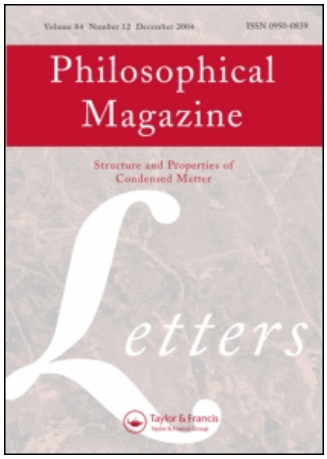

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Reversible transformation of a grain-boundary facet into a rough-to-rough ridge in zinc

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The transition of two first-order facet-to-rough ridges into a single first-order rough-to-rough ridge theoretically predicted for free surfaces has been observed in a slowly migrating grain boundary (GB). The reversible faceting-roughening transition of the [10$\bar{1}$0] tilt GB in a Zn bicrystal has been studied *in situ*. Above $T_{R+} = 673$ K, the slowly migrating GB semi-circle was discontinuously curved, e.g. two rounded (rough) GB portions intersected with a slope discontinuity. Above T_{R+}, a single first-order facet-to-rough GB ridge has been observed. Below $T_{R-} = 668$ K, a facet appeared and intersected with rounded (rough) GB portions with a slope discontinuity. Below T_{R-}, two first-order facet-to-rough GB ridges existed. The GB facet and tangents to the rounded (rough) GB portions were parallel to the closely packed planes of the constrained coincidence sites lattice. The steady state length of the facet increased with decreasing temperature. A hysteresis of about 5 K between roughening temperatures measured on heating, T_{R+}, and on cooling, T_{R-}, was observed. The facet reaches its steady-state length not immediately after a change of sample temperature but with a specific retardation.

1. Introduction

In 1974, Cahn and Hoffman [1] theoretically demonstrated for the first time that two curved (rough) surfaces may intersect along a line with a slope discontinuity. Such a line is called a first-order rough-to-rough ridge. The possibility for the existence of such surface and/or interface line defects clearly followed from the possible geometry of Wulff plots (called also γ-plots). Davidson and den Nijs [2] theoretically analyzed various possible features in the faceting of rough surfaces. The border between a facet and a curved (rough) surface may be of first order (with a slope discontinuity) or of second order (without such a discontinuity) [3, 4]. The first-order facet-to-rough border line may transform into a second-order line in a tricritical point. However, the first-order facet-to-rough border line may also

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continue into a rough surface as a first-order rough-to-rough ridge [2]. In addition, alone-standing rough-to-rough ridges may exist without any intersection with other border lines, finishing in two critical points [2]. To the best of our knowledge, such first-order rough-to-rough ridges have never been experimentally observed before the publication by Straumal *et al*. [5]. In [5], the shape of a cylindrical tilt twin grain boundary in a specially grown Mo bicrystal with two coaxial grains was studied. Cylindrical twin GB with an axis parallel to the common ⟨110⟩ axis of both grains possessed two short symmetrical twin GB facets $(111)_1//(111)_2$ (indices correspond to the grain 1 and grain 2). Elsewhere this GB was rough. The transition of the $(111)_1//(111)_2$ facet into the rough surface was of second order. The rough GBs curved away from the $(111)_1//(111)_2$ facet as x^{β}, with β belonging to the Pokrovsky–Talapov universality class [6]. The rough portions of cylindrical GB contained first-order rough-to-rough ridges in four crystallographically equivalent symmetric positions [5]. However, the theoretically predicted transition from two first-order facet-to-rough ridges into a single first-order rough-to-rough ridge has been never observed before (either for free surfaces nor for GBs). In this work, such a phenomenon was observed experimentally for the first time.

