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Synthesis and crystal structure of $\text{La}_{21}\text{Cr}_{8-2a}\text{Al}_b\text{Ge}_{7-b}\text{C}_{12}$ [$a = 0.22$ (2) and $b = 0.758$ (19)]

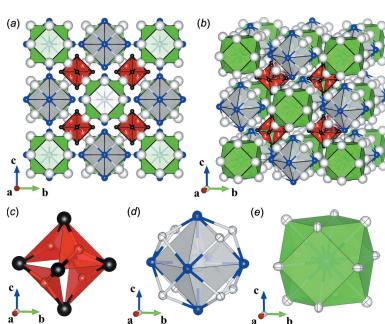
Jaskarun Pabla, Yuri Janssen and Jack W. Simonson*

Department of Physics, Farmingdale State College, Farmingdale, NY 11735, USA. *Correspondence e-mail: jack.simonson@farmingdale.edu

Single crystals of a new multinary chromium carbide, $\text{La}_{21}\text{Cr}_{8-2a}\text{Al}_b\text{Ge}_{7-b}\text{C}_{12}$ (heicosalanthanum octachromium aluminium hexagermanium dodeca-carbide), were grown from an La-rich self flux and were characterized by single-crystal X-ray diffraction. The face-centered cubic crystal structure is composed of isolated and geometrically frustrated regular Cr tetrahedra that are co-centered within regular C octahedra. These mutually separated $\text{Cr}_{4-a}\text{C}_6$ clusters are distributed throughout a three-dimensional framework of Al, Ge, and La. The title compound is isotopic with $\text{La}_{21-\delta}\text{Mn}_8\text{X}_7\text{C}_{12}$ and $R_{21}\text{Fe}_8\text{X}_7\text{C}_{12}$ ($R = \text{La}, \text{Ce}, \text{Pr}; \text{X} = \text{Al}, \text{Bi}, \text{Ge}, \text{Sn}, \text{Sb}, \text{Te}$) and represents the first example of a Cr-based compound with this structure-type.

1. Chemical context

Geometric frustration arises when crystallographic degeneracies lead to the near equalization of competing interatomic interactions. Often, such frustration results in the suppression to an arbitrarily low temperature of any eventual phase transition to an ordered ground state (Gilbert *et al.*, 2016). In the simplest case, this phenomenon occurs when three anti-ferromagnetic exchange-coupled Ising spins are arranged on the vertices of an equilateral triangle, their counterbalanced interactions thereby precluding the transition to mutually energetically favorable magnetic order. The ability to tune the onset of order *via* geometric frustration has been shown to lead to a variety of intriguing properties, including magnetic monopoles (Pan *et al.*, 2016), spin ice states (Hirschberger *et al.*, 2015; Huang *et al.*, 2016), tricritical phenomena (McNally *et al.*, 2015), and quantum criticality (Miiller *et al.*, 2016), with applications ranging from neural networks (Grass *et al.*, 2016), to quantum computing (Katzgraber *et al.*, 2015), to unconventional superconductivity (Glasbrenner *et al.*, 2015). Over the last decades, a class of materials known as pyrochlores has provided a rich ground for studying magnetic frustration due to geometric degeneracies arising from their vertex-linked, regular tetrahedral building blocks (Gardner *et al.*, 2010). The structure of the $\text{La}_{21}\text{Fe}_8\text{Sn}_7\text{C}_{12}$ system also consists regular tetrahedra of Fe, but in this case they are mutually isolated from one another. Here too, geometric frustration has been observed to manifest itself in a spin glass ground state, as inferred from a frequency f -dependent cusp in the real part of measurements of ac magnetic susceptibility χ' near temperature $T = 5$ K (Benbow *et al.*, 2009). On the other hand, if Fe is replaced with Mn as in isostructural $\text{La}_{21}\text{Mn}_8\text{Ge}_{6.2}\text{Al}_{0.8}\text{C}_{12}$,



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similar cusps occurring at $T = 3$ K and 6 K in χ' exhibit no such dependence, even over four orders of magnitude in f , suggesting that only local antiferromagnetic ordering within the Mn_4C_6 cluster arises while the spin glass state remains absent down to $T = 1.8$ K (Zaikina *et al.*, 2011). With the aim of unveiling a new avenue to explore frustrated states within this class of compounds, we present here the synthesis and crystal structure of a new Cr-based analog that is isostructural and likewise geometrically frustrated, $\text{La}_{21}\text{Cr}_{8-2a}\text{Al}_b\text{Ge}_{7-b}\text{C}_{12}$, [$a = 0.22$ (2), $b = 0.758$ (19)].

2. Structural commentary

Fig. 1 shows a polyhedral representation of the crystal structure of the title compound, the geometrically frustrated substructure of which consists of a Cr-capped regular tetrahedron enclosed within a C-capped regular octahedron. Fig. 1a is a depiction of the unit cell from along the crystallographic a axis, and Fig. 1b shows the same from a generic angle above

the ab plane. The structure can be thought to be composed of three building blocks – a geometrically frustrated and Cr-deficient $\text{Cr}_{4-a}\text{C}_6$ unit (Fig. 1c), an La_9Ge_6 unit (Fig. 1d), and an $\text{La}_{12}\text{Al}_b\text{Ge}_{1-b}$ unit (Fig. 1e). These substructures are arranged on four interpenetrating face-centered cubic lattices that originate within the unit cell at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$ for the $\text{Cr}_{4-a}\text{C}_6$ unit, $(\frac{1}{2}, 0, 0)$ for the La_9Ge_6 unit, and $(0, 0, 0)$ for the $\text{La}_{12}\text{Al}_b\text{Ge}_{1-b}$ unit. Accordingly, $\text{La}_{21}\text{Cr}_{8-2a}\text{Al}_b\text{Ge}_{7-b}\text{C}_{12}$ adopts a structure that is effectively a polyatomic analog of the Heusler structure (Graf *et al.*, 2011) with composition X_2YZ , where $X = \text{Cr}_{4-a}\text{C}_6$, $Y = \text{La}_9\text{Ge}_6$, and $Z = \text{La}_{12}\text{Al}_b\text{Ge}_{1-b}$ units. Taken together with the appropriate site occupancies, the title composition is thus obtained as $X_2YZ = \text{La}_{21}\text{Cr}_{8-2a}\text{Al}_b\text{Ge}_{7-b}\text{C}_{12}$.

