

Mixed occupancy: the crystal structure of scheelite-type $\text{LiLu}[\text{MoO}_4]_2$

Ingo Hartenbach^{a*} and Robin F. Hertweck^b

^aUniversity of Stuttgart, Institute of Inorganic Chemistry, Pfaffenwaldring 55, 70569 Stuttgart, Germany, and ^bGymnasium in der Glemsaue, Gröninger Str. 29, 71254 Ditzingen, Germany. *Correspondence e-mail: ingo.hartenbach@iac.uni-stuttgart.de

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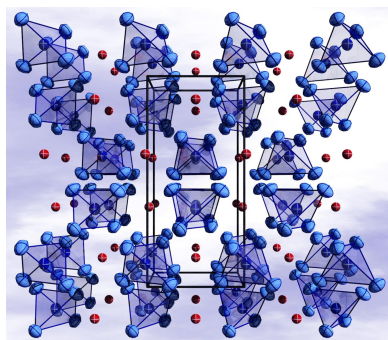
Coarse colorless single crystals of lithium lutetium bis[orthomolybdate(VI)], $\text{LiLu}[\text{MoO}_4]_2$, were obtained as a by-product from a reaction aimed at lithium derivatives of lutetium molybdate. The title compound crystallizes in the scheelite structure type (tetragonal, space group $I4_1/a$) with two formula units per unit cell. The Wyckoff position $4b$ (site symmetry $\bar{4}$) comprises a mixed occupancy of Li^+ and Lu^{3+} cations in a 1:1 ratio. In comparison with a previous powder X-ray study [Cheng *et al.* (2015). *Dalton Trans.* **44**, 18078–18089.] all atoms were refined with anisotropic displacement parameters.

1. Chemical context

The mineral powellite (CaMoO_4) is one of the main sources for molybdenum on this planet. Its tetragonal crystal structure can be described as isotypical with that of the mineral scheelite (CaWO_4) in space group type $I4_1/a$ with the c axis roughly twice as long as the respective a axis (Dickinson, 1920). The predomination of divalent cations, such as alkaline earth metals, can be changed by introducing a mixed occupancy of monovalent (*i.e.* alkali metals) and trivalent cations (*i.e.* rare-earth metals) at the respective Wyckoff position. Since the coordination number of eight around the alkaline earth metal cations in the scheelite structure usually requires larger cations, it is remarkable that the title compound also adopts the scheelite structure type although it comprises the smallest cations of both the alkali metals and the lanthanides.

2. Structural commentary

In the crystal structure of $\text{LiLu}[\text{MoO}_4]_2$ (Fig. 1) the Li^+ and Lu^{3+} cations reside at Wyckoff position $4b$ (site symmetry $\bar{4}$) exhibiting a 1:1 mixed occupancy. The coordination environment around this position is built up by eight oxide anions [$d_{\text{Li/Lu}-\text{O}} = 4 \times 2.369$ (3) and 4×2.371 (3) Å] in the shape of a trigonal dodecahedron (Fig. 2). The Mo^{6+} cations are situated in the centers of oxygen tetrahedra at Wyckoff position $4a$ (site symmetry $\bar{4}$) with distances of 4×1.774 (3) Å. The existence of $\text{LiLu}[\text{MoO}_4]_2$ was first mentioned by Cheng *et al.* (2015), with the crystal structure being refined by the Rietveld method on basis of X-ray data from microcrystalline powder. While their refinement of the lattice parameters [$a = 5.10332$ (11), $c = 11.0829$ (3) Å] resulted in similar values as for the current single-crystal study (see Table 1), no anisotropic displacement parameters of the refined atoms were given in the previous powder study. Furthermore, the structure refinement on basis of single-crystal data not only allows for a more accurate determination of the oxygen site, but also for a



