

Observation of vertex-rounding transition for a crystal in equilibrium: Oxygen-covered tungsten

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Equilibrium crystal shape of oxygen-covered tungsten is followed as a function of temperature using field ion microscopy. In the vicinity of the (111) region, at the temperature 970 ± 70 K, the system undergoes a phase transition from a polyhedral form (sharp edges and sharp vertex) to a rounded form (sharp edges, rounded vertex).

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I. INTRODUCTION

The shape of a crystal in equilibrium depends on the temperature. Theoretical considerations suggest that at 0 K, equilibrium crystal shapes (ECS) are polyhedral.^{1,2} On the other hand, both theory and experiment show that the ECS are almost spherical near the melting point. The detailed evolution of ECS with temperature depends on the particular system studied. According to the three-dimensional Ising model with nearest-neighbor and next-nearest-neighbor interaction,^{1,3-6} there appear to be two basic evolution patterns depicted in Fig. 1. In type-A evolution,^{1,3} the crystal is polyhedral only at 0 K. At arbitrarily low nonzero temperature, facets are separated by rough, rounded regions; no sharp edges or vertices are present on the surface. In type-B evolution (obtained for repulsive next-nearest-neighbor interaction),^{1,3} there exist two characteristic temperatures, the vertex-rounding temperature T_0 and the edge-rounding temperature T_1 . The crystal remains strictly polyhedral up to T_0 . Between T_0 and T_1 , the vertices are smoothly rounded, but the edges remain sharp. Above T_1 , the sharp edges disappear. For high temperatures, both models predict the disappearance of flat facets at the roughening temperature (facet-rounding temperature).

In experiment, the two evolution patterns are difficult to distinguish, because at low temperature it is often impossible to achieve equilibrium due to material transport limitations, while at high temperature the two patterns are similar. Nevertheless, experiments suggest that ⁴He crystals follow type-A evolution,⁵ while NaCl crystals follow type-B evolution (although no images of ECS between T_0 and T_1 have been obtained).⁶

In this Brief Report, we describe how the equilibrium shape of oxygen-covered tungsten (O/W) changes with temperature. We show that the thermal evolution in the vicinity of the [111]-oriented vertex is of type-B, and estimate the vertex-rounding temperature T_0 .

II. EXPERIMENT

In this experiment, the equilibrium crystal was approximated by a [111]-oriented, needle-shaped tungsten crystal (field emitter geometry), with the cone half-angle not exceeding 10° . The apex of the needle was approximately hemispherical, with the average radius of curvature 250 nm

(crystals of smaller radii do not survive thermal cleaning, while larger crystals are difficult to equilibrate). With such crystal geometry, for orientations within 25° of the central direction (in our case, [111]), the average radius of curvature is constant up to $\pm 3\%$.⁷ Therefore, in the vicinity of the (111) pole, the needle crystal is a good approximation of the true equilibrium shape. In this study, we concentrate only on the vicinity of the (111) pole.

The experiment was carried out in a field ion microscope,^{8,9} with the base pressure of 3×10^{-10} Torr. During the thermal shaping of the crystal, the average pressure was higher: 1×10^{-9} Torr, due to the residual presence of the gases used for imaging (helium, neon, krypton) and for adsorption (oxygen).

To observe the equilibrium shape at a temperature T , the following procedure was applied: (1) The crystal was cleaned thermally.¹⁰ (2) The crystal was cooled to 80 K and its surface was covered by oxygen (1.4 ± 0.3 L). (3) The crystal was preannealed at 1500 K for 80 s to achieve a globally faceted shape.¹¹ (4) For technical reasons, the crystal was for a short period (~ 1 min) held at low temperature (near 80 K). (5) The crystal was equilibrated at the temperature of interest T for 80 s. (6) The T equilibrium configuration was frozen by rapid cooling of the crystal to 80 K (the estimated quenching rate is 400 K/s at 1000 K). (7) The crystal surface around the (111) crystal pole was observed by field ion microscopy.

To observe the ECS at a different temperature, the whole

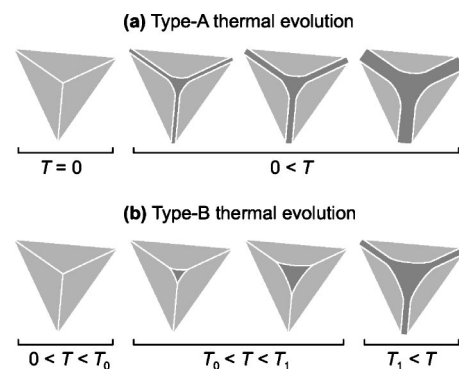


FIG. 1. Thermal evolution of a vertex of equilibrium crystals (Refs. 1 and 3). Dark shading denotes the rough, rounded region. In (b), T_0 denotes the vertex-rounding temperature, and T_1 denotes the edge-rounding temperature.

