In conclusion, it is of importance to note that the proposed method can be readily extended to the cases when the form factors of atoms composing the crystal differ considerably. The improvement of the method would just require the introduction of several density functions for each type of atom and additional computer time.

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A New Type of Satellite in Plagioclases

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Abstract

A new type of satellite has been observed in plagioclases $Ca_xNa_{1-x}[Al_{1+x}Si_{3-x}O_8]$ with $0.5 \le x \le 1$. Their intensities are such that they could be observed only by applying a special focusing technique. They appear in the neighbourhood of some strong reflections with $h + k = 2n$, $l = 2n$. It is shown that the new satellites are most probably caused by a three-dimensional array of domains of two structures, differing only by small displacements of the atoms. Since the translation lattices of the two structures have the same geometry it is concluded that the two structures are twins of an acentric plagioclase correlated with a centre of symmetry. The size of the domains is 80 Å approximately. The diffraction of such submicroscopically intergrown twins is calculated for lamellae and blocks and compared qualitatively with the experimental results. The approximate periodicity of the domains could be destroyed by very long exposure to X-rays.

Introduction

It is well known that plagioclases $Ca_xNa_{1-x}[Al_{1+x}Si_{3-x}O_8]$ exhibit a continuous range of miscibility at high temperatures and tend to unmix at low ones. Since two diffusion processes govern the dynamics of this exsolution the various intermediate stages of unmixing are characterized by complicated structures, forming very complex arrays of domains which will be described here only briefly. With the generally adopted notation for indices with respect to the structure of pure anorthite with $a = 8.18$, $b = 12.88$, $c = 14.17$ Å, $a = 93° 10'$, $\beta = 115° 51'$, $\gamma = 91° 13'$, we call

a reflections $h + k = 2n$, $l = 2n$,
b reflections $h + k = 2n + 1$, $l = 2n + 1$,
c reflections $h + k = 2n$, $l = 2n + 1$,
d reflections $h + k = 2n + 1$, $l = 2n$.

In the composition range $0.5 \le x \le 0.8$ the following types of satellites have been described by Bown & Gay (1958) while supersatellites have been found by Jagodzinski & Korekawa (1965): e satellites

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accompany b reflections (sometimes extinguished), f satellites in the neighbourhood of a reflections, and supersatellites very near to a reflections. The supersatellites correspond to long periodicities with a repeat near to the optical wavelengths and apparently are correlated with the so-called 'Schiller' effect of plagioclases (see Nissen, Eggman & Laves, 1967). A lengthy discussion on the interpretation of e and f satellites has taken place in the literature, ending in various structural proposals by Megaw (1960), Korekawa & Jagodzinski (1967), Smith & Ribbe (1969), Toman & Frueh (1976), Cinnamon & Bailey (1971), Kitamura & Morimoto (1977) and Jagodzinski & Korekawa (1976). Korekawa, Horst & Tagai (1979) performed a structure determination with the e satellites of labradorite, based on the model of Jagodzinski & Korekawa (1976), with the result that the observed and calculated intensities (including extinctions!) agreed. All other models do not obey the extinction rules observed and can have no more than qualitative significance.

In this paper we report on a completely new type of satellite, which is very weak and nearly independent of the chemical composition. So far the satellites have been observed in the composition range $0.5 < x < 1.0$, but it cannot be excluded here that they also occur for $x < 0.5$. These satellites are observed in the vicinity of a reflections and do not show any correlations with the f satellites and supersatellites also accompanying the a-type reflections. Unfortunately, no crystals of the desired quality were available for this extended study.

Experimental results

Crystals of some known and unknown locations including lunar specimens were carefully selected from the bulk material (Table 1). All diffraction pictures were taken by applying a technique described earlier by one of us (Jagodzinski, 1968), allowing for photographs of either high resolution or high intensity. Fig. 1 shows a typical diffraction pattern of the new satellites around the a reflection $0\bar{4}0$ of a plagioclase with $x = 0.7$. This photograph is extremely overexposed and was taken in the high-intensity setting of the X-ray camera. The strong reflection $1,3,\overline{16}$ at high diffraction angles on the left-hand side does not show any indication of the same type of satellite, even if the crystal is rotated from one photograph to the next by very small steps. Most of the pictures were taken with this stepwise rotation around $[100]$, $[\bar{1}00]$ or $[001]$. A typical set of photographs for the reflections 040 and 004, showing the satellites with optimal intensity, is given in Fig. 2. It should be kept in mind that with this technique the reflections 040 and 004 can be cut in four different orientations by the Ewald sphere if one pair of orientations (opposite directions!) is used only; two of

Table 1. *Samples of plagioclases for which the new type of satellite has been observed*

It should be pointed out that the satellite reflections appear in a small angular range. Since oscillation pictures taken at small oscillation angles do not show the satellites the Noromosic technique had to be applied in very small steps and at low angles of aperture of the monochromator. (For that reason the list is incomplete.)

