SH0121

Supplementary Materials

Supp 1. Residual electron density around Li^+ cation in spodumene after the multipolar refinements for the two radiations. Contour intervals 0.1 $eÅ^{-3}$; negative contours are dashed, zero contour omitted. (Fourier summation over data with $0. \leq s \leq 0.9$ $Å^{-1}$).

Supp 2. Experimental (a) and Dynamic (b) deformation electron densities in the Al-O-Si bridge planes : Al-O_1-Si and Al-O_2-Si from MoKα data.
Contour intervals 0.1 $eÅ^{-3}$; negative contours are dashed, zero contour omitted.

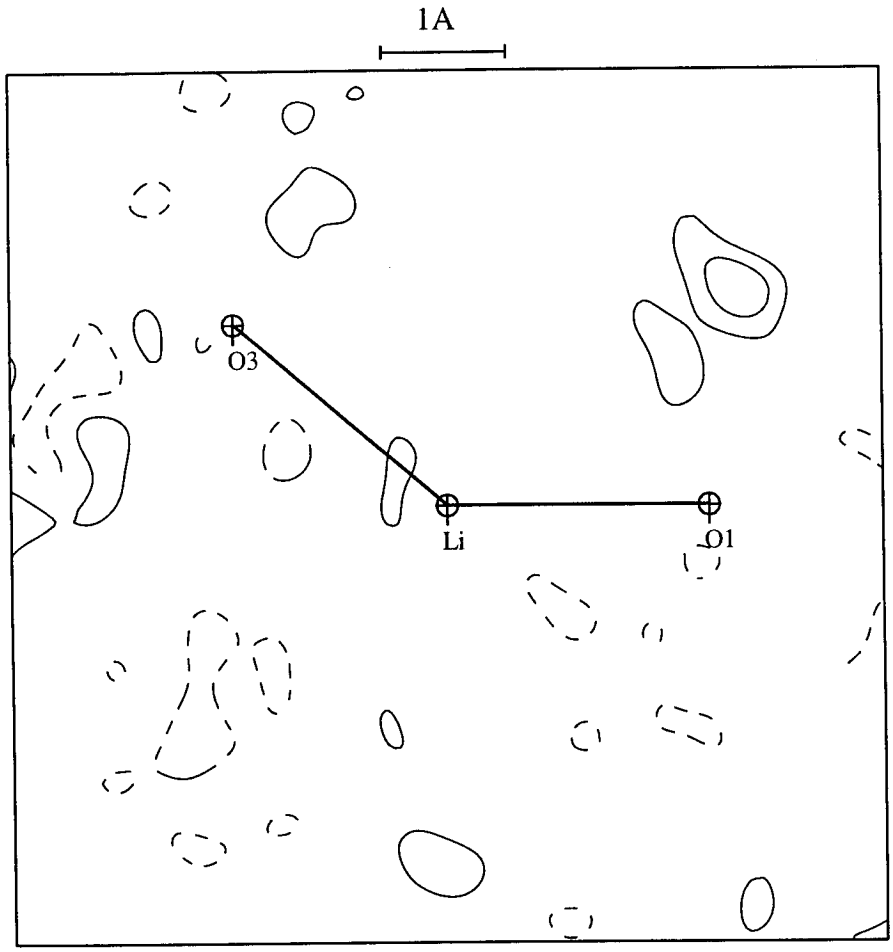
Supp 3. Experimental (a) and Dynamic (b) deformation electron densities in the Al-O-Si bridge planes : Al-O_1-Si and Al-O_2-Si from AgKα data.
Contour intervals 0.1 $eÅ^{-3}$; negative contours are dashed, zero contour omitted.

Supp 4. Experimental (a) and Dynamic (b) deformation electron densities in Si-O_3-Si bridge planes : from MoKα and AgKα data.
Contour intervals 0.1 $eÅ^{-3}$; negative contours are dashed, zero contour omitted.

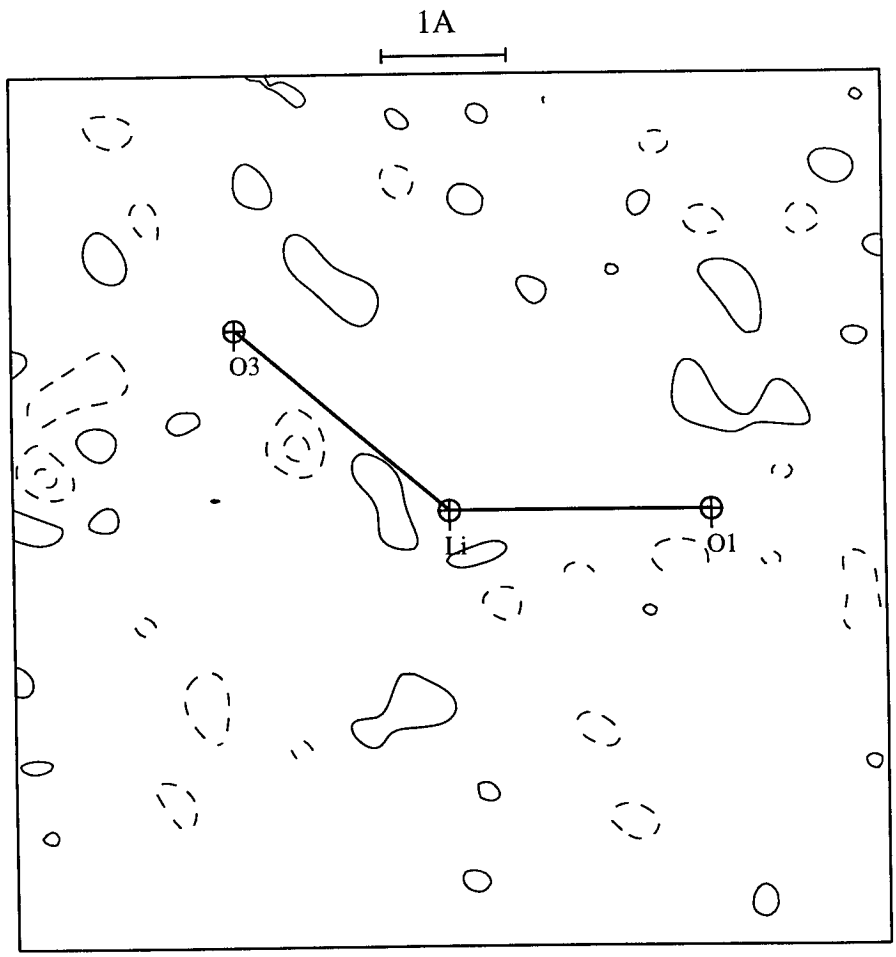
Supp 5. Table of the valence and multipole populations (P_{val} and P_{lm}) and the expansion-contraction coefficients (κ and κ') after multipole refinements 2 and 2' in Table 2. (only significant values, * correspond to the non-refined populations for Aluminium atom).

