

# Electron Density Distribution in Tephroite, $\text{Mn}_2\text{SiO}_4$ : a High-Energy Synchrotron Radiation Study

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Tephroite belongs to the mineral group of olivines and is isotypic to forsterite and fayalite, the Mg- and Fe-end members, respectively of the (Mg, Fe) solid solution series. Thus, it crystallizes in the olivine structure, space group  $Pbnm$ ,  $a_0 = 4.912(1) \text{ \AA}$ ,  $b_0 = 10.598(3) \text{ \AA}$ ,  $c_0 = 6.255(2) \text{ \AA}$ ,  $Z = 4$ . In continuation of our earlier forsterite [1] and fayalite [2] studies we have now carried out room temperature single-crystal diffraction experiments with the aim to complement the earlier results by adding material for a transition element with a closed half shell  $3d^5$  electron configuration. Simultaneously we want to explore the feasibility of combining data recorded from the same crystal, but on different diffraction instruments and with different synchrotron radiation energies.

For the Low-Order reflections, which carry most of the information concerning bond induced charge redistributions, but are notoriously affected by absorption and extinction effects, we have chosen synchrotron radiation of 100.3 keV in order to obtain essentially absorption and extinction free data for the electron density modelling and ensuing topological analysis. The experiment on a sample produced by the Czochalski technique and ground to an approximate sphere of 0.25 mm diameter was performed on the Triple-Crystal-Diffractometer (BW5, [3]).

For a full sphere up to  $\sin\theta/\lambda = 0.382 \text{ \AA}^{-1}$ , 1712 reflections were recorded in a Psi-Scan Mode, i. e. using  $\omega$ -scans and 3 different settings  $\Psi = 0.0^\circ, 0.5^\circ, \text{ and } 1.0^\circ$ . In the following full shell up to  $\sin\theta/\lambda = 0.605 \text{ \AA}^{-1}$ , 1714 reflections were recorded in the conventional bisecting mode. The data reduction including a slight drift correction, but no absorption correction resulted in a set of 309 unique observed reflections ( $I > 4\sigma$ ) with an internal agreement factor  $R(F^2) = 0.0172$ . This value is about two times larger than those in the earlier measurements are. The reason is not yet understood and thorough analysis of the raw data is in progress.

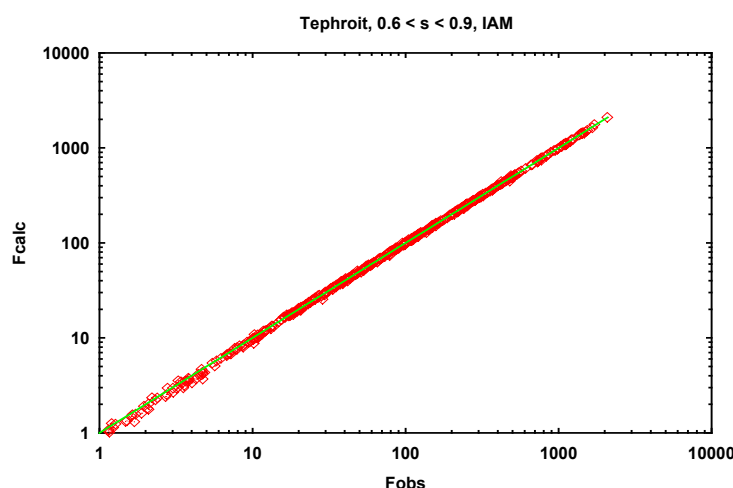


Figure 1.  $F(\text{calc})$  vs.  $F(\text{obs})$  plot of the HO-data

High-Order reflections, which are generally hardly affected by extinction and are dominated by the atomic core electrons, can be used to fix unbiased crystallographic standard parameters. To this purpose, additional data were collected at the Four-Circle-Diffractometer (D3) at a beam energy of 27.56 keV corresponding to a wavelength of  $0.50 \text{ \AA}$ . Exploring a half shell between  $0.60 \text{ \AA}^{-1}$  and

0.99 Å<sup>-1</sup>, 11310 reflections were recorded in the above quoted Psi Scan Mode yielding a set of 493 unique observed reflections with an internal agreement factor  $R(F^2) = 0.0168$ .

Up to date, structure refinements were carried out with the independent atom (IAM) model using SHELXL97 [4]. Applied to the High-Order reflections convergence was reached at  $R1 = 0.0083$ ,  $wR = 0.0214$ ,  $GoF = 1.10$ . Fig. 1 illustrates the quality of these data by a logarithmic  $F(\text{calc})$  vs.  $F(\text{obs})$  plot.

In the next step, a refinement was carried out with the Low-Order reflections alone. Fixing the previously refined atomic standard parameters considered as free from chemical bias, this refinement is expected to show the charge redistribution in terms of dynamic difference density maps. Thus, the only variable to be adjusted is the scale factor. This refinement converged at  $R = 0.0116$  after introducing a small extinction correction. Fig. 2 shows the deformation density distributions associated with the SiO<sub>4</sub>-moiety and the two Mn sites.

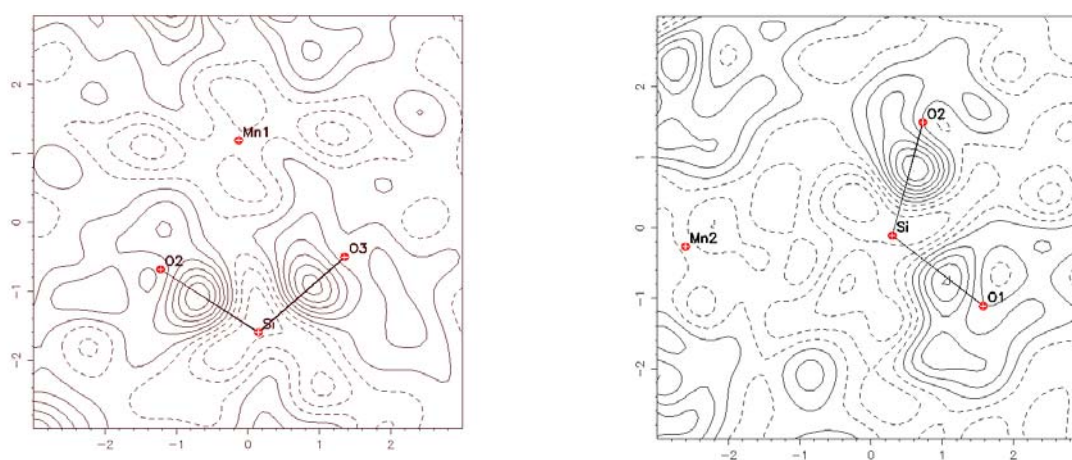


Figure 2 a, b. Deformation density distribution for the two Mn sites. contours at  $0.05 \text{ e } \text{Å}^{-3}$ .

Both maps give clear evidence that Mn, contrary to Fe in fayalite [2], exhibits only little anisotropic 3d-electron density distribution in agreement with the chemical expectation. Modelling of the total density distribution by means of structure refinements with generalized atomic scattering factors and joint data sets is under way.

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## References

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