

An Analysis of Recent Single Crystal X-ray Diffraction Measurements on Calcium Fluoride

BY M. J. COOPER

Materials Physics Division, A.E.R.E., Harwell, Berkshire, England

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An analysis of recent single-crystal X-ray diffraction measurements on calcium fluoride has been carried out by comparing the observed data with those calculated from a theoretical model. A computer program was used which can refine parameters for extinction and anharmonic thermal vibrations in addition to the conventional parameters.

It is shown that for the majority of the experiments in the recent ACA project the angle-dependent deviations between the experiments are consistent with those which would be expected due to a variation in the measured contributions from thermal diffuse scattering. There are discrepancies between experiments for the strongest reflexions, presumably because of errors associated with the use of attenuators, but if these reflexions are excluded the agreement between experiments, allowing for variations in the thermal diffuse scattering contributions, is much better than was indicated by previous analyses. The two remaining experiments and that reported by Zachariassen are in poor agreement with the others and this is attributed to the techniques used, namely an ω -scan with balanced filters in one case and a stationary-crystal, stationary-detector technique in the other two.

Although the effects of anharmonicity on the X-ray intensities are rather small, the data from all experiments are consistent with the magnitude of an anharmonic thermal-vibration parameter, associated with the fluorine atoms, derived from neutron-diffraction measurements.

Introduction

Diffraction measurements on calcium fluoride are of interest because of information which they provide on several physical factors, in particular the anharmonic thermal vibration of the fluorine atoms in this structure (Dawson, Hurley & Maslen, 1967) and the effects of extinction, which is particularly severe in this case (Zachariassen, 1968*a*). It is the purpose of this paper to review critically the recent X-ray diffraction measurements on calcium fluoride and to evaluate the information which can be gained from them.

Extensive single crystal X-ray diffraction measurements on calcium fluoride have been reported recently by workers in eight different laboratories. Of these, seven, as participants in the American Crystallographic Association (ACA) single crystal intensity project, reported measurements obtained from the same single crystal (Abrahams, Alexander, Furnas, Hamilton, Laddell, Okaya, Young & Zalkin, 1967). However, no attempt was made to analyse their results further than a direct comparison between the different measurements. The eighth set of measurements (Zachariassen, 1968*a*) was obtained from a second crystal from those prepared for use in the ACA project, having a radius within one per cent of that of the primary crystal, and was analysed using the recent Zachariassen extinction theory (Zachariassen, 1967; 1968*b*).

A partial analysis of the results of the ACA project was given by Abrahams *et al.* (1967) and a further assessment has been made by Mackenzie & Maslen (1968). However, *both these analyses were based on an incorrect assumption*, namely that 'since the same crystal was used each experimenter made a measure, for

each reflexion, of essentially the same physical quantity (Mackenzie & Maslen, 1968)', and fell far short of the announced purpose of the project which was 'to obtain a quantitative comparison of the absolute accuracy, and the magnitude of the various systematic errors, in the most widely used diffractometer methods for measuring intensities and resulting structure factors (Abrahams *et al.*, 1967)'.

In the present paper the results of a further analysis of these measurements are presented. In this analysis the observed data were compared with the theoretical predictions of a model, the parameters of which were adjusted by a least-squares fitting procedure, and only those parameters which are necessarily the same for all experiments were constrained to be so. A similar analysis of Zachariassen's results was also carried out. These analyses enable a more significant appraisal of the measurements to be made and yield additional information about the crystals studied.

Analysis of the data

(a) A.C.A. project

In both previous analyses of the A.C.A. project it was assumed that all experimenters measured essentially the same quantity for a particular reflexion. However, this assumption ignores completely the fact that one systematic error, that due to thermal diffuse scattering (TDS), is certain to vary from one experiment to another. It has been shown that neglect of TDS effects results in incorrect values of the derived temperature factors (Cooper & Rouse, 1968; Cooper, 1970; Cochran, 1969); indeed almost all published thermal parameters are in error for this reason (Zachariassen,

1969). Since the various experimenters used different techniques and different experimental conditions for their peak and background measurements we can therefore expect the apparent temperature factors for the various sets of measurements to vary within a range consistent with the magnitude of the TDS. This fact should therefore be taken into account in a comparison of the various sets of data. Although Abrahams *et al.* (1967) refer to this type of error in their conclusions, they imply that the effects are small. However, the change in temperature factor (B) which they quote, namely 0.3 \AA^2 , is two-thirds of the value of B_{Ca} and would result in differences in intensity of up to 40%.

