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Supporting information for article:

Anharmonic motions *vs. dynamic* disorder at the Mg ion from the charge densities in pyrope ($Mg_3Al_2Si_3O_{12}$) crystals at 30 K: six of one, half a dozen of the other

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S1. Determination of the cell dimensions

Unit-cell dimensions at 30 K were obtained from a least-squares treatment of 406 Bragg angles (from α_1 and α_2 peaks) of reflections in the range $22.02 < 2\theta_{Mo} < 107.03°$. Cell dimensions were also measured at room temperature before and after cooling of the crystal, using a reduced set of angles, obtained from diffraction profiles centered at both positive and negative 2θ values to minimize the influence of possible errors in the instrumental zeroes. The cell edge was a = 11.4405(3) Å at 30 K and a = 11.4622(7) Å at 292 K.

S2. Details of XRD data collection

Two sets of data were collected in the ω:2θ mode at T = 30.0 ± 0.3 K, with warming to 292 K and change of crystal orientation in between. Graphite-monochromatized Mo Kα radiation (λ=0.71073 Å) was used, and the scan range in 2θ was (3+Δ)°, where Δ is the $K\alpha_1 - \alpha_2$ separation. Backgrounds were measured before and after each scan, for ¼ the scan time on each side of the scan range. Three reference reflections were repeatedly monitored to check instrument and crystal stability.

The first set comprised 3869 reflections measured at a tube setting of 50 kV and 25 mA, plus 474 low-angle (2θ<50°) data collected at a lower current setting (30 kV and 3 mA) to minimize possible problems associated with non-linearity of the counting system when measuring strong reflections. The scan rate was 3 °/min for the measurements at the higher current setting, and 2 °/min for those at the low current setting. The same scan rates were applied to the second data set, where 2832 data were collected at 50 kV and 25 mA, and 311 strong reflections were measured at 30 kV and 3 mA.

At the end of the collection of the first set, and before going to room temperature, an intermediate set of selected reflections was measured at T = 17.6 ± 0.3 K, together with several ψ-scans at the same temperature. The 445 data of this intermediate set, to be used for profile analysis and evaluation of the scan-truncation errors, were not considered in the subsequent reduction of the other two sets of data.

S3. Details of the multipolar model

S3.1. *General discussion*. To calculate the generalized scattering factors (GSF), core and valence monopole one-electron density functions were taken from the Hartree-Fock atomic (neutral) functions tabulated by Clementi and Roetti.[1] The refined inner monopole electron

population coefficient (PCR) was constrained to be equal for all four atoms of the asymmetric unit, while the intermediate monopole electron population coefficient (PVL) was constrained to be equal only for Al and Si atoms. Radial terms for the higher multipoles were single exponentials of the form $r^{nl}\exp(-\alpha r)$. Several different values of n_l (where l is the order of the multipole), were tested for the symmetry-allowed (i.e. non-vanishing) components of the various poles of the four atoms, from dipole (l=1, populated only in the O atom), up to tricontadipole (l=5), introduced into the structure-factor model only for Si and Mg atoms, and null for the site-symmetry of the Al atom. A refinement with extension to hexacontatetrapole terms, l=6, on the latter atom (no l = 6 poles are allowed on Si and Mg atoms) did not improve the least-squares fit and was disregarded. The values of n_l adopted in the final model for the multipole refinement of pyrope are reported in Table S1, together with those of α (shared for all multipoles of each atom), as obtained from some preliminary least-squares refinements, and with the optimized values of κ_0, the radial scaling parameter which apply to the outer (valence) monopoles.

Table S1

Adopted Radial Function Parameters (α and nl) and Refined κ0's.[a]
First Row: Values for the Refinement of Experimental Data; Second Row: Values for the Refinement of Theoretical Structure Factors (see Section S6 below).

	Si	Al	Mg	O
α (bohr-1)	3.488 3.50	3.077 3.039	3.491 3.212	4.446 5.18
n_1				2 2
n_2	4 6		4 4	2 2
n_3	5 6		5 5	3 4
n_4	6 6	6 6	6 6	4 4
n_5	6 6		7 7	
κ_0	1.01(1) 0.984(3)	0.95(2) 0.972(7)	1.14(3) 0.936(12)	0.952(2) 0.9789(5)

[a]The dimensionless scaling parameter κ_0 applies only to the outer (valence) monopole.

Extinction, which affects the diffraction intensities of the stronger reflections, was accounted for by adopting an isotropic model for a Type 1 crystal[2] with a Lorentian distribution of mosaicity. The final, refined extinction parameter corresponds to an average

mosaic spread of 27" of arc. The most affected reflection, (4 0 0), showed a 14.9% reduction in its intensity.

S3.2 *Multipole model parameters*. We have compared five descriptions of the multipolar charge density of pyrope, three for ρ_{EXP} and two for that based on theoretical structure factors, ρ_{MTSF}. The three representations of the experimental electron density distribution were (1) the final model (reported in Table S2), (2) a model without higher GC cumulants, and (3) a model with the n_l and α radial parameters adopted for ρ_{MTSF}. The two sets of parameters describing ρ_{MTSF} were (1) the actual final model (Table S6) and (2) that with the n_l and α radial parameters used for ρ_{EXP}. The main results of the comparison are as follows:
(i) the relevant, statistically highly significant terms of the deformation of ρ_{EXP} remain the same with or without anharmonic contributions to the ADP's. The numerical values of the 48 multipole population parameters plus the 4 scaling coefficients differ only slightly: the average difference between the two models is 1.7 times the pooled standard deviation σ_P (1.05 σ_P for the 25 parameters of the three cations and 2.3 σ_P for the 27 parameters of the O atom).
(ii) In both ρ_{EXP} and ρ_{MTSF}, the effect of changing the radial parameters is a variation of the numerical values of the multipole population coefficients, but the poles with a significant ($> 3\sigma$) population change remain the same with few exceptions: in ρ_{MTSF} only two coefficients (out of 26) become less relevant, while in ρ_{EXP} the decrease of significance is observed for 3 out of the 11 relevant multipole population coefficients of the O atom.
(iii) Most of the deformation features of ρ_{EXP} are common to ρ_{MTSF}, but several significant differences are also observed. Of special note are the following ones: (a) for all four atoms the valence density in ρ_{MTSF} is expanded, while in ρ_{EXP} this occurs only at the Al and O atoms; the largest difference in κ values is observed at the Mg atom (see Table S1). (b) The tricontadipole ($l = 5$) deformation at Si is negligible in ρ_{MTSF}, but significant, for one of the two non-vanishing coefficients, in ρ_{EXP}. (c) All but one coefficient of the hexadecapole of the O atom in ρ_{MTSF} do not exceed 2σ, two of them being virtually null, while in ρ_{EXP} two terms of this pole (different from the one just mentioned in ρ_{MTSF}) are $\geq 4\ \sigma_X$. (d) The unique octopole population coefficient of Mg, equal to 5.5 σ_X in ρ_{EXP}, is $<< \sigma$ in ρ_{MTSF}.

Noticeable similarities between the two multipole charge densities include the highly populated hexadecapole of both Al (that is the only deviation from sphericity allowed for this cation in pyrope within $l \leq 5$) and Mg, the very close (within a 1.1 σ_X) κ value for these atoms, and the statistically very significant tricontadipole ($l = 5$) deformation at Mg.

S4. Details of the weighting scheme for the least-squares refinement

Each intensity was assigned a variance $\sigma^2(I)$ based on counting statistics plus an additional term $(0.01S)^2$, where S is the scan count; this term was suggested by the fluctuation of three reference reflections during data collection. The quantity minimized in all least-squares calculations was $\varepsilon = \Sigma w(F^2_{obs} - k^2F^2_{calc})^2$, based on the 785 reflections with $I > 0$ and with weights w obtained as averages of the $\sigma^{-2}(F^2_{obs})$ of each individual measurement. This weighting scheme was preferred to the canonical w obtained by summing over the individual weights, because some final averaged intensities were coming from few (2 or 3) measurements, while others from up to 15 measures.

S5. Details of least-squares refinement

A total of 93 parameters was refined in the last cycles. They comprise the oxygen coordinates (see Section 3.2 in the main text), 37 terms describing the nuclear displacements, the extinction factor, 4 κ_0 scaling coefficients and 48 multipole population parameters. The refinement process ended with $R(F) = 0.0084$, $R(F^2) = 0.0081$, and goodness-of-fit = 0.7598. Later, a marginally better overall agreement was obtained by adopting the n_l and α values employed in the least-squares refinement of static, theoretical structure factors (see Section 2.5 in the main text), but the resulting κ_0 value for the Mg atom, 1.36(7) was judged as unrealistically large, and this model was rejected. The final parameter values at convergence are available in Table S2, together with several details of the least-squares structure refinement (Table S3-S4), and a list of the 21 final correlation coefficients greater than 0.80 (in absolute value) (Table S5).

Two alternative schemes, leading (as expected) to the same final results, were followed. They are reported in Tables S3 and S4 below. In the first scheme (Table S3), at convergence of the refinement of 65 parameters, comprising the oxygen coordinates, the Uij's of the four atoms, the extinction coefficient, 44 multipole population parameters (up to the

hexadecapole level for all four atoms), and 4 κ_0's, the conventional agreement factor *R(F)* was 0.0092 and $R(F^2)$ = 0.0091. It was then decided to check if the experimental data were carrying information about possible anharmonic contributions to the atomic temperature factors. Therefore, the thermal motion was described with the addition of high-order cumulants, namely third- and fourth-order Gram-Charlier terms, (C_{ijk}'s and D_{ijkl}'s, respectively), besides the usual second-order U_{ij}'s. Refinement of 13 independent third-order coefficients (10 for the O atom, 2 for Si, and 1 for Mg), with all previous parameters kept fixed, reduced *R(F)* to 0.0090. Inclusion and refinement (alone) of further 11 D_{ijkl}'s (6 for Mg and 5 for Al) led to *R(F)* = 0.0089 and $R(F^2)$ = 0.0091. A better agreement between model and experiment was obtained for the 148 low-angle data when the high-order cumulants were kept fixed and four tricontadipole (l=5) terms were added to the multipole expansion, namely 2 terms on each of the Si and Mg atoms. Refinement of the 69 parameters converged to *R(F)* = 0.0088 and $R(F^2)$ = 0.0085. Finally, the 93 analyzed variables were included all together in the least-squares refinement process, which ended with *R(F)* = 0.0084, $R(F^2)$ = 0.0081, and goodness-of-fit = 0.7598. For the 690 data with $F^2 \geq 3\sigma(F^2)$ the agreement index *R(F)* was 0.0066.

