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Supporting information for article:

Experimental observation of charge-shift bond in fluorite CaF_2

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S1. Refinement details.

S1.1. Residual density distribution maps and overall agreement statistics

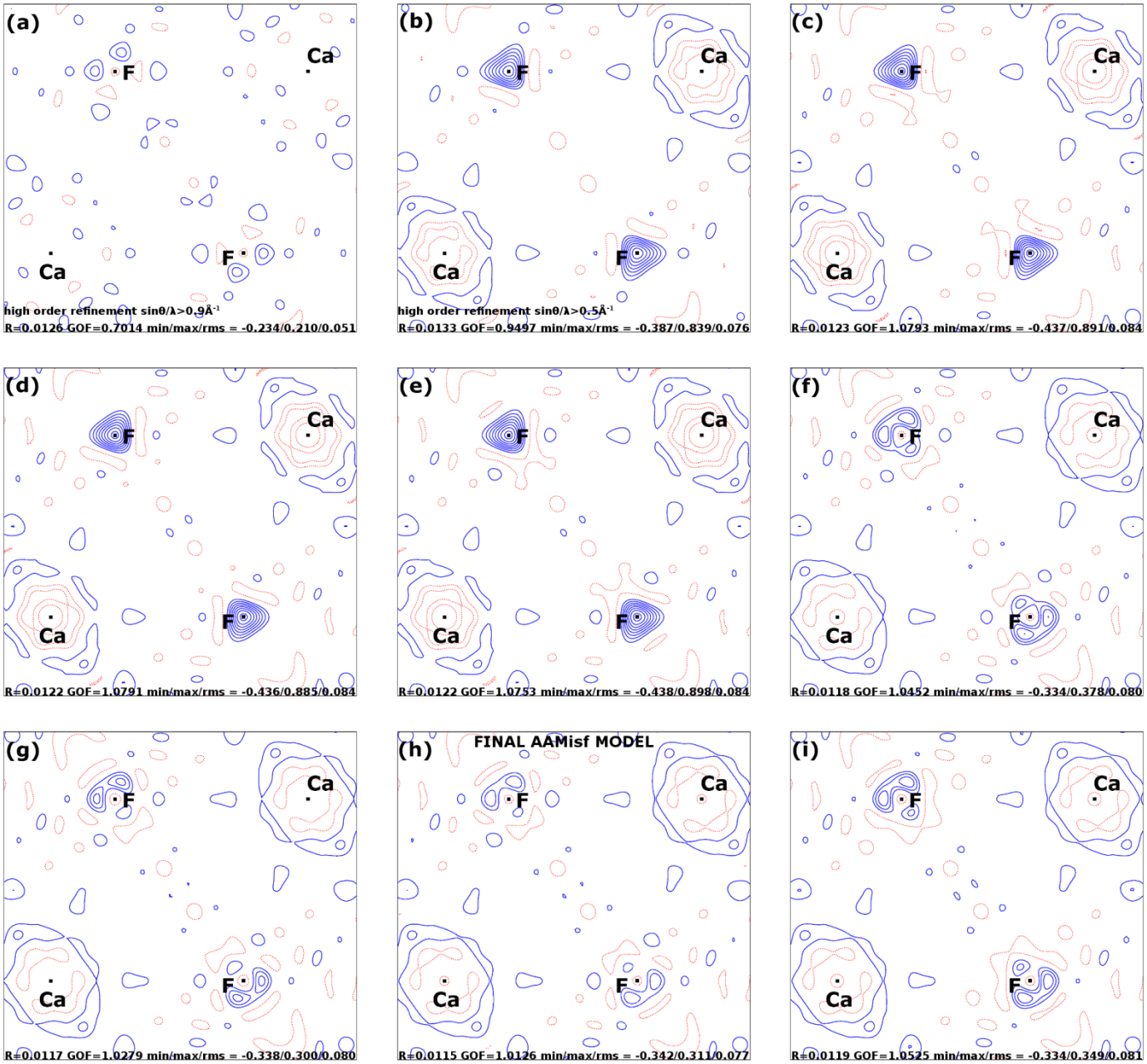

Figure S1 Residual density maps after the refinement steps in AAMisf model. Black squares denote centres of ions. Solid blue lines indicate positive values, red dashed lines negative ones. Contours at ± n·0.1 e Å^{-3} (n =0, 1, 2, …). The agreement statistics R-indices based on F, goodness of fit (GOF) and the min/max/rms residual density are given at the bottom of each figure. Refined parameters: scale factor (s), isotropic displacement parameters (U_{iso}); valence population (P_v); octupole 2- (O2-),