~~**Supp 6.** List of the structure factors of the MoKα data.~~

~~**Supp 7.** List of the structure factors of the AgKα data.~~

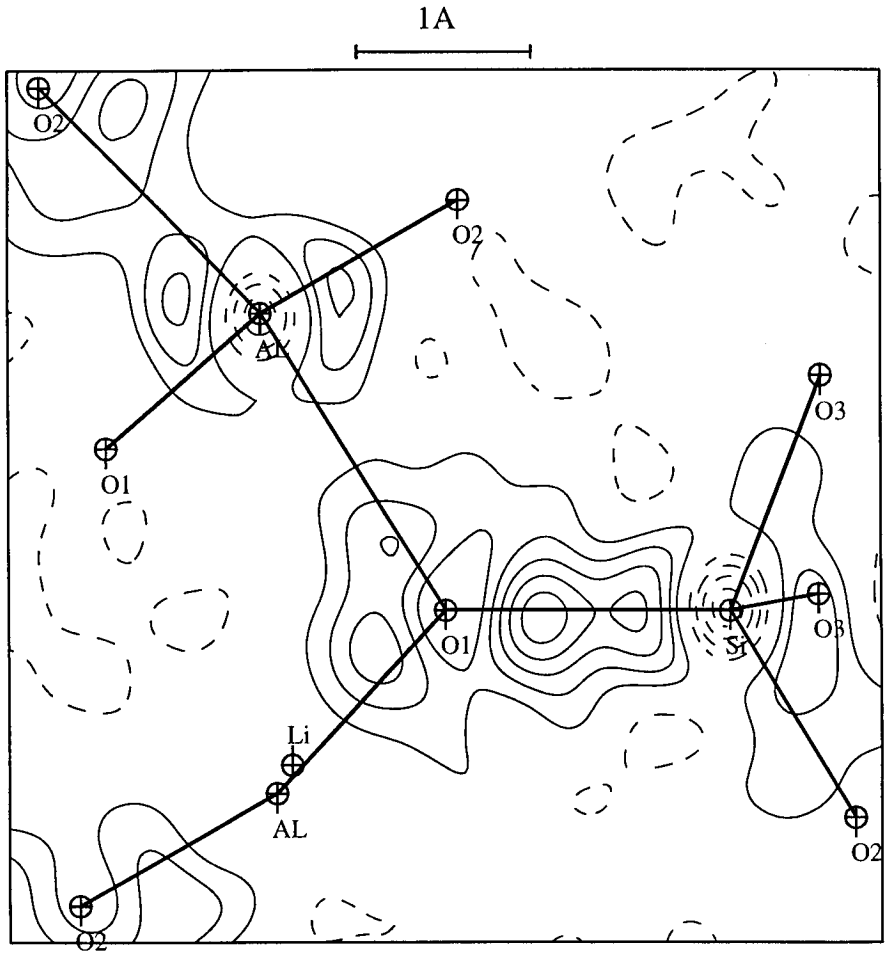