The sequence of the second scheme (Table S4) differs in the starting point: the four tricontadipole terms were added to the multipole expansion since the beginning, before introducing higher-order cumulants into the model. Furthermore, this scheme includes a step (model D) previously not examined. Agreement indices for the various steps of the refinement are reported into the Table.

A list of the final values for the 93 refined parameters has been deposited (cif file) and is available below (Table S2).

S6. Details of the theoretical calculations

As in previous works on garnets by Dovesi *et al*.,[3,4] the B3LYP one-electron Hamiltonian[5,6] has been employed. Consistent Gaussian basis sets of Triple-Zeta Valence with Polarization Quality (TZVP), developed by Peintinger et al. for periodic quantum-chemical solid-state calculations,[7] have been adopted for all the atomic species. Computational conditions (tolerances for the truncation of the infinite Coulomb and exchange sums, SCF convergence criteria, and number of points in the reciprocal space) are reported in the Supporting

Information. The level of accuracy in evaluating the Coulomb and Hartree-Fock exchange series is controlled by five parameters,[8] for which the increased values of 8 8 8 8 16 have been used. Standard SCF convergence criteria have been adopted. The reciprocal space was sampled according to a regular sublattice with a shrinking factor IS equal to 3, corresponding to four independent k vectors in the irreducible Brillouin zone. A 20% mixing of the Fock matrices and an eigenvalue level shift of 1 hartree were applied to accelerate convergence.

Static structure factors for all independent 788 reciprocal-lattice points included within $[(\sin\theta)/\lambda] = 1.14$ Å^{-1} (same *hkl* indices as in the 30 K X-ray experiment) were obtained through the Fourier transform of the periodic density. They were employed in the VALRAY2000 code (see the main text) to derive a multipole-projected charge density distribution of pyrope fully comparable with the experimental density. With the position of the O atom kept fixed and the thermal motion set to zero for all atoms, the number of refined variables in the least-squares procedure was 56 (one κ_0 parameter for each atomic species, plus all 52 independent, non-vanishing multipole population parameters up to and including $l = 5$ poles for Si and Mg, but up only to $l = 4$ poles for Al and O atoms, with no constraints on the monopole populations). As in the case of the experimental structure factors, the criterion for convergence was $\Delta\varepsilon/\varepsilon < 10^{-6}$ in two subsequent cycles. Unit weights were assigned to all reflections, and full second derivatives of ε were included in the least-squares matrix throughout the refinement cycles. Initial values of n_l and α (see Section S3 above) in the radial functions were those adopted for the treatment of the experimental data. After convergence was reached, at $R(F) = 0.0030$, several tests were performed, to improve the agreement, by changing the two radial parameters of each atom according to values reported in the literature for least-squares multipole refinements based on X-ray diffraction intensities of silicates. The values eventually chosen are reported in Table S1 above. The final model led to $R(F) = 0.0026$, $R(F^2) = 0.0023$, and $wR(F^2) = 0.0043$, with a goodness-of-fit of 0.1341 (see the main text, Section 2.4).

S7. Details of the topological analysis

We can summarize the results of the comparisons among the properties of the three charge densities as follows:

(i) As shown in Table 2 and Figure 4 (main text), all $\rho(\mathbf{r})_{bcp}$ values are < 1 and the $\nabla^2\rho(\mathbf{r})_{bcp}$ values are all positive. Only for the Si - O interaction the value of the experimental $\rho(\mathbf{r})_{bcp}$ is smaller than the value in ρ_{THEO}, while for all other interactions ρ_{EXP} is > ρ_{THEO} at the bcp. Conversely, all experimental $\nabla^2\rho(\mathbf{r})_{bcp}$ values are smaller than those in ρ_{THEO}, with the exception of the values at the O2···O3 interaction, that are identical within experimental error. For three of the four M-O interactions the Laplacian of the multipolar ρ_{MTSF} at the bond critical point has a value intermediate between those of the other two charge densities, while for the bcp of the Si-O bond the Laplacian of ρ_{MTSF} coincides with that of ρ_{THEO}. At the bcp's of these four M-O interactions, excellent agreement is shown by the values of the local kinetic energy density $G(\mathbf{r})$ of the two multipolar ρ's, the largest difference, at the Al-O bond, not exceeding 5%. All four $G(\mathbf{r})$ values from ρ_{THEO} are systematically larger than those of ρ_{EXP}, up to 13% for the Si-O interaction.

(ii) By considering the BD and $\rho(\mathbf{r})_{bcp}$ values, and recalling that closed-shell (purely ionic) interactions are associated with positive values of BD, whereas the more BD is negative, the more the bond is covalent and stronger, out of the six contacts of Table 2 (main text) the Si-O interaction shows the largest covalent character, having the most negative BD and the highest $\rho(\mathbf{r})_{bcp}$ values in all the three ρ's. The two O···O interactions, with the smallest $\rho(\mathbf{r})_{bcp}$ in ρ_{EXP} and all six positive BD's, conform the expected closed-shell character. The longest of the two Mg-O bonds shows in ρ_{THEO} a $\rho(\mathbf{r})_{bcp}$ value slightly smaller than that of the O1···O3 interaction and the largest positive BD value, thus suggesting a completely ionic nature. The same conclusion is drawn from the values in ρ_{MTSF}, while, by contrast, a partial character of covalent bond is indicated for this interaction by the corresponding values in ρ_{EXP}. Analogous contrast is shown by the other Mg-O bond, which is characterized as closed-shell in nature in the multipolar ρ based on theoretical structure factors as well as in ρ_{THEO}, but partially covalent in ρ_{EXP} (although to a minor extent than the previous Mg-O bond). Similarly, for the Al-O bond the values of ρ and BD at the bcp in ρ_{EXP} are indicative of a significant covalent character, but, again, this is not confirmed in ρ_{MTSF} and ρ_{THEO}.

(iii) The experimental $\rho(\mathbf{r})_{bcp}$ of the Si-O bond falls within the lower border of a reported[9] scatter plot of experimental Si-O bond lengths *vs* theoretically calculated charge densities at the bcp of this interaction for a variety of silicates, while the experimental $\nabla^2\rho(\mathbf{r})_{bcp}$ is somewhat smaller than the average calculated value as seen in the analogous plot forming,

together with the previous one, Figure 19 in reference 9. The corresponding values in ρ_{THEO} from our present work agree even better with the values of those plots (on the upper and lower borders, respectively), and a good agreement is observed also, in the corresponding diagrams,[9] for the curvatures λ's of the primary density. Less satisfactory agreement is instead shown by $\rho(\mathbf{r})_{bcp}$ in the multipolar charge density ρ_{MTSF}, where, on the other hand, the corresponding $\nabla^2\rho(\mathbf{r})_{bcp}$ coincides (as reported above) with that in ρ_{THEO}.

(iv) For the two Mg-O interactions our calculated values of $\rho(\mathbf{r})_{bcp}$ and $\nabla^2\rho(\mathbf{r})_{bcp}$ in ρ_{THEO} fully conform to those in the plots reported as Fig. 20 of reference 9, from which our experimental values depart significantly, both experimental $\rho(\mathbf{r})_{bcp}$ falling above the scatter diagram of that figure, and both experimental Laplacian falling below.

SUPPORTING INFORMATION

TABLE S2

LIST OF THE FINAL VALUES FOR THE 93 REFINED STRUCTURAL PARAMETERS OF PYROPE FROM A LEAST-SQUARES REFINEMENT BASED ON 785 EXPERIMENTAL STRUCTURE FACTORS (Fobs**2'S):

VALRAY OUTPUT OF THE FINAL CYCLE:

THE CRITERION FOR CONVERGENCE AT CYCLE: 4 1.42824E-08

LEAST SQUARES TERMINATED AT CYCLE 4 CRIT IS LESS THAN 1.000E-06

PARAMETERS AFTER CYCLE 4

*** U-S OR UIJ-S HAVE BEEN MULTIPLIED BY 100 FOR OUTPUT***
*** C-S AND D-S BY 10000 ***

PARAMETER	OLD	CHANGE	NEW	ERROR	SHIFT/ERROR
FC SCL	1.10706	ESTIMATED	1.10706	0.0519020	
G11	0.24544	-0.0000076	0.24543	0.0057161	0.0013
		ATOM TYPE: SI 0 ATOM NAME: 1			
U11	0.18014	-0.0000004	0.18014	0.0020908	0.0002
U22	0.18014	-0.0000004	0.18014	CONSTRAINED	
U33	0.15338	-0.0000004	0.15338	0.0022949	0.0002
C113	0.01278	0.0000000	0.01278	0.0021220	0.0000
C123	-0.01885	0.0000000	-0.01885	0.0039793	0.0000
C223	-0.01278	0.0000000	-0.01278	CONSTRAINED	
KAPPA0	1.00593	0.0000044	1.00593	0.0132568	0.0003
PCORE	2.15621	0.0000004	2.15621	CONSTRAINED	
PL-SH	8.14153	0.0000012	8.14153	CONSTRAINED	
Y00	4.78172	-0.0000848	4.78164	0.2490314	0.0003
Y20	0.58883	0.0000149	0.58885	0.1343236	0.0001
Y32+	-4.41060	-0.0000071	-4.41060	0.4400002	0.0000
Y32-	22.86933	-0.0000214	22.86931	0.9940219	0.0000
Y44+	0.38664	0.0000361	0.38668	0.7028155	0.0001
Y44-	-2.87463	0.0001121	-2.87452	2.3007706	0.0000
Y40	-0.25654	0.0000282	-0.25651	0.7102337	0.0000
Y52+	-13.48023	-0.0000334	-13.48027	4.4084034	0.0000
Y52-	-0.59062	-0.0002194	-0.59084	8.5843500	0.0000
		ATOM TYPE: AL 0 ATOM NAME: 1			
U11	0.21735	-0.0000003	0.21735	0.0038520	0.0001
U22	0.21735	-0.0000003	0.21735	CONSTRAINED	
U33	0.21735	-0.0000003	0.21735	CONSTRAINED	
U12	0.00139	0.0000000	0.00139	0.0025725	0.0000
U13	0.00139	0.0000000	0.00139	CONSTRAINED	
U23	0.00139	0.0000000	0.00139	CONSTRAINED	
D1111	0.00070	0.0000000	0.00070	0.0001095	0.0000
D1112	0.00027	0.0000000	0.00027	0.0002339	0.0000
D1122	0.00071	0.0000000	0.00071	0.0002384	0.0000
D1113	0.00008	0.0000000	0.00008	0.0002236	0.0000
D1123	-0.00002	0.0000000	-0.00002	0.0003449	0.0000
D1133	0.00071	0.0000000	0.00071	CONSTRAINED	
D1222	0.00008	0.0000000	0.00008	CONSTRAINED	
D1223	-0.00002	0.0000000	-0.00002	CONSTRAINED	
D1233	-0.00002	0.0000000	-0.00002	CONSTRAINED	
D1333	0.00027	0.0000000	0.00027	CONSTRAINED	
D2222	0.00070	0.0000000	0.00070	CONSTRAINED	
D2223	0.00027	0.0000000	0.00027	CONSTRAINED	
D2233	0.00071	0.0000000	0.00071	CONSTRAINED	
D2333	0.00008	0.0000000	0.00008	CONSTRAINED	
D3333	0.00070	0.0000000	0.00070	CONSTRAINED	
KAPPA0	0.95480	0.0000029	0.95480	0.0165554	0.0002
PCORE	2.15621	0.0000004	2.15621	CONSTRAINED	
PL-SH	8.14153	0.0000012	8.14153	0.0107828	0.0001

Y00		4.69964	-0.0001067	4.69953	0.3640668	0.0003
Y44+		21.21739	0.0001118	21.21750	1.6202333	0.0001
	Y40	21.21739	0.0001118	21.21750	CONSTRAINED	

ATOM TYPE: MG 0 ATOM NAME: 1

U11		0.48521	-0.0000004	0.48521	0.0072166	0.0001
	U22	0.48521	-0.0000004	0.48521	CONSTRAINED	
U33		0.29818	-0.0000007	0.29818	0.0082258	0.0001
U12		0.09583	0.0000002	0.09583	0.0050923	0.0000
C113		-0.01358	0.0000000	-0.01358	0.0033549	0.0000
	C223	0.01358	0.0000000	0.01358	CONSTRAINED	
D1111		0.00129	0.0000000	0.00129	0.0002189	0.0000
D1112		0.00149	0.0000000	0.00149	0.0003771	0.0000
D1122		0.00397	0.0000000	0.00397	0.0005518	0.0000
D1133		0.00143	0.0000000	0.00143	0.0003927	0.0000
	D1222	0.00149	0.0000000	0.00149	CONSTRAINED	
D1233		0.00089	0.0000000	0.00089	0.0006662	0.0000
	D2222	0.00129	0.0000000	0.00129	CONSTRAINED	
	D2233	0.00143	0.0000000	0.00143	CONSTRAINED	
D3333		0.00080	0.0000000	0.00080	0.0002581	0.0001
KAPPA0		1.14301	0.0000111	1.14302	0.0304537	0.0004
	PCORE	2.15621	0.0000004	2.15621	CONSTRAINED	
PL-SH		8.19390	0.0000010	8.19390	0.0169655	0.0001
Y00		2.43589	-0.0001155	2.43578	0.2935871	0.0004
Y22-		-0.11766	-0.0000098	-0.11767	0.1393995	0.0001
Y20		0.66199	0.0000109	0.66200	0.1453871	0.0001
Y32+		-2.14179	-0.0000071	-2.14179	0.3894317	0.0000
Y44+		-1.24818	0.0000402	-1.24814	0.7165907	0.0001
Y42-		-3.41137	0.0000185	-3.41135	0.7806576	0.0000
Y40		4.47184	0.0000564	4.47190	0.6975714	0.0001
Y54-		29.76447	-0.0000385	29.76443	23.6351457	0.0000
Y52+		37.83823	0.0002767	37.83851	8.6214641	0.0000

ATOM TYPE: O 0 ATOM NAME: 1

X	0.03282	0.0000000	0.03282	0.0000315	0.0001
Y	0.05077	0.0000000	0.05077	0.0000305	0.0000
Z	0.65326	0.0000000	0.65326	0.0000300	0.0000
U11	0.32103	0.0000001	0.32104	0.0038192	0.0000
U22	0.37509	0.0000002	0.37509	0.0037004	0.0000
U33	0.26143	0.0000001	0.26143	0.0037010	0.0000
U12	0.03979	0.0000000	0.03979	0.0016488	0.0000
U13	-0.05697	0.0000000	-0.05697	0.0017029	0.0000
U23	0.00866	0.0000001	0.00866	0.0016530	0.0000
C111	-0.01282	0.0000002	-0.01282	0.0041756	0.0001
C112	0.01315	0.0000000	0.01315	0.0050571	0.0000
C122	-0.00150	0.0000003	-0.00150	0.0051146	0.0001
C113	-0.01571	-0.0000001	-0.01571	0.0048139	0.0000
C123	0.00074	0.0000000	0.00074	0.0058119	0.0000
C133	-0.01447	0.0000002	-0.01447	0.0050082	0.0000
C222	0.00354	0.0000000	0.00354	0.0040898	0.0000
C223	-0.01175	-0.0000001	-0.01175	0.0049906	0.0000
C233	0.01781	0.0000001	0.01782	0.0048571	0.0000
C333	-0.00574	-0.0000001	-0.00574	0.0038857	0.0000
KAPPA0	0.95218	-0.0000002	0.95217	0.0023583	0.0001
PCORE	2.15621	0.0000004	2.15621	0.0050545	0.0001
Y00	6.82887	0.0000033	6.82887	0.0295467	0.0001
Y11+	0.02732	-0.0000015	0.02732	0.0150026	0.0001
Y11-	-0.00809	-0.0000002	-0.00809	0.0145592	0.0000
Y10	0.00050	0.0000005	0.00051	0.0149952	0.0000
Y22+	0.00164	0.0000001	0.00164	0.0066157	0.0000
Y22-	-0.04920	-0.0000003	-0.04920	0.0104672	0.0000
Y21+	-0.03669	0.0000005	-0.03669	0.0128947	0.0000
Y21-	-0.03477	-0.0000010	-0.03477	0.0123021	0.0001
Y20	0.04103	0.0000006	0.04103	0.0111906	0.0001
Y33+	0.02063	0.0000003	0.02063	0.0099701	0.0000
Y33-	-0.08058	0.0000000	-0.08058	0.0097756	0.0000
Y32+	0.12774	0.0000001	0.12774	0.0255528	0.0000
Y32-	-0.34802	0.0000003	-0.34802	0.0551958	0.0000
Y31+	0.03435	0.0000004	0.03435	0.0080093	0.0000
Y31-	-0.05794	-0.0000003	-0.05794	0.0079883	0.0000
Y30	-0.05598	0.0000000	-0.05598	0.0062577	0.0000

Y44+	0.11619	0.0000001	0.11619	0.0208324	0.0000
Y44-	0.16902	-0.0000025	0.16902	0.0857635	0.0000
Y43+	-0.01393	0.0000006	-0.01393	0.0598451	0.0000
Y43-	0.01215	-0.0000024	0.01215	0.0591356	0.0000
Y42+	-0.00368	0.0000007	-0.00368	0.0150932	0.0000
Y42-	0.07899	0.0000000	0.07899	0.0306118	0.0000
Y41+	0.10251	-0.0000002	0.10251	0.0244289	0.0000
Y41-	0.06917	0.0000000	0.06917	0.0225894	0.0000
Y40	-0.00364	0.0000001	-0.00364	0.0176106	0.0000

THE AVERAGE OF SHIFT/ERROR FOR THE 93 PARAMETERS REFINED ON IS 0.0001

THE MAXIMUM OF SHIFT/ERROR FOR THE 93 PARAMETERS REFINED ON IS 0.0013

ESTIMATED AGREEMENT AFTER CYCLE 4

SUM(W*(O-C)**2) IS 3.9945187159E+02

SQRTF(SUM(W*(O-C)**2)/(NO-NV)) IS 0.7598

AGREEMENT FACTORS BEFORE CYCLE 5

SUM(W*(O-C)**2) IS 3.9945187159E+02

SQRTF(SUM(W*(O-C)**2)/(785 - 93)) 0.7598

	NUMERATOR	DENOMINATOR	
R-FACTOR(F):	222.056	26284.598	R(F) = 0.0084
WEIGHTED R-FACTOR(F):	20.997	2590.044	WR(F) = 0.0081
R-FACTOR(F**2):	20466.115	2531464.604	R(F2) = 0.0081
WEIGHTED R-FACTOR(F**2):	19.986	1289.568	WR(F2) = 0.0155

THIS REFINEMENT IS BASED ON F SQUARED

SUPPORTING INFORMATION

TABLE S3

First scheme of the procedure for the least-squares refinement based on 785 experimental F_o^2's.
Models A to E were refined one after the other in succession

Model	A[a]	B[b] = A + 13 C_{ijk}	C[c] = B + 11 D_{ijkl}	D[d] =A+4T	E = D + 13 C_{ijk} + 11 D_{ijhk}
No. of refined parameters	65	14	12	69	93
G11	0.225(6)	0.225(3)	0.225(3)	0.229(6)	0.245(6)
R(F)	0.0092	0.0090	0.0089	0.0088	0.0084
wR(F)	0.0089	0.0086	0.0085	0.0084	0.0081
$R(F^2)$	0.0091	0.0091	0.0091	0.0085	0.0081
$wR(F^2)$	0.0171	0.0165	0.0164	0.0161	0.0155
$\Sigma w(F_o^2-F_c^2)^2$	485.1669	452.8805	445.0729	430.8478	399.4519
GOF[e]	0.8209				0.7598
On 148 data with $(\sin\theta)/\lambda < 0.6486$					
R(F)	0.0064	0.0064	0.0064	0.0060	0.0057
$R(F^2)$	0.0091	0.0090	0.0091	0.0083	0.0080
On 637 data with $(\sin\theta)/\lambda > 0.6486$					
R(F)	0.0110	0.0107	0.0105	0.0105	0.0102
$R(F^2)$	0.0091	0.0091	0.0091	0.0088	0.0077
On 690 data with $F_o^2 > 3\sigma(F_o^2)$					
R(F)	0.0073				0.0066
wR(F)	0.0085				0.0077
$R(F^2)$	0.0090				0.0080
$wR(F^2)$	0.0167				0.0151

[a]The 65 refined parameters of model A comprised the extinction coefficient *G11*, the xyz coordinates of the O atom, 13 U_{ij}'s of the four atoms (6 for O, 2 for Si, 2 for Al, and 3 for Mg), 4 κ_0's (one per atom), and 44 multipole population parameters up to the hexadecapole (l=4) level (26 for O, 7 for Si, 3 for Al, and 8 for Mg, as described in Table S2).

