

A Neutron Diffraction Study of SrF₂ and CaF₂

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Accurate integrated intensities for the Bragg reflexion of neutrons by crystals of SrF₂ and CaF₂, both of which have the cubic fluorite structure, have been measured at room temperature. Measurements were made at three different wavelengths in each case, in order to investigate the effects of extinction, which were found to be quite large, and corrections were made for both extinction and thermal diffuse scattering. The experimental data show significant contributions from a third order anharmonic term in the one particle potential of the fluorine atoms in both cases. This term is consistent with the tetrahedral symmetry of the fluorine atom site and its magnitude was found to be similar to that observed previously for the isostructural BaF₂. Thermal parameters for the three fluorides show that the relative mean-square vibration amplitude of the cations is essentially the same in all three but that for the fluorine ion it increases linearly with the atomic number of the cation neighbour. The ratio of the scattering amplitudes b_{Sr}/b_F was refined to 1.229 (± 0.007), which gives a value for the nuclear scattering amplitude of strontium of $b_{Sr} = 0.688 (\pm 0.013) \times 10^{-12}$ cm, assuming $b_F = 0.560 (\pm 0.010) \times 10^{-12}$ cm.

Introduction

In an earlier paper (Cooper, Rouse & Willis, 1968) we described a series of accurate integrated intensity measurements for the Bragg reflexion of neutrons from BaF₂ at a number of temperatures in the range 20 to 600 °C. The experimental data could only be analysed satisfactorily by considering an anharmonic component in the thermal vibration of the fluorine ions, as allowed by their non-centrosymmetric site symmetry. Similar measurements have since been made at room temperature for crystals of CaF₂ and SrF₂, which also have the fluorite structure, in order to study the thermal vibrations in these and to allow a comparison to be made of the thermal parameters with those obtained previously for BaF₂.

Considerable care was exercised in these measurements in order to achieve data which were considered to be reliable to the required level of accuracy. The appropriate experimental techniques and the sources of systematic error which need to be considered in this type of work have been discussed elsewhere (Cooper & Rouse, 1970*a*). In particular it was found that extinction was quite severe in the crystals studied and a detailed analysis of the data showed that existing theories of extinction were inadequate. Extensive measurements were therefore made at three different wavelengths in each case and the Zachariasen (1967) theory of extinction was extended by the authors. The consideration of extinction effects in the crystals has been discussed in an earlier paper (Cooper & Rouse, 1970*b*) and in the present paper we shall be concerned mainly with the analysis of the data in terms of the thermal vibrations of the atoms.

Theory

Anharmonic thermal vibration in fluorite structures has been considered by Dawson, Hurley & Maslen

(1967) and the relevant theory was summarized in the paper describing the BaF₂ study (Cooper, Rouse & Willis, 1968).

The vibration of each atom j in this structure is assumed to be governed by an effective one-particle potential $V_j(\mathbf{r})$ of the form:

$$V_j(\mathbf{r}) = V_{0j} + \frac{1}{2}\alpha_j(x^2 + y^2 + z^2) + \beta_j(xyz) \quad (1)$$

with $\beta = 0$ except for the fluorine atoms.

x , y and z are the coordinates defining the instantaneous displacement \mathbf{r} of the j th atom, the term in $x^2 + y^2 + z^2$ is the normal harmonic potential with α_j being related to the mean-square displacement of the atom and the third order term has been chosen to conform with the tetrahedral ($\bar{4}3m$) site symmetry of the fluorine atoms. No third order term is possible for the centrosymmetric ($m\bar{3}m$) cation site. The present measurements gave no significant indication of the presence of anisotropic higher order terms in the potential and we shall therefore not consider these here.

For the fluorite structure the reflexions can be divided into three groups depending on the sum of the indices h , k and l . The calculated structure factors for these groups, assuming a potential of the form given in equation (1), are similar to those given previously for BaF₂ [equations (5) of Cooper, Rouse & Willis, 1968], with Ba replaced by Sr or Ca.

The most significant effect on the Bragg reflexions of introducing the anharmonicity parameter β_F is to introduce an additional term in the structure factor for reflexions with $h+k+l = 4n \pm 1$. This additional term is proportional to $b_F\beta_F$ and to the index product $h \times k \times l$. It is positive for $4n+1$ reflexions and negative for $4n-1$ reflexions.

Experimental measurements

The samples used were a spherical single crystal of SrF₂ of radius 1.5 mm, a cylindrical single crystal of

SrF₂ of radius 1.5 mm and length 8 mm, and a cylindrical single crystal of CaF₂ of radius 1.5 mm and length 9 mm. In both cases the axis of the cylinder was parallel to a crystallographic $\langle 110 \rangle$ axis. Two dimensional hkk intensity measurements were made with a Hilger and Watts Mk II automatic neutron diffractometer and in all cases intensities were averaged over a complete two-dimensional set of equivalent reflexions (hkk , $h\bar{k}k$, $h\bar{k}\bar{k}$ and $hk\bar{k}$).

Reflexions were scanned in a θ - 2θ mode using a rectangular detector aperture which was adjusted to reduce the amount of background scattering detected without any loss of Bragg intensity. A number of measurements were repeated with two different aperture widths in order to investigate the dependence of the observed intensity on this. A minimum scan range of $\pm 1.0^\circ$ was used throughout, but for the higher-angle reflexions the scan range was increased in order to avoid any possible loss of Bragg intensity.

