Equilibrium Shapes of Small Lead Crystals: Observation of Pokrovsky-Talapov Critical Behavior

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Equilibrium crystals of Pb in the temperature range 200–300 °C exhibit facets and curved surfaces which are joined at "smooth" edges (no slope discontinuity). Recent theoretical interpretation has suggested that the crystal shape near such edges should show interfacial critical anomalies. Observation via scanning electron microscopy of 2–10-μm Pb crystals reveals a critical exponent which is consistent with theoretical identification as belonging to the Pokrovsky-Talapov universality class.

Although the experimental situation for quantum crystals remains controversial,[1] it is generally believed that macroscopic equilibrium crystals at temperature $T = 0$ are completely faceted (polyhedral). The theoretical picture of the thermal evolution of the equilibrium crystal shape (ECS) of a typical crystal[2,3] is as follows: At nonzero temperatures curved interfacial regions may appear in addition to planar facets. As T increases, facets shrink and eventually disappear,[4] each facet at its own characteristic roughening ("faceting") temperature[5] $T_R(\hat{m})$ ($\hat{m}$ is the facet orientation relative to crystal axes), until at sufficiently high temperature the ECS becomes everywhere smoothly rounded (unless, of course, the system first undergoes a bulk phase change, such as melting). This scenario seems consistent with the present experimental situation, although the difficulty of achieving equilibrium on a laboratory-feasible time scale imposes severe restrictions on the ranges of crystal size and temperature which can be investigated. Indeed, hcp ^{4}He at 0.2–1.5 K is the only system which has been studied through a sequence of faceting transitions and into the everywhere-rounded regime.[6]

This Letter focuses on the ECS in the intermediate regime, where both facets and curved interfacial regions are present. Facets and curved regions then meet at edges, which may be either sharp (slope discontinuity) or smooth (no slope discontinuity). Near a smooth edge the shape of the curved interface varies as [see Fig. 1(a)]

$$y = A (x - x_c)^\theta + \text{higher-order terms.} \quad (1)$$

The position of the edge is given by x_c. The exponent θ is a critical index (see below). Its mean-field value is[7]

$$\theta_{\text{MF}} = 2. \quad (2)$$
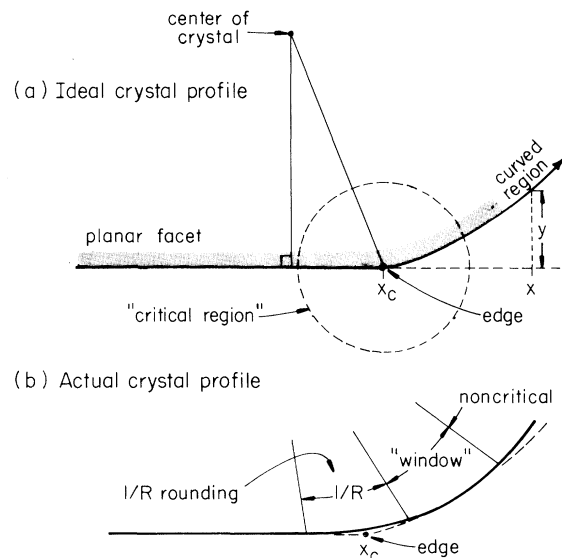
On the other hand, theoretical approaches[2,3,8,9]

FIG. 1. Sketches of (a) ideal and (b) actual crystal profiles through a smooth edge. Ideally ($R \to \infty$), the edge is perfectly sharp and Eq. (1) holds precisely inside the "critical region" ($x - x_c$ small). Actually, the edge is rounded because of finite crystal size, x_c becomes a fit parameter, and only data from the "window" can be used in estimating the index θ.

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which include fluctuations have recently led to the prediction

$$\theta_{\text{theory}} = \tfrac{3}{2}, \tag{3}$$

The value $\theta = \tfrac{3}{2}$ is characteristic of the so-called Pokrovsky-Talapov[10] (or Gruber-Mullins[11, 12]) universality class and should be independent of temperature and facet orientation, provided always that $T < T_R(\hat{m})$.

This Letter reports direct measurement of the exponent θ via scanning electron microscopy (SEM) of 2–10-μm Pb crystals grown, as previously reported,[13–15] on a graphite substrate.[16] We find values of θ which are distinctly below the mean-field prediction (2) and consistent with the theoretical predictions (3). This observation is the first of its kind and the third reported instance[17, 18] of the Pokrovsky-Talapov[10] (Gruber-Mullins[11]) universality class. It also provides confirmation of the connection between interfacial phase transitions and the ECS,[2, 3] which we now review.

