Spatial Dispersion of Lone Electron Pairs? – Experimental Charge Density of Cubic Arsenic(III) Oxide Supporting Information

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Measurement details

Diffraction data were collected on Agilent Technologies Gemini A Ultra diffractometer equipped with an Oxford low temperature device (Oxford Cryosystems Cobra) at 100(2) K. The strategy involved 28 ω scans with a step of 0.25° at five different detector (2ϑ) positions and various φ angle values to increase reflections multiplitcity (redundancy). Images with 2ϑ of 5, 30, 50, 68, 118° were exposed for 5, 5, 20, 40 and 40 s, respectively. The whole possible ω range, i.e. not causing collisions, was scanned at every detector position. Such a strategy resulted

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Table S1: Refinement strategy of multipolar model for the experimental data

Step	Refined parameters	Comments
1	kS	
2	$kS + xyz$	
3	$kS + xyz + U_{ij}$	
4a	$kS + P_v$	10 cycles of block refinement
4b	$kS + \kappa$	
4	$kS + P_v + \kappa$	
5	$kS + P_{lm}$,$l \leq 1$	
6	$kS + P_{lm}$,$l \leq 2$	
7	$kS + P_{lm}$,$l \leq 3$	
8	$kS + P_{lm}$,$l \leq 4$	
9a	$kS + xyz + U_{ij} + P_v + P_{lm}$	50 cycles of block refinement
9b	$kS + \kappa + \kappa'_{As}$	
9	$kS + xyz + U_{ij} + P_v + P_{lm} + \kappa + \kappa'_{As}$	
10a	$kS + xyz_{As}$	50 cycles of block refinement (high
10b	$kS + xyz_O + U_{ij} + C_{ijkAs} + D_{ijklAs}$	correlations between As position and
11a	kS + xyz + $U_{ij} + P_v + P_{lm} + C_{ijkAs} + D_{ijklAs}$	Gram-Charlier coefficients)
11b	$kS + \kappa + \kappa'_{As}$	
11c	$kS + xyz + U_{ij} + P_v + P_{lm} + C_{ijkAs} + D_{ijklAs} + \kappa + \kappa'_{As}$	

in 11534 frames and multiplicity of 53.1 and 63.2 for resolution down to 0.36 and 0.40 Å, respectively. The data were corrected for absorption analytically in the CrysAlis^{PRO}program and merged with SORTAV.