Sample number	Composition (x)	Origin; location	Reflections with satellites
32	0.50	Professor Laves; unknown	040
Sta. Mü.	0.52	Unknown	$0\bar{4}0$
N21	0.585	Valle d'Ossola, Italy	$08\bar{8}$
N103	0.697	Søgnefjord, Norway	$13\bar{2}, 0\bar{4}0$
1447	0.70	Valle d'Ossola, Italy	$0\bar{4}0$
K12	0.75	Professor Laves; India	040
N26	0.786	Valle d'Ossola, Italy	040 $[\bar{1}00]$, 040 $[001]$
75035·49	0.80 ⎫	Lunar sample	$04\bar{2}, 042$
75035·82	0.80 ⎭	75035	040
75075·17	0.80	Lunar sample 75075	066
N23b	0.849	Unknown	$08\bar{0}$
K7 (?)	0.975	Monte Somma, Italy	$004, 0\bar{4}0$
K1	0.98	Minillo, Japan	$0\bar{4}0$
K4	1.0	Pasmeda, Italy	040

them are generated by bringing 040 into the reflection position through rotation around $[100]$ either on the right-hand side or on the left-hand side (alternately $0\bar{4}0$ on the same side). The other two are realized in the same way by changing the direction of the rotation axis from $[100]$ to $[\bar{1}00]$. (The structure has no plane of symmetry!) It should be noted that the pattern of satellites shows two planes of symmetry in spite of the low $\bar{1}$ symmetry of the plagioclases. Deviations are mainly due to a slight misorientation causing a relative displacement of the Bragg peak and its satellites.

Fig. 2 clearly shows the diffraction picture of diffuse planes which contain diffuse streaks and reflections (Figs. 2a–f). Fig. 3 displays a photometer record of the
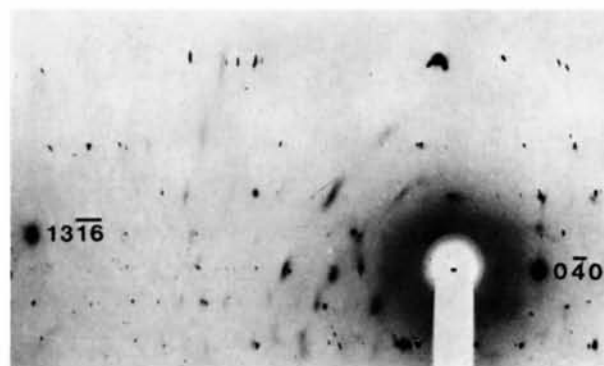

Fig. 1. Diffraction picture of a plagioclase crystal ($x = 0.7$), showing part of the satellite pattern around the reflection $0\bar{4}0$ (right-hand side). Note that the strong reflection $1,3,\overline{16}$ on the left-hand side is not showing any satellite pattern. (Magnification 1 : 0.68.)

reflection $0\bar{4}0$ given in Fig. 2(b), where only six of the eight reflections recorded in Fig. 3 are to be seen.

The reciprocal coordinates of the reflections cannot be given very exactly since all of them are diffuse and it is difficult to determine the maximum of the intensity very accurately in a method taking stepwise diffraction pictures. Table 2 shows these reciprocal coordinates being fairly accurate for h, reasonable for
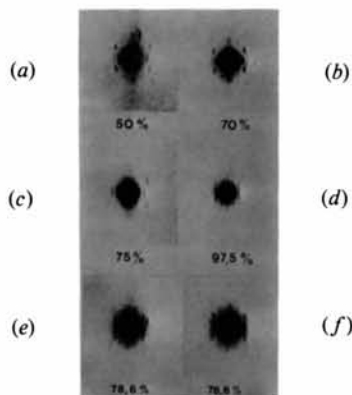

Fig. 2. Satellite pattern of reflections 040 and $0\bar{4}0$, (a),(b),(c),(e),(f), in various orientations of the reciprocal lattice and 004, (d), as a function of the chemical composition. It should be noted that the patterns do not change much more in samples with the same chemical composition when compared with those differing in concentration x: (a) $x = 0.5$, 040 [100]; (b) $x = 0.7$, $0\bar{4}0$ [100]; (c) $x = 0.75$, $0\bar{4}0$ [100]; (d) $x = 0.975$, 004 [$\bar{1}$00]; (e) $x = 0.786$, 040 [$\bar{1}$00]; (f) $x = 0.786$, 040 [001]. (Magnification 1:4.)
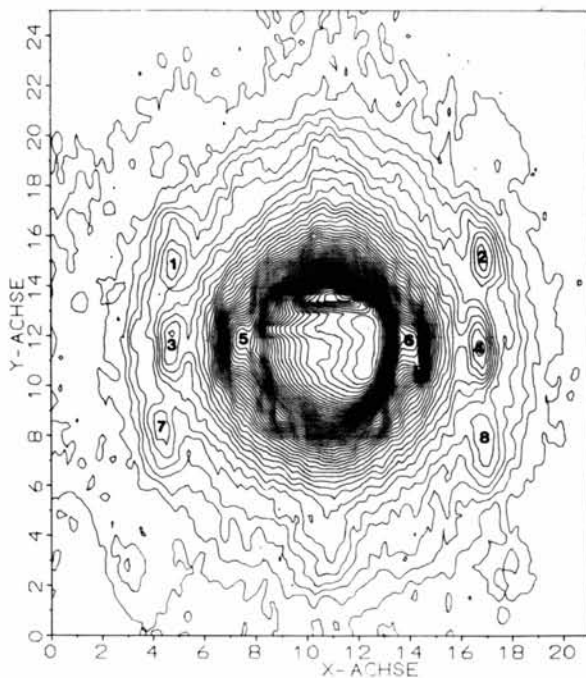

Fig. 3. Photometer record of the photograph given in Fig. 2(b).

