Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

From Symmetry Breaking in the Bulk to Phase Transitions at the Surface: A Quantum-Mechanical Exploration of Li_6PS_5Cl Argyrodite superionic conductor.

Maddalena D' Amore,*,† Loredana Edith Daga,† Riccardo Rocca,†,‡ Mauro Francesco Sgroi,‡ Naiara Leticia Marana,† Silvia Maria Casassa,† Lorenzo Maschio,*,† and Anna Maria Ferrari*,†

†*Dipartimento di Chimica, Università di Torino, Via P. Giuria 5, 10125 Torino, Italy*

‡*Centro Ricerche FIAT S.C.p.A., Strada Torino 50, 10043, Orbassano (To), Italy*

E-mail: maddalena.damore@unito.it; lorenzo.maschio@unito.it; anna.ferrari@unito.it

In this part we provide the structural information about Models numbered as 1 to 4 in main text of the present manuscript and whose lattice details are reported in Table 2 of the same paper.

Supporting Information Available

The following CIF files are available:

- Model 1: CIF file for Model 1 reported in Table 2 of the manuscript;

data-cubic-0-moldraw

_audit_creation_date 2022-06-28

_symmetry_space_group_name_H-M 'F-43M'

_symmetry_Int_Tables_number 216

_symmetry_cell_setting cubic

loop_

_symmetry_equiv_pos_as_xyz

x,y,z

-x,-y,z

-x,y,-z

x,-y,-z

z,x,y

z,-x,-y

-z,-x,y

-z,x,-y

y,z,x

-y,z,-x

y,-z,-x

-y,-z,x

y,x,z

-y,-x,z

y,-x,-z

-y,x,-z

x,z,y

-x,z,-y

-x,-z,y

x,-z,-y

z,y,x

z,-y,-x

-z,y,-x

-z,-y,x

x,y+1/2,z+1/2

-x,-y+1/2,z+1/2

-x,y+1/2,-z+1/2

x,-y+1/2,-z+1/2

z,x+1/2,y+1/2

z,-x+1/2,-y+1/2

-z,-x+1/2,y+1/2

-z,x+1/2,-y+1/2

y,z+1/2,x+1/2

-y,z+1/2,-x+1/2

y,-z+1/2,-x+1/2

-y,-z+1/2,x+1/2

y,x+1/2,z+1/2

-y,-x+1/2,z+1/2

y,-x+1/2,-z+1/2

-y,x+1/2,-z+1/2

x,z+1/2,y+1/2

-x,z+1/2,-y+1/2

-x,-z+1/2,y+1/2

x,-z+1/2,-y+1/2

z,y+1/2,x+1/2

z,-y+1/2,-x+1/2

-z,y+1/2,-x+1/2

-z,-y+1/2,x+1/2

x+1/2,y,z+1/2

-x+1/2,-y,z+1/2

-x+1/2,y,-z+1/2

x+1/2,-y,-z+1/2

z+1/2,x,y+1/2

z+1/2,-x,-y+1/2

-z+1/2,-x,y+1/2

-z+1/2,x,-y+1/2

y+1/2,z,x+1/2

-y+1/2,z,-x+1/2

y+1/2,-z,-x+1/2

-y+1/2,-z,x+1/2

y+1/2,x,z+1/2

-y+1/2,-x,z+1/2

y+1/2,-x,-z+1/2

-y+1/2,x,-z+1/2

x+1/2,z,y+1/2

-x+1/2,z,-y+1/2

-x+1/2,-z,y+1/2

x+1/2,-z,-y+1/2

z+1/2,y,x+1/2

z+1/2,-y,-x+1/2

-z+1/2,y,-x+1/2

-z+1/2,-y,x+1/2

x+1/2,y+1/2,z

-x+1/2,-y+1/2,z

-x+1/2,y+1/2,-z

x+1/2,-y+1/2,-z

z+1/2,x+1/2,y

z+1/2,-x+1/2,-y

-z+1/2,-x+1/2,y

-z+1/2,x+1/2,-y

y+1/2,z+1/2,x

-y+1/2,z+1/2,-x

y+1/2,-z+1/2,-x

-y+1/2,-z+1/2,x

y+1/2,x+1/2,z

-y+1/2,-x+1/2,z

y+1/2,-x+1/2,-z

-y+1/2,x+1/2,-z

x+1/2,z+1/2,y

-x+1/2,z+1/2,-y

-x+1/2,-z+1/2,y

x+1/2,-z+1/2,-y

z+1/2,y+1/2,x

z+1/2,-y+1/2,-x

-z+1/2,y+1/2,-x

-z+1/2,-y+1/2,x

_cell_length_a 10.2536

_cell_length_b 10.2536

_cell_length_c 10.2536

_cell_angle_alpha 90.0000

_cell_angle_beta 90.0000

_cell_angle_gamma 90.0000

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_adp_type

_atom_site_occupancy

Li1 Li -0.97688 -0.75000 -0.75000 0.00000 Uiso 1.00

P1 P -0.50000 -0.50000 -0.50000 0.00000 Uiso 1.00

S1 S -0.75000 -0.75000 -0.75000 0.00000 Uiso 1.00

S2 S -0.61614 -0.38386 -0.61614 0.00000 Uiso 1.00

Cl1 Cl 0.00000 0.00000 0.00000 0.00000 Uiso 1.00

loop_

_geom_bond_atom_site_label_1

_geom_bond_atom_site_label_2

_geom_bond_distance

_geom_bond_site_symmetry_2

_ccdc_geom_bond_type

P1 S2 2.063 . A

P1 S2 2.063 2_445 A

P1 S2 2.063 3_454 A

P1 S2 2.063 4_544 A

- Model 2: CIF file relative to Model 2 reported in Table 2 of the main text of the

manuscript;

data_P1_bulk_magda_scan

_audit_creation_date 2022-06-28

_symmetry_space_group_name_H-M 'P1'

