Crystal Surface Symmetry from Zone-Axis Patterns in Reflection High-Energy-Electron Diffraction

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New experimental techniques, sensitive to crystal surface symmetry, for reflection high-energy-electron diffraction have been developed and applied to the (001) surface of MgO. The techniques map the variation of the intensity of one or more diffracted beams as a function of the incident-beam orientation. The symmetry of these surface zone-axis patterns has been studied theoretically and confirmed experimentally. The techniques are expected to provide a sensitive means of surface characterization.

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The full symmetry inherent in the reflection high-energy-electron diffraction (RHEED) from a crystal surface is more complex than the conventional RHEED experiment can detect and than has previously been realized. We have established these full symmetries for all possible crystal surfaces and developed a set of techniques for displaying them. The patterns—zone-axis patterns—that we obtain, not only display more complete information on the surface symmetry but are expected to have general application to surface identification and structure determination. The experiments are carried out in a transmission electron microscope which means that electron-energy-loss analysis[1] and high-resolution surface imaging[2] can be carried out on the same regions of the sample to complete the surface characterization.

When a parallel electron beam strikes a smooth surface at near-grazing incidence, there is diffracted intensity in the specular beam (related to the incident beam by mirror reflection in the surface) and other diffracted beams.[3] If the direction of the incident beam with respect to the surface is changed, the diffracted beams move and change in intensity. To display the complete symmetry of the situation it is necessary to map this variation of the intensity of the diffracted beams as a function of the angle of the incident beam, for a range of angles close to the symmetry direction. We have developed techniques for doing just this. The symmetry direction in the surface is a zone axis, a direction perpendicular to a row in the reciprocal mesh,[4] and the patterns are called surface zone-axis patterns (ZAPs).

We describe here two methods for obtaining surface ZAPs; a full account of the experimental details will be published separately. The experiments were carried out in a transmission electron microscope (Philips EM420) and, in both cases, it was the flexibility of the instrumentation that made the techniques possible.

In the first method, the pattern is built up sequentially. The incident beam is parallel and is rocked about a point on the surface of the specimen so that the angle that the beam makes with the sample follows a two-dimensional raster; both the grazing angle of incidence and the angle of azimuth are varied. As the incident beam is rocked in this way, coils after the sample are excited so that the specular or some other diffracted beam is made to remain stationary on a detector. The signal from the detector is displayed on a cathode-ray tube that is synchronous with the rocking of the incident beam. Then the intensity of the diffracted beam is mapped as a function of the angle of the incident beam, to produce a surface ZAP. A schematic diagram of the rocking scheme is shown in Fig. 1. This technique has been reported previously[5] and is the analog of a technique developed for diffraction in transmission.[6]

Experiments have been performed with magnesi-

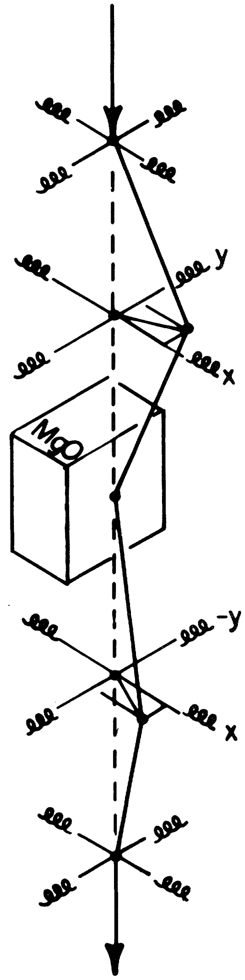

FIG. 1. Schematic diagram of the beam-rocking system used to obtain sequential, surface zone-axis patterns.

um oxide (MgO); this material can be made with clean atomically smooth surfaces by burning magnesium metal in dry air.[7] Specimens were single crystals, cubic in form, about 1 μm on edge; they were supported on a thin carbon foil for mounting in the microscope. The crystals were aligned so that the undeflected beam was parallel to a [010] zone axis of the three-dimensional crystal, parallel to $(0,k)$ of the reciprocal net of the diffracting face. Figure 2 shows a surface zone-axis pattern from MgO with the use of the specular (0,0) beam.

