

Surface Phase Transitions during Martensitic Transformations of Single-Crystal Co

M. Erbudak, E. Wetli,* M. Hochstrasser, D. Pescia, and D. D. Vvedensky†

Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Zürich, CH-8093 Zürich, Switzerland

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The phase transitions of close-packed surfaces that accompany the martensitic transformations between the hexagonal close-packed and face-centered cubic structures of single-crystal Co are observed in real space and in real time with secondary-electron imaging. Simultaneous measurement of the bulk resistivity is used to identify the onset of the bulk transformation. The surface transitions show a broader thermal hysteresis than that of the resistivity, indicating that the martensitic transformation is initiated in the bulk and proceeds slowly to the surface. [S0031-9007(97)03961-6]

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Surface phase transitions that accompany bulk first-order phase transitions can produce a number of intriguing phenomena. Premelting, where a surface disorders below the bulk melting point, has been reported for several open surfaces [1]. There are also transitions, such as the order-disorder transition in Cu_3Au [2], where the order parameter of the surface decreases continuously as the bulk transition temperature is approached [3]. In both of these situations, the behavior of the surface near the transition is smoother than that of the bulk, i.e., the surface “anticipates” the bulk first-order transition. But the reverse situation, where the bulk first-order transition occurs before any transition on the surface, as in the intentional superheating of solids, is also of interest because it provides information about the kinetics of the bulk transformation.

In this Letter, we apply secondary-electron imaging (SEI) to observe the real-space and real-time behavior of the stacking sequence of surface layers during the martensitic transformation of a Co single crystal. By performing simultaneous bulk resistivity measurements to identify the onset of the bulk transformation, we observe that the martensitic transformation is initiated in the bulk and thereafter proceeds toward the surface. The surface transitions are found to share several basic kinetic characteristics with the bulk transformation [4,5], including thermal hysteresis and evidence of athermal effects. In contrast to that of the bulk, however, the hysteresis of the surface *broadens* for *lower* heating and cooling rates.

SEI is a method for obtaining real-space information about the geometric arrangement of atoms near a surface [6]. It involves the excitation of the surface with a beam of electrons having an energy near 2000 eV. (In the present work, the electron energy was 1750 eV.) The backscattered secondary electrons, i.e., those having lost energies up to approximately 100 eV, are imaged on a hemispherical phosphorescent screen. The interpretation of this image is based on the following. The incident electrons are backscattered (elastically and inelastically) by the atoms at and below the surface, which act

as point sources of these secondary electrons. At energies of several keV elastic forward scattering dominates, so the scattered electrons are channeled along the directions of neighbors of their point source [7]. The secondary electrons which emanate from the surface thus produce bright spots on the collector screen. The observed pattern thereby represents a central projection of the real-space atomic arrangement around each source, with many sources contributing incoherently to the pattern. Since a finite region near the surface is imaged, this technique is sensitive not only to the surface atoms, but also to atoms beneath the surface.

Cobalt is known [8] to exist in two allotropic phases, a low-temperature hexagonal close-packed (hcp) phase and a high-temperature face-centered cubic (fcc) phase. The hcp-fcc transformation is reversible and weakly first order, with small changes in enthalpy ($\Delta h \approx 440$ kJ/mol) and volume ($\Delta V/V \approx 0.0036$). The hcp and fcc phases are in equilibrium at $T_{\text{eq}} \approx 422^\circ\text{C}$ [9], but there is considerable thermal hysteresis between the heating and cooling transformations. Because of these characteristics, together with the diffusionless nature of the phase change, this transformation is designated as *martensitic*. Although there are only small differences in the nearest and second-nearest neighbor distances and no differences in the corresponding coordination numbers between the hcp and fcc phases, there is a substantial change in the stacking sequence. Thus, characteristic modifications in microscopic properties, e.g., the electronic structure [10], and macroscopic properties, e.g., the electrical resistivity [8,11] and the work function [12], have been observed to accompany the martensitic transformation. The change in the stacking sequence in the near-surface region can be observed directly with SEI because the depth of the imaging is given by the mean free path of 1750-eV electrons (≈ 15 Å [13]), which corresponds approximately to 5–6 layers.

