

**STATIC EXPERIMENTAL CHARGE DENSITIES - MODEL
DEPENDENCY ON THE DESCRIPTION OF HYDROGEN ATOMS**

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Modeling of hydrogen atoms is a major problem in experimental charge density studies based exclusively of X-ray diffraction. The use of positions from a standard independent atom model refinement or idealized X-H distances based on mean values from neutron-diffraction studies are among the common approaches reported in the literature. The use of an isotropic displacement parameter is also widely applied. The few attempts made to derive ADPs based on X-ray diffraction data have not involved validation by comparison with neutron diffraction values. With offset in multipole models based on high-quality X-ray diffraction data for the two pentoses xylitol and ribitol and a neutron diffraction experiment on xylitol, we have investigated how different approaches to model hydrogen atoms influences the static charge-density model, specifically its topological characteristics. Only small errors in positions are found when idealized X-H distances are used, and these errors do not affect the topological properties of the static charge density. The use of bond lengths from a standard IAM refinement, though, have a significant impact on the charge density, and the use of an isotropic displacement description is a very serious approximation. Estimation of ADPs based on a rigid-body analysis and internal motion from spectroscopic vibrational frequencies proved to be a considerable improvement. With the experience gained from this analysis, we propose a suitable scheme for the description of hydrogen atoms in charge density studies.

Keywords: CHARGE DENSITY HYDROGEN ATOMS MULTIPOLE MODELS

**ELECTRON DENSITY DISTRIBUTION IN FORSTERITE, Mg₂SiO₄: A
REDETERMINATION**

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The room temperature electron density distribution in synthetic Mg₂SiO₄ ($a = 4.752(1)$, $b = 10.192(1)$, $c = 5.9780(5)$ Å, S.G. *Pbnm*, $Z = 4$) has been redetermined using synchrotron radiation of 100.6 keV (beamline BW5 at HASYLAB/DESY, Hamburg) in order to obtain essentially absorption and extinction free data. For a sphere up to $s(\max) = 0.969 \text{ \AA}^{-1}$, 4809 reflections were recorded resulting in a set of 1101 unique observed reflections with an internal agreement factor $R(F^{**2}) = 0.0066$. Structure refinements using VALRAY [1] converged at $R(F) = 0.0062$, $wR(F) = 0.0093$, $GOF = 0.75$ for a multipole model based on fixed HO standard parameters, neutral atoms and multipole expansions up to order $l = 4$. For each atom, the radial expansion coefficients for $l > 0$ were constrained to a common value. The maximum extinction correction was below 1.5 %. The static deformation densities show Si-O bond peaks between 0.34 and 0.41 e/Å³, residual density features being below 0.10 e/Å³. The predominantly closed-shell interaction between Mg and O and the considerable admixture of shared interaction in the Si-O bonds are corroborated by the topological analysis [2] of the model density distribution which revealed bond critical point properties like density values of 0.20 - 0.30 and 1.05 - 1.10 e/Å³ for the Mg-O and Si-O bonds, respectively. Atomic basin calculations resulted in charges $\langle Q(\text{Mg}) \rangle = +1.73$, $Q(\text{Si}) = +3.25$ and $\langle Q(\text{O}) \rangle = -1.68$ e. [1] R.F. Stewart et al. (2000), VALRAY Users Manual. [2] C. Flensburg, D. Madsen (2000), Acta Cryst. A56, 24.

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A SYNCHROTRON STUDY OF CHARGE DENSITY IN β -Si₃N₄

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The true structure of β -Si₃N₄ continues to be a matter of controversy in the published literature. Many conflicting studies of this material alternate between centrosymmetric *P6₃/m* and noncentrosymmetric *P6₃* space groups. The difference lies with the existence, or not, of mirror planes normal to the 3-fold axis. The one independent Si (tetrahedrally sp³ bonded to 4 N atoms) and two independent N (trigonally sp² bonded to 3 Si atoms) atoms all lie on or, very close to this mirror. Here we used high precision electron density imaging with 0.75 Å synchrotron X-radiation at the Photon Factory Tsukuba, to contribute to the debate. A single crystal of maximum dimension 58 μm was examined at BL14A using a fast stacked avalanche photodiode detector (Kishimoto et al 1998). A sphere of data were measured at 293 K to $2\theta = 120^\circ$. The measured data are of high quality, with $R_{\text{merge}} = 0.0284$ from 8577 measurements, reducing to 795 independents. Because the anomalous dispersion is only minor for Si and N, the accentric refinement assumes a monodomain phase rather than refining the Flack parameter. The least squares refinement involved 17 or 24 variables with agreement indices R , wR and S of 0.019, 0.014, 1.98(5) and 0.017, 0.013, 1.84(5) for the *P6₃/m* and *P6₃* settings respectively. Both refinements revealed pronounced $\Delta\rho$ maxima associated with covalent Si-N bonding, but the accentric refinement indicates a 0.040(2) Å shift of one N atom along the 3-fold with the associated $\Delta\rho$ features becoming more regular.

References

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**THE ELECTRON DENSITY AND MAGNETIC PROPERTIES OF AN
IRON-BUTTERFLY COMPLEX**

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In our investigation of basic iron carboxylate complexes [1], we discovered an interesting side-product, [Fe^{III}O₂(C₅H₉O₂)₈(C₆H₇N)₂].2CH₃CN, 1. This compound exhibits an Fe₃(μ³-O) environment, which is suitable for comparison with the previously studied bonding environments in the trinuclear carboxylates [2]. 55130 reflections ($\sin(\theta)/\lambda_{\text{max}} = 1.00 \text{ \AA}^{-1}$) were collected with a crystal temperature of 16 K using a Bruker SMART 6000 CCD detector at the synchrotron beamline X3A1 at NSLS, USA, resulting in 20960 unique reflections with an internal agreement of $R_{\text{int}} = 0.025$. The electron density distribution (EDD) in 1 was modelled employing a multipolar model to give $R(F^2) = 0.025$. In contrast to previous observations [2], the EDD in 1 shows two significantly different Fe^{III}(μ³-O) interactions. The shorter Fe(2)-O(1) exhibits a large accumulation of electron density in the bond, while the longer Fe(1)-O(1) interaction is less directional. This is illustrated by the experimental EDD in the central Fe₂(μ³-O)₂-region, which has a diffuse character (see Figure). The two μ³-O atoms also exhibit an unusually short separation of 2.530(1) Å. A similar observation of enhanced interaction between two metal-bridging oxygens has been made previously from low-resolution synchrotron X-ray data [3]. Support of this work by the Division of Basic Energy Sciences of the U.S. Department of Energy (DE-FG02-86ER45231) is gratefully acknowledged.

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Keywords: CHARGE DENSITY, LOW TEMPERATURE, SYNCHROTRON