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Intensity Averages of Plagioclase Satellites: Distribution in Reciprocal Space

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The directionality of *e* satellite intensity averages in An_{55} plagioclase was studied with the following results: the displacements of atoms responsible for *e* satellites are approximately parallel to the *b* axis, and their magnitude is greater than $\pm 0{\cdot}25$ Å. To explain the observed average intensity, only a small fraction of the atoms is needed to possess displacements of this magnitude. The character of the intensity average distribution for *e* satellites is very different from that for *f* satellites. This suggests that different atoms contribute to each group of reflections.

1. Introduction

In a previous paper Toman & Frueh (1971: hereafter referred to as T & F) have shown that the average intensity of plagioclase satellite reflections (corrected for the angular dependence of atomic scattering factors) depends approximately linearly on the square of the reciprocal lattice vector, and has a positive intercept. This was interpreted as an indication that the presence of satellite reflections is due both to atomic displacements from average atomic positions and the ordered distribution of Ca and Na cations.

This paper extends T & F's paper and its purpose is to show the strong directionality of the distribution of satellite-intensity averages and to offer an interpretation of this directionality.

2. Directionality of intensity-average distribution

2.1. The idea of examining directional properties of the intensity-average distribution of satellite reflections comes from our attempts to generalize Korekawa & Jagodzinski's (1967; hereafter referred to as K & J) model of plagioclase. This model postulates that the Na/Ca distribution among cation sites in the plagioclase structure is represented by two rectangular waves having the same wave vector, differing in phase by π, and operating on cations in such a way that the resulting supercell is face-centered. In this way, their model correctly predicts the positions of *e* and *f* satellites (for terminology, see Bown & Gay, 1958, or the brief summary of T & F), but it has two serious deficiencies when intensities are considered. According to the K & J model:

a. The average intensity (corrected for atomic factor variation) should be constant throughout the reciprocal space.

b. The intensity of both members in every satellite reflection pair should be equal.

Neither of these predictions is borne out by experiment (for *a* see T & F; for *b*, see Megaw, 1960). We attempted to remove these difficulties in a model of a modulated structure, where not only the Na/Ca distribution, but also the atomic displacements from average positions, and one unit-cell-edge length, are modulated by a rectangular wave exactly as in the K & J model.

The resulting amplitude for a satellite reflection pair is: $A(\mathbf{B}_H \pm j\mathbf{B}_T)$

$$= \{1+(-1)^j \exp(\pi i l)+(-1)^j \exp[\pi i(h+k)] + \exp[\pi i(h+k+l)]\} \times \sum_{\text{cells}} \sum_j \alpha_j (\Delta F_H \pm \frac{2\pi}{j} \mathbf{d} \cdot \mathbf{B}_H F_H^{\text{aver}}) \exp[2\pi i \mathbf{X} \cdot (\mathbf{B}_H \pm j\mathbf{B}_T)] \quad (1)$$

Here, $\mathbf{B}_H$ is the reciprocal vector, $\mathbf{B}_T$ is the wave vector of the modulation wave, α_j's are Fourier coefficients describing the form of the wave, *j*'s are integers (1 for *e* satellites, 2 for *f* satellites), $\mathbf{d}$ is a vector describing the change of the unit-cell length due to its modulation, F_H^{aver} is the average structure factor (based on average coordinates of atoms in a quarter of the unit cell: $0 \le x < 1$, $0 \le y < \frac{1}{2}$, $0 \le z < \frac{1}{2}$). ΔF_H is the 'difference' in structure factor due to modulation of positions and of atomic factors, and $\mathbf{X}$ is a position vector of the unit cell in the structure.

Expression (1) predicts the same position of satellites as in the K & J model; moreover, it satisfies the requirements from the previous section:

a. It gives intensity averages proportional to $|\mathbf{B}_H|^2$;

b. The intensity of satellite reflections in the same pair is unequal.

In addition, expression (1) suggests the directionality of the intensity-average distribution through the term containing the scalar product $\mathbf{d} \cdot \mathbf{B}_H$.