Table 2. Determination of reciprocal coordinates of satellites as given in Fig. 3

k' is the coordinate with $0\bar{4}0$ as origin (relative position to main reflection).

Number of satellite	h	k	k'	l
1	0.13	−3.69	+0.31	−0.03
2	0.13	−4.30	−0.30	−0.18
3	0	−3.72	+0.28	+0.07
4	0	−4.28	−0.28	−0.08
5	0	−3.83	+0.17	+0.04
6	0	−4.17	−0.17	−0.04
7	−0.13	−3.69	+0.31	+0.17
8	−0.13	−4.30	−0.30	+0.01

k, but having a possible uncertainty as far as l is concerned. Consequently, it cannot safely be excluded that all reflections have their maximum a little bit displaced such that they belong to a common reciprocal plane passing through the reflection $0\bar{4}0$. This reciprocal plane would correspond roughly to the direction [$3\bar{1}4$]. Figs. 2(a) and (c) show – due to a small misadjustment – a deviation from the vertical plane of symmetry; in both pictures a clear elongation of the reflections numbered 3 and 4 in Fig. 3 is to be seen. Furthermore, the positions of the reflections 1, 2, 7, 8 are distinctly displaced without violating the horizontal plane of symmetry (vertical to [100]), which is not a plane of symmetry of the plagioclase structure. Table 1 shows a review of reflections where satellites of the new type could be detected, but this list is far from being complete, since only a fraction of several thousand a reflections could be checked with the time-consuming Noromosic technique. A comparison of many samples selected from the various locations revealed that only a few crystals displayed the complicated structure of satellites as shown in Figs. 2(a)–(f). Often the pair 5 and 6 (or 3 and 4) were observed only.

After a three months exposure with strictly monochromatic Cu $K\alpha_1$ radiation the superstructure of satellites vanishes, as shown in Fig. 4, where the diffraction picture of both the virgin crystal (a) and the irradiated crystal ($x = 0.7$) (b), is given. This seems to be very important for the structural interpretation of the satellites.

Interpretation

Since the new satellites occur at a distance (shortest) corresponding to $6b \simeq 80$ Å, they should be observable in low-angle diffraction pictures with moderate resolution. Pictures of this kind have been taken by Korekawa (1980), but no satellites of the new type have been reported so far. From this and the sensitivity to X-ray irradiation it may be concluded that small

atomic displacements rather than two superstructures of Ca,Na atoms, different in composition, are the real cause of the satellites. Two or more types of domain with the same lattice geometry have to be introduced in order to explain the unchanged geometry of the translation lattice (sharp *a* reflections!). The most probable structural model meeting these conditions is the following one.

Let us assume that the plagioclases in the composition range considered here are non-centrosymmetric and all samples are submicroscopically twinned according to the twin law of the centre of symmetry. Since the translation group is centrosymmetric the lattice of both structures would not even change its orientation, as holds for other twin laws. The question as to whether an intergrowth of the two twin structures would not lead to an unfavourable lattice energy may easily be answered for complicated lattices: If only one part of the structure is asymmetric and the atoms are situated near planes (which may be highly indexed) of the lattice, forming a closed body, these planes may

(a)

(b)

Fig. 4. Effect of X-ray radiation damage on the satellites: (a) before X-ray exposure (magnification 1:2·2); (b) after three months exposure to monochromatic (1·54 Å) X-rays (magnification 1:2·2).

become a plane of intergrowth with practically identical structures at the planes of intergrowth. As long as only small displacements of atoms are necessary to convert the structure *P*1 to its twin *P*1′, a strain field may transform the structure *P*1 into *P*1′ and *vice versa*. Since all plagioclases (pure anorthite included) are governed by internal strains, the submicroscopical twinning seems to be normal. A very regular arrangement of domains needs some additional assumptions. One possible explanation could be the so-called 'critical nucleus' which may prevent the submicroscopically twinned structure from being dissolved, another explanation might be derived from the assumption that certain asymmetric defects of the structure favour one of the two twins.

As pointed out earlier by Jagodzinski & Korekawa (1973), X-ray diffraction by any arrangement of two different intergrown structures having the same translation lattice may be derived as follows. We introduce the functions

$g(x,y,z) =$ lattice of δ functions representing the translation lattice of both structures,

$f_1(x,y,z)$, $f_2(x,y,z) =$ electron distribution function of the structures *P*1, *P*1′, respectively,

$t(x,y,z) =$ distribution function of domains of the structure *P*1. $1 - t(x,y,z)$ is the corresponding distribution function for *P*1′.

Now the electron distribution function $a(x,y,z)$ is given by (* represents the convolution operation)

$$a(x,y,z) = [g(x,y,z)\,t(x,y,z)] * f_1(x,y,z)$$
$$+ \{g(x,y,z)[1 - t(x,y,z)]\} * f_2(x,y,z),$$

and replacing t and $1 - t$ by

$$t(x,y,z) = \tfrac{1}{2} + \tfrac{1}{2}t'(x,y,z), \qquad (1)$$
$$1 - t(x,y,z) = \tfrac{1}{2} - \tfrac{1}{2}t'(x,y,z),$$

we get

$$a(x,y,z) = g(x,y,z) * \tfrac{1}{2}[f_1(x,y,z) + f_2(x,y,z)]$$
$$+ g(x,y,z)\,t'(x,y,z) * \tfrac{1}{2}[f_1(x,y,z) - f_2(x,y,z)]. \qquad (2)$$