The Co single-crystal specimen used for the measurements reported here has a cylindrical shape with a diameter of 6 mm and a height (along the *c* axis) of 2.5 mm. The crystal was mounted on a resistively heated

oven and its temperature was measured using a Chromel-Alumel thermocouple placed directly on the surface. Four stainless-steel wires of diameter 0.5 mm were placed at the sides of the specimen, two to pass a constant current of 0.3 A and the other two to measure the voltage drop across the sample. The resistance of the specimen ($\approx 6.5 \text{ m}\Omega$ at 670 K) was measured continuously for temperatures between 300 and 870 K with the SEI patterns recorded simultaneously. The surface was first cleaned by Ar^+ bombardment (1500 eV at $0.1 \mu\text{A}/\text{mm}^2$) in an ultrahigh vacuum apparatus described elsewhere [6]. An electron beam was focused on the specimen to a spot size of 0.3 mm, producing a sharp low-energy electron-diffraction (LEED) pattern. Since the display screen has the shape of a spherical segment with limited angular size, only a 104° section of the available solid angle of 2π could be observed. This corresponds to a cone with a polar angle $\theta = 52^\circ$. The SEI pattern was recorded by a charge-coupled-device camera with 375×242 picture elements [14] and an integration time of 1 s. The central portion of the SEI patterns shown below is blocked by the shadow of the electron gun used for the excitation.

Since the lateral arrangement of atoms on the (0001) surface of hcp Co is the same as that on a (111) surface of fcc Co, observing the hcp \rightarrow fcc phase change on the surface is not straightforward. The change in the structure can be detected only by surface methods that are sensitive to at least the top three layers of atoms. LEED can provide conclusive information only with the help of multiple-scattering calculations [15] because the inversion symmetry in reciprocal space means that the threefold symmetry of the fcc lattice cannot be differentiated from the sixfold hcp symmetry using kinematic theory. Rapid data collection (and analysis) is also required to follow the evolution of the surface through the phase transformations. Taken together, these provide stringent criteria for a surface-sensitive technique. Hence, to our knowledge, there have been no reports of *in situ* observations during the martensitic transformation of Co single crystals which are able to distinguish the surface structural transitions from those of the bulk [16].

Figure 1(a) shows an SEI pattern obtained from Co(0001) at 405 K. The characteristic hexagonal structure of the surface of the hcp crystal is apparent from the sixfold symmetry of the pattern. A superimposed central projection including atoms in the top five layers reproduces all of the prominent features of the SEI pattern. The corresponding SEI pattern obtained at elevated temperatures (800 K) from fcc Co is shown in Fig. 1(b). The pattern now has the threefold symmetry of the (111) surface, owing to the change in stacking sequence of the (111) planes. The corresponding central projection again accounts for all of the main features of this SEI pattern. Thus, the transformation of the (0001) surface of hcp Co to the (111) surface of fcc Co is clearly discernible by the change of symmetry in the SEI pattern. In each pattern,

