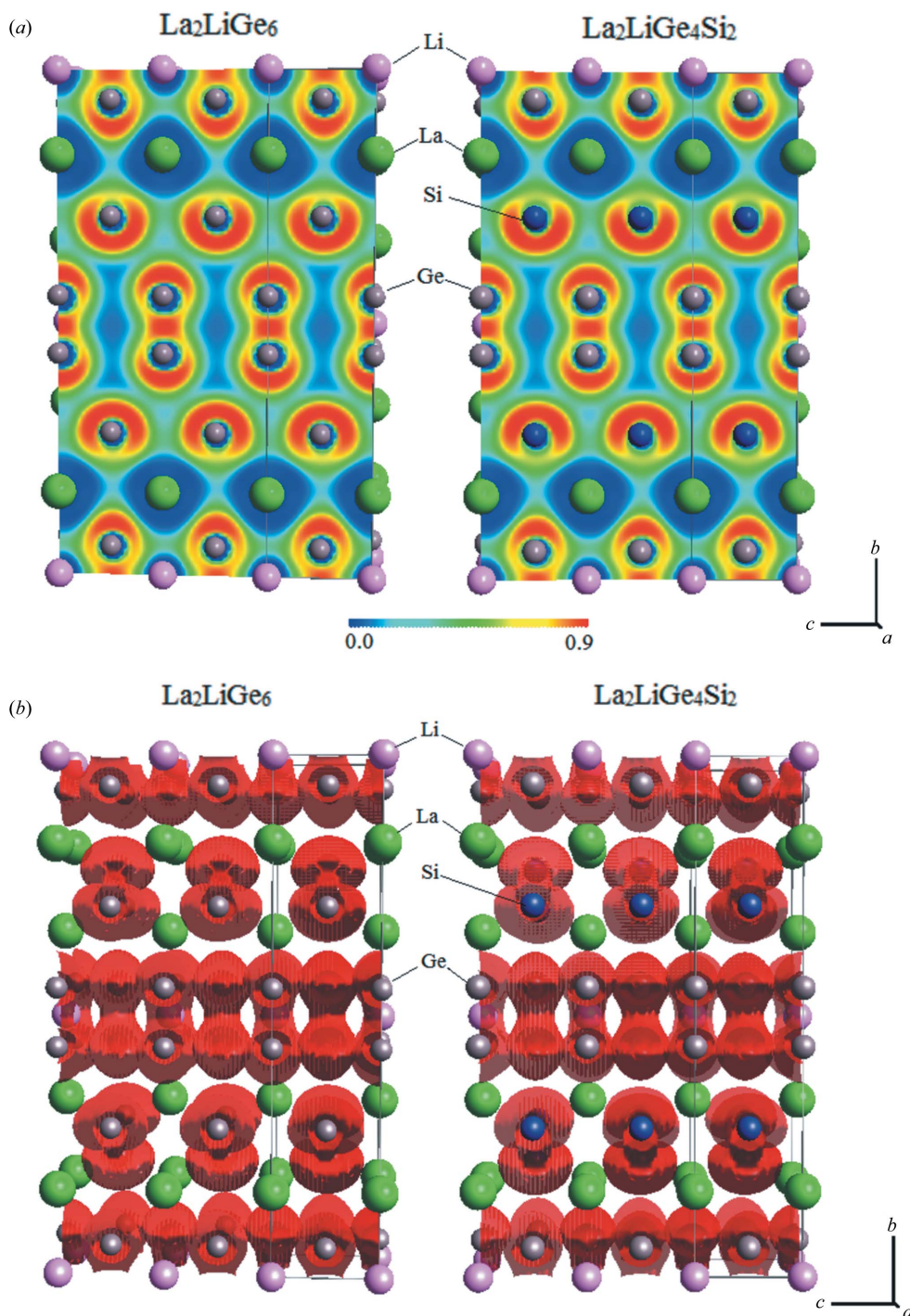


Figure 2
The packing of the AlB_2 , ZrSi_2 and CaF_2 fragment types in the unit cell of $\text{La}_2\text{LiGe}_4\text{Si}_2$, (II).

**Figure 3**

(a) The electron localization function (ELF) mapping and (b) isosurfaces of the ELF around the atoms for La_2LiGe_6 , (I), and $\text{La}_2\text{LiGe}_4\text{Si}_2$, (II).

The La atoms in both structures occupy the $4i$ site and the Li atoms are located on the $2a$ site. In (I), all the Ge atoms occupy $4j$ sites, whereas in (II) one of these sites is fully occupied by Si atoms. Disorder in $\text{La}_2\text{LiGe}_{6-x}$ occurs as the Ge atoms are partially displaced from a single site. The presence of these defects may lead to a limited homogeneity range for $\text{La}_2\text{LiGe}_{6-x}$.

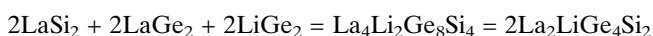
Although (I) and (II) are very similar to the Pr_2LiGe_6 structure (Pavlyuk, Pecharskii & Bodak, 1988) in terms of

having the same space group, the same Wyckoff positions and similar lattice parameters, quaternary (II) cannot be treated as being isostructural with it. According to the classification scheme of Kropyakevich (1977), an ordered variant must be treated as a new structure type.

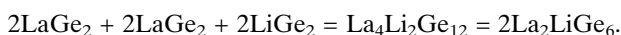
A projection of the unit cell and the coordination polyhedra of the atoms for (II) are shown in Fig. 1. A detailed analysis shows that the Si atom has trigonal prismatic coordination with two additional capping atoms [coordination number

(CN) = 8], *i.e.* Ge1 and Ge2 are enclosed in a tetragonal prism with one added atom (nine-vertex polyhedron). The 17-vertex polyhedron is typical for an La atom and the environment of the Li atom is cubic.

The title compounds may be viewed as the first intermetallic representatives of the novel homologous series based on the CaF_2 , ZrSi_2 and AlB_2 structure types (Fig. 2). The general formula of the ternary series is $R_{m+n}M_kX_{2(k+m+n)}$ and that of the quaternary series is $R_{m+n}M_kX'_{2(k+n)}X''_{2m}$ (m = number of blocks of AlB_2 -type trigonal prisms, n = number of blocks of ZrSi_2 -type empty tetragonal antiprisms and k = number of blocks of CaF_2 -type filled and empty cubes). For the title compounds, $m = n = k = 2$ and the compositions of the fragments are LiGe_2 (for the CaF_2 block), LaGe_2 (for the ZrSi_2 block) and LaGe_2 in (I) or LaSi_2 in (II) (for the AlB_2 block). The combination of these fragments in the unit cell gives the compositions of the title compounds as



or



Among the known structure types similar to the title compounds is Lu_2NiSn_6 (Skolozdra *et al.*, 1985). The main difference between that structure type and the present one is in the location of the trigonal prism and the filled cubes.

The electronic structures of the title compounds were calculated using the tight-binding linear muffin-tin orbital (TB-LMTO) method in the atomic spheres approximation (TB-LMTO-ASA; Andersen, 1975; Andersen & Jepsen, 1984; Andersen *et al.*, 1985, 1986), using the experimental crystallographic data reported here. The exchange and correlation were interpreted in the local density approximation (von Barth & Hedin, 1972).