Measurements were made initially using the sphere of SrF₂ and the cylinder of CaF₂ and the background was measured by making a similar scan with the crystal

Table 1. Neutron diffraction data for SrF₂ sphere at $\lambda = 0.746 \text{ \AA}$

h	k	l	I _o	I _c	$\sigma(I_o)$	γ	α
0	2	2	59172	59488	252	0.259	0.002
4	0	0	(53454)	50466	240	0.331	0.005
4	2	2	44805	44992	221	0.384	0.009
0	4	4	(43153)	40966	217	0.429	0.013
4	4	4	(36188)	35034	200	0.508	0.023
8	0	0	(31199)	30336	188	0.571	0.034
8	2	2	27704	28313	179	0.599	0.040
0	6	6	(34436)	28313	198	0.599	0.040
4	6	6	24277	24763	169	0.647	0.051
8	4	4	-	-	-	-	-
0	8	8	(19422)	18330	160	0.741	0.084
8	6	6	17065	17286	153	0.752	0.091
12	0	0	(22137)	16369	172	0.761	0.099
4	8	8	16513	16369	155	0.761	0.099
12	2	2	15309	15566	153	0.772	0.106
12	4	4	14344	13845	156	0.801	0.127
8	8	8	(14905)	13189	113	0.813	0.139
0	10	10	(15822)	13116	166	0.816	0.147
12	6	6	(18312)	13689	178	0.814	0.159
4	10	10	-	-	-	-	-
1	1	1	31776	30404	138	0.535	0.000
3	1	1	19970	19367	110	0.683	0.003
1	3	3	15438	15258	97	0.744	0.006
5	1	1	13188	12886	91	0.782	0.010
3	3	3	(18039)	13041	145	0.779	0.010
5	3	3	9284	9817	112	0.834	0.020
7	1	1	9160	9015	78	0.849	0.025
1	5	5	8834	8904	77	0.851	0.025
3	5	5	8373	8400	76	0.860	0.030
7	3	3	7518	7650	104	0.873	0.036
5	5	5	(7905)	6651	106	0.891	0.042
9	1	1	6461	6341	99	0.896	0.048
9	3	3	(6684)	5357	101	0.913	0.060
1	7	7	5206	5422	94	0.912	0.060
7	5	5	5862	5886	97	0.905	0.060
3	7	7	5367	5459	95	0.912	0.066
2	0	0	14671	14127	100	0.765	0.001
2	2	2	(10230)	8021	118	0.861	0.003
6	0	0	(13674)	3339	93	0.941	0.016
2	4	4	3119	3339	33	0.941	0.016
6	2	2	3285	2654	37	0.953	0.020
6	4	4	1195	1403	69	0.976	0.037
2	6	6	(1537)	1143	71	0.980	0.042
10	0	0	(2158)	618	77	0.990	0.060
10	2	2	776	502	40	0.992	0.066
6	6	6	(4684)	502	54	0.992	0.066

Table 2. Neutron diffraction data for SrF₂ cylinder at $\lambda = 0.746 \text{ \AA}$

h	k	l	I _o	I _c	$\sigma(I_o)$	γ	α
0	2	2	58004	59513	290	0.270	0.003
4	0	0	53395	51301	267	0.350	0.006
4	2	2	47497	46306	237	0.412	0.011
0	4	4	41910	42461	210	0.464	0.015
4	4	4	36080	36351	180	0.550	0.025
8	0	0	30394	31454	152	0.619	0.036
8	2	2	28784	29321	144	0.649	0.041
0	6	6	29420	29321	147	0.649	0.041
4	6	6	24709	25512	124	0.700	0.052
8	4	4	23317	23828	117	0.722	0.057
0	8	8	18037	18579	90	0.790	0.084
8	6	6	17134	17526	86	0.804	0.089
12	0	0	17362	16715	87	0.817	0.101
4	8	8	16402	16715	82	0.817	0.101
12	2	2	15871	15848	79	0.827	0.105
12	4	4	14062	13929	71	0.850	0.125
8	8	8	12928	13139	126	0.861	0.129
0	10	10	13022	13058	73	0.863	0.138
12	6	6	13756	13479	83	0.858	0.141
4	10	10	13172	13479	71	0.858	0.141
1	1	1	33017	31627	165	0.581	0.001
3	1	1	20382	20139	102	0.741	0.004
1	3	3	15785	15734	79	0.800	0.008
5	1	1	13254	13190	66	0.834	0.012
3	3	3	14002	13355	73	0.832	0.012
5	3	3	9807	9906	55	0.877	0.022
7	1	1	9254	9051	52	0.889	0.027
1	5	5	8985	8936	52	0.891	0.027
3	5	5	8511	8404	51	0.898	0.032
7	3	3	7636	7622	49	0.908	0.038
5	5	5	6560	6490	50	0.923	0.043
9	1	1	6242	6268	45	0.926	0.048
9	3	3	5581	5256	48	0.938	0.059
1	7	7	5374	5322	42	0.937	0.059
7	5	5	5747	5788	43	0.932	0.059
3	7	7	5192	5349	43	0.937	0.064