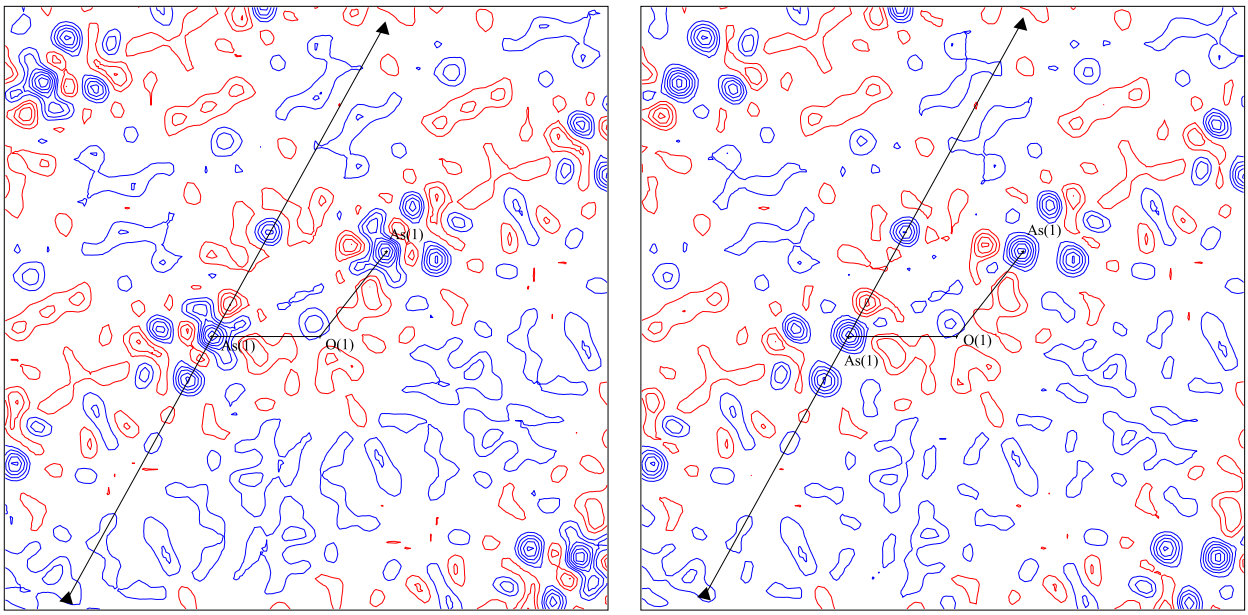

Figure S1: Residual density maps in the As—O—As plane after harmonic and anharmonic treatment of the thermal motion (left and right, respectively). Introduction of the Gram-Charlier coefficients up to the 4^{th} order for arsenic atom reduced the Shashlik-like features around arsenic atom. Contours 0.1 eÅ^{-3}; blue solid lines – positive, red solid lines – negative; the 3 symmetry axis along [111] is marked on the plots.

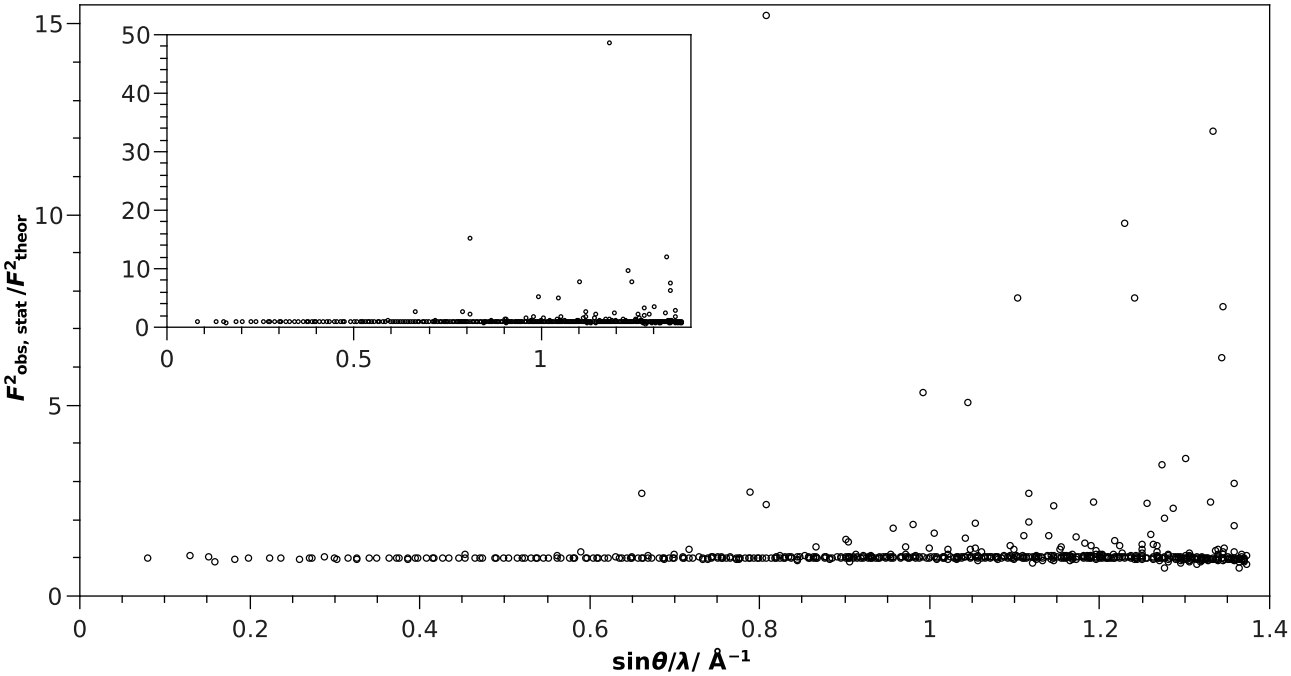

Figure S2: Plot of the $F^2_{\text{obs, stat}}/F^2_{\text{theor}}$ ratio as a function of $\sin\theta/\lambda$. The same graph with a different scale on Y axis is presented in the inset.