MoKα

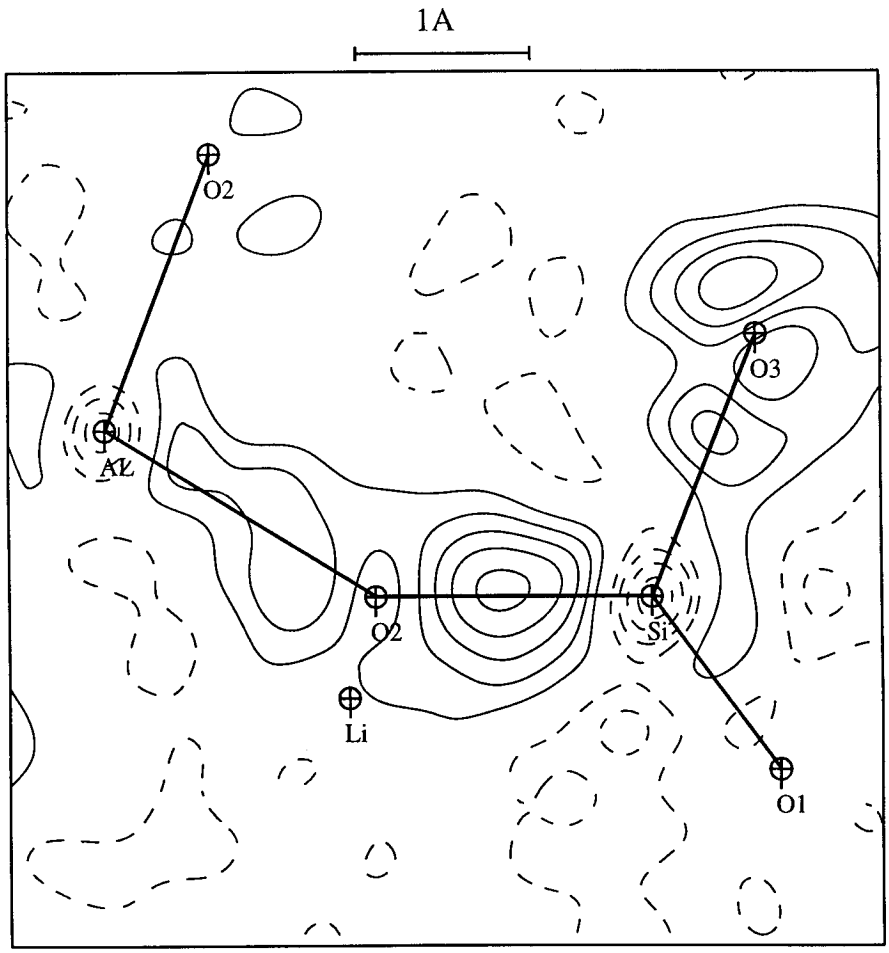


AgKα

Suppl

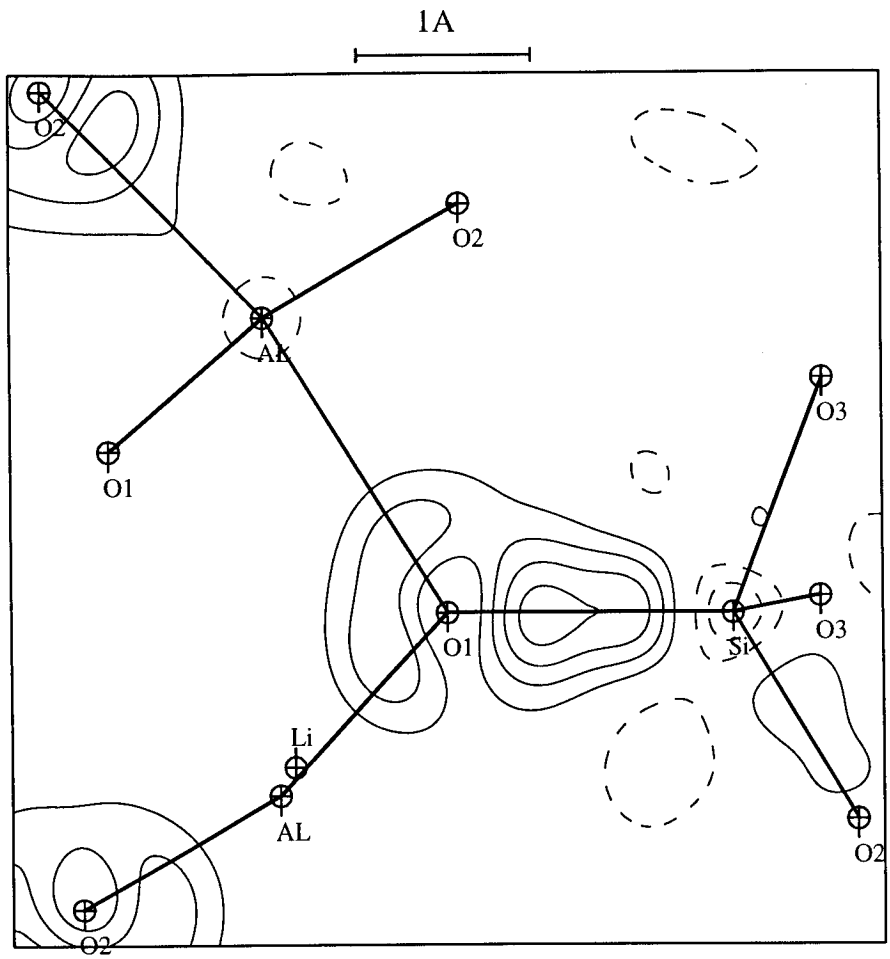


MoKα

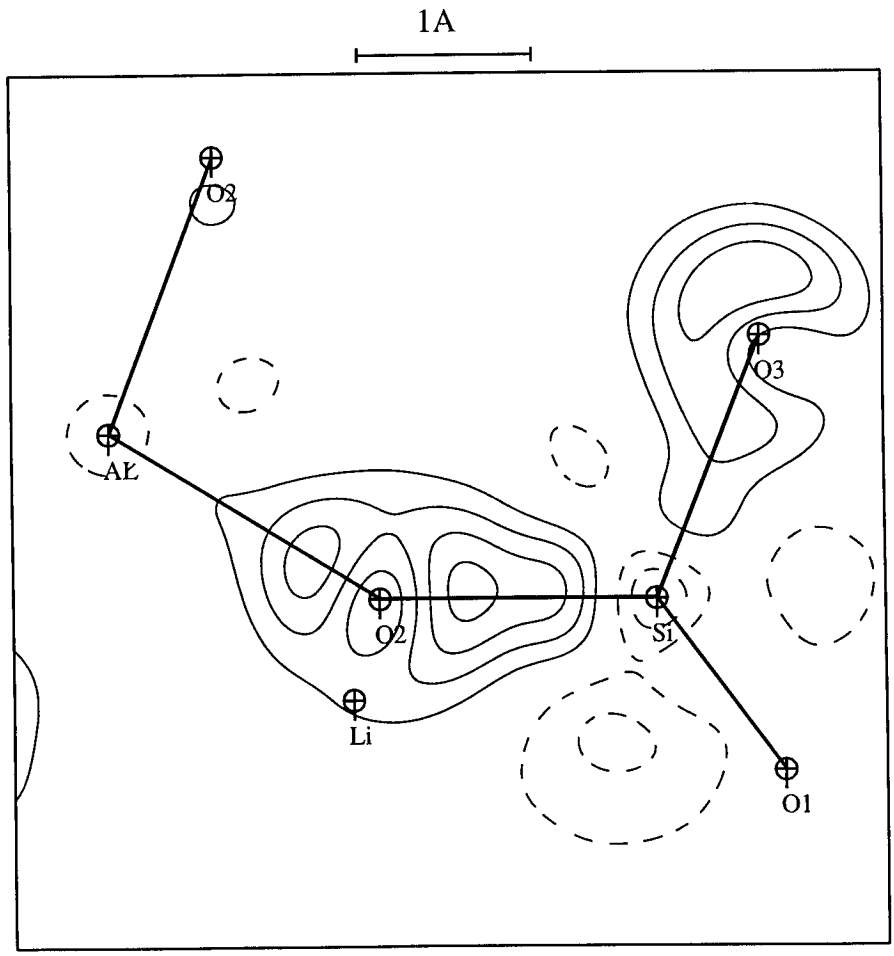


(a)