hexadecapoles 0 and 4+ (H0, H4+), spherical kappa (κ_s). (a) high order refinement ($\sin\theta/\lambda>0.9$ Å^{-1}) of s, U_{iso}^{F}, U_{iso}^{Ca}; (b) high order refinement ($\sin\theta/\lambda>0.5$ Å^{-1}) of s, U_{iso}^{Ca}; (c) s, P_v; (d) s, P_v, O2-; (e) s, P_v, O2-, H0, H4+; (f) s, U_{iso}^{F}, U_{iso}^{Ca}, P_v, O2-, H0, H4+; (g) s, κ_s^{F}; (h) convergence after alternating steps of (f) and (g); (i) s, U_{iso}^{F}, U_{iso}^{Ca} refinement on all data.

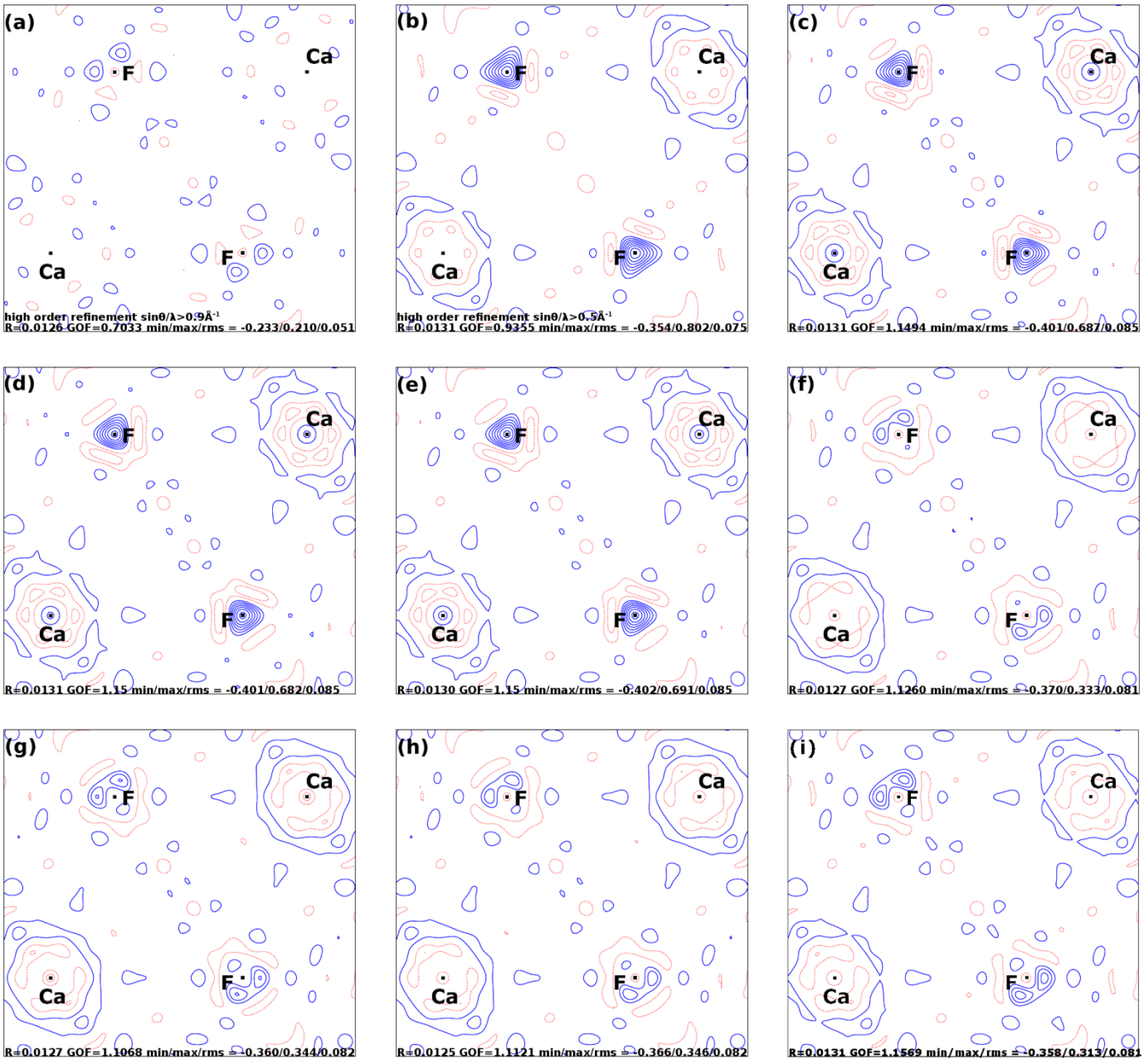

Figure S2 Residual density maps after the refinement steps in AAMasf model. Black squares denote centres of atoms. Solid blue lines indicate positive values, red dashed lines negative ones. Contours at ± n·0.1 eÅ^{-3} (n =0, 1, 2, …). The agreement statistics R-indices based on F, goodness of fit (GOF) and the min/max/rms residual density are given at the bottom of each figure. Refined parameters: scale factor (s), isotropic displacement parameters (U_{iso}); valence population (P_v);

octupole 2-(O2-), hexadecapoles 0 and 4+ (H0, H4+), spherical kappa (κ_s). (a) high order refinement ($\sin\theta/\lambda>0.9$Å^{-1}) of s, U_{iso}^{F}, U_{iso}^{Ca}; (b) high order refinement ($\sin\theta/\lambda>0.5$Å^{-1}) of s, U_{iso}^{Ca}; (c) s, P_v; (d) s. P_v, O2-; (e) s, P_v, O2-, H0, H4+; (f) s. P_v, O2-; (f) s, U_{iso}^{F}, U_{iso}^{Ca}, P_v, O2-, H0, H4+; (g) s, κ_s^{F}; (h) s, U_{iso}^{F}, U_{iso}^{Ca}, P_v, O2-, H0, H4+; (i) s, U_{iso}^{F}, U_{iso}^{Ca} refinement on all data – IAM model.

