Identification of Satellite Faces on Single Crystals of the Incommensurate Structures $\text{Rb}_2\text{ZnBr}_4$ and $\text{Rb}_2\text{ZnCl}_4$

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The modulation of incommensurate structures appears to have macroscopic consequences: On modulated single crystals satellite surfaces have been observed which can be interpreted by extending the classical morphological theory by including superspace group symmetry.

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The morphology of single crystals reveals on a macroscopic scale the microscopic structure of crystalline matter and its space group symmetry. Lattice translational symmetry, in particular, plays a fundamental role in all existing theories on crystal forms. The discovery of incommensurate modulated crystals brings to question whether this modulation (which on the atomic scale breaks lattice periodicity) also has macroscopic consequences, and to what extent morphological theories have to be revised.

In this paper we show that superspace groups (introduced to describe the microscopic symmetry of incommensurate crystal structures) allow a natural generalization of existing geometrical theories on crystal forms, which predicts new morphological features. Preliminary experimental results on $\text{Rb}_2\text{ZnBr}_4$ and $\text{Rb}_2\text{ZnCl}_4$ appear to be consistent with these predictions.

The incommensurate phases of $\text{Rb}_2\text{ZnBr}_4$ and of $\text{Rb}_2\text{ZnCl}_4$ are, as in $\text{KSeO}_4$, characterized by a basic structure with space group $\text{Pcmn}$ and a displacive modulation with wave vector $\mathbf{q}=\gamma \mathbf{c}^*=(0,0,\frac{1}{2}-\delta)=0.3 \mathbf{c}^*$ which is incommensurate with the orthorhombic basic lattice $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$. The superspace symmetry group of $\text{KSeO}_4$ has been determined as $G_s=\text{Pcmn} \cdot \text{Pcmn}$ which in the complete list of $(3+1)$-dimensional superspace groups appears as $62c.9.2$. This same superspace group is also consistent with experimental investigations on $\text{Rb}_2\text{ZnBr}_4$ and $\text{Rb}_2\text{ZnCl}_4$ and so it has been adopted here for both cases.

The morphology of single crystals is classically predicted by the Bravais-Friedel-Donnay-Harker (BFDH) law. According to this law, the crystallographic faces of the form $\{hkl\}$ belonging to the smallest vectors in reciprocal space have the highest morphological importance (MI) or $\text{MI}\{hkl\}>\text{MI}\{h'k'l'\}$ if $|h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*|<|h'\mathbf{a}^*+k'\mathbf{b}^*+l'\mathbf{c}^*|$. The MI $\{hkl\}$ is defined as a measure for the frequency of occurrence of the faces of $\{hkl\}$ and their relative surface area.\(^7\) The DH generalization of the original BF law takes the extinction conditions of the space group into account.

In order to describe the morphology of incommensurate crystals, we generalize the BFDH law to superspace and superspace group symmetry. The proposed generalization implies that crystal faces are oriented perpendicularly to Fourier wave vectors $\mathbf{Q}$ giving sharp diffraction spots and that those faces which get a low $|\mathbf{Q}|$ value by incorporating the superspace group symmetry have a high MI.

In the examples considered here, with a one-dimensional displacive modulation, these $\mathbf{Q}$'s require not three but four basic vectors in reciprocal space: $\mathbf{Q}=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*+m\mathbf{c}^*=(h,k,l,m)$ with $h$, $k$, $l$, and $m$ integers called superspace indices.\(^8\) For $m=0$ one gets the main reflections belonging to the basic structure; the other reflections are the satellites. For the morphology of incommensurate crystals it is therefore convenient to distinguish accordingly between basic and satellite faces. The conditions limiting possible reflections of the superspace group $G_s=\text{Pcmn} \cdot \text{Pcmn}$ are given in Table I (compare Table III of Ref. 3).

Note that by putting $m=0$ one recovers the corresponding selection rules for the basic space group $\text{Pcmn}$.

<table>
<thead>
<tr>
<th>$h\mathbf{0}0\mathbf{0}$, $k=2n$</th>
<th>$0k\mathbf{0}0$, $k=2n$</th>
<th>$00l\mathbf{m}$, $l=2n$</th>
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<tbody>
<tr>
<td>$hh\mathbf{0}0$, $h+k=2n$</td>
<td>$0k\mathbf{l}m$, $l+m=2n$</td>
<td>$h0\mathbf{l}m$, $m=2n$</td>
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</table>

\(^{7}\) The DH generalization of the original BF law takes the extinction conditions of the space group into account.

