

A Neutron Diffraction Study of Anharmonic Temperature Factors in SrF₂

BY SYLVIA L. MAIR* AND Z. BARNEA

School of Physics, University of Melbourne, Parkville 3052, Australia

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

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

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Accurate integrated intensities for the Bragg reflexion of neutrons from two single crystals of SrF₂ have been measured at temperatures between 295 and 1043 °K. Corrections for extinction and thermal diffuse scattering were applied and the experimental data were analysed in terms of a model which includes both harmonic and anharmonic components in the thermal vibrations of the atoms. Significant contributions from the third-order anharmonic term, β_F , in the one-particle potential of the fluorine atoms, consistent with their tetrahedral site symmetry, were observed at all temperatures. At 773 °K significant anisotropic fourth-order components, δ_{Sr} and δ_F , became apparent in the thermal vibration of both the strontium and the fluorine atoms. At this temperature β_F was refined to $-3.45 (\pm 0.11) \times 10^{-12}$ erg Å⁻³, with $\delta_{Sr} = 1.30 (\pm 0.75) \times 10^{-12}$ erg Å⁻⁴ and $\delta_F = 0.84 (\pm 0.29) \times 10^{-12}$ erg Å⁻⁴. The positive signs of the parameters δ_{Sr} and δ_F result from the influence of Coulombic forces on the atomic vibrations.

Introduction

In almost all cases determination of crystal structures is carried out with models which assume harmonic thermal vibrations for all constituent atoms. The thermal vibration of each atom is then constrained such that the time-averaged probability function for the position of an atom is a Gaussian function of the displacement from its equilibrium position and contours of equal probability are ellipsoids. However, in a crystal the neighbours of an atom will of necessity be arranged with a particular symmetry which one would expect to influence the thermal vibration of that atom. This thermal motion will then be modified in such a way that the atom will spend more of its time in the regions of low potential. For an ionic crystal these are determined mainly by the relative influences of the Coulombic and repulsive forces. Such anharmonic components in the thermal vibration will contribute to the Bragg intensities and their effect can be readily recognized in such structures as the fluorite structure. Careful diffraction measurements can thus provide valuable information about the thermal vibration of the atoms and, in particular, about the way in which this is affected by the atomic environment.

In an earlier experiment accurate integrated intensity measurements for the Bragg reflexion of neutrons were made for single crystals of SrF₂ at room temperature (Cooper & Rouse, 1971). The experimental data were analysed to obtain a third-order parameter, β_F , in the potential of the fluorine ions, appropriate to their non-centrosymmetric site symmetry. In this paper we report the results of two further neutron experiments on SrF₂.

The first of these (Experiment *A*) was conducted at the A.A.E.C. Research Establishment, Lucas Heights, Australia and resulted in the determination of a value for β_F , referred to 273 °K, as reported previously (Mair & Barnea, 1971), as well as the temperature variation of the Debye–Waller factors, B_F and B_{Sr} , between 295 and 893 °K. The second (Experiment *B*), carried out at A.E.R.E., Harwell, England, was undertaken in order to investigate further the cubic term, β_F , as well as the fourth-order anharmonic components of the thermal vibration. In the latter experiment extensive measurements were therefore made at 401, 443 and 773 °K.

The cubic anharmonic component is antisymmetric in nature and if we consider the atoms to be constrained by a one-particle potential it is therefore non-zero only for atoms having non-centrosymmetric site symmetry. Its existence in the case of the fluorine ion of SrF₂, which has the cubic fluorite structure, is permitted by the tetrahedral site symmetry of the anion. It represents a preference for the atom to vibrate in directions away from its nearest neighbours, and therefore towards the corners of the tetrahedron which forms the complement to that defined by the nearest neighbour strontium atoms. The anisotropic quartic components are centrosymmetric and are therefore non-zero for atoms having either centrosymmetric or non-centrosymmetric site symmetries. They are again of a nature determined by the atomic site symmetries.

A series of accurate intensity measurements for the Bragg reflexion of neutrons has previously been carried out for the fluorite structures BaF₂ (Cooper, Rouse & Willis, 1968), SrF₂ and CaF₂ (Cooper & Rouse, 1971). These were found to show significant effects arising from the third-order anharmonic component in the thermal vibration of the fluorine ion.

* Present address: Division of Chemical Physics, CSIRO, P.O. Box 160, Clayton, Victoria, Australia 3168.

Although significant anisotropic quartic vibrational effects have been observed for the chlorine ion in KCl (Cooper & Rouse, 1973), they have not previously been observed in the presence of third-order effects. The present experiment is the first demonstration that both cubic and quartic anisotropic effects can be significant in the same structure.

Theory

Using the general structure-factor formalism developed by Dawson (1967), we may write for the structure factor, $F(\mathbf{Q})$, for a particular scattering vector, \mathbf{Q}

$$F(\mathbf{Q}) = \sum_j f_j(\mathbf{Q}) T_j(\mathbf{Q}) \exp(i\mathbf{Q} \cdot \mathbf{r}_j) \quad (1)$$

where $f_j(\mathbf{Q})$ are the scattering factors and $T_j(\mathbf{Q})$ the vibration factors of the atoms at positions \mathbf{r}_j in the unit cell.

For the fluorite structure the reflexions can be divided into three groups, depending on the Miller indices h , k and l , where h , k and l are either all even or all odd. If the strontium atoms are considered to be at 0,0,0 and equivalent sites and the fluorine atoms to be at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ and $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$ and equivalent sites, the calculated structure factors are then

$$F(\mathbf{Q}) = 4b_{\text{Sr}} T_{\text{cSr}} \mp 8b_{\text{F}} T_{\text{cF}} \quad h+k+l=4n \pm 1 \quad (2)$$

$$F(\mathbf{Q}) = 4b_{\text{Sr}} T_{\text{cSr}} + 8b_{\text{F}} T_{\text{cF}} \quad h+k+l=4n \quad (3)$$

$$F(\mathbf{Q}) = 4b_{\text{Sr}} T_{\text{cSr}} - 8b_{\text{F}} T_{\text{cF}} \quad h+k+l=4n+2. \quad (4)$$

In these equations the scattering factors $f_j(\mathbf{Q})$ have been replaced by the nuclear scattering amplitudes, b_j , appropriate to neutron diffraction, and the relations

$$T_{\text{aSr}, j}(\mathbf{Q}) = 0 \quad (5)$$

$$T_{\text{aF}, j}(\mathbf{Q}) = -T_{\text{aF}, j'}(\mathbf{Q}) \quad (6)$$

have been used, where the subscripts j, j' in equation (6) denote sites of type $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ and $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$, respectively.