2·2. To test the prediction of equation (1), we use the intensities of satellite reflections and of *a* reflections collected during the stay of one of us (K. T.)

at the Materials Science Institute, University of Connecticut, Storrs, Connecticut. These measurements were made on a labradorite (with chemical composition corresponding to 55% anorthite, showing sharp *e* and *f* satellites) and are described in more detail by T & F. The set consists of about 2000 reflections of either *e* satellites or *f* satellites and of about 500 *a* reflections; therefore, the set is relatively small, and as such will not allow a completely unrestricted examination of the directionality of satellite-intensity distribution. For this reason, we assumed the axial form of the distribution as indicated by equation (1), and we divided the whole set of measured intensities into three subsets according to the cosine of the angle between $\mathbf{d}'$, the direction of the axis of averaging, and $\mathbf{B}_H$, the reciprocal lattice vector of each reflection ($\frac{2}{3} \leq |\text{cosine}|$, $\frac{1}{3} \leq |\text{cosine}| < \frac{2}{3}$, $0 \leq |\text{cosine}| < \frac{1}{3}$; see Fig. 1.)

In each subset, the average intensity ratio was determined as a function of $|\mathbf{B}_H|^2$ in exactly the same way as in T & F. (Average intensity ratio according to T & F is the local average of satellite intensity divided by the local average of the intensity of *a* reflections.) Because there was no *a priori* knowledge of the direction of the true **d**, calculations were performed for a number of different tentatively chosen $\mathbf{d}'$ vectors. The 011, 010, 100, 110, $1\bar{1}0$, 101, 011, $01\bar{1}$, $\bar{1}11$, and $11\bar{1}$ directions in reciprocal space were chosen as $\mathbf{d}'$ vectors. From equation (1) we can expect that when the direction of the chosen $\mathbf{d}'$ corresponds to the true **d**, the slopes of intensity-average ratio curves in the first, second, and third subset depend linearly on the squares of the average cosines corresponding to these three subsets (*i.e.*, 0·70, 0·26, 0·04). This condition was found to be reasonably well satisfied for $\mathbf{d}'$, corresponding to the b^* axis. (Considering the width of the maximum in Fig. 2, we do not need to distinguish between the direction of the *b* and b^* axes in this paper.) To demonstrate this, Fig. 3 shows not only the average intensity functions for the case where the axis of averaging coincides with the direction of displacement [Fig. 3(*a*)], but also a case where they differ [Fig. 3(*b*)]. Fig. 2 shows the stereographic projection of the intensity-average ratio for $|\mathbf{B}_H|^2 = 0{\cdot}5$ Å^{-2} observed in the first subset for different orientations of $\mathbf{d}'$, which fairly confirms the assumed axial symmetry of the directional dependence of intensity averages of *e* satellites.

The directionality of the intensity distribution of *f* satellites is also fairly definite, with maximum slope for the $01\bar{1}$ direction in reciprocal space. The average intensity of *f* satellites is less than $\frac{1}{10}$ of the average intensity of *e* satellites in our sample; therefore, the difference of directionality of *e* satellite intensity distribution and of *f* satellite intensity distribution may be caused partly, by random errors in measurements of *f* satellite intensities.

2·3. In § 2·2 we described a new experimental observation – the directionality of the distribution of intensity averages of *e* satellites. This observation was a consequence of our study of a model plagioclase, based on a modulated structure. We can ask, therefore, if the observation confirms the modulated structure model, where the unit-cell-edge length was modulated. The answer is no.

Equation (1) not only demands the directionality of intensity averages, but it also prescribes the differences in intensity between individual members of each satellite pair. According to our identification of *d* with the *b* axis of plagioclase, satellite pairs related to reciprocal lattice points *h*0*l* should have equal intensity. Table 1 shows a selection of measured intensities for *e* satellite pairs and it indicates that these intensities are far from being equal. Therefore, the observed directionality of satellite intensities cannot be attributed to the term $\mathbf{d} \cdot \mathbf{B}_H$ in (1), but its origin must be sought in the preferred orientation of atomic displacement in the superstructure.

