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Nonspherical Analysis of the Charge Density of Fluorite

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"The Nonspherical Analysis" by Kurki-Suonio and Ruuskanen (Ann. Acad. Sci. Fennicae A VI **358** (1971)) is applied to the structure amplitudes of CaF_2 measured by Togawa (J. Phys. Soc. Japan **19** (1964) 1696) with weak reflexions of Weiss, Witte and Wölfel (Z. phys. Chem. **10** (1957) 98).

Earlier conclusions of the average compression of the Ca ion and the extension of the F ion are confirmed. The nature of the atomic nonsphericities cannot be verified reliably from the mere data of Togawa because of their incompleteness, while the combined data indicate a slight cubic deformation of fluorine corresponding to angular displacement of about 0.2 el per fluorine atom in total at an average distance of about 1.0 Å from the fluorine nucleus.

§ 1. Introduction

Different methods of analysis[1,5-7] of the X-ray diffraction data of Togawa[6] and Weiss, Witte and Wölfel[7] on fluorite, CaF_2, have led to contradictory statements about the deformation of the crystal atoms.

In "the Nonspherical Analysis" developed by Kurki-Suonio and Ruuskanen,[2] the locality and low order harmonic behaviour of the angular dependence are constraints, which effectively restrict the type of the information to be obtained. Thus a more complete separation of the information from statistical fluctuations is to be expected and a new analysis of the data on CaF_2 by this method is justified.

The study of the strongly covalent diamond type structures is so far the only application of the nonspherical analysis.[2] Therefore, analysis of a crystal of another bonding type such as CaF_2 will be interesting from the point of view of the method itself.

§ 2. Analysis

Fluorite has an FCC-structure with a lattice constant 5.4626 Å and with a three atom basis: Ca at (000), the fluorines F_A and F_B at $\pm\left(\frac{1}{4}\frac{1}{4}\frac{1}{4}\right)$. The site symmetry is cubic for calcium and tetrahedral for fluorine. Thus assuming that the Ca and F atoms follow the symmetry of the field surrounding them we can write their scattering factors as expansions

$$f_{Ca}=f_0+f_4K_4+f_6K_6+f_8K_8+\cdots \qquad (1)$$

and

$$f_{F_A}=f_0+f_3K_3+f_4K_4+f_6K_6+f_7K_7+f_8K_8+\cdots, \qquad (2)$$

where the functions K_n are the cubic harmonics used in the analysis of the diamond structure.[2] The two fluorine atoms, F_A and F_B, are related by inversion. Thus the expansion for f_{F_B} is obtained by changing in (2) the signs of the odd terms, which are pure imaginary.

The data of Togawa[6] are incomplete in the sense that several low angle reflexions have not been observed. This is why we perform an additional analysis of Togawa's values supplemented by the data of Weiss, Witte and Wölfel[7] (WWW). The structure factors are corrected for dispersion according to Cromer.[8] We build a theoretical starting model of separate spherical atoms, corresponding to the theoretical atomic factors of Freeman[9] for Ca^{++} and of Boys[10] for F^-. This choice of the theoretical model is motivated by the fact that a straightforward comparison with the analysis of Kurki-Suonio and Meisalo[1] can be made. On the other hand, the conclusions of our analysis are not affected by the model used. The effect of the starting model can be seen numerically in the spherical component of the atomic factor. We use the temperature parameters $B_{Ca}=0.578$ Å^2, $B_F=0.761$ Å^2 and the scale factor 1.02 obtained by Kurki-Suonio and Meisalo[1] in their analysis of Togawa's values. The experimental and theoretical structure factors, F_o and F_{th}, are given in Table I.

To see the separability of the atoms from their neighbours we calculate the radial charge densities $4\pi r^2\rho_0(r)$ around each atom from the equation

$$\rho_0=\frac{1}{V}\sum F_j\frac{\sin 2\pi b_j r}{2\pi b_j r}\,. \qquad (3)$$

Figure 1 shows the results corresponding to Togawa's data. The addition of the WWW weak reflexions has a negligible effect on these curves.