Ignoring terms of higher order than fourth, the one-particle potential for a crystal having the fluorite structure is

$$\begin{aligned} V_j = & V_{0j} + \frac{1}{2}\alpha_j(x^2 + y^2 + z^2) + \beta_j xyz \\ & + \gamma_j(x^2 + y^2 + z^2)^2 \\ & + \delta_j[x^4 + y^4 + z^4 - \frac{3}{2}(x^2 + y^2 + z^2)^2] \end{aligned} \quad (7)$$

where x , y and z are the coordinates defining the instantaneous displacements, \mathbf{x} , of the j th atom.

The thermal vibration factors for an atom in a potential field defined by equation (7) are then

$$\begin{aligned} T_{c_j}(\mathbf{Q}) = & N_j \exp \left[\frac{-Q^2 k_B T}{2\alpha_j} \right] \left\{ 1 - k_B T \left(\frac{15\gamma_j}{\alpha_j^2} - \frac{\beta_j^2}{2\alpha_j^3} \right) \right. \\ & \left. + (k_B T)^2 \left(\frac{10\gamma_j}{\alpha_j^3} - \frac{\beta_j^2}{2\alpha_j^4} \right) (h^2 + k^2 + l^2) \left(\frac{2\pi}{a_0} \right)^2 \right. \end{aligned}$$

$$\begin{aligned} & \left. - (k_B T)^3 \left(\frac{2\pi}{a_0} \right)^4 \left[\frac{\gamma_j}{\alpha_j^4} (h^2 + k^2 + l^2)^2 \right. \right. \\ & \left. \left. + \frac{\delta_j}{\alpha_j^4} [(h^4 + k^4 + l^4) - 3(h^2 k^2 + k^2 l^2 + l^2 h^2)] \right. \right. \\ & \left. \left. - \frac{\beta_j^2}{\alpha_j^5} (h^2 k^2 + k^2 l^2 + l^2 h^2) \right] \right\} \end{aligned} \quad (8)$$

where

$$N_j = \left[1 - k_B T \left(\frac{15\gamma_j}{\alpha_j^2} - \frac{\beta_j^2}{2\alpha_j^3} \right) \right]^{-1} \quad (9)$$

and

$$T_{a_j}(\mathbf{Q}) = \beta_j \frac{(k_B T)^2}{\alpha_j^3} \left(\frac{2\pi}{a_0} \right)^3 T_{c_j}(\mathbf{Q}) hkl. \quad (10)$$

Equations (8) to (10) have been derived following the methods of Willis (1969), but differ from the results of the latter by the inclusion of the β_j^2 terms in equation (8), which are of the same order as other terms in this equation.

The term in T_{c_j} involving δ_j is the anisotropic quartic term and those in γ_j are the isotropic quartic components. That the isotropic anharmonic effects are closely approximated by a temperature-dependent correction to the harmonic Debye-Waller B factor, B_j , where

$$B_j = \frac{8\pi^2 k_B T}{\alpha_j}, \quad (11)$$

may be seen if T_{c_j} is written in the approximate form obtained by omitting terms of order Q^4 :

$$T_{c_j} = \exp \left\{ \frac{-Q^2 k_B T}{\alpha_j} \left[1 - k_B T \left(\frac{20\gamma_j}{\alpha_j^2} - \frac{\beta_j^2}{\alpha_j^3} \right) \right] \right\}. \quad (12)$$

The temperature dependence of α_j , β_j , γ_j and δ_j is taken into account using the 'quasi-harmonic' approximation, which assumes that changes in volume arising from thermal expansion give rise to proportional changes in the inverse squared frequencies of the normal modes of vibration. This approximation leads to the equations, applicable in the classical limit

$$\frac{\alpha_j}{\alpha_{0j}} = \frac{\beta_j}{\beta_{0j}} = \frac{\gamma_j}{\gamma_{0j}} = \frac{\delta_j}{\delta_{0j}} = (1 - 2\chi\gamma_G \Delta T), \quad (13)$$

where γ_G is the Grüneisen constant, χ is the volume coefficient of expansion, α_{0j} , β_{0j} , γ_{0j} and δ_{0j} are the values of the potential parameters at a reference temperature, ΔT is the difference between the actual and reference temperatures, and it is assumed that $2\chi\gamma_G \Delta T \ll 1$.

From equations (12) and (13), an effective harmonic parameter, α_j^{eff} , may be defined.

$$\alpha_j^{\text{eff}} = \alpha_{0j} (1 - 2\chi\gamma_G \Delta T) \left[1 + k_B T \left(\frac{20\gamma_j}{\alpha_j^2} - \frac{\beta_j^2}{\alpha_j^3} \right) \right] \quad (14)$$

and it is this parameter which is obtained if isotropic

anharmonic effects and thermal expansion effects are ignored.

Experimental measurements

(a) Experiment A

The sample used in Experiment A was a single crystal of SrF₂ in the shape of a cube of dimensions 4 × 4 × 4 mm. It was mounted in a vacuum furnace (Barnea & Towers, 1971) attached to the 4H2 automatic neutron diffractometer at the HIFAR reactor, A.A.E.C. Research Establishment, Lucas Heights. The temperature was measured using a thermocouple in contact with the sample and a calibration was made to assess temperature gradients. Over 40 reflexions, each measurement consisting of the average for two equivalents ($hkl, \bar{h}\bar{k}\bar{l}$), were collected at each of four temperatures in the range 295 to 895°K using an incident wavelength of 0.979 Å. In order to obtain an estimate of the cubic anharmonic term, β_F , certain reflexions of type $4n \pm 1$ were measured at additional temperatures up to 1043°K. The reflexions chosen were members of pairs which are equivalent in the harmonic approximation, but differ in intensity if the cubic anharmonic term is non-zero (Mair & Barnea, 1971).

All reflexions were scanned in a θ - 2θ mode using a detector aperture adjusted to reduce the amount of background scattering detected without loss of Bragg intensity. The scan range was $\pm 1.5^\circ$ for all reflexions. The background was measured by taking stationary counts at 3° on either side of the Bragg peak.