2. Experimental

A Zn $[10\bar{1}0]$ flat bicrystal was grown from Zn of 99.999 wt% purity using a modified Bridgman technique [7–9]. It contained two tilt GBs with a misorientation angle θ of 30°. Two 30° GBs grew parallel to one another, forming a loop (figure 1). Both flat and curved GB parts were perpendicular to the surface of the sample. The $[10\bar{1}0]$ axes in both grains were also perpendicular to the surface of the sample. The GB loop moved under the action of constant capillary driving force determined by the width of the middle grain (grain 2 in figure 1). The shape of the migrating GB loop was studied in the temperature range between 633 and 683 K *in situ* in a hot stage of a light microscope using polarized light. The temperature was stabilized within ±0.5 K. Temperature steps between isothermal anneals were 5 or 10 K. The duration of isothermal anneals was 120 or 180 s. The 'new' temperature of a hot stage and sample stabilized in a few seconds. The samples were protected from oxidation by a nitrogen atmosphere of high purity (99.999%). Before measurements, the samples were electropolished in a 30-ml H_3PO_4 + 70-ml C_2H_5OH solution (voltage 9 V, current density 5 mA/cm^2). A polarization filter in the reflected beam permitted a distinction to be made between different orientations of the grains by differing intensities of the reflected light. The GB shape was recorded in the course of experiment by a colour video camera connected to the microscope and a video recorder.

3. Results

The c/a value, where a is the lattice spacing in the basal plane (0001) and c is the lattice spacing in a direction perpendicular to the (0001) plane, is irrational in Zn.

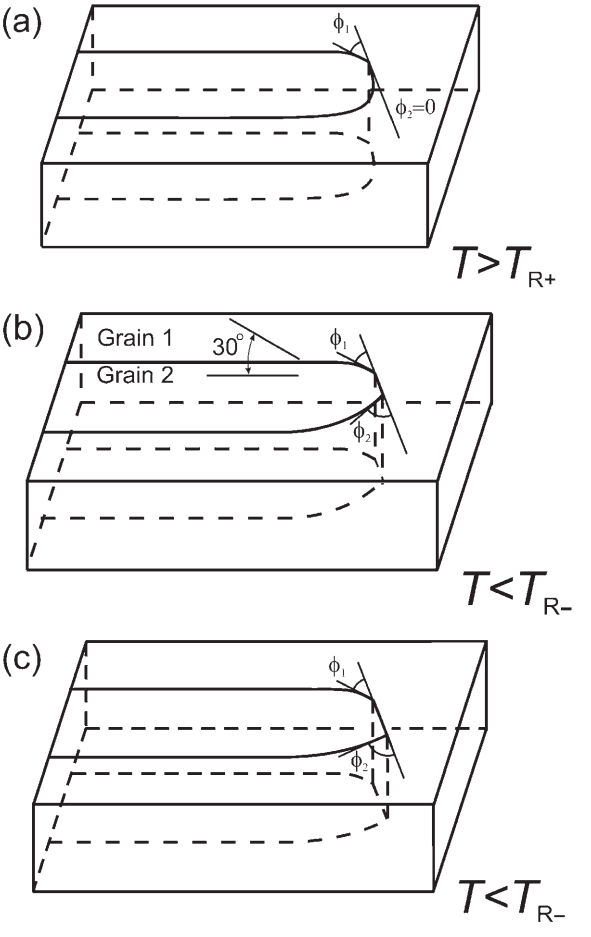

Figure 1. Scheme of the Zn bicrystal containing the 30° [10$\bar{1}$0] tilt GB. The GB consists of two parallel portions and a half-loop. (a) GB with first-order rough-to-rough ridge above T_{R+}. (b) GB with a short facet and two first-order facet-to-rough ridges slightly below T_{R-}. The orientation of basal plane (0001) in both grains and the misorientation angle of 30° are also shown. (c) GB with a long facet and two first-order facet-to-rough ridges well below T_{R-}. The angles ϕ_1 and ϕ_2 between facet and tangents to the upper (ϕ_1) and lower (ϕ_2) curved (rough) GB portions are also shown.

