References

BACON, G. E., CURRY, N. A. & WILSON, S. A. (1964). *Proc. Roy. Soc.* A**279**, 98–110.

BAZHULIN, A. & RAKHINOV, M. (1967). *Sov. Phys. Solid State*, **8**, 1719–1722.

BONADEO, H. & D'ALESSIO, E. (1975). *Lattice Dynamics and Intermolecular Forces*, Int. School Phys. 'Enrico Fermi' LV, New York. New York: Academic Press.

BORN, M. & HUANG, K. (1954). *Dynamical Theory of Crystal Lattices*. Oxford Univ. Press.

BREE, A., KYDD, R. A., MISRA, T. N. & VILKOS, V. V. B. (1971). *Spectrochim. Acta*, A**27**, 2315–2332.

BREE, A., SOLVEN, F. G. & VILKOS, V. V. B. (1972). *J. Mol. Spectrosc.* **44**, 298–319.

CAMERMAN, A. & TROTTER, J. (1965). *Acta Cryst.* **18**, 636–643.

CRUICKSHANK, D. W. J. (1957). *Acta Cryst.* **10**, 504–508.

FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFFRITTI, G. B. (1973). *J. Chem. Phys.* **59**, 5088–5101.

HAGLER, A. T. & LIFSON, A. (1974). *Acta Cryst.* B**30**, 1336–1341.

HULER, E. & ZUNGER, A. (1975). *Phys. Rev.* (*B*), **12**, 5878–5889.

LEIBFRIED, G. & LUDWIG, W. (1961). *Solid State Phys.* **12**, 275–444.

MASON, R. (1964). *Acta Cryst.* **17**, 547–555.

PAWLEY, G. S. (1967). *Phys. Stat. Sol.* **20**, 347–360.

PAWLEY, G. S. (1972). *Phys. Stat. Sol.* (*b*), **49**, 475–488.

PAWLEY, G. S. & CYVIN, S. J. (1970). *J. Chem. Phys.* **52**, 4073–4077.

RINALDI, R. P. & PAWLEY, G. S. (1975). *J. Phys. C: Solid State Phys.* **8**, 599–616.

SANQUER, M. & MESSAGER, J. C. (1975). *Mol. Cryst. Liq. Cryst.* **29**, 285–294.

SATATY, Y. A. & RON, A. (1976). *J. Chem. Phys.* **65**, 1578–1580.

SATATY, Y. A., RON, A. & BRITH, M. (1973). *Chem. Phys. Lett.* **23**, 500–503.

SCHERINGER, C. (1974). *Acta Cryst.* A**30**, 359–363.

SUZUKI, M., YOKAYAMA, T. & ITO, M. (1968). *Spectrochim. Acta*, A**24**, 1091–1107.

TADDEI, G., BONADEO, H., MARZOCCHI, M. P. & CALIFANO, S. (1973). *J. Chem. Phys.* **58**, 966–978.

TROTTER, J. (1963). *Acta Cryst.* **16**, 605–608.

WILLIAMS, D. E. (1965). *J. Chem. Phys.* **43**, 4424–4426.

WILLIAMS, D. E. (1970). *Trans. Amer. Cryst. Assoc.* **6**, 21–33.

WILLIAMS, D. E. (1972). *Acta Cryst.* A**28**, 629–635.

WILLIAMS, D. E. (1974). *Acta Cryst.* A**30**, 71–77.

WILLIAMS, D. E. & STARR, T. L. (1977). *Comput. Chem.* To be published.

ZALLEN, R., GRIFFITHS, C. H., SLADE, M. L., HAYEK, M. & BRAFMAN, O. (1976). *Chem. Phys. Lett.* **39**, 85–89.

Acta Cryst. (1977). A**33**, 776–783

An X-ray Diffraction Study of NaF

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NaF gives rise to very weak odd-index reflexions in X-ray diffraction. These reflexions have been studied to determine the best models for electron distribution in the NaF crystal. Data were obtained from a single crystal at room temperature for Ag $K\alpha$, Mo $K\alpha$, Cu $K\alpha$ and Co $K\alpha$ radiations. Least-squares analyses were made on the Ag $K\alpha$ and Mo $K\alpha$ data. Scattering factors for Hartree–Fock singly charged free ions allowed a good fit to the data, and there was a marginal improvement of the fit with similar scattering factors modified for effects of crystalline environment. The mean thermal parameter for the ions was $\bar{B}=0{\cdot}905\pm0{\cdot}025$ Å^2. An attempt to account for the wavelength dependence of intensities of the strong reflexions, with current theories of extinction, was unsuccessful.

1. Introduction

The structure of NaF was established early in the history of X-ray crystallography. There are nevertheless a number of pertinent questions which might be answered from a careful study of the intensities of the various reflexions. These questions include:

1. How can the data be processed to yield structure factors on the correct scale?
2. What are the values of the thermal parameters B_{Na} and B_F?
3. How are the intensities affected by extinction in any particular crystal?
4. To what extent are the tabulated atomic/ionic scattering factors adequate for describing the diffraction? This question relates to the suitability of various models for the electron distribution in NaF.