Table 1. *Selection of measured intensities for e satellite pairs*

Closest reciprocal lattice point*	I_{e+}†	I_{e-}‡	Closest reciprocal lattice point*	I_{e+}†	I_{e-}‡
$10\bar{7}$	1·18	3·00	307	1·82	2·10
$10\bar{5}$	1·70	absent	$50\bar{7}$	2·25	absent
$10\bar{3}$	0·60	1·44	$50\bar{5}$	absent	0·35
$10\bar{1}$	absent	absent	503	0·14	absent
101	0·20	0·75	$50\bar{1}$	0·45	absent
103	2·54	1·52	501	0·13	absent
105	absent	1·70	503	absent	1·13
107	4·62	3·55	505	0·61	absent
$30\bar{7}$	3·62	0·16	507	1·76	0·40
$30\bar{5}$	1·09	4·26	$70\bar{7}$	1·77	0·95
$30\bar{3}$	0·72	1·49	$70\bar{5}$	absent	1·60
$30\bar{1}$	0·10	0·12	$70\bar{3}$	absent	0·08
301	0·40	absent	$70\bar{1}$	0·39	0·28
303	0·53	0·62	701	0·12	absent
305	0·30	0·61			

* Referred to anorthite axes
† Satellite at $h+0{\cdot}06\ k+0{\cdot}05\ l-0{\cdot}22$; relative scale.
‡ Satellite at $h-0{\cdot}06\ k-0{\cdot}05\ l+0{\cdot}22$; the same scale as for I_{e+}.

This result does not disqualify the ideas of the modulated structures in plagioclases in general; it means merely that ways other than the modulation of

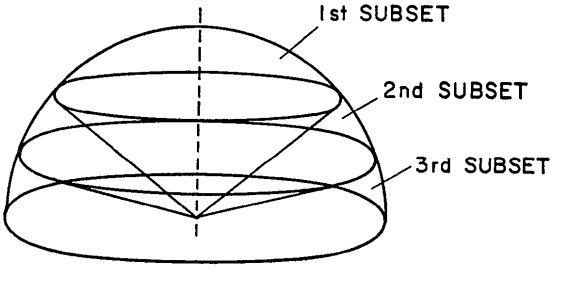

Fig. 1. Axial averaging, limits of subsets.

unit-cell-edge length must be used to obtain different intensity values for individual members in each satellite pair.

3. Directionality of atomic displacements

In the previous section, we described the directionality of intensity-average ratios found experimentally, and we concluded that they are probably related to the directionality of atomic displacements from average positions in individual subcells of the plagioclase superstructure.

To examine this idea, we use a more general model of a crystal with a superstructure such as the one discussed by T & F; the modulated structure can be considered a special case of this model. Let us start with equation (2) of T & F's paper and simplify it by expanding the exponential function, and using the fact that $\sum_{pqr} \Phi^H_{pqr}=0$. We have, for 'difference' reflections:

$$
\begin{aligned}
|F|^2 = & \sum_{jk} \exp\left[2\pi i \mathbf{B}_H \cdot (\xi_j - \xi_k)\right] \\
& \times \sum_{pqr} \sum_{p'q'r'} \delta_{pqrj}\delta_{p'q'r'k}\, \Phi^H_{pqr}\Phi^{*H}_{p'q'r'} \\
& - \frac{4\pi^2}{2!} \sum_{jk} f_j f_k \exp\left[2\pi i \mathbf{B}_H \cdot (\xi_j - \xi_k)\right] \\
& \times \sum_{pqr} \sum_{p'q'r'} |(\Delta_{pqrj} - \Delta_{p'q'r'k}) \cdot \mathbf{B}_H|^2 \Phi^H_{pqr}\Phi^{*H}_{p'q'r'} \\
& + \frac{16\pi^4}{4!} \sum f_j f_k \exp\left[2\pi i \mathbf{B}_H \cdot (\xi_j - \xi_k)\right] \\
& \times \sum_{pqr} \sum_{p'q'r'} |(\Delta_{pqrj} - \Delta_{p'q'r'k}) \cdot \mathbf{B}_H|^4 \Phi^H_{pqr}\Phi^{*H}_{p'q'r'} \ldots \qquad (2)
\end{aligned}
$$

where all symbols have the same meaning as in T & F's paper. (δ_{pqrj} is the difference of the atomic scattering factor of the jth atom site in the pqrth subcell with respect to f_j, the average atomic scattering factor associated with this site; vector $\Delta pqrj$ has similar meaning regarding the atomic displacements; Φ_{pqr} is the phase factor depending on the reciprocal lattice vector $\mathbf{B}_H$ and on the position of the origin of the pqrth cell in the superstructure, *etc.*). For further details, see T & F's paper.

