# *In Situ* Observation of a Roughening Transition of the $(10\bar{1}2)$ Satellite Crystal Surface of Modulated $((CH_3)_4N)_2ZnCl_4$

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The first microscopic observation of a roughening transition *on* a crystal surface is reported. The surface involved is a so-called satellite face of a modulated $((CH_3)_4N)_2ZnCl_4$ crystal. The orientation of such a face is directly coupled to the length of the structural modulation wave vector **q**. At a change of **q** the stable satellite orientations change. Applying *in situ* optical microscopy we observed growth and etch features on the $(10\bar{1}2)$ satellite face; at the first commensurate-commensurate phase transition the roughening features suggest a *sudden* decrease of the edge free energy to zero.

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The notion that crystal form is determined by the crystal lattice and its symmetry is the historical basis of modern crystallography. Given the fundamental difference between surface and bulk properties the success of early crystallographers is quite remarkable.

Recent experiments show the influence of temperature on crystal form. Above a certain critical temperature a flat crystal face may disappear. The resulting rounding of crystals has been observed, e.g., on a hcp $^4$He crystal in equilibrium with its superfluid,[1] and on an adamantane crystal approximately in equilibrium with its vapor.[2] Also the rounding of solution-grown organic crystals in nonequilibrium conditions has been reported.[3] The theory of the so-called roughening transition is extensively studied. With the use of Ising models, computer simulations of stepped surfaces[4] indicate that above the roughening temperature $T_R$ the edge free energy $\gamma$ becomes zero and the steps lose their identity. In the Wulff plot, the orientational plot of the surface free energy, a cusped minimum becomes rounded above $T_R$ (see Rottman and Wortis[5] for a review). The relation between $\gamma$ and $T_R$ was made more explicit by van der Eerden and Knops.[6] Also, the character of the phase transition has been suggested to be of infinite order.[7] Recently, with use of the fact that the roughening temperature is close to the critical temperature of a two-dimensional Ising lattice, a method has been developed to estimate the roughening temperature of more complicated (non-Kossel-type) crystal surfaces.[8]

Here, I present the first direct microscopic observations of the changes occurring on a crystal surface during a roughening transition. However, in this case the vanishing of the edge free energy is not due to a change in temperature, but results from a change in crystal structure. More precisely, from a change in the wavelength of the displacive modulation in $((CH_3)_4N)_2ZnCl_4$ (here indicated as TMA-ZC). Consequently the transition is not of the Kosterlitz-Thouless (continuous order) type, but rather it is first order. Hence, from now on we shall generalize the notion of a roughening transition as any transition where the step free energy vanishes.

TMA-ZC, a $K_2SO_4$-type structure, shows a sequence of modulated phases.[9] All these phases can be characterized as a combination of a relatively unperturbed basic structure and a displacive modulation wave vector $\mathbf{q} = \gamma \mathbf{c}^*$, with $\gamma$ taking several *commensurate* and *incommensurate* values (Table I).

The existence of extra, so-called satellite faces related to the length of the modulation wave and the supersymmetry of the crystal has been reported.[10,11] In the [010] zone of TMA-ZC, only the very small (1002) and $(10\bar{1}2)$ satellite faces were identified.[11] Large satellite faces were found on the mineral crystal calaverite.[12]

Extending the classical geometrical morphological laws to modulated crystals, faces have to be labeled by four integers $(hklm)$. These integers indicate the face normals, which are parallel to the Fourier wave vectors $\mathbf{k} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$ describing the crystal density distribution. In contrast to the main faces $(hkl0)$ whose orientation is not affected by the modulation wave, *satellite faces (hklm) change in orientation with respect to (hkl0) upon a change of* **q**. Indeed on TMA-ZC the change in length of the modulation wavelength as a function of temperature could be monitored by measuring the relative orientation of the satellite faces at different temperatures.[11] This approach to the mor-

TABLE I. The various phases of TMA-ZC between 0 and 30 °C. The wave vector **q** is taken along the pseudohexagonal axis, **c**, and the polarization is along the shortest axis, **b**.