The geometrically frustrated Cr-deficient $\text{Cr}_{4-a}\text{C}_6$ unit shown in Fig. 1c is composed of a single inequivalent Cr position and a single C position. Accordingly, nearest neighbor Cr–C distances are uniformly 1.949 (5) Å, in good agreement with nearest neighbor distances in binary Cr carbides. Like-

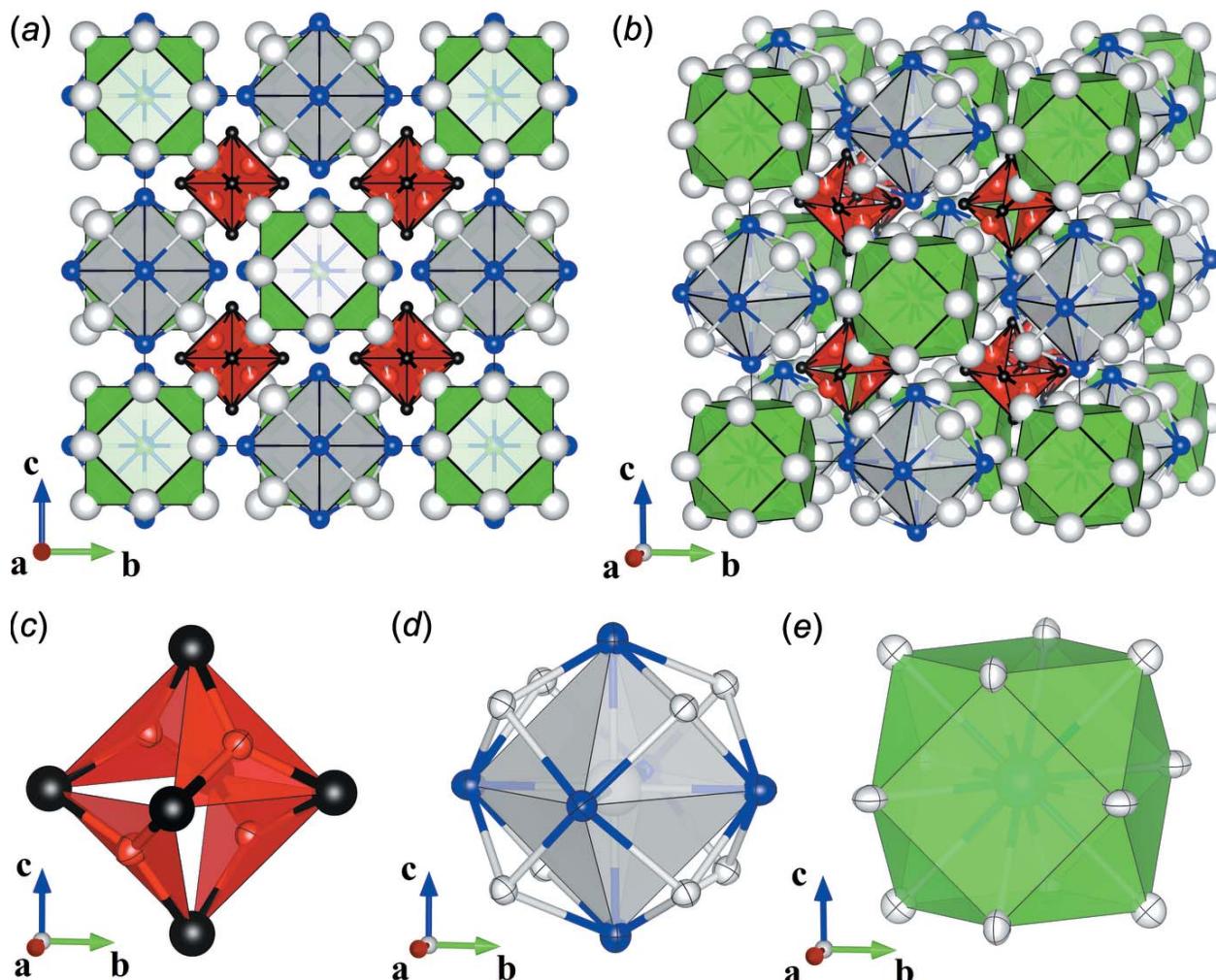


Figure 1

(a) A view of the crystal structure of $\text{La}_{21}\text{Cr}_{8-2a}\text{Al}_b\text{Ge}_{7-b}\text{C}_{12}$ along [100]. (b) The same crystal structure from an arbitrary view above the ab plane. (c) Cr-deficient $\text{Cr}_{4-a}\text{C}_6$ substructure depicted as four tetrahedrally arranged and vertex-linked CrC_3 plaquettes. (d) La^3 coordination polyhedron. (e) Al^2/Ge^2 coordination polyhedron. In all sub-figures, colors are as follows: La (white), Cr (red), Al (green), Ge (blue), and C (black). Polyhedra are colored according to the central element. In c–e, the ellipsoids correspond to 99% probability.

wise, all Cr–Cr distances within the substructure are similarly identical at 2.4821 (9) Å, only slightly smaller than the 2.512 Å nearest neighbor distance observed in Cr metal (Gorbunoff *et al.*, 2009). Perhaps more interesting, however, is this relative proximity when compared with the 2.878 Å that separates neighboring Cr in the frustrated Kagomé planes of $\text{SrCr}_{8-x}\text{Ga}_{4+x}\text{O}_{19}$, a seminal example of a geometrically frustrated magnetic system (Broholm *et al.*, 1990).