The ECS is a geometrical expression of interfacial thermodynamics. Wulff[19] and Herring[4] showed how the dependence of the interfacial free energy per unit area $f_i(T,\hat{m})$ on the interfacial orientation $\hat{m}$ determines the ECS $r(T,\hat{h})$ (r is the radius to the interface from the center of the crystal in the direction $\hat{h}$) of a macroscopic crystalline inclusion in two-phase coexistence. Andreev[7] recently made explicit the sense in which Wulff's construction is simply a Legendre transform,[20] so that $f_i,\hat{m}$ and $r,\hat{h}$ are thermodynamically conjugate pairs and the relation $\hat{m}(T,\hat{h})$, defined by the Wulff construction, is an equation of state. From this perspective $r(T,\hat{h})$ is a free energy and its singularities, which at fixed T are just the crystal edges discussed above, define an interfacial phase diagram.[2, 3] Sharp edges correspond to first-order phase transitions and smooth edges, to second-order phase transitions. Behavior near a smooth edge, as in Eq. (1), is critical behavior, and θ is a critical exponent. The prediction $\theta = \tfrac{3}{2}$ rests on the propositions[2, 3, 8, 9] that (a) as long as the bulk correlation length is small, the interface can be modeled as a two-dimensional surface and (b) the dominant excitations of this surface are "steps" or "ledges."[21] The dynamics of this step/ledge system was first studied by Gruber and Mullins.[11, 12] Pokrovsky and Talapov[10] studied the corresponding excitations (domain walls) in the commensurate-incommensurate transition.

Equilibrium lead crystals in the range 2–10 μm were grown on a single-crystal graphite substrate by a method described in detail elsewhere.[13–15] The

process is carried out under ultrahigh vacuum[22] (UHV) and involves (i) in situ cleavage of the graphite crystal, (ii) room-temperature deposition of a 3000-Å film of 99.999+%-pure lead from a molybdenum crucible, (iii) melting of the lead film (during which it breaks up into 2–10-μm liquid droplets), (iv) cooling to at least 75 °C below the melting temperature of lead (327 °C) to solidify, (v) annealing at a fixed temperature (200–300 °C) until the equilibrium crystal shape is reached, and, finally, (vi) rapid cooling to room temperature. Step (iv) is required to overcome the tendency of liquid Pb to supercool, which would otherwise prevent direct crystallization of the higher-temperature (275–300 °C) crystals.[15, 23] Annealing times in step (v) necessary to achieve equilibrium vary in the range 1–10 h but are always long with respect to the cooling time in step (vi) (typically less than 30 s to cool to 120 °C), so the final shape achieved is that characteristic of the annealing temperature in step (v). Equilibrium during step (v) takes place via surface self-diffusion.[13] The evidence that the final forms attain are, indeed, equilibrium shapes is that (a) no further time evolution is detectable, (b) different thermal histories lead to the same final shape,[13, 14] (c) crystals of different sizes have identical shapes, and (d) the observed ECS exhibits the lattice point-group symmetry (except, of course, that part of the complete ECS is truncated by the substrate[16]). Gravitational effects are expected to be negligible for small crystals, which is consistent with point (d).

Once grown, the equilibrium crystals were observed by SEM.[24] In the temperature range studied, they are cubo-octahedra exhibiting clearly defined {111} and {100} planar facets, separated by curved surfaces with smooth edges. They sit epitaxially on the substrate with {111}Pb ∥ {001}Gr and ⟨1̄10⟩Pb ∥ ⟨010⟩Gr. The facets shrink with increasing temperature, and at 300 °C the {100} facet is hardly visible. In order to see edge profiles, it is necessary to align the direction of observation accurately parallel to the plane of the facet. When this is done, the facet appears strikingly linear (straight),[24] except for small $1/R$ effects near the edges (see below). The pictures were originally taken with other purposes in mind.[13–15] We have studied four photographs with particular care. Our best data are from a single 9-μm crystal annealed at 300 °C for 4 h and viewed along the ⟨110⟩Pb direction, which sets the {111} facets in profile. This presents {111}/curved edges, which we analyze in detail below. To provide the raw data, a photographic enlargement ($\sim 3 \times 10^4 \times$ from the original

crystal) of the SEM picture was digitized on an Auto-trol digitizer. The approximately fifty digitized data points[25] (Fig. 2) cover an angular range of roughly ± 18° about the edge studied.