The present analysis of the A.C.A. project therefore assumed only that the extinction is identical for each set of data. The scattering factors used were those given in *International Tables for X-ray Crystallography* (1962) for Ca^{2+} and F^- ions, with $\Delta f'_{\text{Ca}}=0.2$ and $\Delta f''_{\text{Ca}}=0.33$ (this term was neglected except for the weakest reflexions). Observed $|F|^2$ values were taken from Table 1 of Mackenzie & Maslen (1968) and a weighting scheme with $\sigma(|F|^2)=0.02 |F|^2$ was used. A least-squares computer program, comparing observed and calculated intensities† and employing a search algorithm procedure (Powell, 1965), was used to refine the remaining parameters. This program, written ini-

tially for a limited number of cubic space groups, can refine anharmonic thermal vibration parameters, up to fourth order, for each atom (see Dawson, Hurley & Maslen, 1967) and the extinction parameter r^* in the Zachariasen theory (Zachariasen, 1967, 1968b), for a spherical or cylindrical crystal.

Initially all data were used except for the anomalous 111 and 022 reflexions of experiment 1 and an harmonic model was assumed (all anharmonic thermal parameters constrained to be zero). The immediate conclusions from a study of the results of this refinement are, in agreement with those of Mackenzie & Maslen, that experiment 6 is poor and that the agreement of the low angle reflexions for the remaining experiments is also poor. It was decided, therefore, to adopt the use of a concordant subset of data, as defined by Mackenzie & Maslen, in the further analysis. This subset consists of all data for reflexions for which $27 \leq S(=h^2 + k^2 + l^2) \leq 108$. No further analysis of experiment 6 was carried out.

The preliminary harmonic refinement was therefore repeated for the remaining experiments, using only the concordant subset of data. The parameters obtained are given in Table 1.

A is an agreement factor defined as

$$A = \sqrt{\sum \{w(I_o - I_c)\}^2 / (n - m)}, \quad (1)$$

where I_o and I_c are the observed and calculated intensities respectively, w is the weight given to a particular observed intensity, n is the number of observations and

† Since the experimental data were published only as $|F|^2$ or $|F|$, all references to intensities in this paper are to quantities $|F|^2 \text{ cosec } 2\theta$.

Table 1. Parameters obtained from harmonic refinement of ACA concordant subset

	Experiment						
	1	2	3	4	5	7	
B_{Ca}	0.458	0.515	0.530	0.455	0.479	0.445 \AA^2	
$\sigma(B_{\text{Ca}})$	0.011	0.014	0.018	0.008	0.008	0.008	
B_{F}	0.710	0.739	0.812	0.706	0.710	0.705	
$\sigma(B_{\text{F}})$	0.011	0.014	0.019	0.008	0.008	0.009	
r^*	1.39	1.81	1.36	1.30	1.35	1.23	
$\sigma(r^*)$	0.09	0.16	0.15	0.06	0.06	0.06	
s	8.69	9.35	8.65	8.19	8.47	8.02	
$\sigma(s)$	0.20	0.30	0.32	0.14	0.14	0.14	
A	1.11	1.16	1.50	0.83	1.00	0.81	
R_1	2.12	1.92	2.83	1.48	1.91	1.27%	
R_1^w	0.95	1.75	1.79	0.88	1.35	1.53%	

Table 2. Parameters obtained from harmonic refinement of ACA concordant subset with $r^* = 1.33 \times 10^{-4} \text{ cm}$

	Experiment						
	1	2	3	4	5	7	
B_{Ca}	0.453	0.477	0.528	0.458	0.477	0.453 \AA^2	
$\sigma(B_{\text{Ca}})$	0.009	0.009	0.013	0.007	0.008	0.005	
B_{F}	0.708	0.730	0.814	0.706	0.709	0.707	
$\sigma(B_{\text{F}})$	0.014	0.014	0.021	0.010	0.012	0.007	
s	8.56	8.40	8.60	8.25	8.43	8.22	
$\sigma(s)$	0.08	0.08	0.11	0.05	0.07	0.04	
A	1.10	1.34	1.47	0.82	0.99	0.81	
R_1	2.12	2.15	2.83	1.50	1.89	1.40%	
R_1^w	1.07	2.28	1.83	0.87	1.37	1.55%	