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There have been previous studies directed towards one or more of the above questions. Meisalo & Merisalo (1966) used powder specimens so that intensities would not be affected by extinction. In an analysis employing Hartree–Fock free-ion scattering factors they obtained for the thermal parameters $B_{Na}=B_F=1{\cdot}08\pm0{\cdot}07$ Å^2 and were able to comment that certain other scattering factors gave a less satisfactory fit to their data. The results have been examined further by Aikala & Mansikka (1971, 1972).

Sharma (1974*a*, *b*, 1975) studied a single crystal of NaF. He concluded that the thermal parameters were $B_{Na}=0{\cdot}893\pm0{\cdot}021$, $B_F=0{\cdot}912\pm0{\cdot}054$ Å^2. He found that the intensities were diminished by extinction, and concluded that his crystal exhibited type II extinction behaviour (Zachariasen, 1967). Sharma found that the scattering factors given in *International Tables for X-ray Crystallography* (1962) allowed a good fit to his data, but there are reasons (Killean, 1976) to treat at least this aspect of the work with caution.

The primary motivation for the present work has been an interest in the question of the adequacy of theoretical scattering factors. There appear to be good prospects that accurate experimental data from NaF can indeed provide critical evaluation of these scattering factors. The odd-index reflexions (indices h,k,l, all odd) are expected to prove particularly valuable, for these reflexions involve the difference between the scattering factor for the ten-electron Na^+ ion and that for the ten-electron F^- ion. The difference is small and relatively sensitive (at least at low Bragg angles) to the details of the electron distributions assumed. Although these odd-index reflexions are so weak that they should be little affected by extinction, they are by no means too weak to be measured. For NaF, several models for the electron distribution have been proposed, and corresponding to these models there are several sets of scattering factors available: those considered in this paper are indicated in Table 1. It will be shown in the following sections that certain scattering factors are quite definitely preferred to others.

On account of correlations, an assessment of the scattering factors cannot proceed in ignorance of the scale, the thermal parameters, or the effects of extinction. Therefore, a discussion of these is included.

The potential of the odd-index reflexions for probing the electron distribution in NaF was clearly recognized by the late Dr B. Dawson (private communication); it is as a result of his encouragement that we have undertaken the measurements reported below.

2. Experimental method

2.1 *Crystal preparation*

Crystals of NaF (Univar, Ajax Chemicals) were grown by evaporation of a solution in de-ionized distilled water. A crystal $0{\cdot}096\times0{\cdot}074\times0{\cdot}076$ mm was selected and, after careful checking of its diffraction pattern, used for data collection.

2.2 *Apparatus*

An automated four-circle diffractometer, with a Stoe goniostat, was used in conjunction with a high-stability Philips 1140 X-ray generator. The detector was a hyper-pure *n*-type Si solid-state device, kept at liquid-nitrogen temperature (Beech & Eberhardt, 1973). With such a detector, the characteristic radiation from a target or, in fact, any energy band can be selected on the basis of pulse height alone. No filters or monochromators are required. As the cryogenic reservoir for the detector was bulky, limitations were imposed on the setting angles. In particular, 2θ was limited to $\sim90°$, which restricted the accessible reflexions with longer wavelengths.

2.3 *Background determination*

The problems associated with background determination with a solid-state detector have been described by Howard & Jones (1976) who, with Hope (1975), have found that incorrect evaluation of the background level leads to gross overestimation of integrated intensity, especially at low Bragg angles. If

Table 1. *Scattering factors considered in this work*

Scattering factors (with abbreviations used in the text)	Source	Model for electron distribution from which scattering factors have been derived
Hartree–Fock neutral atoms (HF^0)	Cromer & Mann (1968)	Solutions of the Hartree–Fock equations for free neutral atoms Na^0 and F^0.
Hartree–Fock ions (HF)	Cromer & Mann (1968)	Solutions of the Hartree–Fock equations for the free ions Na^+ and F^-.
Dirac–Slater ions (DS)	Cromer & Waber (1965)	Solutions of the Dirac equation (incorporating relativistic effects) for the free ions Na^+ and F^-, but with Slater's approximation for the exchange terms.
Poly-detor ions (PD)	Dawson (1961)	Solutions for the free ions Na^+ and F^- which incorporate effects of Coulomb repulsion between electrons. The F^- ion is considerably contracted compared with the Hartree–Fock F^- ion.
Aikala & Mansikka Model 1 (AM1)	Aikala & Mansikka (1972)	Modification of the Hartree–Fock free ions which incorporates a contraction of the 2*p* orbital of the F^- ion in the crystal as compared with the same orbital in the free ion.
Aikala & Mansikka Model 2 (AM2)	Aikala & Mansikka (1972)	Further modification (beyond AM1) to take account of the overlap of the wave functions within the crystal environment.

our conclusions are to have any significance, estimation of true background, *i.e.* the white radiation level, is of paramount importance. By careful adjustment of the energy bandwidth of the pulse-height discriminator at the energy of the characteristic radiation, sufficient white radiation was accepted to allow accurate assessment of background. Fig. 1 shows representative θ–2θ scans for Mo $K\alpha$ radiation and indicates how allowance has been made for background.

