

Identification of Satellite Faces on Single Crystals of the Incommensurate Structures Rb_2ZnBr_4 and Rb_2ZnCl_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 Rb_2ZnBr_4 and Rb_2ZnCl_4 appear to be consistent with these predictions.

The incommensurate phases of Rb_2ZnBr_4 and of Rb_2ZnCl_4 are, as in K_2SeO_4 , characterized by a basic structure with space group $Pcmm$ and a displacive modulation with wave vector $\vec{q} = \gamma\vec{c}^* = (0, 0, \frac{1}{3} - \delta) \approx 0.3\vec{c}^*$ which is incommensurate with the orthorhombic basic lattice Λ^* .¹ The superspace symmetry group of K_2SeO_4 has been determined² as $G_s = P_{ss1}^{-Pcmm}$ which in the complete list of (3+1)-dimensional superspace groups³ appears as 62c.9.2. This same superspace group is also consistent with experimental investigations on Rb_2ZnBr_4 ⁴ and Rb_2ZnCl_4 ⁵ 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.⁶ 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 $|(h\vec{a}^* + k\vec{b}^* + l\vec{c}^*)| < |(h'\vec{a}^* + k'\vec{b}^* + l'\vec{c}^*)|$. The $\text{MI}\{hkl\}$ 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 \vec{Q} giving sharp diffraction spots and that those faces which get a low $|\vec{Q}|$ value by incorporating the superspace group symmetry have a high MI.

In the examples considered here, with a one-dimensional displacive modulation, these \vec{Q} 's require not three but four basic vectors in reciprocal space: $\vec{Q} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* + m\vec{q} = (h, k, l, m)$ 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 P_{ss1}^{-Pcmm} 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 $Pcmm$.

TABLE I. Conditions limiting possible reflections for the superspace group P_{ss1}^{-Pcmm} . [There are no conditions for all other terms, the general one being $(h, k, l, m) = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* + m\vec{q}$, with $\vec{a}^*, \vec{b}^*, \vec{c}^*$ orthorhombic and $\vec{q} = \gamma\vec{c}^*$ incommensurate. For the subgroup $P_{s1}^{-Pc2_1^n}$ the last condition drops out.]

$h000, h = 2n$
$0k00, k = 2n$
$00lm, l = 2n$
$hk00, h + k = 2n$
$0klm, l + m = 2n$
$h0lm, m = 2n$

In order to check the relevance of the generalized BFDH law given above we have studied the faces on single crystals of Rb_2ZnBr_4 and Rb_2ZnCl_4 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 Rb_2ZnBr_4 and by assuming proportionality for the corresponding ones of Rb_2ZnCl_4 . The crystals were grown by slow evaporation from aqueous solution at $\pm 30^\circ\text{C}$.

In Table II the comparison between the observed

TABLE II. Crystal faces observed and identified according to superspace group selection rules valid for $P_s \Gamma \Gamma^{Pc2_1^n}$. The angles ρ and φ are measured from the \hat{c}^* and the \hat{a}^* axis, respectively. The vector length $|\vec{Q}|$ is calculated using the parameters of Rb_2ZnBr_4 . Type B means basic face; type S, satellite face.

Sample	Orientation				Face indices h k l m	Donnay Harker law $ \vec{Q} $ in Å ⁻¹	Type
	observed ρ φ	assigned ρ φ					
Rb_2ZnBr_4	0 90	0 90	0 0 0 2	0.062	S		
	92 0	90 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 0 1	0.155	S		
	0 90	0 90	0 0 2 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		
Rb_2ZnCl_4 (I)	0 90	0 90	0 0 0 2	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		
	64 61	65 63	1 1 1 $\bar{1}$	0.168	S		
	57 33	56 34	2 0 1 0	0.182	B		
	55 65	56 66	1 1 1 0	0.184	B		
	0 90	0 90	0 0 2 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	B		
	90 29	90 30	$\bar{3}$ 1 0 0	0.261	B		
	90 90	90 90	0 2 0 0	0.264	B		
	75 33	75 34	$\bar{3}$ 1 1 $\bar{1}$	0.271	S		
	81 78	84 74	1 2 0 1 ?	0.277	S		
	69 80	69 75	1 2 1 0 ?	0.293	B		
Rb_2ZnCl_4 (II)	0 90	0 90	0 0 0 2	0.062	S		
	71 21	68 22	1 0 0 1	0.081	S		
	37 53	36 54	1 0 1 0	0.127	B		
	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 0 1	0.155	S		
	55 65	56 66	1 1 1 0	0.184	B		
	0 90	0 90	0 0 2 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					

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 ($hkl0$) 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 Rb_2ZnBr_4 are much larger in size than on Rb_2ZnCl_4 , which can simply be understood by regarding the growth conditions of the particular crystals: 30°C is just around the transition point of Rb_2ZnCl_4 while it is 50° below the transition point of Rb_2ZnBr_4 with consequently a much stronger manifestation of the modulation.