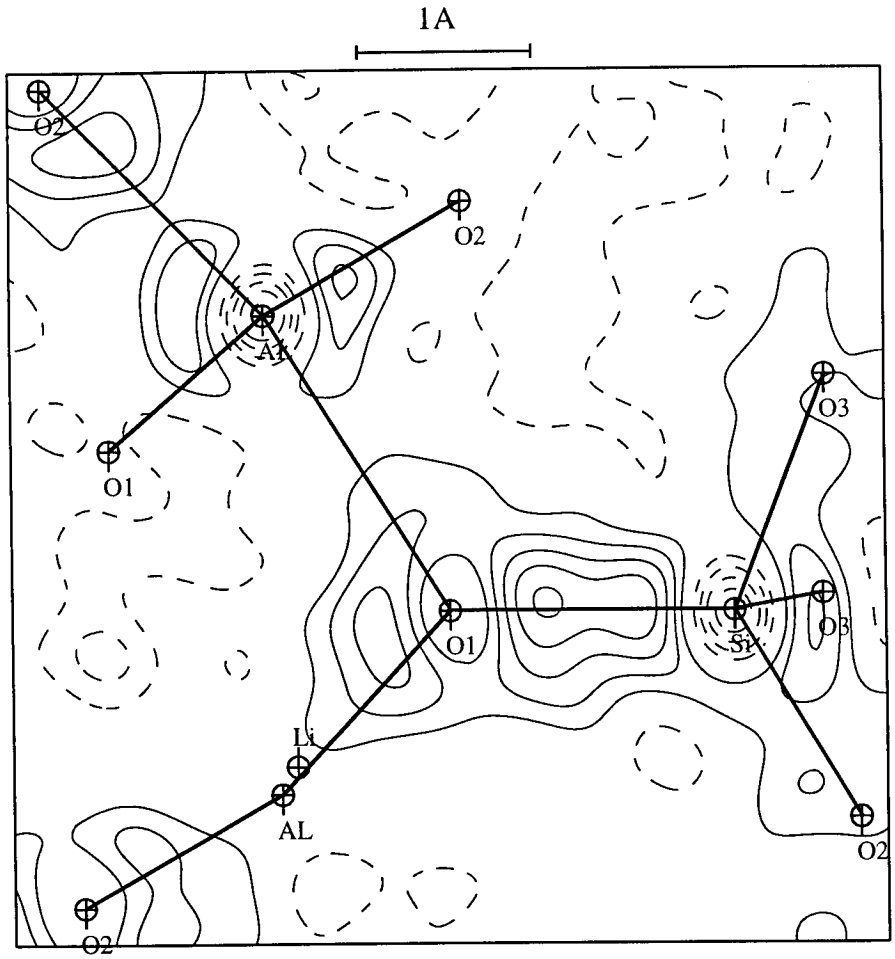
Supp 2



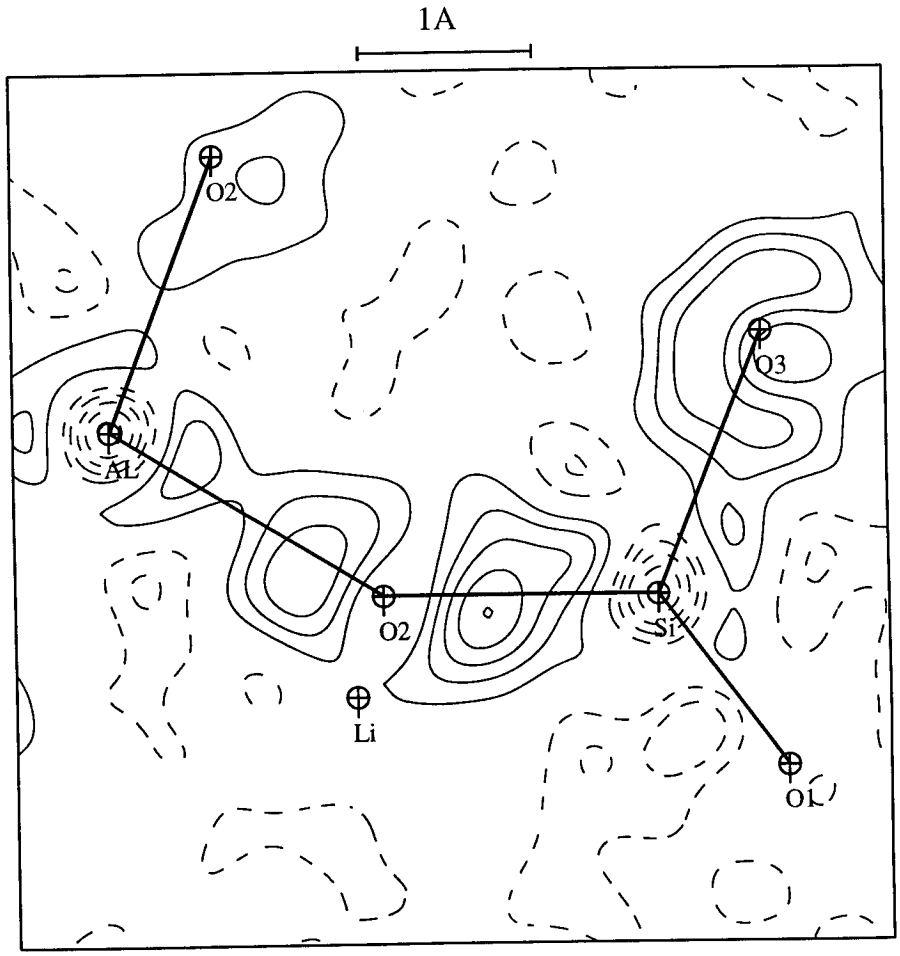
MoKa



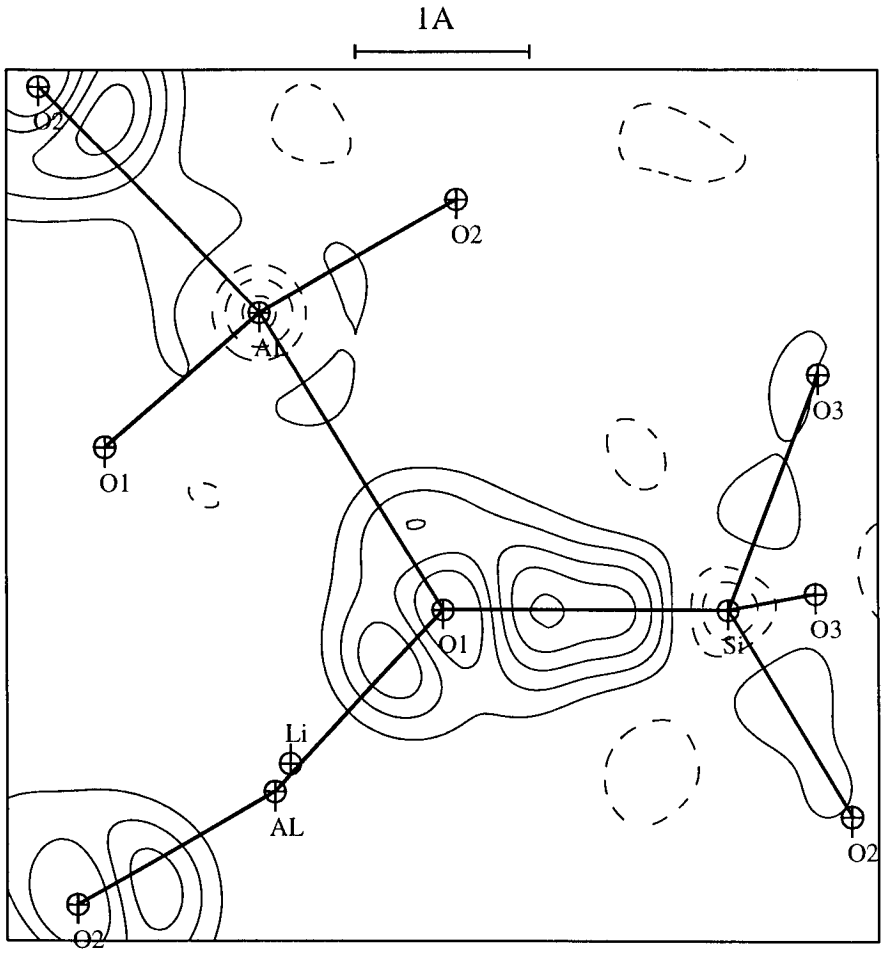
(b)