mis-set by 2° . However, certain anomalies were observed in the background scattering from the SrF₂ sphere at the shortest wavelength and further measurements were therefore made using the SrF₂ cylinder at this wavelength. Anomalies in the background were again observed. These took the form of an additional background scattering along a radial (θ - 2θ) direction through certain reciprocal lattice points. The extra intensity was essentially independent of angle and in order to eliminate the effect on the apparent Bragg intensities a conventional type of background measurement was made at the extremities of the scan through the Bragg reflexion. Similar, but smaller, anomalies were observed at the longer wavelengths but the effect of these could, in most cases, be ignored. However, the magnitude of the effect at short wavelengths emphasizes the care which needs to be exercised over the background measurements if the diffuse scattering in the vicinity of the Bragg peaks is significantly anisotropic.

Data analysis

(a) Method of analysis

The sets of observed data were analysed using the Harwell TAILS computer program, which was developed originally for the analysis of data involving effects due to anharmonic thermal vibrations and requiring possible corrections for extinction and thermal diffuse scattering. The program determines the values of the varied parameters which minimize the quantity S ,

given by

$$S = \sum_i [w_i(I_{oi} - I_{ci})]^2 \quad (2)$$

where I_{oi} is the observed background-corrected intensity of the i th reflexion, I_{ci} is the corresponding computed quantity and w_i is the weight given to the observation.

It should be noted that for spherical or cylindrical crystals no corrections, apart from the subtraction of the normal background, are made to the observed intensities; corrections for all systematic effects are made to the computed intensities. Minimization of S is effected by the search algorithm of Powell (1965), implemented in the subroutine *VAO2A* of the Harwell subroutine library. This algorithm does not necessitate the computation of partial derivatives.

Provision is made for including corrections for the effects of absorption, extinction and thermal diffuse scattering, the calculated intensity being given by

Table 3. Neutron diffraction data for SrF₂ sphere at $\lambda=0.865 \text{ \AA}$

h	k	l	I_o	I_c	$\sigma(I_o)$	γ	α
0	2	2	221818	221921	337	0.208	0.002
4	0	0	196238	193516	318	0.263	0.005
4	2	2	175756	176872	302	0.310	0.009
0	4	4	160841	164991	288	0.352	0.013
4	4	4	145686	146420	274	0.423	0.023
8	0	0	129974	131438	260	0.483	0.034
8	2	2	121490	125023	251	0.509	0.039
0	6	6	123547	125023	254	0.509	0.039
4	6	6	111749	113963	342	0.556	0.050
8	4	4	109408	109034	340	0.573	0.058
0	8	8	98922	95524	232	0.623	0.085
8	6	6	96026	94408	229	0.632	0.090
12	0	0	96140	94529	188	0.638	0.096
4	8	8	96813	94529	189	0.638	0.096
12	2	2	98739	97110	236	0.639	0.104
1	1	1	122859	120407	248	0.445	0.000
3	1	1	83053	80861	204	0.594	0.003
1	3	3	67226	65546	151	0.662	0.006
5	1	1	57531	56661	140	0.706	0.010
3	3	3	59130	57284	142	0.703	0.010
5	3	3	40443	44840	119	0.770	0.020
7	1	1	41429	41753	121	0.787	0.025
1	5	5	41014	41273	120	0.789	0.025
3	5	5	39192	39470	144	0.800	0.030
7	3	3	35816	36546	113	0.816	0.036
5	5	5	32901	31947	109	0.839	0.041
9	1	1	30619	31413	105	0.844	0.047
9	3	3	27608	27644	127	0.861	0.060
1	7	7	27116	27964	126	0.860	0.060
7	5	5	29198	30237	129	0.849	0.060
3	7	7	27462	28670	127	0.854	0.067
11	1	1	25872	25853	126	0.869	0.081
5	7	7	21127	23628	116	0.879	0.081
9	5	5	23755	23507	100	0.881	0.087
11	3	3	25317	26246	107	0.870	0.092
7	7	7	29559	28893	115	0.860	0.100
1	9	9	29087	29130	115	0.862	0.108
13	1	1	37344	36594	163	0.833	0.111
11	5	5	39812	39836	165	0.821	0.111
3	9	9	40137	39471	165	0.822	0.111
2	0	0	61583	60583	124	0.688	0.001
2	2	2	36436	35985	96	0.806	0.003
6	0	0	18404	15893	71	0.913	0.016
2	4	4	15028	15893	66	0.913	0.016
6	2	2	12185	12813	60	0.930	0.020
6	4	4	6392	7068	42	0.962	0.036
2	6	6	5418	5850	37	0.969	0.042
10	0	0	(4094)	3355	40	0.982	0.061
10	2	2	2623	2794	35	0.985	0.068
6	6	6	(4635)	2794	40	0.985	0.068
10	4	4	1348	1621	27	0.991	0.088
2	8	8	1310	1621	27	0.991	0.088