The remaining substructures, namely the La_9Ge_6 unit shown in Fig. 1*d* and the $\text{La}_{12}\text{Al}_b\text{Ge}_{1-b}$ unit shown in Fig. 1*e* form cages about their central La3 and Al2/Ge2 sites respectively. The cage-like nature of this configuration is clear from the large anisotropic displacement parameters U_{ed} corresponding to these two central sites, as has been previously observed in isostructural materials (Benbow *et al.*, 2009; Zaikina *et al.*, 2011). These sites are likely characterized by strong rattling modes of the central loosely bound atom, such as is observed in skutterudite compounds (Sergueev *et al.*, 2015). Not surprisingly, the distance between central La3 and its nearest neighbor Ge1 is a rather long, 3.41450 (13) Å. The central Al2/Ge2 site is even further – 3.8858 (2) Å from its nearest neighbor La1. A brief review of the crystallographic literature finds nearest neighbor bond lengths in La–Ge binaries to be typically on the order of only 3.0 to 3.2 Å, far smaller than either of these distances, which lends credence to the emerging picture of a stuffed, skutterudite-like arrangement.

3. Synthesis and crystallization

$\text{La}_{21}\text{Cr}_{8-a}\text{Al}_b\text{Ge}_{7-b}\text{C}_{12}$ crystals were grown from a self flux of excess La (Alfa Aesar, 00175) and the following chemicals: Cr (Alfa Aesar, 38494), Ge (Strategic Metal, SM1301-B), and graphite (McMaster-Carr 9121K71) in an La:Cr:Ge:C atomic ratio of 561:214:76:149. The growth process was carried out in Al_2O_3 crucibles sealed within fused quartz ampoules under high purity Ar gas. Ampoules were heated to 1423 K over a period of four h, left to soak at that temperature for an additional four h, and cooled to 1173 K over 50 h to induce nucleation and to promote crystal growth. The ampoule was then quickly centrifuged at 2000 r.p.m. for several seconds to separate the solid crystals from the liquid La-rich solution. Crystals took the form of well-faceted tablets with metallic luster.

4. Refinement details

Details regarding the crystal itself, as well as data collection and structural refinement are presented in Table 1. No evidence for twin domains was observed, and all sites with the exception of C were refined with anisotropic displacement parameters. Here permitting anisotropic displacement parameters did not appreciably improve the refinement. Two reflections, $(\bar{1}\bar{1}1)$ and $(00\bar{2})$, required manual culling due to beamstop clipping.

Table 1
Experimental details.

Crystal data	
Chemical formula	$\text{La}_{21}\text{Cr}_{7.556}\text{Al}_{0.758}\text{Ge}_{6.242}\text{C}_{12}$
M_r	3927.6
Crystal system, space group	Cubic, $Fm\bar{3}m$
Temperature (K)	294
a (Å)	16.4048 (6)
V (Å ³)	4414.8 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	25.76
Crystal size (mm)	0.12 × 0.11 × 0.07
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Numerical (<i>SADABS</i> ; Bruker, 2008)
T_{\min} , T_{\max}	0.342, 0.527
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	40979, 328, 321
R_{int}	0.041
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	0.670
Refinement	
$R[F > 3\sigma(F)]$, $wR(F)$, S	0.012, 0.045, 1.91
No. of reflections	328
No. of parameters	21
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	1.07, -0.83

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SUPERFLIP* (Palatinus & Chapuis, 2007), *JANA2006* (Petříček *et al.*, 2014), *VESTA* (Momma & Izumi, 2011) and *publCIF* (Westrip, 2010).

The refinement was improved when the Ge2 site was permitted to be mixed with Al. In this case, Al and Ge coordinates and displacement parameters were constrained to be equal, and the sum of the Al and Ge occupancies was constrained to unity. The refined Al:Ge ratio 0.758 (19):6.242 (19) is in excellent agreement with observed ratios of 0.83 (2):6.17 (2) in $\text{La}_{21}\text{MnAl}_b\text{Ge}_{7-b}\text{C}_{12}$ (Zaikina *et al.*, 2011) and somewhat lower than the reported ratio of 2.1:4.9 in $\text{La}_{21}\text{FeAl}_b\text{Ge}_{7-b}\text{C}_{12}$ (Benbow *et al.*, 2009). Like the Mn-based analog, however, we observe no evidence to suggest that the Ge1 site is mixed, as was the case with the more Al-rich $\text{La}_{21}\text{FeAl}_b\text{Ge}_{7-b}\text{C}_{12}$. Regardless of any quantitative differences, the potential for Al – apparently extracted by an La-rich flux from Al_2O_3 growth crucibles – to mix with Ge appears to be a universal phenomenon in this class of compounds. It remains unclear if Al is required to stabilize the Ge-containing examples of these phases, which have not been reported in its absence.

In addition to mixing on the Al2/Ge2 site, excess charge was observed in Fourier maps when the Cr site was constrained to full occupancy, and the refinement was substantially improved when this parameter was subsequently freed. Permitting instead partial occupancy of Al on the Cr site did not appreciably improve the refinement. No evidence for mixed or non-unity occupancy was found for any of the La sites, despite previously published density functional theory calculations that found a composition of $\text{La}_{20}\text{Mn}_8\text{Te}_7\text{C}_{12}$ to be stabilized by the shift of the Fermi energy to a pseudogap in the density of states (Zaikina *et al.*, 2011). Our final refined composition is

then $\text{La}_{21}\text{Cr}_{8-2a}\text{Al}_b\text{Ge}_{7-b}\text{C}_{12}$ with the occupancy parameters $a = 0.22$ (2) and $b = 0.758$ (19).