Introducing the Fourier transforms $A(h,k,l)$, $G(h,k,l)$, $T'(h,k,l)$, $F_1(h,k,l)$, $F_2(h,k,l)$, corresponding to functions in crystal space represented by the corresponding small letters, we can calculate the diffraction pattern given by the distribution (2)
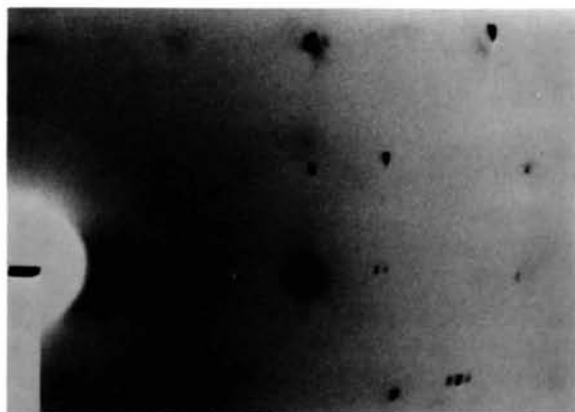
$$A(h,k,l) = G(h,k,l)\,\bar{F}(h,k,l)$$
$$+ [G(h,k,l) * T'(h,k,l)]\,\Delta F(h,k,l), \qquad (3)$$

where

$$\bar{F}(h,k,l) = \tfrac{1}{2}[F_1(h,k,l) + F_2(h,k,l)]$$
$$\Delta F(h,k,l) = \tfrac{1}{2}[F_1(h,k,l) - F_2(h,k,l)].$$
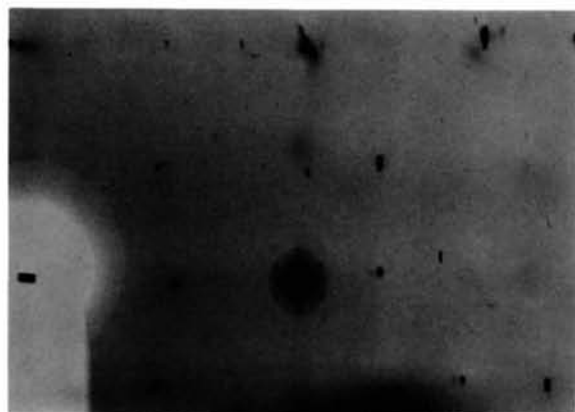
The first term in (3) describes the sharp reflections, the structure factors of which are given by the average of the two structures; the second term gives, on account of the convolution operation of the reciprocal lattice G with T' diffuse reflections, or satellite reflections if $t'(x,y,z)$ has some periodicities. It should be pointed out that $\int t'(x,y,z)\,dx\,dy\,dz = 0$ in the case of equal volumes of each type of domain. As a consequence, no contribution of the second term in (3) to sharp reflections is to be expected in this particular case, which seems to be typical for our model of a crystal twinned submicroscopically.

Let us now calculate some cases for periodical domain structures that might be relevant to our problem. As has been pointed out above, any twin problem is a question of boundary energies. As long as only one such boundary exists a lamellar arrangement of domains parallel to the interface of lowest energy will be realized. Two conditions determine a favourable boundary: (1) The congruence of the lattice at the face of intergrowth; (2) the topology of the two structures at the boundary. Now we consider the diffraction of a crystal containing two types of lamellae, N_1, N_2 and unit cells with structure factors F_1, F_2, respectively. Let $\mathbf{a}$ be the vector normal (or nearly normal) to the boundary, we have

$$A(h,k,l)$$

$$= R\left(\bar{F}\,\frac{\sin \pi N(N_1 + N_2)\,h}{\sin \pi h}\right.$$

$$+ \Delta F\,\frac{\sin \pi N(N_1 + N_2)\,h}{\sin \pi(N_1 + N_2)\,h}$$

$$\left. \times \left\{ -i\,\frac{\exp\left[i\pi(N_1 - N_2)\,h\right] - \cos \pi(N_1 + N_2)\,h}{\sin \pi h}\right\}\right).$$

$$(4)$$

R represents the two-dimensional lattice in reciprocal space according to the periodic structure parallel to the lamellae (vectors $\mathbf{b}$, $\mathbf{c}$), N is the total number of lamellae.

In accordance with (3), the first term describes the sharp main reflections (h = integer), while the second one gives the satellites at the positions $h = v/(N_1 + N_2)$, where v is an integer; the term in curly brackets also determines the structure factors of the satellites and becomes

$$-i\,\frac{\exp\left[i\pi v(N_1 - N_2)/(N_1 + N_2)\right] + (-1)^{v+1}}{\sin \pi v/(N_1 + N_2)}.\quad(5)$$

This gives the solutions, for v even,

$$\left[2\,\frac{\sin \pi vC}{\sin \pi v/(N_1 + N_2)}\right] \text{ with } C = \frac{1}{2}\frac{N_1 - N_2}{N_1 + N_2},\quad(6a)$$

and, for v odd,

$$\left[-2i\,\frac{\cos \pi vC}{\sin \pi v/(N_1 + N_2)}\right].\quad(6b)$$

In the case $N_1 = N_2$ we have $C = 0$ and the term in (6a) vanishes, which means that even satellites are extinguished if $v \neq 0$. As long as $v \ll N_1 + N_2$, the intensity of the satellites becomes approximately

$$\frac{(N_1 + N_2)^2}{\pi^2}\frac{1}{v^2}\,|\Delta F|^2,\quad(6c)$$

indicating a rapid decrease with increasing order of the satellites. Naturally, the domain structure is not strictly periodic and one may imagine that an additional statistic breaks the extinction rule given in (6a). Furthermore, it can be shown that $\bar{F}$ also contributes to the structure amplitudes of satellites in the non-periodic case.