Table 4. Neutron diffraction data for SrF₂ sphere at $\lambda=1.077 \text{ \AA}$

h	k	l	I_o	I_c	$\sigma(I_o)$	γ	α
0	2	2	294346	285272	388	0.145	0.002
4	0	0	266011	262515	369	0.195	0.006
4	2	2	240189	252265	351	0.238	0.010
0	4	4	226715	244029	342	0.274	0.015
4	4	4	217637	232111	334	0.335	0.025
8	0	0	204726	223945	325	0.380	0.037
8	2	2	204785	219796	326	0.394	0.043
0	6	6	207672	219796	328	0.394	0.043
4	6	6	215435	227390	334	0.421	0.052
8	4	4	229563	241839	345	0.426	0.058
1	1	1	164210	159773	184	0.334	0.001
3	1	1	121007	115253	176	0.473	0.003
1	3	3	101324	98078	144	0.543	0.007
5	1	1	90211	88180	125	0.592	0.012
3	3	3	92581	89046	127	0.588	0.012
5	3	3	75129	74396	115	0.656	0.022
7	1	1	71607	71735	112	0.675	0.027
1	5	5	71687	71005	112	0.678	0.027
3	5	5	70855	70400	112	0.687	0.034
7	3	3	68396	67383	110	0.694	0.039
5	5	5	64664	62024	118	0.713	0.045
9	1	1	66193	64895	120	0.710	0.052
9	3	3	74166	70260	116	0.702	0.059
1	7	7	74796	71003	117	0.700	0.059
7	5	5	79003	76186	119	0.686	0.059
3	7	7	97042	90240	146	0.657	0.066
2	0	0	93359	88897	127	0.571	0.001
2	2	2	57688	56788	100	0.709	0.004
6	0	0	27321	28215	77	0.854	0.017
2	4	4	26297	28215	77	0.854	0.017
6	2	2	22146	23541	79	0.879	0.023
6	4	4	13851	14669	66	0.922	0.040
2	6	6	12207	12842	63	0.931	0.045
10	0	0	10065	10199	63	0.947	0.059
10	2	2	11541	11307	70	0.942	0.065
6	6	6	11634	11307	70	0.942	0.065

$$I_c = sA_\mu(\gamma + \alpha)|F_c|^2 \operatorname{cosec} 2\theta \quad (3)$$

where s is the scale factor, A_μ is the absorption factor, γ the extinction factor and α the thermal diffuse scattering factor.

The absorption factor for a spherical or cylindrical crystal is obtained by interpolation in stored tables of A_μ as a function of μR and $\sin^2 \theta$, where R is the radius of the crystal. Tables appropriate to neutron diffraction measurements have been published elsewhere (Rouse, Cooper, York & Chakera, 1970). For other shapes of crystals it is necessary to correct the observed intensities for absorption.

The extinction factor is that defined by the Zachariasen (1967) theory as modified by the authors [Cooper & Rouse, 1970*b*, equations (29), (34), (15) and (20*d*)].

The thermal diffuse scattering factor is calculated using the isotropic approximation of the authors (Cooper & Rouse, 1968) for first order scattering, but it should be noted that this approximation is not valid if the neutron velocity is appreciably less than that of the phonons concerned (see Cooper, 1971).

(b) Results

Absorption was sufficiently small in the crystals studied ($\mu R < 0.01$) for A_μ to be considered the same for all reflexions and this factor was therefore considered as part of the scaling factor. Thermal diffuse scattering corrections were calculated using the elastic

constant values given by Gerlich (1964) for SrF₂ and by Huffman & Norwood (1960) for CaF₂. No correction was applied for CaF₂ at 1.339 Å since at this wavelength the neutrons are faster than all sound velocities in the crystal.

The parameters which were considered as possible variable quantities were the scale factor, the scattering amplitude of the cation, the harmonic thermal parameters for each ion, the anharmonic thermal parameter for the fluorine ion and the effective domain radius. Of these, the following were considered to be well de-

