Supplemental material to "Packing of Adsorbed Molecules in Microporous Polymorphs Aluminium Methylphosphonates α and β"

Christian Schumacher, Jorge Gonzalez, Paul A. Wright and Nigel A. Seaton

Structure refinement of AlMePO-α

A sample of fully deuterated AlMePO-α, $Al_2(CD_3PO_3)_3$, phase pure by X-ray powder diffraction, made with perdeuterated methylphosphonic acid, was heated under vacuum to remove all adsorbed molecules and sealed in a thin-walled quartz tube. Neutron powder diffraction data were collected at 2K on the High Resolution Powder Diffraction (HRPD) station at ISIS, the Rutherford Appleton Laboratory, with the quartz tube held in a vanadium can. Data were recorded on two banks of detectors positioned at 89.3° and 168.3° in 2θ, over the time-of-flight window 40 to 120 ms and refined using the GSAS suite of programs.

The neutron diffraction data, collected as two diffraction patterns, was initially refined using crystallographic parameters available from the room temperature single crystal X-ray structure determination and default values for the instrumental parameters. Background was measured input manually for the two histograms. The analysis was a 2-phase refinement, in which scattering from the vanadium can was included. Initially constrained refinement of the aluminium methyl phosphonate structure was performed, in which the atomic parameters were allowed to vary, and the constraints were gradually removed. Refinements of lattice parameters was performed throughout, while profile coefficients were refined alternately with isotropic temperature factors of the atoms, which were constrained to be equal for atoms of the same kind. The final fit was acceptable, with total R_{wp} values for fits to the two histograms taken being 3.3 and 2.8 %, respectively. The fits to the two histograms of data are shown in figures S1a and S1b. The final refined atomic coordinates and thermal parameters are given in Table S1, and selected bond lengths and angles are given in Tables S2 and S3. The deuterium atom positions were located, and are expected to be fixed at this temperature from other studies, but at 77 K (the temperature of the nitrogen adsorption) they would be rotating very rapidly.

Figure S1. Fitted profiles of the powder time-of-flight (40 - 120 ms) pulsed neutron diffraction data collected on dehydrated AlMePO-α at 2 K on detectors at (above) 168° 2θ and (below) 89° 2θ. R_{wp} values for the two profiles are 3.3 and 2.8%, respectively.