Table 3. Parameters obtained from anharmonic refinement of ACA concordant subset with $r^* = 1.33 \times 10^{-4}$ cm

	Experiment					
	1	2	3	4	5	7
B_{Ca}	0.452	0.477	0.527	0.459	0.479	0.453 Å ²
$\sigma(B_{Ca})$	0.008	0.007	0.012	0.006	0.008	0.005
B_F	0.707	0.728	0.812	0.707	0.711	0.706
$\sigma(B_F)$	0.012	0.009	0.018	0.009	0.013	0.007
$-\beta_F$	3.53	6.21	5.28	2.49	3.80	3.93
$\sigma(\beta_F)$	3.25	1.64	3.18	2.15	0.61	1.72
						} $\times 10^{-12}$ erg.Å ⁻³
s	8.56	8.41	8.59	8.25	8.44	8.22
$\sigma(s)$	0.07	0.05	0.10	0.05	0.07	0.04
A	1.10	1.28	1.44	0.82	0.97	0.80
R_1	2.07	2.02	2.74	1.48	1.88	1.37%
R^w_1	1.00	2.03	1.78	0.83	1.28	1.47%

Table 4. $|F_o|^2$ and $|F_c|^2$ values

(a) ACA experiments 1,2 and 3

hkl	S	Experiment					
		1		2		3	
		$ F_o ^2$	$ F_c ^2$	$ F_o ^2$	$ F_c ^2$	$ F_o ^2$	$ F_c ^2$
111	3	314.1		494.8	540.2	576.2	539.4
002	4	4.5	2.1	5.2	2.0	5.5	2.4
022	8	663.4		1058.9	1054.5	1082.3	1049.7
113	11	462.3	509.7	473.2	508.5	495.9	505.8
222	12	41.3	35.1	44.2	34.9	45.1	35.0
004	16	850.7	884.1	867.7	881.3	909.7	873.1
133	19	423.9	437.2	403.8	434.8	456.5	430.4
224	24	719.0	752.1	710.2	748.2	727.2	737.5
333	27	362.1	383.1	362.8	381.0	379.7	375.6
115	27	376.0	382.0	363.3	379.1	362.3	373.4
044	32	679.3	655.7	645.1	650.9	695.7	638.1
135	35	330.8	340.8	326.8	337.7	325.9	331.0
006	36	77.7	77.1	76.8	75.8	78.9	75.8
244	36	78.6	77.1	78.1	75.8	79.2	75.8
335	43	302.1	305.7	299.9	300.8	277.4	292.6
266	44	81.2	79.7	80.2	78.2	76.0	77.7
444	48	522.8	524.5	506.5	518.2	481.6	501.7
155	51	279.5	277.4	282.3	272.4	268.6	263.5
117	51	284.3	278.0	283.4	273.9	259.1	265.0
355	59	254.7	253.4	250.0	250.0	239.2	240.8
137	59	244.5	251.6	251.7	246.5	234.1	236.9
008	64	450.4	429.0	432.6	421.5	408.4	402.5
337	67	228.9	229.8	229.9	225.7	215.2	216.0
446	68	73.0	72.7	70.8	70.5	68.5	69.1
066	72	398.9	389.1	379.2	381.3	369.4	361.5
228	72	396.8	389.1	382.9	381.3	359.6	361.5
555	75	202.4	205.1	197.8	198.3	189.2	187.6
226	76	67.8	67.8	68.3	65.5	63.4	64.1
119	83	187.9	186.8	179.9	181.5	171.4	171.0
466	88	315.1	318.9	310.8	310.7	292.1	289.9
448	96	285.8	288.2	273.2	280.0	255.8	259.2
177	99	150.6	150.7	147.1	145.0	137.3	134.7
339	99	150.5	150.3	141.1	144.4	136.5	134.0
557	99	152.5	153.2	150.4	149.6	141.0	139.8
0,0,10	100	52.0	51.8	49.9	49.6	47.1	47.6
377	107	-	-	134.3	133.2	-	-
666	108	45.9	46.6	42.8	44.5	43.3	42.5
2,2,10	108	46.4	46.6	43.4	44.5	41.7	42.5
1,1,11	123			99.8	103.8		
577	123			100.2	100.0		
088	128			181.3	180.7		
559	131			86.8	89.4		
288	132			30.8	31.9		
4,4,10	132			29.5	31.9		
668	136			151.7	161.1		

m is the number of refined parameters. R_1 is a discrepancy factor, defined as

$$R_1 = \Sigma |I_o - I_c| / \Sigma I_o, \quad (2)$$

R_1^w is a weighted discrepancy factor, defined as

$$R_1^w = \Sigma (w^2 |I_o - I_c|) / \Sigma (w^2 I_o), \quad (3)$$

and s is a scale factor.