The La and Li atoms donate their electrons to the Ge and Si atoms. Therefore, positive charge density can be observed around the rare earth and Li atoms, and negative charge density is present around the Ge atoms in phase (I) or the Ge and Si atoms in phase (II) (Fig. 3). The dominant type of bonding in this compound is metallic. However, Ge–Ge and Si–Si covalent dumbbells are also observed. Similar covalent dumbbells were observed in $\text{La}_4\text{Mg}_5\text{Ge}_6$ (Solokha *et al.*, 2012), $\text{Tb}_4\text{Zn}_5\text{Ge}_6$ (Chumak *et al.*, 2006) and $\text{Gd}_4\text{Zn}_5\text{Ge}_6$ (Kranenberg *et al.*, 2001).

The total and partial densities of states for La_2LiGe_6 and $\text{La}_2\text{LiGe}_4\text{Si}_2$ (Figs. 4a and 4b, respectively) in the region below E_F exhibit significant mixing between the La and Ge sites in phase (I), and a decrease of this mixing in the case of phase (II). The region above E_F consists mostly of La 5d orbitals and Ge *p* orbitals. The Si and Ge *s*-type states are mainly close to the lower valence band (from -12.0 eV to <-7.5 eV). The higher occupation number of electronic states at the Fermi level for La_2LiGe_6 than for $\text{La}_2\text{LiGe}_4\text{Si}_2$ indicates a more metallic behaviour.

The crystal orbital Hamilton population (COHP) and integrated COHP (iCOHP) calculations were used to obtain a

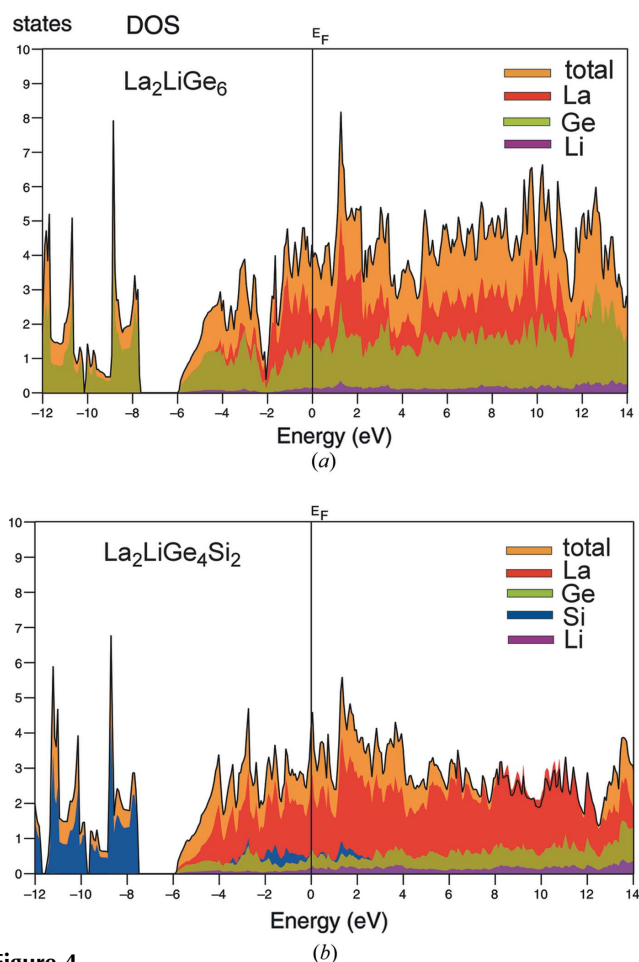


Figure 4
The total and partial density of states for (a) La_2LiGe_6 , (I), and (b) $\text{La}_2\text{LiGe}_4\text{Si}_2$, (II).

quantitative evaluation of the bonding strength between the different types of atoms. From the COHP curves for both phases (Fig. 5), it can be concluded that the strongest interactions are between Ge1–Ge1 atoms [$\delta = 2.451$ Å and $-\text{iCOHP} = 3.425$ eV for (I), and $\delta = 2.381$ Å and $-\text{iCOHP} = 3.796$ eV for (II)] and between Ge2–Ge2 atoms [$\delta = 2.423$ Å and $-\text{iCOHP} = 3.441$ eV for (I), and $\delta = 2.389$ Å and $-\text{iCOHP} = 3.547$ eV for (II)]. These atoms in both structures are enclosed by a tetragonal prism. The Si1···Si1 interaction in (II) ($\delta = 2.581$ Å and $-\text{iCOHP} = 2.162$ eV) and the Ge3···Ge3 interaction in (I) ($\delta = 2.594$ Å and $-\text{iCOHP} = 2.060$ eV), which are enclosed by a trigonal prism, are weak. These results indicate that the strength of Ge···Ge and Si···Si covalent interactions depends significantly on the type of coordination.

Experimental

Lanthanum, lithium, germanium and silicon, all with a nominal purity greater than 99.9 wt.%, were used as starting materials. First, pieces of the pure metals with stoichiometries $\text{La}_{22}\text{Li}_{12}\text{Ge}_{66}$, $\text{La}_{22}\text{Li}_{12}\text{Ge}_{60}\text{Si}_6$ and $\text{La}_{22}\text{Li}_{12}\text{Ge}_{44}\text{Si}_{12}$ were pressed into pellets, which were then enclosed in a tantalum crucible and placed in a resistance furnace with a thermocouple controller. The heating rate from room

