Experimental Electron Density Distribution and QTAIM Topological Analysis for the Perovskite Mineral: *Sulphohalite* – $Na_6(SO_4)_2FCl$

Agata Wróbel, dr Roman Gajda, prof. dr hab. Krzysztof Woźniak.
Department of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Poland

Outline

The acquaintance of *modern crystallography* onto *mineralogy* will be approached by endeavouring in an experimental charge density study for the double antiperovskite mineral – *sulphohalite* [$Na_6(SO_4)_2FCl$]. *High-resolution* X-ray diffraction data was collected employing **Ag*Kα*** radiation (λ = 0.56087 Å) to a resolution of **0.3941 Å** at **100K**. The crystal structure was solved by direct methods implementation based on merged SHELX data – in compliance with the *Independent Atom Model* (**IAM**). *Electron density* (**ED**) distribution – **ρ(r)** was modelled, as proposed in the Hansen-Coppens formalism, by consecutive least-square multipolar refinements. The *quality* of collected data and computed **ED** model was assesed; conclusively it proved to be of high grade.

High-resolution data collection and ED refinement

Table 1. Crystal data for *sulphohalite*.

Crystal	*Sulphohalite*
Chemical Formula	$Na_6(SO_4)_2FCl$
Formula molecular mass [g/mol]	384.51
Crystal System	Cubic
Space Group	$Fm\bar{3}m$
a [Å]	10.03124(7)
Volume [Å^3]	1009.40(2)
Z	4
D_x [g/cm^3]	2.530
μ[mm^{-1}]	0.552
F(000)	752.0
Crystal size [mm^3]	0.129 × 0.081 × 0.070

Table 2. Data collection for *sulphohalite*.

Data collection	*Sulphohalite*
Temperature [K]	100(2)
Radiation type	Ag Kα (λ = 0.56087 Å)
2Θ range for data collection [°]	5.55 to 89.306
Diffractometer	Agilent Technologies SuperNova
Absorption correction	SCALE3 ABSPACK
T_{min}, T_{max}	0.5019, 1.0000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5847, 477, 477
R_{int}, R_{sigma}	0.0675, 0.0263
Index Ranges	-25 ≤ h ≤ 25; -25 ≤ k ≤ 25; -25 ≤ l ≤ 25
$\sin\theta/\lambda_{max}$ (Å^{-1})	0.500

Table 3. Refinement features for the *Independent Atom Model* (**IAM**) and the *Multipole Model* (**MM**).

Refinement	IAM	MM
Data / restraints / parameters	477 / 0 / 10	477 / 22 / 33
Goodness-of-fit on F^2	1.0390	2.8895
Final *R* indexes [$I \geq 2\sigma(I)$] on F^2	R_1 = 0.0292; wR_2 = 0.0496	R_1 = 0.0188; wR_2 = 0.0423
Final *R* indexes [all data] on F^2	R_1 = 0.0323; wR_2 = 0.0830	R_1 = 0.0229; wR_2 = 0.0698
Largest diff. peak/hole[e·Å^{-3}]	0.488 / -1.477	0.402 / -0.846

Crystal structure

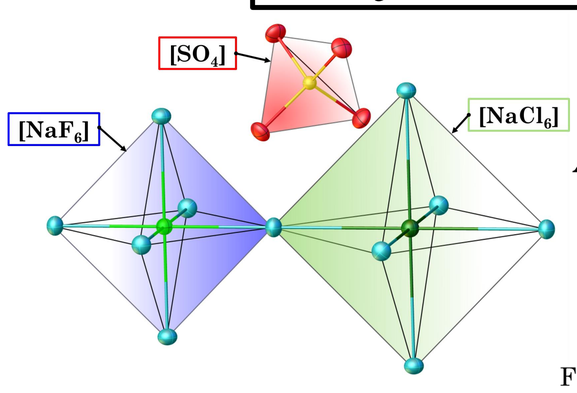


Fig 1. The crystal structure of *sulphohalite* is presented as a polyhedral construct. Displacement ellipsoids are drawn at a 60% probability level.

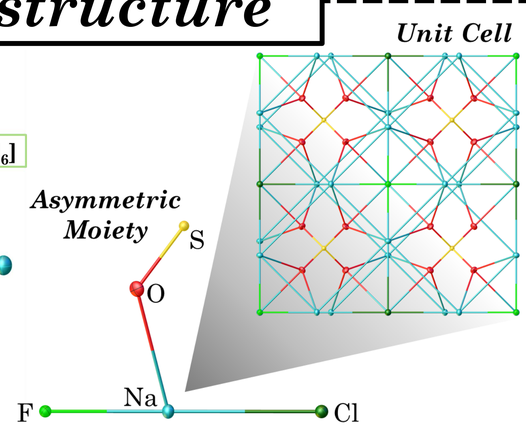
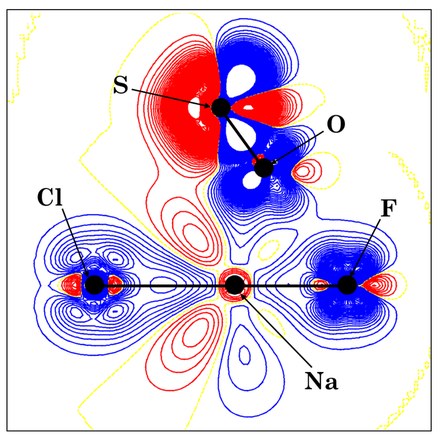


Fig 2. The asymmetric moiety and the unit cell of the *sulphohalite* crystal. Displacement ellipsoids are drawn at a 60% probability level.