Therefore, the exact coincidence sites lattice (CSL) exists in Zn only for GBs with rotation around [0001] axis. In all other cases, the so-called constrained coincidence sites lattice (CCSL) exists [10]. The section of CCSLs perpendicular to [10$\bar{1}$0] tilt axis is shown in figure 2d for a GB with a misorientation angle of 30°. Filled and empty circles mark the sites of two misoriented Zn lattices. Large black circles mark the CCSL sites. The sites of both lattices do not coincide exactly; the difference reaches a few per cent of the lattice spacing. This situation is similar to the near-coincidence GBs in materials with the cubic lattice, when the misorientation angle is close but not equal to that of exact coincidence θ_Σ, but is

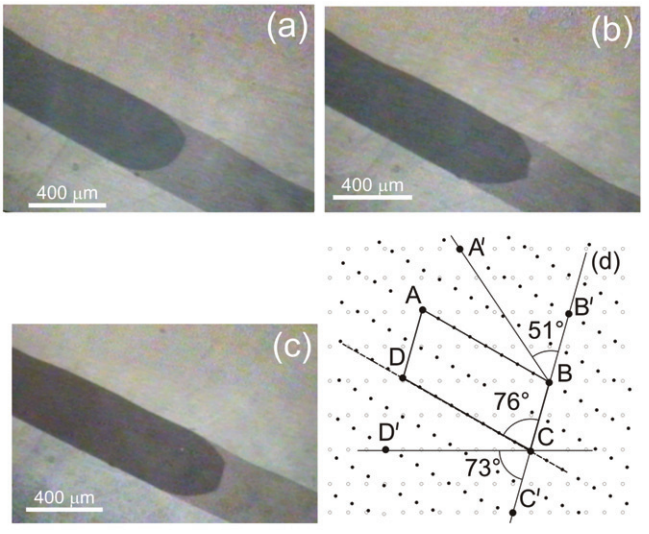

Figure 2. Micrograph of 30° [10$\bar{1}$0] tilt GB. (a) The first-order rough-to-rough ridge, $T = 678$ K above T_{R+}. (b) The short facet and two first-order facet-to-rough ridges, $T = 673$ K. (c) The long facet and two first-order facet-to-rough ridges, $T = 643$ K below T_{R-}. Grain width a and projection of facet length a_f are also shown. (d) Section of CCSL perpendicular to the [10$\bar{1}$0] tilt axis for the GB with misorientation angle $\theta = 30°$ in Zn. Filled and empty circles mark the sites of two misoriented Zn lattices. Large circles mark the sites of the CCSL. The inverse density of coincidence sites is $\Sigma = 15$ [10]. Unit cell of respective CCSL (ABCD), position of basal plane (0001) for grain 2 (CD, dashed line; *cf*. figure 1b) and position of CCSL plane BC parallel to the facet in the moving GB part are also shown. CCSL planes CD′ and BA′ are nearly parallel to the tangents to the lower and upper rounded GB portions in their intersection points with a facet (below T_{R+}) or with each other (above T_{R+}).

still inside the existence area of special GBs [8, 11]. The inverse density of coincidence sites is $\Sigma = 15$ for the studied $\theta = 30°$ GB [10]. The GB facet observed in the moving GB loop at low annealing temperatures (figure 2b, c) is parallel to the closest-packed CCSL plane (BC in figure 2d). The as-grown long GB portions were parallel to another closely-packed CCSL plane (CD in figure 2d). Both planes form an angle of 76°. The c/a ratio in Zn is temperature dependent [12]. The CCSL in figure 2a is shown for 690 K.