Since all experiments were on the same crystal the values of the extinction parameter r^* should be identical. With the exception of experiment 2 the values obtained are in very good agreement and a fixed value of $r^* = 1.33 \times 10^{-4}$ cm was chosen for a further har-

monic refinement, the results of which are given in Table 2.

A final anharmonic refinement was then carried out with r^* fixed at 1.33×10^{-4} cm and with the anharmonic thermal vibration parameter β_F allowed to refine from a starting value of -3.0×10^{-12} erg \AA^{-3} (see Cooper, Rouse & Willis, 1968). The results of this refinement are given in Table 3 and may be compared directly with the results of the corresponding harmonic refinement in Table 2. It can be seen that the inclusion of this anharmonicity parameter β_F , corresponding to a tetrahedral distortion of the probability density (thermal vibration) function of the fluorine atoms consistent with the site symmetry, has a negligible effect on the

Table 4 (cont.)

(b) ACA experiments 4, 5 and 7

Experiment 4		Experiment 5		Experiment 7		Extinction factor y (exp. 2)	hkl
$ F_o ^2$	$ F_c ^2$	$ F_o ^2$	$ F_c ^2$	$ F_o ^2$	$ F_c ^2$		
494.8	540.5	508.8	540.2	—	—	0.205	111
4.7	2.0	4.7	1.9	—	—	0.998	002
1047.0	1055.9	1050.5	1055.0	927.5	1056.1	0.170	022
459.9	509.3	472.3	508.3	494.9	509.7	0.365	113
40.5	34.3	39.4	33.7	41.7	35.1	0.927	222
855.3	883.6	855.2	882.0	—	—	0.267	004
404.1	436.7	421.0	434.9	430.5	437.1	0.482	133
727.5	751.4	730.3	749.1	742.9	752.1	0.353	224
364.7	382.0	365.3	380.1	380.1	383.1	0.566	333
377.0	381.3	367.6	379.0	386.0	381.9	0.568	115
673.2	654.8	675.8	651.9	680.6	655.7	0.428	044
336.3	339.6	333.3	337.0	—	—	0.632	135
77.4	76.4	75.1	74.6	75.4	77.0	0.900	006
77.7	76.4	75.0	74.6	78.0	77.0	0.900	244
301.5	305.0	295.4	301.4	300.2	305.5	0.684	335
78.9	78.8	78.2	76.7	80.8	79.5	0.905	226
526.3	523.3	531.1	519.4	515.8	524.6	0.548	444
278.1	276.2	284.3	272.5	276.0	277.2	0.724	155
277.2	276.7	274.9	273.3	276.4	278.0	0.723	117
251.7	251.6	246.3	248.3	249.8	253.5	0.754	355
251.5	250.4	247.9	246.3	—	—	0.757	137
440.0	427.6	429.5	422.7	431.7	428.9	0.636	008
225.3	228.1	221.4	224.4	226.5	229.8	0.783	337
70.6	71.7	69.8	69.1	71.5	72.6	0.926	446
399.0	387.5	385.0	382.5	394.6	389.1	0.672	066
391.4	387.5	385.9	382.5	394.0	389.1	0.672	228
199.6	204.2	196.0	199.3	202.4	204.8	0.812	555
67.0	66.8	63.7	64.1	—	—	0.933	266
186.6	185.3	180.8	181.0	188.8	186.6	0.830	119
315.5	317.2	307.9	311.8	319.8	319.0	0.733	466
288.0	286.5	277.2	281.1	288.1	288.2	0.759	448
149.4	149.4	145.1	144.9	150.9	150.5	0.866	177
147.7	149.2	145.7	144.6	149.4	150.1	0.867	339
151.2	151.1	147.9	147.5	153.0	153.4	0.863	557
51.2	50.7	46.8	48.2	53.0	51.6	0.952	0,0,10
133.6	135.3	132.9	131.6	—	—	0.878	377
45.4	45.6	43.0	43.1	45.4	46.5	0.957	666
45.7	45.6	44.0	43.1	47.4	46.5	0.957	2,2,10
109.0	107.1	—	—	—	—	0.904	1,1,11
106.0	105.7	—	—	—	—	0.907	577
196.5	186.9	—	—	—	—	0.837	088
95.1	94.5	—	—	—	—	0.915	559
33.3	33.0	—	—	—	—	0.969	288
31.3	33.0	—	—	—	—	0.969	4,4,10
177.8	167.1	—	—	—	—	0.849	668