2.4 *Data collection*

The crystal was mounted in a general orientation with respect to the φ axis of the goniostat. All measurements were made at $\sim 20\,^{\circ}C$. The lattice parameter was determined as 4·630 Å. Integrated intensities for four wavelengths (Ag $K\alpha$, set I; Mo $K\alpha$, set II; Cu $K\alpha$, set III; Co $K\alpha$, set IV) were measured, in the bisecting mode, by a θ–2θ step-scan method (Elcombe, Cox, Pryor & Moore, 1971). Except for the high-angle odd-index reflexions for Ag $K\alpha$, which were too weak to be measured, all reflexions accessible within the instrumental limits were scanned. Details of data collection have been deposited.* As a check for the absence of multiple diffraction, azimuthal scans were recorded for several reflexions with special attention to the low-angle odd-index reflexions. No variation from the intensity recorded in the bisecting position could be detected.

2.5 *Data processing*

Integrated intensities were reduced to F_o^2 and $\sigma(F_o^2)$.* These values were corrected further for first-order thermal diffuse scattering (Rouse & Cooper, 1968). Instrumental constants for this calculation were: detector aperture diameter 3·8 mm (the circular aperture was approximated to a square of equivalent area), crystal-to-detector distance 120 mm. Positions of background measurement are recorded in the Supplementary Publication. Elastic constants used were those listed in the *American Institute of Physics Handbook* (1972). The corrections ranged from 0·05 % for 111 with Ag $K\alpha$ radiation to 9 % for 10,0,0.

Equivalent reflexions were averaged for each wavelength to obtain the data sets included in Table 2. The estimated standard deviation was taken as the greater of those calculated from Poisson statistics and from variation from the mean intensity of an equivalent set.

Inspection of the four data sets indicated there was secondary extinction and, for III and IV, possibly anisotropic extinction. For the latter two, {200} and {220} were not accepted on our statistical criteria for equivalence of intensity. Since some estimation of extinction was required for III and IV, a mean F_o^2 was calculated for these two reflexions without regard to statistical equivalence.

3. Least-squares analyses

The method of least-squares was used to determine the best fit to F_o^2 by $|F_c'|^2 = yS^2|F_c|^2$ where y is an extinction correction involving the isotropic extinction parameter g (see §4.3 and Coppens & Hamilton, 1970); S is a scale factor, there being one such factor for each of the four data sets;

$$F_c = 4[f_{Na} \exp(-B_{Na} \sin^2\theta/\lambda^2) \pm f_F \exp(-B_F \sin^2\theta/\lambda^2)],$$

B_{Na} and B_F are the thermal parameters, f_{Na} and f_F are the scattering factors for atoms or ions, and include anomalous dispersion terms (Cromer & Liberman,

* Details of the method of data collection, scan widths, data reduction, estimation of errors and a listing of the F_o^2 values for each wavelength have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32621 (14 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester, CH1 1NZ, England.

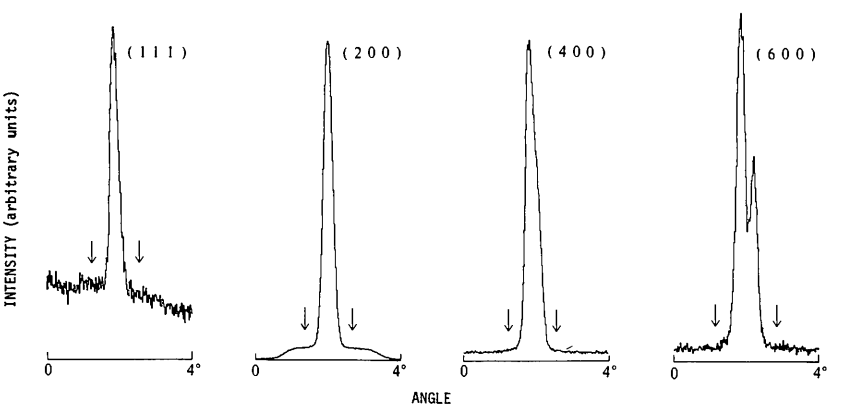

Fig. 1. θ–2θ scans of representative reflexions with Mo $K\alpha$ radiation. The arrows indicate the scan limits for intensity measurement and the positions of measurement for background estimation.

1970); the signs + and − refer to even- and odd-index reflexions respectively.

An analysis was made with each of the six combinations of scattering factors given in Table 1. In all refinements, the function minimized was $\Sigma w(|F_o|^2-|F_c'|^2)^2$ with $w=\sigma(F_o^2)^{-2}$.