In figures 2b and c, the 76° facet in the slowly moving part of GB is shown (see also schemes in figures 1b and c). The rounded rough GB portions separated the 76° facet and both flat as-grown GBs. The edges between the flat 76° GB facet and the rounded rough regions were not smooth; they revealed slope discontinuities. In other words, the derivative of the GB line (and also that of the GB free enthalpy) has a break. It is an indication that the transition between the 76° facet and the rough GBs is of first order. The angles ϕ_1 and ϕ_2 formed by the facet and the tangents to the upper and lower rounded (rough) GB portions (figures 1b and c) characterize the slope discontinuities at the 'upper' (1) and 'lower' (2) edges. No low-angle GBs were observed at the discontinuities, i.e. the discontinuities are not caused by the GB triple junctions. The absence of low-angle GBs at the discontinuities in the studied samples has been proved both optically (no contrast in the polarized light during

in situ studies) and metallographically (by etching of the sample after migration experiments). The low-angle GBs were not visible. Previously, we proved by electron-backscattering diffraction (EBSD) that low-angle GBs can be visualized by these methods if the GB misorientation is above 2°.

The length of the 76° facet continuously decreased with increasing temperature (figure 3a). At $T_{R+} = 673$ K, the roughening transition proceeded and the 76° facet completely disappeared. The angle ϕ_2 increased from 40° to 70° and dropped down to zero at $T_{R+} = 673$ K (figure 3b). The tangent to the lower rounded GB portion was almost parallel to one of the closely-packed CCSL planes (CD′ in figure 2d), and the value of $\phi_2 = 70°$ at $T_{R+} = 673$ K was very close to the angle of 73° between CC′ and CD′ planes of CCSL (figure 2d). The angle ϕ_1 decreased from 55° to 42° and did not significantly change at $T_{R+} = 673$ K. The mean position of the tangent to the upper rounded GB portion is almost parallel to the closely-packed CCSL plane BA′ (figure 2d). The mean value of $\phi_1 = 48°$ was very close to the angle of 51° between A′B and BB′ planes (figure 2d).

Above $T_{R+} = 673$ K, the moving GB part contained two rounded (rough) GB portions. They intersected along the line with a slope discontinuity (figures 1a and 2a). The tangent to the lower rounded GB portion was parallel to the CB plane of the CCSL. The angle ϕ_1 between two rounded GB portions decreased further from 42° to 35°. The 76° facet appeared again at $T_{R-} = 668$ K on cooling. The angle ϕ_2 increased at $T_{R-} = 668$ K from zero to 40° (figure 3c). The angle ϕ_1 increased on cooling from 45° to 55°. A hysteresis of about 5 K between roughening temperatures during heating T_{R+} and during cooling T_{R-} was observed. This is the second indication that the transition between the 76° facet and rough GB is of first order.

In figure 4, the dependences of the facet length and discontinuity angles ϕ_1 and ϕ_2 on the annealing time are shown. The zero-time point (0 s) corresponds to the time when the temperature of the sample and hot stage became stable after 5–10 K heating (or cooling) from the temperature of the previous anneal. It took about 80 s before the facet disappeared at 673 K after heating from 663 K (figures 4a, b). The angle ϕ_2 followed the behaviour of a facet (i.e. ϕ_2 decreased from 70° to zero at 673 K; figure 4b). The angle ϕ_1 fluctuated around a constant value of 42°. It took about 60 s before the facet appeared at 668 K after cooling from 673 K (figures 4c, d). The angle ϕ_2 increased from zero to 35–55° at 668 K (figure 4d). The angle ϕ_1 fluctuated around a constant value of 42°. In other words, the facet did not reach its steady state length immediately after a change of sample temperature, but only after a certain delay.

4. Discussion

An important difference exists between the Wulff approach for the equilibrium crystal shape of free surfaces (and interphase boundaries) and grain boundaries (GBs). The equilibrium crystal shape defined by the Wulff procedure corresponds to a minimum in the free enthalpy for a crystal having a constant volume. An isolated grain cannot conserve its volume if a GB is mobile. A free GB always moves to the centre of its curvature under a capillary driving force. However, the Wulff approach can be successfully applied to small deviations from equilibrium.