_symmetry_Int_Tables_number 1

_symmetry_cell_setting triclinic

loop_

_symmetry_equiv_pos_as_xyz

x,y,z

_cell_length_a 9.9631

_cell_length_b 10.0511

_cell_length_c 10.0134

_cell_angle_alpha 87.8917

_cell_angle_beta 89.0432

_cell_angle_gamma 86.8056

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_adp_type

_atom_site_occupancy

LI1 Li -0.19848 -0.21316 -0.04110 0.00000 Uiso 1.00

LI2 Li 0.17518 -0.19335 0.01524 0.00000 Uiso 1.00

LI3 Li -0.02781 -0.27700 -0.32003 0.00000 Uiso 1.00

LI4 Li -0.30275 -0.01573 -0.29047 0.00000 Uiso 1.00

LI5 Li 0.02834 0.18037 -0.17561 0.00000 Uiso 1.00

LI6 Li 0.30002 0.02200 -0.30309 0.00000 Uiso 1.00

P7 P 0.49751 -0.49448 -0.49877 0.00000 Uiso 1.00

CL8 Cl 0.00809 0.01679 0.03528 0.00000 Uiso 1.00

S9 S -0.25820 -0.24983 -0.26129 0.00000 Uiso 1.00

S10 S 0.13150 -0.11613 -0.38847 0.00000 Uiso 1.00

S11 S -0.11941 0.12111 -0.37128 0.00000 Uiso 1.00

S12 S 0.10305 -0.36830 -0.12404 0.00000 Uiso 1.00

S13 S 0.38229 -0.11478 -0.10840 0.00000 Uiso 1.00

- Model 3: CIF file relative to Model 3 reported in Table 2 of the main text of the manuscript;

data_li48h_ahlrichs_cif_scon

_audit_creation_date 2022-06-28

_symmetry_space_group_name_H-M 'P1'

_symmetry_Int_Tables_number 1

_symmetry_cell_setting triclinic

loop_

_symmetry_equiv_pos_as_xyz

x,y,z

_cell_length_a 10.0434

_cell_length_b 10.0126

_cell_length_c 9.9573

_cell_angle_alpha 90.8839

_cell_angle_beta 93.1369

_cell_angle_gamma 87.9161

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_adp_type

_atom_site_occupancy

LI1 Li -0.21924 -0.17587 -0.02563 0.00000 Uiso 1.00

LI2 Li -0.17670 0.17918 0.03077 0.00000 Uiso 1.00

LI3 Li -0.01834 -0.19367 -0.19806 0.00000 Uiso 1.00

LI4 Li 0.19740 -0.01156 0.17750 0.00000 Uiso 1.00

LI5 Li 0.21508 0.04501 -0.19449 0.00000 Uiso 1.00

LI6 Li 0.01924 -0.20520 0.19950 0.00000 Uiso 1.00

P7 P 0.49824 -0.49734 0.49982 0.00000 Uiso 1.00

CL8 Cl -0.01226 -0.03121 0.00965 0.00000 Uiso 1.00

S9 S -0.24669 -0.23520 -0.25574 0.00000 Uiso 1.00

S10 S 0.12004 -0.10759 -0.36613 0.00000 Uiso 1.00

S11 S -0.12786 0.12808 -0.39455 0.00000 Uiso 1.00

S12 S 0.11879 -0.38782 -0.11572 0.00000 Uiso 1.00

S13 S 0.38230 -0.12461 -0.11692 0.00000 Uiso 1.00

- Model 4: CIF file relative to Model 4 reported in Table 2 of the main text of the manuscript;

data_su_li48h_2sym_ahlrichs_cif

_audit_creation_date 2022-06-28

_audit_creation_method 'Moldraw'

_symmetry_space_group_name_H-M 'PM'

_symmetry_Int_Tables_number 6

_symmetry_cell_setting monoclinic

loop_

_symmetry_equiv_pos_as_xyz

x,y,z

_cell_length_a 9.7768

_cell_length_b 9.7768

_cell_length_c 10.6982

_cell_angle_alpha 90.0203

_cell_angle_beta 90.0203

_cell_angle_gamma 92.4085

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_adp_type

_atom_site_occupancy

LI1 Li -0.15480 0.15453 0.04537 0.00000 Uiso 1.00

LI2 Li 0.15453 -0.15480 0.04537 0.00000 Uiso 1.00

LI3 Li -0.02220 -0.22162 -0.20183 0.00000 Uiso 1.00

LI4 Li -0.22162 -0.02220 -0.20183 0.00000 Uiso 1.00

LI5 Li 0.02241 0.22195 -0.20179 0.00000 Uiso 1.00

LI6 Li 0.22195 0.02241 -0.20179 0.00000 Uiso 1.00

P7 P 0.49995 0.49995 -0.47039 0.00000 Uiso 1.00

CL8 Cl -0.00009 -0.00009 -0.06388 0.00000 Uiso 1.00

S9 S -0.24996 -0.24996 -0.26900 0.00000 Uiso 1.00

S10 S 0.12461 -0.12457 -0.37264 0.00000 Uiso 1.00

S11 S -0.12457 0.12461 -0.37264 0.00000 Uiso 1.00

S12 S 0.12434 -0.37566 -0.08741 0.00000 Uiso 1.00

S13 S 0.37543 -0.12457 -0.08733 0.00000 Uiso 1.00