Table I. The theoretical structure factors F_{th} and the experimental dispersion corrected structure factors F_o of Togawa supplemented by the data of Weiss, Witte and Wölfel (WWW).

h	k	l	$\sin\theta/\lambda$	F_{th}	F_o
1	1	1	0.1585	61.24	61.60
2	0	0	0.1831	0.00	1.72(WWW)
2	2	0	0.2589	94.20	94.24
3	1	1	0.3036	44.04	44.28
2	2	2	0.3171	6.28	7.64(WWW)
4	0	0	0.3661	68.20	66.68
3	3	1	0.3990	35.12	35.48
4	2	0	0.4093	8.40	9.52(WWW)
4	2	2	0.4484	54.20	54.12
3	3	3	0.4756	29.88	29.80
5	1	1	0.4756	29.88	29.80
4	4	0	0.5178	45.64	45.08
5	3	1	0.5415	26.48	26.68
4	4	2	0.5492	9.76	10.20(WWW)
6	0	0	0.5492	9.76	10.20(WWW)
6	2	0	0.5789	39.84	39.48
5	3	3	0.6002	23.96	23.68

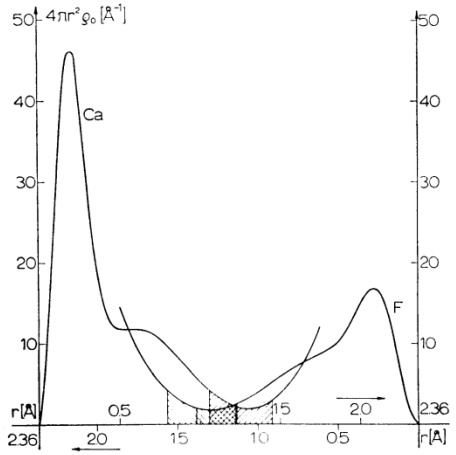

Fig. 1. Radial charge densities $4\pi r^2\rho_0(r)$ of Ca and F with an indication of the integrated electron numbers of the peaks, as calculated from Togawa's data.

To eliminate termination errors ρ_0 was first calculated for a Gaussian model crystal[1] and the result was corrected by difference series (3), with the differences $F_o - F_{Gauss}$ as coefficients.

The radial scattering factors f_n in the series (1) and (2) are calculated from the series

$$f_n(b)=\frac{(4\pi)^2R^3}{VA_n}\sum_j F_jK_n(u_jv_j) \times\frac{xj_{n+1}(x)j_n(x_j)-x_jj_{n+1}(x_j)j_n(x)}{x^2-x_j^2} \quad (4)$$

which is an exact formula for a charge distribution within a sphere of radius R in the crystal. Here $j_n(x)$ is the spherical Bessel function, $x=2\pi Rb$ and $A_n=\int K_n^2 d\Omega$. For this calculation we choose on the basis of Fig. 1 the radii $R_{Ca}=1.48$ Å$=0.63\ d$ and $R_F=1.67$ Å$=0.71\ d$, where d is the nearest neighbour distance $=2.36$ Å. This choice takes into account the earlier experiences[2,3] that slightly "too large" spheres are most favourable for this analysis. The results of a difference series calculation using Togawa's data are shown in Fig. 2 up to the 8th order. Figure 3 gives the same results for data supplemented by the WWW weak reflexions. The error bars show experimental inaccuracy. The results indicate that both of the data are consistent with the assumption of low order harmonic angular behaviour of the atoms although the higher orders are slightly larger in case of the supplemented data. Thus, according to our "nonspherical standard of adequacy"[2] the data of Togawa can be expected to be accurate enough to contain information about asphericities and the WWW weak reflexions fit reasonably well with the nonspherical behaviour of Togawa's data to make

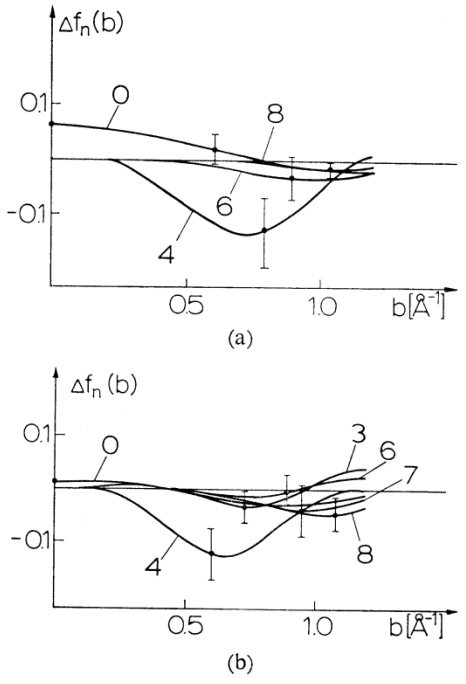

Fig. 2. The radial atomic factors Δf_n of (a) calcium, within the radius $R=1.48$ Å, $n=0$, 4, 6, 8 (b) fluorine, within the radius $R=1.67$ Å, $n=0$, 3, 4, 6, 7, 8. Results of a single difference series calculation from Togawa's data.

the nonspherical analysis reasonable also in case of the combined data. This justifies an analysis based on the assumption that the higher order components, $n>4$, are negligible.