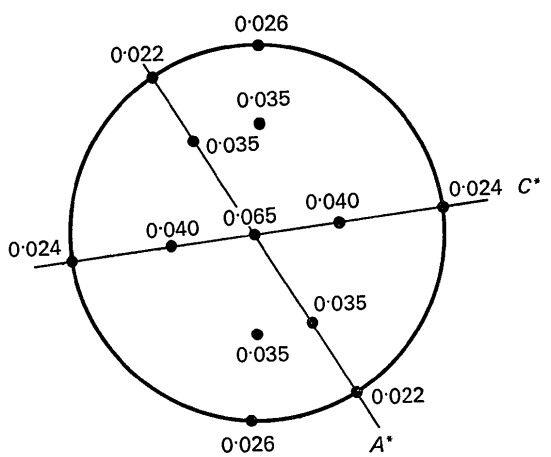

Fig. 2. The stereographic projection of the intensity-average ratio for $|B_H|^2=0{\cdot}5$ Å^{-2}, as found in the first subset for different orientations of the axis of averaging.

To compare expression (2) above with axial averages of measured satellite intensities described in § 2·2, it is necessary to perform the same axial averaging on it that was performed on the experimental set of satellite intensities (Fig. 1).

If $|\mathbf{B}_H|$ is not too small (>0·6 Å^{-1}), and if $|\xi_j - \xi_k|$ are generally greater than 2·2 Å, then the axial averaging leads to the result in which terms where $j \neq k$ can be neglected, and equation (2) changes to:

$$
\begin{aligned}
\langle I_a \rangle = & (N^2 \textstyle\sum f_j^2)^{-1} [\sum_j \sum_{pqr} \sum_{p'q'r'} \Phi^a_{pqr}\Phi^{*a}_{pqr}\delta_{pqrj}\delta_{p'q'r'j} \\
& - \frac{4\pi^2|\mathbf{B}|^2}{3!} \sum_j f_j^2 \sum_{pqr} \sum_{p'q'r'} \Phi^a_{pqr}\Phi^{*a}_{p'q'r'} |\Delta_{pqrj} - \Delta_{p'q'r'j}|^2 \\
& \times R_{pqr,\,p'q'r'j} + \frac{16\pi^4|B|^4}{5!} \sum f_j^2 \sum_{jpqr} \sum_{p'q'r'} \Phi^a_{pqr}\Phi^{*a}_{p'q'r'} \\
& \times |\Delta_{pqrj} - \Delta_{p'q'r'j}|^4 \, S_{pqr,\,p'q'r'j}] \,. \qquad (3)
\end{aligned}
$$

Here, the term $N^2 \sum_j f_j^2$ was introduced (see T & F) to scale-measured values, and to remove the dependence of intensity averages on the reciprocal vector by way of the scattering factors; furthermore,

$$
\begin{aligned}
R_{pqr,\,p'q'r'j} &= \tfrac{1}{2}A \sin^2 \Psi_{pqr,\,p'q'r'j} + B \cos^2 \Psi_{pqr,\,p'q'r'j}; \\
S_{pqr,\,p'q'r'j} &= \tfrac{3}{8}C \sin^4 \Psi_{pqr,\,p'q'r'j} + \tfrac{3}{4}D \sin^4 2\Psi_{pqr,\,p'q'r'j} \\
&\quad + E \cos^4 \Psi_{pqr,\,p'q'r'j} \,,
\end{aligned}
$$

and $\Psi_{pqr,\,p'q'r'j}$ is the angle between the vectors $\Delta_{pqrj} - \Delta_{p'q'r'j}$ and $\mathbf{d}'$, the axis of averaging. A, B, C, D, and E, which are functions of limits or subsets (Fig. 1) are given in Table 2.

