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Observation of Bands of Faces on Incommensurate Rb_2ZnBr_4 Single Crystals

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The macroscopic consequences of displacive modulation on the morphology of incommensurate single crystals are confirmed. Bands of faces in the neighborhood of stable normal crystal faces have been observed on spherically shaped Rb_2ZnBr_4 crystals. An interpretation is given in terms of classical morphological theory extended to include (four-dimensional) superspace group symmetry. This leads to the view that the formation of these bands involves, at least partly, so-called satellite faces and gives a simple explanation of why the set of bands has a lower point-group symmetry than the set of normal faces.

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As observed first by de Wolff and collaborators,[1] incommensurate single crystals of Rb_2ZnBr_4 and Rb_2ZnCl_4 grown in an aqueous solution show morphological features due to their modulation in the form of so-called satellite faces. These satellite faces could be interpreted[2] by extension of the classical geometrical theories of Bravais,[3] Friedel,[4] and Donnay and Harker.[5]

On the basis of the Bravais-Friedel-Donnay-Harker law, a fairly large number of satellite faces is expected to have about the same morphological importance. Their simultaneous appearance is favored by use of spherically shaped single crystals as the initial growth form. Indeed, as reported below, with this technique a number of growth bands could be made visible in addition to the normal faces. A normal face appears as a depression on the growing sphere. Satellite faces appear within a strip of ledged faces forming a kind of staircase, which will here be called a "staircase band" (or simply a "band") of faces, the faces being called "steps." Bands of this kind have also been observed on a number of inorganic single crystals like ADP ($NH_4H_2PO_4$) and KDP (KH_2PO_4)[6,7] (see Fig. 1), and on crystalline metals like cadmium and zinc.[8]

For the sphere experiments two large, transparent, single crystals of Rb_2ZnBr_4 were selected and polished into half spheres of about 1 cm diam with poles along the $\langle 101\rangle$ and $\langle 110\rangle$ directions, respectively. Because of inversion symmetry half a sphere already contains all relevant information. After growth for about 1 h in a slightly supersaturated solution at about 30 °C, beautiful faces and bands could be observed. Goniometer measurements allowed the faces to be indexed as (100), (001), (201), (111), (110), and (310). These are normally expected crystal faces in crystals of the K_2SO_4 structure type.[9] As far as the observations allowed us to conclude, all these faces obey the *mmm* point-group symmetry of the average crystal structure (space group *Pcmn*).

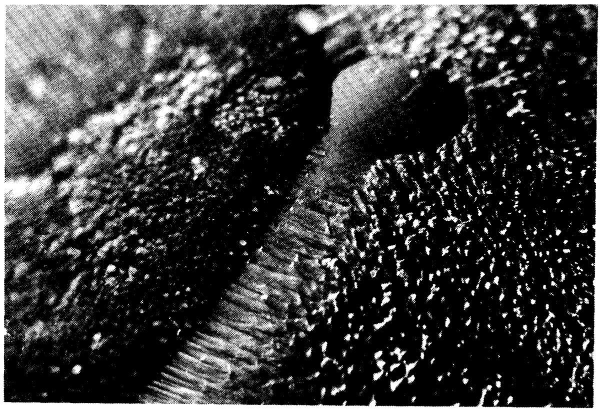

FIG. 1. Growth process on a single-crystal sphere of KDP showing the appearance of a normal crystal face and of a staircase band of faces.

In contrast to these faces, the bands have point-group symmetry 222 only. These bands produce vague reflections with varying orientations along well-defined zones (Fig. 2). Thus goniometric reflections definitely exclude the possibility of staircase bands with steps built up from normal faces only.

The most important set of bands (A) appears in the [010] zone in the region comprised between the faces (101) and (10$\bar{1}$) and includes the main faces (100) and (201). This band consists of about a hundred steps. A second set of bands (B) is found in the [1$\bar{1}$0] zone. It clearly shows a 222 point-group symmetry. On the first sphere grown, only small bands formed asymmetrically around (110). The second experiment, however, revealed a band which started at (111) and contained (110) without reaching (11$\bar{1}$). The number of steps in this band is much smaller than in the case of band A. This second band contains, in particular, the satellite face (1101) already observed on other single crystals.[2] (The four-index symbols are explained further on.) The third and weakest set of bands (C) is located around (310) in the [001] zone. These bands do not end in a normal low-index face and upon growing they decrease and disappear rapidly.