That extinction rules govern the diffraction pattern may easily be shown in the simple model where the domains are blocks of equal size (N_1, N_2, N_3 = number of unit cells in the block) and have a periodically alternating arrangement in three translation directions (a kind of NaCl structure of two kinds of domains). The model gives the following structure amplitudes:

$$A(h,k,l) = \frac{\sin \pi(2N_1)Nh}{\sin \pi(2N_1)\,h}\frac{\sin \pi(2N_2)\,Nk}{\sin \pi(2N_2)\,k}$$

$$\times \frac{\sin \pi(2N_3)\,Nl}{\sin \pi(2N_3)\,l}$$

$$\times \left\{\frac{\sin \pi N_1\,h}{\sin \pi h}\frac{\sin \pi N_2\,k}{\sin \pi k}\frac{\sin \pi N_3\,l}{\sin \pi l}\right.$$

$$\times [1 + \exp 2\pi i(N_1\,h + N_2\,k)$$

$$+ \exp 2\pi i\,(N_1\,h + N_3\,l)$$

$$+ \exp 2\pi i(N_2\,k + N_3\,l)]$$

$$\left.\times [(\bar{F} + \Delta F) + (\exp 2\pi iN_1\,h)(\bar{F} - \Delta F)]\right\}$$

$$= R\{B \times [S] \times [F]\}.\quad(7)$$

N is the number of supercells in the three translation directions. The first factor R in (7) yields maxima for

$$h = \frac{v_1}{2N_1},\quad k = \frac{v_2}{2N_2},\quad l = \frac{v_3}{2N_3}.$$

Since the factor in the first square bracket, S, is 4 or 0 according to a face-centred extinction rule, v_1, v_2, v_3 are all even or all odd.

Again, the factor B is 0 when all v_i are even, $v_1 = v_2 = v_3 = 0$ excepted. If v_i are odd, then

$$A(h,k,l) = \left(\frac{2}{\pi}\right)^3\frac{N_1 N_2 N_3}{v_1 v_2 v_3}8\Delta F(h,k,l).\quad(8)$$

This again confirms the extinction rule and the decrease of intensities with increasing v_i in agreement with the lamellar model.

From (7) it becomes evident that the diffraction of a periodic, or almost periodic, three-dimensional array of domains based on the same translation lattice is a kind of resonance phenomenon of the two terms R and B. R determines the position of the satellites, one of them coinciding with the reflections of the strictly ordered sublattice (main reflection). This reflection has the structure factor $\bar{F}$ corresponding to the averaged structure of the two structures of domains. $B\Delta F$ determines the structure factor of the remaining satellites. Since B has secondary maxima and minima, and even zeroes which are strongly dependent on the dimensions of the domains, and ΔF does not vary rapidly when compared with B, the diffraction pattern may be very complex if the array of domains is disordered. As long as R is based on a strictly periodic superstructure, the satellite pattern around each main reflection should be equivalent. In the nonperiodic case the maxima given by R become diffuse and a typical resonance behaviour with displacements of satellites and a change of their intensity has to be expected.

Fig. 5 shows the behaviour of B for the three-dimensional block model in the first 'zone' of diffuse scattering, schematically displaying diffuse planes and rods, or peaks, respectively, at the intersections of the maxima of the three subterms of B according to (7). It may well be that a similar plane is given by the reflections 1, 2, 7 and 8 in Fig. 3 (compare Figs. 2a–c); if this were true, the diffuse plane should produce a 'ring', which seems to be present in Fig. 2(c). The different sections through the main reflections 040 and 004 given in Figs. 2(d)–(f) display very clearly the diffuse planes, most probably due to deviations from the strictly periodic superlattice of the domains in the third translation direction. Since $\mathbf{c}$ is nearly normal to

b, the diffuse planes cut the Ewald sphere nearly vertically in Fig. 2(d) and produce diffuse streaks. The distance of the diffuse streaks yields a second domain size, again about 80 Å. The existence of more than the four maxima described above indicates that there are more than three pairs of boundaries. Obviously diffraction in this particular case will become more complex, although the general decrease in intensity should remain unaffected. The calculation of the shape factor B according to (7) is not easy, and we do not intend to give a more general calculation of diffraction patterns as long as sufficiently reliable experimental data are not available for comparison with adequate theoretical models. Fig. 6 shows some possible models demonstrating the difficulties to be expected. Obviously the approximate rhombic symmetry observed in the diffraction pattern is due to a pseudosymmetry of the energies of interfaces. Several planes seem to compete with the strain energy and the topology of domains forming polyhedra. If the stable domain form cannot completely fill the three-dimensional space, either different polyhedra or similar polyhedra with less-stable interfaces have to be formed. This can lead to a change of the morphological symmetry of a single domain. Fig. 6 demonstrates some examples of such

(a)

(b)

