

06.2-5 EXTINCTION IN THE  $KMF_3$  PEROVSKITES

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The effect of extinction on the electron distribution in the  $KMF_3$  perovskites,  $M = Mn, Fe, Co, Ni$  &  $Cu$  was investigated using previously published data. The first four members of the series are isostructural and crystallize in the space group  $Pm\bar{3}m$ . There is little evidence for anisotropy in the magnitudes of the structure factors of equivalent reflections. Inclusion of anisotropic extinction parameters during refinement improved the  $R$  factors slightly, but  $\Delta\rho$  maps assuming isotropic extinction are almost identical to those based on an anisotropic model. Hence the extinction for these structures is essentially isotropic.

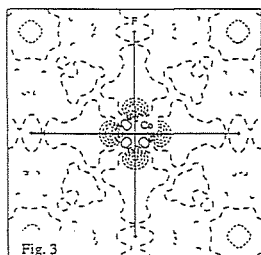
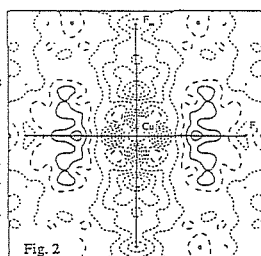
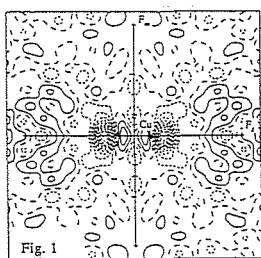
The  $Cu$  member is potentially an exception. It is a Jahn-Teller system and crystallizes in the lower symmetry space group  $I4/mcm$ . Hence there is more likelihood of anisotropy in the parameters for this compound. There is strong anisotropy in the extinction parameters published for  $KCuF_3$ . This is not supported by our observations. The spread in the magnitudes of the structure factors of equivalent reflections is not large. Difference density maps evaluated assuming anisotropic extinction are not internally consistent. There is a heavy depletion of density along the short  $Cu-F_s$  bond, a weak depletion of density along the slightly longer  $Cu-F_m$  bond (Fig. 1) and a weak accumulation of density along the longest  $Cu-F_l$  bond (not shown). The large differences in the topology near the bonds is not consistent with the small differences in their lengths, especially as all have similar environments. The topologies of the density along vectors joining the  $Cu$  atom and the second nearest neighbour  $K$  atoms are also inconsistent with those for the other members of the series.

The  $KCuF_3$  data has been reanalysed assuming an isotropic extinction model. The residual indices ( $R = .015$  and  $R_w = .017$ ) were comparable to those previously published. As shown in Fig. 2 the topology of the density along the  $Cu-F_s$  and

$Cu-F_m$  bonds are now virtually the same, as one would expect, except near the bond midpoint. The secondary minima observed along  $Cu-F_m$  is also observed in other  $Cu-X$  bonds, while the maxima along the  $Cu-F_s$  bond is an artefact of the extinction correction (the  $220$  reflection is not adequately corrected by either the isotropic or anisotropic models). The difference density is now consistent with those of the other members of the series as seen by comparing the maps above with that of the  $Co$  member shown in Fig. 3.

Anisotropic extinction parameters should not be included in a refinement simply on the basis that it lowers the  $R$  factors. Analysing the spread of intensities amongst equivalent reflections is far more reliable as an indicator for the presence of anisotropic extinction. The danger of incorrect diagnosis may be reduced by correlating results from related structures. Ideally, however, one should study the mosaic distribution by more definitive methods such as two dimensional scans of the diffraction profiles.

The assistance of Professors F. Marumo and K. Tanaka and their colleagues is gratefully acknowledged.



## 06.2-6 THE INFLUENCE OF STRONG ELECTRIC FIELDS ON THE ELECTRON DENSITY DISTRIBUTION OF MOLECULAR IONS.

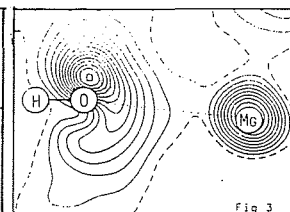
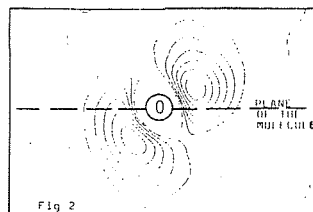
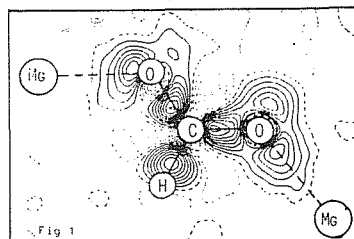
By J. van der Meulen and D. Feil, Chem. Phys. Lab., University of Twente, Enschede, Netherlands.

The dynamic electron density map of  $Mg$ -formate. $2H_2O$  shows the effect of the electric field of the  $Mg$ -ions on the lone-pair densities of the various  $C=O$  groups (fig. 1).

A striking feature is a lone pair system rotated out of the plane of the formate group (fig. 2), similar to the one observed by Stevens in formamide. Another effect of the strong fields in the crystal is the asymmetric electron density distribution in water (fig. 3).

A Hartree-Fock-Slater study of the  $Mg^{++}-HCOO^- - Mg^{++}$  unit, using an extended basis set, confirms the effect

on the lone pair densities. The atomic charges obtained by the stockholder method are compared for the observed and the calculated charge distributions.



## 06.2-7 DEFORMATION ELECTROSTATIC PROPERTIES OF

L-ALANINE FROM SINGLE-CRYSTAL X-RAY DIFFRACTION DATA AT 23 K. By R. Destro and R. E. Marsh, A.A. Noyes Lab. of Chemical Physics, California Institute of Technology, Pasadena, California, USA.

From a crystal of  $l$ -alanine, ground to a sphere and mounted on a four-circle diffractometer modified for low-temperature measurements, three complete data sets to  $\sin \theta/\lambda = 1.08 \text{ \AA}^{-1}$  were collected at  $23 \pm 1 \text{ K}$ . The measured intensities were corrected for the effects of scan truncation by a method we have recently developed. Least-squares refinement of a rigid pseudoatom model at the octopole level gave excellent agreement between observed and calculated intensities ( $R = 0.020$  and  $wR = 0.016$  for all 2519 reflections with  $I > 0$ ). Electron population parameters resulting from the multipole refinement correspond to charge distributions and bond polarities of the carboxylate group which differ significantly from the values predicted by previous theoretical calculations. Several chemically significant features, including those of the hydrogen bonds network, have been enlightened by experimental deformation maps, both of charge density and electrostatic potential. All features of the maps closely match the electron population analysis of the multipole model.