\(^{8}\) For $m=0$ one gets the main reflections belonging to the basic structure; the other reflections are the satellites. For the morphology of incommensurate crystals it is therefore convenient to distinguish accordingly between basic and satellite faces. The conditions limiting possible reflections of the superspace group $G_s=\text{Pcmn} \cdot \text{Pcmn}$ are given in Table I (compare Table III of Ref. 3).

Note that by putting $m=0$ one recovers the corresponding selection rules for the basic space group $\text{Pcmn}$.
In order to check the relevance of the generalized BFDH law given above we have studied the faces on single crystals of Rb₂ZnBr₄ and Rb₂ZnCl₄ with the help of an optical goniometer and indexed the observed faces by using the cell parameters \( a = 13.33 \), \( b = 7.656 \), and \( c = 9.707 \) Å and \( q = 0.3c^* \) of Rb₂ZnBr₄ and by assuming proportionality for the corresponding ones of Rb₂ZnCl₄. The crystals were grown by slow evaporation from aqueous solution at \( \pm 30^\circ \mathrm{C} \).

In Table II the comparison between the observed crystal faces and their identification in accordance with the superspace group are given in the order of preference according to the generalized BFDH law. It can be seen that in addition to the basic faces \((hklO)\) corresponding to the basic space-group symmetry, satellite faces are observed on all the investigated crystals. In Fig. 1 photographs are shown of two examples of such satellite faces. Those observed on Rb₂ZnBr₄ are much larger in size than on Rb₂ZnCl₄, which can simply be understood by regarding the growth conditions of the particular crystals: 30°C is just around the transition point of Rb₂ZnCl₄ while it is 50°C below the transition point of Rb₂ZnBr₄ with consequently a much stronger manifestation of the modulation.

**TABLE II. Crystal faces observed and identified according to superspace group selection rules valid for \( P_{a \overline{1}} P_{c 1} n^4 \).** The angles \( \phi \) and \( \varphi \) are measured from the \( \mathbf{c}^* \) and the \( \mathbf{a}^* \) axes, respectively. The vector length \( |Q| \) is calculated using the parameters of Rb₂ZnBr₄. Type \( B \) means basic face; type \( S \), satellite face.

| Sample       | Orientation | Face indices \((hklO)\) | Donnay-Barkley \( |Q| \) in Å | Type |
|--------------|-------------|------------------------|-----------------------------|------|
| Rb₂ZnBr₄     | 0 90        | 0 90 0 0 0 0 2 0       | 0.062                       | S    |
|              | 92 0        | 90 0 0 2 0 0 0         | 0.150                       | B    |
|              | 90 60       | 90 60 1 1 0 0          | 0.152                       | B    |
|              | 80 61       | 78 61 1 1 1 1          | 0.155                       | S    |
|              | 0 90        | 0 90 0 0 2 0 0          | 0.206                       | B    |
|              | 90 31       | 90 30 3 1 0 0          | 0.261                       | B    |
|              | 90 87       | 90 90 0 2 0 0           | 0.264                       | B    |
| Rb₂ZnCl₄     | 0 90        | 0 90 0 0 0 0 2 0       | 0.062                       | S    |
|              | 90 0        | 90 0 2 0 0 0           | 0.150                       | B    |
|              | 90 60       | 90 60 1 1 0 0          | 0.152                       | B    |
| (1)          | 94 61       | 65 63 1 1 1 1          | 0.168                       | S    |
|              | 37 33       | 36 34 2 0 1 0          | 0.182                       | B    |
|              | 35 65       | 56 66 1 1 1 1          | 0.184                       | B    |
|              | 0 90        | 0 90 0 0 2 0 0          | 0.206                       | B    |
|              | 83 7        | 82 8 3 0 0 1           | 0.227                       | S    |
|              | 36 73       | 36 73 1 1 2 0          | 0.256                       | S    |
|              | 90 29       | 90 30 1 1 0 0          | 0.261                       | B    |
|              | 90 90       | 90 90 0 2 0 0           | 0.264                       | B    |
|              | 75 33       | 75 34 1 1 1 1          | 0.271                       | S    |
|              | 81 78       | 84 74 1 2 0 1 1        | 0.277                       | S    |
|              | 69 80       | 69 75 1 2 1 0 2        | 0.293                       | B    |
| Rb₂ZnCl₄     | 0 90        | 0 90 0 0 0 0 2 0       | 0.062                       | S    |
| (11)         | 71 21       | 68 22 1 0 0 1 0        | 0.081                       | S    |
|              | 37 53       | 36 54 1 0 1 0          | 0.127                       | S    |
|              | 90 0        | 90 0 2 0 0 0           | 0.150                       | B    |
|              | 90 60       | 90 60 1 1 0 0          | 0.152                       | B    |
|              | 77 65       | 78 61 1 1 1 1          | 0.155                       | S    |
|              | 55 65       | 56 66 1 1 1 0          | 0.184                       | B    |
|              | 0 90        | 0 90 0 0 2 0 0          | 0.206                       | B    |
|              | 83 7        | 82 8 3 0 0 1           | 0.227                       | S    |
|              | 90 30       | 90 30 3 1 0 0          | 0.261                       | B    |
|              | 19 84       | non identified         |                             |      |
|              | 84 9        | non identified         |                             |      |