Table 2. *Functions of limits or subsets*

	1st subset	2nd subset	3rd subset
A	0·79	2·22	2·89
B	2·11	0·68	0·11
C	5·11	25·11	4·68
D	8·22	8·22	1·55
E	23·44	3·44	0·01

If vectors $\Delta_{pqrj} - \Delta_{p'q'r'j}$ were distributed in all directions with equal probability, *i.e.*, $\langle \sin^2 \Psi \rangle = \frac{2}{3}$, $\langle \cos^2 \Psi \rangle = \frac{1}{3}$, $\langle \sin^4 \Psi \rangle = \frac{8}{15}$, $\langle \sin^2 2\Psi \rangle = \frac{8}{15}$, and $\langle \cos^4 \Psi \rangle = \frac{1}{5}$, then equation (2) in this paper becomes identical to equation (4) in T & F's paper. If the vectors $\Delta_{pqrj} - \Delta_{p'q'r'j}$ are preferentially clustered around direction $\mathbf{d}$, then the axial averaging where $\mathbf{d}'$ coincides with this preferred direction has the largest slope in the first subset, a medium one in the second, and the smallest slope in the third. In an extreme case, where all im-

portant $\Delta_{pqrj}-\Delta_{p'q'r'j}$ vectors are parallel with the direction of axis **d'**, the ratio of slopes would be 1:0·37:0·05. In the present case, with 010 as the axis of averaging, the slope in the first subset was found to be $15{\cdot}2\times10^{-2}$ Å^2, in the second subset $4{\cdot}8\times10^{-2}$ Å^2 and in the third subset $3{\cdot}0\times10^{-2}$ Å^2, which corresponds to the ratio of 1:0.32:0·20.

This means that in our sample of plagioclase, the directions of displacements of atoms contributing most to *e* satellites are close to the *b* axis. For comparison, let us calculate the ratio of slopes for a model, where five vectors of equal length are distributed in such a way that one points exactly along the axis of averaging, while the remaining four are at 30° to it. Using equation (3), we obtain for the ratio of slopes: 1:0·47:0·20; this, compared with the experimentally determined ratios, suggests that in our sample of plagioclase, the displacement vectors that are most important for the intensity of *e* satellites are at least as clustered about the *b* axis as in this model.

4. Interpretations

4·1. In our previous paper (T & F), we have shown that the intensity of *e* satellite reflections in plagioclase (An_{55}) is due to the ordering of Na and Ca ions in cation sites and to the displacements of atoms from averaging positions. The present paper shows that the distribution of these displacements is highly directional; most important displacements (important as contributions to *e* satellite intensity) are approximately parallel to the *b* axis.

The magnitude of these displacements can be estimated from the curvature of the average intensity-ratio function (Fig. 2). For simplicity, let us rewrite equation (3) as $\langle I\rangle=\alpha+\beta|\mathbf{B}_H|^2+\gamma|\mathbf{B}_H|^4$; if we assume that $|\Delta_{pqr}|$ are equal for all atoms in the structure (or that $|\Delta_{pqr}|$ are equal for one kind of atom and negligible for other kinds of atoms), we have the ratio of γ/β:

$$\gamma/\beta=-\frac{4\pi^2}{5}\frac{E}{B}|\Delta|^2$$

From Fig. 2 we have $\gamma/\beta=-0{\cdot}54$, which gives 0·24 Å for the $|\Delta|$ displacement.

We can arrive at the same conclusion from Fig. 3 and equation (3) in T & F's paper. The intensity averages in Fig. 3 approach the constant value, if $|B_H|$ is close to, or longer than, 1 Å. From equation (3) of T & F we see that this happens if the value of the sine is larger than π, which in turn gives $|\Delta|\sim0{\cdot}25$Å.

4·2. To interpret our results in terms of a model of plagioclase structure, let us consider 'average' structures of feldspars, which are obtained if the electron density function is calculated from *a* reflections only. By neglecting 'difference' reflections, the information about location of individual subcells is omitted and the electron density map gives the structure of an 'average' subcell, where peaks are located on average positions, and the only way the differences between individual subcells are displayed is in the form of atomic peaks.