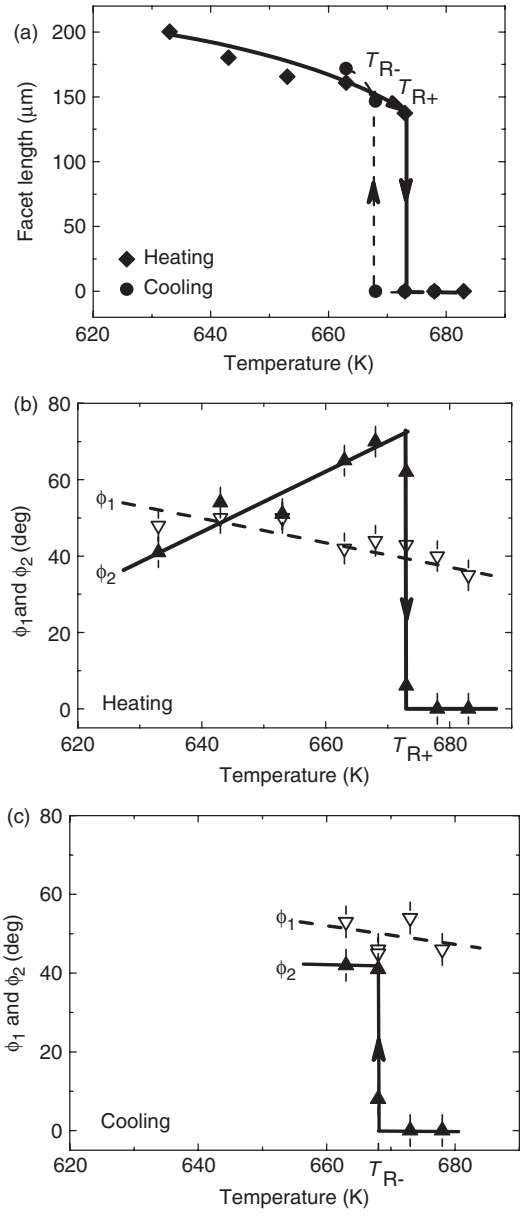

Figure 3. (a) Temperature dependence of GB facet steady-state length by heating and cooling. (b) Temperature dependence of ϕ_1 and ϕ_2 angles on heating. (c) Temperature dependence of ϕ_1 and ϕ_2 angles on cooling.

Particularly, it allows a description of the shape of a slowly growing (or slowly dissolving) crystal [13]. Similarly, the γ-plots also allowed an adequate description of GB faceting and roughening by using the coincidence site lattice (superlattice which is common for crystal lattices of both grains forming a GB) [14–17]. However, this approach is eligible only for small deviations from equilibrium, i.e. for slow GB