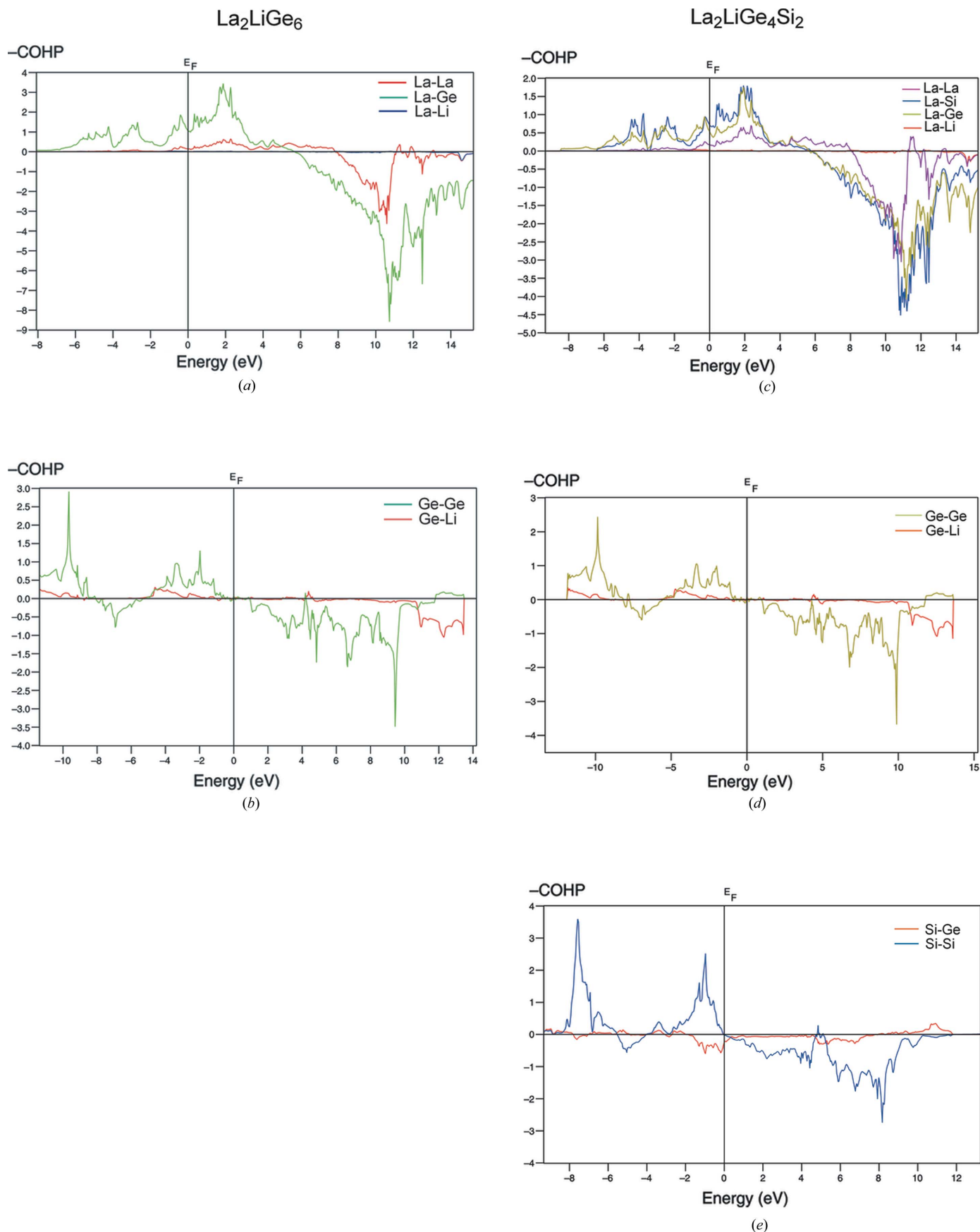


Figure 5
-COHP curves for La_2LiGe_6 , (I) [parts (a) and (b)], and $\text{La}_2\text{LiGe}_4\text{Si}_2$, (II) [parts (c), (d) and (e)].

temperature to 670 K was 5 K min⁻¹. The alloy was kept at this temperature for 2 d and then the temperature was increased from 670 to 1070 K over a period of 1 h. The alloy was then annealed at this temperature for 6 h and cooled slowly to room temperature. After these melting and annealing procedures, the total weight loss was less than 2%. Small good quality single crystals of (I) and (II) were isolated from the La₂₂Li₁₂Ge₆₆ and La₂₂Li₁₂Ge₄₄Si₁₂ alloys.

Compound (I)

Crystal data

La ₂ LiGe _{5.79}	$V = 388.20 (2) \text{ \AA}^3$
$M_r = 1410.11$	$Z = 1$
Orthorhombic, <i>Cmmm</i>	Mo $K\alpha$ radiation
$a = 4.1871 (1) \text{ \AA}$	$\mu = 32.73 \text{ mm}^{-1}$
$b = 21.1132 (6) \text{ \AA}$	$T = 293 \text{ K}$
$c = 4.3912 (1) \text{ \AA}$	$0.14 \times 0.12 \times 0.02 \text{ mm}$

Data collection

Oxford Xcalibur3 CCD area-detector diffractometer	1770 measured reflections
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	290 independent reflections
$T_{\min} = 0.015$, $T_{\max} = 0.528$	289 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	21 parameters
$wR(F^2) = 0.059$	$\Delta\rho_{\max} = 1.20 \text{ e \AA}^{-3}$
$S = 1.20$	$\Delta\rho_{\min} = -0.98 \text{ e \AA}^{-3}$
290 reflections	

Compound (II)

Crystal data

La ₂ LiGe ₄ Si ₂	$V = 381.75 (2) \text{ \AA}^3$
$M_r = 631.38$	$Z = 2$
Orthorhombic, <i>Cmmm</i>	Mo $K\alpha$ radiation
$a = 4.1462 (1) \text{ \AA}$	$\mu = 26.69 \text{ mm}^{-1}$
$b = 21.0674 (6) \text{ \AA}$	$T = 293 \text{ K}$
$c = 4.3704 (1) \text{ \AA}$	$0.12 \times 0.09 \times 0.03 \text{ mm}$

Data collection

Oxford Xcalibur3 CCD area-detector diffractometer	1770 measured reflections
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	290 independent reflections
$T_{\min} = 0.074$, $T_{\max} = 0.451$	289 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.073$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$	18 parameters
$wR(F^2) = 0.045$	$\Delta\rho_{\max} = 1.15 \text{ e \AA}^{-3}$
$S = 1.20$	$\Delta\rho_{\min} = -1.62 \text{ e \AA}^{-3}$
290 reflections	

The structures of (I) and (II) were solved after applying an analytical absorption correction. In the first stage of the structure solution, the positions of the La, Ge and Si atoms were obtained correctly by direct methods. For (I), the residual factor $R1$ was 0.030 after refinement of the La and Ge atoms, and the highest difference

peak was 6.54 e \AA^{-3} . For (II), $R1$ was 0.032 after refinement of the La, Ge and Si atoms, and the highest difference peak was 7.58 e \AA^{-3} . The remaining Li atoms were located in subsequent difference Fourier syntheses and, after refinement of their parameters, $R1$ reduced to 0.024 for (I) and 0.020 for (II), and the highest difference peaks decreased to 1.20 e \AA^{-3} for (I) and 1.15 e \AA^{-3} for (II). However, in (I), the Ge1 position showed a displacement parameter considerably different from those of the other Ge atoms, suggesting that this position is only partially occupied by the Ge atom. The site-occupancy factor for Ge1 was refined to 0.896 (8).

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3108). Services for accessing these data are described at the back of the journal.