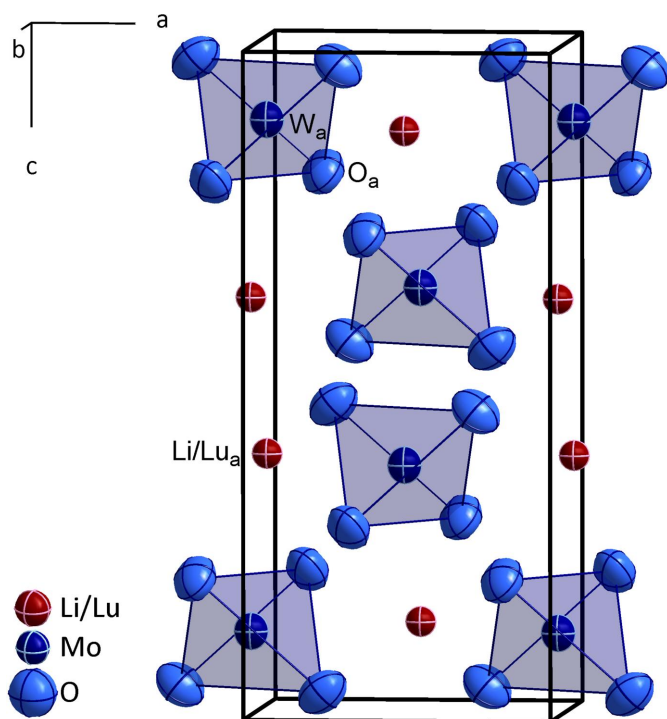


Figure 1
The augmented unit cell of $\text{LiLu}[\text{MoO}_4]_2$ in a view approximately along $[010]$, with the $[\text{MoO}_4]^{2-}$ anions in polyhedral representation and displacement ellipsoids drawn at the 95% probability level. Atomic positions marked with the subscript "a" build up the asymmetric unit.

rather precise determination of the Li:Lu ratio found at Wyckoff position $4b$ (occupancy ratio 0.483 Li:0.517 Lu when refined freely). For electroneutrality, the site occupancies were fixed to ideal values (0.5:0.5) in the final refinement step.

Since Na^+ and K^+ cations are larger than Li^+ cations and thus closer to the size of Ln^{3+} cations, it is not astonishing that the crystal volumes of $\text{NaLn}[\text{MoO}_4]_2$ and $\text{KLn}[\text{MoO}_4]_2$ compounds are considerably larger than those of the respective $\text{LiLn}[\text{MoO}_4]_2$ series. In case of the larger lanthanoids, lithium-containing scheelite-type structures according to the formula $\text{LiLn}[\text{MoO}_4]_2$ with $\text{Ln} = \text{Ce}^{3+}$ (Egorova *et al.*, 1982) and Nd^{3+} (Kolitsch, 2001) are known so far, while for Yb^{3+} as a representative of the smaller lanthanides, the crystal structure shows deviations from the Laue group $4/m$, crystallizing in space group $\bar{4}$ (Volkov *et al.*, 2005; Armand *et al.*, 2021). In all the aforementioned compounds, the rather small Li^+ cations assume a mixed occupancy with the respective lanthanoid, which is also found in the crystal structures of *e.g.* $\text{LiLn}_5[\text{W}_8\text{O}_{32}]$ for $\text{Ln} = \text{Y}$ (Dorn *et al.*, 2017) and Dy–Lu (Dorn *et al.*, 2021). However, in these structures the Li^+ cations show a sixfold coordination in contrast to the scheelite-type title compound with a coordination number of eight.

3. Synthesis and crystallization

Colorless single crystals of $\text{LiLu}[\text{MoO}_4]_2$, which remain stable towards atmospheric influences, were obtained as a by-

Table 1
Experimental details.

