

s2.m2.p5.la **Joint analysis of charge and momentum densities.** P.J. Becker, J.M. Gillet, C. Fluteaux, P. Cortona. *SPMS, Ecole Centrale Paris and CNRS, Grande Voie des Vignes, 92295 Chatenay Malabry Cedex France.*
Keywords: charge spin densities.

Charge density studies, based on X Ray Bragg scattering, lead to a fair description in terms of atom centered contributions; this includes symmetry relaxation effects due to neighboring atoms, and effective radial behavior of pseudoatomic densities. However, it does not elucidate the mechanisms of delocalisation of electrons associated with orbital coupling among different atoms. A test study on MgO was performed by some of us (1), based on accurate structure factors by convergent electron diffraction (2); it revealed the relevance of model ions based on a DFT calculation for ionic solids (3) and the ambiguity concerning the origin of incomplete charge transfer.

We proposed the possibility of refining directional Compton profiles –DCP– (4), in terms of parameters that are directly involved in the description of the wavefunction. In particular, anisotropies among DCPs are very sensitive to the coupling among different atomic orbitals. We measured 8 different DCPs for MgO (5) from which we proposed an analytical reconstruction of the 3D momentum density (6). We then performed two refinement strategies; one based on the 3D density, another on the profiles themselves. With only very few parameters (effective screening constants of valence orbitals, coupling between O and Mg valence orbitals), we get a very fair description of anisotropic features in momentum space. The O-Mg coupling is small (about 0.2), but plays a crucial role towards anisotropies of DCPs. Effective screening constants agree well with those obtained from structure factor refinement.

We presently develop a joint refinement among both types of information.

It is clear from this study that combining charge and momentum density studies allows for a full description of bonding and cohesive mechanisms in solids.

s3.m2.p6.la **A modulated structure determination and refinement using marginal diffraction data.** A.D. Rae, A.J. Edwards, *Research School of Chemistry, Australian National University, Canberra, Australia*, A.F. Williams, C.J. Matthews, *Department of Inorganic Chemistry, University of Geneva, CH1211 Genève 4 Switzerland.*
Keywords: computing, refinement, modelling.

Low temperature data from very small triclinic crystals ($280 \times 10^{-6} \text{ mm}^3$) of ethane-1-(1H,3H-benzimidazol-2-ylidium-2-(3'-methyl-1H'-benzimidazol-2'-ylidium) dichloride trihydrate ($\text{N}_4\text{C}_{17}\text{H}_{18}^{2+} \cdot 2\text{Cl}^- \cdot 3\text{H}_2\text{O}$, a 6.749(1), b 9.538(2) c 16.257(3) Å, α 89.52(1), β 80.23(1), γ 71.02(1)°, z 2, $P-1$, $Mo\ K\alpha$, 200 K) were collected on a Nonius CCD diffractometer with 13741 reflections yielding 2201 independent reflections. Using standard procedures, only 65 of the 753 merged reflections with $I_{\text{obs}} > 3\sigma(I)$ had $k+l$ odd. The cation has pseudo $2/m$ symmetry but is necessarily non centrosymmetric. A parent structure, however, is readily determined in space group $A-1$ as a 1:1 disordered structure corresponding to the Fourier transform of the $k+l$ even reflections. A methyl group is attached to one N whereas the other three N are all hosts to water Hydrogen bonding that also links the Cl ions. Only the methyl group and its pseudosymmetrically related water are not badly overlapped in the disordered $A-1$ structure.

Two different orderings are physically possible and allow either (i) $A1$, with displacive modulation lowering the symmetry to $P1$ or (ii) $P-1$. The correct structure was determined by comparative constrained refinement (*RAELS96*) using only those reflections with $I_{\text{calc}} > 3\sigma(I)$. $R(F) = 0.082$ for 626 $k+l$ even reflections, 0.403 for just 27 $k+l$ odd reflections, and 2.22 for 84 reflections with $I_{\text{obs}} < 3\sigma(I)$. For the purpose of Least Squares, but not refinement statistics, these latter reflections had I_{obs} reset to $3\sigma(I)$. The preferred structure is largely justified by the data fit to the weakest reflections, and a minimisation of the intensity of the $k+l$ odd reflections without resorting to stacking faults. This used just 61 variables for the $P-1$ model. Expanding the model appears to make little difference and simply creates noise.

Certain observations can be made about the quality of the data fit and the error estimates. The goodness of fit, 3.5, was best for the strong $k+l$ even reflections but not much worse for the remainder. No individual measurements could be classified as very well determined. We question the wisdom of assuming multiple measurement of reflections improves statistical reliability of weak reflections and will present an argument for saying that if ($p+b$) and b are sampled equally, then the result of n measurements with different geometries gives a mean value for p of $\langle p \rangle$ with variance

$$\text{var}(p) = (1/n) \langle p+b \rangle + \langle b \rangle$$

ie. The variance can not be lower than $\langle b \rangle$, the average variance of the background. You can not do better than the quality of the scale being used.

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