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supporting information

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Synthesis and crystal structure of $\text{La}_{21}\text{Cr}_{8-2a}\text{Al}_b\text{Ge}_{7-b}\text{C}_{12}$ [$a = 0.22$ (2) and $b = 0.758$ (19)]

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Computing details

Data collection: *APEX2* (Bruker, 2007) and *SAINT* (Bruker, 2007); cell refinement: *APEX2* (Bruker, 2007) and *SAINT* (Bruker, 2007); data reduction: *APEX2* (Bruker, 2007) and *SAINT* (Bruker, 2007); program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2014); molecular graphics: *VESTA* (Momma & Izumi, 2011); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Henicosalanthanum octachromium aluminium hexagermanium dodecacarbide

Crystal data

$\text{La}_{21}\text{Cr}_{7.556}\text{Al}_{0.758}\text{Ge}_{6.242}\text{C}_{12}$	$D_x = 5.909 \text{ Mg m}^{-3}$
$M_r = 3927.6$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Cubic, $Fm\bar{3}m$	Cell parameters from 9327 reflections
Hall symbol: -F 4 2 3	$\theta = 5.0\text{--}56.7^\circ$
$a = 16.4048$ (6) \AA	$\mu = 25.76 \text{ mm}^{-1}$
$V = 4414.8$ (5) \AA^3	$T = 294 \text{ K}$
$Z = 4$	Plate, metallic_black
$F(000) = 6639.4$	$0.12 \times 0.11 \times 0.07 \text{ mm}$

Data collection

Bruker APEXII CCD	40979 measured reflections
diffractometer	328 independent reflections
Radiation source: X-ray tube	321 reflections with $I > 3\sigma(I)$
Graphite monochromator	$R_{\text{int}} = 0.041$
ω and φ scans	$\theta_{\text{max}} = 28.4^\circ$, $\theta_{\text{min}} = 2.2^\circ$
Absorption correction: numerical (<i>SADABS</i> ; Bruker, 2008)	$h = -21 \rightarrow 21$
$T_{\text{min}} = 0.342$, $T_{\text{max}} = 0.527$	$k = -21 \rightarrow 21$
	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(I) + 0.0004I^2)$
$R[F > 3\sigma(F)] = 0.012$	$(\Delta/\sigma)_{\text{max}} = 0.015$
$wR(F) = 0.045$	$\Delta\rho_{\text{max}} = 1.07 \text{ e \AA}^{-3}$
$S = 1.91$	$\Delta\rho_{\text{min}} = -0.83 \text{ e \AA}^{-3}$
328 reflections	Extinction correction: B-C type 2 (Becker & Coppens, 1974)
21 parameters	Extinction coefficient: 810 (150)
0 restraints	
1 constraint	

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
La1	0	0.167496 (14)	0.167496 (14)	0.01125 (10)	
La2	0.369379 (15)	0.369379 (15)	0.369379 (15)	0.00984 (9)	
La3	0.5	0.5	0.5	0.0384 (3)	
Ge1	0.29186 (6)	0	0	0.0121 (2)	
Cr1	0.19651 (4)	0.19651 (4)	0.19651 (4)	0.0068 (2)	0.944 (5)
Ge2	0	0	0	0.0323 (12)	0.242 (19)
Al2	0	0	0	0.0323 (12)	0.758 (19)
C1	0.1049 (4)	0.25	0.25	0.0127 (11)*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La1	0.0074 (2)	0.01315 (17)	0.01315 (17)	0	0	0.00046 (13)
La2	0.00984 (15)	0.00984 (15)	0.00984 (15)	-0.00052 (8)	-0.00052 (8)	-0.00052 (8)
La3	0.0384 (4)	0.0384 (4)	0.0384 (4)	0	0	0
Ge1	0.0139 (5)	0.0112 (3)	0.0112 (3)	0	0	0
Cr1	0.0068 (3)	0.0068 (3)	0.0068 (3)	0.0008 (2)	0.0008 (2)	0.0008 (2)
Ge2	0.032 (2)	0.032 (2)	0.032 (2)	0	0	0
Al2	0.032 (2)	0.032 (2)	0.032 (2)	0	0	0

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

La1—La1 ⁱ	3.8282 (4)	La2—Ge1 ^{xiii}	3.2864 (5)
La1—La1 ⁱⁱ	3.8859 (3)	La2—Ge1 ^{xiv}	3.2864 (5)
La1—La1 ⁱⁱⁱ	3.8859 (3)	La2—Cr1 ^{vi}	3.2216 (7)
La1—La1 ^{iv}	3.8859 (3)	La2—Cr1 ^{vii}	3.2216 (7)
La1—La1 ^v	3.8859 (3)	La2—Cr1 ⁱ	3.2216 (7)
La1—La2 ^{vi}	3.9907 (4)	La2—C1 ^{vi}	2.8015 (9)
La1—La2 ^{vii}	3.9907 (4)	La2—C1 ^{xv}	2.8015 (9)
La1—La2 ^{viii}	3.9907 (4)	La2—C1 ^{xvi}	2.8015 (9)
La1—La2 ^{ix}	3.9907 (4)	Cr1—Cr1 ^{vi}	2.4821 (9)
La1—Cr1	3.2932 (7)	Cr1—Cr1 ^{vii}	2.4821 (9)
La1—Cr1 ^x	3.2932 (7)	Cr1—Cr1 ⁱ	2.4821 (9)
La1—C1	2.574 (4)	Cr1—C1	1.949 (5)
La1—C1 ^{xi}	2.574 (4)	Cr1—C1 ⁱⁱ	1.949 (5)
La2—La3	3.7115 (3)	Cr1—C1 ^{iv}	1.949 (5)
La2—Ge1 ^{xii}	3.2864 (5)		
La1 ⁱ —La1—La1 ⁱⁱ	120.000 (6)	La3—La2—Cr1 ^{vii}	153.589 (14)
La1 ⁱ —La1—La1 ⁱⁱⁱ	120.000 (6)	La3—La2—Cr1 ⁱ	153.589 (14)
La1 ⁱ —La1—La1 ^{iv}	120.000 (6)	La3—La2—C1 ^{vi}	136.07 (12)
La1 ⁱ —La1—La1 ^v	120.000 (6)	La3—La2—C1 ^{xv}	136.07 (12)
La1 ⁱ —La1—La2 ^{vi}	61.339 (6)	La3—La2—C1 ^{xvi}	136.07 (12)
La1 ⁱ —La1—La2 ^{vii}	61.339 (6)	Ge1 ^{xii} —La2—Ge1 ^{xiii}	94.557 (15)
La1 ⁱ —La1—La2 ^{viii}	61.339 (6)	Ge1 ^{xii} —La2—Ge1 ^{xiv}	94.557 (15)