Crystal data	$\text{LiLu}[\text{MoO}_4]_2$
Chemical formula	501.79
M_r	Tetragonal, $I4_1/a$
Crystal system, space group	293
Temperature (K)	5.1052 (3), 11.0800 (7)
a, c (\AA)	288.78 (4)
V (\AA^3)	2
Z	$\text{Ag } K\alpha, \lambda = 0.56083 \text{ \AA}$
Radiation type	25.07
μ (mm^{-1})	$0.14 \times 0.09 \times 0.08$
Crystal size (mm)	
Data collection	Stoe Stadivari
Diffractometer	Multi-scan [<i>X-RED32</i> (Stoe & Cie, 2019) using Gaussian integration, analogous to Coppens (1970). Afterwards scaling of reflection intensities was performed within <i>LANA</i> (Koziskova <i>et al.</i> , 2016)]
Absorption correction	
T_{\min}, T_{\max}	0.031, 0.155
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4315, 352, 162
R_{int}	0.037
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.833
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.019, 0.048, 0.96
No. of reflections	352
No. of parameters	15
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e \AA^{-3})	1.14, -1.22

Computer programs: *X-AREA* (Stoe & Cie, 2019), *LANA* (Koziskova *et al.*, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *DIAMOND* (Brandenburg & Putz, 2023) and *publCIF* (Westrip, 2010).

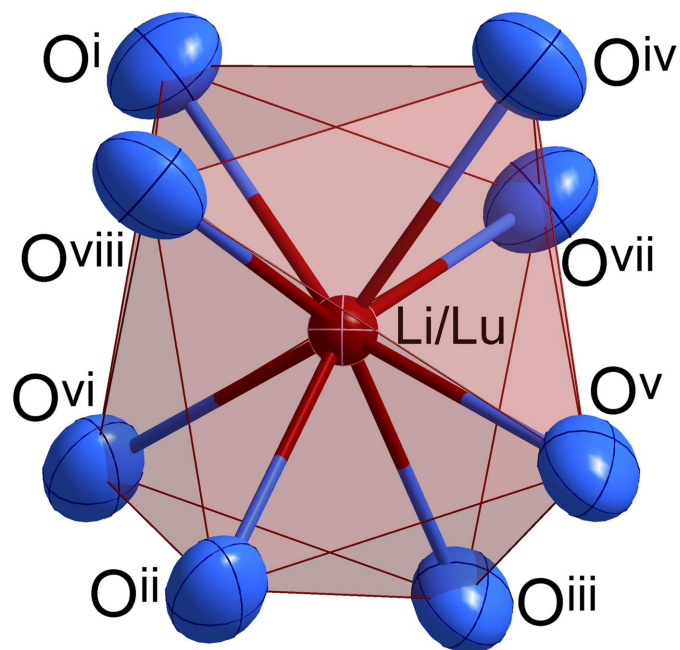


Figure 2
Oxidic coordination environment around the mixed cationic $\text{Li}^+/\text{Lu}^{3+}$ position in the shape of a trigonal dodecahedron; displacement ellipsoids are drawn at the 95% probability level [Symmetry codes: (i) $y - \frac{1}{4}, -x + \frac{3}{4}, z + \frac{3}{4}$; (ii) $x - \frac{1}{2}, y, -z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-y + \frac{1}{4}, x - \frac{1}{4}, z + \frac{3}{4}$; (v) $x - \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2}$; (vi) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (vii) $-y + \frac{3}{4}, x - \frac{1}{4}, -z + \frac{3}{4}$; (viii) $y - \frac{3}{4}, -x + \frac{3}{4}, -z + \frac{3}{4}$].

product of synthesis attempts for $\text{LiLu}_5[\text{Mo}_8\text{O}_{32}]$. Lithium chloride, lutetium sesquioxide and molybdenum trioxide in molar ratios of 3:8:24 were fused together in evacuated silica ampoules and treated with a stepwise temperature program with a peak value of 1123 K for four days. After a slow cooling ramp of another four days, the desired compound was obtained as a microcrystalline powder with single crystals of the title compound found in the bulk.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The 1:1 ratio of Li^+ and Lu^{3+} was reached by fixed occupation factors (0.5:0.5) of the respective atoms at Wyckoff position 4b.