[b]The 14 refined parameters were the extinction coefficient G11 and 13 third-order cumulants C_{ijk}'s.

[c]The 12 refined parameters were the extinction coefficient G11 and 11 fourth-order cumulants D_{ijkl}'s (6 for Mg and 5 for Al).

[d]Model D included the third- and fourth-order cumulants resulting from the refinements of models B and C into the calculation of the structure factors, but not into the refinement process. The 69 refined parameters were those of model A plus two tricontadipole (l=5) terms for each of the Si and Mg atoms.

[e]The goodness-of-fit (GOF) is $[\Sigma w(F_o^2-F_c^2)^2/(785-NV)]^{½}$, where NV is the number of refined variables.

SUPPORTING INFORMATION

TABLE S4

Procedure for the least-squares refinement based on 785 experimental F_o^2's.

Models A to E were refined one after the other in succession

Model	A[a]	B[b] = A + 13 C_{ijk}	C[c] = B	D[d]=C+6D_{ijhk} (Mg)	E[e]=D+5D_{ijhk} (Al)
No. of refined parameters	69	14	82	88	93
G11	0.230(6)	0.230(3)	0.228(6)	0.236(6)	0.248(6)
R(F)	0.0091	0.0089	0.0089	0.0086	0.0084
wR(F)	0.0088	0.0085	0.0084	0.0082	0.0081
$R(F^2)$	0.0086	0.0086	0.0087	0.0083	0.0081
$wR(F^2)$	0.0169	0.0163	0.0162	0.0157	0.0155
$\Sigma w(F_o^2-F_c^2)^2$	472.4482	442.2310	433.8940	412.2807	399.4519
GOF[f]	0.8123		0.7856	0.7691	0.7598
On 148 data with $(\sin\theta)/\lambda < 0.6486$					
R(F)	0.0062	0.0061	0.0060	0.0058	0.0057
$R(F^2)$	0.0084	0.0083	0.0085	0.0083	0.0080
On 637 data with $(\sin\theta)/\lambda > 0.6486$					
R(F)	0.0110	0.0106	0.0107	0.0104	0.0102
$R(F^2)$	0.0090	0.0090	0.0089	0.0085	0.0082
On 690 data with $F_o^2 > 3\sigma(F_o^2)$					
R(F)	0.0072				0.0066
wR(F)	0.0084				0.0077
$R(F^2)$	0.0086				0.0080
$wR(F^2)$	0.0164				0.0151

[a]The 69 refined parameters of model A comprised the extinction coefficient *G11*, the *xyz* coordinates of the O atom, 13 U_{ij}'s of the four atoms (6 for O, 2 for Si, 2 for Al, and 3 for Mg), 4 κ_0's (one per atom), 44 multipole population parameters up to the hexadecapole (l=4) level (26 for O, 7 for Si, 3 for Al, and 8 for Mg), plus 2 tricontadipole (l=5) terms for each of the Si and Mg atoms (see Table S2 for the constraints imposed to non-unique variables).

[b]The 14 refined parameters were 13 third-order cumulants C_{ijk}'s (2 for Si, 1 for Mg and 10 for O) and the extinction coefficient *G11*. All the other 68 parameters of model A were kept fixed

[c]The 82 parameters of model B (69+13 C_{ijk}'s) were refined altogether.

[d]The 88 refined parameters of model D were those of model C plus 6 fourth-order cumulants for atom Mg.

[e]Model E = Final model included the 88 parameters of model D plus five fourth-order cumulants for atom Al.

[f]The goodness-of-fit (*GOF*) is $[\Sigma w(F_o^2-F_c^2)^2/(785-NV)]^{½}$, where NV is the number of refined variables.

SUPPORTING INFORMATION

TABLE S5

FINAL LEAST-SQUARES REFINEMENT OF PYROPE: LIST OF THE 21 LARGEST CORRELATION COEFFICIENTS

AGREEMENT FACTORS BEFORE CYCLE 5

SUM(W*(O-C)**2) IS 3.9945187159E+02

SQRTF(SUM(W*(O-C)**2)/(785 - 93)) 0.7598

	NUMERATOR	DENOMINATOR	
R-FACTOR(F):	222.056	26284.598	R(F) = 0.0084
WEIGHTED R-FACTOR(F):	20.997	2590.044	WR(F) = 0.0081
R-FACTOR(F**2):	20466.115	2531464.604	R(F2) = 0.0081
WEIGHTED R-FACTOR(F**2):	19.986	1289.568	WR(F2) = 0.0155

THIS REFINEMENT IS BASED ON F SQUARED

CORRELATION MATRIX

CORRELATION COEFFICIENTS GREATER THAN 0.8

ATOM	PARAMETER	ATOM	PARAMETER	CORRELATION
SI	01 KAPPA0	SI	01 Y00	-0.85263
SI	01 Y00	AL	01 Y00	0.86833
MG	01 U11	MG	01 D1111	0.85866
MG	01 U12	MG	01 D1112	0.89551
MG	01 U33	MG	01 D3333	0.87191
SI	01 KAPPA0	MG	01 Y00	-0.80466
SI	**01 Y00**	**MG**	**01 Y00**	**0.94303**
AL	01 Y00	MG	01 Y00	0.83624
O	**01 X**	**O**	**01 C111**	**0.91225**
O	**01 Y**	**O**	**01 C222**	**0.90937**
O	**01 Z**	**O**	**01 C333**	**0.90740**
SI	01 U11	O	01 PCORE	0.81673
O	01 U11	O	01 PCORE	0.83001
O	01 U22	O	01 PCORE	0.83915
O	01 U33	O	01 PCORE	0.83984
O	01 KAPPA0	O	01 PCORE	-0.88460
O	01 KAPPA0	O	01 Y00	-0.87073
O	**01 X**	**O**	**01 Y11+**	**-0.91577**
O	01 C111	O	01 Y11+	-0.80382
O	01 Y	O	01 Y11-	-0.90620
O	01 Z	O	01 Y10	-0.89886

SUPPORTING INFORMATION

TABLE S6

LIST OF THE FINAL VALUES FOR THE 56 REFINED STRUCTURAL PARAMETERS OF PYROPE FROM A LEAST-SQUARES REFINEMENT BASED ON 788 THEORETICAL STRUCTURE FACTORS (F_{theo}^2's).

VALRAY output of the final cycle:

THE CRITERION FOR CONVERGENCE AT CYCLE: 3 9.39051E-08

LEAST SQUARES TERMINATED AT CYCLE 3 CRIT IS LESS THAN 1.000E-06

PARAMETERS AFTER CYCLE 3

PARAMETER	OLD	CHANGE	NEW	ERROR	SHIFT/ERROR
FC SCL	1.00916	ESTIMATED	1.00916	0.0100472	
ATOM TYPE: SI 0 ATOM NAME: 1					
KAPPA0	0.98405	0.0000004	0.98405	0.0030660	0.0001
PCORE	1.94420	-0.0000029	1.94419	0.0009417	0.0030
PL-SH	7.93919	0.0000003	7.93919	0.0027619	0.0001
Y00	3.79475	-0.0000098	3.79474	0.0424617	0.0002
Y20	1.86254	0.0000139	1.86255	0.1122769	0.0001
Y32+	-12.65756	-0.0000219	-12.65758	0.3318180	0.0001
Y32-	33.43201	-0.0000026	33.43200	0.6937791	0.0000
Y44+	-0.60043	0.0000068	-0.60043	0.2031311	0.0000
Y44-	-7.56410	0.0000295	-7.56407	0.9800151	0.0000
Y40	-3.97447	-0.0000017	-3.97447	0.1968691	0.0000
Y52+	-1.56393	0.0000220	-1.56391	1.8813830	0.0000
Y52-	3.57369	-0.0000399	3.57365	3.9962985	0.0000
ATOM TYPE: AL 0 ATOM NAME: 1					
KAPPA0	0.97180	0.0000008	0.97180	0.0066373	0.0001
PCORE	1.95051	-0.0000023	1.95050	0.0009042	0.0025
PL-SH	7.96226	0.0000004	7.96226	0.0029527	0.0001
Y00	2.54125	-0.0000201	2.54123	0.0645973	0.0003
Y44+	5.53068	-0.0000296	5.53065	0.3207207	0.0001
Y40	5.53068	-0.0000296	5.53065	CONSTRAINED	
ATOM TYPE: MG 0 ATOM NAME: 1					
KAPPA0	0.93606	0.0000003	0.93606	0.0121718	0.0000
PCORE	1.95253	-0.0000017	1.95253	0.0007467	0.0023
PL-SH	7.98539	0.0000001	7.98539	0.0030527	0.0000
Y00	1.48200	-0.0000178	1.48198	0.0878580	0.0002
Y22-	-0.09886	-0.0000009	-0.09886	0.0783594	0.0000
Y20	0.32833	-0.0000001	0.32833	0.0598683	0.0000
Y32+	0.08953	0.0000203	0.08955	0.2606704	0.0001
Y44+	2.52891	0.0000205	2.52893	0.3106165	0.0001
Y42-	-8.63096	0.0000129	-8.63095	0.5927498	0.0000
Y40	0.10007	-0.0000288	0.10005	0.2761203	0.0001
Y54-	-76.83424	0.0000526	-76.83419	18.1973514	0.0000
Y52+	50.47871	-0.0001978	50.47851	5.6668579	0.0000
ATOM TYPE: O 0 ATOM NAME: 1					
KAPPA0	0.97894	0.0000000	0.97894	0.0005468	0.0000
PCORE	1.99531	-0.0000004	1.99531	0.0004086	0.0009
Y00	6.47392	0.0000003	6.47392	0.0077534	0.0000
Y11+	-0.05553	0.0000000	-0.05553	0.0017635	0.0000
Y11-	0.04372	-0.0000001	0.04372	0.0016576	0.0000
Y10	-0.04421	0.0000000	-0.04421	0.0017733	0.0000
Y22+	-0.01434	0.0000001	-0.01434	0.0011788	0.0000