(b) Experiment B

The sample used in Experiment B was one of those used in the earlier room-temperature experiments (Cooper & Rouse, 1971). It was a cylindrical single crystal of SrF₂ of radius 1.5 mm and length 8 mm, with its axis parallel to a crystallographic $\langle 011 \rangle$ axis. Two-dimensional hkk intensity measurements were made at 401, 443 and 773°K with a Hilger and Watts Mk II automatic neutron diffractometer at the PLUTO reactor, A.E.R.E. Harwell. The incident wavelength was 1.071 Å. In all cases intensities were averaged over a complete two-dimensional set of equivalent reflexions ($hkk, \bar{h}k\bar{k}, h\bar{k}\bar{k}, \bar{h}\bar{k}k$).

The crystal was mounted in a sealed silica tube in a small split-coil platinum resistance furnace with a hot zone constant in temperature to within $\pm 5^\circ$. The temperature of the sample, as determined by a thermocouple placed in contact with it, was automatically controlled to within very narrow limits.

The reflexions were scanned in a θ - 2θ mode as in Experiment A, but with scan ranges of ± 0.8 , ± 1.0 and $\pm 1.2^\circ$, the higher scan ranges being used for the higher-angle reflexions to avoid any loss of Bragg intensity. The background was measured by making a similar scan with the crystal mis-set by 2° . The data were collected with considerable care, repeated measurements being made when necessary to improve the counting statistics.

Data analysis

(a) Methods of analysis

The sets of observed data from both experiments were analysed by basically similar procedures. Those from Experiment A were processed using the least-squares computer program *ORFLS* (Busing, Martin & Levy, 1962) modified by S. Mair to include anharmonic effects and by Dr M. Fehlmann to include the extinction correction of Zachariasen (1967). The program determines the values of the varied parameters which minimize the quantity S_1 given by:

$$S_1 = \sum_i [w_i(F_{oi} - F_{ci})]^2 \quad (15)$$

where F_{oi} is the observed structure factor corrected for background and thermal diffuse scattering, F_{ci} is the corresponding computed quantity and w_i is the weight given to the i th observation. The thermal diffuse scattering was calculated in a separate program using the isotropic approximation of Cooper & Rouse (1968), valid for neutron velocities greater than those of the phonons concerned (Cooper, 1971).

The data for Experiment B were analysed using the Harwell *TAILS* computer program, which is designed to analyse data involving effects due to anharmonic thermal vibrations and requiring possible corrections for extinction and thermal diffuse scattering. The quantity minimized in this case is:

$$S_2 = \sum_i [w_i(I_{oi} - I_{ci})]^2, \quad (16)$$

where I_{oi} is the observed background corrected intensity of the i th reflexion, I_{ci} is the computed intensity and w_i is the weight given to the observation. Minimization of S_2 is effected by the search algorithm of Powell (1965), which does not necessitate the computation of partial derivatives.

The calculated intensity is given by:

$$I_c = sA_\mu(y + \alpha) |F_c|^2 \operatorname{cosec} 2\theta \quad (17)$$

where s is the scale factor, A_μ the absorption factor, y the extinction factor and α the thermal-diffuse-scattering factor. The extinction factor is that defined by the Zachariasen (1967) theory, modified by Cooper & Rouse (1970). The thermal-diffuse-scattering factor is calculated using the isotropic approximation (Cooper & Rouse, 1968).

(b) Results

Absorption was sufficiently small in both crystals ($\mu R < 0.01$) for A_μ to be effectively constant for all reflexions and this factor was therefore considered part of the scaling factor. Thermal-diffuse-scattering corrections were calculated using the elastic constants given by Gerlich (1964), extrapolated to the temperature concerned.

The parameters which were varied simultaneously at each temperature were the scale factor, the harmonic thermal parameters (α_j), the domain radius (r^*), the cubic anharmonic parameter (β_j) and, in the case of Experiment *B*, the quartic anharmonic parameters (δ_j). The ratio of the nuclear scattering amplitude of strontium to that of fluorine was taken to be 1.229, as refined from the earlier room-temperature data on SrF₂ (Cooper & Rouse, 1972).

Initially the refinement of the data was made using weights given by the reciprocals of the estimated standard deviations. Owing to the severity of the extinction in the data of Experiment *B*, systematic differences existed between observed and calculated intensities of the strongest reflexions. This was consistent with earlier indications (Cooper & Rouse, 1971), that the analytical expression for y is not appropriate for a cylindrical crystal where extinction is very severe. For this reason a weighting scheme which gave less weight to these intensities was considered desirable for these data sets. An adaptation of the system given by Cruickshank (1965) was therefore used to provide a set of self-consistent weights appro-

priate to the quantity S_2 minimized. This required adjustment of weights to ensure that the quantity $w^2(I_o - I_c)^2$ had constant averages in groups of increasing I_o . The final analysis at each of the three temperatures involved was therefore made with such a set of self-consistent weights calculated from the results of a refinement using the original weighting system. The introduction of this weighting scheme caused small changes in both the parameters and their standard deviations, but the parameter changes were well within the corresponding standard deviations.

The extinction in the sample used in Experiment *A* was appreciably lower than that in the sample used in Experiment *B*. The effect of the somewhat different treatment of the extinction in Experiment *A* was therefore not significant. A small but significant decrease in the extinction (as measured by the effective domain radius) with increasing temperature was noted for both crystals.

The parameter β_F was significant for all data above room temperature and δ_F and δ_{Sr} were significant for the 773°K data. β_F has a direct influence only on the reflexions of type $4n \pm 1$ whereas δ_F and δ_{Sr} have their

