

On the Origin of Plagioclase Satellite Reflections

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The theory of intensity-average ratio of 'difference' reflections is presented for a crystal having a large supercell. Its application to plagioclase satellites shows the dominant effect of atomic displacements on the intensity of satellites. The non-zero intercept on the intensity-average ratio curve suggests strongly that there is segregation of Na and Ca ions into separate subcells.

Introduction

The satellites observed on diffraction diagrams of plagioclase of intermediate composition have been the object of many crystallographic studies since their discovery by Chao & Taylor (1940). A brief review of the diffraction effects and of the terminology used in describing the effects is given in the Appendix.

At present, two theories of satellites in plagioclase diffraction patterns are prominent:

1. The stacking-fault model by Megaw (1960), where the displacements of atoms are considered responsible for satellites, and no ordered arrangement of the Ca and Na ions is postulated.
2. The modulated-structure model by Korekawa & Jagodzinski (1967), where the segregation of Na and Ca ions, and the regular fluctuations of electron density connected with it, are supposed to be the cause of satellites. In this model, atomic displacements are not considered significant.

Unfortunately, both models are based on qualitative estimates of intensity only. Korekawa & Jagodzinski claim in their paper that the normalized observed intensity of satellites depends only slightly on the Bragg angle, and they consider it as a confirmation of their model. Smith & Ribbe (1969) in their review of the plagioclase problem accept Korekawa & Jagodzinski's opinion about the intensity dependence of satellites, but point out that this can also be in agreement with Megaw's model because of the great magnitude of atom displacements in individual subcells of the latter's model.

The object of this paper is, first, to show how the intensity averages of reflections vary with the absolute value of the reciprocal vector for a crystal whose unit cell consists of a number of subcells; and, second, to compare this result with our experimental data from bytownite and labradorite.

Intensity averages

We introduce the theory of intensity averages in more general terms, because it may have application to other structural studies involving supercells.

Let us suppose that the unit cell of our crystal is a large supercell consisting of $n=n_1 \cdot n_2 \cdot n_3$ subcells. The origin of the pqr th subcell is at

$$\mathbf{r}_{pqr} = \frac{p}{n_1} \mathbf{a} + \frac{q}{n_2} \mathbf{b} + \frac{r}{n_3} \mathbf{c}.$$

where p, q, r are integers ($0 \leq p \leq n_1$ and similarly for q and r); n_1, n_2 , and n_3 are numbers of subcells along the edge of the supercell, and \mathbf{a}, \mathbf{b} , and \mathbf{c} are cell edges of the supercell. The subcells are assumed to have identical numbers of atoms and very similar structures. For instance, the position of the j th atom in the pqr th subcell is $\xi_j + \Delta_{pqrj}$, and in the $p'q'r'$ subcell it is $\xi_j + \Delta_{p'q'r'j}$, where Δ_{pqrj} and $\Delta_{p'q'r'j}$ are small compared with ξ_j . The atomic scattering factor of the j th atom in the pqr th subcell is $f_j + \delta_{pqrj}$, where f_j is the average scattering factor when the average is taken over all j th atoms in all subcells. In this way, our model is capable of expressing substitutions of atoms in different subcells.

The structure factor F_H of a reflection characterized by reciprocal lattice vector \mathbf{B}_H (subscript H symbolizes the reciprocal lattice point hkl) can be written:

$$F_H = \sum_{p=0}^{n_1-1} \sum_{q=0}^{n_2-1} \sum_{r=0}^{n_3-1} \Phi_{pqr}^{(H)} F_{pqr}^{(H)}. \quad (1)$$