3.1 *Scale factor*

No attempt was made to determine experimentally an absolute scale for each wavelength (see §4.1). To eliminate differences which might occur in derived parameters if I and II were analysed separately, they were placed on a common scale as follows:

Full-matrix least-squares refinement varying (i) a scale factor for each of I and II, (ii) B for each atom and using (iii) only data with $(\sin\theta)\lambda^{-1}>0{\cdot}7$ and (iv) HF scattering factors was carried out. In this range, observations should be unaffected by extinction and calculated structure factors are insensitive to the model assumed. The process was repeated with PD. In the two calculations, the ratio of the two scale factors was the same. This confirmed that a relative scale, independent of model, could be defined to 0·9% accuracy [95% confidence level (Hamilton, 1965)]. I and II in Table 2 have been put on the common scale. Subsequently, except for extinction purposes, I and II were treated as the one data set I,II.

3.2 *Refinement for each model with* Ag $K\alpha$, Mo $K\alpha$

In the absence of an absolute scale and definitive values for B_{Na} and B_F, and since scale and B's have appreciable correlation, the following procedure was adopted. Least-squares refinement was carried out for each scattering factor model and, for each model, a single overall scale, the individual B's, and g for each wavelength were varied. The refinements involved 67 observations and 5 variable parameters.

For the HF^0 and DS models, g(Ag $K\alpha$) refined to a small negative value. The calculation for these two models was repeated with g(Ag $K\alpha$) fixed at 0.

3.3 Cu $K\alpha$ *and* Co $K\alpha$ *data*

These data were used to obtain information on extinction. Anticipating our results (see §4.4), we found

Table 2. *Observed and calculated structure factors for* NaF

Calculations are for Ag $K\alpha$ radiation and assume $B_{Na}=0{\cdot}901$, $B_F=0{\cdot}908$ Å^2, and AM2 scattering factors.

				Ag $K\alpha$		Mo $K\alpha$		Cu $K\alpha$		Co $K\alpha$	
h	k	l	F_c^2	F_o^2	$\sigma(F_o^2)$	F_o^2	$\sigma(F_o^2)$	F_o^2	$\sigma(F_o^2)$	F_o^2	$\sigma(F_o^2)$
1	1	1	26·16	26·26	0·54	25·92	0·20	28·26	0·17	27·98	0·40
2	0	0	3237·19	3057·12	13·34	2913·39	18·82	2348·20	23·21	2063·53	53·32
2	2	0	1911·88	1858·96	3·35	1821·04	2·87	1631·31	7·47	1562·73	22·80
3	1	1	40·39	41·02	0·24	40·88	0·20	43·18	0·27	43·71	0·26
2	2	2	1227·41	1232·80	1·76	1184·36	2·44	1106·86	9·27		
4	0	0	834·26	830·05	1·77	805·96	3·23	773·87	6·28		
3	3	1	24·88	24·82	0·24	25·46	0·17	25·89	0·28		
4	2	0	592·86	589·71	0·98	582·77	1·05				
4	2	2	436·40	436·89	0·69	436·38	1·05				
3	3	3	13·60	12·81	0·35	13·75	0·37				
5	1	1	13·60	13·19	0·21	13·45	0·22				
4	4	0	257·13	255·24	1·20	256·92	1·20				
5	3	1	7·33	7·24	0·28	7·22	0·17				
4	4	2	203·94	206·22	0·68	202·63	0·87				
6	0	0	203·94	207·84	1·25	205·87	1·65				
6	2	0	164·60	165·93	0·69	164·68	0·95				
5	3	3	4·01	3·95	0·34	3·99	0·22				
6	2	2	134·96	134·38	0·74	134·91	0·76				
4	4	4	112·07	112·26	1·32	111·30	1·17				
5	5	1	2·24	1·38	0·34	2·41	0·33				
7	1	1	2·24	2·28	0·42	2·40	0·34				
6	4	0	94·12	93·33	0·56	94·52	0·77				
6	4	2	79·80	80·00	0·49	81·05	0·53				
5	5	3	1·30	1·13	0·35	1·05	0·32				
7	3	1	1·30	0·94	0·26	1·28	0·24				
8	0	0	58·73	59·36	0·78	60·65	1·12				
7	3	3	0·77	0·50	0·37	1·13	0·35				
6	4	4	50·86	51·14	0·54	52·44	0·65				
8	2	0	50·86	50·23	0·54	51·24	0·57				
6	6	0	44·32	43·18	1·21						
8	2	2	44·32	45·20	1·00						
6	6	2	38·79	39·13	0·77						
8	4	0	34·08	35·42	0·78						
8	4	2	30·04	29·12	0·57						
6	6	4	26·57	26·69	0·91						
8	4	4	20·94	22·67	0·78						
8	6	0	18·65	18·76	0·78						
10	0	0	18·65	18·36	1·50						

AM2 gave the best fit for I, II. Fixing the B's from this model, a scale factor was refined for the odd-index reflexions of each of III and IV. It was assumed that these reflexions would be insensitive to extinction. Subsequently, with scale and B values fixed for each set, g was refined.

4. Results and discussion

Table 3 shows values for the parameters (each with e.s.d.) from refinement on I, II (see §3.2). The calculated structure factors for AM2 are in Table 2.