La1 ⁱ —La1—La2 ^{ix}	61.339 (6)	Ge1 ^{xii} —La2—Cr1 ^{vi}	131.521 (19)
La1 ⁱ —La1—Cr1	78.207 (12)	Ge1 ^{xii} —La2—Cr1 ^{vii}	131.521 (19)
La1 ⁱ —La1—Cr1 ^x	78.207 (12)	Ge1 ^{xii} —La2—Cr1 ⁱ	95.56 (2)
La1 ⁱ —La1—C1	41.96 (10)	Ge1 ^{xii} —La2—C1 ^{vi}	165.90 (12)
La1 ⁱ —La1—C1 ^{xi}	41.96 (10)	Ge1 ^{xii} —La2—C1 ^{xv}	95.00 (8)
La1 ⁱⁱ —La1—La1 ⁱⁱⁱ	90.000 (7)	Ge1 ^{xii} —La2—C1 ^{xvi}	95.00 (8)
La1 ⁱⁱ —La1—La1 ^{iv}	60.000 (5)	Ge1 ^{xiii} —La2—Ge1 ^{xiv}	94.557 (15)
La1 ⁱⁱ —La1—La1 ^v	120.000 (7)	Ge1 ^{xiii} —La2—Cr1 ^{vi}	131.521 (19)
La1 ⁱⁱ —La1—La2 ^{vi}	60.865 (6)	Ge1 ^{xiii} —La2—Cr1 ^{vii}	95.56 (2)
La1 ⁱⁱ —La1—La2 ^{vii}	101.955 (5)	Ge1 ^{xiii} —La2—Cr1 ⁱ	131.521 (19)
La1 ⁱⁱ —La1—La2 ^{viii}	165.127 (7)	Ge1 ^{xiii} —La2—C1 ^{vi}	95.00 (8)
La1 ⁱⁱ —La1—La2 ^{ix}	105.813 (7)	Ge1 ^{xiii} —La2—C1 ^{xv}	165.90 (12)
La1 ⁱⁱ —La1—Cr1	53.844 (12)	Ge1 ^{xiii} —La2—C1 ^{xvi}	95.00 (8)
La1 ⁱⁱ —La1—Cr1 ^x	142.596 (13)	Ge1 ^{xiv} —La2—Cr1 ^{vi}	95.56 (2)
La1 ⁱⁱ —La1—C1	84.21 (8)	Ge1 ^{xiv} —La2—Cr1 ^{vii}	131.521 (19)
La1 ⁱⁱ —La1—C1 ^{xi}	147.63 (4)	Ge1 ^{xiv} —La2—Cr1 ⁱ	131.521 (19)
La1 ⁱⁱⁱ —La1—La1 ^{iv}	120.000 (7)	Ge1 ^{xiv} —La2—C1 ^{vi}	95.00 (8)
La1 ⁱⁱⁱ —La1—La1 ^v	60.000 (5)	Ge1 ^{xiv} —La2—C1 ^{xv}	95.00 (8)
La1 ⁱⁱⁱ —La1—La2 ^{vi}	105.813 (7)	Ge1 ^{xiv} —La2—C1 ^{xvi}	165.90 (12)
La1 ⁱⁱⁱ —La1—La2 ^{vii}	165.127 (7)	Cr1 ^{vi} —La2—Cr1 ^{vii}	45.314 (17)
La1 ⁱⁱⁱ —La1—La2 ^{viii}	101.955 (5)	Cr1 ^{vi} —La2—Cr1 ⁱ	45.314 (17)
La1 ⁱⁱⁱ —La1—La2 ^{ix}	60.865 (6)	Cr1 ^{vi} —La2—C1 ^{vi}	36.93 (9)
La1 ⁱⁱⁱ —La1—Cr1	142.596 (13)	Cr1 ^{vi} —La2—C1 ^{xv}	36.93 (9)
La1 ⁱⁱⁱ —La1—Cr1 ^x	53.844 (12)	Cr1 ^{vi} —La2—C1 ^{xvi}	70.34 (12)
La1 ⁱⁱⁱ —La1—C1	147.63 (4)	Cr1 ^{vii} —La2—Cr1 ⁱ	45.314 (17)
La1 ⁱⁱⁱ —La1—C1 ^{xi}	84.21 (8)	Cr1 ^{vii} —La2—C1 ^{vi}	36.93 (9)
La1 ^{iv} —La1—La1 ^v	90.000 (7)	Cr1 ^{vii} —La2—C1 ^{xv}	70.34 (12)
La1 ^{iv} —La1—La2 ^{vi}	101.955 (5)	Cr1 ^{vii} —La2—C1 ^{xvi}	36.93 (9)
La1 ^{iv} —La1—La2 ^{vii}	60.865 (6)	Cr1 ⁱ —La2—C1 ^{vi}	70.34 (12)
La1 ^{iv} —La1—La2 ^{viii}	105.813 (7)	Cr1 ⁱ —La2—C1 ^{xv}	36.93 (9)
La1 ^{iv} —La1—La2 ^{ix}	165.127 (7)	Cr1 ⁱ —La2—C1 ^{xvi}	36.93 (9)
La1 ^{iv} —La1—Cr1	53.844 (12)	C1 ^{vi} —La2—C1 ^{xv}	73.86 (13)
La1 ^{iv} —La1—Cr1 ^x	142.596 (13)	C1 ^{vi} —La2—C1 ^{xvi}	73.86 (13)
La1 ^{iv} —La1—C1	84.21 (8)	C1 ^{xv} —La2—C1 ^{xvi}	73.86 (13)
La1 ^{iv} —La1—C1 ^{xi}	147.63 (4)	La2—La3—La2 ^{ix}	109.471 (6)
La1 ^v —La1—La2 ^{vi}	165.127 (7)	La2—La3—La2 ^{xx}	109.471 (6)
La1 ^v —La1—La2 ^{vii}	105.813 (7)	La2—La3—La2 ^{xxi}	109.471 (6)
La1 ^v —La1—La2 ^{viii}	60.865 (6)	La2—La3—La2 ^{xxii}	70.529 (6)
La1 ^v —La1—La2 ^{ix}	101.955 (5)	La2—La3—La2 ^{xxiii}	180.0 (5)
La1 ^v —La1—Cr1	142.596 (13)	La2—La3—La2 ^{xxiv}	70.529 (6)
La1 ^v —La1—Cr1 ^x	53.844 (12)	La2—La3—La2 ^{xxv}	70.529 (6)
La1 ^v —La1—C1	147.63 (4)	La2 ^{xix} —La3—La2 ^{xx}	109.471 (6)
La1 ^v —La1—C1 ^{xi}	84.21 (8)	La2 ^{xix} —La3—La2 ^{xi}	109.471 (6)
La2 ^{vi} —La1—La2 ^{vii}	87.896 (6)	La2 ^{xix} —La3—La2 ^{xxii}	180.0 (5)
La2 ^{vi} —La1—La2 ^{viii}	122.677 (8)	La2 ^{xix} —La3—La2 ^{xxiii}	70.529 (6)
La2 ^{vi} —La1—La2 ^{ix}	64.952 (7)	La2 ^{xix} —La3—La2 ^{xxiv}	70.529 (6)
La2 ^{vi} —La1—Cr1	51.418 (12)	La2 ^{xix} —La3—La2 ^{xxv}	70.529 (6)
La2 ^{vi} —La1—Cr1 ^x	115.315 (13)	La2 ^{xx} —La3—La2 ^{xxi}	109.471 (6)