Table 5. Neutron diffraction data for CaF₂ cylinder at $\lambda=0.877$ Å

h	k	l	I _o	I _c	$\sigma(I_o)$	y	α
0	2	2	32844	27262	192	0.086	0.002
4	0	0	26498	25480	174	0.117	0.006
4	2	2	23485	24727	164	0.144	0.011
0	4	4	23853	24245	165	0.169	0.016
4	4	4	20967	23525	155	0.215	0.027
8	0	0	19952	22798	153	0.257	0.040
8	2	2	18986	22459	151	0.277	0.046
0	6	6	19938	22459	154	0.277	0.046
4	6	6	19725	22124	156	0.314	0.061
8	4	4	19234	22024	154	0.331	0.067
0	8	8	23163	23567	172	0.376	0.092
8	6	6	26205	25433	182	0.378	0.098
1	1	1	12896	12270	96	0.251	0.000
3	1	1	8799	9504	78	0.385	0.003
1	3	3	8456	8341	78	0.463	0.007
5	1	1	6902	7597	72	0.517	0.011
3	3	3	7502	7681	74	0.512	0.011
5	3	3	5538	6459	67	0.602	0.020
			5936	6493	91	0.602	0.024
7	1	1	5800	6202	69	0.624	0.026
			5889	6241	92	0.624	0.030
1	5	5	6222	6123	70	0.628	0.026
			6224	6161	93	0.628	0.030
3	5	5	6008	6029	70	0.639	0.031
			5895	6072	90	0.639	0.036
7	3	3	5438	5708	70	0.662	0.037
			5444	5754	63	0.662	0.042
5	5	5	5370	5035	73	0.703	0.042
			5472	5077	64	0.703	0.048
9	1	1	5130	5103	74	0.704	0.048
			5190	5149	90	0.704	0.055
9	3	3	5042	4687	72	0.736	0.058
			5009	4734	52	0.736	0.066
1	7	7	5152	4754	73	0.733	0.058
			5105	4802	64	0.733	0.066
7	5	5	5460	5228	74	0.708	0.058
			5452	5282	65	0.708	0.066
3	7	7	5534	5101	80	0.717	0.066
			5546	5161	70	0.717	0.075
11	1	1	5282	4885	89	0.737	0.075
			5302	4944	61	0.737	0.085
5	7	7	4604	4356	88	0.763	0.075
			4698	4406	59	0.763	0.085
9	5	5	5531	4579	85	0.754	0.078
			5587	4632	74	0.754	0.088
11	3	3	6876	5756	131	0.702	0.087
			6798	5836	82	0.702	0.098
2	0	0	14826	14072	100	0.204	0.001
2	2	2	12162	11272	89	0.306	0.003
6	0	0	8549	8285	78	0.490	0.016
2	4	4	8540	8285	78	0.490	0.016
6	2	2	7380	7623	74	0.537	0.021
6	4	4	6072	5986	73	0.647	0.037
2	6	6	6153	5544	76	0.676	0.043
			5985	5593	95	0.676	0.049
10	0	0	5296	4532	72	0.745	0.059
10	2	2	4676	4296	78	0.759	0.067
			4829	4344	54	0.759	0.076
6	6	6	5266	4296	80	0.759	0.067
			5067	4344	55	0.759	0.076
10	4	4	4969	4011	82	0.782	0.079
			4750	4055	57	0.782	0.088
2	8	8	4438	4011	81	0.782	0.079
			4650	4055	57	0.782	0.088

Table 6. Neutron diffraction data for CaF₂ cylinder at $\lambda=1.078$ Å

h	k	l	I _o	I _c	$\sigma(I_o)$	y	α
0	2	2	26484	23102	30	0.119	0.002
4	0	0	21710	21686	28	0.161	0.006
4	2	2	19508	21151	26	0.197	0.010
0	4	4	20070	20904	27	0.229	0.015
4	4	4	18982	20663	22	0.283	0.025
8	0	0	19311	21213	32	0.328	0.036
8	2	2	20396	21766	26	0.344	0.041
0	6	6	21276	21766	47	0.344	0.041
4	6	6	26816	25543	53	0.362	0.048
1	1	1	9825	10269	23	0.345	0.001
3	1	1	6939	7717	19	0.505	0.003
1	3	3	6770	6618	19	0.583	0.008
5	1	1	5765	5963	18	0.632	0.012
3	3	3	6102	6042	18	0.628	0.012
5	3	3	5244	5059	17	0.698	0.022
7	1	1	5368	4929	17	0.709	0.027
1	5	5	5597	4858	17	0.713	0.027
3	5	5	5817	4940	18	0.716	0.033
7	3	3	5723	4851	18	0.726	0.038
5	5	5	5820	4487	18	0.747	0.043
9	1	1	6226	4993	26	0.729	0.049
2	0	0	11876	11825	25	0.280	0.001
2	2	2	9509	9381	22	0.410	0.004
6	0	0	6966	6681	19	0.601	0.017
2	4	4	7293	6681	20	0.600	0.017
6	2	2	6607	6133	15	0.638	0.022
6	4	4	6394	5139	15	0.711	0.039
2	6	6	6653	5018	19	0.721	0.043

termined already and therefore not needing to be refined: $b_{Ca}=0.488 \times 10^{-12}$ cm (Atoji, 1961) and α_{Ca} and α_F for CaF₂ as given by $B_{Ca}=0.507$ Å² and $B_F=0.697$ Å² which were derived from the values given by Elcombe & Pryor (1970). The scattering amplitude of fluorine was taken to be $b_F=0.56 \times 10^{-12}$ cm (Donaldson, 1964), but it should be noted that, since the scale factor is refined, only the ratio of the scattering amplitudes of the cation and the anion can be determined from the analysis.

Of the remaining parameters only the effective domain radius and the scale factor vary with the wavelength. However, the original version of the program does not permit joint refinement of data collected at different wavelengths and initial analysis was carried out treating the data for the various wavelengths separately. Good agreement was obtained for the values of the parameters which are independent of the wavelength and a weighted mean value was determined in each case. The analysis was then repeated with these parameters fixed at their weighted mean values, in the following order: (i) cation scattering amplitude, (ii) harmonic thermal parameters (iii) anharmonic thermal parameter. In order to determine the values of β_F most precisely analyses were made of the odd-index reflexions only, since only these are dependent on this parameter. The final analysis of all the data was carried out with only the effective domain radius and the scale factor as variable parameters.

Analyses including anisotropic fourth order thermal parameters for each ion gave consistent values of these, as appropriate to the site symmetries, but in no case were the effects large enough to be considered significant.