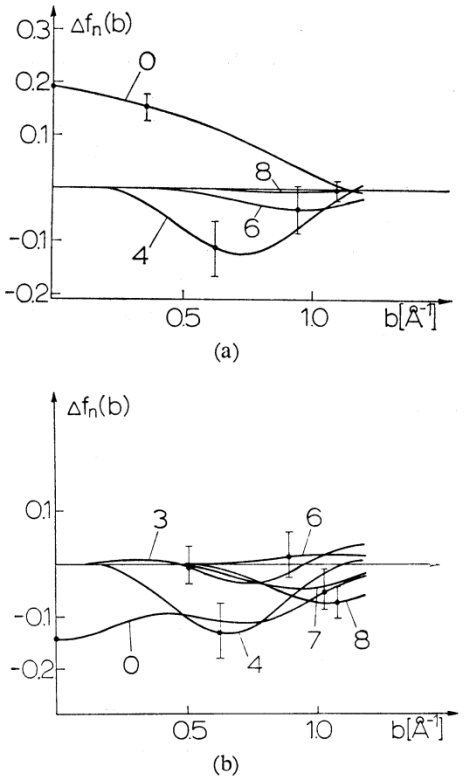

Fig. 3. The radial atomic factors Δf_n of (a) calcium, within the radius $R=1.48$ Å, $n=0$, 4, 6, 8, (b) fluorine, within the radius $R=1.67$ Å, $n=0, 3, 4, 6, 7, 8$. Results of a single difference series calculation from Togawa's data supplemented by the WWW weak reflections.

Single application of eq. (4) to calculate the low order components ($n=0$, 3, 4) from the data is probably not sufficient to produce an interpretation compatible with the data. This is particularly the case when the spheres used overlap. Similarly in case of incomplete data, the analysis is expected to produce estimates for the absent structure amplitudes, and another calculation by taking these into account would yield a more accurate result. We are thus led to an iterative procedure, where theoretical structure amplitudes are corrected by Δf_n ($n=0$, 3, 4) from eq. (4) and then used as theoretical values of a new loop of calculation. This procedure will converge to a model compatible with the data. This prepared model represents the results of our analysis giving the experimental information transformed into atomic scattering amplitudes of local atoms with low order harmonic behaviour.

§ 3. Results and Discussion

Comparison of Fig. 1 with the corresponding results on diamond and silicon[2] shows that the situation is now essentially different. Both fluorine and calcium are now well separated from their surroundings by distinct low minima in their radial charge density distributions. The radii of best separation defined by these minima are $R_{Ca}\approx R_F\approx 1.30$ Å. The integrated electron numbers within these radii were calculated from the series

$$Z(R)=\frac{4\pi R^3}{V}\sum F_j\frac{j_1(2\pi b_j r)}{2\pi b_j r} \qquad (5)$$

using a similar Gaussian procedure as in the case of eq. (3). The results correspond to the degrees of ionization $n_{Ca}=+1.85$ and $n_F=-0.85$ (1.75 and -0.80 if the WWW weak reflexions are included). The radial densities at the minima give $dn_{Ca}/dR_{Ca}=1.7\,el/$Å and $dn_F/dR_F=1.8\,el/$Å which give a relative measure for the conceptual uncertainty of the crystal atom. These are essentially experimental results not dependent on comparison with different models.[5]

X-ray diffraction data give, thus, full support to the general belief that fluorite is an ionic compound $Ca^{2+}F_2^-$. This is demonstrated in Fig. 1 by drawing limits within which the ions contain 18 ± 0.5 and 10 ± 0.5 electrons corresponding to Ca^{2+} and F^- respectively.

The numbers obtained can be compared with the corresponding results given by Kurki-Suonio and Salmo[4] for the alkali halides KBr, NaF, LiF, and the metal oxides MnO, CoO, NiO. No systematic differences in the degree of ionization are observed; it is reasonably close to the ideal values in all cases. The separability of the ions, however, suggests a systematic change in the nature of the bond in crystals. The positive ion Ca^{2+} is less clearly separable than the singly ionized alkali ions in the halides, but is rather clearly separable compared with the doubly ionized ions in metal oxides. In case of the fluorine ion, the situation in CaF_2 is very similar to that in NaF ($dn_F/dR_F=2.0\,el/$Å) and LiF ($dn_F/dR_F=1.8\,el/$Å).