Here, $\Phi_{pqr}^{(H)}$ is the phase factor, $\exp [2\pi i \mathbf{B}_H \cdot \mathbf{r}_{pqr}]$, and $F_{pqr}^{(H)}$ is the structure factor of the pqr th subcell, $\sum (f_j + \delta_{pqrj}) \exp [2\pi i \mathbf{B}_H \cdot (\xi_j + \Delta_{pqrj})]$. Let us consider the phase factors $\Phi_{pqr}^{(H)}$. It is obvious from their form that all reflections can be subdivided into n ($n = n_1 n_2 n_3$) groups according to their indices so that all reflections within a given group have the same set of phase factors. One group among them always has all phase factors equal to unity (strong, 'summation' reflections) and $n-1$ groups of reflections each satisfying the relation $\sum_{pqr} \Phi_{pqr}^{(H)} = 0$ (where summation extends over all subcells). Reflections belonging to

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these $n-1$ groups are 'difference' reflections; they are weak if the differences between subcells are small, and are absent if the structural differences between subcells disappear.

Using expression (1), the intensity of a reflection is, therefore:

$$|F_H|^2 = \sum_{jk} \left\{ \sum_{pqr} \sum_{p'q'r'} \Phi_{pqr}^{(H)} \Phi_{p'q'r'}^{*(H)} (f_j + \delta_{pqrj}) (f_k + \delta_{p'q'r'k}) \right. \\ \left. \times \exp [2\pi i \mathbf{B}_H \cdot (\xi_j - \xi_k + \Delta_{pqrj} - \Delta_{p'q'r'k})] \right\}. \quad (2)$$

Let us take the average of \mathbf{B}_H within individual groups of 'difference' reflections separately. The symbol H in expression (2), which represented indices of a reflection, is therefore replaced by a symbol of a group of reflections. As usual in similar calculations, terms with $j \neq k$ average to zero. If we further assume that vectors \mathbf{B}_H (within the spherical shell of reciprocal space in which the average is being taken) have any orientation with equal probability, we have:

$$|\bar{F}|_\alpha^2 = \sum_j \left[\sum_{pqr} \sum_{p'q'r'} \Phi_{pqr}^\alpha \Phi_{p'q'r'}^{*\alpha} (f_j + \delta_{pqrj}) (f_j + \delta_{p'q'r'j}) \frac{\sin 2\pi |\mathbf{B}_H| \cdot |\Delta_{pqrj} - \Delta_{p'q'r'j}|}{2\pi |\bar{\mathbf{B}}_H| \cdot |\Delta_{pqrj} - \Delta_{p'q'r'j}|} \right]. \quad (3)$$

Here, α means that average was taken over the α th group of reflections. As products $|\mathbf{B}| \cdot |\Delta_{pqrj} - \Delta_{p'q'r'j}|$ are assumed to be small in our type of supercell, the power series expansion for $\sin x/x$ can be used. If terms beyond the 4th power are ignored, equation (3) becomes:

$$|\bar{F}|_\alpha^2 = \sum_j \left[\sum_{pqr} \sum_{p'q'r'} \Phi_{pqr}^\alpha \Phi_{p'q'r'}^{*\alpha} (f_j + \delta_{pqrj}) (f_j + \delta_{p'q'r'j}) \right. \\ \left. + \delta_{p'q'r'j} \right] - \frac{4\pi^2 |\mathbf{B}|^2}{3!} \sum_j \left[\sum_{pqr} \sum_{p'q'r'} \Phi_{pqr}^\alpha \right. \\ \left. \times \Phi_{p'q'r'}^{*\alpha} (f_j + \delta_{pqrj}) (f_j + \delta_{p'q'r'j}) \right. \\ \left. \times |\Delta_{pqrj} - \Delta_{p'q'r'j}|^2 \right] + \frac{16\pi^4 |\mathbf{B}|^4}{5!} \\ \times \sum_j \left[\sum_{pqr} \sum_{p'q'r'1} \Phi_{pqr}^\alpha \Phi_{p'q'r'}^{*\alpha} (f_j + \delta_{pqrj}) \right. \\ \left. \times (f_j + \delta_{p'q'r'j}) \times |\Delta_{pqrj} - \Delta_{p'q'r'j}|^4 \right]. \quad (4)$$

This rather complicated expression is simplified substantially if we specify the number of subcells. To obtain better insight into its properties, let us examine two special cases: the case of a supercell consisting of two subcells, and the case of a supercell consisting of four subcells.