Table 7. Neutron diffraction data for CaF₂ cylinder at $\lambda=1.339 \text{ \AA}$

h	k	l	I _o	I _c	$\sigma(I_o)$	γ	α
0	2	2	50384	46591	25	0.138	0
4	0	0	41854	44760	23	0.189	0
4	2	2	37752	44721	26	0.232	0
0	4	4	39324	45399	26	0.266	0
4	4	4	49042	50983	28	0.318	0
1	1	1	19731	19959	20	0.384	0
3	1	1	13816	14824	17	0.546	0
1	3	3	13562	12780	17	0.618	0
5	1	1	12352	11691	16	0.656	0
3	3	3	12572	11851	16	0.651	0
5	3	3	12388	10817	16	0.694	0
7	1	1	16127	11566	19	0.681	0
1	5	5	16834	11404	19	0.685	0
3	5	5	23600	13977	25	0.633	0
2	0	0	24475	23101	22	0.314	0
2	2	2	18600	18288	20	0.450	0
6	0	0	15461	13627	23	0.613	0
2	4	4	16053	13627	24	0.613	0
6	2	2	17580	13227	21	0.634	0

Discussion

The experimental data are summarized in Tables 1 to 4 for SrF₂ and Tables 5 to 7 for CaF₂. These tables list the observed and calculated background-corrected intensities, the standard deviation of the observed intensity based on counting statistics, together with the values of the extinction and thermal diffuse scattering factors for each reflexion. Values given in brackets in Tables 1 and 3 include a significant contribution from the anomalous diffuse scattering and were therefore excluded from the analysis. The final values for the fundamental parameters are listed in Table 8 and the derived values of the structure factors are given in Table 9 for SrF₂ and Table 10 for CaF₂. In order to give an indication of the overall agreement, the values of the conventional discrepancy index,

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad (4)$$

are listed for the various sets of data in Table 11.

Table 8. Final values of fundamental parameters for SrF₂ and CaF₂

	SrF ₂	CaF ₂	
b_M	0.688 (0.013)	0.488	$\times 10^{-12} \text{ cm}$
α_M	5.63 (0.11)	6.30	$\times 10^{-12} \text{ erg. \AA}^{-2}$
α_F	3.77 (0.06)	4.58	$\times 10^{-12} \text{ erg. \AA}^{-2}$
$-\beta_F$	3.95 (0.46)	5.66 (1.16)	$\times 10^{-12} \text{ erg. \AA}^{-3}$

It can be seen from Tables 9 and 10 that there is, in general, excellent agreement between the F_o values derived from the various sets of data, in spite of the magnitude of the extinction corrections involved (see the γ values given in Tables 1 to 7). The good agreement between the two sets of F_o values obtained for SrF₂ at 0.746 Å, excluding those measurements affected by the anomalous diffuse scattering, is particularly striking, especially since the measurements were made on two crystals, one of which was a sphere and the other a cylinder, so that not only is the magnitude of

the extinction different in the two cases but the form of the correction formula is also different.

The measurements as a whole quite convincingly support the extensions made to the Zachariasen theory, which we have discussed elsewhere (Cooper & Rouse, 1970b), particularly the inclusion of the angular dependent function $f(\theta)$. Indeed, analysis using the original Zachariasen formulation gave R values which were larger by a factor of about 2 or 3 (see Cooper & Rouse, 1970b). Extinction was particularly severe for the calcium fluoride crystal and the final agreement obtained in that case is inferior to that obtained for the strontium fluoride data. However, there are still some systematic differences between the observed and calculated intensities of the strongest reflexions which indicate that an analytical expression for γ may not be appropriate for a cylindrical crystal if the extinction is very severe. It should be noted, however, that the analytical functions considered are indistinguishable when the extinction is relatively small and that they only become unsatisfactory when the extinction is very large.

Table 9. Neutron structure factors for SrF₂

h	k	l	0.746Å	0.865Å	1.077Å	F _c	
			F ₁	F ₂	F ₃		F ₄
0	2	2	6.903	6.833	6.919	7.030	6.921
4	0	0		6.758	6.664	6.668	6.624
4	2	2	6.326	6.421	6.315	6.186	6.340
0	4	4		6.029	5.991	5.849	6.068
4	4	4		5.540	5.547	5.385	5.561
8	0	0		5.010	5.069	4.873	5.097
8	2	2	4.828	4.836	4.811	4.711	4.880
0	6	6		4.889	4.852	4.744	4.880
4	6	6	4.431	4.404	4.432	4.356	4.475
8	4	4		4.240	4.293	4.176	4.286
0	8	8		3.555	3.671		3.608
8	6	6	3.434	3.417	3.486	3.456	3.456
12	0	0		3.375	3.339		3.311
4	8	8	3.326	3.280	3.351	3.311	3.311
12	2	2	3.146	3.175	3.199		3.173
12	4	4	2.842	2.805			2.792
8	8	8		2.544			2.565
0	10	0		2.155			2.158
12	6	6		2.282			2.259
4	10	10		2.233			2.259
1	1	1	2.777	2.776	2.744	2.754	2.747
3	1	1	2.670	2.645	2.665	2.694	2.629
1	3	3	2.550	2.539	2.567	2.576	2.535
5	1	1	2.482	2.459	2.472	2.481	2.453
3	3	3		2.531	2.511	2.520	2.472
5	3	3	2.210	2.261	2.158	2.283	2.272
7	1	1	2.241	2.243	2.214	2.221	2.223
1	5	5	2.198	2.213	2.200	2.218	2.207
3	5	5	2.178	2.195	2.174	2.188	2.181
7	3	3	2.085	2.105	2.082	2.119	2.103
5	5	5		1.963	1.982	1.994	1.953
9	1	1	1.954	1.932	1.911	1.955	1.936
9	3	3		1.838	1.782	1.832	1.783
1	7	7	1.759	1.804	1.768	1.842	1.795
7	5	5	1.873	1.871	1.845	1.912	1.877
3	7	7	1.789	1.766	1.766	1.871	1.804
11	1	1		1.643			1.642
5	7	7		1.476			1.561
9	5	5		1.525			1.517
11	3	3		1.532			1.560
7	7	7		1.592			1.574
1	9	9		1.363			1.364
13	1	1		1.349			1.335
11	5	5		1.402			1.403
3	9	9		1.407			1.395
2	0	0	1.694		1.676	1.704	1.663
2	2	2		1.548		1.550	1.538
6	0	0		1.300		1.189	1.208
2	4	4	1.167		1.175	1.166	1.208
6	2	2	1.236		1.054	1.078	1.111
6	4	4	0.789		0.813	0.831	0.855
2	6	6		0.751		0.761	0.781
10	0	0				0.580	0.584
10	2	2			0.510	0.532	0.526
6	6	6				0.534	0.526
10	4	4			0.343		0.376
2	8	8			0.338		0.376