In the modulated phase (at room temperature) the crystal of Rb_2ZnBr_4 has a (3 + 1)-dimensional superspace symmetry group[2] possibly given by $Pcmn(00\gamma)(ss\bar{1})$, or alternatively $Pc2_1n(00\gamma)(s\bar{1}\bar{1})$, implying an orthohombic average structure with space-group $Pcmn$ (or $Pc2_1n$) with unit cell parameters $a = 13.33$ Å, $b = 7.656$ Å, and $c = 9.707$ Å. The modulation wave vector is $\vec{q} = \gamma\vec{c}^* = 0.3\vec{c}^*$. Despite the fact that γ is only approximately 0.3 at 30 °C, that value has been adopted in what follows. The Fourier wave vectors of the matter distribution of the crystal have the general form $\vec{k} = (hklm) = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* + m\vec{q}$ with h, k, l, m integers. The superspace group symmetry given above implies restrictions on the set of possible combinations (systematic extinction rules), but these restrictions have been disregarded here, because the experimental data so far available do not allow their detailed verification. (See Janner and co-workers[10] for more details on the superspace approach.) The interpretation of the bands is based on the following extension of the Bravais-Friedel-Donnay-Harker law:

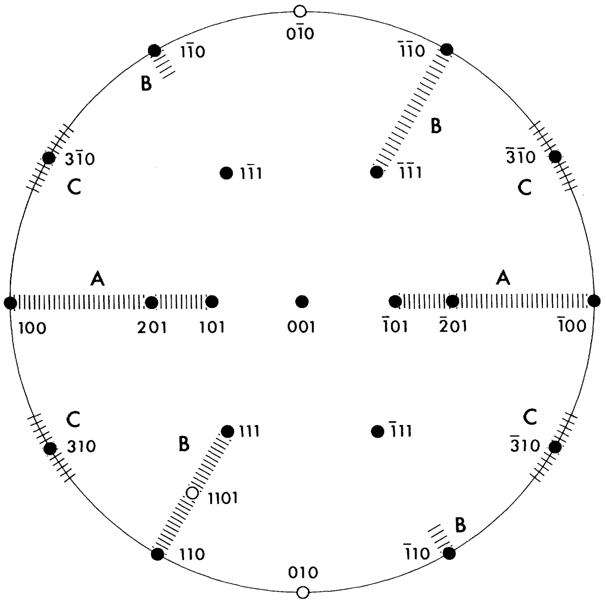

FIG. 2. Stereogram of a single-crystal sphere of Rb_2ZnBr_4 showing the location of observed (solid circles) and expected (open circles) normal faces and staircase bands of faces (hatched areas). The morphologically important satellite face (1101) is also indicated.

(1) Crystal faces correspond in the three-dimensional space to fronts of Fourier matter waves. The intersection between real space and lattice hyperplanes with indices ($hklm$) in four-dimensional superspace corresponds to crystal faces normal to Fourier wave vectors $\vec{k} = (hklm)$.[3]

(2) The morphological importance of a given set of symmetry-related faces is greater for smaller values $|\vec{k}|$ of the wave vectors involved.[4] For normal faces ($m = 0$), this means that the indices should be small. The corresponding condition implying that the morphological importance of satellite faces decreases for increasing values

of *m* does not follow directly from the Friedel law, but is plausible if interpreted in terms of magnitude of the Fourier components.

(3) Reflections forbidden by superspace (four-dimensional) symmetry imply vanishing of those Fourier components and also low morphological importance of the corresponding faces.[5]

Faces with $m=0$ are labeled as usual by (hkl) only, and are called normal faces, whereas those with $m\neq 0$ are denoted as satellite faces. The wave vectors of satellite faces deviate only slightly in length from those of the nearby main faces. Thus, bands of satellite faces around morphologically important normal faces are expected, especially in the zones parallel to a strong periodic bond chain.[11] In particular for Rb_2ZnBr_4, in the approximation given by $\gamma=0.3$, there are (disregarding possible extinction rules) nine different satellite faces between (hkl) and $(hk\,l+1)$ with *m* values varying between -5 and $+5$:

lm	00	$1\bar{3}$	$\bar{1}4$	01	$1\bar{2}$	$\bar{1}5$	02	$1\bar{1}$	$2\bar{4}$	03	10
$l+\gamma m$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0

We call such a set of satellite faces a family, labeled by the two limiting normal faces. In general a band is thought to consist of the union of several such families of satellite faces. Even if a detailed identification of the individual satellite faces within a band is very difficult and has not yet been made, to recognize globally the families involved is fairly straightforward. In Table I an example is given of how band *A* can be built up from two kinds of families having $h=1$ and 2, respectively: i.e., (100)–(101), (200)–(201), and (201)–(202). It can be seen that a whole band of faces can be constructed in this way, even if we restrict ourselves to *m* values lower than 4. A number of satellite faces occurring in these bands have also been observed in naturally shaped single crystals of Rb_2ZnBr_4 and of Rb_2ZnCl_4.[12] From the plot of the $|\vec{k}|$ values (Fig. 3) it can be recognized that the morphological importance of faces diminishes fairly strong from (101) to (001).