**FIG. 1.** Photographic images of incommensurate single crystals. (a) Rb₂ZnBr₄. (b) Rb₂ZnCl₄, sample I. In the schematic drawing corresponding with each photograph, the \((3 + 1)\)-dimensional indices are used; those of the satellite faces are underlined.
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Rb$_2$ZnCl$_4$ might indicate the presence of an addi­
the experimental data presented in Table n. A
excellent agreement with the high MI of this face.
agreement with the classical laws of crystallography for incom­
mental accuracy. Here we also omit discussion of other
incommensurate displacive modulation means that this
manifests itself on a macroscopic scale. We have shown that the superspace-group
for the interpretation of the morphological data. For a strict check of the proposed generalized
BFDH law, a much larger number of crystals
need to be measured which will be done in the near future. In addition we will try to give a phy­sical interpretation of the generalized BFDH law
by studying the bond structure of slices by using
the Hartman-Perdok theory$^{11}$ as a tool and by
introducing modulation in crystal growth models.
Useful discussions with T. Janssen and J. van
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also indebted to P. M. de Wolff for telling us the
evidence of satellite faces in Rb$_2$ZnBr$_4$. Part of
this work was supported by the Stichting Funda­menteel Onderzoek der Materie.

In conclusion, the satellite faces identified on
single crystals with clearly recognized incom­mensurate
satellite faces to the basic structure and try to
find rational indices $hkl$ fitting within the experi­mental accuracy. However, then only fairly
large integers are consistent with the underlying incommensurability, making the law of rational
indices questionable. Furthermore, according to
the BFDH law, these faces get a low MI because
of the large $|\mathbf{Q}|$ values involved. Experimental
observations reported here, even limited so far
to a small number of samples, show that this is
definitely not the case. Instead one finds a global
agreement with the generalized BFDH law, which
implies that small superspace indices are the
morphological important ones. This confirms to
a high extent the relevance of a suitably general­
ized law of rational indices, i.e., the validity of
the classical laws of crystallography for incom­mensurate crystals as well, if one properly ex­tends the dimension of the space used for the
description.$^8$ Consider, for example, Rb$_2$ZnBr$_4$,
with the observed basic forms \{200\}, \{110\},
\{002\}, \{310\}, and \{020\}. The smallest $|\mathbf{Q}|$ value involved here is $|\mathbf{Q}| = 0.075$, the largest is
$|\mathbf{Q}| = 0.264$. In addition to these faces there
is a very well developed face which if considered
as a basic face gets indices (331) or higher
and accordingly $|\mathbf{Q}| \geq |\mathbf{Q}| = 0.467$. Consider­­ing it as a satellite face (as first done by de Wolff
and collaborators$^{10}$) it gets four indices (1101)
with a much shorter length of the corresponding
reciprocal vector $|\mathbf{Q}| = 0.155$. This is in
excellent agreement with the high MI of this face.
Other examples can easily be reconstructed from the experimental data presented in Table II. A
small but systematic deviation of the satellites of
Rb$_2$ZnCl$_4$ might indicate the presence of an addi­tional component of the modulation wave vector of
about 0.1Å$^*$. Such a component is not compatible
with an orthorhombic (3 + 1) dimensional super­
space group and requires either a monoclinic dis­
tortion or a (3 + 2) dimensional superspace. Both
possibilities have been disregarded in the present
analysis. Here we also omit discussion of other
striking morphological observations (bend faces,
growth bands, etc.) fitting, in principle at least,
with theoretical expectations for incommensurate
structures but which are not yet properly inter­
preted.

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