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Mixed occupancy: the crystal structure of scheelite-type LiLu[MoO₄]₂

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Computing details

Lithium lutetium bis[orthomolybdate(VI)]

Crystal data

LiLu[MoO₄]₂

$M_r = 501.79$

Tetragonal, $I4_1/a$

$a = 5.1052$ (3) Å

$c = 11.0800$ (7) Å

$V = 288.78$ (4) Å³

$Z = 2$

$F(000) = 444$

$D_x = 5.771$ Mg m⁻³

Ag $K\alpha$ radiation, $\lambda = 0.56083$ Å

Cell parameters from 2522 reflections

$\theta = 3.5$ – 31.7°

$\mu = 25.07$ mm⁻¹

$T = 293$ K

Coarse, colorless

$0.14 \times 0.09 \times 0.08$ mm

Data collection

Stoe Stadivari

diffractometer

Radiation source: Axo Ag

Graded multilayer mirror monochromator

Detector resolution: 5.81 pixels mm⁻¹

rotation method, ω scans

Absorption correction: multi-scan

[X-Red32 (Stoe & Cie, 2019) using Gaussian integration, analogous to Coppens (1970).

Afterwards scaling of reflection intensities was performed within *LANA* (Koziskova *et al.*, 2016)]

$T_{\min} = 0.031$, $T_{\max} = 0.155$

4315 measured reflections

352 independent reflections

162 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 27.9^\circ$, $\theta_{\min} = 3.5^\circ$

$h = -8 \rightarrow 8$

$k = -8 \rightarrow 8$

$l = -15 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.019$

$wR(F^2) = 0.048$

$S = 0.96$

352 reflections

15 parameters

0 restraints

$w = 1/[\sigma^2(F_o^2) + (0.0206P)^2 + 1.1482P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.14$ e Å⁻³

$\Delta\rho_{\min} = -1.22$ e Å⁻³

Extinction correction: SHELXL (Sheldrick

2015b), $F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.044 (2)

Special details

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

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Li	0.000000	0.250000	0.625000	0.00754 (18)	0.5
Lu	0.000000	0.250000	0.625000	0.00754 (18)	0.5
Mo	0.000000	0.250000	0.125000	0.01028 (19)	
O	0.2480 (4)	0.4067 (5)	0.0394 (2)	0.0175 (6)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Li	0.0075 (2)	0.0075 (2)	0.0075 (3)	0.000	0.000	0.000
Lu	0.0075 (2)	0.0075 (2)	0.0075 (3)	0.000	0.000	0.000
Mo	0.0097 (2)	0.0097 (2)	0.0114 (3)	0.000	0.000	0.000
O	0.0203 (15)	0.0157 (14)	0.0177 (13)	-0.0012 (12)	0.0049 (11)	0.0027 (14)

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

Li—O ⁱ	2.369 (3)	Lu—O ^v	2.371 (3)
Li—O ⁱⁱ	2.369 (3)	Lu—O ^{vi}	2.371 (3)
Li—O ⁱⁱⁱ	2.369 (3)	Lu—O ^{vii}	2.371 (3)
Li—O ^{iv}	2.369 (3)	Lu—O ^{viii}	2.371 (3)
Li—O ^v	2.371 (3)	Lu—Lu ^{ix}	3.7668 (2)
Li—O ^{vi}	2.371 (3)	Lu—Lu ^x	3.7668 (2)
Li—O ^{vii}	2.371 (3)	Lu—Lu ^{xi}	3.7668 (2)
Li—O ^{viii}	2.371 (3)	Lu—Lu ^{xii}	3.7668 (2)
Lu—O ⁱ	2.369 (3)	Mo—O ^{xiii}	1.774 (3)
Lu—O ⁱⁱ	2.369 (3)	Mo—O ^{xiv}	1.774 (3)
Lu—O ⁱⁱⁱ	2.369 (3)	Mo—O ^{xv}	1.774 (3)
Lu—O ^{iv}	2.369 (3)	Mo—O	1.774 (3)
O ⁱ —Li—O ⁱⁱ	126.20 (9)	O ^{iv} —Lu—O ^{viii}	74.75 (12)
O ⁱ —Li—O ⁱⁱⁱ	126.20 (9)	O ^v —Lu—O ^{viii}	99.23 (6)
O ⁱⁱ —Li—O ⁱⁱⁱ	79.57 (15)	O ^{vi} —Lu—O ^{viii}	99.23 (6)
O ⁱ —Li—O ^{iv}	79.57 (15)	O ^{vii} —Lu—O ^{viii}	132.78 (15)
O ⁱⁱ —Li—O ^{iv}	126.20 (9)	O ⁱ —Lu—Lu ^{ix}	158.93 (7)
O ⁱⁱⁱ —Li—O ^{iv}	126.20 (9)	O ⁱⁱ —Lu—Lu ^{ix}	70.38 (7)
O ⁱ —Li—O ^v	153.18 (13)	O ⁱⁱⁱ —Lu—Lu ^{ix}	37.40 (7)
O ⁱⁱ —Li—O ^v	69.36 (7)	O ^{iv} —Lu—Lu ^{ix}	101.37 (7)
O ⁱⁱⁱ —Li—O ^v	74.75 (12)	O ^v —Lu—Lu ^{ix}	37.35 (7)
O ^{iv} —Li—O ^v	73.93 (6)	O ^{vi} —Lu—Lu ^{ix}	101.88 (8)
O ⁱ —Li—O ^{vi}	73.93 (6)	O ^{vii} —Lu—Lu ^{ix}	85.81 (7)