Deformation of ED – Δρ(r)



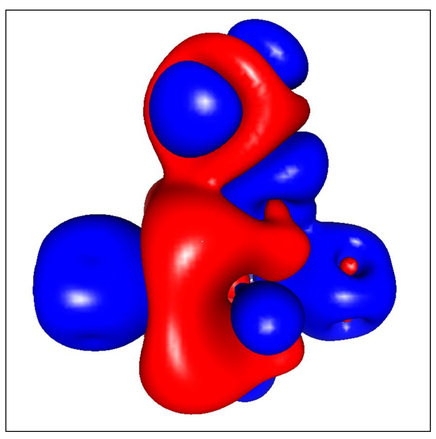


Fig 3. 2D and **3D** Static Deformation of **ED** maps – calculated based on the subtraction of the **IAM** from the **MM** model and projected on to the (01$\bar{1}$) plane. *Positive* and *negative* values of the function are correspondingly denoted by blue and red. Standard contour levels are drawn up to ± **0.001 e·Å^{-3}.** *Zero* contour lines are presented in yellow. 3D surface corresponds to the isovalue**: ± 0.001 e·Å^{-3}.**

Atomic Basins (AB's)

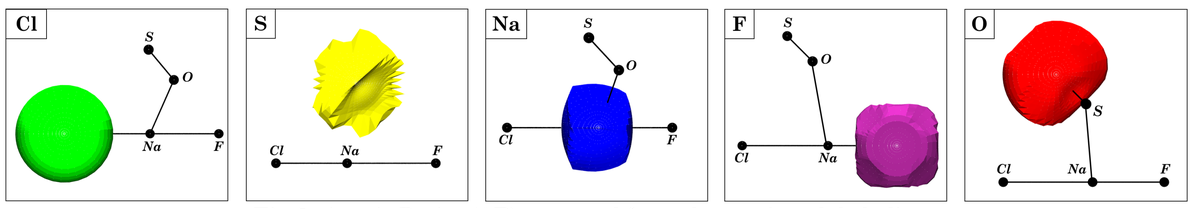


Fig 5. *Atomic Basins* (**AB**) computed for each atom in *sulphohalite*.

Table 7. Computed **AB** volumes and charges.

Atom	V_{ab} [Å^3]	Q_{ab} [e$^-$]
Cl	38.920	-0.836
S	5.656	3.168
Na	7.931	0.910
F	14.178	-1.334
O	17.416	-1.227

Table 8. Percentage of "*unaccounted*" unit cell volume by experimental **AB**.

Unit cell volume	V [Å^3]	V [%]
$V = a^3$	1009.389	100.0
$\Sigma(n \cdot V_{ab})$	1005.293	99.594
$\Delta[V - \Sigma(n \cdot V_{ab})]$	4.095	**0.406**

Table 9. Percentage of "*unaccounted*" unit cell charge by experimental **AB**.

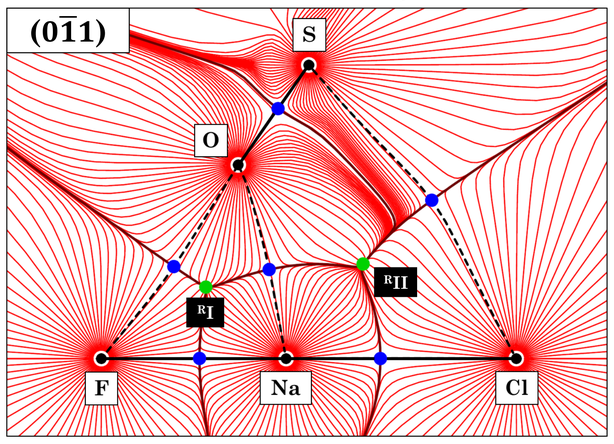
Unit cell charge	*n* [e$^-$]	*n* [%]
Number of electrons $-\Sigma(n \cdot Z)$	752.0	100.0
Number of "*unaccounted*" electrons $-\Sigma(n \cdot Q_{ab})$	-0.750	**0.010**

Table 10. *Atomic Lagrangian* – **L**, for computed **AB** in the *sulphohalite* crystal.