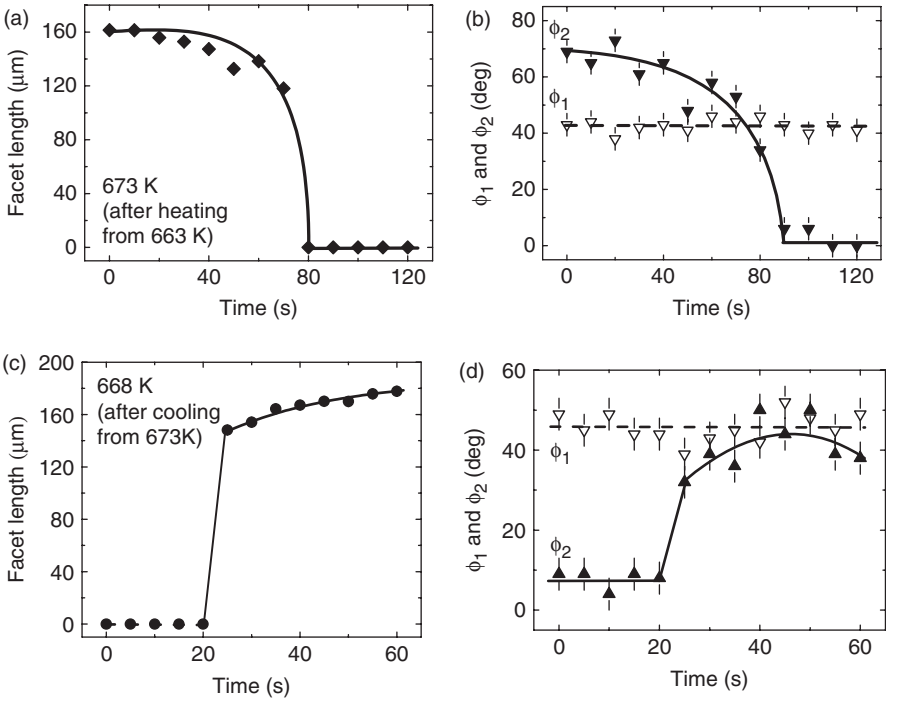

Figure 4. Dependence of the facet length and of the angles ϕ_1 and ϕ_2 on the annealing time after stabilization of temperature. (a) The facet length and (b) angles ϕ_1 and ϕ_2 at 673 K after heating from 663 K. The facet disappears only after 80 s. (c) The facet length and (d) angles ϕ_1 and ϕ_2 at 668 K after cooling from 673 K. The facet appears after 20 s and reaches its steady-state length only after 60 s.

migration. If a GB moves with high speed, its shape would be controlled mainly by the mobility and not by the energy of facets and rough portions [8, 9, 17, 18]. Another factor influencing the shape of a moving GB is the thermal etching groove (similar to the classic Mullins groove) appearing where the GB intersects the free surface of metallographic observation [19]. The influence of this groove on the moving GBs in Zn has been studied previously [8]. Fortunately, the rate of the groove growth is much slower than that of GB migration. As a result, if a capillary driving force for the GB motion is high enough (as in this work), a moving GB can break away from the thermal groove. In this case, a thermal groove does not influence the GB mobility and GB shape.

We discuss first the disappearance of a GB facet with increasing temperature. The idea of a faceting-roughening transition for free crystal surfaces was firstly proposed by Burton *et al.* [20]. They supposed that the free energy of an elementary step for each crystal surface decreases with increasing temperature on account of the thermal fluctuations (configurational enthropy). As a result, a specific roughening temperature T_R exists for each singular crystal face. At T_R, the free energy of the elementary step at the surface falls to zero. As a result, a plane surface becomes unstable above T_R. T_R is different for different surfaces, the highest T_R corresponding to the surfaces with the lowest Miller indices. For GBs, a CSL

(i.e. a superlattice formed by the lattices of two grains) plays a role similar to that which a crystal lattice plays for the free surface. In other words, GB facets are almost always parallel to the CSL planes that are densely packed with coincidence sites. Close to the coincidence misorientations, the GB faceting appears together with the so-called special GB properties [11]. According to the idea of Burton *et al*. [20], a surface facet has to gradually disappear by $T \rightarrow T_R$. Given the difficult experimental conditions required, surface roughening (i.e. the vanishing of surface facets) was directly observed for the first time more than 30 years later in the growth of solid ^{4}He crystals [21]. The gradual disappearance of a GB facet was observed for the first time in triple junctions formed by three [10$\bar{1}$0] tilt GBs in Zn with misorientation angles θ of 43°, 37° and 6° [7]. However, the GB facet disappeared in a very narrow temperature interval of only 17 K [7]. In the mean-field approximation proposed by Andreev [22], the radius of the facet, R, has to decrease close to the T_R according to the square-root law $R \sim \tau^{0.5}$, where $\tau = |T_{R-} - T|/T_R$. A more sophisticated theory, based on the solid-on-solid (SOS) model, supposed a weaker temperature dependence of T_R of the form $R \sim \exp(c\tau^{-0.5})$, thus exhibiting an essential singularity [23]. The $R(T)$ dependence for the ^{4}He facets follows the SOS law. In our case, the mean-field Andreev approximation describes well the GB facet growth during cooling (figure 3a). GB facet growth on cooling was not observed in [7]. The GB facet shortening observed in this work by heating (figure 3a) is better described by the SOS model, in contrast to the observations in [7]. The 37° [10$\bar{1}$0] tilt GB remained rough and curved following a temperature decrease, thus showing the possibility for substantial undercooling of the rough GB facet.