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supplementary materials

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(I) dilanthanum lithium hexagermanide

Crystal data

$\text{La}_2\text{LiGe}_{5.79}$	$F(000) = 605.2$
$M_r = 1410.11$	$D_x = 6.032 \text{ Mg m}^{-3}$
Orthorhombic, <i>Cmmm</i>	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-C 2 2$	Cell parameters from 289 reflections
$a = 4.1871 (1) \text{ \AA}$	$\theta = 3.9\text{--}27.6^\circ$
$b = 21.1132 (6) \text{ \AA}$	$\mu = 32.73 \text{ mm}^{-1}$
$c = 4.3912 (1) \text{ \AA}$	$T = 293 \text{ K}$
$V = 388.20 (2) \text{ \AA}^3$	Plate, metallic dark grey
$Z = 1$	$0.14 \times 0.12 \times 0.02 \text{ mm}$

Data collection

Oxford Xcalibur3 CCD area-detector diffractometer	1770 measured reflections
Radiation source: fine-focus sealed tube	290 independent reflections
Graphite monochromator	289 reflections with $I > 2\sigma(I)$
Detector resolution: 0 pixels mm^{-1}	$R_{\text{int}} = 0.034$
ω scans	$\theta_{\text{max}} = 27.6^\circ$, $\theta_{\text{min}} = 3.9^\circ$
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	$h = -5 \rightarrow 5$
$T_{\text{min}} = 0.015$, $T_{\text{max}} = 0.528$	$k = -27 \rightarrow 27$
	$l = -5 \rightarrow 5$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.024$	$w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 14.9101P]$
$wR(F^2) = 0.059$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.20$	$(\Delta/\sigma)_{\text{max}} < 0.001$
290 reflections	$\Delta\rho_{\text{max}} = 1.20 \text{ e \AA}^{-3}$
21 parameters	$\Delta\rho_{\text{min}} = -0.98 \text{ e \AA}^{-3}$
0 restraints	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
La1	0.0000	0.16551 (3)	0.0000	0.0114 (2)	
Ge1	0.0000	0.05806 (7)	0.5000	0.0179 (5)	0.896 (8)
Ge2	0.0000	0.44262 (6)	0.0000	0.0152 (3)	
Ge3	0.0000	0.28626 (6)	0.5000	0.0155 (3)	
Li1	0.0000	0.0000	0.0000	0.018 (6)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La1	0.0096 (3)	0.0127 (3)	0.0118 (3)	0.000	0.000	0.000
Ge1	0.0164 (8)	0.0201 (8)	0.0171 (8)	0.000	0.000	0.000
Ge2	0.0131 (6)	0.0185 (6)	0.0140 (6)	0.000	0.000	0.000
Ge3	0.0132 (6)	0.0194 (6)	0.0139 (6)	0.000	0.000	0.000
Li1	0.022 (15)	0.015 (13)	0.018 (15)	0.000	0.000	0.000

Geometric parameters (\AA , $^\circ$)

La1—Ge2 ⁱ	3.0975 (10)	Ge2—La1 ⁱ	3.0975 (10)
La1—Ge2 ⁱⁱ	3.0975 (10)	Ge2—La1 ⁱⁱ	3.0975 (10)
La1—Ge1 ⁱⁱⁱ	3.1571 (12)	Ge3—Ge3 ^v	2.5936 (16)
La1—Ge1	3.1571 (12)	Ge3—Ge3 ^{iv}	2.5936 (16)
La1—Ge3 ^{iv}	3.2001 (5)	Ge3—La1 ^{iv}	3.2001 (5)
La1—Ge3 ⁱ	3.2001 (5)	Ge3—La1 ⁱ	3.2001 (5)
La1—Ge3 ^v	3.2001 (5)	Ge3—La1 ⁱⁱ	3.2001 (5)
La1—Ge3 ⁱⁱ	3.2001 (5)	Ge3—La1 ^v	3.2001 (5)
La1—Ge3	3.3646 (11)	Ge3—La1 ^{vii}	3.3646 (11)
La1—Ge3 ⁱⁱⁱ	3.3646 (11)	Li1—Ge2 ⁱⁱ	2.4188 (6)
La1—Li1	3.4944 (6)	Li1—Ge2 ^{xi}	2.4188 (6)
Ge1—Ge1 ^{vi}	2.451 (3)	Li1—Ge2 ⁱ	2.4188 (6)
Ge1—Li1	2.5146 (7)	Li1—Ge2 ^{xii}	2.4188 (6)
Ge1—Li1 ^{vii}	2.5146 (7)	Li1—Ge1 ^{xiii}	2.5146 (7)
Ge1—La1 ^{vii}	3.1571 (12)	Li1—Ge1 ^{vi}	2.5146 (7)
Ge2—Li1 ^{viii}	2.4188 (6)	Li1—Ge1 ⁱⁱⁱ	2.5146 (7)
Ge2—Li1 ^{ix}	2.4188 (6)	Li1—La1 ^{xiii}	3.4944 (6)
Ge2—Ge2 ^x	2.423 (3)		
Ge2 ⁱ —La1—Ge2 ⁱⁱ	85.04 (3)	Li1 ^{ix} —Ge2—La1 ⁱ	77.534 (14)
Ge2 ⁱ —La1—Ge1 ⁱⁱⁱ	58.022 (17)	Ge2 ^x —Ge2—La1 ⁱ	137.478 (17)
Ge2 ⁱⁱ —La1—Ge1 ⁱⁱⁱ	58.022 (17)	Li1 ^{viii} —Ge2—La1 ⁱⁱ	77.534 (14)
Ge2 ⁱ —La1—Ge1	58.022 (17)	Li1 ^{ix} —Ge2—La1 ⁱⁱ	162.58 (4)
Ge2 ⁱⁱ —La1—Ge1	58.022 (17)	Ge2 ^x —Ge2—La1 ⁱⁱ	137.478 (17)
Ge1 ⁱⁱⁱ —La1—Ge1	88.13 (4)	La1 ⁱ —Ge2—La1 ⁱⁱ	85.04 (3)