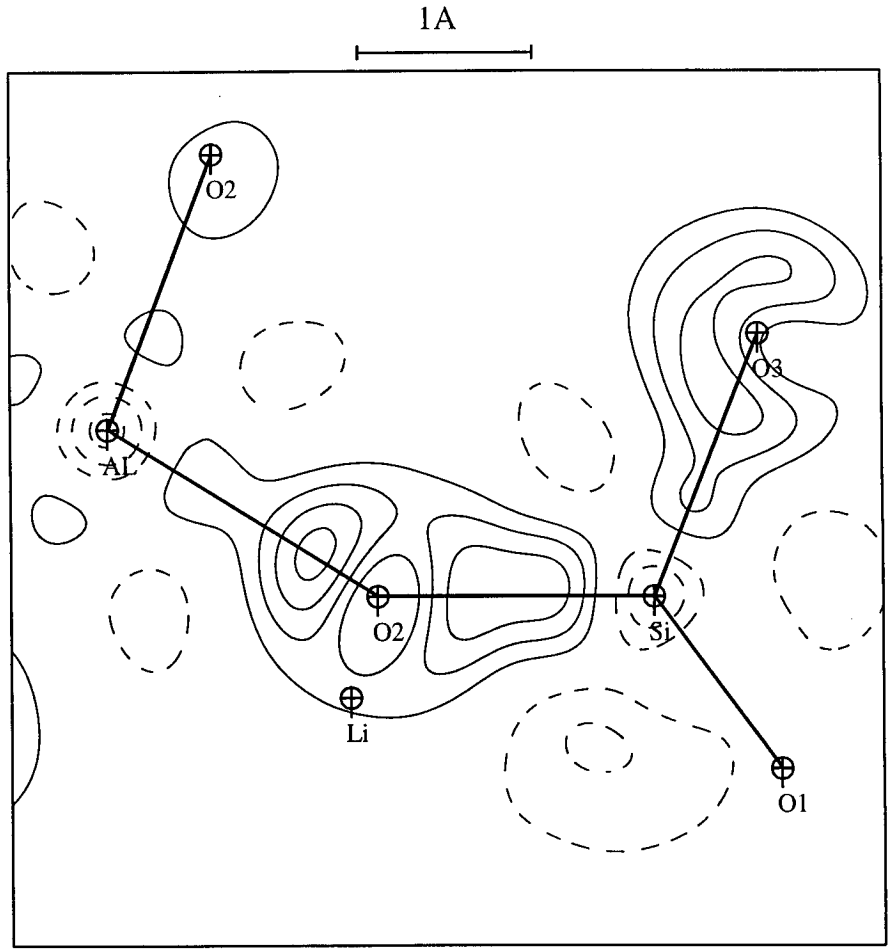
AgKα



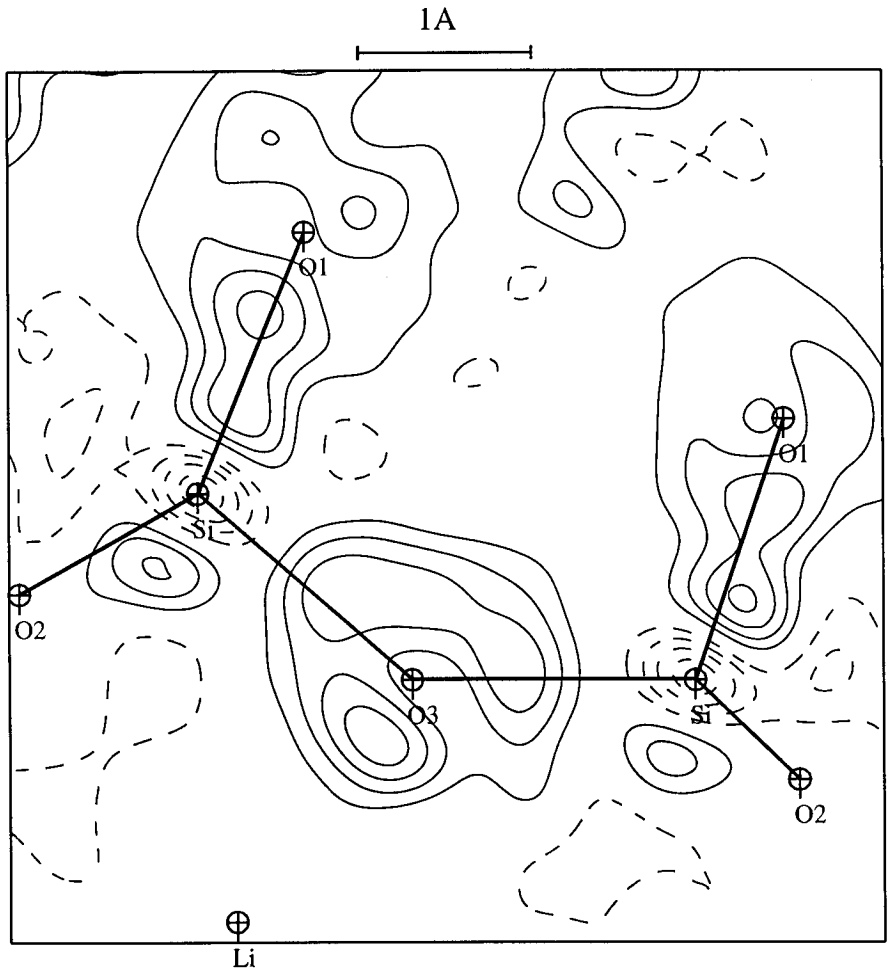
(a)