| IV | III | II | I |
|---|---|---|---|
| $q = \frac{1}{3}\mathbf{c}^*$ | $q = \frac{2}{5}\mathbf{c}^*$ | $q \simeq 0.42\mathbf{c}^*$ | para |
| $T > 181$ K | $T > 276.5$ K | $T > 279$ K | $T > 293$ K |
| $P112_1/n$ | $Pc2_1n$ | ? | $Pcmn$ |

phology of modulated crystals is inspired by the superspace approach introduced for the diffraction pattern of incommensurate crystals by de Wolff, Janner, and Janssen.[13] It can be shown that for TMA-ZC and related $K_2SO_4$-type compounds the whole sequence of modulated structures can be described by one superspace group.[11,14]

In the incommensurate case the concept of closely packed lattice planes (Bravais) is completely lost for satellite orientations; thus, the nature of a satellite face remained unclear up to now. Does a satellite surface behave like a normal, main surface? Generally, on normal, main faces growth steps develop around screw dislocations to form the so-called growth spirals, first predicted by Frank.[15] Upon dissolution, steep etch pits are formed around screw and edge dislocations. These features have been extensively studied experimentally by both *in situ* and *ex situ* optical microscopy.[16] From theory it is clear that neither steep etch pits nor growth spirals can occur on surfaces with a zero edge free energy $\gamma$. Hence, to study the nature of a satellite face, we started an *in situ* investigation of the surface morphology of the $(10\bar{1}\bar{2})$ satellite face of TMA-ZC in the $T$ range between 0 and 10 °C and looked in particular for the existence of growth spirals.

Lately the possibilities to apply optical *in situ* microscopical techniques have increased enormously.[17] By recording the image on video tape with use of an analog contrast amplifier, it has been shown[18] that, with differential interference contrast microscopy, the kinetic behavior of growth steps as low as 100 Å can be observed. In the present study, oblique illumination microscopy[18] with conventional optics was used; it gives about the same vertical resolution as differential interference contrast microscopy. Even better results can be obtained by application of specially designed optics.[19]

After cutting a crystal, grown in the phase I at about 30 °C, along approximately the $(10\bar{1}\bar{2})$ orientation, the crystal is placed in a thermostated, stagnant-solution, growth cell[20] filled with a saturated TMA-ZC solution. Upon growth, the cut crystal surface develops into small isles of satellite faces partly bounded by strong main faces. The orientation of the grown satellite face can be checked quite accurately by optical goniometry *(ex situ)*.

The most important result of these observations is that indeed growth spirals and etch pits, circular in shape, can be observed in the incommensurate phase II and the commensurate phases III and IV, implying that the edge free energy of the $(10\bar{1}\bar{2})$ satellite face is larger than zero in each of the three modulated phases investigated here. In Fig. 1 a growth spiral is shown rotating on a $(10\bar{1}\bar{2})$ facet of a crystal growing in its incommensurate phase. The behavior of the growth spiral is quite normal. Upon increasing the supersaturation (by lowering the temperature in the growth cell) the rotational velocity of the spiral increases and the step distance decreases, eventually preventing observation of the spiral.

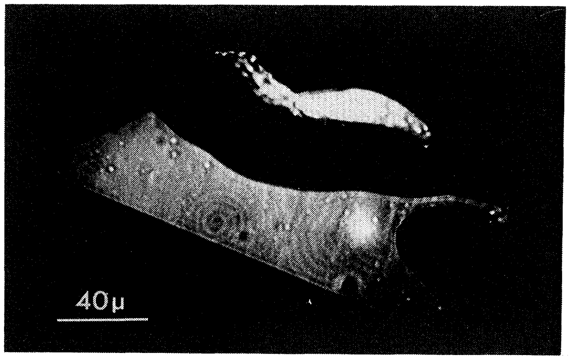

FIG. 1. *In situ* observation of a growth spiral on an *incommensurate* $(10\bar{1}\bar{2})$ face of $((CH_3)_4N)_2ZnCl_4$. $T = 8.1$ °C.

Apart from spirals and etch pits, the occurrence of so-called hollow cores[21] is also an indication that $\gamma$ is nonzero. These holes in the crystal surface may develop around strong dislocations. Their radius increases with decreasing supersaturation while their equilibrium radius is inversely proportional to $\gamma$ and approximately given by [21]

$$r_0 = (\mu b^2)/(8\pi^2\gamma), \tag{1}$$

with $\mu$ being the shear modulus and $b$ the dislocation's Burgers vector. Hollow cores can be explained by a reduction of the effective supersaturation due to the stress in the dislocation center. Indeed, in the satellite crystal surface we observed holes which, once formed, expand upon lowering the supersaturation. Below the equilibrium temperature the hollow cores suddenly open up and form etch pits, a process already observed more quantitatively by van der Hoek, van Enckevort, and van der Linden.[22] Such hollow cores could not be observed on several TMA-ZC main faces in any of the three modulated phases, which suggests that though $\gamma(10\bar{1}\bar{2})$ is larger than zero it is much smaller than the edge free energy of a main crystal face.