other refined parameters. In each case β_F refines to a value in the range -2.4 to -6.2×10^{-12} erg \AA^{-3} , but for most experiments the data are such that the value obtained cannot be regarded as very significant.† Neutron diffraction data for calcium fluoride lead to values of β_F in the range -5.7 to -7.2×10^{-12} erg \AA^{-3} (Dawson, Hurley & Maslen, 1967; Cooper & Rouse, 1970a) and the X-ray data are certainly consistent with values of β_F in this range.

The values of $|F_0|^2$ and $|F_c|^2$, scaled to the values of $|F_0|^2$ given for experiment 1, are listed in Table 4.

(b) Zachariasen data

The data of set I of Zachariasen's (1968a) Table 1, which may be compared directly with the data from the A.C.A. project, were analysed in a similar way, using (a) data for reflexions in the Mackenzie & Maslen 'concordant subset' only, and (b) all data. The results of this analysis for both harmonic and anharmonic refinements are given in Table 5. As in the case of the A.C.A. project, agreement is much better for the concordant subset than for data outside this. The concordant subset gives a value of $\beta_F = -5.32 (\pm 1.16) \times 10^{-12}$ erg \AA^{-3} , which is again in agreement with the values obtained from neutron diffraction data.

Discussion

Examination of Tables 3 and 5 confirms that the different experiments do, in general, provide different values for the thermal parameters B_{Ca} and B_F . Apart from experiments 3 and 6, the accuracy of which was questioned by the previous analyses, the A.C.A. data give B values within a range, for each atom, of less than 0.03\AA^2 . Calculation of TDS corrections for typical

experimental conditions using an isotropic approximation (Cooper & Rouse, 1968) indicate that, for calcium fluoride, neglect of these is likely to lead to an underestimation of the isotropic temperature factors with a probable range of ΔB of 0.05 to 0.08\AA^2 . The observed range of B values, which gives rise to differences in intensity between experiments of several per cent, is therefore consistent with these calculations. Correction for TDS is likely to increase the observed temperature factors to about $B_{Ca} \approx 0.53 \text{\AA}^2$ and $B_F \approx 0.78 \text{\AA}^2$. Experiments 3 and 6 and the Zachariasen data all give significantly larger B values. However, the second and third of these experiments both used a stationary-crystal, stationary-detector technique, which is believed to be less reliable than the other techniques used and experiment 3 also used a technique of doubtful reliability (Mackenzie & Maslen, 1968).

Agreement between observed and calculated intensities is excellent for the concordant subset in all cases (excluding experiment 6). There is some indication that the differences become dependent on the intensity at low angle. We should note, however, that because of the nature of the structure there is a direct correlation between intensity and scattering angle within three groups of reflexions ($h+k+l=4n$, $4n \pm 1$ and $4n+2$) and it is probable that these systematic differences arise from an inadequacy of the extinction theory when the extinction becomes severe (see Cooper & Rouse, 1970b).

Agreement for the lowest angle reflexions, with $s < 27$ (outside the concordant subset), is poor. However, it should be noted that this group of eight reflexions contains the five strongest and also the two with the smallest $|F|^2$ values. As pointed out in the previous analyses the disagreement between experiments for the strongest reflexions is probably due to errors associated with the determination of attenuator factors. It is well known that the use of attenuators can result in a marked change in the spectrum of the radiation and extreme care must therefore be taken (see e.g. Batterman, Chipman & DeMarco, 1961); in the A.C.A. project

† It should be noted that the significance of β_F values would be increased by omitting the even index reflexions, which are independent of β_F , from the refinement (see Cooper & Panke, 1970).