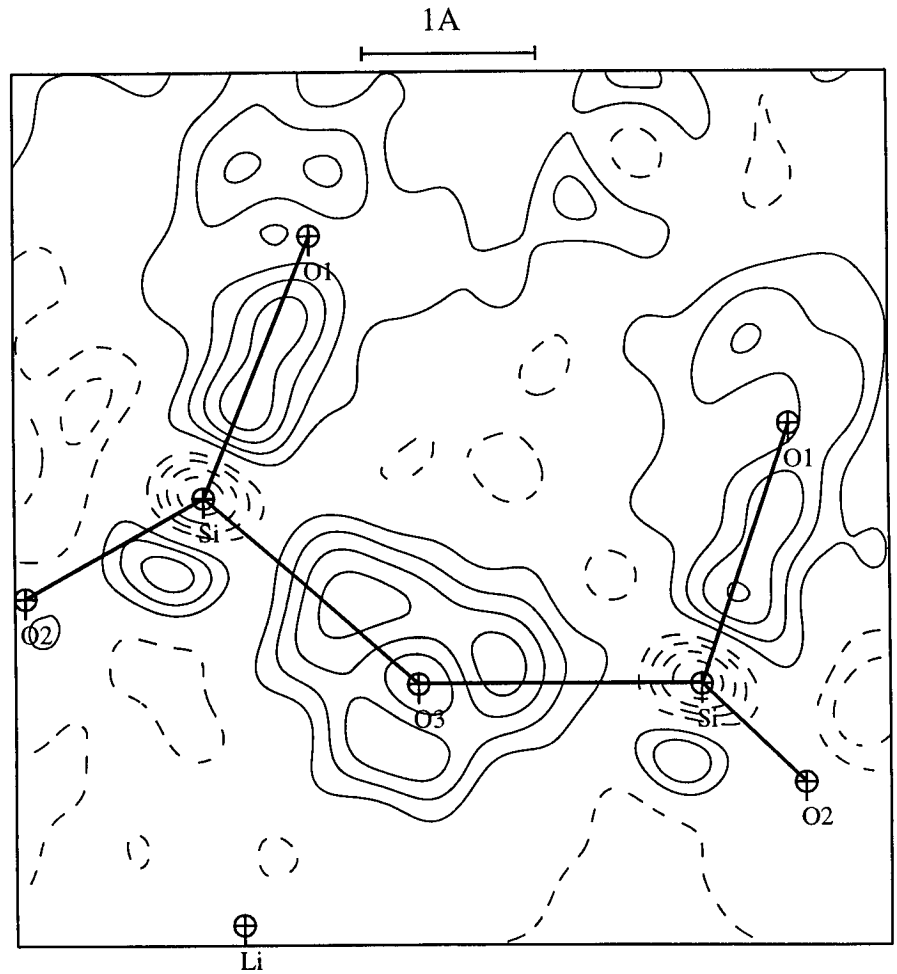
AgKα



(b)