Table 1. Observed and calculated intensities for SrF₂ at 295°K (Experiment *A*)

h	k	l	I_o	I_c	$\sigma(I_o)$	y	α
0	2	2	146942	142478	276.4	0.3321	0.0043
0	0	4	107766	116955	240.5	0.4039	0.0105
2	2	4	99929	101936	232.2	0.4506	0.0177
0	4	4	90946	90487	221.1	0.4817	0.0254
0	2	6	83907	81109	211.9	0.5017	0.0334
4	4	4	71807	73430	281.9	0.5153	0.0416
2	4	6	70559	67301	197.7	0.5250	0.0499
0	0	8	65371	62602	190.7	0.5382	0.0582
0	6	6	61106	59174	185.9	0.5522	0.0663
2	2	8	62325	59174	186.8	0.5522	0.0663
0	4	8	58710	56838	182.6	0.5691	0.0743
4	6	6	55067	55396	251.5	0.5880	0.0817
4	4	8	53161	54689	247.4	0.6060	0.0886
2	6	8	51994	54619	174.6	0.6197	0.0945
0	2	10	51175	54619	173.2	0.6197	0.0945
1	1	1	62177	60502	185.7	0.5695	0.0012
1	1	3	37453	37936	151.5	0.7128	0.0065
1	3	3	30862	30327	87.9	0.7712	0.0131
1	1	5	25575	25806	128.1	0.8028	0.0205
3	3	3	25142	25806	129.4	0.8028	0.0205
1	3	5	22154	22635	98.0	0.8207	0.0283
3	3	5	19958	20263	114.7	0.8308	0.0364
1	5	5	20012	18444	115.3	0.8370	0.0447
1	1	7	19994	18444	113.5	0.8370	0.0447
1	3	7	17321	17043	110.8	0.8424	0.0530
3	5	5	17472	17043	111.6	0.8424	0.0530
3	3	7	17073	15976	108.3	0.8481	0.0613
5	5	5	15180	15190	104.5	0.8553	0.0693
1	5	7	15906	15190	106.9	0.8553	0.0693
1	1	9	14944	14642	103.4	0.8635	0.0771
3	5	7	14382	14642	103.1	0.8635	0.0771
1	3	9	14264	14311	102.3	0.8719	0.0844
1	7	7	12945	1419c	101.8	0.8788	0.0910
3	3	9	13459	1419c	100.7	0.8788	0.0910
5	5	7	14165	14196	104.2	0.8788	0.0910
0	0	2	24924	26405	128.2	0.7745	0.0017
2	2	2	13469	15123	108.2	0.8731	0.0073
0	2	4	11336	10755	95.7	0.9116	0.0140
0	0	6	5817	6419	77.2	0.9449	0.0293
2	4	4	5890	6419	79.2	0.9449	0.0293
2	2	6	4907	5144	75.3	0.9536	0.0375
0	4	6	5194	4180	60.4	0.9603	0.0457
4	4	6	3231	2841	97.4	0.9711	0.0623
0	2	8	3007	2841	67.1	0.9711	0.0623
2	6	6	2509	2367	94.2	0.9759	0.0703
2	4	8	2100	1985	63.9	0.9805	0.0781
0	0	10	1173	1424	63.1	0.9871	0.0917
0	6	8	1217	1424	64.8	0.9871	0.0917

Table 2. Observed and calculated intensities for SrF₂ at 493°K (Experiment *A*)

h	k	l	I_o	I_c	$\sigma(I_o)$	y	α
0	2	2	141004	138651	273.0	0.3712	0.0073
0	0	4	100585	109554	234.5	0.4573	0.0179
2	2	4	89930	91844	226.2	0.5166	0.0301
0	4	4	78024	78445	210.7	0.5591	0.0432
0	2	6	68741	67667	196.5	0.5902	0.0569
4	4	4	58963	58929	186.8	0.6145	0.0709
2	4	6	54427	51906	182.5	0.6361	0.0851
0	0	8	48306	46306	169.0	0.6575	0.0992
0	6	6	44757	41874	169.5	0.6807	0.1132
2	2	8	43915	41874	168.5	0.6807	0.1132
0	4	8	40213	38353	164.3	0.7060	0.1268
4	6	6	35597	35551	153.9	0.7321	0.1397
4	4	8	32431	33313	148.5	0.7569	0.1516
2	6	8	30172	31575	146.3	0.7774	0.1619
0	2	10	29495	31575	142.6	0.7774	0.1619
1	1	1	58364	57997	190.4	0.6121	0.0020
1	1	3	34271	35045	149.4	0.7559	0.0110
1	3	3	27139	26584	64.2	0.8161	0.0224
1	1	5	21905	21829	126.5	0.8476	0.0349
3	3	3	22694	22465	125.8	0.8433	0.0349
1	3	5	18649	18783	115.5	0.8642	0.0483
3	3	5	14018	15376	104.3	0.8825	0.0621
1	5	5	15368	13752	107.8	0.8889	0.0762
1	1	7	15374	14138	108.7	0.8861	0.0762
1	3	7	12820	12305	102.6	0.8960	0.0904
3	5	5	13980	13327	106.5	0.8877	0.0904
3	3	7	11009	11908	96.9	0.8965	0.1045
5	5	5	9597	9324	95.4	0.9181	0.1183
1	5	7	11350	10642	98.8	0.9070	0.1183
1	1	9	9065	9515	97.8	0.9184	0.1317
3	5	7	8999	8801	91.9	0.9244	0.1317
1	3	9	9598	9173	93.9	0.9244	0.1443
1	7	7	7803	8229	91.3	0.9350	0.1557
3	3	9	7838	8027	89.8	0.9367	0.1557
5	5	7	9672	9701	96.7	0.9238	0.1557
3	7	7	8809	9174	81.1	0.9309	0.1653
0	0	2	7238	7989	87.1	0.9395	0.1653
0	0	2	23113	24089	126.6	0.8124	0.0029
2	2	2	10558	12282	109.3	0.9065	0.0124
0	2	4	8550	7782	94.2	0.9423	0.0239
0	0	6	3119	3619	71.8	0.9723	0.0500
2	4	4	3087	3619	86.1	0.9723	0.0500
2	2	6	2278	2525	83.8	0.9797	0.0638
0	4	6	2649	1763	77.6	0.9849	0.0780
4	4	6	1108	837	73.9	0.9925	0.1062
0	2	8	887	837	68.6	0.9925	0.1062
2	6	6	588	561	76.2	0.9951	0.1200
2	4	8	508	364	73.7	0.9971	0.1333
0	6	8	104	129	73.6	0.9993	0.1570

greatest effect on the high-angle $4n+2$ type reflexions. The two quartic parameters are correlated and have opposite effects on the intensities of these reflexions. It was found that δ_F had by far the greater influence, with the result that δ_{Sr} could only be refined correctly in the presence of a non-zero δ_F .

Discussion

Tables 1 to 4 summarize the data analysis for Experiment *A*, Tables 5 to 7 that for Experiment *B*. The tables list the observed and calculated background-corrected intensities, the standard deviations, $\sigma(I_o)$, of the observed intensities, based on counting statistics, the thermal-diffuse-scattering corrections, α , and the extinction factor, y .