Atom	*Cl*	*S*	*Na*	*F*	*O*
Atomic Lagrangian - **L**	$1.401 \cdot 10^{-2}$	$1.042 \cdot 10^{-3}$	$1.726 \cdot 10^{-3}$	$1.460 \cdot 10^{-3}$	$4.899 \cdot 10^{-3}$

QTAIM – Topological Analysis

Gradient Vector Field of ED – ∇ρ(r)



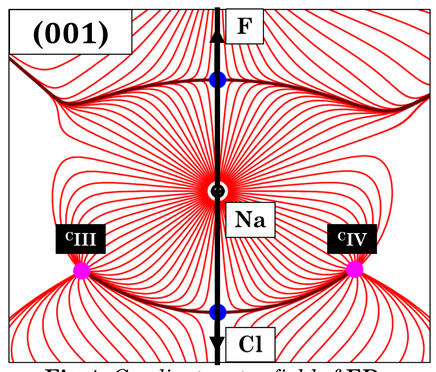


Fig 4. *Gradient vector field* of **ED**, drawn for two planes in the crystal of *sulphohalite*. *Bond*, *Ring* and *Cage* **CP's** are respectively denoted by blue, green, and magenta circles. Interatomic bonding is presented by black lines; whereas bonding paths are depicted by black dashed lines.

Laplacian of ED – ∇²ρ(r)

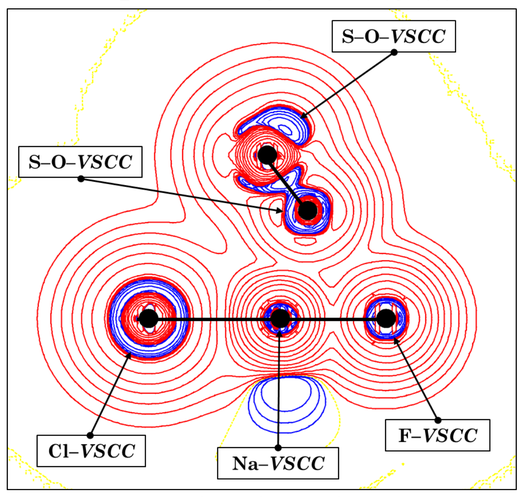


Fig 6. *Valence Shell Charge Concentrations* **(VSCC's)**, denoted on the **2D** *Laplacian* of **ED** contour plot drawn onto the *sulphohalite's* (01$\bar{1}$) plane. Logarithmic contour levels are drawn up to ± **0.001 e·Å^{-3}.** *Positive* and *negative* values of the function are correspondingly denoted by blue and red. *Zero* contour lines are presented in yellow.

Critical Points (CP's)

Table 4. *Bond Critical Point* (**BCP**) features.

BCP *type*	$\rho(r_{BCP})$ [e·Å^{-3}]	$\nabla^2\rho(r_{BCP})$ [e·Å^{-5}]	Ellipticity - ε
Cl···S	0.008	0.120	0.090
Cl···Na	0.126	0.575	0.000
S–O	2.484	-31.00	0.002
Na···O	0.129	1.931	0.197
Na···F	0.207	3.022	0.000
F···O	0.061	0.868	0.340

Table 5. *Ring Critical Point* (**RCP**) features.

RCP *type*	$\rho(r_{RCP})$ [e·Å^{-3}]	$\nabla^2\rho(r_{RCP})$ [e·Å^{-5}]
^{R}I	0.0520	R0.912
^{R}II	-0.0018	0.332
^{R}III, ^{R}IV, ^{R}V	-0.0070	0.201

Table 6. *Cage Critical Point* (**CCP**) features.

CCP *type*	$\rho(r_{CCP})$ [e·Å^{-3}]	$\nabla^2\rho(r_{CCP})$ [e·Å^{-5}]
^{C}I, ^{C}II	-0.025	0.514
^{C}III, ^{C}IV	-0.026	0.401

Interatomic Interactions

Table 11. Evaluation of the nature of interatomic interactions according to the *dichotomous* classification.

Interatomic Interaction	*Cl···S*	*Cl···Na*	*S–O*	*Na···O*	*Na···F*	*F···O*
$\nabla^2\rho(r_{BCP})$ [e·Å^{-5}]	> 0	> 0	< 0	> 0	> 0	> 0
VSCC overlap at BP	No	No	Yes	No	No	No
Outcome	*Closed-Shell*	*Closed-Shell*	*Shared-Shell*	*Closed-Shell*	*Closed-Shell*	*Closed-Shell*

Conclusions

Topological analysis according to the *Quantum Theory of Atoms in Molecules* – **QTAIM** was undertaken based on the experimentally attained distribution of charge. *Atomic basins* (**AB's**) were delineated based on the *zero flux surfaces* (**ZFS's**) denoted on the *gradient vector field* of **ED – ∇ρ(r)**. The appertaining volumes and charges of each basin were computed by full-volume integration. Following, *critical points* (**CP's**) were identified as local extrema of the **∇ρ(r)** function, and classified based on the *Laplacian* of **ED – ∇²ρ(r).** Morse's '*characteristic set*' condition was met. The study of *primary bundles* (**PB's**), as proposed by Pendás, revealed the interconnection between **AB's** and **CP's** onto *basins of attraction* or *basins of repulsion*. The nature of interatomic interactions was assessed through the *dichotomous* classification. The **S–O** contact was acknowledged as a *covalent* with a shared-shell. The remaining contacts were characterized as *non-covalent* closed-shell (**Cl···Na**, **Na···O** and **Na···F**) or *weak van der Waals* closed-shell (**Cl···S** and **F···O**).

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