In the second method, the surface ZAP is formed in parallel. A strong lens, very close to the specimen, is used to focus the illumination onto the sample with an angle of convergence that is comparable to, although less than, the smallest operating Bragg angle. In the absence of a specimen this would produce a disk in the diffraction plane. With

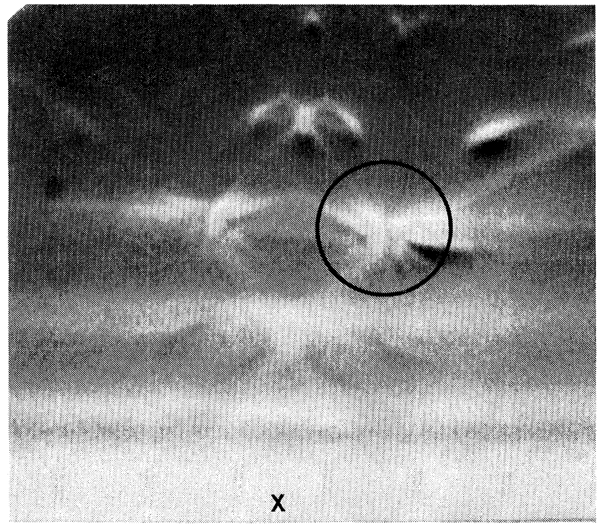

FIG. 2. Surface zone-axis pattern in the specular beam from MgO at 100 kV. (The circle marks the region corresponding to the field of view in the specular beam of Fig. 4). The orientation marked x is parallel to the [010] zone axis.

the specimen in place and the focused beam incident on the surface, an array of disks is produced: One disk is associated with each diffracted beam.[8] This is shown schematically in Fig. 3. Within each disk the variation of intensity of the corresponding diffracted beam as a function of the angle of the incident beam is mapped; it is a surface zone-axis pattern. An example of a surface ZAP from MgO, obtained in this way, is shown in Fig. 4. This method is the analog of convergent-beam diffraction (for a review see Steeds[9]) in transmission electron microscopy.

In the double-rocking method a wide angular range can be displayed but only for one diffracted beam at a time. In the convergent-beam method the angular range is limited by the need to avoid overlap of the disks, but all the operating diffracted beams are mapped at the same time.

By two independent methods, a graphical construction and group theory applied to a quantum mechanical formulation of the problem, that are analogous to those used in the transmission case,[10] we have shown that there are five possible symmetries that surface ZAPs can display and that these are in a one-to-one correspondence with the five possible symmetries of a RHEED diffraction experiment. The symmetry of a RHEED experiment is the symmetry of a semi-infinite crystal with a designated direction (corresponding to the chosen zone axis) in its surface. The five point symmetries correspond to no symmetry, a mirror perpendicular to

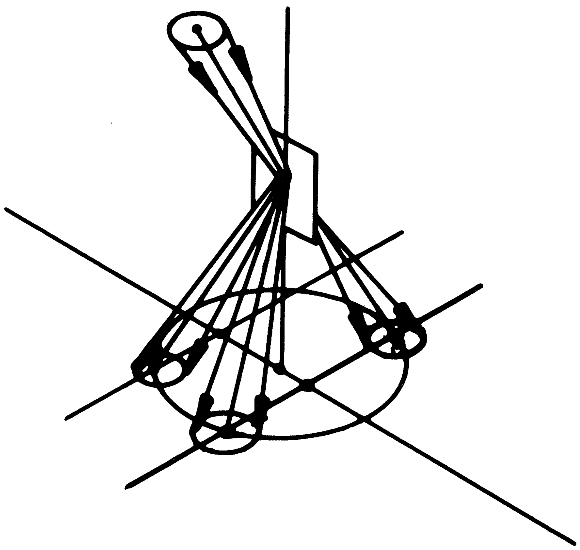

FIG. 3. Schematic diagram to show the formation of a surface convergent-beam pattern.