Table 5. Parameters obtained from refinement of Zachariasen's data

	Harmonic refinement		Anharmonic refinement	
	Subset	All data	Subset	All data
B_{Ca}	0.550	0.609	0.552	0.614 \AA^2
$\sigma(B_{Ca})$	0.019	0.046	0.008	0.045
B_F	0.788	0.810	0.790	0.808
$\sigma(B_F)$	0.017	0.039	0.007	0.038
$-\beta_F$	—	—	5.32	5.35
$\sigma(\beta_F)$	—	—	1.08	7.51
			} $\times 10^{-12}$ erg \AA^{-3}	
r^*	0.97	1.59	0.98	1.64
$\sigma(r^*)$	0.12	0.34	0.04	0.33
			} $\times 10^{-4}$ cm	
s	8.14	9.44	8.16	9.55
$\sigma(s)$	0.30	0.83	0.12	0.82
A	0.98	2.71	0.86	2.70
R_1	1.48	4.56	1.37	4.43%
R_w	1.52	3.71	1.22	3.55%

only two experiments (5 and 7) used attenuators of the same material. In the case of the weak 002 and 222 reflexions the structure factor is the difference between the partial structure factor for four calcium atoms and that for eight fluorine atoms and at very low scattering angles these are almost equal. The calculated intensity is therefore extremely sensitive to the model used. These weak reflexions will also be particularly susceptible to errors due to multiple reflexion effects (see Coppens, 1968).

Since the theoretical model is slightly different for each experiment it is desirable to test the consistency of the deviations from the calculated intensities so that an estimation of the agreement between experiments can be obtained which is independent of any systematic deviations from the model. To do this an inter-experiment discrepancy factor R_{ij} has been calculated, *viz.*

$$R_{ij} = \frac{\sum |(F_{oi}^2 - F_{ci}^2) - (F_{oj}^2 - F_{cj}^2)|}{\sum (F_o^2)}, \quad (4)$$

where i and j are the numbers of the two experiments, F_o^2 is the mean value of F_o^2 for a particular reflexion averaged over all experiments, and the summations are carried out over all reflexions in the concordant subset. The values obtained for R_{ij} are given in Table 6. It can be seen that there are very few R_{ij} values, other than those involving experiment 3, which exceed the mean R_1 factor (see Table 3) for the two experiments concerned. It may therefore be concluded that agreement between experiments is, in general, better than agreement with the model used. This is reasonable in view of the limitations of the model. It would also appear that the agreement between experiments, allowing for variation in the thermal diffuse scattering contribution, is much better than was indicated by the previous analyses.

Table 6. R_{ij} factors for ACA concordant subset (%)

Experiment	Experiment					
	1	2	3	4	5	7
1	—	2.02	2.58	0.99	1.44	1.47
2	2.02	—	2.93	1.99	1.96	2.45
3	2.58	2.93	—	2.46	2.27	2.21
4	0.99	1.99	2.46	—	1.08	1.35
5	1.44	1.96	2.27	1.08	—	1.57
7	1.47	2.45	2.21	1.35	1.57	—

Agreement for the 'concordant subset' of Zachariassen's data is excellent. The value of the extinction parameter is somewhat smaller than that obtained by Zachariassen but the thermal parameters B_{Ca} and B_F are in excellent agreement. The values of these are, however, significantly larger than those obtained for the majority of the A.C.A. experiments and this experiment must therefore be coupled with the A.C.A. experiment 6, which used a similar stationary crystal, stationary detector technique. It seems, therefore, that this technique is particularly susceptible to large errors, although it may be possible for these to be absorbed, to a large extent, in the thermal parameters.

Conclusions

Of the seven A.C.A. experiments two (experiments 3 and 6) are obviously of inferior quality, as was concluded by Mackenzie & Maslen (1968). It seems reasonable to suppose that this is a result of the techniques which were used in these experiments, namely the ω -scan with balanced filters (experiment 3) and the stationary-crystal, stationary-detector technique (experiment 6). The Zachariassen experiment, which used the latter technique, although giving better agreement with a theoretical model, still gives apparently incorrect values for the thermal parameters.