Bonzel and Edmuns [24] proposed a novel calculation method for the kink and step free-energies based on the known temperature dependence of the facet radius. We will attempt to transfer this method to the case of GB facets. A change of temperature would change the step free-energy and, hence, also the facet radius $R(T)$. The following relationship between facet radii R and step free-energies f is then valid:

$$\frac{f(T)}{f(0)} = \frac{R(T)}{R(0)}. \tag{1}$$

The temperature dependence of the step free-energy related to kink formation is given in the framework of an Ising model [25–27] (for $T < 0.8\varepsilon_k/k$, where ε_k is the kink formation energy) as:

$$f(T) = f(0) - 2kT \exp\left(-\frac{\varepsilon}{kT}\right). \tag{2}$$

Combining both equations (1) and (2) and rewriting the expression such that a ratio of facet radii appears on the left, we have [17]:

$$\frac{T_m}{T}\left(1 - \frac{R(T)}{R(0)}\right) = \frac{2kT_m}{f(0)} \exp\left(-\frac{\varepsilon}{kT}\right), \tag{3}$$

where T_m is the melting temperature. If measurements of the $R(T)$ for a certain facet can be carried out for a range of temperatures, a plot of $\ln[T_m(T(1 - R(T)/R(0))]$ *versus* $1/T$ should yield a straight line according to equation (3). The intersection on the ordinate of $\ln[2kT_m/f(0)]$ gives the step free-energy at zero temperature $f(0)$,

and the slope of the line gives ε_k/k. Let us suppose that $R(0)$ is equal to the maximal possible length of the GB facet (about 200 μm; *cf*. figure 2). In this case the Bonzel plot yields a rather low value for the step free-energy at zero temperature of $f(0) = 10^{-4}$ eV/atom. Typical $f(0)$ values for the surfaces lie in the interval between 0.01 and 0.8 eV (obtained in theoretical calculations [28]) and about 0.1 eV (obtained experimentally for Pb(111) surfaces [29]). The slope of the Bonzel plots yields, in our case, also a rather low value for the kink energy $\varepsilon_k = 3 \times 10^{-4}$ eV. In the case of Pb(111) surfaces, ε_k is about 0.05 eV [29]. The reason for the low values obtained for $f(0)$ and ε_k may be because we calculated the slope very close to the T_R temperature, where the validity of the Bonzel method is questionable. In the future, we will try to find GBs in Zn where the facet length substantially decreases with increasing temperature (as that of Pb facets reported in [29]), but does not fall to zero.

In using the Andreev, SOS and Bonzel approaches, it should be noted that they were developed for stationary equilibrium surfaces and not for moving GBs. The case of steady-state migrating GBs is more similar to the classic case of the shape of a growing or dissolving crystal [13]. The GB migration can drastically influence the GB shape and the shortening of the facet with increasing temperature [17, 18]. The most important difference between the GB phenomena observed in this work and experiments on surface roughening is that, whereas the facet disappears by heating, two first-order facet-to-rough ridges do not disappear but merge into a single first-order rough-to-rough ridge. To the best of our knowledge, this phenomenon has never been reported before. The first-order rough-to-rough ridges observed in this work form a class of line defects that can influence the mobility of grain boundaries as do grain boundary triple lines, especially in nanograined materials [8, 30]. Hence, their further study may have practical importance.

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