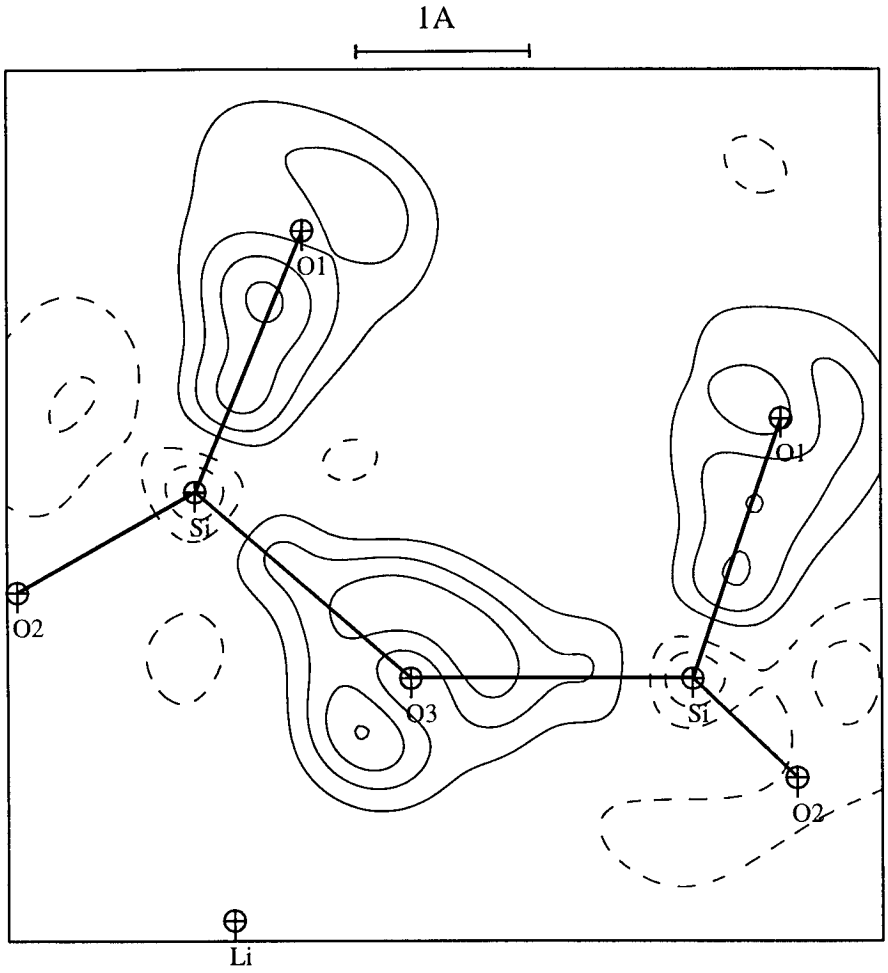
MoKα



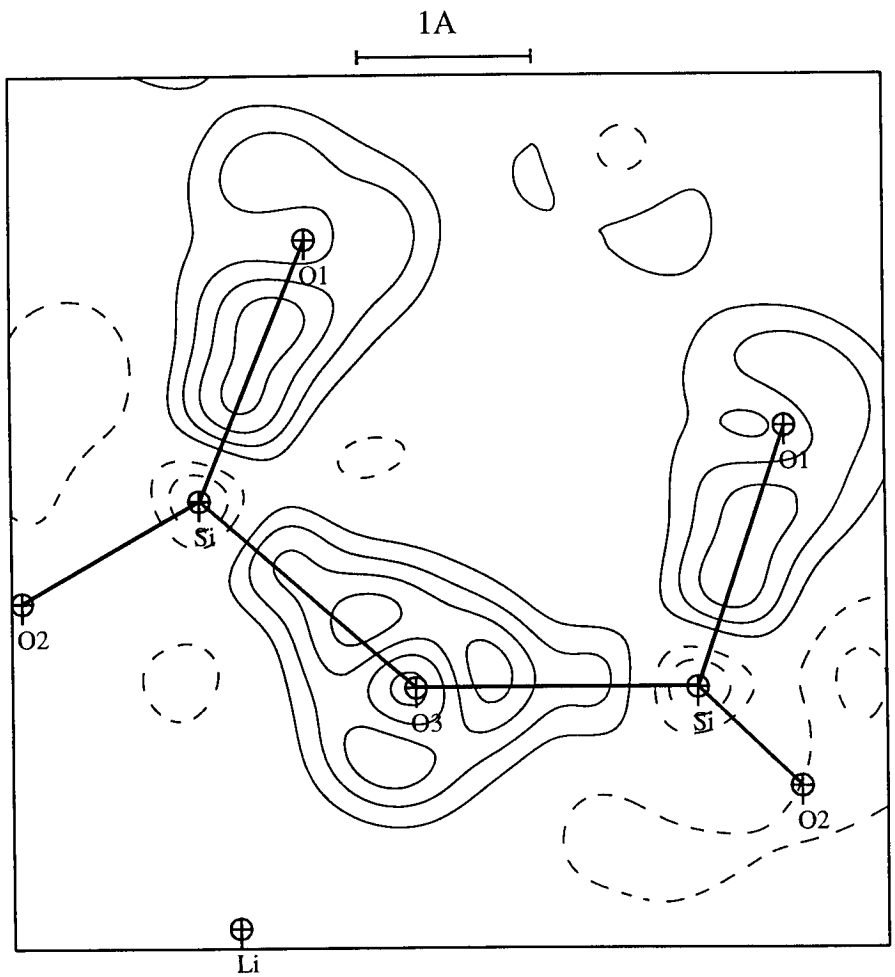
AgKα

(a)

Supp 4



MoKα



AgKα

(b)

Supp 4

	Si	Al	O_1	O_2	O_3	Li
κ	1.08(1)	1.00(3)	0.968(3)	0.970(3)	0.968(3)	1.0
κ'	0.95(1)	0.97(4)	1.04(6)	0.86(5)	0.95(5)	
P_{val}	3.00(7)	2.24(6)	6.58(4)	6.57(5)	6.72(4)	
P_{11}	-	*	-0.02(1)	-	-	
P_{1-1}	0.04(2)	*	0.01(1)	0.01(1)	-	
P_{10}	-	*	-	-	-0.03(1)	
P_{20}	-0.20(3)	0.01(2)	0.02(1)	-0.03(1)	-0.03(1)	
P_{21}	-	*	-	-	-0.04(1)	
P_{2-1}	-	-0.03(2)	-0.01(1)	0.05(1)	0.03(1)	
P_{22}	0.03(2)	-0.03(1)	0.03(1)	0.02(1)	-	
P_{2-2}	-0.13(2)	*	-	-0.02(1)	0.03(1)	
P_{30}	0.03(2)	*	0.01(1)	-	-0.02(1)	
P_{31}	-0.21(2)	0.04(1)	-0.02(1)	-0.01(1)	0.02(1)	
P_{3-1}	-0.29(2)	*	-0.02(1)	-0.01(1)	-0.01(1)	
P_{32}	-	*	-	-0.01(1)	-	
P_{3-2}	-	0.01(1)	-0.02(1)	-	-	
P_{33}	0.31(2)	0.03(1)	0.01(1)	-	0.02(1)	
P_{3-3}	0.04(2)	*	-0.01(1)	-0.02(1)	-	
P_{40}	0.09(2)	0.09(2)				
P_{41}	0.04(1)	*				
P_{4-1}	-0.06(2)	0.00(1)				
P_{42}	-0.02(2)	0.04(2)				
P_{4-2}	0.16(2)	*				
P_{43}	-	*				
P_{4-3}	-	-0.04(2)				
P_{44}	0.03(1)	-0.08(2)				