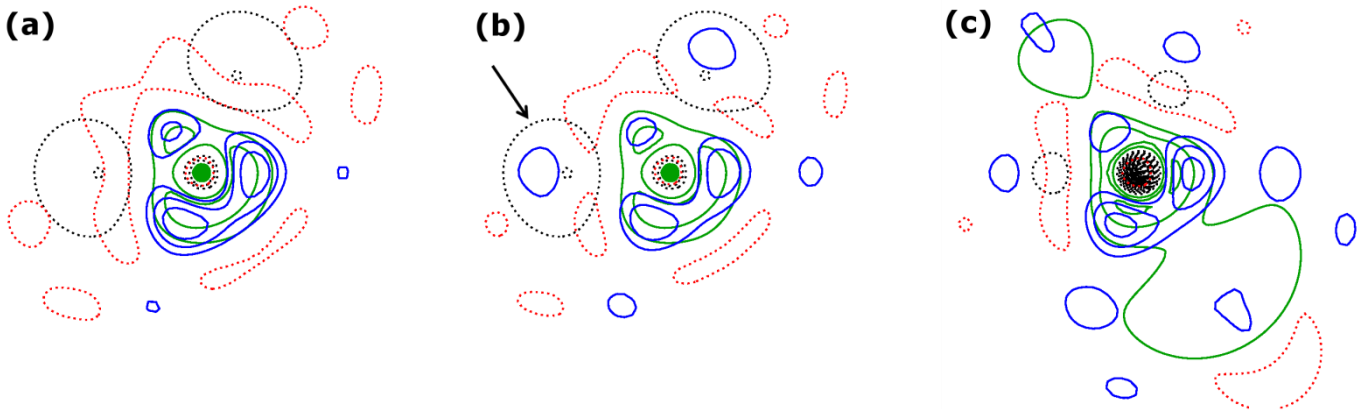

Figure S3 An overlay of deformation density map on residual density map for fluoride ion. For residual density maps solid blue lines indicate positive values, red dashed lines negative. For deformation density maps solid green and dashed black lines indicate positive and negative values, respectively. Contours at ± n·0.1 eÅ^{-3} (n =0, 1, 2, …); (a) residual density map of procrystal model with scattering factors for ions (Pisf), deformation density map defined as AAMisf-Pisf model; (b) residual density map for final AAMisf, deformation density map defined as AAMisf-Pisf (c) residual density map of IAM, deformation density as AAMisf-IAM.

A blue isocontour of 0.1 eÅ^{-3}, indicated by the black arrow can be found in Figure S3(b) for the residual density map. The dashed black isocontours of -0.2 eÅ^{-3} coming from the deformation density map is located in the vicinity. There is a slight overestimation of charge depletion in the AAMisf in this area. However, Figures S3(a) and S3(c) rationalise depletion of charge in this region. The obtained values of refined parameters is a compromise between real charge depletion and decreased flexibility of the model due to a very high symmetry in fluorite.

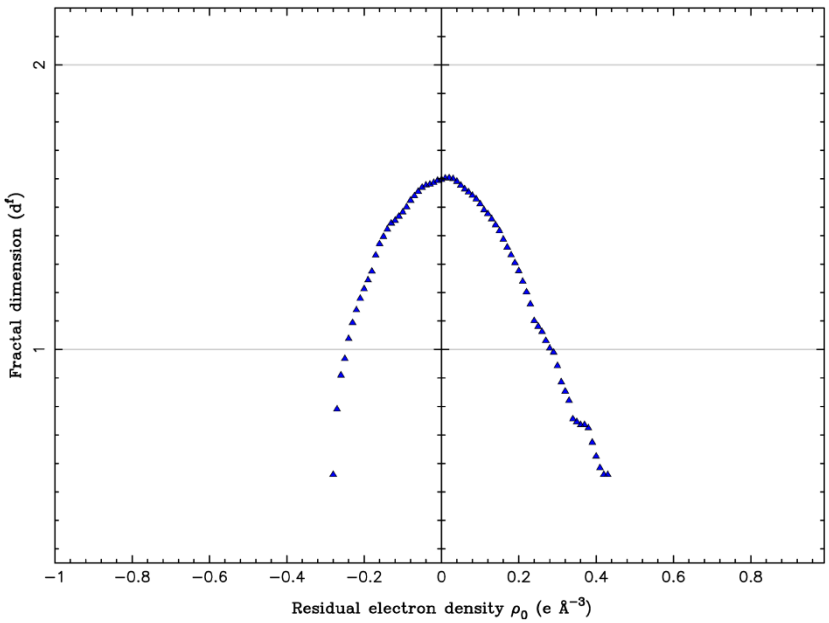

Figure S4 Fractal dimension plot of residual density from Figure S1(h) for AAMisf. Plot was generated in PIXELstats software (Meindl & Henn, 2008).

Residual density maxima close to F nuclei (Figure S1) indicate that the multipole model did not have enough flexibility to completely describe aspherical character of charge density distribution around fluoride ion. Nevertheless the overall trend is preserved, only asphericity may be slightly more complex than multipole model is able to describe. Refinement of κ' for an octupole and hexadecapoles led to exceptionally large values of these parameters (1.77 and 8.97, respectively) and did not improve significantly the residual density around fluoride. Moreover after numerous iterations of alternate refinements of kappa parameters in one cycle and multipole parameters together with displacement parameters in the following cycle, did not converge to the final stable values but were continuously increasing.