Y22-	0.03833	0.0000000	0.03833	0.0023663	0.0000
Y21+	-0.07798	0.0000000	-0.07798	0.0023166	0.0000
Y21-	0.00935	0.0000000	0.00935	0.0024373	0.0000
Y20	-0.00307	0.0000001	-0.00307	0.0020297	0.0000
Y33+	0.00137	0.0000001	0.00137	0.0035168	0.0000
Y33-	-0.03194	0.0000000	-0.03194	0.0035994	0.0000
Y32+	0.08392	0.0000003	0.08392	0.0091555	0.0000
Y32-	-0.06530	-0.0000002	-0.06530	0.0164259	0.0000
Y31+	0.01063	0.0000001	0.01063	0.0028398	0.0000
Y31-	-0.02122	0.0000000	-0.02122	0.0028585	0.0000
Y30	-0.02330	-0.0000001	-0.02330	0.0022361	0.0001
Y44+	0.00593	0.0000000	0.00593	0.0037787	0.0000
Y44-	-0.02326	-0.0000002	-0.02326	0.0163690	0.0000
Y43+	0.01049	-0.0000002	0.01049	0.0110720	0.0000
Y43-	-0.02366	0.0000001	-0.02366	0.0117518	0.0000
Y42+	-0.00011	0.0000000	-0.00011	0.0029654	0.0000
Y42-	-0.00681	0.0000001	-0.00681	0.0061183	0.0000
Y41+	0.00200	-0.0000001	0.00200	0.0043845	0.0000
Y41-	0.01427	0.0000000	0.01427	0.0044186	0.0000
Y40	0.00010	0.0000000	0.00010	0.0030737	0.0000

THE AVERAGE OF SHIFT/ERROR FOR THE 56 PARAMETERS REFINED ON IS 0.0002
THE MAXIMUM OF SHIFT/ERROR FOR THE 56 PARAMETERS REFINED ON IS 0.0030

AGREEMENT FACTORS BEFORE CYCLE 4 FROM FILE WRITTEN 8 TIMES.

SUM(W*(O-C)**2) IS 1.3157367469E+01

SQRTF(SUM(W*(O-C)**2)/(788 - 56)) 0.1341

	NUMERATOR	DENOMINATOR	
R-FACTOR(F):	72.747	28221.686	R(F) = 0.0026
WEIGHTED R-FACTOR(F):	3.757	1688.303	WR(F) = 0.0022
R-FACTOR(F**2):	6534.498	2850367.271	R(F2) = 0.0023
WEIGHTED R-FACTOR(F**2):	3.627	840.044	WR(F2) = 0.0043

THIS REFINEMENT IS BASED ON F SQUARED

CORRELATION MATRIX

CORRELATION COEFFICIENTS GREATER THAN 0.70700

ATOM	PARAMETER	ATOM	PARAMETER	CORRELATION
SI 01	PCORE	SI 01	PL-SH	-0.84219
SI 01	KAPPA0	SI 01	Y00	-0.80482
AL 01	PCORE	AL 01	PL-SH	-0.77577
AL 01	KAPPA0	AL 01	Y00	-0.83451
MG 01	PCORE	MG 01	PL-SH	-0.71464
MG 01	KAPPA0	MG 01	Y00	-0.72773
O 01	KAPPA0	O 01	Y00	-0.89733

TABLE S7. Properties of the (3,+1) Ring Critical Points in ρ_{EXP} (first row), ρ_{MTSF} (second row), and ρ_{THEO} (third row) of pyrope[a]

RCP No.	1	2	3	4	5	6	7
Multiplicity	96	96	96	48	48	48	96
x	0.1061(14) 0.0994(4) 0.09864	0.0988(12) 0.0893(2) 0.08979	0.1018(25) 0.0801(2) 0.07930	0.0943(24) 0.0719(3) 0.07056	0.0 0.0 0.0	0.2823(14) 0.2837(6) NF[b]	NF[b] NF[b] 0.02733
y	0.4073(10) 0.4096(3) 0.42350	0.2485(6) 0.2486(2) 0.24981	0.2267(13) 0.2363(6) 0.23613	0.3443(24) 0.3219(3) 0.32056	0.250 0.250 0.250	0.0323(14) 0.0337(6) NF[b]	NF[b] NF[b] 0.08445
z	0.3723(10) 0.3694(3) 0.37184	0.1632(5) 0.1576(1) 0.15715	0.0513(20) 0.0693(3) 0.07110	0.125 0.125 0.125	0.0298(9) 0.0356(1) 0.03476	0.375 0.375 NF[b]	NF[b] NF[b] 0.34113
ρ_{rcp}	0.140(8) 0.123(2) 0.0837	0.19(1) 0.121(3) 0.1005	0.16(1) 0.114(3) 0.0964	0.144(9) 0.104(2) 0.0808	0.22(1) 0.154(3) 0.1383	0.112(8) 0.102(2) NF[b]	NF[b] NF[b] 0.054
$\nabla^2\rho_{rcp}$	1.27(2) 1.114(4) 1.1978	1.06(3) 1.303(7) 1.5797	1.35(2) 1.068(7) 1.4293	1.22(2) 0.831(6) 1.1580	1.52(4) 2.156(8) 2.3677	0.79(2) 0.675(4) NF[b]	NF[b] NF[b] 0.692
λ_1	-0.135(4) -0.129(1) -0.1769	-0.33(1) -0.220(3) -0.3298	-0.264(5) -0.161(2) -0.2975	-0.183(4) -0.112(2) -0.2081	-0.45(2) -0.361(3) -0.4870	-0.044(3) -0.059(1) /	/ / -0.0214
λ_2	0.156(5) 0.134(1) 0.3928	0.54(2) 0.467(2) 0.7178	0.14(2) 0.490(2) 0.6811	0.14(2) 0.453(8) 0.6640	0.67(1) 0.501(3) 1.0287	0.111(2) 0.088(1) /	/ / 0.1265
λ_3	1.25(1) 1.109(3) 0.9818	0.85(1) 1.056(8) 1.1916	1.47(1) 0.739(5) 1.0458	1.270(9) 0.491(2) 0.7021	1.29(4) 2.017(9) 1.8260	0.72(2) 0.647(4) /	/ / 0.5872
Distance of the closest anion	1.769 / Si 1.738 / Si 1.673 / Si	1.212 / Mg 1.088 / Mg 1.091 / Mg	1.462 / Mg 1.127 / Mg 1.108 / Mg	1.525 / Mg 1.163 / Mg 1.142 / Mg	1.089 / Mg 1.023 / Mg 1.032 / Mg	1.819 / Si 1.812 / Si /	/ / 1.808 / Mg
Distances of the 2 closest O atoms	1.435 , 1.513 1.442 , 1.561 1.503 , 1.598	1.433 , 1.480 1.489 , 1.542 1.478 , 1.552	1.388 , 1.404 1.496 , 1.543 1.501 , 1.555	1.429 , 1.429 1.557 , 1.557 1.567 , 1.567	1.441 , 1.441 1.475 , 1.475 1.470 , 1.470	1.703 , 1.703 1.717 , 1.717 /	/ / 1.673 , 1.695
S_{E_M}[c]	0.088	0.126	0.354	0.373	0.066	0.023	/
S_{E_T}[d]	0.204	0.125	0.359	0.384	0.057	/	/

[a] *x, y, z*: fractional coordinates of the RCP. Electron density ρ_{rcp} in eÅ^{-3}; its Hessian eigenvalues (λ_1, λ_2, and λ_3) and the corresponding Laplacian ($\nabla^2\rho_{rcp}$) in eÅ^{-5}. Distances between critical points and atoms in Å. Estimated standard deviations in parentheses refer to the last quoted digit.

[b] NF = not found

[c] Separation (Å) between RCP in ρ_{EXP} and ρ_{MTSF}.

[d] Separation (Å) between RCP in ρ_{EXP} and ρ_{THEO}.