O ⁱⁱ —Li—O ^{vi}	74.75 (12)	O ^{viii} —Lu—Lu ^{ix}	131.46 (8)
O ⁱⁱⁱ —Li—O ^{vi}	69.36 (7)	O ⁱ —Lu—Lu ^x	37.40 (7)
O ^{iv} —Li—O ^{vi}	153.18 (13)	O ⁱⁱ —Lu—Lu ^x	158.93 (7)
O ^v —Li—O ^{vi}	132.78 (15)	O ⁱⁱⁱ —Lu—Lu ^x	101.37 (7)
O ⁱ —Li—O ^{vii}	74.75 (12)	O ^{iv} —Lu—Lu ^x	70.38 (8)
O ⁱⁱ —Li—O ^{vii}	153.18 (13)	O ^v —Lu—Lu ^x	131.46 (7)
O ⁱⁱⁱ —Li—O ^{vii}	73.93 (6)	O ^{vi} —Lu—Lu ^x	85.81 (7)
O ^{iv} —Li—O ^{vii}	69.36 (7)	O ^{vii} —Lu—Lu ^x	37.35 (7)
O ^v —Li—O ^{vii}	99.23 (6)	O ^{viii} —Lu—Lu ^x	101.88 (8)
O ^{vi} —Li—O ^{vii}	99.23 (6)	Lu ^{ix} —Lu—Lu ^x	122.737 (3)
O ⁱ —Li—O ^{viii}	69.36 (7)	O ⁱ —Lu—Lu ^{xi}	70.38 (8)
O ⁱⁱ —Li—O ^{viii}	73.93 (6)	O ⁱⁱ —Lu—Lu ^{xi}	101.37 (7)
O ⁱⁱⁱ —Li—O ^{viii}	153.18 (13)	O ⁱⁱⁱ —Lu—Lu ^{xi}	158.93 (7)
O ^{iv} —Li—O ^{viii}	74.75 (12)	O ^{iv} —Lu—Lu ^{xi}	37.40 (7)
O ^v —Li—O ^{viii}	99.23 (6)	O ^v —Lu—Lu ^{xi}	85.81 (7)
O ^{vi} —Li—O ^{viii}	99.23 (6)	O ^{vi} —Lu—Lu ^{xi}	131.46 (7)
O ^{vii} —Li—O ^{viii}	132.78 (15)	O ^{vii} —Lu—Lu ^{xi}	101.88 (8)
O ⁱ —Lu—O ⁱⁱ	126.20 (9)	O ^{viii} —Lu—Lu ^{xi}	37.35 (7)
O ⁱ —Lu—O ⁱⁱⁱ	126.20 (9)	Lu ^{ix} —Lu—Lu ^{xi}	122.737 (3)
O ⁱⁱ —Lu—O ⁱⁱⁱ	79.57 (15)	Lu ^x —Lu—Lu ^{xi}	85.322 (6)
O ⁱ —Lu—O ^{iv}	79.57 (15)	O ⁱ —Lu—Lu ^{xii}	101.37 (7)
O ⁱⁱ —Lu—O ^{iv}	126.20 (9)	O ⁱⁱ —Lu—Lu ^{xii}	37.40 (7)
O ⁱⁱⁱ —Lu—O ^{iv}	126.20 (9)	O ⁱⁱⁱ —Lu—Lu ^{xii}	70.38 (7)
O ⁱ —Lu—O ^v	153.18 (13)	O ^{iv} —Lu—Lu ^{xii}	158.93 (7)