Table 8 lists the parameters obtained at the various temperatures, together with their standard deviations, including for comparison the earlier room-temperature (295°K) results. It may be noted that the Debye-Waller *B* factors and the value of β_F for the latter, which were derived from data collected under essentially the same conditions as for Experiment *B*, are in close agreement with those obtained at the same temperature from the data of Experiment *A*, conducted under different

Table 3. *Observed and calculated intensities for SrF₂ at 693°K (Experiment A)*

h k l	I_o	I_c	$\sigma(I_o)$	y	α
0 2 2	139165	136633	269.4	0.4123	0.0105
0 0 4	96892	102541	229.5	0.5153	0.0258
2 2 4	80107	81476	210.2	0.5897	0.0434
0 4 4	66193	65836	192.4	0.6455	0.0623
0 2 6	54643	53696	174.8	0.6884	0.0820
4 4 4	44265	44164	161.3	0.7229	0.1023
2 4 6	37902	37452	151.5	0.7530	0.1228
0 0 8	31579	30782	140.1	0.7813	0.1433
0 6 6	27244	26098	133.3	0.8090	0.1635
2 2 8	27048	26098	131.1	0.8090	0.1635
0 4 8	22678	22351	124.9	0.8358	0.1832
4 6 6	19411	19323	118.1	0.8608	0.2020
4 4 8	16597	16873	111.1	0.8827	0.2194
2 6 8	13966	14916	106.0	0.9004	0.2348
0 2 10	13849	14916	106.0	0.9004	0.2348
1 1 1	58227	57299	180.4	0.6506	0.0028
1 1 3	31829	32955	143.4	0.7930	0.0159
1 3 3	23797	23336	79.9	0.8546	0.0322
1 1 5	18897	18425	115.8	0.8845	0.0503
3 3 3	20139	19931	120.1	0.8753	0.0503
1 3 5	15462	15635	106.0	0.8988	0.0696
3 3 5	11222	11179	94.9	0.9236	0.0896
1 5 5	10894	9896	94.5	0.9286	0.1099
1 1 7	11480	10645	94.9	0.9232	0.1099
1 3 7	8552	8532	89.0	0.9353	0.1305
3 5 5	10502	10432	95.4	0.9214	0.1305
3 3 7	8980	8749	89.9	0.9320	0.1509
5 5 5	5071	5150	79.4	0.9598	0.1710
1 5 7	7405	6322	84.9	0.9433	0.1710
1 1 9	5704	5845	79.2	0.9550	0.1904
3 5 7	4531	4808	75.9	0.9631	0.1904
1 3 9	5496	5577	78.8	0.9585	0.2087
1 7 7	3812	4402	75.7	0.9689	0.2255
3 3 9	3600	4147	74.8	0.9707	0.2255
5 5 7	5936	6382	82.1	0.9545	0.2255
1 5 9	3337	4092	73.3	0.9724	0.2399
3 7 7	4865	5570	112.2	0.9618	0.2399
0 0 2	21662	22900	123.2	0.8398	0.0416
2 2 2	8330	9544	94.8	0.9351	0.0178
0 2 4	5727	5052	80.7	0.9666	0.0344
0 0 6	931	1512	61.1	0.9897	0.0721
2 4 4	1199	1512	64.2	0.9897	0.0721
2 2 6	577	789	59.2	0.9945	0.0921
0 4 6	1008	379	123.1	0.9973	0.1125

experimental conditions. This would seem to support the validity of the comparison of results from the two experiments.

Table 4. *Observed and calculated intensities for SrF₂ at 893°K (Experiment A)*

h k l	I_o	I_c	$\sigma(I_o)$	y	α
0 2 2	126376	132450	257.7	0.4219	0.0138
0 0 4	93896	94512	225.9	0.5402	0.0340
2 2 4	73544	70991	203.1	0.6295	0.0572
0 4 4	49056	50932	135.9	0.6981	0.0821
0 2 6	41762	41213	156.1	0.7510	0.1081
4 4 4	33267	31681	143.1	0.7932	0.1349
2 4 6	26180	24530	130.3	0.8281	0.1620
0 0 8	19893	19142	117.2	0.8587	0.1891
0 6 6	14168	15057	86.0	0.8856	0.2159
2 2 8	15688	15057	107.6	0.8856	0.2159
0 4 8	11766	11942	99.9	0.9091	0.2420
4 6 6	9347	9556	93.1	0.9288	0.2671
4 4 8	8049	7722	88.6	0.9446	0.2905
2 6 8	5482	6319	82.8	0.9566	0.3114
0 2 10	5513	6319	80.9	0.9566	0.3114
1 1 1	59965	57100	182.2	0.6529	0.0037
1 1 3	30137	31571	139.2	0.8012	0.0209
1 3 3	20435	20582	64.3	0.8710	0.0425
1 1 5	16122	15537	109.7	0.9021	0.0664
3 3 3	19104	18032	116.9	0.8872	0.0664
1 3 5	12841	13015	100.1	0.9096	0.0917
3 3 5	7769	7697	85.3	0.9474	0.1181
1 5 5	6873	6770	118.9	0.9511	0.1450
1 1 7	8579	7760	87.4	0.9461	0.1450
1 3 7	5600	5569	65.9	0.9579	0.1721
3 5 5	8108	7974	72.6	0.9399	0.1721
3 3 7	6433	6155	82.8	0.9520	0.1992
5 5 5	2463	2453	69.7	0.9812	0.2258
1 5 7	3875	4572	74.3	0.9640	0.2258
1 1 9	3198	3269	71.5	0.9746	0.2516
3 5 7	2276	2289	56.4	0.9825	0.2516
1 3 9	2993	3073	71.2	0.9769	0.2761
1 7 7	1304	2066	67.4	0.9855	0.2986
3 3 9	1810	1860	66.2	0.9870	0.2986
5 5 7	3232	3800	73.5	0.9726	0.2986
1 5 9	1454	1820	93.0	0.9876	0.3183
3 7 7	2030	3005	100.1	0.9793	0.3183
0 0 2	20023	21170	120.9	0.8521	0.0055
2 2 2	6058	7924	91.9	0.9461	0.0234
0 2 4	3611	3531	74.4	0.9767	0.0453
2 4 4	233	650	87.1	0.9956	0.0950
0 4 6	522	52	49.1	0.9995	0.1484
2 4 8	117	84	57.5	0.9995	0.2547

