

Phase refinement with EDEN: Point defect structure in inorganic crystals

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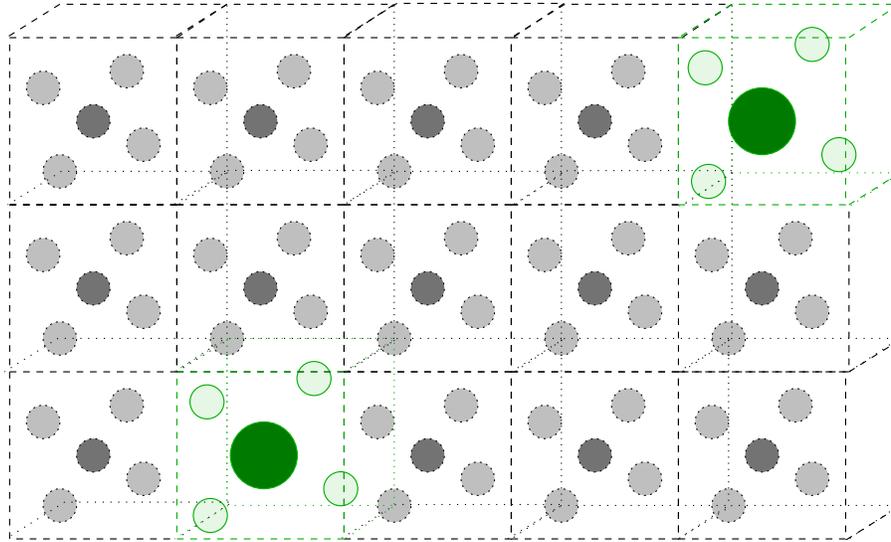
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How to make non-periodic objects
look periodic.

Point defects



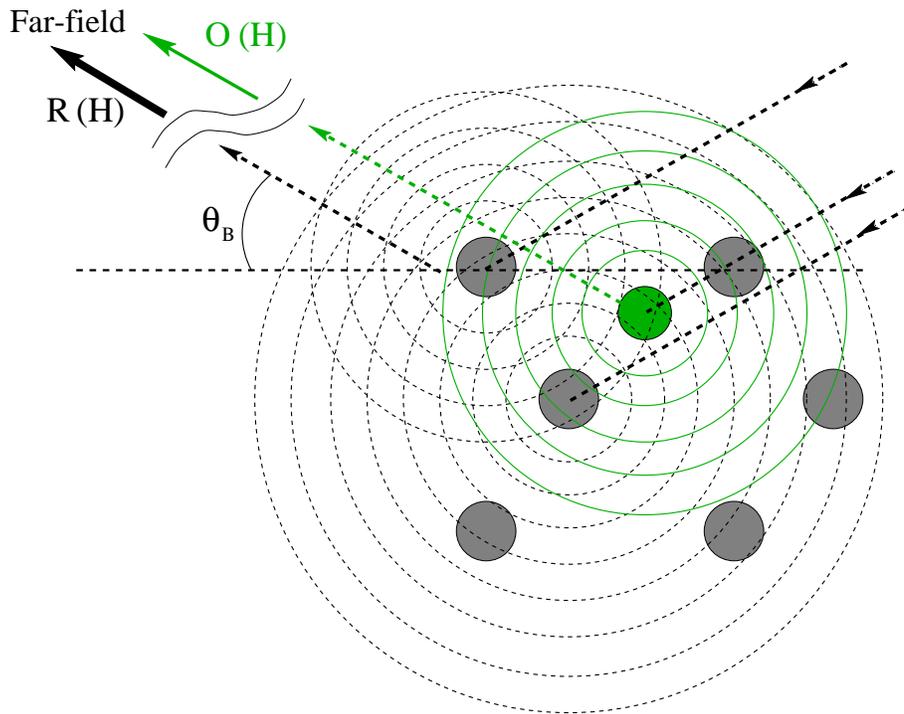
- randomly spread objects eg. vacancies, interstitial or substituted atoms
- local distortion of atomic arrangement
- no clustering, no translational order
- low concentration

A holographic approach

an idea by A. Szöke, Lawrence Livermore Lab.