Band *B* is probably made up from two kinds of families having $h=k=1$ and $h=k=2$, though the $|\vec{k}|$ values are a bit high in the latter case. The reduction of symmetry in this band cannot be explained on the basis of $|\vec{k}|$ values only, but admits a simple interpretation in terms of superspace-group symmetry. According to the superspace-group approach, what one can see macroscopically is a point group (conventionally denoted by K_E and representing the so-called external part of the superspace point group K_S), which in general is a subgroup of the point group K_0 of the average structure. In terms of modulation, one gets such a symmetry reduction in particular when modulation waves with the same wave vector $\vec{q}$ but different relative phases coexist in the crystal.[13] This interpretation still has to be verified by a better fit of the diffraction data available for Rb_2ZnBr_4 crystals, under the assumption of a superspace group having (external) point-group symmetry 222 instead of *mmm* or *m*2*m*, as considered until now.[2] Let us remark that this inter-

TABLE I. Expected low-index satellite faces in the zone [010] as a function of their angle ρ with respect to the face (001).

ρ	*hklm*	*hklm*	ρ	*hklm*	*hklm*
90.0	100	200	55.5	$10\bar{1}5$	201
86.1	···	$201\bar{3}$	52.9	···	$202\bar{3}$
82.2	$101\bar{3}$	$20\bar{1}4$	50.5	1002	2004
78.4	···	2001	48.2	···	2011
74.6	$10\bar{1}4$	$201\bar{2}$	46.1	$101\bar{1}$	$202\bar{2}$
71.0	···	$20\bar{1}5$	44.2	···	2005
67.6	1001	2002	42.3	$102\bar{4}$	2012
64.3	···	$201\bar{1}$	40.6	···	$202\bar{1}$
61.2	$101\bar{2}$	$202\bar{4}$	39.0	1003	$203\bar{4}$
58.2	···	2003	37.5	···	2013
			36.1	101	202

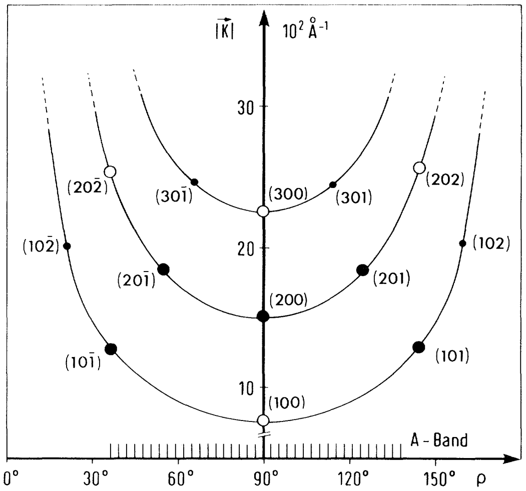

FIG. 3. Variation in wave-vector length for various families of satellite faces expected to build up the observed *A* band. Large black circles indicate observed normal faces, small black circles the expected faces, and open circles the forbidden ones.

pretation is consistent with the observed *mmm* point symmetry of the normal faces. These indeed reflect the symmetry of the average structure even in the modulated case, whereas this is not so, in general, for the satellite faces.

Band *C* cannot be explained on the basis of the present theory without the assumption of an additional small-amplitude modulation in the $\vec{a}^*$ axis.

Concluding, it is amazing how much can be said on the basis of the purely geometrical Bravais-Friedel-Donnay-Harker law only, even concerning such subtle properties as superspace symmetry elements, as implied by the point-group symmetry of the configuration of band *B*. Probably also the abrupt ending of the bands at (101) and (111) can be explained by structural arguments. If we consider the satellite faces as being stabilized by the presence of two faces with high morphological importance, and not by only one, then clearly the situation at either side of (111) and of (101), respectively, is different and may explain the ending.

This analysis applies both to incommensurate and to commensurate (long-period) modulated crystals. This means that the precise role of incommensurability in the morphology has to be elucidated further. We even expect that under favorable conditions (e.g., near edges formed by normal faces) bands of satellite faces should appear in naturally grown incommensurate single crystals, as suggested by the experiments of Uyeda.[14]

It has to be stressed that the interpretation given here of the new morphological features observed in incommensurate Rb_2ZnBr_4, though consistent, need not to be the whole truth of the story. No satisfactory explanation for the bands on ADP and KDP, nor on cadmium or zinc crystals, could be given, as all those crystals are not known to be modulated, and no such periodic lattice distortion could yet be established from x-ray diffraction experiments. In any case, crystal-sphere experiments seem to be of importance for the further investigation of structural properties.

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FIG. 1. Growth process on a single-crystal sphere of KDP showing the appearance of a normal crystal face and of a staircase band of faces.