Table 5. *Observed and calculated intensities for SrF₂ at 401°K (Experiment B)*

h k l	I_o	I_c	$\sigma(I_o)$	y	α
4 2 2	758288	780201	720	0.2710	0.0139
4 4 0	696400	737776	757	0.3135	0.0204
4 4 4	633707	673225	658	0.3891	0.0342
8 0 0	580904	620849	626	0.4501	0.0481
8 2 2	577082	602788	770	0.4754	0.0546
0 6 6	572551	603252	772	0.4752	0.0546
8 4 4	563532	596935	762	0.5155	0.0681
4 6 6	575891	585995	775	0.5088	0.0652
2 0 0	306788	290485	306	0.6522	0.0011
2 2 2	172697	173848	246	0.7976	0.0053
6 0 0	70196	70106	138	0.9215	0.0238
2 4 4	68617	70316	151	0.9213	0.0238
6 2 2	54622	54689	156	0.9397	0.0307
6 4 4	29260	27577	136	0.9705	0.0550
2 6 6	23675	22237	114	0.9764	0.0620
10 0 0	13516	12635	64	0.9868	0.0813
1 1 1	562193	520383	620	0.3743	0.0007
3 1 1	404662	379397	524	0.5460	0.0047
1 3 3	321554	316116	366	0.6291	0.0101
5 1 1	287457	276774	446	0.6811	0.0163
3 3 3	283831	280656	443	0.6766	0.0163
5 3 3	225095	221761	394	0.7541	0.0298
7 1 1	209058	209730	381	0.7710	0.0369
1 5 5	201288	206590	293	0.7743	0.0369
3 5 5	203945	202098	295	0.7816	0.0438
7 3 3	190858	191218	448	0.7977	0.0541
5 5 5	170105	168142	424	0.8238	0.0612
9 1 1	176257	173906	431	0.8195	0.0676
9 3 3	179574	178335	437	0.8205	0.0811
1 7 7	181685	180931	441	0.8180	0.0811
7 5 5	200992	199340	462	0.8006	0.0811

Table 9 lists the discrepancy indices

$$R_1^w = \left(\frac{\sum_i w_i^2 |F_{oi} - F_{ci}|^2}{\sum_i w_i^2 F_{oi}^2} \right)^{1/2} \quad (18a)$$

for the data of Experiment *A* and

$$R_2^w = \frac{\sum_i (w_i^2 |I_{oi} - I_{ci}|)}{\sum_i w_i^2 I_{oi}} \quad (18b)$$

for Experiment *B*. To illustrate the significance of the quartic terms at 773°K the *R* values are also included for a model in which δ_{sr} and δ_F are set to zero. Using

the tables of Hamilton (1965) and the relevant *R* value ratios the improvement of fit resulting from the inclusion of the quartic anisotropic parameters may be assessed. This yields the result that δ_{sr} and δ_F are jointly significant at a level of 0.005.

The effect of the quartic anisotropic terms upon the Bragg intensities is quite specific. For SrF₂ at 773°K the 10,0,0 reflexion was increased in intensity above its harmonically expected value by as much as 26%. The reflexions showing the largest changes tend to be those with the lowest intensities, in the category having Miller indices summing to $4n+2$. The $4n \pm 1$ reflexions are affected least, partly because they are independent of δ_F . δ_F has a far greater influence than δ_{sr} . This is not surprising as the δ_j enter the intensity expression as

Table 6. Observed and calculated intensities for SrF₂ at 443°K (Experiment *B*)

h	k	l	<i>I</i> ₀	<i>I</i> _c	$\sigma(I_0)$	<i>y</i>	α
4	2	2	804110	838129	912	0.2713	0.0159
4	4	0	746298	788259	715	0.3161	0.0235
4	4	4	669583	709952	850	0.3971	0.0400
8	0	0	618358	643973	798	0.4641	0.0568
8	2	2	596628	619969	784	0.4922	0.0649
0	6	6	591517	620743	780	0.4918	0.0649
8	4	4	587451	596585	550	0.5397	0.0830
4	6	6	597907	591933	555	0.5306	0.0786
2	0	0	326610	315816	582	0.6458	0.0012
2	2	2	185046	185806	467	0.7977	0.0060
6	0	0	67732	68864	274	0.9281	0.0275
2	4	4	67887	69212	246	0.9278	0.0275
6	2	2	52828	51990	174	0.9466	0.0358
6	4	4	25948	23233	132	0.9769	0.0609
2	6	6	19745	17808	120	0.9824	0.0687
10	0	0	9735	7996	61	0.9923	0.0902
1	1	1	601328	564443	786	0.3664	0.0008
3	1	1	431844	411675	670	0.5394	0.0053
1	3	3	343436	341279	535	0.6260	0.0115
5	1	1	298944	297393	561	0.6804	0.0187
3	3	3	300810	302973	561	0.6743	0.0187
5	3	3	234650	233612	350	0.7589	0.0347
7	1	1	223335	221128	338	0.7756	0.0432
1	5	5	214980	216711	317	0.7800	0.0432
3	5	5	213639	213607	336	0.7858	0.0516
7	3	3	198160	199268	323	0.8038	0.0599
5	5	5	169454	168536	300	0.8356	0.0678
9	1	1	174737	175959	304	0.8300	0.0748
9	3	3	175962	175044	308	0.8359	0.0899
1	7	7	179880	178448	311	0.8328	0.0899
7	5	5	203850	202718	330	0.8114	0.0899

Table 7. Observed and calculated intensities for SrF₂ at 773°K (Experiment *B*)