O ⁱⁱ —Lu—O ^v	69.36 (7)	O ^v —Lu—Lu ^{xii}	101.88 (8)
O ⁱⁱⁱ —Lu—O ^v	74.75 (12)	O ^{vi} —Lu—Lu ^{xii}	37.35 (7)
O ^{iv} —Lu—O ^v	73.93 (6)	O ^{vii} —Lu—Lu ^{xii}	131.46 (7)
O ⁱ —Lu—O ^{vi}	73.93 (6)	O ^{viii} —Lu—Lu ^{xii}	85.81 (7)
O ⁱⁱ —Lu—O ^{vi}	74.75 (12)	Lu ^{ix} —Lu—Lu ^{xii}	85.322 (5)
O ⁱⁱⁱ —Lu—O ^{vi}	69.36 (7)	Lu ^x —Lu—Lu ^{xii}	122.737 (3)
O ^{iv} —Lu—O ^{vi}	153.18 (13)	Lu ^{xi} —Lu—Lu ^{xii}	122.737 (3)
O ^v —Lu—O ^{vi}	132.78 (15)	O ^{xiii} —Mo—O ^{xiv}	106.65 (10)
O ⁱ —Lu—O ^{vii}	74.75 (12)	O ^{xiii} —Mo—O ^{xv}	106.65 (10)
O ⁱⁱ —Lu—O ^{vii}	153.18 (13)	O ^{xiv} —Mo—O ^{xv}	115.3 (2)
O ⁱⁱⁱ —Lu—O ^{vii}	73.93 (6)	O ^{xiii} —Mo—O	115.3 (2)
O ^{iv} —Lu—O ^{vii}	69.36 (7)	O ^{xiv} —Mo—O	106.65 (10)
O ^v —Lu—O ^{vii}	99.23 (6)	O ^{xv} —Mo—O	106.65 (10)
O ^{vi} —Lu—O ^{vii}	99.23 (6)	Mo—O—Li ⁱⁱⁱ	130.25 (16)
O ⁱ —Lu—O ^{viii}	69.36 (7)	Mo—O—Li ^{xvi}	120.42 (15)
O ⁱⁱ —Lu—O ^{viii}	73.93 (6)	Li ⁱⁱⁱ —O—Li ^{xvi}	105.25 (12)
O ⁱⁱⁱ —Lu—O ^{viii}	153.18 (13)		

Symmetry codes: (i) $y-1/4, -x+3/4, z+3/4$; (ii) $x-1/2, y, -z+1/2$; (iii) $-x+1/2, -y+1/2, -z+1/2$; (iv) $-y+1/4, x-1/4, z+3/4$; (v) $x-1/2, y-1/2, z+1/2$; (vi) $-x+1/2, -y+1, z+1/2$; (vii) $-y+3/4, x-1/4, -z+3/4$; (viii) $y-3/4, -x+3/4, -z+3/4$; (ix) $-x, -y, -z+1$; (x) $-x+1/2, -y+1/2, -z+3/2$; (xi) $-x-1/2, -y+1/2, -z+3/2$; (xii) $-x, -y+1, -z+1$; (xiii) $-x, -y+1/2, z$; (xiv) $-y+1/4, x+1/4, -z+1/4$; (xv) $y-1/4, -x+1/4, -z+1/4$; (xvi) $x+1/2, y+1/2, z-1/2$.