In the case of the strontium fluoride data there was no correlation between the extinction and any of the thermal parameters and the reliability of the values obtained for these parameters will therefore not be affected by the magnitude of the extinction. On the other hand, in the case of the calcium fluoride data some correlation was found to occur between the extinction and the harmonic thermal vibration parameter for the calcium atoms, α_{Ca} . Because of this correlation, values of the harmonic thermal vibration parameters for both ions were subsequently fixed at values calculated from the temperature factors listed by Elcombe & Pryor (1970), which were determined from phonon frequency measurements. The value of β_F was not affected by the extinction.

With the present measurements we have now completed a series of accurate neutron diffraction measurements at room temperature for the series of isostructural fluorides of calcium, strontium and barium. The neutron scattering amplitudes and thermal parameters which have been derived from these measurements are listed in Table 12, together with the ratios of $-\beta_F$ and α_M to α_F and the values of B and B/a^2 , where a is the unit-cell dimension. The quantities in brackets are the standard deviations of refined parameters or functions derived from refined parameters. The parameters for CaF_2 which have no tabulated standard deviation were not refined, but were held fixed at the given values for

the reasons discussed above. It is interesting to note the systematic trends which are observed across this table. The value of the harmonic thermal parameter of both ions decreases as the atomic number of the cation increases and the unit cell becomes larger, although the value of α_F decreases more rapidly than the corresponding value for the cation. The value of the anharmonic thermal parameter, $-\beta_F$, also decreases. Although the ratio of $-\beta_F$ to α_F decreases, it is in no case significantly different from the weighted mean value of $1.04 (\pm 0.07) \text{ \AA}^{-1}$.

Table 11. *Discrepancy index values (%)*

	SrF ₂	CaF ₂
F_1	0.90	} 4.14
F_2	1.01	
F_3	1.07	
F_4	2.21	

The mean-square vibration amplitude of the ions, $\langle u^2 \rangle$, is proportional to their temperature factor B and thus inversely proportional to the harmonic thermal parameter α . Thus the mean-square vibration amplitudes of the ions increase as the atomic number of the cation increases. However, the unit-cell size also increases and it is therefore convenient to consider the relative mean-square vibration amplitude, which is proportional to the ratio B/a^2 given in Table 12. It can be seen that this ratio is essentially constant for the cations but that the ratio for the fluorine ion increases linearly with the atomic number of the cation.

It is interesting to compare the behaviour of the relative mean-square vibration amplitudes in these fluorite structures with that obtained for certain alkali halides. Menz (1968) determined the values of B/a^2 for the ions Li^+ , Na^+ , F^- and Cl^- from electron diffraction measurements on LiF , $LiCl$, NaF and $NaCl$ and concluded that the ratio was inversely proportional to the ionic mass. However, the values obtained for fluorine conflicted with this general conclusion and Linkoaho (1969) has more recently calculated B/a^2 values from accurate room temperature X-ray diffraction measurements on the above halides together with KCl , KBr and $RbCl$. From these more extensive measurements Linkoaho concludes that, apart from a relatively high value for Li^+ , the ratio B/a^2 seems to be constant, independent of the ionic mass. However, he shows that, in every case, the ratio for an individual ion increases when the number of electrons in its neighbours increases and in the case of Cl^- , for which four values were available the increase was very linear. He also points out that the latter trend is also apparent in the measurements of Menz (1968). There is thus a very striking similarity between the behaviour of the relative mean-square vibration amplitudes in the fluorite and the alkali halide structures.