La2 ^{vi} —La1—C1	44.302 (12)	La2 ^{xx} —La3—La2 ^{xxii}	70.529 (6)
La2 ^{vi} —La1—C1 ^{xi}	90.13 (7)	La2 ^{xx} —La3—La2 ^{xxiii}	70.529 (6)
La2 ^{vii} —La1—La2 ^{viii}	64.952 (7)	La2 ^{xx} —La3—La2 ^{xxiv}	180.0 (5)
La2 ^{vii} —La1—La2 ^{ix}	122.677 (8)	La2 ^{xx} —La3—La2 ^{xxv}	70.529 (6)
La2 ^{vii} —La1—Cr1	51.418 (12)	La2 ^{xxi} —La3—La2 ^{xxii}	70.529 (6)
La2 ^{vii} —La1—Cr1 ^x	115.315 (13)	La2 ^{xxi} —La3—La2 ^{xxiii}	70.529 (6)
La2 ^{vii} —La1—C1	44.302 (12)	La2 ^{xxi} —La3—La2 ^{xxiv}	70.529 (6)
La2 ^{vii} —La1—C1 ^{xi}	90.13 (7)	La2 ^{xxi} —La3—La2 ^{xxv}	180.0 (5)
La2 ^{viii} —La1—La2 ^{ix}	87.896 (6)	La2 ^{xxii} —La3—La2 ^{xxiii}	109.471 (6)
La2 ^{viii} —La1—Cr1	115.314 (13)	La2 ^{xxii} —La3—La2 ^{xxiv}	109.471 (6)
La2 ^{viii} —La1—Cr1 ^x	51.418 (12)	La2 ^{xxii} —La3—La2 ^{xxv}	109.471 (6)
La2 ^{viii} —La1—C1	90.13 (7)	La2 ^{xxiii} —La3—La2 ^{xxiv}	109.471 (6)
La2 ^{viii} —La1—C1 ^{xi}	44.302 (12)	La2 ^{xxiii} —La3—La2 ^{xxv}	109.471 (6)
La2 ^{ix} —La1—Cr1	115.314 (13)	La2 ^{xxiv} —La3—La2 ^{xxv}	109.471 (6)
La2 ^{ix} —La1—Cr1 ^x	51.418 (12)	La2 ^{xxvi} —Ge1—La2 ⁱ	134.47 (3)
La2 ^{ix} —La1—C1	90.13 (7)	La2 ^{xxvi} —Ge1—La2 ^{xxvii}	81.389 (12)
La2 ^{ix} —La1—C1 ^{xi}	44.302 (12)	La2 ^{xxvi} —Ge1—La2 ^{xxviii}	81.389 (12)
Cr1—La1—Cr1 ^x	156.414 (18)	La2 ⁱ —Ge1—La2 ^{xxvii}	81.389 (12)
Cr1—La1—C1	36.25 (10)	La2 ⁱ —Ge1—La2 ^{xxviii}	81.389 (12)
Cr1—La1—C1 ^{xi}	120.16 (10)	La2 ^{xxvii} —Ge1—La2 ^{xxviii}	134.47 (3)
Cr1 ^x —La1—C1	120.16 (10)	La1—Cr1—La1 ⁱⁱ	72.313 (15)
Cr1 ^x —La1—C1 ^{xi}	36.25 (10)	La1—Cr1—La1 ^{iv}	72.313 (15)
C1—La1—C1 ^{xi}	83.91 (14)	La1—Cr1—La2 ^{vi}	75.541 (15)
La1 ^{vi} —La2—La1 ^{vii}	57.323 (6)	La1—Cr1—La2 ^{vii}	75.541 (15)
La1 ^{vi} —La2—La1 ^{xv}	113.653 (7)	La1—Cr1—La2 ⁱ	139.88 (2)
La1 ^{vi} —La2—La1 ^{xvii}	58.269 (6)	La1—Cr1—Cr1 ^{vi}	142.60 (3)
La1 ^{vi} —La2—La1 ^{xvi}	113.653 (7)	La1—Cr1—Cr1 ^{vii}	142.60 (3)
La1 ^{vi} —La2—La1 ^{xviii}	150.254 (8)	La1—Cr1—Cr1 ⁱ	101.79 (3)
La1 ^{vi} —La2—La3	104.871 (7)	La1—Cr1—C1	51.34 (11)
La1 ^{vi} —La2—Ge1 ^{xii}	147.964 (10)	La1—Cr1—C1 ⁱⁱ	113.23 (9)
La1 ^{vi} —La2—Ge1 ^{xiii}	97.605 (8)	La1—Cr1—C1 ^{iv}	113.23 (9)
La1 ^{vi} —La2—Ge1 ^{xiv}	55.083 (13)	La1 ⁱⁱ —Cr1—La1 ^{iv}	72.313 (15)
La1 ^{vi} —La2—Cr1 ^{vi}	53.041 (13)	La1 ⁱⁱ —Cr1—La2 ^{vi}	75.541 (15)
La1 ^{vi} —La2—Cr1 ^{vii}	76.602 (13)	La1 ⁱⁱ —Cr1—La2 ^{vii}	139.88 (2)
La1 ^{vi} —La2—Cr1 ⁱ	98.244 (13)	La1 ⁱⁱ —Cr1—La2 ⁱ	75.541 (15)
La1 ^{vi} —La2—C1 ^{vi}	39.92 (8)	La1 ⁱⁱ —Cr1—Cr1 ^{vi}	142.60 (3)
La1 ^{vi} —La2—C1 ^{xv}	79.52 (2)	La1 ⁱⁱ —Cr1—Cr1 ^{vii}	101.79 (3)
La1 ^{vi} —La2—C1 ^{xvi}	113.23 (10)	La1 ⁱⁱ —Cr1—Cr1 ⁱ	142.60 (3)
La1 ^{vii} —La2—La1 ^{xv}	150.254 (8)	La1 ⁱⁱ —Cr1—C1	113.23 (9)
La1 ^{vii} —La2—La1 ^{xvii}	113.653 (7)	La1 ⁱⁱ —Cr1—C1 ⁱⁱ	51.34 (11)
La1 ^{vii} —La2—La1 ^{xvi}	58.269 (6)	La1 ⁱⁱ —Cr1—C1 ^{iv}	113.23 (9)
La1 ^{vii} —La2—La1 ^{xviii}	113.653 (7)	La1 ^{iv} —Cr1—La2 ^{vi}	139.88 (2)
La1 ^{vii} —La2—La3	104.871 (7)	La1 ^{iv} —Cr1—La2 ^{vii}	75.541 (15)
La1 ^{vii} —La2—Ge1 ^{xii}	147.964 (10)	La1 ^{iv} —Cr1—La2 ⁱ	75.541 (15)
La1 ^{vii} —La2—Ge1 ^{xiii}	55.083 (13)	La1 ^{iv} —Cr1—Cr1 ^{vi}	101.79 (3)
La1 ^{vii} —La2—Ge1 ^{xiv}	97.605 (8)	La1 ^{iv} —Cr1—Cr1 ^{vii}	142.60 (3)
La1 ^{vii} —La2—Cr1 ^{vi}	76.602 (13)	La1 ^{iv} —Cr1—Cr1 ⁱ	142.60 (3)
La1 ^{vii} —La2—Cr1 ^{vii}	53.041 (13)	La1 ^{iv} —Cr1—C1	113.23 (9)