Ge ²ⁱ —La1—Ge ^{3iv}	132.59 (2)	Ge ^{3v} —Ge3—Ge ^{3iv}	107.64 (9)
Ge ²ⁱⁱ —La1—Ge ^{3iv}	78.02 (2)	Ge ^{3v} —Ge3—La1 ^{iv}	135.72 (2)
Ge1 ⁱⁱⁱ —La1—Ge ^{3iv}	134.90 (2)	Ge ^{3iv} —Ge3—La1 ^{iv}	70.111 (17)
Ge1—La1—Ge ^{3iv}	75.61 (2)	Ge ^{3v} —Ge3—La1 ⁱ	70.111 (17)
Ge ²ⁱ —La1—Ge ³ⁱ	78.02 (2)	Ge ^{3iv} —Ge3—La1 ⁱ	135.72 (2)
Ge ²ⁱⁱ —La1—Ge ³ⁱ	132.59 (2)	La1 ^{iv} —Ge3—La1 ⁱ	142.89 (5)
Ge1 ⁱⁱⁱ —La1—Ge ³ⁱ	75.61 (2)	Ge ^{3v} —Ge3—La1 ⁱⁱ	135.72 (2)
Ge1—La1—Ge ³ⁱ	134.90 (2)	Ge ^{3iv} —Ge3—La1 ⁱⁱ	70.111 (17)
Ge ^{3iv} —La1—Ge ³ⁱ	142.89 (5)	La1 ^{iv} —Ge3—La1 ⁱⁱ	86.644 (16)
Ge ²ⁱ —La1—Ge ^{3v}	78.02 (2)	La1 ⁱ —Ge3—La1 ⁱⁱ	81.719 (14)
Ge ²ⁱⁱ —La1—Ge ^{3v}	132.59 (2)	Ge ^{3v} —Ge3—La1 ^v	70.111 (17)
Ge1 ⁱⁱⁱ —La1—Ge ^{3v}	134.90 (2)	Ge ^{3iv} —Ge3—La1 ^v	135.72 (2)
Ge1—La1—Ge ^{3v}	75.61 (2)	La1 ^{iv} —Ge3—La1 ^v	81.719 (14)
Ge ^{3iv} —La1—Ge ^{3v}	81.719 (14)	La1 ⁱ —Ge3—La1 ^v	86.644 (16)
Ge ³ⁱ —La1—Ge ^{3v}	86.644 (16)	La1 ⁱⁱ —Ge3—La1 ^v	142.89 (5)
Ge ²ⁱ —La1—Ge ³ⁱⁱ	132.59 (2)	Ge ^{3v} —Ge3—La1	63.43 (4)
Ge ²ⁱⁱ —La1—Ge ³ⁱⁱ	78.02 (2)	Ge ^{3iv} —Ge3—La1	63.43 (4)
Ge1 ⁱⁱⁱ —La1—Ge ³ⁱⁱ	75.61 (2)	La1 ^{iv} —Ge3—La1	133.54 (2)
Ge1—La1—Ge ³ⁱⁱ	134.90 (2)	La1 ⁱ —Ge3—La1	78.078 (17)
Ge ^{3iv} —La1—Ge ³ⁱⁱ	86.644 (16)	La1 ⁱⁱ —Ge3—La1	78.078 (17)
Ge ³ⁱ —La1—Ge ³ⁱⁱ	81.719 (14)	La1 ^v —Ge3—La1	133.54 (2)
Ge ^{3v} —La1—Ge ³ⁱⁱ	142.89 (5)	Ge ^{3v} —Ge3—La1 ^{vii}	63.43 (4)
Ge ²ⁱ —La1—Ge3	123.949 (13)	Ge ^{3iv} —Ge3—La1 ^{vii}	63.43 (4)
Ge ²ⁱⁱ —La1—Ge3	123.949 (13)	La1 ^{iv} —Ge3—La1 ^{vii}	78.078 (17)
Ge1 ⁱⁱⁱ —La1—Ge3	176.67 (3)	La1 ⁱ —Ge3—La1 ^{vii}	133.54 (2)
Ge1—La1—Ge3	95.20 (2)	La1 ⁱⁱ —Ge3—La1 ^{vii}	133.54 (2)
Ge ^{3iv} —La1—Ge3	46.46 (2)	La1 ^v —Ge3—La1 ^{vii}	78.078 (17)
Ge ³ⁱ —La1—Ge3	101.922 (17)	La1—Ge3—La1 ^{vii}	81.47 (3)
Ge ^{3v} —La1—Ge3	46.46 (2)	Ge ²ⁱⁱ —Li1—Ge ^{2xi}	180.00 (5)
Ge ³ⁱⁱ —La1—Ge3	101.922 (17)	Ge ²ⁱⁱ —Li1—Ge ²ⁱ	119.89 (5)
Ge ²ⁱ —La1—Ge ³ⁱⁱⁱ	123.949 (13)	Ge ^{2xi} —Li1—Ge ²ⁱ	60.11 (5)
Ge ²ⁱⁱ —La1—Ge ³ⁱⁱⁱ	123.949 (13)	Ge ²ⁱⁱ —Li1—Ge ^{2xii}	60.11 (5)
Ge1 ⁱⁱⁱ —La1—Ge ³ⁱⁱⁱ	95.20 (2)	Ge ^{2xi} —Li1—Ge ^{2xii}	119.89 (5)
Ge1—La1—Ge ³ⁱⁱⁱ	176.67 (3)	Ge ²ⁱ —Li1—Ge ^{2xii}	180.00 (5)
Ge ^{3iv} —La1—Ge ³ⁱⁱⁱ	101.922 (17)	Ge ²ⁱⁱ —Li1—Ge1 ^{xiii}	104.131 (17)
Ge ³ⁱ —La1—Ge ³ⁱⁱⁱ	46.46 (2)	Ge ^{2xi} —Li1—Ge1 ^{xiii}	75.869 (17)
Ge ^{3v} —La1—Ge ³ⁱⁱⁱ	101.922 (17)	Ge ²ⁱ —Li1—Ge1 ^{xiii}	104.131 (17)
Ge ³ⁱⁱ —La1—Ge ³ⁱⁱⁱ	46.46 (2)	Ge ^{2xii} —Li1—Ge1 ^{xiii}	75.869 (17)
Ge3—La1—Ge ³ⁱⁱⁱ	81.47 (3)	Ge ²ⁱⁱ —Li1—Ge1	75.869 (17)
Ge ²ⁱ —La1—Li1	42.522 (17)	Ge ^{2xi} —Li1—Ge1	104.131 (17)
Ge ²ⁱⁱ —La1—Li1	42.522 (17)	Ge ²ⁱ —Li1—Ge1	75.869 (17)
Ge1 ⁱⁱⁱ —La1—Li1	44.06 (2)	Ge ^{2xii} —Li1—Ge1	104.131 (17)
Ge1—La1—Li1	44.06 (2)	Ge1 ^{xiii} —Li1—Ge1	180.00 (6)
Ge ^{3iv} —La1—Li1	108.56 (2)	Ge ²ⁱⁱ —Li1—Ge1 ^{vi}	104.131 (17)
Ge ³ⁱ —La1—Li1	108.56 (2)	Ge ^{2xi} —Li1—Ge1 ^{vi}	75.869 (17)
Ge ^{3v} —La1—Li1	108.56 (2)	Ge ²ⁱ —Li1—Ge1 ^{vi}	104.131 (17)
Ge ³ⁱⁱ —La1—Li1	108.56 (2)	Ge ^{2xii} —Li1—Ge1 ^{vi}	75.869 (17)
Ge3—La1—Li1	139.265 (16)	Ge1 ^{xiii} —Li1—Ge1 ^{vi}	121.65 (6)
Ge ³ⁱⁱⁱ —La1—Li1	139.265 (16)	Ge1—Li1—Ge1 ^{vi}	58.35 (6)