Two subcells in a supercell

For simplicity, $n_1=2$, $n_2=1$, $n_3=1$. Vectors determining the positions of subcells in the supercell are $\mathbf{r}_{000}=\mathbf{0}$ and $\mathbf{r}_{100}=\frac{1}{2}\mathbf{a}$. We have two groups of reflections according to phase factors: the 'summation' reflections for h even, and the 'difference' reflections for h odd (Table 1).

Table 1. Phase factors for a supercell consisting of two subcells

	Φ_{000}	Φ_{100}
h even	1	1
h odd	1	-1

Inserting Φ 's into (4), we have for 'summation' reflections approximately:

$$|\bar{F}|_+^2 = 4 \sum f_j^2 \quad (5)$$

for 'difference' reflections we have:

$$|\bar{F}|_-^2 = 4 \left[\sum_j \delta_j^2 + \frac{8\pi^2 |\mathbf{B}|^2}{3!} \sum_j f_j^2 \Delta_j^2 - \frac{128\pi^4 |\mathbf{B}|^4}{5!} \times \sum_j f_j^2 \Delta_j^4 \right]. \quad (6)$$

Intensity averages as given by equations (5) and (6) depend on the absolute value of the reciprocal vector both directly and through atomic scattering factors. Fortunately, the dependence on atomic scattering factors can be removed if we assume that $f_j = Z_j f$, where Z_j is the number of electrons in the j th atom and f is a function common to all atoms in the unit cell. The ratio of the intensity average of 'difference' reflections to the intensity average of 'summation' reflections is then:

$$\frac{|\bar{F}|_-^2}{|\bar{F}|_+^2} = \left(\sum_j Z_j^2 \right)^{-1} \left[\sum_j \Delta Z_j^2 + \frac{8\pi^2 |\mathbf{B}|^2}{3!} \times \sum_j Z_j^2 \Delta_j^2 - \frac{128\pi^4 |\mathbf{B}|^4}{5!} \sum_j Z_j^2 \Delta_j^4 \right]. \quad (7)$$

Let us discuss the meaning of equation (7). If there are no differences in the occupation of atomic positions in different subcells, and if all Δ 's are small, then the intensity-average ratio is proportional to the square of the reciprocal vector \mathbf{B} . If Δ 's are small, but some $\Delta Z_j \neq 0$ (e.g., one subcell has the j th position occupied by Na ions and the other by Ca ions), then the intensity-average ratio is linearly dependent on $|\mathbf{B}|^2$ with a non-zero intercept. If, on the other hand, Δ 's are larger, the 4th power term is no longer negligible and the slope of the intensity-average ratio decreases progressively. This is readily understandable, because if the structures of both subcells were unrelated, the ratios would be unity.

Four subcells in a supercell

Here we assume $n_1=2, n_2=2, n_3=1$. Position vectors of the subcells are $\mathbf{r}_{000}=0, \mathbf{r}_{100}=\frac{1}{2}\mathbf{a}, \mathbf{r}_{010}=\frac{1}{2}\mathbf{b}, \mathbf{r}_{110}=\frac{1}{2}(\mathbf{a}+\mathbf{b})$. In this case there are four groups of reflections: one group of 'summation' reflections for both h and k even (a reflections), and three groups of 'difference' reflections (b, c and d reflections) (Table 2).