4.1 *The scale*

How near are the F_o^2 recorded in Table 2 to absolute scale? The scale is strongly correlated with the other parameters, and the least-squares scale also depends on the particular scattering factors used. (In contrast, the relative scale of the Ag $K\alpha$ to Mo $K\alpha$ data, as determined from the high-angle data, was insensitive to model assumed.)

An estimate of the accuracy of the scale was obtained in the following way. Under the assumption that AM2 scattering factors gave a correct description of the ions, least-squares refinements were carried out with the scale fixed at successive values near the optimum, while the other parameters were allowed to vary. For each value of scale, the quantity

$$wR=[\sum w(|F_o|^2-|F_c'|^2)^2/\sum w|F_o|^4]^{1/2}$$

was determined and the plausibility of each value of scale was assessed by testing the ratio of wR to wR for the optimum fit against the tables given by Hamilton (1965). The ratio was compared with $\mathscr{R}_{1,62,0\cdot05}$. (This procedure is very similar to that used previously to determine the accuracy of the relative scale.) The procedure was repeated, it being assumed successively that AM1 and HF were the correct scattering factors. The final result for the scale was $1\cdot000\pm0\cdot013$ where the errors are intended to indicate 95% confidence limits. With this error and the previously mentioned error of 0·9% in the relative scale taken into account, the entries in Table 2 under Ag $K\alpha$ are thought to be on the correct scale to an accuracy of about 3% (corresponding to 1·5% in F_o).

Consideration was given to experimental determination of the absolute scale. Stevens & Coppens (1975) have made experimental measurements of the scale (on F_o) to an accuracy of about 1%. There would be some interest in measuring the scale to this accuracy as a check on our results. However, the results for scale included in Table 3 indicate that, to be of assistance in distinguishing among the better models for the electron distribution, the absolute scale would need to be determined with an accuracy approaching 0·1%.

4.2 *The thermal parameters*

Isotropic thermal parameters B_{Na} and B_F were determined in the least-squares refinement and are recorded in Table 3. However, we prefer to consider the values of $\bar{B}=\frac{1}{2}(B_{Na}+B_F)$ and $\Delta B=\frac{1}{2}(B_F-B_{Na})$.

The approximation which assumes high temperatures and only near-neighbour forces leads to $\Delta B=0$ (Willis & Pryor, 1975). In practice, we expect ΔB to be small, so that $\bar{B}$ should approximate both B_{Na} and B_F.

The parameter $\bar{B}$ is highly correlated with the scale and is correlated to a lesser extent with the extinction parameters, but (as can be seen from Table 3) it is not unduly affected by the choice of scattering factors. The value of $\bar{B}$ is determined largely from the even-index data. To establish confidence limits for the value of $\bar{B}$ we carried through an analysis similar to that described in §4.1, once again allowing for the possibility that any of HF, AM1, or AM2 might be the correct model for the electron distribution. The result is $\bar{B}=0\cdot905\pm0\cdot025$ Å^2 where again the errors are intended to correspond to 95% confidence limits.

The parameter ΔB is determined largely from the odd-index data. The value obtained depends markedly on which scattering factors are used in the fit. Conversely, we would expect that any independent definitive information concerning ΔB would be of considerable value in assessing the scattering factors. Values for ΔB are available from Table 3. As to confidence limits, we have used Hamilton's R-ratio tests to examine the hypothesis $\Delta B=0$. For AM2, AM1 and HF scattering factors the ratios are 1·007, 1·043 and 1·264 respectively. Consulting the tables (Hamilton, 1965) for values of $\mathscr{R}_{1,62,\alpha}$ we find that for AM2 the hypothesis is not rejected, for AM1 the hypothesis is rejected at the

Table 3. *The least-squares derived parameters for each type of scattering factor (see text)*

Intensity data used were collected with Ag $K\alpha$ and Mo $K\alpha$ radiations.

	Scattering factor					
	AM2	AM1	HF	PD	DS	HF^0
Scale ($\times10^3$)	1000 (1)	996 (1)	1008 (2)	1001 (2)	964 (1)	993 (2)
B_{Na} ($\times10^3$)	901 (5)	893 (5)	925 (5)	914 (6)	885 (5)	891 (7)
B_F ($\times10^3$)	908 (4)	911 (4)	872 (4)	915 (5)	946 (5)	853 (7)
g_{Ag} ($\times10^{-1}$)	9 (1)	10 (2)	10 (2)	14 (2)	—	—
g_{Mo} ($\times10^{-1}$)	18 (1)	18 (1)	18 (1)	21 (1)	9 (1)	9 (1)
$\Sigma w\Delta^2$	373	406	537	1105	1415	4577
$\Sigma w\Delta^2_{odd}$	44	75	195	742	858	4144
$\Sigma w\Delta^2_{even}$	329	331	342	363	557	463

2·5% significance level, and for HF the hypothesis is very definitely rejected. Thus, given AM2 scattering factors, the sign of ΔB is not really determined, given AM1 scattering factors, we could say $\Delta B \geq 0$ with 97·5% confidence, while given HF scattering factors we could say definitely that $\Delta B < 0$.