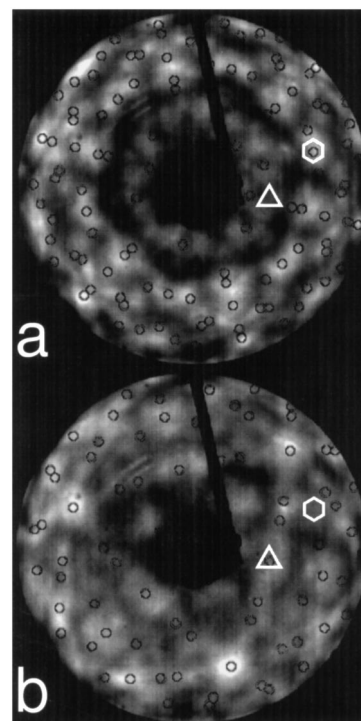


FIG. 1. (a) SEI pattern of backscattered electrons from Co(0001) in the hcp phase obtained at 1750 eV with normal incidence. (b) Analogous pattern obtained from the same Co surface at 800 K shows that the surface has transformed to the fcc structure. The open circles superimposed on each pattern are obtained from central projections for the appropriate bulk crystal structures. The hexagons and triangles mark hcp- and fcc-characteristic directions, respectively, as described in the text.

a hexagon marks the position of an hcp-characteristic direction at $\theta = 31.5^\circ$, i.e., one of the $\langle 11\bar{2}1 \rangle$ directions along which the electron intensity I_{hcp} is measured in a cone with an opening angle of 2° . Similarly, the triangles mark the position of an fcc-characteristic direction at $\theta = 19.5^\circ$, one of the three $\langle 211 \rangle$ directions along which the I_{fcc} is measured.

Figure 2 shows the temperature dependence of the ratio $A = I_{\text{hcp}}/I_{\text{fcc}}$. A is normalized to unity at room temperature, i.e., Fig. 1(a), and to zero at the high-temperature end, i.e., Fig. 1(b). Each A point represents an individual SEI measurement. The arrows show the direction of the temperature change. Also shown is the bulk resistivity ρ of the Co crystal, which has been transformed by subtracting a parabolic background and normalized to unity for the hcp phase and zero for the fcc phase. The inset shows the raw resistivity data. The bulk resistivity is seen to change abruptly near 700 K during heating and near 660 K during cooling. The data shown in Fig. 2 were obtained at a heating/cooling rate of 2.5 K/h. At 400 K/h, the width of the bulk hysteresis increases to approximately 60 K with a pronounced smoothing of the lower temperature branch of the transition. The

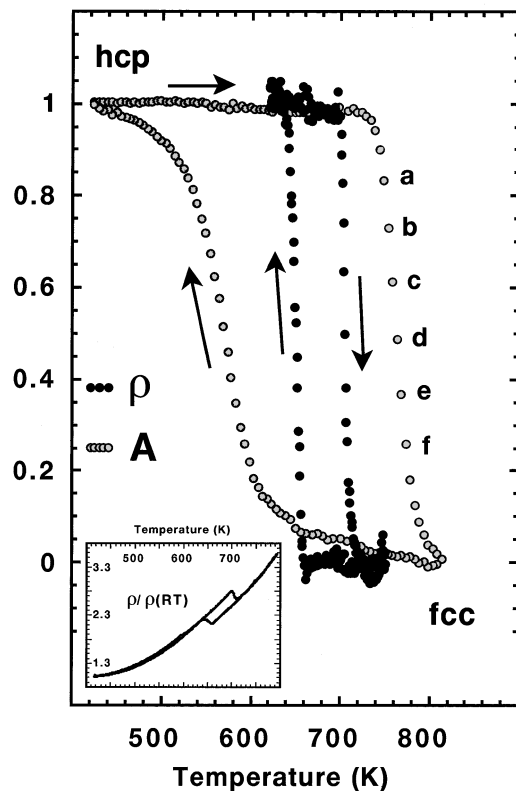


FIG. 2. The electrical resistivity ρ and the surface spot intensity A (right ordinate) as a function of T . ρ and A are both normalized to unity for the hcp phase and zero for the fcc. The resistivity is used to record the bulk phase transitions. The inset shows the raw data for $\rho(T)/\rho(RT)$. A is the intensity of backscattered electrons along an hcp-characteristic direction divided by the intensity along an fcc-characteristic direction. Hence, large (low) values of A are associated with the hcp (fcc) structure at the surface as indicated by the characteristic images shown in Fig. 1.

