pke (Springer-Verlag, Berlin, 1980).

⁵M. Postel and J. C. Riess, *J. Phys. Chem.* **81**, 2634 (1977).

⁶J. K. Kjems *et al.*, *Phys. Rev. B* **13**, 1446 (1976); R. D. Diehl, M. F. Toney, and S. C. Fain, *Phys. Rev. Lett.* **48**, 177 (1982); J. P. McTague and M. Nielsen, *Phys. Rev. Lett.* **37**, 596 (1976); I. Marlow *et al.*, *J. Phys. (Paris), Colloq.* **38**, C4-19 (1977); A. D. Migone, M. H. W. Chan, and J. R. Boyer, *Physica (Utrecht)* **108B**, 787 (1981).

⁷S. F. O'Shea and M. L. Klein, *Chem. Phys. Lett.* **66**, 381 (1979); O. G. Mouritsen and A. J. Berlinsky, *Phys. Rev. Lett.* **48**, 181 (1982); R. K. Kalia, P. Vashishta, and S. D. Mahanti, *Phys. Rev. Lett.* **49**, 676 (1982); S. F. O'Shea and M. L. Klein, *J. Chem. Phys.* **71**, 2399 (1979).

⁸Piotr Pierański *et al.*, *Philos. Mag. A* **37**, 107

(1978).

⁹One molecule moves in a cell bounded by its neighbors fixed in their lattice positions and orientations. The area $v_f(\varphi)$ accessible for the molecular center at a given orientation φ of this molecule is approximated by an ellipse. Integrating $v_f(\varphi)$ over φ one obtains v_f . See also J. A. Barker, *Lattice Theories of the Fluid State*, edited by J. S. Rowlinson (Pergamon, Oxford, 1963).

¹⁰M. Parrinello and A. Rahman, *Phys. Rev. Lett.* **45**, 1196 (1980).

¹¹G. S. Pawley and G. W. Thomas, *Phys. Rev. Lett.* **48**, 410 (1982).

¹²Hexamers, pentamers, trimers, and dimers were studied. About hexamers, see A. C. Brańka, Piotr Pierański, and K. W. Wojciechowski, *J. Phys. Chem. Solids* **43**, 817 (1982).

Observation of Bands of Faces on Incommensurate Rb_2ZnBr_4 Single Crystals

B. Dam, A. Janner, P. Bennema, W. H. v. d. Linden, and Th. Rasing ^(a)

Faculty of Science, Catholic University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

(Received 29 September 1982)

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.

PACS numbers: 61.50.Em, 61.50.Cj

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 interpreted² 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 ($\text{NH}_4\text{H}_2\text{PO}_4$) 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 $Pcmm$).

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 $(hkl+1)$ with m values varying between -5 and $+5$:

lm	00	13	14	01	12	15	02	11	24	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

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	1015	201
86.1	...	2013	52.9	...	2023
82.2	1013	2014	50.5	1002	2004
78.4	...	2001	48.2	...	2011
74.6	1014	2012	46.1	1011	2022
71.0	...	2015	44.2	...	2005
67.6	1001	2002	42.3	1024	2012
64.3	...	2011	40.6	...	2021
61.2	1012	2024	39.0	1003	2034
58.2	...	2003	37.5	...	2013
			36.1	101	202

$(201)-(202)$. 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 $m2m$, as considered until now.² Let us remark that this inter-

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.

Part of this work has been supported by the Netherlands Foundation for Pure Research (ZWO/FOM-SON).

^(a)Present address: Physics Department, University of California, Berkeley, Cal. 94720.

¹P. M. de Wolff, private communication.

²A. Janner, Th. Rasing, P. Bennema, and W. H. van der Linden, *Phys. Rev. Lett.* **45**, 1700 (1980).

³A. Bravais, *J. Ec. Polytech. (Paris)* **19**, 1 (1850).

⁴G. Friedel, *Bull. Soc. Fr. Mineral.* **30**, 326 (1907).

⁵G. D. H. Donnay and D. Harker, *Am. Mineral.* **22**, 446 (1937).

⁶P. Bennema, *Z. Kristallogr.* **121**, 312 (1965).

⁷B. Dam, P. Bennema, W. J. P. van Enkevort, and A. Janner, in *Extended Abstracts of the Proceedings of the International Conference on Crystal Growth, Moscow, 1980* (unpublished), Vol. 4, p. 18.

⁸S. Budurov and N. Stoichev, in *Growth of Crystals*, edited by N. N. Sheftal (Consultants Bureau, New York, 1968), Vol. 5A, p. 110.

⁹P. Groth, *Chemische Kristallographie* (W. Engelmann, Leipzig, 1906), Vol. 2, pp. 337–358.

¹⁰A. Janner and T. Janssen, *Acta Crystallogr. Sec. A* **36**, 399, 408 (1980); P. M. de Wolff, T. Janssen, and A. Janner, *Acta Crystallogr. Sec. A* **37**, 625 (1981).

¹¹P. Hartman and W. G. Perdok, *Acta Crystallogr.* **8**, 42, 521 (1955).

¹²Th. Rasing, thesis, University of Nijmegen, 1982 (unpublished).

¹³A. Janner and B. W. v. Beest, in *Proceedings of the Eleventh International Colloquium on Group Theoretical Methods in Physics, Istanbul, 23–28 August 1982* (to be published).

¹⁴R. Uyeda, in *Collected Abstracts of the Proceedings of the Twelfth International Congress of Crystallography, Ottawa, Canada, August 1981* (to be published).

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.