La1 ^{vii} —La2—Cr1 ⁱ	98.244 (13)	La1 ^{iv} —Cr1—C1 ⁱⁱ	113.23 (9)
La1 ^{vii} —La2—C1 ^{vi}	39.92 (8)	La1 ^{iv} —Cr1—C1 ^{iv}	51.34 (11)
La1 ^{vii} —La2—C1 ^{xv}	113.23 (10)	La2 ^{vi} —Cr1—La2 ^{vii}	118.56 (2)
La1 ^{vii} —La2—C1 ^{xvi}	79.52 (2)	La2 ^{vi} —Cr1—La2 ⁱ	118.56 (2)
La1 ^{xv} —La2—La1 ^{xvii}	57.323 (6)	La2 ^{vi} —Cr1—Cr1 ^{vi}	118.32 (3)
La1 ^{xv} —La2—La1 ^{xvi}	113.653 (7)	La2 ^{vi} —Cr1—Cr1 ^{viii}	67.34 (2)
La1 ^{xv} —La2—La1 ^{xviii}	58.269 (6)	La2 ^{vi} —Cr1—Cr1 ⁱ	67.34 (2)
La1 ^{xv} —La2—La3	104.871 (7)	La2 ^{vi} —Cr1—C1	59.74 (2)
La1 ^{xv} —La2—Ge1 ^{xii}	55.083 (13)	La2 ^{vi} —Cr1—C1 ⁱⁱ	59.74 (2)
La1 ^{xv} —La2—Ge1 ^{xiii}	147.964 (10)	La2 ^{vi} —Cr1—C1 ^{iv}	168.77 (11)
La1 ^{xv} —La2—Ge1 ^{xiv}	97.605 (8)	La2 ^{vii} —Cr1—La2 ⁱ	118.56 (2)
La1 ^{xv} —La2—Cr1 ^{vi}	76.602 (13)	La2 ^{vii} —Cr1—Cr1 ^{vi}	67.34 (2)
La1 ^{xv} —La2—Cr1 ^{vii}	98.244 (13)	La2 ^{vii} —Cr1—Cr1 ^{viii}	118.32 (3)
La1 ^{xv} —La2—Cr1 ⁱ	53.041 (13)	La2 ^{vii} —Cr1—Cr1 ⁱ	67.34 (2)
La1 ^{xv} —La2—C1 ^{vi}	113.23 (10)	La2 ^{vii} —Cr1—C1	59.74 (2)
La1 ^{xv} —La2—C1 ^{xv}	39.92 (8)	La2 ^{vii} —Cr1—C1 ⁱⁱ	168.77 (11)
La1 ^{xv} —La2—C1 ^{xvi}	79.52 (2)	La2 ^{vii} —Cr1—C1 ^{iv}	59.74 (2)
La1 ^{xvii} —La2—La1 ^{xvi}	150.254 (8)	La2 ⁱ —Cr1—Cr1 ^{vi}	67.34 (2)
La1 ^{xvii} —La2—La1 ^{xviii}	113.653 (7)	La2 ⁱ —Cr1—Cr1 ^{viii}	67.34 (2)
La1 ^{xvii} —La2—La3	104.871 (7)	La2 ⁱ —Cr1—Cr1 ⁱ	118.32 (3)
La1 ^{xvii} —La2—Ge1 ^{xii}	97.605 (8)	La2 ⁱ —Cr1—C1	168.77 (11)
La1 ^{xvii} —La2—Ge1 ^{xiii}	147.964 (10)	La2 ⁱ —Cr1—C1 ⁱⁱ	59.74 (2)
La1 ^{xvii} —La2—Ge1 ^{xiv}	55.083 (13)	La2 ⁱ —Cr1—C1 ^{iv}	59.74 (2)
La1 ^{xvii} —La2—Cr1 ^{vi}	53.041 (13)	Cr1 ^{vi} —Cr1—Cr1 ^{viii}	60.00 (3)
La1 ^{xvii} —La2—Cr1 ^{vii}	98.244 (13)	Cr1 ^{vi} —Cr1—Cr1 ⁱ	60.00 (3)
La1 ^{xvii} —La2—Cr1 ⁱ	76.602 (13)	Cr1 ^{vi} —Cr1—C1	103.11 (10)
La1 ^{xvii} —La2—C1 ^{vi}	79.52 (2)	Cr1 ^{vi} —Cr1—C1 ⁱⁱ	103.11 (10)
La1 ^{xvii} —La2—C1 ^{xv}	39.92 (8)	Cr1 ^{vi} —Cr1—C1 ^{iv}	50.45 (11)
La1 ^{xvii} —La2—C1 ^{xvi}	113.23 (10)	Cr1 ^{vii} —Cr1—Cr1 ⁱ	60.00 (3)
La1 ^{xvi} —La2—La1 ^{xviii}	57.323 (6)	Cr1 ^{vii} —Cr1—C1	103.11 (10)
La1 ^{xvi} —La2—La3	104.871 (7)	Cr1 ^{vii} —Cr1—C1 ⁱⁱ	50.45 (11)
La1 ^{xvi} —La2—Ge1 ^{xii}	97.605 (8)	Cr1 ^{vii} —Cr1—C1 ^{iv}	103.11 (10)
La1 ^{xvi} —La2—Ge1 ^{xiii}	55.083 (13)	Cr1 ⁱ —Cr1—C1	50.45 (11)
La1 ^{xvi} —La2—Ge1 ^{xiv}	147.964 (10)	Cr1 ⁱ —Cr1—C1 ⁱⁱ	103.11 (10)
La1 ^{xvi} —La2—Cr1 ^{vi}	98.244 (13)	Cr1 ⁱ —Cr1—C1 ^{iv}	103.11 (10)
La1 ^{xvi} —La2—Cr1 ^{vii}	53.041 (13)	C1—Cr1—C1 ⁱⁱ	119.45 (4)
La1 ^{xvi} —La2—Cr1 ⁱ	76.602 (13)	C1—Cr1—C1 ^{iv}	119.45 (4)
La1 ^{xvi} —La2—C1 ^{vi}	79.52 (2)	C1 ⁱⁱ —Cr1—C1 ^{iv}	119.45 (4)
La1 ^{xvi} —La2—C1 ^{xv}	113.23 (10)	La1—C1—La1 ⁱ	96.09 (19)
La1 ^{xvi} —La2—C1 ^{xvi}	39.92 (8)	La1—C1—La2 ^{vi}	95.78 (7)
La1 ^{xviii} —La2—La3	104.871 (7)	La1—C1—La2 ^{vii}	95.78 (7)
La1 ^{xviii} —La2—Ge1 ^{xii}	55.083 (13)	La1—C1—Cr1	92.41 (2)
La1 ^{xviii} —La2—Ge1 ^{xiii}	97.605 (8)	La1—C1—Cr1 ⁱ	171.5 (2)
La1 ^{xviii} —La2—Ge1 ^{xiv}	147.964 (10)	La1 ⁱ —C1—La2 ^{vi}	95.78 (7)
La1 ^{xviii} —La2—Cr1 ^{vi}	98.244 (13)	La1 ⁱ —C1—La2 ^{vii}	95.78 (7)
La1 ^{xviii} —La2—Cr1 ^{vii}	76.602 (13)	La1 ⁱ —C1—Cr1	171.5 (2)
La1 ^{xviii} —La2—Cr1 ⁱ	53.041 (13)	La1 ⁱ —C1—Cr1 ⁱ	92.41 (2)
La1 ^{xviii} —La2—C1 ^{vi}	113.23 (10)	La2 ^{vi} —C1—La2 ^{vii}	162.7 (2)