temperature dependence of A also shows a hysteresis, but one that is distinctly broader in temperature than that of the bulk. The surface transition at high temperature is also seen to be much sharper than that at the lower temperature, in contrast to bulk. At a *lower* heating rate, we observe a clear *broadening* of the surface thermal hysteresis, while the bulk hysteresis *narrows*. Besides the broader hysteresis, this is the most conspicuous difference between the surface and the bulk behavior. But there is an important similarity between the surface and bulk transitions: the presence of an athermal component of the transition [4,5], i.e., the transformations proceed, albeit slowly, only as long as the temperature is changing. If the sample temperature is held fixed, no changes are observed in the SEI pattern for waiting times of up to one hour [17].

Figure 3 displays six SEI patterns obtained at temperatures after the onset of the hcp \rightarrow fcc transition in the two-phase regime. The difference between successive patterns is small, showing the gradual change of the relative contributions from hcp- and fcc-stacking se-

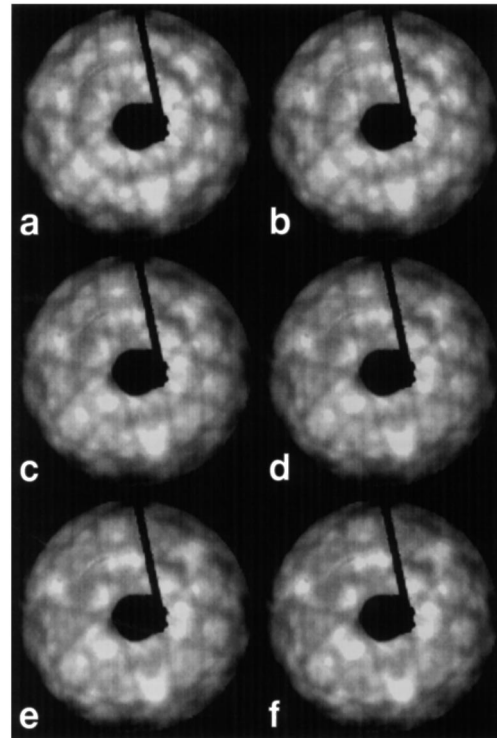


FIG. 3. Sequence of SEI patterns after the onset of the hcp-to-fcc surface transition. The positions of panels (a)–(f) are indicated in Fig. 2.

quences near the surface. This reflects the subtle structural changes that are occurring near the surface, i.e., short-range order is retained throughout the transition. Furthermore, the high definition of the LEED spots (measured under the same conditions) is indicative of the retention of long-range order as well. Both of these factors are entirely consistent with the sliding of (111) planes, which is believed to be the mechanism behind the martensitic transition [5].

Our SEI and resistivity measurements appear to indicate that the surface transition corresponds to the late stages of the martensitic transformation. The abrupt changes in the resistivity are therefore associated with the initial stages of the bulk transformation. Analogous abrupt changes and hysteresis have been seen in other measurements of electronic [10–12] and structural [16] properties, but in each case of which we are aware, the measurement has either had a non-negligible bulk contribution [10–12] or the experimental conditions did not permit the surface transitions to be resolved from those of the bulk [16]. It is apparent from Fig. 2 that any measurement with an appreciable contribution from the bulk will exhibit abrupt changes upon heating and cooling through the hcp-fcc transformation. But the origins of the transformation occurring at different temperatures on the surface than in the bulk remain unclear. One possibility is that the thermal equilibrium transition temperature of the

surface is effectively higher than that in the bulk [3,18]. A second possibility is that the sliding of the planes is better pinned at the surface than in bulk, giving rise to a more stable “metastable” state. We hope that our direct-space observations will stimulate further theoretical and experimental work on this important class of transitions for which many questions remain unanswered.

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*Present address: Physikinstitut, Universität Zürich-Irchel, CH-8057 Zürich, Switzerland.

†Permanent address: The Blackett Laboratory, Imperial College, London SW7 2BZ, United Kingdom.

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