Ref.: Holographic Methods in X-ray Crystallography. II

Acta Cryst. A49, 853-866, (1993).



$$R(\vec{h}) = \sum \int_{UC} \rho_{known}(\vec{r}) \exp(2\pi i \vec{h} \vec{r}) d^3 r$$

$$O(\vec{h}) = \sum \int_{UC} \rho_{unknown}(\vec{r}) \exp(2\pi i \vec{h} \vec{r}) d^3 r$$

$$\begin{aligned} I(\theta_B) &\propto |F(\vec{h})|^2 = |R(\vec{h}) + O(\vec{h})|^2 \\ &= |R(\vec{h})|^2 + R(\vec{h})O^*(\vec{h}) + R^*(\vec{h})O(\vec{h}) + |O(\vec{h})|^2 \end{aligned}$$

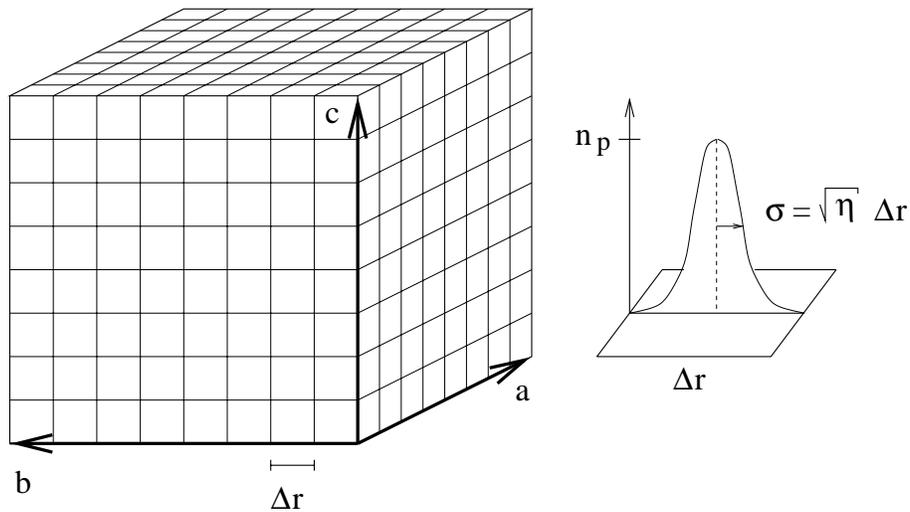


EDEN

unknown electron density $\rho_{unknown}$ is decomposed into a set of (Gauss) basis functions of unknown magnitude n_p

$$\rho_{unknown} \approx \rho_{approx} = (\pi\eta\Delta r^2)^{-\frac{3}{2}} \sum_{p=1}^P n_p \exp\left(-\frac{(\vec{r} - \vec{r}_p)^2}{\eta\Delta r^2}\right)$$

$$n_p \geq 0 \quad (\text{electron density is positive})$$



$$\begin{aligned}
H(\vec{h}) &= |F(\vec{h})|^2 - |R(\vec{h})|^2 \\
&= \sum_{p=1}^P n_p \exp[-\eta(\pi \Delta r |\vec{h}|)^2] \\
&\quad \times [R(\vec{h}) \exp(-2\pi i \vec{h} \vec{r}_p) + R^*(\vec{h}) \exp(2\pi i \vec{h} \vec{r}_p)] \\
&\quad + \sum_{p,q=1}^P n_p n_q \exp[-2\eta(\pi \Delta r |\vec{h}|)^2] \\
&\quad \times \exp[2\pi i \vec{h}(\vec{r}_p - \vec{r}_q)]
\end{aligned}$$

- set of quadratic equations
- P unknowns $n_1 \dots n_p$ which are the equivalent electron scattering strength in the p^{th} voxel
- No. of equations = No. of measured reflections
- with the constraint $n_p \geq 0$ the problem is solved by minimizing a cost function

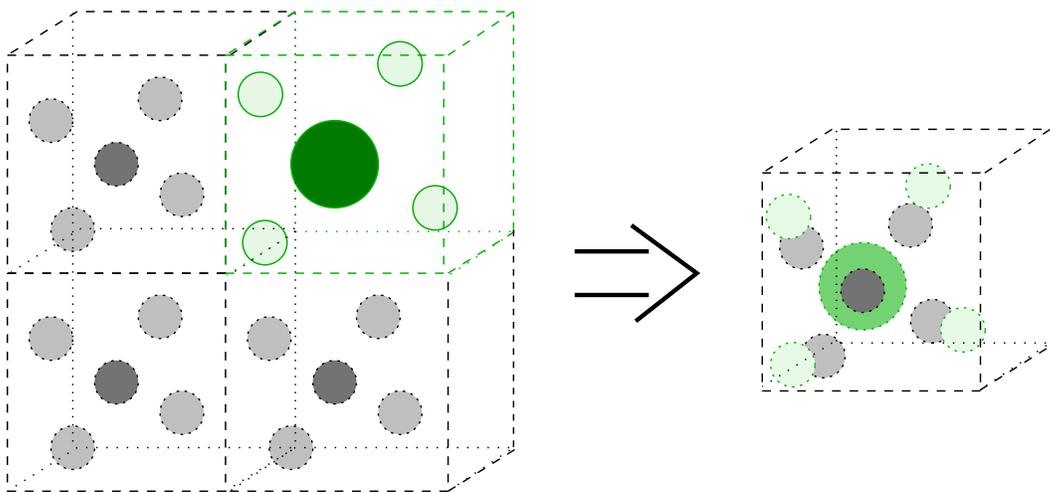


The average crystal

The scattering pattern will be produced by the 'average crystal'.