The difference series procedure used in this analysis means a comparison of the real crystal with a model built of theoretical free ions Ca^{2+} and F^-. It is found by the above statements that the model is reasonable for such a calculation. The results of iteration shown in Figs. 4 and 5 are in full agreement with the statements since

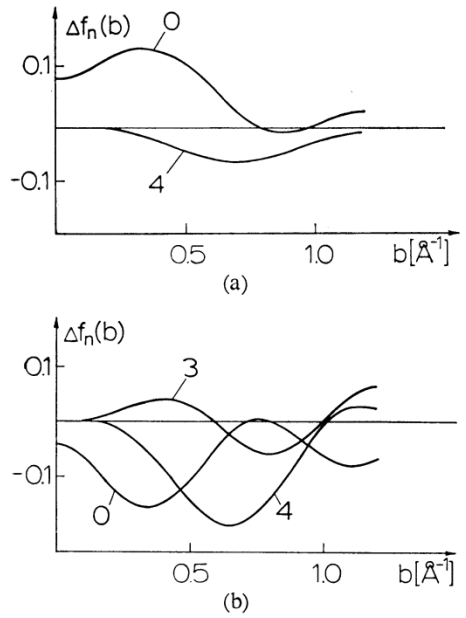

Fig. 4. The radial atomic factors; (a) Δf_0, $\Delta f_3/i$, Δf_4 of Ca within the radius $R=1.48$ Å; (b) Δf_0, $\Delta f_3/i$, Δf_4 of F within the radius $R=1.67$ Å. Results of an iterative calculation from Togawa's data.

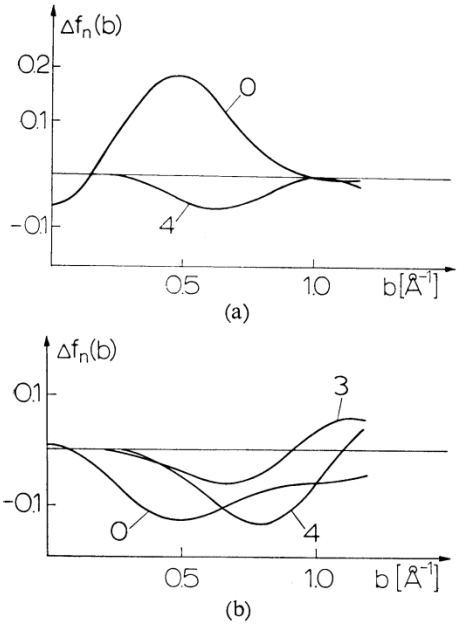

Fig. 5. The radial atomic factors; (a) Δf_0, Δf_4 of Ca within the radius $R=1.48$ Å; (b) Δf_0, $\Delta f_3/i$, Δf_4 of F within the radius $R=1.67$ Å. Results of an iterative calculation from Togawa's data supplemented by the WWW weak reflections.

$\Delta f_0(0)\approx 0$ for both ions.

To control the convergence properties of the iteration procedure and to get an idea of the significance of the results a series of calculations was made just as in the case of diamond and silicon.[2] We used different radii and also slightly different procedures varying the order in which the different components were taken into account in the iteration.

The problem of convergence is qualitatively similar to that of the diamond structure. The iteration will necessarily diverge if the radii are too large. When equal radii were used for both ions the critical value was found to be about $R=0.69\,d$, where d is the nearest neighbour distance. This is clearly smaller than the corresponding critical radius in the diamond structure,[2] obviously, because the overlapping volume of the spheres is now larger due to the larger number of neighbours.

The final prepared models obtained in the analysis of Togawa's data using different radii and different procedures varied within rather wide limits as compared to experimental inaccuracies, which are indicated by the error bars in Fig. 2. Thus the incompleteness of the data dominates the problem of reliability of the results. Different interpretations with slight cubic deformations of the fourth order in either of the ions or in both of them seem equally possible. Still, qualitatively, an average spherical compression of Ca and an extension of F seem to be a common feature in all prepared models and can be regarded as a definite indication of the data.

Thus, contrary to the conclusion of the paper by Kurki-Suonio and Meisalo,[1] where the experimental errors were considered to dominate, the nature of nonsphericities of the atoms cannot be reliably derived from Togawa's data. This analysis indicates at least, however, that the interpretation of Togawa's data merely by spherical atoms is not satisfactory.