h	k	l	<i>I</i> ₀	<i>I</i> _c	$\sigma(I_0)$	<i>y</i>	α
4	2	2	924412	938979	996	0.3603	0.0279
0	4	4	809272	822094	937	0.4387	0.0410
4	4	4	612068	627072	809	0.5821	0.0691
8	0	0	444141	447711	701	0.7066	0.0973
2	0	0	373306	368267	628	0.7114	0.0022
2	2	2	171060	170654	463	0.8708	0.0107
6	0	0	25641	24316	169	0.9825	0.0479
2	4	4	25995	27033	167	0.9805	0.0479
6	2	2	14317	13060	157	0.9908	0.0620
6	4	4	1476	1209	94	0.9992	0.1113
0	6	6	395641	404282	476	0.7423	0.1186
8	2	2	389543	393757	473	0.7485	0.1186
2	6	6	1624	223	95	0.9999	0.1257
4	6	6	315986	319362	617	0.8019	0.1531
8	4	4	287715	284920	435	0.8252	0.1637
10	0	0	2081	2105	96	0.9987	0.1671
1	1	1	758252	730676	885	0.4150	0.0014
3	1	1	507058	495344	743	0.6122	0.0094
1	3	3	372173	370094	640	0.7184	0.0203
5	1	1	297205	297893	587	0.7786	0.0327
3	3	3	323961	322130	605	0.7604	0.0327
5	3	3	180051	181976	606	0.8709	0.0602
7	1	1	172497	173151	464	0.8795	0.0744
1	5	5	159571	160951	448	0.8880	0.0744
3	5	5	173137	172041	460	0.8819	0.0886
7	3	3	145021	144001	318	0.9037	0.1094
5	5	5	80490	81287	262	0.9463	0.1240
9	1	1	93625	94292	269	0.9388	0.1449
7	5	5	115222	116099	305	0.9269	0.1664
1	7	7	78077	76349	271	0.9516	0.1664
9	3	3	73228	70506	377	0.9553	0.1664

Table 8. Values of refined parameters for SrF₂

Temperature (°K)	293	295	401	443	493	693	773	893
Estimated error in temperature (°K)	± 2	± 2	± 8	± 8	± 10	± 15	± 5	± 15
<i>B</i> _{sr} (Å ²)	0.567	0.576	0.753	0.845	0.941	1.368	1.612	1.930
$\sigma(B_{sr}) \times 10^{12}$ (erg Å ⁻²)*	0.011	0.021	0.018	0.013	0.025	0.027	0.009	0.045
<i>B</i> _F (Å ²)	0.846	0.878	1.112	1.251	1.450	2.208	2.397	3.026
$\sigma(B_F) \times 10^{12}$ (erg Å ⁻²)	0.013	0.024	0.022	0.019	0.028	0.030	0.014	0.051
$\alpha_{sr} \times 10^{12}$ (erg Å ⁻²)	5.63	5.58	5.80	5.71	5.71	5.52	5.19	5.04
$\sigma(\alpha_{sr}) \times 10^{12}$ (erg Å ⁻²)	0.11	0.20	0.14	0.09	0.15	0.11	0.03	0.12
$\alpha_F \times 10^{12}$ (erg Å ⁻²)	3.77	3.66	3.93	3.86	3.70	3.42	3.49	3.22
$\sigma(\alpha_F) \times 10^{12}$ (erg Å ⁻²)	0.06	0.10	0.08	0.06	0.07	0.05	0.02	0.05
$-\beta_F \times 10^{12}$ (erg Å ⁻³)	3.95	3.8†	3.32	3.49	3.7†	3.59	3.45	3.64
$\sigma(\beta_F) \times 10^{12}$ (erg Å ⁻³)	0.46	0.4	0.38	0.12	0.4	0.49	0.11	0.39
$\delta_{sr} \times 10^{12}$ (erg Å ⁻⁴)							1.30	
$\sigma(\delta_{sr}) \times 10^{12}$ (erg Å ⁻⁴)							0.75	
$\delta_F \times 10^{12}$ (erg Å ⁻⁴)							0.84	
$\sigma(\delta_F) \times 10^{12}$ (erg Å ⁻⁴)							0.29	

* $\sigma(P)$ is the standard deviation of parameter *P*.

† β_F values obtained assuming quasi-harmonic temperature dependence (Mair & Barnea, 1971).

Table 9. *Discrepancy index values*

Experiment A		Experiment B	
Temperature (°K)	R _F ²	Temperature (°K)	R _{Sr} ²
293	2.4	401	1.65
493	2.5	443	1.30
693	2.1	773	1.72
893	2.9	773	2.60*

* Agreement factor if δ_{Sr} and δ_F are omitted from refinement.

δ_j/α_j^4 [see equation (8)], which is over three times larger for the fluorine atoms than for the strontium atoms.

Consideration of the definition of the effective one-particle potential [equation (7)] will show that positive values of δ_j indicate that the j th atom is vibrating preferentially along the eight $\langle 111 \rangle$ directions. This is in contradiction to the prediction of Willis (1969), who states that such a situation is appropriate to atoms with octahedral coordination, as in the rock-salt structure. This prediction is based on the assumption that the atoms will always prefer to vibrate in directions away from their nearest neighbours, which is indeed the case for the cubic anisotropic vibration. Whilst such an assumption is justifiable for atoms having point masses and zero charge, Coulombic forces must certainly be considered for a highly ionic compound such as SrF₂. The repulsive core-core interaction will cause atoms to vibrate along $\langle 100 \rangle$ directions, towards atoms of the same species, and hence tend to make δ_j negative. Coulombic forces will inhibit such motion, causing preferred motion along $\langle 111 \rangle$ directions, towards atoms of the opposite species, with resulting positive δ_j values, as have been obtained experimentally. The experimental results therefore indicate that the Coulombic forces have greater influence on the quartic vibrations than the repulsive forces between cores.

It is true that in the case of cubic anisotropic vibration the results indicate that the repulsive forces dominate the Coulombic forces. In this case, however, the repulsive forces cause motion diametrically away from the nearest neighbours. The steric lowering of the energy is therefore much more effective than for quartic motion, which must always be centrosymmetric.

The cubic anisotropic parameter, β_F , is significant at the 0.005 level for all data above room temperature, its inclusion becoming increasingly necessary with rise in temperature for fitting the odd-index data.

It is clear from equations (8) and (9) that the temperature factor contains an isotropic quartic term, γ_j , as well as the anisotropic quartic term, δ_j , refined in the least-squares analysis of the data at 773°K. Reference to equations (11) to (14) will, however, show that this quartic term appears to first order as a change in the Debye-Waller B factor, or, equivalently, in the inversely related parameter, α_j . It is therefore not possible to refine α_j and γ_j together, as they are too highly correlated. A value for γ_j may, however, be obtained if α_j is fixed at some predetermined, harmonic value, corrected for thermal-expansion effects. This procedure was followed for KCl by Cooper & Rouse (1973). For

SrF₂, however, no theoretical harmonic values of the Debye-Waller B factors have been calculated, so that it was not possible to separate out the anharmonic contributions to the α_j or B_j values.