Ge ²ⁱ —La ¹ —La ¹ⁱⁱ	167.88 (2)	Ge ²ⁱⁱ —Li ¹ —Ge ¹ⁱⁱⁱ	75.869 (17)
Ge ²ⁱⁱ —La ¹ —La ¹ⁱⁱ	107.074 (16)	Ge ^{2xi} —Li ¹ —Ge ¹ⁱⁱⁱ	104.131 (17)
Ge ¹ⁱⁱⁱ —La ¹ —La ¹ⁱⁱ	128.299 (15)	Ge ²ⁱ —Li ¹ —Ge ¹ⁱⁱⁱ	75.869 (17)
Ge ¹ —La ¹ —La ¹ⁱⁱ	128.299 (15)	Ge ^{2xii} —Li ¹ —Ge ¹ⁱⁱⁱ	104.131 (17)
Ge ^{3iv} —La ¹ —La ¹ⁱⁱ	52.73 (2)	Ge ^{1xiii} —Li ¹ —Ge ¹ⁱⁱⁱ	58.35 (6)
Ge ³ⁱ —La ¹ —La ¹ⁱⁱ	93.24 (3)	Ge ¹ —Li ¹ —Ge ¹ⁱⁱⁱ	121.65 (6)
Ge ^{3v} —La ¹ —La ¹ⁱⁱ	93.24 (3)	Ge ^{1vi} —Li ¹ —Ge ¹ⁱⁱⁱ	180.00 (6)
Ge ³ⁱⁱ —La ¹ —La ¹ⁱⁱ	52.73 (2)	Ge ²ⁱⁱ —Li ¹ —La ^{1xiii}	120.06 (3)
Ge ³ —La ¹ —La ¹ⁱⁱ	49.191 (15)	Ge ^{2xi} —Li ¹ —La ^{1xiii}	59.94 (3)
Ge ³ⁱⁱⁱ —La ¹ —La ¹ⁱⁱ	49.191 (15)	Ge ²ⁱ —Li ¹ —La ^{1xiii}	120.06 (3)
Li ¹ —La ¹ —La ¹ⁱⁱ	149.597 (9)	Ge ^{2xii} —Li ¹ —La ^{1xiii}	59.94 (3)
Ge ^{1vi} —Ge ¹ —Li ¹	60.83 (3)	Ge ^{1xiii} —Li ¹ —La ^{1xiii}	60.83 (3)
Ge ^{1vi} —Ge ¹ —Li ^{1vii}	60.83 (3)	Ge ¹ —Li ¹ —La ^{1xiii}	119.17 (3)
Li ¹ —Ge ¹ —Li ^{1vii}	121.65 (6)	Ge ^{1vi} —Li ¹ —La ^{1xiii}	60.83 (3)
Ge ^{1vi} —Ge ¹ —La ^{1vii}	135.94 (2)	Ge ¹ⁱⁱⁱ —Li ¹ —La ^{1xiii}	119.17 (3)
Li ¹ —Ge ¹ —La ^{1vii}	163.24 (5)	Ge ²ⁱⁱ —Li ¹ —La ¹	59.94 (3)
Li ^{1vii} —Ge ¹ —La ^{1vii}	75.110 (14)	Ge ^{2xi} —Li ¹ —La ¹	120.06 (3)
Ge ^{1vi} —Ge ¹ —La ¹	135.94 (2)	Ge ²ⁱ —Li ¹ —La ¹	59.94 (3)
Li ¹ —Ge ¹ —La ¹	75.110 (14)	Ge ^{2xii} —Li ¹ —La ¹	120.06 (3)
Li ^{1vii} —Ge ¹ —La ¹	163.24 (5)	Ge ^{1xiii} —Li ¹ —La ¹	119.17 (3)
La ^{1vii} —Ge ¹ —La ¹	88.13 (4)	Ge ¹ —Li ¹ —La ¹	60.83 (3)
Li ^{1viii} —Ge ² —Li ^{1ix}	119.89 (5)	Ge ^{1vi} —Li ¹ —La ¹	119.17 (3)
Li ^{1viii} —Ge ² —Ge ^{2x}	59.94 (3)	Ge ¹ⁱⁱⁱ —Li ¹ —La ¹	60.83 (3)
Li ^{1ix} —Ge ² —Ge ^{2x}	59.94 (3)	La ^{1xiii} —Li ¹ —La ¹	180.0
Li ^{1viii} —Ge ² —La ¹ⁱ	162.58 (4)		

Symmetry codes: (i) $-x-1/2, -y+1/2, -z$; (ii) $-x+1/2, -y+1/2, -z$; (iii) $x, y, z-1$; (iv) $-x+1/2, -y+1/2, -z+1$; (v) $-x-1/2, -y+1/2, -z+1$; (vi) $-x, -y, -z+1$; (vii) $x, y, z+1$; (viii) $x+1/2, y+1/2, z$; (ix) $x-1/2, y+1/2, z$; (x) $-x, -y+1, -z$; (xi) $x-1/2, y-1/2, z$; (xii) $x+1/2, y-1/2, z$; (xiii) $-x, -y, -z$.

(II) dilanthanum lithium tetragermanium disilicide

Crystal data

La₂LiGe₄Si₂
M_r = 631.38
 Orthorhombic, *Cmmm*
 Hall symbol: $-C\ 2\ 2$
a = 4.1462 (1) Å
b = 21.0674 (6) Å
c = 4.3704 (1) Å
V = 381.75 (2) Å³
Z = 2

F(000) = 546
D_x = 5.493 Mg m⁻³
 Mo *Kα* radiation, λ = 0.71073 Å
 Cell parameters from 289 reflections
 θ = 3.9–27.8°
 μ = 26.69 mm⁻¹
T = 293 K
 Plate, metallic dark grey
 0.12 × 0.09 × 0.03 mm

Data collection

Oxford Xcalibur3 CCD area-detector
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 Detector resolution: 0 pixels mm⁻¹
 ω scans
 Absorption correction: analytical
 (*CrysAlis RED*; Oxford Diffraction, 2008)
T_{min} = 0.074, *T_{max}* = 0.451

1770 measured reflections
 290 independent reflections
 289 reflections with $I > 2\sigma(I)$
R_{int} = 0.073
 θ_{\max} = 27.8°, θ_{\min} = 3.9°
h = $-5 \rightarrow 5$
k = $-27 \rightarrow 27$
l = $-5 \rightarrow 5$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.045$
 $S = 1.20$
 290 reflections
 18 parameters
 0 restraints

Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map
 $w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 0.5539P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.15 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.62 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
La1	0.0000	0.165371 (18)	0.0000	0.01556 (16)
Ge1	0.0000	0.05651 (3)	0.5000	0.0146 (2)
Ge2	0.0000	0.44330 (3)	0.0000	0.0140 (2)
Si1	0.0000	0.28647 (10)	0.5000	0.0159 (4)
Li1	0.0000	0.0000	0.0000	0.011 (3)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La1	0.01094 (19)	0.0230 (2)	0.0128 (3)	0.000	0.000	0.000
Ge1	0.0125 (3)	0.0203 (4)	0.0112 (5)	0.000	0.000	0.000
Ge2	0.0122 (3)	0.0193 (4)	0.0105 (4)	0.000	0.000	0.000
Si1	0.0131 (7)	0.0249 (9)	0.0099 (12)	0.000	0.000	0.000

Geometric parameters (\AA , $^\circ$)

La1—Ge2 ⁱ	3.0885 (6)	Ge2—La1 ⁱ	3.0885 (6)
La1—Ge2 ⁱⁱ	3.0885 (6)	Ge2—La1 ⁱⁱ	3.0885 (6)
La1—Ge1 ⁱⁱⁱ	3.1679 (6)	Si1—Si1 ^v	2.581 (2)
La1—Ge1	3.1679 (6)	Si1—Si1 ^{iv}	2.581 (2)
La1—Si1 ^{iv}	3.1784 (7)	Si1—La1 ^{iv}	3.1784 (7)
La1—Si1 ⁱ	3.1784 (7)	Si1—La1 ⁱ	3.1784 (7)
La1—Si1 ^v	3.1784 (7)	Si1—La1 ^v	3.1784 (7)
La1—Si1 ⁱⁱ	3.1784 (7)	Si1—La1 ⁱⁱ	3.1784 (7)
La1—Si1	3.3592 (16)	Si1—La1 ^{vii}	3.3592 (16)
La1—Si1 ⁱⁱⁱ	3.3592 (16)	Li1—Ge2 ⁱⁱ	2.3926 (3)
La1—Li1	3.4839 (4)	Li1—Ge2 ^{xi}	2.3926 (3)