Our value for $\bar{B}$ is in agreement with that obtained, with PD scattering factors, by Sharma (1975), $\bar{B} = 0{\cdot}903$ Å^2, but is lower than the $\bar{B} = 1{\cdot}08 \pm 0{\cdot}07$ Å^2 quoted by Meisalo & Merisalo (1966). The reason for the discrepancy is not clear, but it may be related to the difficulty of determining the background levels in the powder method. Theoretical values for room temperature have been derived from the experimental phonon dispersion (Buyers, 1967) and other data by Reid & Smith (1970) who give $\bar{B} = 0{\cdot}8678$, $\Delta B = -0{\cdot}0007$, and by Sneh & Dayal (1975) who give $\bar{B} = 0{\cdot}95$, $\Delta B = +0{\cdot}05$ Å^2.

4.3 *Extinction*

For the least-squares analysis, the Zachariasen (1967) extinction correction was included. This correction factor is

$$y = (1 + 2p_2 x_0/p_1)^{-1/2}$$

where

$$p_1 = 1 + \cos^2 2\theta, \quad p_2 = 1 + \cos^4 2\theta,$$

$$x_0 = gQ_0 \bar{T},$$

$$Q_0 = \left(\frac{e^2 F_c}{mc^2 V}\right)^2 \frac{\lambda^3}{\sin 2\theta},$$

and $\bar{T}$ is the effective mean path length. The parameter g is determined in the least-squares analysis. For the joint refinement of the Ag $K\alpha$ and Mo $K\alpha$ data, we allowed g to assume independent values for the two wavelengths. These results for g have been recorded in Table 3.

Refinements of the Cu $K\alpha$ and Co $K\alpha$ data (see §3.3) gave for the isotropic extinction parameter the values $g = 15\ (1) \times 10$ and $g = 16\ (1) \times 10$ respectively.

Becker & Coppens (1974) have indicated that the Zachariasen extinction correction is applicable only when extinction is not severe and, for type II extinction, the correction factor should be amended to incorporate

$$x_0 = gQ_0 \bar{T} \sin 2\theta.$$

Assuming this different θ dependence, a least-squares refinement for our Ag $K\alpha$/Mo $K\alpha$ data, with AM2 scattering factors, led to the results

$$\text{Scale} = 1{\cdot}005\ (2),\ B_{Na} = 0{\cdot}911\ (5),\ B_F = 0{\cdot}912\ (5),$$

$$g_{Ag} = 41\ (6) \times 10,\ g_{Mo} = 51\ (4) \times 10,$$

$$\Sigma w\Delta^2 = 328,\ \Sigma w\Delta^2_{odd} = 40,\ \Sigma w\Delta^2_{even} = 288.$$

The scale and thermal parameters are not very different from those shown in Table 3 for the AM2 scattering factors, while the values of $\Sigma w\Delta^2$ indicate no significant difference in the fit. However, the numerical values for the extinction parameters are larger than in Table 3.

The F_o^2 for the strong reflexions (Table 2) show a systematic dependence on wavelength which is attributed to extinction. An attempt was made to compare this wavelength dependence with the theoretical predictions for type I and type II secondary extinction from Zachariasen (1967) and from Becker & Coppens (1974). None of these predictions on wavelength dependence was clearly applicable in our case. This somewhat disheartening result is consistent with conclusions reached by Cooper & Rouse (1976) following a much more extensive analysis of neutron data from SrF_2.

4.4 *Models for electron distribution*

The quality of the fit provided by each model and its corresponding set of scattering factors was judged according to the values of $\Sigma w\Delta^2$ (Table 3), rather than on values of R.† In Table 3, $\Sigma w\Delta^2$ has been subdivided to show the contributions $\Sigma w\Delta^2_{even}$ from the even- and $\Sigma w\Delta^2_{odd}$ from the odd-index reflexions. Notable features are the relatively constant values of $\Sigma w\Delta^2_{even}$, and the dramatic variation from model to model of $\Sigma w\Delta^2_{odd}$. The former feature indicates that, by variations of the assumptions for extinction and thermal parameters, any model will give a reasonable fit to even-index data. By contrast, the variation of $\Sigma w\Delta^2_{odd}$ (anticipated in §1) is a result of the particular sensitivity of the odd-index reflexions to the model assumed. From the values of $\Sigma w\Delta^2_{odd}$ in Table 3, we conclude that AM2, AM1 and HF are the best models, while PD, DS and HF^0 are untenable.

The fits to the odd-index data provided by the different models are examined in another way in Fig. 2. The curves represent the calculated intensities for the odd-index reflexions according to (best fits of) the different models, whereas the points represent the experimentally measured odd-index data. We see in this figure a suggestion that AM2 provides the best fit to the data but, in view of the size of the estimated standard deviations, we do not believe that models AM1 or HF are excluded. On the other hand, it seems clear that PD, DS and HF^0 do not allow acceptable fits to the data and should be rejected. Our conclusions rest heavily on a comparison of calculated and observed intensities of the 111 and 113 reflexions. We had anticipated that these would be the most crucial reflexions (§1), and measured them with considerable care (see, for instance, §2.3 and §2.4).