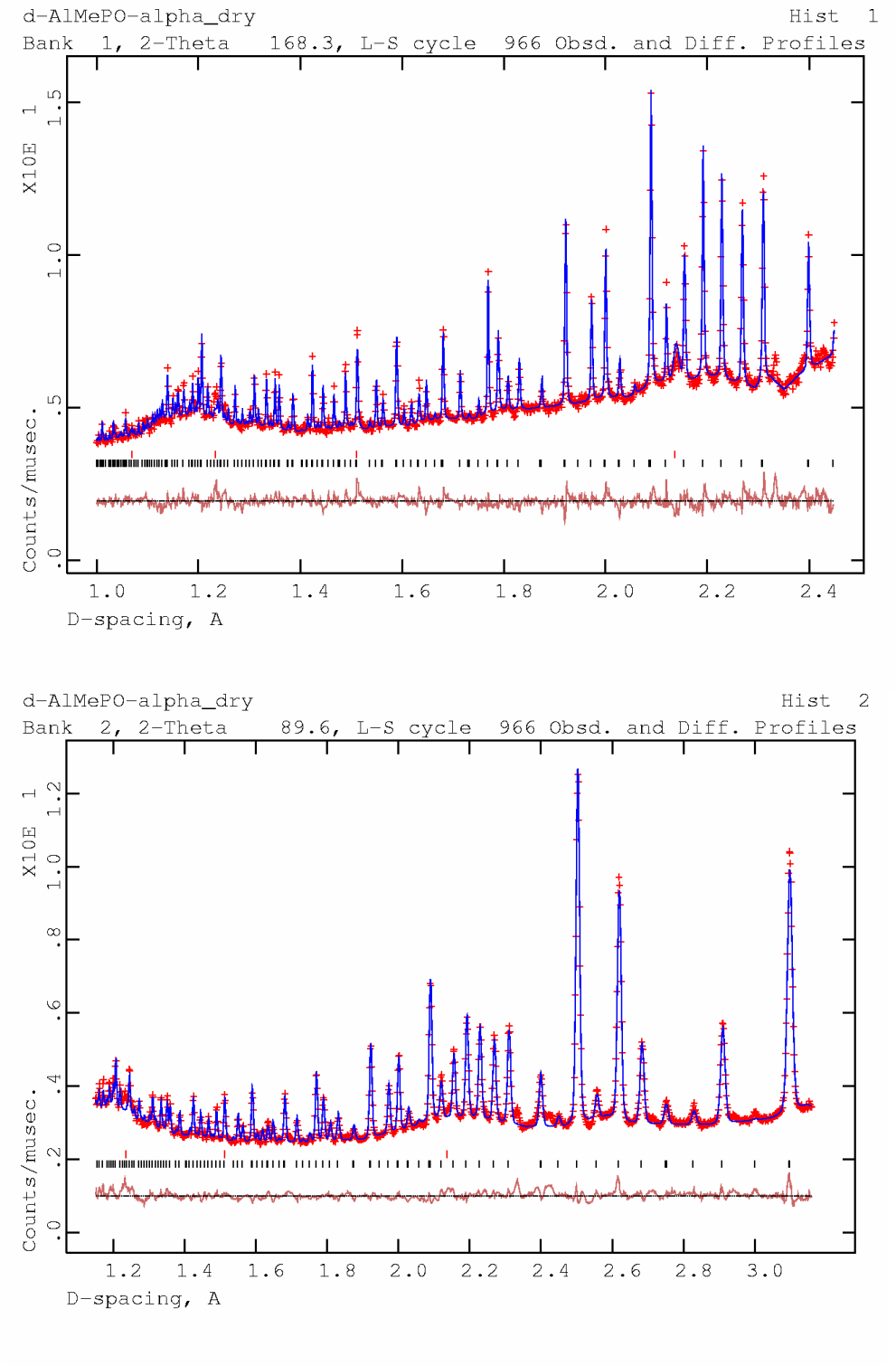

Table S1. Refined fractional atomic coordinates and thermal parameters of AlMePO-α at 2 K (P 31c, a = 1.38593(1) nm, c = 0.84766(1) nm).

Atom	x	y	z	U_{iso}
Al1	0.6666	0.3333	0.5000	0.049(5)
Al2	0.6024(11)	0.5029(11)	0.0631(20)	0.049(5)
P1	0.6473(7)	0.5262(7)	0.7131(16)	0.012(1)
P2	0.8041(8)	0.5281(8)	0.2333(17)	0.012(1)
O1	0.6289(7)	0.4222(7)	0.6260(14)	0.042(1)
O2	0.6221(8)	0.5966(8)	0.6020(19)	0.042(1)
O3	0.5845(8)	0.4868(12)	0.8667(18)	0.042(1)
O4	0.7530(7)	0.4670(7)	0.3790(15)	0.042(1)
O5	0.8952(8)	0.5050(8)	0.1621(18)	0.042(1)
O6	0.7293(11)	0.5341(11)	0.1165(18)	0.042(1)
C1	0.7896(9)	0.5936(14)	0.7404(27)	0.040(2)
C2	0.9015(13)	0.6694(12)	0.3037(22)	0.040(2)
D1a	0.8148(12)	0.6688(15)	0.8007(20)	0.10(1)
D1b	0.8438(13)	0.6226(12)	0.6475(23)	0.10(1)
D1c	0.8237(11)	0.5592(13)	0.8225(21)	0.10(1)
D2a	0.9353(15)	0.7198(13)	0.1952(22)	0.10(1)
D2b	0.9597(13)	0.6747(13)	0.3858(26)	0.10(1)
D2c	0.8423(12)	0.6900(14)	0.3577(21)	0.10(1)

Table S2. Selected bond distances for AlMePO-α at 2 K

Bond	Distance / nm	Bond	Distance / nm
Al1 - O1	0.189(1)	Al2 - O2	0.172(1)
Al1 - O1	0.189(1)	Al2 - O3	0.168(1)
Al1 - O1	0.189(1)	Al2 - O5	0.174(1)
Al1 - O4	0.192(1)	Al2 - O6	0.165(1)
Al1 - O4	0.192(1)		
Al1 - O4	0.192(1)		
P1 - O1	0.152(1)	P2 - O4	0.147(1)
P1 - O2	0.152(1)	P2 - O5	0.156(1)
P1 - O3	0.151(1)	P2 - O6	0.146(1)
P1 - C1	0.172(2)	P2 - C2	0.183(2)
C1 - D1a	0.105(1)	C2 - D2a	0.111(1)
C1 - D1b	0.102(1)	C2 - D2b	0.104(1)
C1 - D1c	0.108(1)	C2 - D2c	0.109(1)

Table S3. Selected bond angles for AlMePO-α at 2 K

Atom1-Atom2-Atom3	Angle / °	Atom1-Atom2-Atom3	Angle / °
O1 - Al1 - O1	91.2(5)	O2 - Al2 - O3	104.0(8)
O1 - Al1 - O1	91.2(5)	O2 - Al2 - O5	109.7(8)
O1 - Al1 - O4	85.1(5)	O2 - Al2 - O6	104.5(9)
O1 - Al1 - O4	89.5(5)	O3 - Al2 - O5	110.7(9)
O1 - Al1 - O1	91.2(5)	O3 - Al2 - O6	111.9(8)
O1 - Al1 - O4	85.1(5)	O5 - Al2 - O6	115.0(11)
O1 - Al1 - O4	89.5(5)		
O1 - Al1 - O4	89.5(5)		
O1 - Al1 - O4	85.1(5)		
O4 - Al1 - O4	94.2(5)		
O1 - P1 - O2	108.9(7)	O4 - P2 - O5	114.0(8)
O1 - P1 - O3	106.4(8)	O4 - P2 - O6	116.7(8)
O2 - P1 - O3	119.5(8)	O5 - P2 - O6	114.5(9)
O1 - P1 - C1	100.5(9)	O4 - P2 - C2	103.1(9)
O2 - P1 - C1	107.7(9)	O5 - P2 - C2	97.0(9)
O3 - P1 - C1	112.1(9)	O6 - P2 - C2	108.8(9)