Fig. 6. Two more complicated arrangements of two kinds of domains (shaded and unshaded areas) having more than four boundaries in the principal zone. (a) Pair of lower symmetry, (b) complicated array with high symmetry.
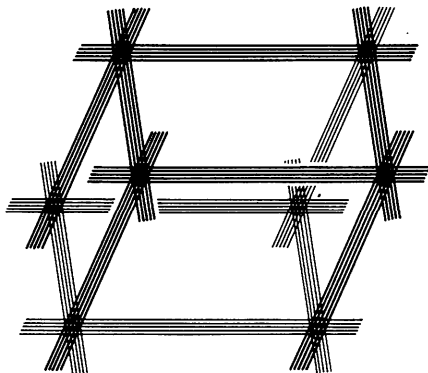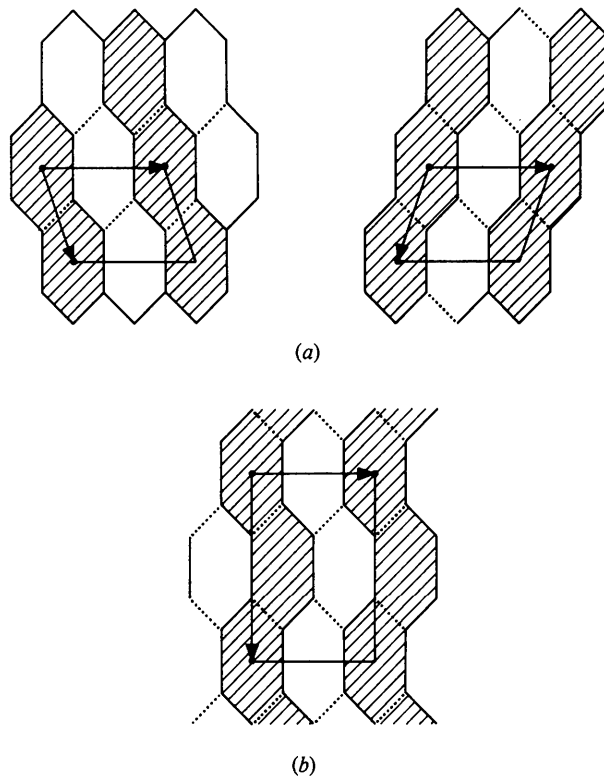

Fig. 5. Diffraction (schematically drawn) of a disordered three-dimensional periodic array of blocks. The (central) main reflection is not shown because of its high intensity. The diffuse lines and planes vanish if the array is strictly periodic.

space-filling polyhedra without claiming that they explain the diffraction pattern observed. Fig. 6(a) shows a pair of equivalent superstructures leading to rhombic symmetry, as does Fig. 6(b) for a more complicated single array of domains. It is supposed that similar arrangements are responsible for the symmetry and the very complex positions and intensities of the satellite pattern observed.

We have not yet made any assumption on the nature of $\bar{F}$ and ΔF in our calculations. Consequently all conclusions drawn so far are of general validity as long as only two types of domain occur. Let us now discuss the partial structure factors $\bar{F}$, ΔF in the case of centrosymmetric twins where all atoms are near the centrosymmetric position. Here we introduce for the nearly centrosymmetric pair of atoms the vectors $\mathbf{r}_{\nu_1}$, $\mathbf{r}_{\nu_2}$ and define (Fig. 7)

$$\mathbf{r}_\nu = \frac{\mathbf{r}_{\nu_1} - \mathbf{r}_{\nu_2}}{2} \quad \text{and} \quad \Delta\mathbf{r}_\nu = \frac{\mathbf{r}_{\nu_1} + \mathbf{r}_{\nu_2}}{2}.$$

Then we have

$$\mathbf{r}_{\nu_1} = \mathbf{r}_\nu + \Delta\mathbf{r}_\nu \quad \text{and} \quad \mathbf{r}_{\nu_2} = -\mathbf{r}_\nu + \Delta\mathbf{r}_\nu,$$

which means that the structure becomes centrosymmetric only if $\Delta\mathbf{r}_\nu = 0$. With this definition we get the two structure factors and $\bar{F}$, ΔF:

$$F_1(\mathbf{h}) = 2\sum_\nu f_\nu \exp(2\pi i \mathbf{h}\Delta\mathbf{r}_\nu)\cos 2\pi\mathbf{h}\mathbf{r}_\nu$$

$$F_2(\mathbf{h}) = 2\sum_\nu f_\nu \exp(-2\pi i \mathbf{h}\Delta\mathbf{r}_\nu)\cos 2\pi\mathbf{h}\mathbf{r}_\nu = F_1^*(\mathbf{h})$$

$$\bar{F}(\mathbf{h}) = 2\sum_\nu f_\nu \cos 2\pi\mathbf{h}\mathbf{r}_\nu \cos 2\pi\mathbf{h}\Delta\mathbf{r}_\nu \qquad (9a)$$

$$\Delta F(\mathbf{h}) = 2i\sum_\nu f_\nu \cos 2\pi\mathbf{h}\mathbf{r}_\nu \sin 2\pi\mathbf{h}\Delta\mathbf{r}_\nu, \qquad (9b)$$

with the definitions for $\bar{F}$ and ΔF:

$$\bar{F} = \tfrac{1}{2}(F_1 + F_2), \quad \Delta F = \tfrac{1}{2}(F_1 - F_2).$$

Developing (9) for small $\mathbf{h}\Delta\mathbf{r}_\nu$ we get

$$\bar{F} = 2\sum_\nu f_\nu \cos 2\pi\mathbf{h}\mathbf{r}_\nu[1 - 2\pi^2(\mathbf{h}\Delta\mathbf{r}_\nu)^2] \qquad (10a)$$