If we neglect the eight lowest angle reflexions, which include the five strongest and the two with smallest $|F|^2$ values, the remaining experiments are in excellent agreement, apart from small variations in the thermal parameters. The magnitude of these variations, however, is consistent with that expected as a result of variations in the amount of thermal diffuse scattering which is included in the measurements. However, this cannot be checked rigorously unless full details of the experimental conditions are known.* For these five experiments the R_1 factors (equation 2) lie in the range 1.37 to 2.07% and the R_{ij} factors (equation 4) lie in the range 0.99 to 2.45%, indicating that correlation of the observed systematic angular variation with TDS effects gives a much better agreement between these experiments than was indicated by the previous analyses. Disagreement between experiments for the strongest low angle reflexions is probably due to errors associated with the use of attenuators.

The present analysis confirms the severity of the extinction in these crystals (see Table 4) and in view of the approximations involved in the extinction theory it is remarkable that such good agreement between observed and calculated intensities can be achieved over so large a range of intensity. It should be noted, however, that extinction can give rise to errors in the scale factor and in the thermal parameters (in this case in B_{Ca} only).

Consistent values of the anharmonicity parameter β_F are obtained for all experiments. However, the effects of this anharmonicity on the X-ray intensities are rather small and in most cases the accuracy of the data is insufficient to give a large significance to this parameter. The values obtained are, however, in close agreement with those determined from neutron diffraction data for this type of compound.

In conclusion, it is suggested that a proper consideration of predictable systematic effects, particularly those due to thermal diffuse scattering, would enable a project such as the A.C.A. single-crystal intensity project to achieve its announced purpose.

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Extinction in X-ray and Neutron Diffraction

BY M. J. COOPER AND K. D. ROUSE

Materials Physics Division, A.E.R.E., Harwell, Berkshire, England

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Accurate neutron-diffraction measurements from crystals suffering from severe extinction have been used to test the recent general theory of extinction of Zachariasen (*Acta Cryst.* (1967). **23**, 558). Analysis of these measurements indicates that certain of the approximations made in the theory are not generally valid and result in systematic deviations between theory and experiment, namely a marked angle-dependent effect and an inadequacy of the theory for strong extinction. The original theory is therefore extended to take these factors into account and to give agreement with the observed data.

Introduction

Theoretical formulae for the Bragg intensities of diffracted X-rays or neutrons have been derived rigorously only in the limiting cases of an ideally perfect crystal (the dynamical theory) and an ideally imperfect crystal (the kinematical theory). In general a given crystal will lie somewhere between these two extreme cases and modification of the kinematical theory is necessary to take into account the degree of perfection of the crystal. The treatment is normally based on the mosaic model for which the crystal is assumed to consist of a number of small perfect crystal domains, each slightly mis-oriented with respect to its neighbours.

Zachariasen (1967) has recently described a general theory of X-ray diffraction in crystals, based on an approximate treatment of the coupling between incident and diffracted beams. In this theory he derives a general formula for the intensity diffracted by a finite perfect crystal and hence the intensity diffracted by a finite mosaic crystal. Because of the complexity of the problem a number of approximations are introduced and the ultimate test of this theory is therefore, as Zachariasen states, a test of its agreement with experi-

ment. Zachariasen himself has carried out a number of experimental tests using X-ray diffraction data (see Zachariasen, 1968*a*, *b*, *c*, 1969) and has obtained excellent agreement for the crystals studied: lithium fluoride, quartz, phenakite, hambergite and calcium fluoride. In addition, other experimental X-ray diffraction tests have provided good agreement with the theory (see *e.g.* Chandrasekhar, Ramaseshan & Singh, 1969).

The Zachariasen formulae have also been applied to accurate neutron diffraction measurements on several crystals. These include barium fluoride (Cooper, Rouse & Willis, 1968) and strontium fluoride and calcium fluoride (Cooper & Rouse, 1970). For barium fluoride only limited strongly extinguished data were collected but the theory held up to a level of extinction of about 16 per cent in intensity (at $\lambda = 1.038 \text{ \AA}$). For calcium fluoride complete two-dimensional *hkk* data were collected initially at a wavelength of 0.877 \AA and a preliminary analysis gave a value of r^* [see equations (16)] comparable to that obtained by Zachariasen (1968*b*). However, once again the theory did not correct the strongest intensities adequately and so a more extensive study was undertaken. Complete two-dimensional neu-