Ge1—Ge1 ^{vi}	2.3808 (14)	Li1—Ge2 ⁱ	2.3926 (3)
Ge1—Li1	2.4884 (3)	Li1—Ge2 ^{xii}	2.3926 (3)
Ge1—Li1 ^{vii}	2.4884 (3)	Li1—Ge1 ^{xiii}	2.4884 (3)
Ge1—La1 ^{vii}	3.1679 (6)	Li1—Ge1 ⁱⁱⁱ	2.4884 (3)
Ge2—Ge2 ^{viii}	2.3891 (14)	Li1—Ge1 ^{vi}	2.4884 (3)
Ge2—Li1 ^{ix}	2.3926 (3)	Li1—La1 ^{xiii}	3.4839 (4)
Ge2—Li1 ^x	2.3926 (3)		
Ge2 ⁱ —La1—Ge2 ⁱⁱ	84.32 (2)	Li1 ^{ix} —Ge2—La1 ⁱ	162.11 (2)
Ge2 ⁱ —La1—Ge1 ⁱⁱⁱ	57.543 (9)	Li1 ^x —Ge2—La1 ⁱ	77.789 (8)
Ge2 ⁱⁱ —La1—Ge1 ⁱⁱⁱ	57.543 (9)	Ge2 ^{viii} —Ge2—La1 ⁱⁱ	137.838 (10)
Ge2 ⁱ —La1—Ge1	57.543 (9)	Li1 ^{ix} —Ge2—La1 ⁱⁱ	77.789 (8)
Ge2 ⁱⁱ —La1—Ge1	57.543 (9)	Li1 ^x —Ge2—La1 ⁱⁱ	162.11 (2)
Ge1 ⁱⁱⁱ —La1—Ge1	87.23 (2)	La1 ⁱ —Ge2—La1 ⁱⁱ	84.32 (2)
Ge2 ⁱ —La1—Si1 ^{iv}	132.41 (3)	Si1 ^v —Si1—Si1 ^{iv}	106.90 (15)
Ge2 ⁱⁱ —La1—Si1 ^{iv}	78.39 (3)	Si1 ^v —Si1—La1 ^{iv}	135.57 (3)
Ge1 ⁱⁱⁱ —La1—Si1 ^{iv}	134.86 (3)	Si1 ^{iv} —Si1—La1 ^{iv}	70.49 (2)
Ge1—La1—Si1 ^{iv}	75.93 (3)	Si1 ^v —Si1—La1 ⁱ	70.49 (2)
Ge2 ⁱ —La1—Si1 ⁱ	78.39 (3)	Si1 ^{iv} —Si1—La1 ⁱ	135.57 (3)
Ge2 ⁱⁱ —La1—Si1 ⁱ	132.41 (3)	La1 ^{iv} —Si1—La1 ⁱ	142.77 (7)
Ge1 ⁱⁱⁱ —La1—Si1 ⁱ	75.93 (3)	Si1 ^v —Si1—La1 ^v	70.49 (2)
Ge1—La1—Si1 ⁱ	134.86 (3)	Si1 ^{iv} —Si1—La1 ^v	135.57 (3)
Si1 ^{iv} —La1—Si1 ⁱ	142.77 (7)	La1 ^{iv} —Si1—La1 ^v	81.42 (2)
Ge2 ⁱ —La1—Si1 ^v	78.39 (3)	La1 ⁱ —Si1—La1 ^v	86.87 (2)
Ge2 ⁱⁱ —La1—Si1 ^v	132.41 (3)	Si1 ^v —Si1—La1 ⁱⁱ	135.57 (3)
Ge1 ⁱⁱⁱ —La1—Si1 ^v	134.86 (3)	Si1 ^{iv} —Si1—La1 ⁱⁱ	70.49 (2)
Ge1—La1—Si1 ^v	75.93 (3)	La1 ^{iv} —Si1—La1 ⁱⁱ	86.87 (2)
Si1 ^{iv} —La1—Si1 ^v	81.42 (2)	La1 ⁱ —Si1—La1 ⁱⁱ	81.42 (2)
Si1 ⁱ —La1—Si1 ^v	86.87 (2)	La1 ^v —Si1—La1 ⁱⁱ	142.77 (7)
Ge2 ⁱ —La1—Si1 ⁱⁱ	132.41 (3)	Si1 ^v —Si1—La1	63.11 (6)
Ge2 ⁱⁱ —La1—Si1 ⁱⁱ	78.39 (3)	Si1 ^{iv} —Si1—La1	63.11 (6)
Ge1 ⁱⁱⁱ —La1—Si1 ⁱⁱ	75.93 (3)	La1 ^{iv} —Si1—La1	133.60 (4)
Ge1—La1—Si1 ⁱⁱ	134.86 (3)	La1 ⁱ —Si1—La1	78.182 (18)
Si1 ^{iv} —La1—Si1 ⁱⁱ	86.87 (2)	La1 ^v —Si1—La1	133.60 (4)
Si1 ⁱ —La1—Si1 ⁱⁱ	81.42 (2)	La1 ⁱⁱ —Si1—La1	78.182 (18)
Si1 ^v —La1—Si1 ⁱⁱ	142.77 (7)	Si1 ^v —Si1—La1 ^{vii}	63.11 (6)
Ge2 ⁱ —La1—Si1	124.262 (14)	Si1 ^{iv} —Si1—La1 ^{vii}	63.11 (6)
Ge2 ⁱⁱ —La1—Si1	124.262 (14)	La1 ^{iv} —Si1—La1 ^{vii}	78.182 (18)
Ge1 ⁱⁱⁱ —La1—Si1	176.97 (3)	La1 ⁱ —Si1—La1 ^{vii}	133.60 (4)
Ge1—La1—Si1	95.81 (2)	La1 ^v —Si1—La1 ^{vii}	78.182 (18)
Si1 ^{iv} —La1—Si1	46.40 (4)	La1 ⁱⁱ —Si1—La1 ^{vii}	133.60 (4)
Si1 ⁱ —La1—Si1	101.818 (17)	La1—Si1—La1 ^{vii}	81.16 (5)
Si1 ^v —La1—Si1	46.40 (4)	Ge2 ⁱⁱ —Li1—Ge2 ^{xi}	180.00 (3)
Si1 ⁱⁱ —La1—Si1	101.818 (18)	Ge2 ⁱⁱ —Li1—Ge2 ⁱ	120.10 (3)
Ge2 ⁱ —La1—Si1 ⁱⁱⁱ	124.262 (14)	Ge2 ^{xi} —Li1—Ge2 ⁱ	59.90 (3)
Ge2 ⁱⁱ —La1—Si1 ⁱⁱⁱ	124.262 (14)	Ge2 ⁱⁱ —Li1—Ge2 ^{xii}	59.90 (3)
Ge1 ⁱⁱⁱ —La1—Si1 ⁱⁱⁱ	95.81 (2)	Ge2 ^{xi} —Li1—Ge2 ^{xii}	120.10 (3)
Ge1—La1—Si1 ⁱⁱⁱ	176.97 (3)	Ge2 ⁱ —Li1—Ge2 ^{xii}	180.00 (3)
Si1 ^{iv} —La1—Si1 ⁱⁱⁱ	101.818 (18)	Ge2 ⁱⁱ —Li1—Ge1 ^{xiii}	103.818 (9)

