The effect of extinction on the electron distribution in the KMF₃ perovskites, Mn, Mn, Fe, Co, Ni & Cu, was investigated using previously published data. The first four members of the series are isosymmetric and crystallizes in the space group Pm₃m. 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 no 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 anisotropic extinction are not internally consistent. There is a heavy depletion of density along the short Cu-F₁ bond, a weak depletion of density along the slightly longer Cu-F₃ bond (Fig. 1) and a weak accumulation of density along the longest Cu-F₃ bond (not shown). The large differences in the topology near the bonds is consistent with those for the other members of the series.

The KCuF₃ data has been reanalysed assuming an isotropic extinction model. The residual indices (K=0.015 and Rₑ=0.017) were comparable to those previously published. As shown in Fig. 2 the topology of the density along the Cu-F₁ and Cu-F₃ bonds are now virtually the same, as one would expect, except near the bond midpoint. The secondary minima observed along Cu-F₃ is also observed in other Cu-X bonds, while the maxima along the Cu-F₁ bond is an artifact 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 that of the Cu 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. Analyzing 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.

06.2-5 EXTINCTION IN THE KMF₃ PEROVSKITES by N. Spadaccini and E.N. Maalen, Crystallography Centre, University of Western Australia, Australia.

The dynamic electron density map of Mg-formate.2H₂O 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 Mg²⁺-HCOO⁻·Mg⁺⁺ unit, using an extended basis set, on the lone pair densities. The atomic charges obtained by the stockholder method are compared for the observed and the calculated charge distributions.

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

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

The dynamic electron density map of Mg-formate.2H₂O 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 Mg²⁺-HCOO⁻·Mg⁺⁺ unit, using an extended basis set, 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 2θ = 1.08 Å⁻¹ were collected at 23±1 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 pseudomolecule 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 D>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 chemical 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.