Table 2. Phase factors for a supercell consisting of four subcells

		Φ_{000}	Φ_{100}	Φ_{010}	Φ_{110}
h even, k even	a	1	1	1	1
h even, k odd	b	1	1	-1	-1
h odd, k even	c	1	-1	-1	-1
h odd, k odd	d	1	-1	-1	1

Inserting Φ 's into (4) we have for the intensity-average ratio for b reflections:

$$\frac{|F|_b^2}{|F|_a^2} = \frac{1}{16} \left(\sum_j Z_j^2 \right)^{-1} \left[\sum_j (\Delta Z_{1j} + \Delta Z_{2j}) - (\Delta Z_{3j} + \Delta Z_{4j}) \right]^2 + \frac{8\pi^2 |\mathbf{B}|^2}{3!} \sum_j Z_j^2 [|\Delta_{1j} - \Delta_{2j}|^2 + |\Delta_{3j} - \Delta_{4j}|^2 - |\Delta_{1j} - \Delta_{3j}|^2 - |\Delta_{1j} - \Delta_{4j}|^2 - |\Delta_{2j} - \Delta_{3j}|^2 - |\Delta_{2j} - \Delta_{4j}|^2] - \frac{32\pi^4 |\mathbf{B}|^4}{5!} \sum_j Z_j^2 [|\Delta_{1j} - \Delta_{2j}|^4 + |\Delta_{3j} - \Delta_{4j}|^4 - |\Delta_{1j} - \Delta_{3j}|^4 - |\Delta_{1j} - \Delta_{4j}|^4 - |\Delta_{2j} - \Delta_{3j}|^4 - |\Delta_{2j} - \Delta_{4j}|^4]. \quad (8)$$

Similarly, the intensity-average ratio for c reflections is obtained if we interchange indices 2 and 3 in this expression.

Equation (8) leads to conclusions similar to those derived from (7), but here there is one important difference. The presence or absence of an intercept on the intensity-average ratio plot depends not only on the separation of atoms into different subcells, but, for a particular group of 'difference' reflections, also on the manner in which they are distributed among four subcells. For instance, let us assume that the j th atom in subcells 1 and 2 is Na and in subcells 3 and 4 it is Ca. Then, the intensity-average ratio of b reflections has an intercept, whereas the intensity-average plots for c and d reflections have zero intercepts. By the same token, slopes also can be different for different groups of reflections.

Experimental study of intensity-average ratio

Bytownite

We decided to verify our theoretical results on bytownite, because its crystal structure was studied in detail by Fleet, Chandrasekhar & Megaw (1966) and can be assumed to have been solved. Our measurements of integrated intensity were performed on a Picker

automatic diffractometer with Mo $K\alpha$ radiation. Limits of collecting data were set at $2\theta \leq 90^\circ$; measurements were performed in ω -scan using a graphite crystal monochromator and an amplitude analyzer. Integrated intensities were corrected for Lorentz and polarization factors; absorption correction was not computed because in average-intensity ratios its influence cancels out. The 080 reflection was used as a standard throughout all measurements.

The crystal fragment used had an approximate cubic shape with an edge about 0.05 mm long. The diffraction pattern consisted mostly of a reflections ($h+k$ even, l even) and b reflections ($h+k$ odd, l odd). Only

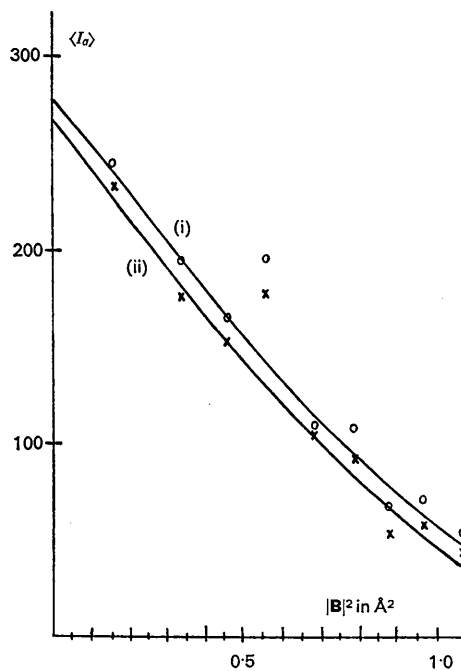


Fig. 1. Intensity averages of a reflections; (i) bytownite, (ii) labradorite.