Inspection of the satellite faces observed in Rb_2ZnCl_4 shows that a better interpretation can be obtained if the condition $h0lm$, $m = 2n$, is omitted. This supports the alternative superspace group $G_s' = P_s \Gamma \Gamma^{Pc2_1^n}$ (equivalent with 33c.9.1 of Ref. 3), which shares with $P_{ss} \Gamma^{Pc2_1^n}$ all other conditions. The satellite faces of Rb_2ZnBr_4 are compatible with both superspace groups. It is interesting to note that $Pc2_1^n$ (the basic space group of G_s') is also the symmetry group of the low-temperature commensurate phase (the lock-in phase) for both compounds, while structure refinements indicate that it might also be the average space group of the incommensurate phase.^{1,9} (One gets the average structure by neglecting satellite reflections, whereas in the basic structure one disregards modulation. Often, but not

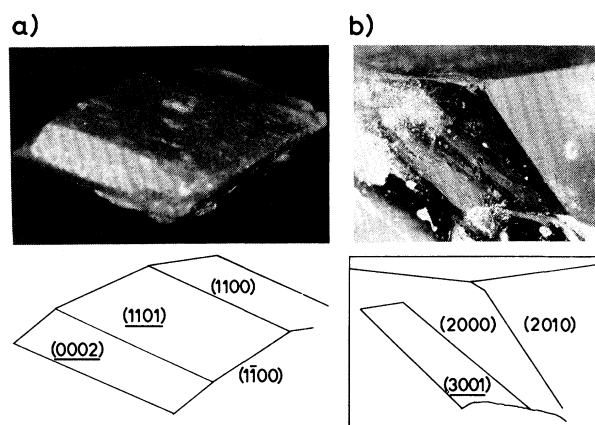


FIG. 1. Photographic images of incommensurate single crystals. (a) Rb_2ZnBr_4 . (b) Rb_2ZnCl_4 , sample I. In the schematic drawing corresponding with each photograph, the $(3+1)$ -dimensional indices are used; those of the satellite faces are underlined.

always, average and basic space groups coincide.)

In principle one can try to refer \vec{Q} vectors of 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 $|\vec{Q}|$ 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 generalized 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_2ZnBr_4 , with the observed basic forms $\{200\}$, $\{110\}$, $\{002\}$, $\{310\}$, and $\{020\}$. The smallest $|\vec{Q}|$ value involved here is $|(2, 0, 0)| = 0.15$, the largest is $|(0, 2, 0)| = 0.264$. 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 $|\vec{Q}| \geq |(3, 3, 1)| = 0.467$. Considering it as a satellite face (as first done by de Wolff and collaborators¹⁰) it gets four indices (1101) with a much shorter length of the corresponding reciprocal vector $|(1, 1, 0, 1)| = 0.155$. 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_2ZnCl_4 might indicate the presence of an additional component of the modulation wave vector of about $0.1\vec{a}^*$. Such a component is not compatible with an orthorhombic (3+1) dimensional superspace group and requires either a monoclinic distortion 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 interpreted.

In conclusion, the satellite faces identified on single crystals with clearly recognized incommensurate displacive modulation means that this modulation manifests itself on a macroscopic scale. We have shown that the superspace-group approach gives a very useful frame of reference 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 theory¹¹ as a tool and by introducing modulation in crystal growth models.

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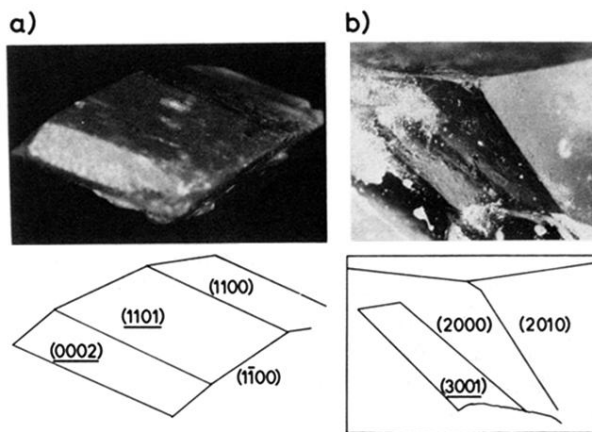


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