P_{4-4}	0.07(2)	*				

MoKα data (multipole refinement 2 in Table 2)

	Si	Al	O_1	O_2	O_3	Li
κ	1.12(1)	1.34(4)	0.960(3)	0.958(3)	0.963(3)	1.0
κ'	0.93(1)	0.91(3)	0.98(6)	0.89(5)	1.00(7)	
P_{val}	2.95(8)	1.44(4)	6.75(4)	6.77(5)	6.81(5)	
P_{11}	-	*	-0.03(1)	-0.04(1)	0.02(1)	
P_{1-1}	0.08(3)	*	-	0.03(1)	-	
P_{10}	0.03(3)	*	-	-	-0.02(1)	
P_{20}	-0.15(3)	0.08(3)	-	-	-0.04(1)	
P_{21}	-	*	-0.02(1)	-	-0.03(1)	
P_{2-1}	-0.10(2)	-0.04(2)	-	0.03(1)	-	
P_{22}	0.04(3)	-0.04(2)	0.02(1)	0.02(1)	-	
P_{2-2}	-0.17(3)	*	-0.01(1)	-0.03(1)	-	
P_{30}	0.07(2)	*	0.01(1)	-	-0.02(1)	
P_{31}	-0.22(2)	0.04(2)	-0.01(1)	-	0.02(1)	
P_{3-1}	-0.30(2)	*	-0.02(1)	-0.01(1)	-	
P_{32}	-	*	0.02(1)	-	-	
P_{3-2}	-	0.03(2)	-0.02(1)	-0.02(1)	-	
P_{33}	0.36(2)	0.01(2)	0.04(1)	-	0.03(1)	
P_{3-3}	0.04(2)	*	-	-0.01(1)	-0.01(1)	
P_{40}	0.12(3)	0.06(2)				
P_{41}	-	*				
P_{4-1}	-	0.01(2)				
P_{42}	-0.02(2)	0.01(2)				
P_{4-2}	0.20(2)	*				
P_{43}	-0.02(2)	*				
P_{4-3}	0.02(2)	-0.07(2)				
P_{44}	0.03(2)	-0.13(2)				
P_{4-4}	-	*				

AgKα data (multipole refinement 2' in Table 2)

SUPP 5