$$\Delta F = 4\pi i \sum_\nu f_\nu \cos 2\pi\mathbf{h}\mathbf{r}_\nu[\mathbf{h}\Delta\mathbf{r}_\nu], \qquad (10b)$$

with

$$\Delta\mathbf{r}_\nu = \Delta\mathbf{r}_\nu' + \overline{\Delta\mathbf{r}}, \quad \overline{\Delta\mathbf{r}} = \sum_\nu \Delta\mathbf{r}_\nu$$

and

$$\sum_\nu \Delta\mathbf{r}_\nu' = 0,$$

$$\Delta F = 4\pi i \left(\mathbf{h}\overline{\Delta\mathbf{r}} \sum_\nu f_\nu \cos 2\pi\mathbf{h}\mathbf{r}_\nu + \sum_\nu f_\nu [\cos 2\pi\mathbf{h}\mathbf{r}_\nu] \mathbf{h}\Delta\mathbf{r}_\nu' \right).$$

$$(10c)$$

The first term in (10c) shows satellites proportional to the structure factor of the centrosymmetric structure which is very near to $\bar{F}$, as given in (10a). Since $\sum_\nu \Delta\mathbf{r}_\nu' = 0$, the second term behaves completely differently, but it is smaller than the first term unless $\mathbf{h}\Delta\mathbf{r}_\nu = 0$. Furthermore, it may have the same or the opposite sign with respect to the first term. For weak reflections $\bar{F}$ the first term will be weak anyway, but the second term may become large if many terms $f_\nu \cos 2\pi\mathbf{h}\mathbf{r}_\nu$ are large and have opposite signs being reversed by an opposite sign of $(\mathbf{h}\Delta\mathbf{r}_\nu')$, but this again is not very probable. Therefore the observation of satellites near strong reflections is more probable than for others, but only strong reflections with large $\mathbf{h}\Delta\mathbf{r}_\nu$ show the satellites. This agrees well with the observation of satellites near strong a reflections. Furthermore, (9c) predicts a linear increase of the intensities of satellites with increasing $|\mathbf{h}| = 2\sin\theta/\lambda$. This seems to be in contradiction to the observation that no strong a reflections with satellites could be observed at large diffraction angles. But this fact may be explained in terms of the proposed model: According to (6c) and (8) both the lamellar model and the three-dimensional block model yield odd satellites only if both twins occur with the same probability and their intensities decrease with increasing order. This behaviour is independent of the diffraction angle. The diffuse scattering due to disorder (e.g. strains of the lattice, thermal diffuse scattering, etc.) spreads from the Bragg peak into the reciprocal space with increasing diffraction angle. Its increase in intensity lies in the same order of magnitude because it is also caused by displacements. Therefore it may be expected that the satellites are vanishing in the diffuse background owing to disorder scattering or thermal diffuse scattering.
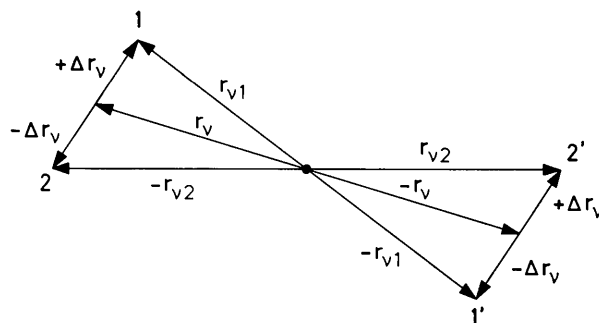

Fig. 7. Position of vectors of pairs of domains as discussed in equations (10) and (12).

Now let us briefly discuss why the solution of our structural model could not be found by solving the structure with the aid of an acentric model. Kalus (1978) has redetermined the structure of pure anorthite, with neutron and X-ray data; the signs of the structure factors of a reflections were determined by direct methods, and the signs of b and c reflections were calculated in various cycles. Curiously, two centrosymmetric structures came up with displacements of a few atoms, differing significantly before the weak d reflections were introduced. After they had been taken into account the two structures coalesced into one. The final reliability factor was 5·5% for X-ray data (7952 reflections) and 3·7% for neutron data (2188 reflections). It would seem to be hopeless to omit the centre of symmetry in a new refinement for the following reasons:

1. The data have been collected on very good diffractometers, yet no satellites could be detected (effect is too weak!). Consequently, the integrated intensities of satellites *and* main reflections had been measured.

2. The structure factor of (10a) represents a maximum for any sets of small displacement vectors [all $(h\Delta r_v)^2$ are positive!]. Consequently, a nearly correct set of displacement vectors has to be used for the refinement of the acentric structure according to (10a) (averaged structure).

3. It cannot be assumed that the use of integrated intensities of main reflections and satellites yields the correct acentric structure. Equation (10a) gives a contribution independent of the sign of $h\Delta r_v$. This means a reduction in intensity for $|\bar{F}|^2$, at least for the strong reflections. Since the sign of $h\Delta r_v$ is important for (10b), determining the intensity of satellites, it is possible that the intensity of the satellites is zero ($\Delta F = 0$), while (10a) yields a decrease of $\bar{F}$. This means that the invariant integrated intensity of the complete reciprocal space is not constant in the case of a single reflection and its satellites. Consequently, the only chance to solve the structure is a careful measurement of the intensities of satellites (including extinctions), and determination of displacement vectors according to (10b) or (10c). But this perhaps could be done if a crystal with a perfectly periodic domain structure were found, and the thermal diffuse scattering were avoided by cooling down the crystal to liquid-helium temperature.