Work in progress on two structures, An_{48} andesine by Hall, Kempster, Megaw & Taylor, and An_{28} oligoclase by Phillips & Ribbe, has been reported by Smith & Ribbe (on the basis of private communications, 1970) as showing that in both cases the Na/Ca peaks are irregular and broadened out.

More detailed information about the form of the cation peak is contained in the discussion of the albite structures by Ribbe, Megaw & Taylor (1969). Sodium peaks on electron density maps of high-albite are strongly elongated in a direction at 40° to the *b* axis. This has been interpreted as either an effect of extremely anisotropic heat motion or (which is more likely) as a manifestation of a superstructure, where disordered subcells differ (among other things) in sodium positions. The estimate of the magnitude of displacements as reported by Ribbe *et al.* (1969), depends on

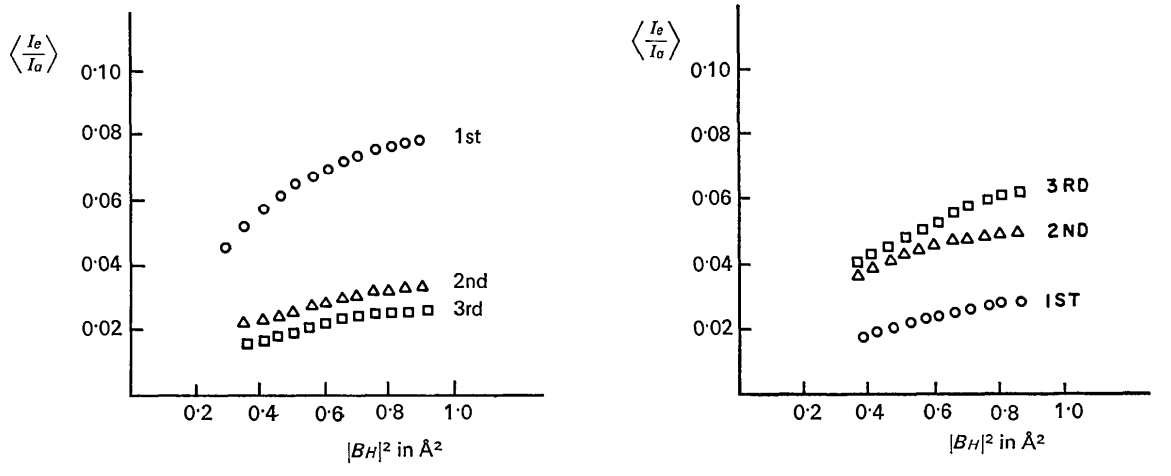

Fig. 3. Axial averaging of intensity of *e* satellites. (*a*) axis of averaging 010, (*b*) axis of averaging 100.

the method of refinement, but is close to $\pm 0{\cdot}3$ Å.

Bearing this in mind, let us now look at the results of our study of intensity averages of *e* satellites. The largest contribution to the intensity of *e* satellites comes from displacements of atoms from average positions by about 0·25 Å, and the direction of the displacement is approximately parallel to the *b* axis.

On the other hand, the examination of 'average' structures revealed that the largest distortions of atomic peaks (suggesting largest displacements of atoms from average positions in individual subcells) are associated with the cation positions. Peaks representing other atoms are considerably less affected. Also, the magnitude and direction of the cation displacement from 'average' structures roughly correspond to our findings, based on a completely different source of information.

These considerations encourage us to express what seems to us a highly plausible hypothesis: the intensity of *e* satellites comes mostly from:

a. the ordered distribution of Na and Ca cations among cation sites in subcells;

b. the ordered distribution of displacements of cations. These displacements are approximately parallel to the *b* axis and their magnitude is about $\pm 0{\cdot}25$ Å.

This is what can be derived from the statistical examination of intensities. The definition of the supercell and its subdivision into subcells can be made only from examining geometrical aspects of satellite distribution in reciprocal space. At present, two major theories deal with this equestion (Megaw, 1960; Korekawa & Jagodzinski, 1967), both correctly describing the positions of satellites and offering mechanisms for explaining changes in their position with chemical composition; but neither theory is elaborated enough to give detailed predictions of satellite intensities.