Si1 ⁱ —La1—Si1 ⁱⁱⁱ	46.40 (4)	Ge2 ^{xi} —Li1—Ge1 ^{xiii}	76.182 (9)
Si1 ^v —La1—Si1 ⁱⁱⁱ	101.818 (18)	Ge2 ⁱ —Li1—Ge1 ^{xiii}	103.818 (9)
Si1 ⁱⁱ —La1—Si1 ⁱⁱⁱ	46.40 (4)	Ge2 ^{xii} —Li1—Ge1 ^{xiii}	76.182 (9)
Si1—La1—Si1 ⁱⁱⁱ	81.16 (5)	Ge2 ⁱⁱ —Li1—Ge1	76.182 (9)
Ge2 ⁱ —La1—Li1	42.161 (10)	Ge2 ^{xi} —Li1—Ge1	103.818 (9)
Ge2 ⁱⁱ —La1—Li1	42.161 (10)	Ge2 ⁱ —Li1—Ge1	76.182 (9)
Ge1 ⁱⁱⁱ —La1—Li1	43.615 (10)	Ge2 ^{xii} —Li1—Ge1	103.818 (9)
Ge1—La1—Li1	43.615 (10)	Ge1 ^{xiii} —Li1—Ge1	180.00 (3)
Si1 ^{iv} —La1—Li1	108.61 (4)	Ge2 ⁱⁱ —Li1—Ge1 ⁱⁱⁱ	76.182 (9)
Si1 ⁱ —La1—Li1	108.61 (4)	Ge2 ^{xi} —Li1—Ge1 ⁱⁱⁱ	103.818 (9)
Si1 ^v —La1—Li1	108.61 (4)	Ge2 ⁱ —Li1—Ge1 ⁱⁱⁱ	76.182 (9)
Si1 ⁱⁱ —La1—Li1	108.61 (4)	Ge2 ^{xii} —Li1—Ge1 ⁱⁱⁱ	103.818 (9)
Si1—La1—Li1	139.42 (2)	Ge1 ^{xiii} —Li1—Ge1 ⁱⁱⁱ	57.16 (3)
Si1 ⁱⁱⁱ —La1—Li1	139.42 (2)	Ge1—Li1—Ge1 ⁱⁱⁱ	122.84 (3)
Ge2 ⁱ —La1—La1 ⁱⁱ	168.011 (13)	Ge2 ⁱⁱ —Li1—Ge1 ^{vi}	103.818 (9)
Ge2 ⁱⁱ —La1—La1 ⁱⁱ	107.666 (9)	Ge2 ^{xi} —Li1—Ge1 ^{vi}	76.182 (9)
Ge1 ⁱⁱⁱ —La1—La1 ⁱⁱ	128.749 (7)	Ge2 ⁱ —Li1—Ge1 ^{vi}	103.818 (9)
Ge1—La1—La1 ⁱⁱ	128.749 (7)	Ge2 ^{xii} —Li1—Ge1 ^{vi}	76.182 (9)
Si1 ^{iv} —La1—La1 ⁱⁱ	52.86 (3)	Ge1 ^{xiii} —Li1—Ge1 ^{vi}	122.84 (3)
Si1 ⁱ —La1—La1 ⁱⁱ	92.97 (4)	Ge1—Li1—Ge1 ^{vi}	57.16 (3)
Si1 ^v —La1—La1 ⁱⁱ	92.97 (4)	Ge1 ⁱⁱⁱ —Li1—Ge1 ^{vi}	180.00 (3)
Si1 ⁱⁱ —La1—La1 ⁱⁱ	52.86 (3)	Ge2 ⁱⁱ —Li1—La1 ^{xiii}	119.951 (14)
Si1—La1—La1 ⁱⁱ	48.959 (18)	Ge2 ^{xi} —Li1—La1 ^{xiii}	60.049 (14)
Si1 ⁱⁱⁱ —La1—La1 ⁱⁱ	48.959 (18)	Ge2 ⁱ —Li1—La1 ^{xiii}	119.951 (14)
Li1—La1—La1 ⁱⁱ	149.827 (5)	Ge2 ^{xii} —Li1—La1 ^{xiii}	60.049 (14)
Ge1 ^{vi} —Ge1—Li1	61.420 (14)	Ge1 ^{xiii} —Li1—La1 ^{xiii}	61.420 (14)
Ge1 ^{vi} —Ge1—Li1 ^{vii}	61.420 (14)	Ge1—Li1—La1 ^{xiii}	118.580 (14)
Li1—Ge1—Li1 ^{vii}	122.84 (3)	Ge1 ⁱⁱⁱ —Li1—La1 ^{xiii}	118.580 (14)
Ge1 ^{vi} —Ge1—La1 ^{vii}	136.385 (10)	Ge1 ^{vi} —Li1—La1 ^{xiii}	61.420 (14)
Li1—Ge1—La1 ^{vii}	162.19 (2)	Ge2 ⁱⁱ —Li1—La1	60.049 (14)
Li1 ^{vii} —Ge1—La1 ^{vii}	74.965 (7)	Ge2 ^{xi} —Li1—La1	119.951 (14)
Ge1 ^{vi} —Ge1—La1	136.385 (10)	Ge2 ⁱ —Li1—La1	60.049 (14)
Li1—Ge1—La1	74.965 (8)	Ge2 ^{xii} —Li1—La1	119.951 (14)
Li1 ^{vii} —Ge1—La1	162.19 (2)	Ge1 ^{xiii} —Li1—La1	118.580 (14)
La1 ^{vii} —Ge1—La1	87.23 (2)	Ge1—Li1—La1	61.420 (14)
Ge2 ^{viii} —Ge2—Li1 ^{ix}	60.049 (14)	Ge1 ⁱⁱⁱ —Li1—La1	61.420 (14)
Ge2 ^{viii} —Ge2—Li1 ^x	60.049 (14)	Ge1 ^{vi} —Li1—La1	118.580 (14)
Li1 ^{ix} —Ge2—Li1 ^x	120.10 (3)	La1 ^{xiii} —Li1—La1	180.0
Ge2 ^{viii} —Ge2—La1 ⁱ	137.838 (10)		

Symmetry codes: (i) $-x-1/2, -y+1/2, -z$; (ii) $-x+1/2, -y+1/2, -z$; (iii) $x, y, z-1$; (iv) $-x+1/2, -y+1/2, -z+1$; (v) $-x-1/2, -y+1/2, -z+1$; (vi) $-x, -y, -z+1$; (vii) $x, y, z+1$; (viii) $-x, -y+1, -z$; (ix) $x+1/2, y+1/2, z$; (x) $x-1/2, y+1/2, z$; (xi) $x-1/2, y-1/2, z$; (xii) $x+1/2, y-1/2, z$; (xiii) $-x, -y, -z$.