These surface morphological features support the idea that the $(10\bar{1}\bar{2})$ satellite face is a thermodynamically stable equilibrium form in each modulated phase. Hence each change in $\mathbf{q}$ implies an instability of the old $(10\bar{1}\bar{2})$ orientation with respect to the new one. Still, neither within the incommensurate phase nor at the incommensurate-commensurate transition were any peculiar surface features detected. The satellite face rotates over ~3° during this process, but optical goniometry showed that this tilting is a very slow process. Only after growing the crystal for about one day at constant temperature does the surface fully adopt its equilibrium orientation.

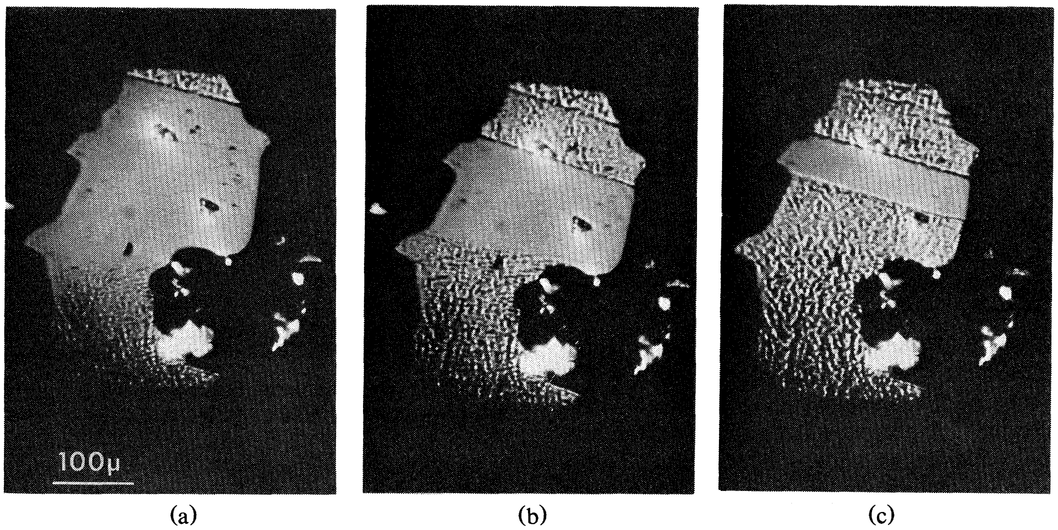

FIG. 2. *In situ* observation of the consecutive stages of the roughening of a $(10\overline{1}\overline{2})$ face of TMA-ZC at a change of the modulation wave vector $\mathbf{q}$ from $\frac{2}{5}\mathbf{c}^*$ to $\frac{1}{3}\mathbf{c}^*$. Roughening proceeds from both the upper and the lower edge of the satellite face, the boundary separating the rough and flat surface parts being along [010].

At the commensurate-commensurate transition $\mathbf{q}$ jumps from $\mathbf{q}=\frac{2}{5}\mathbf{c}^*$ to $\mathbf{q}=\frac{1}{3}\mathbf{c}^*$. Correspondingly the $(10\overline{1}\overline{2})$ satellite face rotates with respect to the main (0010) face over 9.5° in orientation. This is indeed found to be a discontinuous process. At 3.9 °C the satellite surface is seen to roughen. In Fig. 2 a sequence of pictures taken from the video screen illustrates this process. The central, flat $(10\overline{1}\overline{2})$ surface is found to disintegrate from two sides. Though we are not exactly at equilibrium (upon lowering the temperature the supersaturation of the solution increases), the coexistence of flat and disintegrated surface areas suggests that the roughening process is a first-order transition. On some facets, rotating growth spirals were observed while at the sides of the facet the roughening had set in already. At the rough surface no layer growth can be observed. The boundary line separating the two phases in Fig. 2 preferentially lies along [010]. Curiously enough the lower phase boundary in Fig. 2 proceeds continuously, while the upper boundary seems to be temporarily pinned sometimes and moves stepwise. Only on very smooth surfaces can such two-phase regions be observed. Otherwise the surface transition proceeds from distorted areas and quickly covers the whole satellite surface. Hence the coexistence of smooth and disintegrated rough surfaces is not likely to be due to a temperature gradient or to the proceeding bulk transition. This suggests that the surface itself undergoes a first-order transition.