Equation (10a) also cautions us in structure determination of acentric structures and reveals once more that the Wilson test is not an adequate means to secure a moderate deviation from a centrosymmetric structure with intensities

$$|F_1|^2 = |\bar{F}|^2 + |\Delta F|^2. \qquad (11)$$

This means that the decrease of $\bar{F}$, as given in (10a), is partly balanced by $|\Delta F|^2$ as stated in (10c). Con-

sequently we may conclude that the structure factors of a slightly acentric structure differ from those of its centrosymmetric counterpart in their phases rather than in their amplitudes; in other words, slightly acentric structures are homometric with their centrosymmetric counterpart.

It should be pointed out that a similar discussion could be conducted on behalf of two different centrosymmetric structures with the same chemical composition, but differing slightly in their atomic positions. With (Fig. 7)

$$\mathbf{r}_{v_1} = \mathbf{r}_v + \Delta \mathbf{r}_v, -\mathbf{r}_{v_1},$$

and

$$-\mathbf{r}_{v_2} = \mathbf{r}_v - \Delta \mathbf{r}_v, \mathbf{r}_{v_2}$$

(two similar centrosymmetric structures), we get

$$\bar{F} = 2 \sum_v f_v \cos 2\pi h \mathbf{r}_v \cos 2\pi h \Delta \mathbf{r}_v \qquad (12a)$$

$$\Delta F = 2 \sum_v f_v \sin 2\pi h \mathbf{r}_v \sin 2\pi h \Delta \mathbf{r}_v. \qquad (12b)$$

Equations (12) may be discussed in a similar way to before. Obviously, the difference lies in (12b), which cannot be split by introducing $\Delta r'$ in two terms such that one of them is proportional to a structure factor of the averaged structure as observed experimentally. Furthermore, the energetic equivalence of the two structures could not be understood.

Obviously, in the particular case of plagioclases a quantitative comparison of observed intensities with calculated ones is tedious, and we do not intend to sacrifice so much time on additional experimental measurements and theoretical evaluations when the displacements are so slight. From a theoretical point of view it would be interesting to know the physical or chemical reasons for this strange behaviour.

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SHORT COMMUNICATIONS

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Significance of calculated cluster conformations of benzene: comment on a publication by D. E. Williams.

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Abstract

Results of potential-energy minimization, applied to clusters of benzene molecules, have been reported recently by Williams [*Acta Cryst.* (1980), A36, 715–723]. Two stable tridecamer clusters were found and compared with a 13-molecule fragment from crystalline orthorhombic benzene. In this comment the significance of such a comparison is discussed and related to the size of the clusters.

Introduction

The potential energy of a limited number (N) of molecules is a complicated function of the $6N$ molecular coordinates, even if the molecular interaction is represented by a simple model. In general, there will be more than one minimum and the result of a minimization procedure will therefore be dependent on the starting point in configuration space, the initial configuration. Since each minimum that can be localized corresponds to a definite conformation of N molecules in a cluster, the problem arises of establishing the significance of different cluster conformations, relative to one another, particularly in connection with molecular complexation and crystallization. This significance cannot be derived from a direct comparison with experimental material, since no detailed information concerning the structure of small molecular clusters is available.

The procedure adopted by Williams (1980) to find optimum conformations for clusters of benzene molecules, ranging in size from $N = 2$ to $N = 15$, consists of finding the optimum conformation of an N cluster by adding two molecules to an optimized ($N - 2$) cluster, starting with $N =$

3. One molecule is kept fixed at the origin; pairs of additional molecules are related by a centre of symmetry at the origin. In two instances ($N = 7$ and $N = 13$) the results are not unique. In this comment we will fix our attention on the 13-molecule clusters, since they may be considered as a central molecule with a completed coordination shell. Two criteria are applied by Williams to distinguish between clusters of equal size: (*a*) the energy E_r of the central molecule and (*b*) the behaviour of E_r in the sequence $N = 3$, 5, . . .,13. It is assumed by Williams that the cluster with the lowest value of E_r and with the most regular decrease of $E_r(N)$ in the 'history' of the cluster, could lead to crystallite formation, whereas other clusters could be broken up by thermal agitation. The cluster that is supposed to play a role in crystallite formation is subsequently compared with the observed crystal structure of orthorhombic benzene.

Although the criteria applied by Williams may be justifiable, they do not appear to be decisive, in view of the small differences in energy and the small number of molecules under consideration. It is the purpose of this comment to investigate whether a comparison with the observed crystal structure is feasible and if it can support Williams's assumption concerning crystallite formation.

Although a cluster conformation can be compared with a fragment of the observed crystal structure, there is little reason to expect the structure of a cluster to be very similar to that of such a fragment, when the number of molecules is small. In the case of benzene, all 13 molecules in a crystal fragment, consisting of a central molecule and its first coordination shell, are equivalent and have the same environment. This environment is not present in a 13-molecule cluster; nearly all molecules are 'surface molecules', and the conformation may therefore be dominated by surface effects.

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