The accuracy of the SrF_2 measurements was sufficient for a reliable value of the ratio of the nuclear scattering amplitudes to be determined. The resultant values was $b_{Sr}/b_F = 1.229 (\pm 0.007)$, which gives a value

Table 10. *Neutron structure factors for CaF₂*

			0.877Å	1.078Å	1.339Å		
h	k	l	F_1	F_2	F_3	F_4	F_c
0	2	2		6.764	6.598	6.408	6.162
4	0	0		6.021	5.907	5.709	5.504
4	2	2		5.513	5.433	5.198	5.657
0	4	4		5.376	5.311	5.045	5.420
4	4	4		4.698	4.770	4.881	4.977
8	0	0		4.275	4.361		4.570
8	2	2		4.027	4.240		4.380
0	6	6		4.127	4.330		4.380
4	6	6		3.799	4.122		4.023
8	4	4		3.603			3.856
0	8	8		3.227			3.255
8	6	6		3.167			3.120
1	1	1	1.975		1.885	1.917	1.927
3	1	1	1.794		1.768	1.800	1.865
1	3	3	1.808		1.816	1.849	1.795
5	1	1	1.656		1.709	1.786	1.738
3	3	3	1.735		1.764	1.808	1.756
5	3	3	1.434	1.533	1.632	1.716	1.603
7	1	1	1.523	1.530	1.644	1.860	1.575
1	5	5	1.572	1.568	1.674	1.895	1.560
3	5	5	1.551	1.531	1.688	2.019	1.554
7	3	3	1.461	1.456	1.625		1.496
5	5	5	1.411	1.419	1.556		1.367
9	1	1	1.372	1.374	1.528		1.368
9	3	3	1.299	1.288			1.252
1	7	7	1.316	1.303			1.264
7	5	5	1.376	1.368			1.345
5	7	7	1.344	1.338			1.291
11	1	1	1.207	1.202			1.161
5	7	7	1.110	1.114			1.079
5	5	5	1.154	1.153			1.050
11	3	3	1.214	1.198			1.110
2	0	0	2.522		2.463	2.529	2.457
2	2	2	2.412		2.338	2.341	2.322
6	0	0	1.986		1.997	2.083	1.955
2	4	4	1.985		2.043	2.122	1.955
6	2	2	1.816		1.916	2.128	1.846
6	4	4	1.560		1.728		1.549
2	6	6	1.539	1.511	1.682		1.461
10	0	0	1.321				1.222
10	2	2	1.200	1.213			1.151
6	6	6	1.274	1.243			1.151
10	4	4	1.067	1.037			0.958
2	8	8	1.008	1.026			0.958

Table 12. Neutron scattering amplitudes and thermal parameters obtained for CaF₂, SrF₂ and BaF₂

	CaF ₂	SrF ₂	BaF ₂	
b_M	0.488	0.688 (0.013)	0.522 (0.13)	$\times 10^{-12}$ cm
α_M	6.30	5.63 (0.011)	4.71 (0.04)	$\times 10^{-12}$ erg. \AA^{-2}
α_F	4.58	3.77 (0.06)	3.04 (0.01)	$\times 10^{-12}$ erg. \AA^{-2}
$-\beta_F$	5.66 (1.16)	3.95 (0.46)	3.06 (0.26)	$\times 10^{-12}$ erg. \AA^{-3}
$-\beta_F/\alpha_F$	1.24 (0.25)	1.05 (0.12)	1.01 (0.09)	\AA^{-1}
α_M/α_F	1.38	1.49 (0.03)	1.55 (0.01)	
B_M	0.507	0.567 (0.011)	0.678 (0.005)	\AA^2
B_F	0.697	0.846 (0.013)	1.048 (0.004)	\AA^2
B_M/a^2	1.70	1.69 (0.03)	1.76 (0.01)	$\times 10^{-2}$
B_F/a^2	2.34	2.51 (0.04)	2.73 (0.01)	$\times 10^{-2}$

for the nuclear scattering amplitude of strontium of $b_{Sr} = 0.688 (\pm 0.013) \times 10^{-12}$ cm, assuming a value of $b_F = 0.560 (\pm 0.010) \times 10^{-12}$ cm. The new value of b_{Sr} is appreciably larger than the previously tabulated values of 0.57×10^{-12} cm (*International Tables for X-ray Crystallography*, 1962) and 0.656×10^{-12} cm (The Neutron Diffraction Commission, 1969), but is in excellent agreement with the value of $0.683 (\pm 0.007) \times 10^{-12}$ cm given by Loopstra & Rietveld (1969).

The present measurements give further confirmation of the importance of anharmonic effects for atoms occupying tetrahedral sites in the fluorite structure and it is to be expected that these considerations can be extended to other types of structure. Neutron diffraction measurements on a number of other relatively simple structures are in progress to investigate this further.

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An Improved Absorption Correction Procedure for X-ray Intensity Data from a Poorly Defined Single Crystal

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A mathematical technique is described which combats the inaccuracies in absorption corrections applied to single-crystal X-ray diffraction data due to indefinite location of the crystal faces.

Introduction

The purpose of this paper is to demonstrate the feasibility of correcting errors inherent in the calculation of absorption corrections. Here a method is described for calculating the magnitude of the absorption error associated with the fixing of the planes defining a crystal.

The effectiveness of the method is studied by using a least-squares correlation of common reflexions obtained from different data collection geometries. The orientation of the defining planes of a crystal may reasonably be regarded as without error and only the