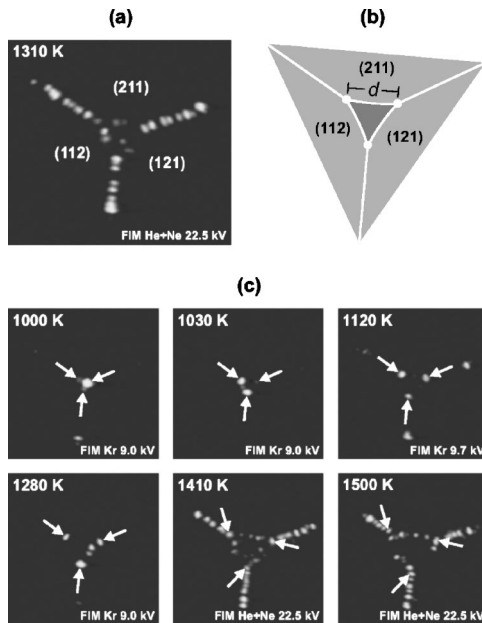


FIG. 2. Thermal evolution of an oxygen-covered tungsten crystal. (a) Microscopic image of the vicinity of the (111) pole. The {211} facets form a pyramid pointing in the [111] direction. (b) A model corresponding to (a). The degree of vertex rounding can be characterized by the distance d between the edge end points. (c) The distance between the edge end points (indicated by arrows) increases with temperature.

procedure was repeated (including crystal cleaning) to avoid possible contamination of the surface by residual gases.

III. RESULTS

Figure 2(a) shows an example of a microscopic image of the crystal equilibrated at $T=1310$ K. Only the area around the (111) pole is shown. The surface configuration seen in the image is a good approximation of the ECS, with possible minor differences due to nonzero time of quenching. The edges connecting the {211} facets are sharp on the atomic scale, but the (211)-(121)-(112) pyramid is incomplete—the vertex is missing. In Fig. 2(b), we propose a corresponding model of the surface, with a rough, rounded vertex region. Figure 2(c) demonstrates that the area of the rough region increases with temperature, in accord with the theory of ECS.¹

In order to demonstrate better the changes of the rough area with temperature, we characterize the degree of vertex rounding by measuring the distance d between the edge end points [Fig. 2(b)]. This distance is plotted in Fig. 3 against the temperature. In measuring d , we have neglected local variations in magnification of the microscope;^{9,10} for this reason, the nanometer scale in Fig. 3 is only approximate, and the lengths are probably overestimated for low values of d . By slight extrapolation of the plotted data, we obtain the vertex-rounding temperature $T_0=970\pm 70$ K.

IV. DISCUSSION

We have studied the thermal evolution of an *adsorbate-covered* metal crystal, a system more complex than—already

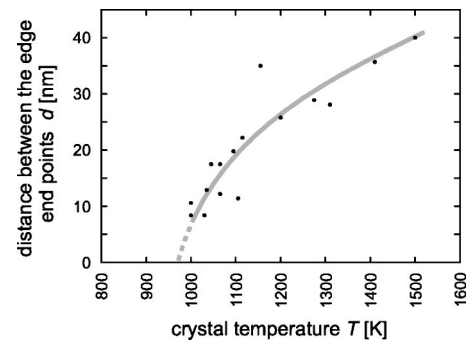


FIG. 3. The size of the rough region at the (111) crystal pole, characterized by the distance d between the edge end points, increases with temperature.

difficult to describe theoretically—a *pure* metal crystal. Is the presence of an adsorbate essential for the vertex-rounding transition to occur on real crystals? The answer is most probably no. However, oxygen adsorption on tungsten greatly increases the anisotropy of the surface free energy in the vicinity of the (111) pole. In effect, while between 1000 K and 1200 K the {211} facets of pure tungsten are separated by rounded regions,^{10,12} the oxygen-covered tungsten develops sharp edges between the {211} facets (Fig. 2), and most probably a sharp (111) vertex below ~ 970 K (Fig. 3). It is possible that *pure* tungsten also undergoes a vertex-rounding transition of similar type, but at much lower temperature, where equilibrium cannot be achieved by surface self-diffusion.

The oxygen coverage, corresponding to 1.4 L exposure applied in this study, does not exceed 5×10^{14} molecules/cm². At such coverage, desorption of oxygen at temperatures not exceeding 1500 K is negligible,¹³ so the adsorbate film during the thermal evolution of the crystal is stable.