The formation of a new $(10\overline{1}\overline{2})$ facet orientation conforming to the new wave vector $\mathbf{q}=\frac{1}{3}\mathbf{c}^*$ again takes a long time (about one day). However, if one increases the temperature shortly after the phase transition to the old phase again, the disintegrated rough surface (upon which no growth features can be discerned) quickly recovers. Small isles are formed which gradually coalesce into a single flat satellite surface. No hysteresis could be observed in this process.

As stated before, the observed roughening is not a roughening transition in the sense of the Ising models described at the beginning of this Letter. In the first place we are dealing here with only a near-equilibrium situation. Secondly, roughening due to a structural change generally corresponds to a change in the Wulff plot such that a sharply cusped minimum is transformed into a curve without a minimum for the surface free energy in that orientation. Such a transition in the surface free energy is in accordance with the first-order character of the transition observed; i.e., the coexistence of flat and roughened surface areas.

In conclusion, the thermodynamic stability (i.e., $\gamma > 0$) of the $(10\overline{1}\overline{2})$ satellite face is established in the *incommensurate* and in the first two *commensurate* phases of TMA-ZC. The delicate orientational dependence of satellite faces on the length of $\mathbf{q}$ again shows the remarkable connection between crystal structure and surface stability. Note that the amplitude of the displacements in the modulation wave is only of the order of tenths of an angstrom. This poses a challenge to understand the bonding nature of the satellite faces.

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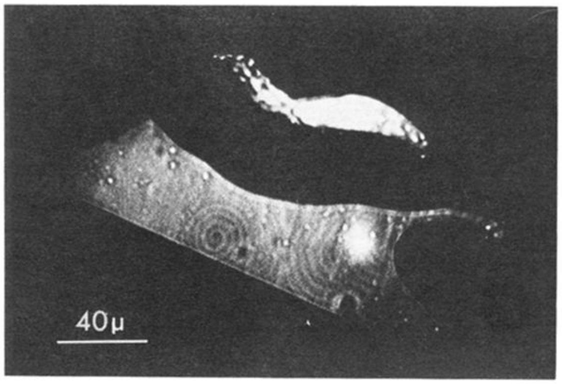

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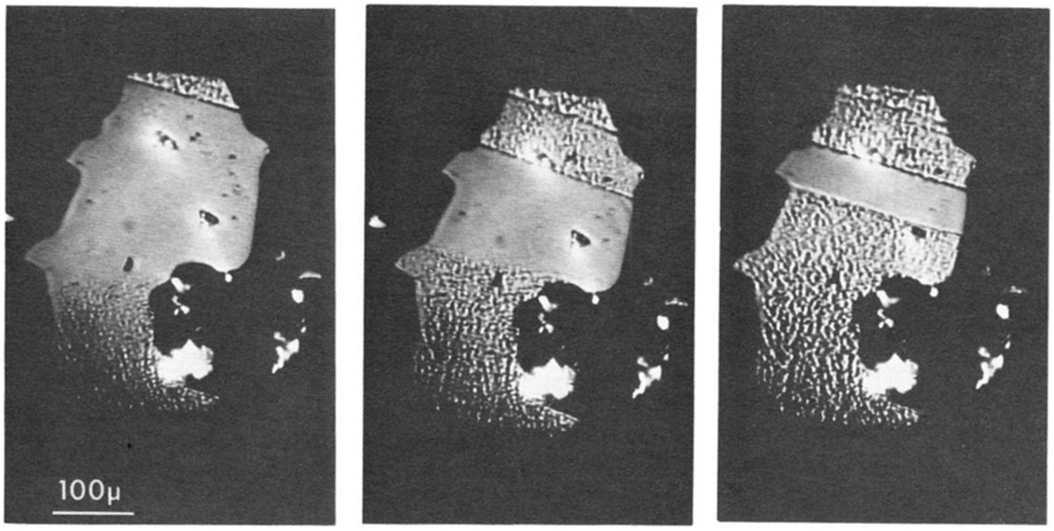

(a) (b) (c)

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