Our conclusions concerning the models are plausible. There is certainly little support for the idea that NaF comprises neutral Na and F atoms, so the definite rejection of HF^0 is in some ways reassuring. It can be seen from Fig. 2 that rejection depends almost entirely on the measurement of the 111 reflexion. In the

† $R = \Sigma||F_o|^2 - |F_c'|^2|/\Sigma|F_o|^2$ is of little value at this level of accuracy. The variation of R over the six models is 0·0107 to 0·0126. In fact HF^0, the worst model based on our criteria, gives the lowest R.

absence of this peculiarly weak low-angle reflexion, it would have been difficult to distinguish from the X-ray measurements between neutral atoms and singly-charged ions. On the other hand, the Hartree–Fock calculations for singly-charged Na^+ and F^- ions are expected to give a good description of the electron distribution in the solid, and the HF scattering factors indeed provide a reasonable fit to the odd-index data. The results show that Dirac–Slater ions are unsatisfactory, which is consistent with the consensus that relativistic effects are small for light atoms, whereas Slater's approximation overestimates the effects of exchange. Poly-detor ions are intended as improvements on Hartree–Fock free ions to the extent that electron correlation effects due to Coulomb repulsion are included. However, Dawson (1961) recognized that the approximations made in the poly-detor calculation impose artificial contraction on the electron distribution especially for the F^- ion. Our results show that these limitations of the poly-detor calculations outweigh the advantages. The models AM1 and AM2 represent modifications of the HF model to take account of the crystalline environment in NaF, even if at zero temperature. Our results indicate preference for AM2 over AM1 and HF, but it is not clear that the preference is significant.

Throughout the analysis, spherically symmetric scattering factors have been assumed. No attempt has been made to determine aspherical contributions through least-squares analysis. There is no evidence from the pairs of reflexions occurring at equal angles (for instance 333 and 511) of any departure from spherical symmetry.

Finally, we compare our conclusions about models with those from the earlier work. Meisalo & Merisalo (1966) concluded that HF scattering factors were preferable to PD ones, which is in accord with our conclusions. Aikala & Mansikka (1972) have obtained marginally better fits to the Meisalo & Merisalo data with models AM1 and AM2. Sharma (1974*a*, *b*) has used PD scattering factors to fit his data, and does obtain a good fit to his low-angle odd-index data. In this respect his work is at variance with ours. For the 111 reflexion, his observed intensity is evidently about 25% less than ours. We are not able to offer any explanation for the discrepancy.

5. Summary and conclusions

We have measured intensities of the X-ray reflexions from a crystal of NaF at room temperature with four wavelengths. No direct determination of scale was attempted.

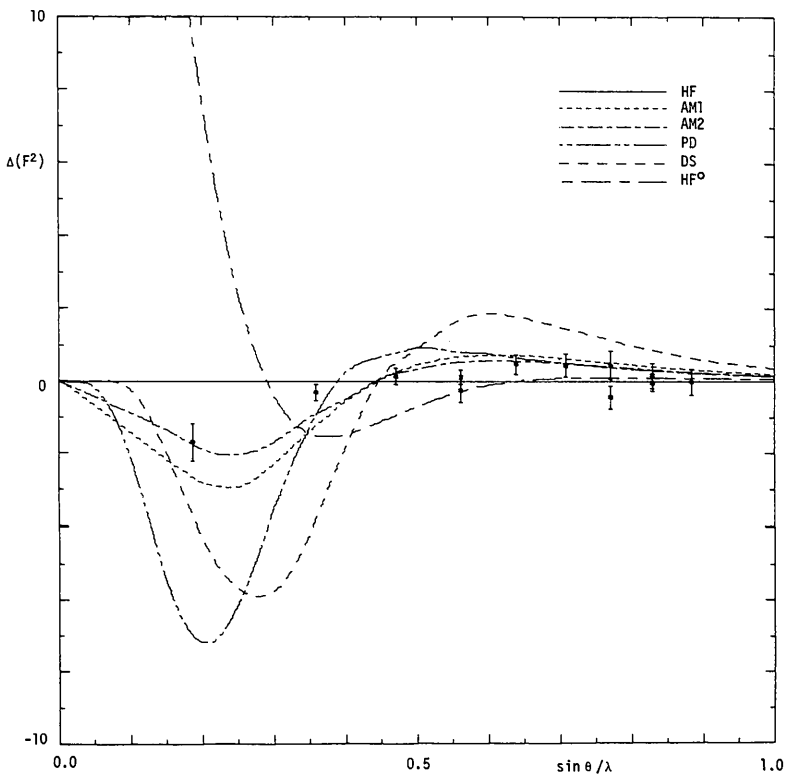

Fig. 2. This figure shows $|F_c'|^2$ (model) $-$ $|F_c'|^2$ (HF) for the odd-index reflexions and Ag $K\alpha$ radiation as a function of $(\sin\theta)/\lambda$. The curves are associated with the different models, and each corresponds to a best fit to all the data. The HF curve was taken as reference and is shown as the axis. The points * represent $F_o^2(\mathrm{Ag}) - |F_c'|^2(\mathrm{HF})$ and the error bars represent the estimated standard deviations in $F_o^2(\mathrm{Ag})$.