TABLE S8 Properties of the (3,+3) Cage Critical Points (CCPs) in ρ_{EXP} (first row), ρ_{MTSF} (second row), and ρ_{THEO} (third row) of pyrope[a]

CCP No.	1	2	3
Multiplicity	96	16	48
x	0.0029(24) 0.0458(12) 0.03468	0.125 0.125 0.125	NF[b] NF[b] 0.29952
y	0.0930(14) 0.0746(5) 0.08223	0.125 0.125 0.125	NF[b] NF[b] 0.04953
z	0.3151(23) 0.3357(10) 0.34585	0.125 0.125 0.125	NF[b] NF[b] 0.375
ρ_{ccp}	0.108(8) 0.089(2) 0.0541	0.076(9) 0.062(3) 0.0223	NF[b] NF[b] 0.041
$\nabla^2\rho_{ccp}$	0.764(22) 0.557(3) 0.6952	0.437(20) 0.291(4) 0.3238	NF[b] NF[b] 0.600
λ_1	0.044(3) 0.052(1) 0.02572	0.141(9) 0.085(2) 0.0989	/ / 0.0553
λ_2	0.145(7) 0.080(2) 0.1156	0.141(9) 0.085(2) 0.0989	/ / 0.1549
λ_3	0.575(13) 0.425(1) 0.5540	0.155(6) 0.121(2) 0.1260	/ / 0.3903
Distance of the two closest anions	1.907(Mg); 1.923 (Si) 1.585(Mg); 2.122 (Si) 1.776(Mg); 1.988(Si)	2.022(Mg); 2.477 (Al) 2.022(Mg); 2.477 (Al) 2.022(Mg); 2.477(Al)	/ / 1.764(Si); 1.764(Si)
Distances of the 2 closest O atoms	1.663; 1.733 1.655; 1.698 1.678; 1.707	2.021; 2.021 2.021; 2.021 2.021; 2.021	/ / 1.886; 1.886
Separation between CCP in ρ_{EXP} and ρ_{MTSF}	0.58	0	/
Separation between CCP in ρ_{EXP} and ρ_{THEO}	0.52	0	/

[a] Units and esd's as in Table S7.
[b] NF = not found.

TABLE S9. Calculated vibrational spectra (cm^{-1}) at 30 K. The IRREP column includes the active irreducible representations.

DFT/B3LYP		DFT/PBE	
Freq (cm^{-1})	IRREP	Freq (cm^{-1})	IRREP
124.7029	(F2g)	138.557	(F1u)
124.7029	(F2g)	138.557	(F1u)
124.7029	(F2g)	138.557	(F1u)
132.7367	(F1u)	144.7775	(Bu)
132.7367	(F1u)	150.1265	(F1u)
132.7367	(F1u)	150.1265	(F1u)
136.1018	(F2u)	150.1265	(F1u)
136.1018	(F2u)	154.0749	(F2g)
136.1018	(F2u)	154.0749	(F2g)
139.0066	(F1u)	154.0749	(F2g)
139.0066	(F1u)	163.0904	(F2u)
139.0066	(F1u)	163.0904	(F2u)
142.8628	(Bu)	163.0904	(F2u)
169.8182	(F1g)	181.8734	(F1g)
169.8182	(F1g)	181.8734	(F1g)
169.8182	(F1g)	181.8734	(F1g)
174.275	(F1g)	182.9139	(F2g)
174.275	(F1g)	182.9139	(F2g)
174.275	(F1g)	182.9139	(F2g)
176.0986	(F2g)	190.2198	(F1g)
176.0986	(F2g)	190.2198	(F1g)
176.0986	(F2g)	190.2198	(F1g)
195.9023	(F1u)	206.2591	(F1u)
195.9023	(F1u)	206.2591	(F1u)
195.9023	(F1u)	206.2591	(F1u)
204.4296	(F1g)	209.245	(Eg)
204.4296	(F1g)	209.245	(Eg)
204.4296	(F1g)	210.2644	(F2u)
210.7029	(F2g)	210.2644	(F2u)
210.7029	(F2g)	210.2644	(F2u)
210.7029	(F2g)	211.1496	(Eu)
211.8023	(F2u)	211.1496	(Eu)
211.8023	(F2u)	212.7766	(F1g)
211.8023	(F2u)	212.7766	(F1g)
213.7128	(Eg)	212.7766	(F1g)
213.7128	(Eg)	213.421	(F2g)
215.4651	(Eu)	213.421	(F2g)
215.4651	(Eu)	213.421	(F2g)
218.4961	(F1u)	225.1307	(F1u)
218.4961	(F1u)	225.1307	(F1u)

218.4961	(F1u)	225.1307	(F1u)
224.4871	(F2u)	226	(F2u)
224.4871	(F2u)	226	(F2u)
224.4871	(F2u)	226	(F2u)
244.6072	(Bg)	239.8153	(Bg)
263.9303	(F1u)	260.3334	(F1u)
263.9303	(F1u)	260.3334	(F1u)
263.9303	(F1u)	260.3334	(F1u)
267.7422	(F2u)	262.921	(F2u)
267.7422	(F2u)	262.921	(F2u)
267.7422	(F2u)	262.921	(F2u)
273.1478	(F2g)	274.305	(F2g)
273.1478	(F2g)	274.305	(F2g)
273.1478	(F2g)	274.305	(F2g)
278.9481	(F1g)	280.6915	(F1g)
278.9481	(F1g)	280.6915	(F1g)
278.9481	(F1g)	280.6915	(F1g)
293.9985	(F1g)	286.9314	(F1g)
293.9985	(F1g)	286.9314	(F1g)
293.9985	(F1g)	286.9314	(F1g)
294.0904	(F2u)	289.1322	(F2u)
294.0904	(F2u)	289.1322	(F2u)
294.0904	(F2u)	289.1322	(F2u)
311.3712	(Eg)	310.3513	(Eu)
311.3712	(Eg)	310.3513	(Eu)
313.7668	(Eu)	312.6398	(Eg)
313.7668	(Eu)	312.6398	(Eg)
319.6575	(Bg)	314.559	(F2g)
320.8803	(Au)	314.559	(F2g)
323.2248	(F2g)	314.559	(F2g)
323.2248	(F2g)	316.1705	(Au)
323.2248	(F2g)	324.1023	(Bg)
328.0325	(Bu)	328.3191	(Bu)
337.4539	(F1g)	333.3251	(F1u)
337.4539	(F1g)	333.3251	(F1u)
337.4539	(F1g)	333.3251	(F1u)
342.4738	(F2u)	334.6741	(F1g)
342.4738	(F2u)	334.6741	(F1g)
342.4738	(F2u)	334.6741	(F1g)
343.8861	(F1u)	338.5559	(F2u)
343.8861	(F1u)	338.5559	(F2u)
343.8861	(F1u)	338.5559	(F2u)
346.785	(Eg)	341.8555	(F1g)
346.785	(Eg)	341.8555	(F1g)
348.9313	(F1g)	341.8555	(F1g)

348.9313	(F1g)	345.3771	(Eg)
348.9313	(F1g)	345.3771	(Eg)
350.2559	(F1u)	345.6793	(F2u)
350.2559	(F1u)	345.6793	(F2u)
350.2559	(F1u)	345.6793	(F2u)
352.4243	(F2u)	346.2116	(F1u)
352.4243	(F2u)	346.2116	(F1u)
352.4243	(F2u)	346.2116	(F1u)
355.9949	(Eu)	346.5623	(Eu)
355.9949	(Eu)	346.5623	(Eu)
359.728	(F2g)	352.7179	(F2g)
359.728	(F2g)	352.7179	(F2g)
359.728	(F2g)	352.7179	(F2g)
360.9929	(Ag)	361.5383	(Ag)
377.5704	(Eu)	370.9608	(Eu)
377.5704	(Eu)	370.9608	(Eu)
385.2484	(Eg)	375.9214	(F1g)
385.2484	(Eg)	375.9214	(F1g)
385.3385	(Au)	375.9214	(F1g)
385.6279	(F1g)	377.0622	(F1u)
385.6279	(F1g)	377.0622	(F1u)
385.6279	(F1g)	377.0622	(F1u)
387.8294	(F1u)	377.6877	(Au)
387.8294	(F1u)	381.4513	(Eg)
387.8294	(F1u)	381.4513	(Eg)
393.6132	(Bu)	382.1601	(Bu)
393.8348	(F2g)	389.665	(F2g)
393.8348	(F2g)	389.665	(F2g)
393.8348	(F2g)	389.665	(F2g)
408.505	(F2u)	400.9317	(F2u)
408.505	(F2u)	400.9317	(F2u)
408.505	(F2u)	400.9317	(F2u)
428.8864	(F1u)	411.8187	(F1u)
428.8864	(F1u)	411.8187	(F1u)
428.8864	(F1u)	411.8187	(F1u)
441.3122	(Eu)	423.7633	(Eu)
441.3122	(Eu)	423.7633	(Eu)
450.2469	(Bg)	437.7143	(Bg)
462.4036	(F2u)	452.1133	(F2u)
462.4036	(F2u)	452.1133	(F2u)
462.4036	(F2u)	452.1133	(F2u)
467.624	(F1u)	455.7722	(F1u)
467.624	(F1u)	455.7722	(F1u)
467.624	(F1u)	455.7722	(F1u)
470.1678	(Au)	457.8887	(Au)

477.363	(F1g)	463.983	(F1g)
477.363	(F1g)	463.983	(F1g)
477.363	(F1g)	463.983	(F1g)
481.1834	(F1u)	464.7599	(F1u)
481.1834	(F1u)	464.7599	(F1u)
481.1834	(F1u)	464.7599	(F1u)
497.2775	(F2g)	482.4204	(F2g)
497.2775	(F2g)	482.4204	(F2g)
497.2775	(F2g)	482.4204	(F2g)
504.303	(F1g)	488.1015	(F1g)
504.303	(F1g)	488.1015	(F1g)
504.303	(F1g)	488.1015	(F1g)
510.9308	(F2g)	494.2588	(F2g)
510.9308	(F2g)	494.2588	(F2g)
510.9308	(F2g)	494.2588	(F2g)
512.2171	(F2u)	497.1654	(F2u)
512.2171	(F2u)	497.1654	(F2u)
512.2171	(F2u)	497.1654	(F2u)
513.5977	(Eu)	507.2624	(Eu)
513.5977	(Eu)	507.2624	(Eu)
527.0024	(Bu)	509.0379	(Eg)
527.8059	(Eg)	509.0379	(Eg)
527.8059	(Eg)	519.1686	(Bu)
545.1693	(F2u)	533.842	(F2u)
545.1693	(F2u)	533.842	(F2u)
545.1693	(F2u)	533.842	(F2u)
546.5131	(F1u)	542.0741	(F1u)
546.5131	(F1u)	542.0741	(F1u)
546.5131	(F1u)	542.0741	(F1u)
562.6367	(Eu)	548.9023	(Eu)
562.6367	(Eu)	548.9023	(Eu)
570.0066	(Ag)	550.1212	(Ag)
582.7842	(F1g)	559.5844	(Bg)
582.7842	(F1g)	562.5656	(F1g)
582.7842	(F1g)	562.5656	(F1g)
583.795	(Bg)	562.5656	(F1g)
593.9879	(F1u)	584.6703	(F2g)
593.9879	(F1u)	584.6703	(F2g)
593.9879	(F1u)	584.6703	(F2g)
607.491	(F2g)	585.7031	(F1u)
607.491	(F2g)	585.7031	(F1u)
607.491	(F2g)	585.7031	(F1u)
635.0118	(Eg)	609.5331	(Eg)
635.0118	(Eg)	609.5331	(Eg)
649.1855	(F2u)	626.8147	(F2g)