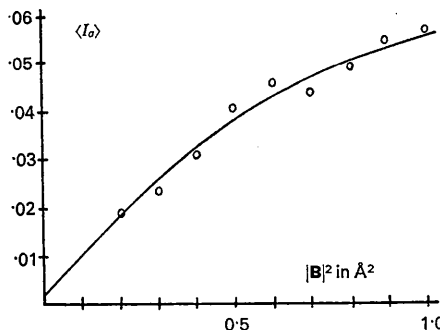


Fig. 2. Intensity-average ratio for b reflections of bytownite; experimental points and a curve fitted by the least-squares method.

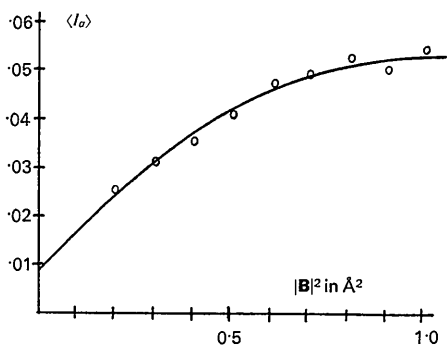


Fig. 3. Intensity-average ratio for e satellites of labradorite; experimental points and a curve fitted by the least-squares method.

a few, very diffuse c reflections ($h+k$ even, l odd) were observed. The chemical composition of the fragment has not yet been determined by chemical analysis, but from the lattice parameters and the general properties of the diffraction pattern, its composition is expected to be close to 80% anorthite.

In our measurements, both a reflections and b reflections were measured. The a reflections were strong and represent the 'summation' group of reflections; b reflections were generally weaker and represent the 'difference' group of reflections. The c reflections are not included in this paper because their number is so limited (only three) that they do not represent a statistically meaningful set. As can be seen from Fig. 1, the average intensity of a reflections deviates from an ideal smooth curve. In the subsequent measurement of labradorite intensities, we observed almost exactly the same deviations; therefore, we conclude that these deviations are not caused by errors in measurements, but by structural properties of subcells. As the best representation of $\sum f_j^2$, we therefore took the smoothed values of intensity averages of a reflections in both cases. From this smoothed curve and from our intensity averages of b reflections, the ratios were computed. Their dependence on $|B|^2$ is shown in Fig. 2.

The curve has the form expected from our theoretical calculations and from Megaw's structure. The intercept, slope, and the coefficient at $|B|^4$ of the experimental curve were determined by least-squares methods and are shown in Table 3. The model given by Megaw leads to $0, 8.2 \times 10^{-2}$ and -0.8×10^{-2} for intercept, slope, and the coefficient at $|B|^4$, respectively. The difference in the intercept is probably insignificant; agree-

ment between slopes is fairly good, but the agreement between coefficients at $|B|^4$ is only qualitative. This may be attributed to the 'out-of-step' nature of bytownite. In our computation of coefficients, we simplified the Fleet *et al.* model and considered bytownite as composed only of two subcells where atomic positions related by $\frac{1}{2}(a+b+c)$ were averaged. On Δ 's obtained in this way, our formula from the preceding section was applied.

Labradorite

Similar measurements were performed on a crystal of labradorite from Labrador, Canada (Collection of the Department of Geology, University of Connecticut, Storrs). Its diffraction pattern exhibited, in addition to a reflections, a set of sharp, strong e satellites and a set of slightly more diffuse and weaker f satellites. In a separate study, the form and position of f satellites were measured for the same crystal. The results (0.125, 0.102, -0.438 , expressed as fractions of a conventional reciprocal unit cell of anorthite) compared with Table 1 of Megaw (1960, p. 159) indicate the composition of the crystal as being close to 55% anorthite.

The technique of intensity measurements here was exactly the same as used on bytownite. Results are given in Figs. 1, 3 and 4. In Table 3, intercepts, slopes and coefficients at $|B|^4$ together with standard deviations are given as determined by least-squares methods for e and f satellites.