Least-squares analyses were carried out with each of six combinations of scattering factors. The major analyses employed the Ag $K\alpha$ and Mo $K\alpha$ data. The analyses established the scale for each data set, and the mean isotropic thermal parameter for the ions as $\bar{B}=0{\cdot}905\pm0{\cdot}025$ Å^2, a result not unduly affected by the choice of scattering factors. Although the observations incorporate the effects of extinction and its dependence on wavelength, no definitive commentary upon the theories has emerged. Our primary interest in this work has been the assessment of the various scattering factors (Table 1), and thereby of the corresponding models for the electron distribution in the crystal. This assessment was possible, mainly through the sensitive dependence of the weak 111 and 311 reflexions on the model assumed. We found that the Hartree–Fock scattering factors for free ions allowed a reasonable fit to data, and there was a marginal (perhaps not significant) improvement of the fit when these scattering factors were modified to incorporate effects of the crystal environment (Aikala & Mansikka, 1972). No satisfactory fits were obtained with Hartree–Fock neutral atoms, with Dirac–Slater ions, or with polydetor ions. There was no evidence that the scattering factors showed deviations from spherical symmetry.

Though there are sound reasons to accept Hartree–Fock calculations as giving excellent descriptions of the electron distributions in the free Na^+ and F^- ions, we believe it significant to have demonstrated that the same calculations suffice to approximate the ions as they actually exist in the NaF crystal. Our result provides some vindication for the widespread use of Hartree–Fock calculations for the description of ions and of particular electron orbitals in solids.

There is a suggestion from our work of *slight* deviation of the actual electron distribution in the crystal from Hartree–Fock free ion distributions. This suggestion might be confirmed from structure factor data if (for instance) the thermal parameters were precisely and independently known, but confirmation is more likely to be provided from measurements of the Compton profile (Paakkari, Kohonen, Aikala, Mansikka & Mikkola, 1974).

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References

AIKALA, O. & MANSIKKA, K. (1971). *Phys. kondens. Mater.* **13**, 59–66.

AIKALA, O. & MANSIKKA, K. (1972). *Phys. kondens. Mater.* **14**, 105–110.

American Institute of Physics Handbook (1972). P. **2**–52. Edited by D. E. GRAY. New York: McGraw-Hill.

BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* A**30**, 148–153.

BEECH, A. MCG. & EBERHARDT, J. E. (1973). Australian Atomic Energy Commission Report AAEC/E297.

BUYERS, W. J. L. (1967). *Phys. Rev.* **153**, 923–930.

COOPER, M. J. & ROUSE, K. D. (1976). *Acta Cryst.* A**32**, 806–812.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

CROMER, D. T. & LIBERMAN, G. (1970). *J. Chem. Phys.* **53**, 1891–1898; and Los Alamos Scientific Laboratory Report LA-4403. See also *International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.

CROMER, D. T. & MANN, J. B. (1968). Los Alamos Scientific Laboratory Report LA-3816.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

DAWSON, B. (1961). *Acta Cryst.* **14**, 1117–1120. See also *International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.

ELCOMBE, M. M., COX, G. W., PRYOR, A. W. & MOORE, F. H. (1971). Australian Atomic Energy Commission Report AAEC/TM578.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510. See also *International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.

HOPE, H. (1975). *Anomalous Scattering.* Edited by S. RAMASESHAN & S. C. ABRAHAMS, pp. 293–305. Copenhagen: Munksgaard.

HOWARD, C. J. & JONES, R. D. G. (1976). *J. Appl. Cryst.* **9**, 235.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

KILLEAN, R. C. G. (1976). *Acta Cryst.* A**32**, 510.

MEISALO, V. & MERISALO, M. (1966). *Ann. Acad. Sci. Fenn.* AVI, **211**.

PAAKKARI, T., KOHONEN, E. L., AIKALA, O., MANSIKKA, K. & MIKKOLA, S. (1974). *Phys. Fenn.* **9**, 207–221.

REID, J. S. & SMITH, T. (1970). *J. Phys. Chem. Solids*, **31**, 2689–2697.

ROUSE, K. D. & COOPER, M. J. (1968). United Kingdom Atomic Energy Research Establishment Report AERE-R5725.

SHARMA, V. C. (1974*a*). *Acta Cryst.* A**30**, 278–280.

SHARMA, V. C. (1974*b*). *Acta Cryst.* A**30**, 299–300.

SHARMA, V. C. (1975). *Acta Cryst.* A**31**, 157.

SNEH & DAYAL, B. (1975). *Phys. Stat. Sol.* (*b*), **67**, 125–128.

STEVENS, E. D. & COPPENS, P. (1975). *Acta Cryst.* A**31**, 612–619.

WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, p. 122. Cambridge Univ. Press.

ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.