Theoretical values for the Debye-Waller B factors have been obtained through shell-model calculations by Elcombe (1972). These calculations use phonon-dispersion measurements and several other physical quantities, all measured at room temperature. The values obtained by Elcombe at 300°K will therefore contain the anharmonic effects incorporated into the room-temperature frequencies. These are the self-energy terms in the anharmonic Debye-Waller factor [discussed by Cowley (1961)] and correspond in the effective one-particle-potential model to the terms in γ_j/α_j^2 and β_j^2/α_j^3 occurring in equation (12).

Thermal-expansion corrections are probably included to some extent also, as the other physical quantities are room-temperature values. A direct comparison between the Debye-Waller factors obtained through our refinements of α_{Sr} and α_F at 295°K and those calculated by Elcombe at 300°K is therefore valid. The values of Elcombe are

$$B_{Sr} = 0.546 \text{ \AA}^2, \quad B_F = 0.810 \text{ \AA}^2,$$

which are, respectively, 5 and 7% lower than the values

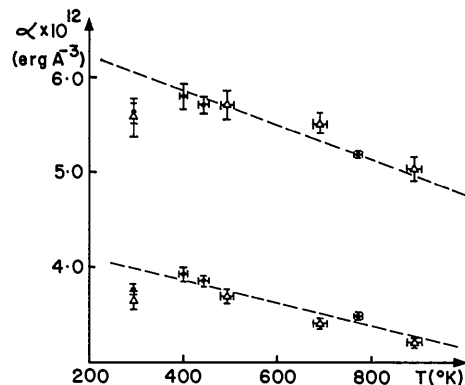


Fig. 1. Temperature dependence of α_{Sr} and α_F – Experiment A, triangles; Experiment B, circles.

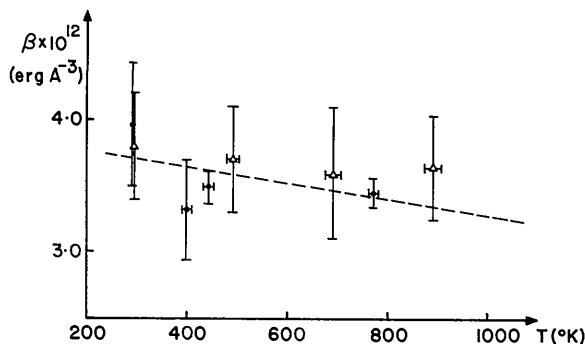


Fig. 2. Temperature dependence of β_F – Experiment A, triangles; Experiment B, circles.

obtained from Experiment *A*. Such good agreement is generally not obtained between observed and calculated Debye–Waller factors.

The refined parameters α_{sr} , α_{F} and β_{F} listed in Table 8 have been plotted against temperature in Figs. 1 and 2. The triangles distinguish the points from Experiment *A*. If we assume that γ_j is negative, as is the case for KCl (Cooper & Rouse, 1973), then we may rewrite equation (14), giving the temperature dependence of the refined α_j , as

$$\alpha_j^{\text{eff}} = \alpha_{0j} [1 - 2\chi\gamma_G \Delta T - \varepsilon_j(T)] \quad (19)$$

where $\varepsilon_j(T) \geq 0$.

If we assume for the moment that $\varepsilon_j(T)$ is zero, we are able to fit both the α_{sr} and the α_{F} curves of Fig. 1 by a straight line corresponding to a $\chi\gamma_G$ value of $1.54 \times 10^{-4} \text{K}^{-1}$, as shown. The room-temperature values lie well below this line, but this is quite consistent with what we expect as quantum effects become larger. The value of $\chi\gamma_G$ from the measurements of Bailey & Yates (1967) is, however, $0.85 \times 10^{-4} \text{K}^{-1}$. Even allowing a 12% error in our $\chi\gamma_G$ value our result is still well removed from that of Bailey & Yates. We conclude from this that the anharmonic effects described by $\varepsilon_j(T)$ are having a significant effect on the Debye–Waller factors. This was also the case in the corresponding BaF_2 results of Cooper, Rouse & Willis (1968), where a value of $1.8 \times 10^{-4} \text{K}^{-1}$ was obtained for $\chi\gamma_G$, compared with a value of $0.84 \times 10^{-4} \text{K}^{-1}$ given by Bailey & Yates.

The β_{F} temperature dependence, plotted in Fig. 2, is not as well-defined. Nevertheless, the results are consistent with the quasi-harmonic model, as shown by the line, corresponding to the $\chi\gamma_G$ of Bailey & Yates, drawn through the points. A line of gradient as steep as that describing the temperature dependence of α_{sr} and α_{F} is not consistent with the measurement. This supports the interpretation that the α_j and β_j all obey the quasi-harmonic model, but that the refined α_j values contain additional anharmonic terms.

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References

- BAILEY, A. C. & YATES, B. (1967). *Proc. Phys. Soc.* **91**, 390–398.
 BARNEA, Z. & TOWERS, G. R. (1971). *J. Appl. Cryst.* **4**, 75–76.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 COOPER, M. J. (1971). *Acta Cryst.* **A27**, 148–157.
 COOPER, M. J. & ROUSE, K. D. (1968). *Acta Cryst.* **A24**, 405–410.
 COOPER, M. J. & ROUSE, K. D. (1970). *Acta Cryst.* **A26**, 214–223.
 COOPER, M. J. & ROUSE, K. D. (1971). *Acta Cryst.* **A27**, 622–628.
 COOPER, M. J. & ROUSE, K. D. (1972). *Z. Kristallogr.* **135**, 316–317.
 COOPER, M. J. & ROUSE, K. D. (1973). *Acta Cryst.* **A29**, 514–520.
 COOPER, M. J., ROUSE, K. D. & WILLIS, B. T. M. (1968). *Acta Cryst.* **A24**, 484–493.
 COWLEY, R. A. (1963). *Advanc. Phys.* **12**, 421–480.
 CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*, Edited by J. S. ROLLETT, chap. 14. Oxford: Pergamon Press.
 DAWSON, B. (1967). *Proc. Roy. Soc.* **A298**, 255–263.
 ELCOMBE, M. M. (1972). *J. Phys. C* **5**, 2702–2710.
 GERLICH, D. (1964). *Phys. Rev.* **136**, A, 1366–1368.
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
 MAIR, S. L. & BARNEA, Z. (1971). *Phys. Lett.* **35** A, 286–287.
 POWELL, M. J. D. (1965). *Comput. J.* **7**, 303–307.
 WILLIS, B. T. M. (1969). *Acta Cryst.* **A25**, 277–300.
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.