4·3. Let us return to our hypothesis expressed above, and let us try to check whether the observed value of β ($15{\cdot}2\times10^{-2}$ Å^2) can be obtained if we assume that the only contribution to *e* satellite intensities comes from cations displaced by $\pm 0{\cdot}3$ Å.

From equation (3) we have

$$\beta = -\frac{16\pi^2}{3!} f^2 B |\Delta|^2 \sum_{pqr} \sum_{p'q'r'} \Phi^a_{pqr} \Phi^{*a}_{p'q'r'} / N^2 \sum f^2.$$

Obviously, the value of the double sum depends on the distribution of displacements over subcells in the superstructure; therefore it cannot be evaluated without a detailed model of the superstructure. However, if we assume that there are only two kinds of displacements in our structure ($+\Delta$ and $-\Delta$), it can be easily shown that one extreme value of the double sum is zero and the other is $-2/\pi^2/N^2$.

Inserting appropriate values in the last equation, we have ($|\Delta|^2$ assumed at 0·09 Å^2), $\beta = \frac{16}{3}\,\frac{240}{1496}\,\frac{19}{9}\,0{\cdot}09 = 16{\cdot}2\times10^{-2}$, which shows that the observed value of the slope of the intensity-average ratio can easily be obtained if only the cations are considered to have large displacements ($\pm 0{\cdot}3$ Å).

4·4. Another problem, which is discussed briefly here, is the different character of the experimentally found intensity distributions of *e* and *f* satellites. In the case of *e* satellites, the preferred orientation of displacements is 010; the intensity-average function is strongly curved (indicating large displacements) and has a definite intercept (indicating ordering of atoms with appreciably different scattering factor). In the case of *f* satellites, the preferred orientation of displacements is close to $01\bar{1}$ (in reciprocal space); the intensity-average function is only slightly curved, its slope is relatively low (only about $\frac{1}{10}$ of the slope of intensity-average function for *e* satellites), and it has no intercept (for details, see T & F).

This apparent inconsistency of results can be readily understood by using equation (3). For *e* satellites, the set of Φ^e_{pqr} (phase factors) is different from the set of phase factors for *f* satellites. It is possible that the structure of the set of Φ^e_{pqr} and the structure of the set of large (cation) displacements $|\Delta_{pqr}-\Delta_{p'q'r'}|_{\text{cation}}$ are such that their contribution to *e* satellites is large and their contribution to *f* satellites is small; if this is true, the distribution of average intensities of *e* satellites reflects predominantly the arrangements of cations, and the distribution of *f* satellites reflects the distribution of the remaining atoms, which seems to be our case.

Proving this idea entails accepting a definite model of the supercell structure of plagioclase, which lies beyond the scope of this statistical study. On the other hand, we can easily show with a hypothetical example that the assumption presented in the previous paragraph is entirely plausible. Let us imagine the supercell consisting of a row of nine subcells (Megaw's model, very much simplified); the *f* satellites occur if the reciprocal lattice point coordinate is $n\pm\frac{1}{9}$ (where n is an integer), and the *e* satellites occur if the reciprocal lattice point coordinate is $n\pm\frac{4}{9}$. Further, let us assume that the cation displacements are distributed among nine subcells in this way: $+\Delta$, $-\Delta$, $+\Delta$, $-\Delta$, 0, $+\Delta$, $-\Delta$, $+\Delta$, $-\Delta$. For *f* satellites, the nine phase factors are: 1, $\exp 2\pi i\,\frac{1}{9}$, $\exp 2\pi i\,\frac{2}{9}$, $\exp 2\pi i\,\frac{3}{9}$, $\exp 2\pi i\,\frac{4}{9}$, $\exp 2\pi i\,\frac{5}{9}$, $\exp 2\pi i\,\frac{6}{9}$, $\exp 2\pi i\,\frac{7}{9}$, and $\exp 2\pi i\,\frac{8}{9}$. If we combine phase factors and displacements to obtain the double sum from equation (2), we get for *f* satellites:

$\sum_p \sum_{p'} \Phi^f_p \Phi^f_{p'} |\Delta_p - \Delta_{p'}|^2 = 0$. For *e* satellites, the set of phase factors is 1, $\exp 2\pi i\,\frac{4}{9}$, $\exp 2\pi i\,\frac{8}{9}$, $\exp 2\pi i\,\frac{3}{9}$, $\exp 2\pi i\,\frac{7}{9}$, $\exp 2\pi i\,\frac{2}{9}$, $\exp 2\pi i\,\frac{6}{9}$, $\exp 2\pi i\,\frac{1}{9}$, and $\exp 2\pi i\,\frac{5}{9}$, and the double sum is

$$\sum_p \sum_{p'} \Phi^e_p \Phi^{*e}_{p'} |\Delta_p - \Delta_{p'}|^2 = -66{\cdot}78\,\Delta^2.$$

5. Summary

In summary, the following appears to be experimentally well-established:

a. The intensity of the *e* satellites in an An_{55} plagioclase owes its main contributions to atomic displacements and Ca/Na ordering (shown in T & F's paper).
b. Displacements responsible for *e* satellites in an An_{55} plagioclase are preferentially oriented approximately parallel to the *b* axis (shown in § 3·1) and are larger than ±0·25 Å (shown in § 4·1).
c. To obtain the experimental value of the average intensity of *e* satellites, only a small portion of the atoms is required to have displacements as large as ±0·3 Å (shown in § 4·3).

The following hypotheses appear to be plausible:

a. Atoms displaced by ±0·25 Å in the direction of the *b* axis and contributing strongly to *e* satellites are Na/Ca cations (discussed in § 4·2 and § 4·3).
b. Na/Ca cations contribute strongly to *e* satellites but weakly to *f* satellites, which explains differences found in the intensity distribution of *e* and *f* satellites (discussed in § 4·4).

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Crystal Structure of Bis(cyclopentadienyl)beryllium at −120° *

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The crystal structure of bis(cyclopentadienyl)beryllium, $Be(C_5H_5)_2$ has been determined from X-ray diffraction photographs taken at −120°C. The crystals are monoclinic, space group $P2_1/n$, with cell dimensions $a=5{\cdot}95$ (3), $b=7{\cdot}51$ (2), $c=8{\cdot}94$ (3) Å and $\beta=92{\cdot}8$ (5)°. There are two molecules per unit cell. The final R value is 0·105. The two cyclopentadienyl rings are related by a centre to form a 'slip' sandwich. The normal distance between rings is 3·33 Å. Two alternate positions are related by a centre for the disordered beryllium atoms. The Be is π-bonded to one of the rings with all Be–C distances equal to 1·94 (4) Å. However, the Be appears to be σ-bonded to C(5′) of the other ring, with a Be–C distance of 1·81 (5) Å. This Be–C bond is normal to the plane of the ring. In the cyclopentadienyl rings, the carbon and hydrogen atoms are all coplanar, except H(5′). The observed H(5) positions suggest that the C(5′)–H(5′) bond forms an angle of about 30° with the plane, when C(5′) is σ-bonded to Be. The calculated dipole moment, based on this structure, is in good agreement with the measured values.

Introduction

The compound bis(cyclopentadienyl)beryllium was first synthesized by Fischer & Hofmann (1959). It has been found to have a dipole moment of 2·46D in benzene and 2·24D in cyclohexane (Fischer & Schreiner, 1959). Careful electron diffraction studies of the gas phase of this compound (Almenningen, Bastiansen & Haaland, 1964; Haaland, 1968) showed that the molecule is of C_{5v} symmetry, with the rings parallel and staggered. The Be atom occupies two alternative positions on the fivefold axis. However, since the structure in the solid state may not be the same as in the vapour state, and since it has been found that this compound has a very large temperature factor ($B\simeq 18$) at room temperature (Wong, Chao, Chih & Lee, 1969), a low temperature X-ray diffraction study of this compound was undertaken.

Experimental

The compound was synthesized in this laboratory by the method of Fischer & Hofmann (1959). It is very sensitive to air and moisture. Single crystals were grown in thin-walled pyrex capillaries. Usually, they grow with the [111] direction parallel to the capillary axis, but sometimes with [100] or [001].

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