649.1855	(F2u)	626.8147	(F2g)
649.1855	(F2u)	626.8147	(F2g)
654.0024	(F2g)	633.6892	(F2u)
654.0024	(F2g)	633.6892	(F2u)
654.0024	(F2g)	633.6892	(F2u)
660.1252	(F2u)	640.0929	(F2u)
660.1252	(F2u)	640.0929	(F2u)
660.1252	(F2u)	640.0929	(F2u)
668.8076	(Eu)	644.433	(Eu)
668.8076	(Eu)	644.433	(Eu)
679.6386	(F1u)	661.1084	(F1u)
679.6386	(F1u)	661.1084	(F1u)
679.6386	(F1u)	661.1084	(F1u)
724.7215	(Au)	708.2627	(Au)
872.5582	(F1g)	849.8976	(Eg)
872.5582	(F1g)	849.8976	(Eg)
872.5582	(F1g)	854.6889	(F1g)
874.8591	(Eg)	854.6889	(F1g)
874.8591	(Eg)	854.6889	(F1g)
889.536	(F2g)	869.4916	(F2u)
889.536	(F2g)	869.4916	(F2u)
889.536	(F2g)	869.4916	(F2u)
889.701	(F2u)	871.3153	(F2g)
889.701	(F2u)	871.3153	(F2g)
889.701	(F2u)	871.3153	(F2g)
891.9232	(F1u)	871.5286	(F1g)
891.9232	(F1u)	871.5286	(F1g)
891.9232	(F1u)	871.5286	(F1g)
896.9961	(F1g)	873.0313	(F1u)
896.9961	(F1g)	873.0313	(F1u)
896.9961	(F1g)	873.0313	(F1u)
923.293	(Bu)	897.4285	(Eu)
923.6366	(Eu)	897.4285	(Eu)
923.6366	(Eu)	899.7119	(Bu)
923.9133	(F1u)	903.8292	(F1u)
923.9133	(F1u)	903.8292	(F1u)
923.9133	(F1u)	903.8292	(F1u)
925.2395	(F2g)	905.0054	(F2g)
925.2395	(F2g)	905.0054	(F2g)
925.2395	(F2g)	905.0054	(F2g)
930.5022	(F2u)	907.7201	(F2u)
930.5022	(F2u)	907.7201	(F2u)
930.5022	(F2u)	907.7201	(F2u)
939.4091	(Ag)	910.0289	(Ag)
963.5265	(Eu)	941.3953	(Eu)

963.5265	(Eu)	941.3953	(Eu)
965.5766	(Eg)	943.5961	(Eg)
965.5766	(Eg)	943.5961	(Eg)
975.5202	(F2u)	951.3436	(F2u)
975.5202	(F2u)	951.3436	(F2u)
975.5202	(F2u)	951.3436	(F2u)
993.4567	(F1g)	967.6903	(F1g)
993.4567	(F1g)	967.6903	(F1g)
993.4567	(F1g)	967.6903	(F1g)
997.5773	(F1u)	974.7122	(F1u)
997.5773	(F1u)	974.7122	(F1u)
997.5773	(F1u)	974.7122	(F1u)
1053.1599	(Bg)	1026.7557	(Bg)
1069.6725	(Au)	1040.9893	(Au)
1087.7217	(F2g)	1057.4804	(F2g)
1087.7217	(F2g)	1057.4804	(F2g)
1087.7217	(F2g)	1057.4804	(F2g)

TABLE S10. Results of the 96h–disordered model (DIS96h)

LIST OF THE FINAL VALUES FOR THE 28 REFINED STRUCTURAL PARAMETERS OF PYROPE FROM A LEAST-SQUARES REFINEMENT BASED ON 785 EXPERIMENTAL STRUCTURE FACTORS (Fobs**2'S):

VALRAY OUTPUT OF THE FINAL CYCLE:

THE CRITERION FOR CONVERGENCE AT CYCLE: 33 1.11629E-08

LEAST SQUARES TERMINATED AT CYCLE 33 CRIT IS LESS THAN 1.000E-06

PARAMETERS AFTER CYCLE 33

*** U-S OR UIJ-S HAVE BEEN MULTIPLIED BY 100 FOR OUTPUT***
*** C-S AND D-S BY 10000 ***

PARAMETER	OLD	CHANGE	NEW	ERROR	SHIFT/ERROR
FC SCL	1.14816	ESTIMATED	1.14813	0.0721600	
G11	0.24219	0.0000103	0.24220	0.0084021	0.0012
ATOM TYPE: SI 0	ATOM NAME: 1				
U11	0.20531	0.0000000	0.20531	0.0025134	0.0000
U22	0.20531	0.0000000	0.20531	CONSTRAINED	
U33	0.18218	0.0000000	0.18218	0.0030397	0.0000
KAPPA0	0.99646	0.0000372	0.99650	0.0176893	0.0021
PCORE	2.24554	0.0000030	2.24555	CONSTRAINED	
PL-SH	8.00841	0.0000088	8.00842	CONSTRAINED	
Y00	5.07776	-0.0007929	5.07697	0.3772427	0.0021
ATOM TYPE: AL 0	ATOM NAME: 1				
U11	0.23478	0.0000001	0.23478	0.0025626	0.0000
U22	0.23478	0.0000001	0.23478	CONSTRAINED	
U33	0.23478	0.0000001	0.23478	CONSTRAINED	
U12	-0.00198	0.0000000	-0.00198	0.0015341	0.0000
U13	-0.00198	0.0000000	-0.00198	CONSTRAINED	
U23	-0.00198	0.0000000	-0.00198	CONSTRAINED	
KAPPA0	1.05442	0.0000437	1.05446	0.0229089	0.0019
PCORE	2.24554	0.0000030	2.24555	0.0054285	0.0005
PL-SH	8.00841	0.0000088	8.00842	0.0156032	0.0006
Y00	4.05065	-0.0008840	4.04976	0.4182838	0.0021
ATOM TYPE: MG 0	ATOM NAME: 1				
X	0.00574	0.0000002	0.00574	0.0003782	0.0004
Y	0.25092	0.0000000	0.25092	0.0000804	0.0004
Z	0.12492	0.0000000	0.12492	0.0001101	0.0000
U11	0.11181	-0.0000272	0.11178	0.0641695	0.0004
KAPPA0	1.11982	0.0000527	1.11987	0.0305332	0.0017
PCORE	2.24554	0.0000030	2.24555	CONSTRAINED	
PL-SH	8.00841	0.0000088	8.00842	CONSTRAINED	
Y00	3.44809	-0.0009800	3.44711	0.4407151	0.0022
ATOM TYPE: O 0	ATOM NAME: 1				
X	0.03291	0.0000000	0.03291	0.0000091	0.0001
Y	0.05072	0.0000000	0.05072	0.0000090	0.0000
Z	0.65332	0.0000000	0.65332	0.0000089	0.0001
U11	0.37672	0.0000012	0.37672	0.0043038	0.0003
U22	0.42781	0.0000011	0.42781	0.0043268	0.0003
U33	0.31941	0.0000014	0.31941	0.0042628	0.0003
U12	0.03459	-0.0000001	0.03459	0.0021502	0.0000
U13	-0.05876	0.0000001	-0.05876	0.0021760	0.0001

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U23                0.00391     -0.0000001    0.00391    0.0021161       0.0001
KAPPA0             0.91490     -0.0000016    0.91489    0.0026303       0.0006
PCORE              2.24554      0.0000030    2.24555  CONSTRAINED
Y00                7.24798      0.0000351    7.24802    0.0403097       0.0009

THE AVERAGE OF SHIFT/ERROR FOR THE   28 PARAMETERS REFINED ON IS        0.0007

THE MAXIMUM OF SHIFT/ERROR FOR THE   28 PARAMETERS REFINED ON IS        0.0022

ESTIMATED AGREEMENT AFTER CYCLE  33

SUM(W*(O-C)**2) IS  1.3293528112E+03

SQRTF(SUM(W*(O-C)**2)/(NO-NV)) IS     1.3252

AGREEMENT FACTORS BEFORE CYCLE  34 FROM FILE WRITTEN     3 TIMES.