The critical feature of incompleness of Togawa's data can also be seen when the fit of the prepared models with the experimental structure amplitudes is considered. A complete fit like that shown in Fig. 6 was obtained with different radii and different procedures. The situation is similar to the analyses of the data of DeMarco and Weiss[11] on Si and Ge, as was reported by Kurki-Suonio and Ruuskanen (1971).[2] This shows that the data are not dense enough in the reciprocal space to build up a clear systematic behaviour, so that all statistical fluctuations of the data are infiltrated into the results, and the method is not able to separate the information from the background noise.

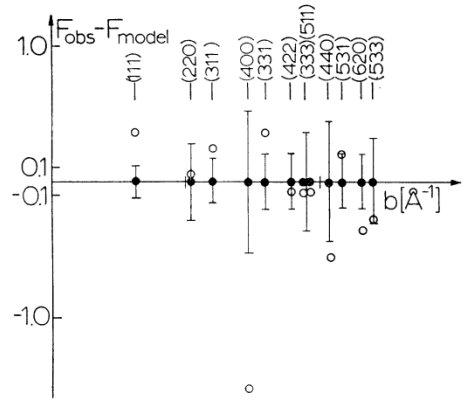

Fig. 6. The deviations of the experimental structure amplitudes from the original theoretical model (open circles) and from the final model (solid circles) obtained by an iterative analysis of Togawa's data with radii $R_{Ca}=1.48$Å, $R_F=1.67$Å.

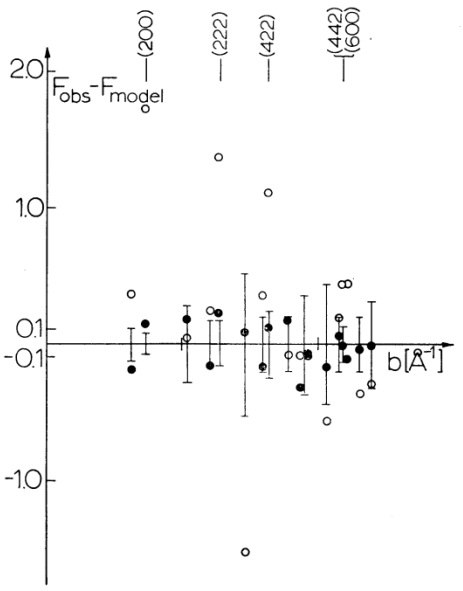

Fig. 7. The deviations of the experimental structure amplitudes from the original theoretical model (open circles) and from the final model (solid circles) obtained by an iterative analysis of Togawa's data supplemented by the WWW weak reflexions, with radii $R_{Ca}=1.48$ Å, $R_F=1.67$ Å.

In case of the combined data the situation is different. Now, clearly, the experimental inaccuracy dominates and Fig. 5 with the error bars of Fig. 3 shows the results indicated by the data. The spherical compression of the Ca ion and the extension of the F ion are confirmed. The fourth order cubic deformation of fluorine is also evident. The corresponding redistribution of the electrons depends on the behaviour of the harmonic K_4. K_4 has positive maxima in the directions of the cubic crystal axes and negative minima in the bond and antibond directions.[2] Thus $f_4(b)$ obtained corresponds to a transfer of electrons from the lobes along the cubic crystal axes to the bond and antibond directions. The total of $Z_4=0.2$ electrons per fluorine atom displaced in this way is obtained by numerical integration of the curve $f_4(b)$.* Similarly $\langle r\rangle_4$**$=1.0$ Å$=0.43\ d$ is obtained for the effective distance of this deformation component from the nucleus. This indicates concentration of the deformed electrons in the proximity of the midpoint between the Ca and F atoms. The third order tetrahedral component of fluorine and the cubic deformation of calcium are too weak to be positively verified.

* $Z_4=\int\limits_{K_4>0} K_4\,\mathrm{d}\Omega \int \rho_4(r)r^2\mathrm{d}r=1.37\int_0^\infty f_4(b)\frac{1}{b}\mathrm{d}b.$

** $Z_4\langle r\rangle_4=\int\limits_{K_4>0} K_4\mathrm{d}\Omega \int \rho_4(r)r^3\mathrm{d}r=0.90\int_0^\infty f_4(b)\frac{1}{b^2}\mathrm{d}b.$

The fit of this prepared model to the data is shown in Fig. 7. The residual differences are small enough to be interpreted as the statistical background noise left, when the information is separated by letting the assumptions of locality and low order harmonic behaviour of the atoms to be effective to define the signal shape.

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