Table S2: Highest peaks and deepest holes in the residual density after multipolar modelling of experimental structure factors.

peak		x	y	z	height
PK(1)	is 0.03 A from As(1)	0,7728	0.7728	0.773	0.66
PK(2)	is 0.84 A from As(1)	0.7273	0.7273	0.7273	0.53
PK(3)	.....	0.125	0.125	0.125	0.53
PK(4)	is 0.89 A from As(1)	0.8163	0.7238	0.7238	0.49
PK(5)	is 0.25 A from O(1)	0.875	0.8715	0.7222	0.23
PK(6)	.....	0.549	0.0034	0.0047	0.23
PK(7)	.....	0.625	0.001	0.125	0.22
PK(8)	.....	0.0955	0.0077	0.0077	0.21
PK(9)	.....	0.6662	0.0838	0.0838	0.20
PK(10)	.....	0.9656	0.4649	0.1108	0.17
HL(1)	is 0.64 A from As(1)	0.8049	0.8049	0.8049	−0.44
HL(2)	.....	0.814	0.043	0.0601	−0.31
HL(3)	is 0.81 A from As(1)	0.809	0.8056	0.7188	−0.29
HL(4)	.....	0.9102	0.0885	0.0885	−0.24
HL(5)	.....	0.656	0.0118	0.0518	−0.23
HL(6)	.....	0.1152	0.0576	0.0576	−0.19
HL(7)	.....	0.125	0.4316	0.125	−0.18
HL(8)	.....	0.9573	0.0004	0.0424	−0.11
HL(9)	.....	0.9367	0.4738	0.0949	−0.09
HL(10)	.....	0.7893	0.0035	0.2893	−0.08

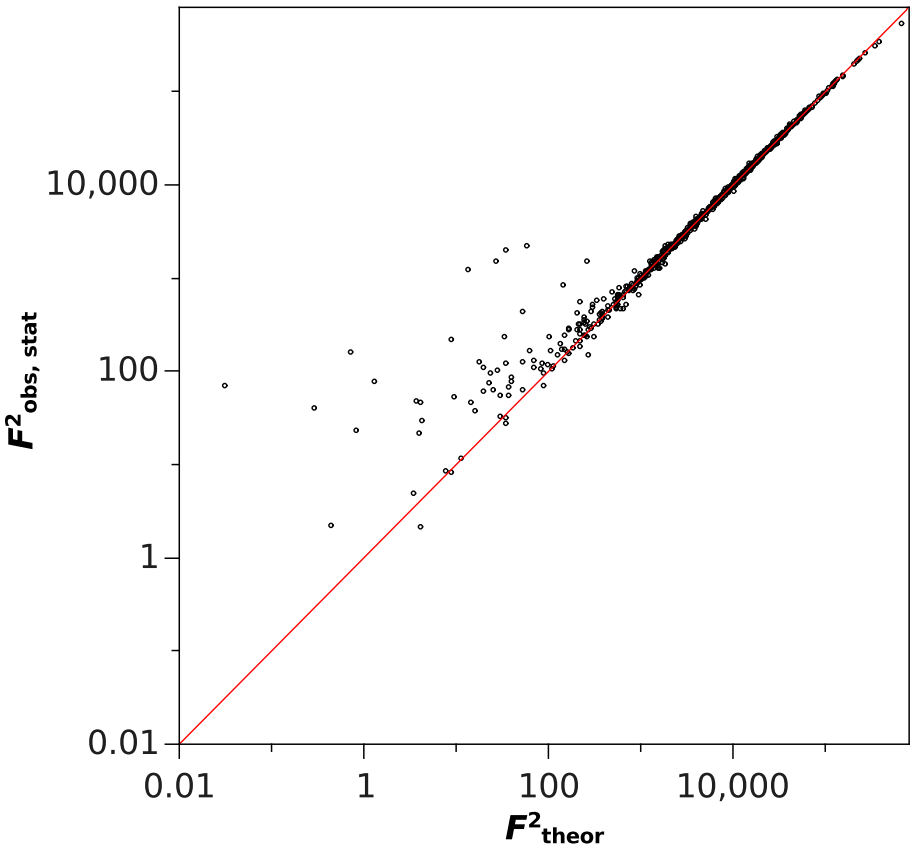

Figure S3: Comparison of $F^2_{\text{obs, stat}}$ with F^2_{theor} depicting very good agreement for strong reflections and some discrepancies for the very weak ones.