$$\rho(\vec{r}) = w_1\rho_1(\vec{r}) + (1 - w_1)\rho_2(\vec{r})$$

This is a projection of the (non-periodic) defect structure into the (periodic) unit cell.



Experimental details

Sc_2O_3 :

space group: $Ia\bar{3}$ (cubic)
lattice const.: 9.865 Å
dopants: Er < 1%
No. of atoms: 16 formula units
sites: Sc: 8a and 24d, O: 48e

data:

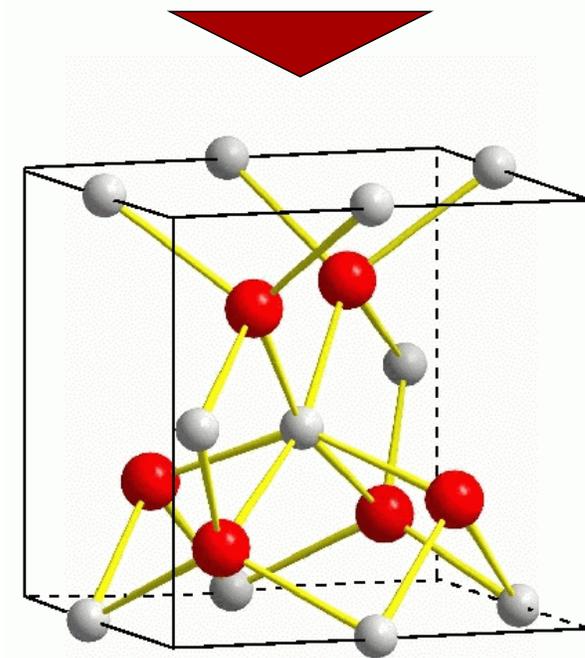
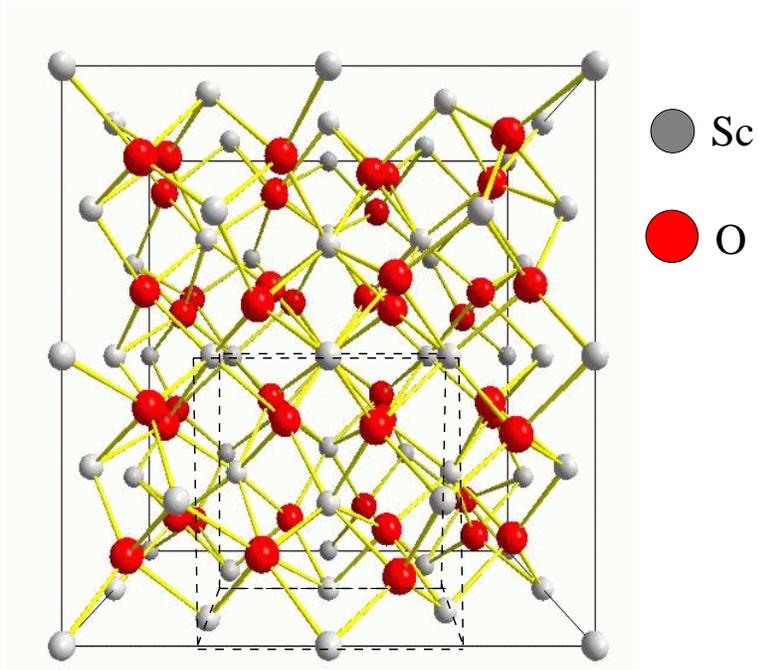
crystal size: $\approx 200 \mu\text{m}$
beamline: 4-circle diffractometer
D3 at HASYLAB
resolution: up to $0.57 \text{ \AA}^{-1} \frac{\sin \theta}{\lambda}$
energy: 31 KeV

refinement:

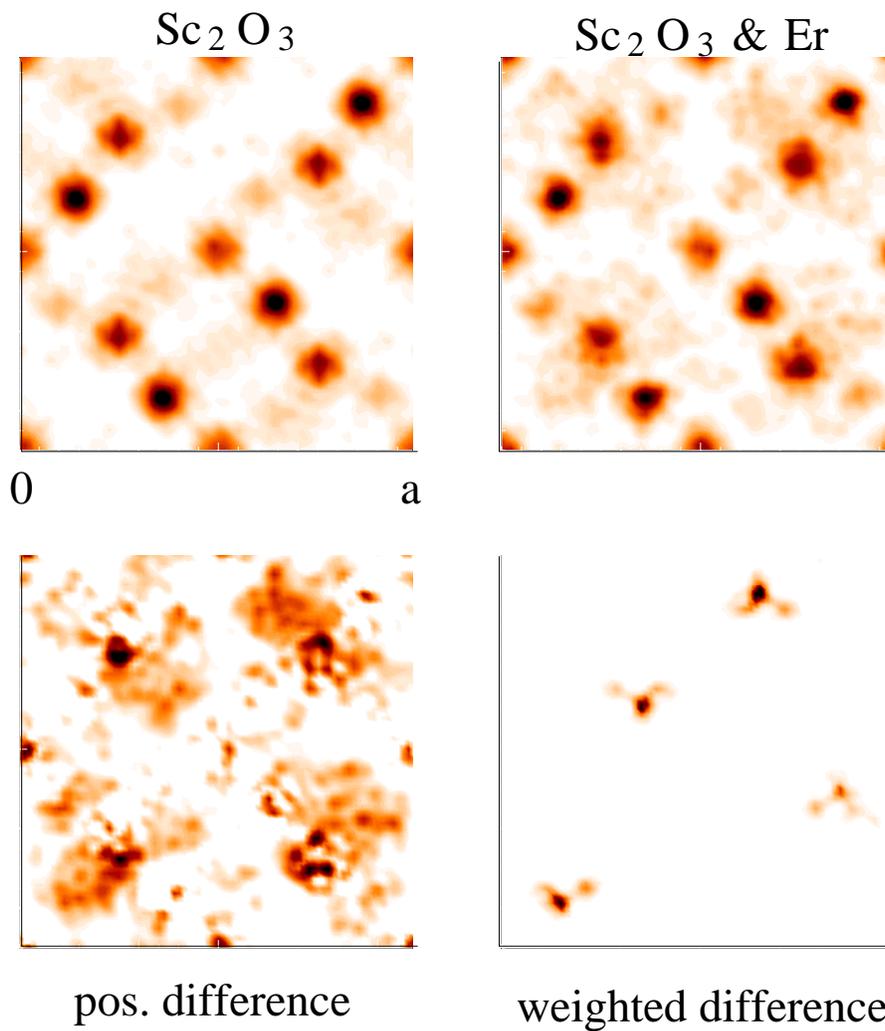
solving grid: $40 \times 40 \times 40$
extinction: $x=0.048$
R-factor: 2 % (doped),
3 % (undoped)