Analysis of crystal-shape data near a smooth edge is similar to that of thermal phase-transition data near a critical point. Data points far from the edge cannot be expected to be fitted by the form of Eq. (1), because higher-order (correction-to-scaling) terms become important. Similarly, data very close to the edge are contaminated by finite-size or "$1/R$" effects due to atomic-scale rounding of the ideally singular edge structure.[2,26] This has two consequences: First, the actual position of the edge (x_c) becomes fuzzy and must be treated as a fitting parameter; second, there is at best a window of data [Fig. 1(b)] which should be fitted by Eq. (1). Our procedure is to choose a window and then determine θ by a three-parameter (A,x_c,θ) least-squares fit. Figure 2 illustrates the sensitivity of θ to the choice of window. Notice that the effective value of θ increases at both ends: Windows that extend to small $x - x_c$ see $1/R$ rounding of the singularity; those that extend to large $x - x_c$ begin to see the macroscopic closure of the crystal outline. Between these extremes is a region of low effective θ (ex-
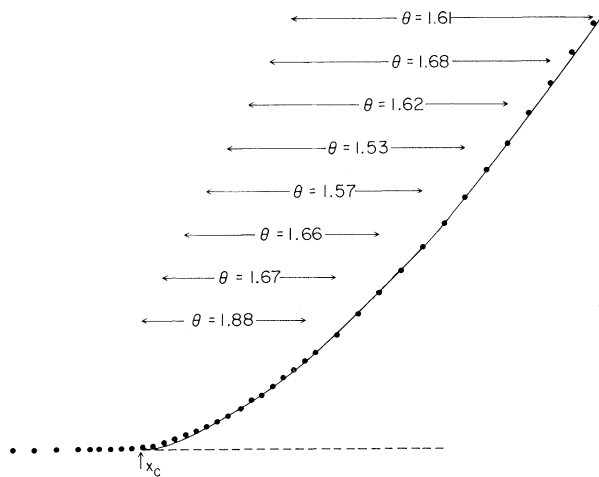

FIG. 2. Data for our best crystal. Dots are digitized data points from photograph. Least-squares fits by Eq. (1), performed over the ranges shown by the arrows (approximately 0.8 μm), produced the values of θ indicated. The solid line plots the best-fit function or the $\theta = 1.53$ window. The corresponding nominal edge is at x_c, as shown. The best-fit function lies slightly outside the crystal profile both at $x \simeq x_c$ ($1/R$ rounding) and far from the edge (corrections to scaling). Best-fit functions for nearby "windows" also produce good fits to the data, provided θ lies in the range (4).

tending in angular measure between 4° and 13° from the edge) which we interpret as the true critical region. Figure 2 shows the fit to the data points provided by least-squares analysis of the $\theta_{\rm eff} = 1.53$ window.

Without better control of the correction terms, it is impossible to make a precise estimate of θ. On the basis of Fig. 2 and additional supporting analysis,[27] we quote rather conservatively

$$\theta = 1.60 \pm 0.15. \qquad (4)$$

This is consistent with the theoretical prediction (3) [but difficult to reconcile with the mean-field result (2)]. Analysis of other crystals and at other annealing temperatures continues to show a region of lower effective θ (as in Fig. 2) and gives results consistent with (4) but with wider uncertainties.

Better control of correction terms would allow a more precise estimate than Eq. (4). Experimentally, this would call for analysis of identically prepared crystals of different sizes to pick up the $1/R$ corrections. In practice this will be limited by the long equilibration times necessary for large crystals.[13-15] Theoretical estimates for $1/R$ corrections are not to the best of our knowledge now available. Similarly, at large $x - x_c$, it would be useful to know the correction-to-scaling exponent[28] for the Pokrovsy-Talapov (Gruber-Mullins) universality class. Additional observations of other facets, temperatures, and materials seem called for. We note in closing that not all observed edges are of the smooth type studied here. Gold,[24] in particular, shows sharp edges, which have only very recently begun to receive theoretical attention.[2,3]

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[26]The ideal singularity in shape [Eq. (1)] occurs only in the "thermodynamic limit," as the crystal size becomes macroscopically large ($R \to \infty$).

[27]We have also done ln-ln analysis and direct graphical fits, with similar results.

[28]Probably these corrections go as $1 + O((x - x_c)^{1/2})$ because of the free-fermion character of the Pokrovsky-Talapov fixed point. W. F. Saam, private communication.