SUM(W*(O-C)**2) IS       1.3293527765E+03

SQRTF(SUM(W*(O-C)**2)/(   785 -   28))    1.3252

                                   NUMERATOR   DENOMINATOR

R-FACTOR(F):                         324.260     26284.598      R(F) = 0.0123

WEIGHTED R-FACTOR(F):                 38.026      2590.044     WR(F) = 0.0147

R-FACTOR(F**2):                     32834.633   2531464.604     R(F2) = 0.0130

WEIGHTED R-FACTOR(F**2):              36.460      1289.568    WR(F2) = 0.0283

THIS REFINEMENT IS BASED ON F SQUARED
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TABLE S11. Results of the 48f–disordered model (DIS48F)

LIST OF THE FINAL VALUES FOR THE 26 REFINED STRUCTURAL PARAMETERS OF PYROPE FROM A LEAST-SQUARES REFINEMENT BASED ON 785 EXPERIMENTAL STRUCTURE FACTORS (Fobs**2'S):

VALRAY OUTPUT OF THE FINAL CYCLE:

THE CRITERION FOR CONVERGENCE AT CYCLE: 26 9.72386E-09

LEAST SQUARES TERMINATED AT CYCLE 26 CRIT IS LESS THAN 1.000E-06

PARAMETERS AFTER CYCLE 26

*** U-S OR UIJ-S HAVE BEEN MULTIPLIED BY 100 FOR OUTPUT***
*** C-S AND D-S BY 10000 ***

PARAMETER	OLD	CHANGE	NEW	ERROR	SHIFT/ERROR
FC SCL	1.14716	ESTIMATED	1.14716	0.0861932	
G11	0.23819	-0.0000156	0.23817	0.0100474	0.0016
ATOM TYPE: SI 0 ATOM NAME: 1					
U11	0.20566	-0.0000005	0.20566	0.0029985	0.0002
U22	0.20566	-0.0000005	0.20566	CONSTRAINED	
U33	0.18348	-0.0000005	0.18347	0.0036395	0.0001
KAPPA0	0.99722	-0.0000009	0.99722	0.0211278	0.0000
PCORE	2.24735	0.0000009	2.24735	CONSTRAINED	
PL-SH	8.00311	0.0000025	8.00312	CONSTRAINED	
Y00	5.03754	0.0000269	5.03757	0.4509619	0.0001
ATOM TYPE: AL 0 ATOM NAME: 1					
U11	0.23593	-0.0000004	0.23593	0.0030537	0.0001
U22	0.23593	-0.0000004	0.23593	CONSTRAINED	
U33	0.23593	-0.0000004	0.23593	CONSTRAINED	
U12	-0.00101	0.0000000	-0.00101	0.0018577	0.0000
U13	-0.00101	0.0000000	-0.00101	CONSTRAINED	
U23	-0.00101	0.0000000	-0.00101	CONSTRAINED	
KAPPA0	1.05541	-0.0000007	1.05541	0.0276028	0.0000
PCORE	2.24735	0.0000009	2.24735	0.0065012	0.0001
PL-SH	8.00311	0.0000025	8.00312	0.0188469	0.0001
Y00	4.00635	0.0000261	4.00638	0.5002960	0.0001
ATOM TYPE: MG 0 ATOM NAME: 1					
Z	0.12491	0.0000000	0.12491	0.0001279	0.0000
U11	0.58672	-0.0000006	0.58672	0.0093625	0.0001
KAPPA0	1.10892	-0.0000007	1.10892	0.0349301	0.0000
PCORE	2.24735	0.0000009	2.24735	CONSTRAINED	
PL-SH	8.00311	0.0000025	8.00312	CONSTRAINED	
Y00	3.45853	0.0000329	3.45856	0.5258224	0.0001
ATOM TYPE: O 0 ATOM NAME: 1					
X	0.03292	0.0000000	0.03292	0.0000110	0.0000
Y	0.05073	0.0000000	0.05073	0.0000109	0.0000
Z	0.65333	0.0000000	0.65333	0.0000107	0.0000
U11	0.37713	0.0000004	0.37713	0.0051804	0.0001
U22	0.43136	0.0000004	0.43136	0.0052011	0.0001
U33	0.32104	0.0000004	0.32104	0.0051483	0.0001
U12	0.03368	0.0000000	0.03368	0.0026052	0.0000
U13	-0.06302	0.0000000	-0.06302	0.0026227	0.0000
U23	0.00696	0.0000000	0.00696	0.0025554	0.0000

```
KAPPA0             0.91422     -0.0000003    0.91422    0.0031580       0.0001
PCORE              2.24735      0.0000009    2.24735  CONSTRAINED
Y00                7.24647      0.0000032    7.24647    0.0485002       0.0001

THE AVERAGE OF SHIFT/ERROR FOR THE   26 PARAMETERS REFINED ON IS        0.0001

THE MAXIMUM OF SHIFT/ERROR FOR THE   26 PARAMETERS REFINED ON IS        0.0016

ESTIMATED AGREEMENT AFTER CYCLE  26

SUM(W*(O-C)**2) IS  1.9496328959E+03

SQRTF(SUM(W*(O-C)**2)/(NO-NV)) IS     1.6027

AGREEMENT FACTORS BEFORE CYCLE  27 FROM FILE WRITTEN     3 TIMES.

SUM(W*(O-C)**2) IS       1.9496328853E+03

SQRTF(SUM(W*(O-C)**2)/(   785 -   26))    1.6027

                                    NUMERATOR   DENOMINATOR

R-FACTOR(F):                          397.107     26284.598      R(F) = 0.0151

WEIGHTED R-FACTOR(F):                  45.901      2590.044     WR(F) = 0.0177

R-FACTOR(F**2):                     34628.318   2531464.604     R(F2) = 0.0137

WEIGHTED R-FACTOR(F**2):               44.155      1289.568    WR(F2) = 0.0342

THIS REFINEMENT IS BASED ON F SQUARED
```

TABLE S12. Results of the monopole-only, harmonic ordered model (24c).

LIST OF THE FINAL VALUES FOR THE 27 REFINED STRUCTURAL PARAMETERS OF PYROPE FROM A LEAST-SQUARES REFINEMENT BASED ON 785 EXPERIMENTAL STRUCTURE FACTORS (Fobs**2'S):

VALRAY OUTPUT OF THE FINAL CYCLE:

THE CRITERION FOR CONVERGENCE AT CYCLE: 11 4.16078E-07

LEAST SQUARES TERMINATED AT CYCLE 11 CRIT IS LESS THAN 1.000E-06

*** U-S OR UIJ-S HAVE BEEN MULTIPLIED BY 100 FOR OUTPUT***

PARAMETER	OLD	CHANGE	NEW	ERROR	SHIFT/ERROR
FC SCL	1.12905	ESTIMATED	1.12903	0.0688615	
G11	0.21839	-0.0000719	0.21832	0.0073685	0.0098
ATOM TYPE: SI 0 ATOM NAME: 1					
U11	0.17606	-0.0000040	0.17606	0.0030124	0.0013
U22	0.17606	-0.0000040	0.17606	CONSTRAINED	
U33	0.15351	-0.0000040	0.15350	0.0033773	0.0012
KAPPA0	0.97835	0.0000243	0.97838	0.0154883	0.0016
PCORE	2.16144	0.0000032	2.16144	CONSTRAINED	
PL-SH	8.06997	0.0000118	8.06998	CONSTRAINED	
Y00	5.12718	-0.0005468	5.12664	0.3557882	0.0015
ATOM TYPE: AL 0 ATOM NAME: 1					
U11	0.19967	-0.0000032	0.19967	0.0033068	0.0010
U22	0.19967	-0.0000032	0.19967	CONSTRAINED	
U33	0.19967	-0.0000032	0.19967	CONSTRAINED	
U12	-0.00146	0.0000000	-0.00146	0.0014099	0.0000
U13	-0.00146	0.0000000	-0.00146	CONSTRAINED	
U23	-0.00146	0.0000000	-0.00146	CONSTRAINED	
KAPPA0	1.01342	0.0000180	1.01343	0.0197999	0.0009
PCORE	2.16144	0.0000032	2.16144	0.0074167	0.0004
PL-SH	8.06997	0.0000118	8.06998	0.0147609	0.0008
Y00	4.27153	-0.0005652	4.27096	0.4120978	0.0014
ATOM TYPE: MG 0 ATOM NAME: 1					
U11	0.43865	-0.0000026	0.43865	0.0041730	0.0006
U22	0.43865	-0.0000026	0.43865	CONSTRAINED	
U33	0.28185	-0.0000025	0.28184	0.0046907	0.0005
U12	0.07483	-0.0000001	0.07483	0.0026335	0.0000
KAPPA0	1.05393	0.0000176	1.05394	0.0265969	0.0007
PCORE	2.16144	0.0000032	2.16144	CONSTRAINED	
PL-SH	8.06997	0.0000118	8.06998	CONSTRAINED	
Y00	3.49852	-0.0006361	3.49789	0.4201430	0.0015
ATOM TYPE: O 0 ATOM NAME: 1					
X	0.03291	0.0000000	0.03291	0.0000084	0.0000
Y	0.05072	0.0000000	0.05072	0.0000083	0.0000
Z	0.65332	0.0000000	0.65332	0.0000081	0.0001
U11	0.32279	0.0000007	0.32279	0.0053006	0.0001
U22	0.37506	0.0000006	0.37506	0.0052811	0.0001
U33	0.26642	0.0000007	0.26642	0.0052412	0.0001
U12	0.03379	0.0000000	0.03379	0.0019675	0.0000
U13	-0.05922	0.0000000	-0.05922	0.0019885	0.0000

```
U23                0.00470      0.0000000    0.00470    0.0019355       0.0000
KAPPA0             0.94635     -0.0000010    0.94635    0.0032178       0.0003
PCORE              2.16144      0.0000032    2.16144  CONSTRAINED
Y00                6.96682      0.0000168    6.96683    0.0383905       0.0004

THE AVERAGE OF SHIFT/ERROR FOR THE   27 PARAMETERS REFINED ON IS        0.0009

THE MAXIMUM OF SHIFT/ERROR FOR THE   27 PARAMETERS REFINED ON IS        0.0098

ESTIMATED AGREEMENT AFTER CYCLE  11

SUM(W*(O-C)**2) IS  1.1230870096E+03

SQRTF(SUM(W*(O-C)**2)/(NO-NV)) IS     1.2172

AGREEMENT FACTORS BEFORE CYCLE  12 FROM FILE WRITTEN     8 TIMES.

SUM(W*(O-C)**2) IS       1.1230870088E+03

SQRTF(SUM(W*(O-C)**2)/(   785 -   27))    1.2172

                                   NUMERATOR   DENOMINATOR

R-FACTOR(F):                         284.886     26284.598      R(F) = 0.0108

WEIGHTED R-FACTOR(F):                 34.960      2590.044     WR(F) = 0.0135

R-FACTOR(F**2):                    29500.588   2531464.604     R(F2) = 0.0117

WEIGHTED R-FACTOR(F**2):              33.512      1289.568    WR(F2) = 0.0260

THIS REFINEMENT IS BASED ON F SQUARED
```

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