La1 ^{xviii} —La2—C1 ^{xv}	79.52 (2)	La2 ^{vi} —C1—Cr1	83.33 (10)
La1 ^{xviii} —La2—C1 ^{xvi}	39.92 (8)	La2 ^{vi} —C1—Cr1 ⁱ	83.33 (10)
La3—La2—Ge1 ^{xii}	58.029 (15)	La2 ^{vii} —C1—Cr1	83.33 (10)
La3—La2—Ge1 ^{xiii}	58.029 (15)	La2 ^{vii} —C1—Cr1 ⁱ	83.33 (10)
La3—La2—Ge1 ^{xiv}	58.029 (15)	Cr1—C1—Cr1 ⁱ	79.1 (2)
La3—La2—Cr1 ^{vi}	153.589 (14)		

Symmetry codes: (i) $x, -y+1/2, -z+1/2$; (ii) z, x, y ; (iii) $-z, -x, y$; (iv) y, z, x ; (v) $-y, z, -x$; (vi) $-x+1/2, -y+1/2, z$; (vii) $-x+1/2, y, -z+1/2$; (viii) $y-1/2, x, -z+1/2$; (ix) $y-1/2, -x+1/2, z$; (x) $-y, x, z$; (xi) $-x, z, y$; (xii) $x, y+1/2, z+1/2$; (xiii) $z+1/2, x, y+1/2$; (xiv) $y+1/2, z+1/2, x$; (xv) $z, -x+1/2, -y+1/2$; (xvi) $-y+1/2, z, -x+1/2$; (xvii) $-z+1/2, -x+1/2, y$; (xviii) $y, -z+1/2, -x+1/2$; (xix) $-x+1, -y+1, z$; (xx) $-x+1, y, -z+1$; (xxi) $x, -y+1, -z+1$; (xxii) $y, x, -z+1$; (xxiii) $-y+1, -x+1, -z+1$; (xxiv) $y, -x+1, z$; (xxv) $y-1/2, x, z$; (xxvi) $x, y-1/2, z-1/2$; (xxvii) $y, x-1/2, -z+1/2$; (xxviii) $y, -x+1/2, z-1/2$.