Oxygen adsorption on a flat W(111) crystal face has been described in the literature.^{14–17} At temperatures above 800 K, the O/W(111) system is unstable and undergoes massive hill-and-valley faceting, exposing {211} facets. According to the theory of ECS,^{1,18} this means that, at least at 800 K, the (111) facet is absent from the equilibrium form of O/W, which is consistent with the results presented here.

At the transition temperature, the (111) vertex is surrounded by three {211} facets. The adsorption of oxygen on W(211) has been described in the literature.^{19–26} Oxygen exposure of 1.4 L causes the formation of 0.5–1.5 geometric monolayers of oxygen atoms on W(211). At low temperatures, the adsorbate forms ordered phases: $p(2 \times 1)$, $p(1 \times 1)$, and $p(1 \times 2)$, depending on the coverage. However, above 900 K the adsorbate is disordered at all coverages—it forms a two-dimensional lattice gas.^{23,25}

In Sec. I, we put our results in the context of models of thermal evolution of *pure* crystals. To the best of our knowledge, in the literature so far there have been no reports of models of thermal evolution of ECS with adsorbate (although zero-temperature models of ECS with adsorbate have been described^{27,28}). It should also be noted that such small crystals as the one studied here possibly can display finite-size effects, in contrast to the often studied “thermodynamic

limit" case.¹ Recently, a simple Monte Carlo solid-on-solid bcc model has been described,²⁹ which is in accord with certain features of the experimentally observed adsorbate-induced faceting. The extension of this model to curved surfaces is under development.³⁰

To the best of our knowledge, the thermal evolution of the ECS vertex described in Sec. III has not yet been observed for pure or adsorbate-covered metal crystals. The edges of ECS of pure metals always appear rounded in the microscopic images.³¹ It seems that such crystals either exhibit type-A evolution, or the temperatures studied are higher than the edge-rounding temperature. On the other hand, annealed adsorbate-covered crystals often develop sharp edges between the facets and sharp vertices,^{32–34} but the temperature-dependent vertex rounding has not been reported. The sharpness of the vertices observed in some adsorbate-induced faceting experiments may be due to low annealing temperatures (below the vertex-rounding temperature), or due to low quenching rates (nonequilibrium effect: the vertex is rebuilt during cooling).

In our study, the average radius of curvature of the crystal (see Sec. II) is an order of magnitude smaller than in a typical ECS experiment.³¹ Because of this small size, thermal equilibration of the crystal is possible at relatively low temperatures. We have found that 80 s of annealing is sufficient to obtain equilibrium, at least around the (111) pole, already at 1400 K,¹¹ that is, at $\sim 40\%$ of the substrate melting temperature. At the same time, the quenching rate is high (see Sec. II). We believe that in this case the overall outline of the ECS is preserved during quenching, although reconfigurations within a few interatomic distances are possible. We have verified that, for the crystal studied here, lowering of the quenching rate leads to a different shape: the vertex is significantly sharper.

Our view that the overall outline of the ECS is preserved during quenching may not be valid for temperatures above

1500 K, where surface diffusion is very efficient. The images of O/W annealed at 1640–1800 K show a complex structure,¹¹ which may be due to nonequilibrium processes occurring during quenching.

Although the thermal vertex rounding for adsorption systems has not been reported previously, there appears to be a close correspondence of the O/W vertex rounding described in this work and the results reported by Song *et al.*³⁵ for a planar O/Mo(111) system. They have reported the reversible planar/faceted phase transition at ~ 950 K (oxygen dosage: 0.8 L). A similar transition occurs in Oleksy's Monte Carlo model.²⁹ Oxygen-induced faceting is similar on Mo(111) and W(111) substrates,^{16,17,35} so a planar/faceted transition is also expected for O/W(111).³⁶ We believe that the temperature of the planar/faceted transition is equal to the vertex-rounding temperature of the ECS, if the adsorbate coverage is the same. We hope that this hypothesis will be addressed both by theorists and experimentalists.

In light of the observations of the planar/faceted transition, a question arises: is the vertex *rounded* for O/W ECS above 970 K, or is it *truncated* by a flat (111) facet? It is not possible to address this question on the basis of our microscopic images, because of insufficient microscope resolution, because of possible image distortions,^{9,10} and because of the possibility of atomic-scale reconstruction of this area during quenching. However, the Monte Carlo model²⁹ shows that the phase above the transition temperature is not flat after all, exhibiting large variations from the ideal bcc(111) structure, while still being able to produce the bcc(111) low-energy electron diffraction spots [see Figs. 5(b) and 9 in Ref. 29]. For this reason, we believe that the thermal evolution of the oxygen-covered tungsten crystal can be effectively described by the type-B scheme (rough, rounded vertex, sharp edges).

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