The Structure of Sc_2O_3

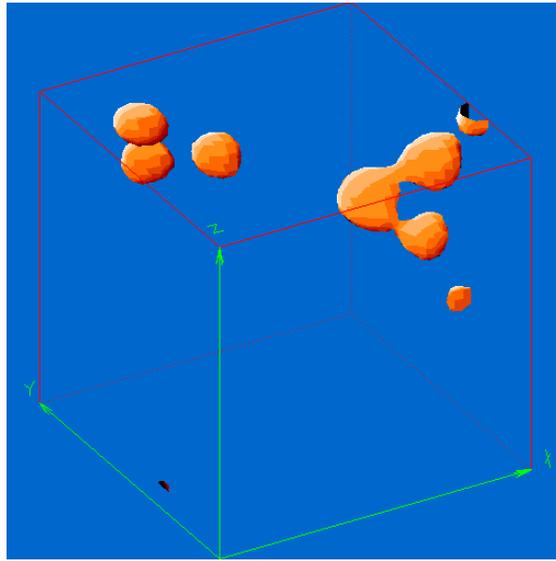


cut through electron density
in $z = 0.0625$

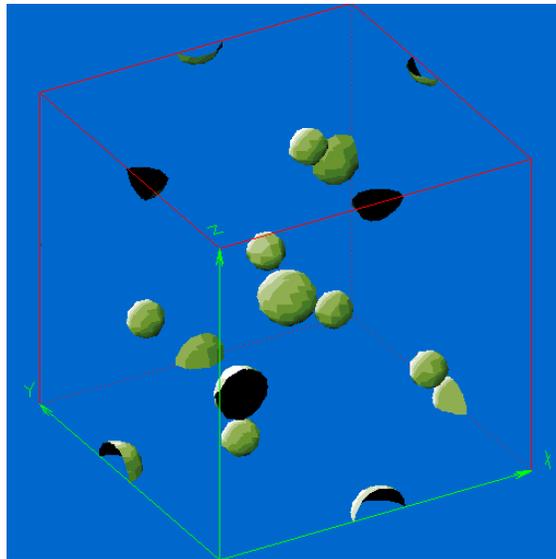


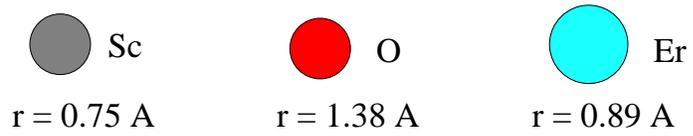
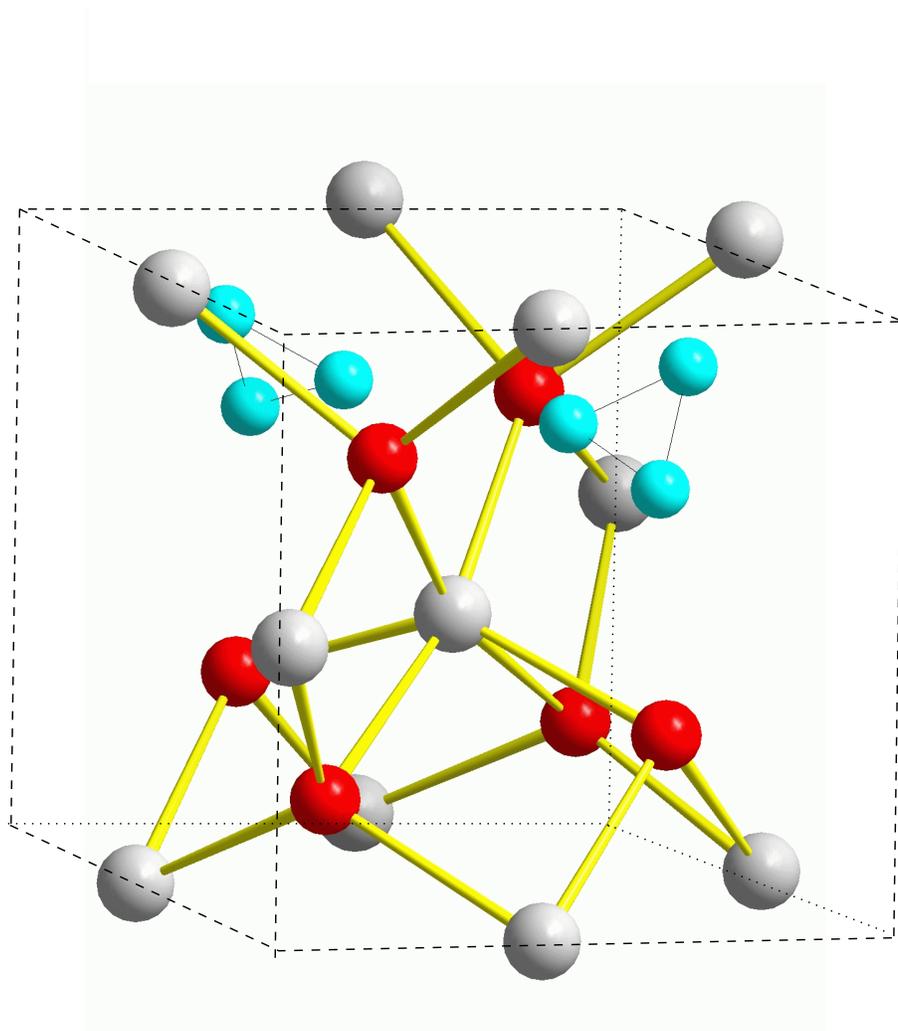
Er positions: convol. weighted difference

$$\frac{\text{Sc}_2\text{O}_3 \text{ \& Er} - \text{Sc}_2\text{O}_3}{\text{Sc}_2\text{O}_3}$$



1/8 of the Sc_2O_3 - structure





Summary

- EDEN is well suited for resolving small changes of electron density, as they are e.g. caused by point defects.
- In this approach, all information can be used and no prior assumption about the defect structure itself has to be made.
- This method has been used to compare an Er-doped Sc_2O_3 to an undoped crystal.
- A displaced Er-position, coupled with an oxygen vacancy has been found.
- This is consistent with spectroscopy-based observations.