Let us consider first the intercepts. The intercept of the e satellite curve is fairly large and, with regard to its standard deviation, it can probably be considered as significant. If we assume the chemical composition as being close to 50% anorthite, the maximum theoretical value of the intercept is $16:1496 = 1.07 \times 10^{-2}$, and, as can be shown, it does not depend on the number of subcells in the supercell.

Agreement between this value and our experimental value is not perfect, but we see that the experimental value is of the right magnitude. The obvious interpretation is that an ordered arrangement of Na and Ca ions is present in our sample. The fact that for f satellites the intercept is negligible does not contradict this conclusion because, as we have shown earlier, even when complete separation of atoms in subcells takes place, some groups of 'difference' reflections do not have intercepts in the plot of intensity-average ratio.

The slope for e satellites is comparable with the slope observed for bytownite; for f satellites it is about 10 times smaller.

Table 3. Resulting intercepts, slopes, and coefficients at B^4 as determined by least-squares methods.

Substance	Type of reflections	Standard deviations are in brackets.		
		Intercept	Slope	Coefficient at B^4
Bytownite	b	0.17 (0.48)	8.90 (1.78)	3.58 (1.46)
Labradorite	e satellite	0.85 (0.39)	8.63 (1.46)	4.09 (1.20)
Labradorite	f satellite	0.04 (0.10)	0.69 (0.40)	0.02 (0.32)

(multiply all values by 10^{-2})

Conclusions

The results of our statistical examination of intensity-average ratios of e and f satellites of a labradorite crystal can be summarized as follows:

1. There is little doubt that atomic displacements of the same order of magnitude as in bytownite are present in the labradorite and are the main cause of e and f satellites.

2. The presence of the intercept of reasonable magnitude in the plot for e satellites indicates segregation of Na and Ca ions in our sample.

3. The method of intensity-average ratios enables us to obtain information about the segregation of atoms in plagioclase in a simple way, unbiased by prior assumptions about the nature of disorder. Therefore, it seems worthwhile to repeat these measurements on other samples of plagioclase exhibiting e satellites.

APPENDIX

The X-ray diffraction effects produced by the plagioclase feldspars are best summarized in the paper by Bown & Gay (1958). They describe six groups of reflections: a , b , c and d reflections, which have integral indices in an anorthite-like reciprocal lattice, and the e and f reflections which are satellites whose positions depend upon the chemical composition but cannot be expressed by integral indices.

The reflections a , b , c and d are defined as follows:

a	have $h+k$ even	l even
b	have $h+k$ odd	l odd
c	have $h+k$ even	l odd
d	have $h+k$ odd	l even.

Monoclinic, C -centered feldspars have only a reflections; a and b reflections are present in body-centered triclinic feldspars, and primitive anorthite exhibits reflections from all four groups.

Satellites occur in pairs centered about the a reflections or the b reflections of the anorthite-like reciprocal lattice. The e satellites are centered about the b reflec-

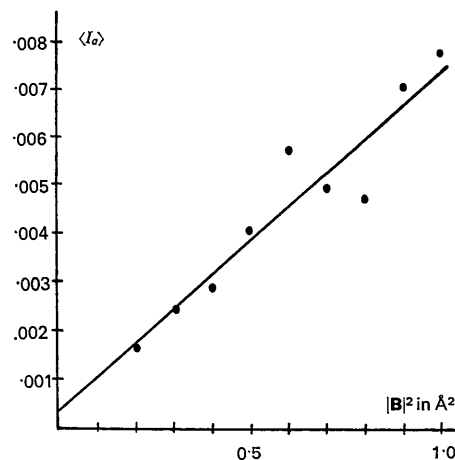


Fig. 4. Intensity-average ratio for f satellites of labradorite; experimental points and a curve fitted by the least-squares method.

tions; f satellites are those centered about the a reflections. The vector separating the f satellites in a given pair has exactly the same orientation, but twice the magnitude, of the similar vector between a pair of e satellites.

There is no obvious pattern to the variation of satellite intensity throughout the reciprocal space, and neither the Megaw nor the Korekawa-Jagodzinski model is adequate to interpret this variation.

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