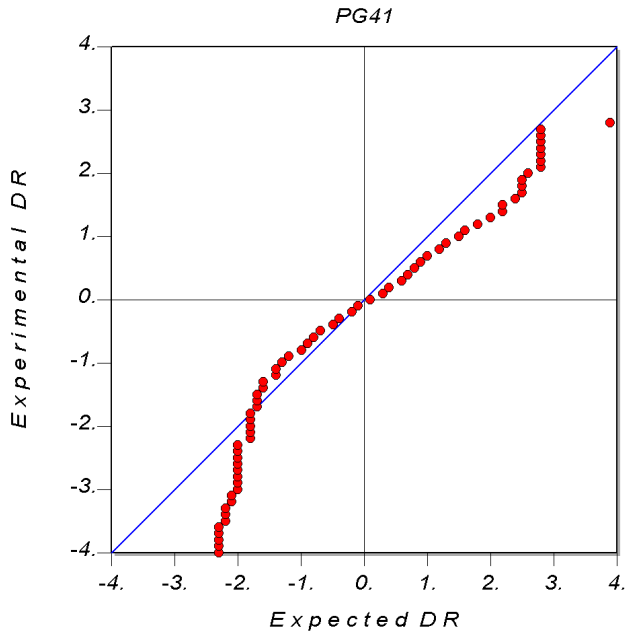

Figure S4: Normal probability plot for experimental structure factors after multipolar modelling (**exp_MM**).

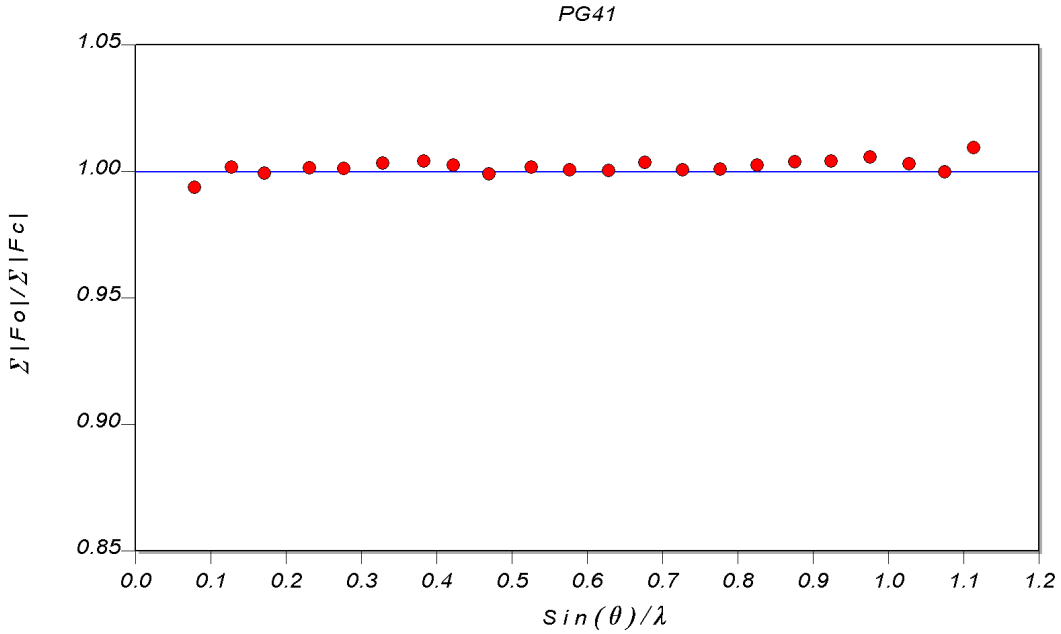

Figure S5: Scale factor variability ($\sum |F_{\text{obs}}| / \sum |F_{\text{calc}}|$) as a function of $\sin\theta/\lambda$ for the multipolar model (**exp_MM**)