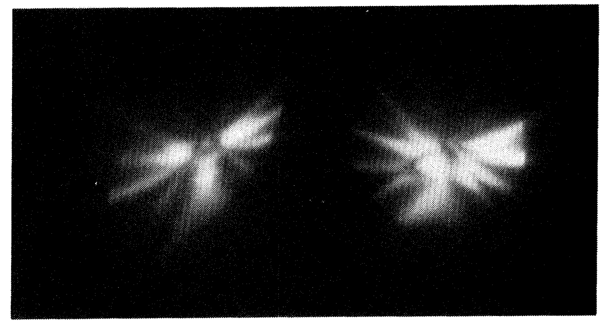

FIG. 4. Surface convergent-beam zone-axis pattern from MgO at 100 kV. The specular beam is to the right. There is a "topological" mirror in the (1,0) reflection, to the left.

the surface (parallel or perpendicular to the zone axis), a twofold axis perpendicular to the surface, and a twofold axis combined with both mirrors. In standard notation these are written 1, m, $1m$, 12, and $mm2$.

Each of these produces a distinct symmetry in the RHEED diffraction at the zone axis. By analogy with the transmission case we call them "RHEED diffraction groups" and designate them as 1, m, m_R, 2_R, and $2_R mm_R$. The interrelations of intensity that they represent are complex; the diffracted intensity in one beam may be related to the intensity in a different beam for a different orientation of the incident beam. The details of the derivation and results will be published separately; a few points should be noted, however.

The results obtained for the diffraction symmetries require the application of the principle of reciprocity.[11] In particular, the mirror in the (1,0) reflection of Fig. 4 would not be present if reciprocity were not applicable. This mirror is not, perhaps, immediately apparent. The geometry of RHEED diffraction is, with the exception of the specular beam, rather complex. For example, the symmetry-related points in $(h,0)$ beams do not lie on points that are mirror related with respect to the line of symmetry of the pattern (the line at $G/2$). The points lie at equal perpendicular distances from the symmetry line but are displaced parallel to the line so that the pattern is skewed, and what results is not a "metric symmetry" but a "topological symmetry."[12] Also, we should point out that not all the symmetry relations mentioned above have yet been observed by us, and, indeed, we anticipate that some of them may be difficult to see. This is because the projection approximation is sometimes valid in RHEED as it is in transmission. When the projection approximation holds, instead of one of five diffraction groups, only one of two projection diffraction groups $(m_R, 2_R mm_R)$ can be observed.

In addition to the symmetries of the patterns, we have proved that "forbidden reflections" due to glide planes will contain dark lines analogous to those found in transmission-electron-diffraction patterns[13] and predicted for low-energy-electron diffraction.[14] If the point group element m comes from a glide plane rather than a mirror there can be a dark line in $(h,0)$ while a glide in $1m$ can give a dark line in the $(0,k)$ reflection.

In principle, the observation of the dynamic absences as well as the detection of the centering of the unit cell [by comparing the positions of $(h,1)$ reflections with those of $(h,0)$ reflections] would make it possible to distinguish each of the seventeen space groups of a surface structure. It remains to be established how often this is possible in practice and how frequently the projection approximation restricts the information available.

The surface area sampled by the beam is elongated in the incident-beam direction (dependent on the angle of incidence) to perhaps thirty times its width. The width, in these experiments, was 40 nm in the convergent-beam mode and 200 nm in the rocking mode. The surface would have to be free from twins and other defects over this area to give accurate symmetry information. Surface imaging should allow such areas to be selected. The depth of the sample that contributes to the pattern is believed to be just a few atom layers; it is strongly dependent on incident angle, but only weakly dependent on beam energy.[15]

The results obtained on MgO are compatible with a surface symmetry that is unchanged from the exposed bulk structure.

We have concentrated on the use of surface ZAPs for improved symmetry determination. However, we anticipate that their usefulness will be wider than this implies. As can be seen, these figures are complex. Their richness suggests the possibility of recognizing surfaces from their RHEED ZAPs and, through comparison of the patterns with computer simulation,[15] of studying surface structure itself. Moreover, since the experiments are carried out in an electron microscope, it will be practical to combine this improved diffraction information with the complementary information available in surface imaging and electron-energy-loss analysis. We anticipate that the new technique will provide a sensitive means of characterizing surface structures. We see potential applications for studies of surface relaxation, absorption, epitaxy, and diffusion.

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[3]The other beams are displaced from the specular beam by $\vec{G}$, a vector in the two-dimensional mesh reciprocal to the surface net; the component of the wave vector perpendicular to the surface is fixed by energy conservation.

[4]This is by analogy with the zone axis of a three-dimensional crystal, which is a direction perpendicular to a plane in the reciprocal lattice.

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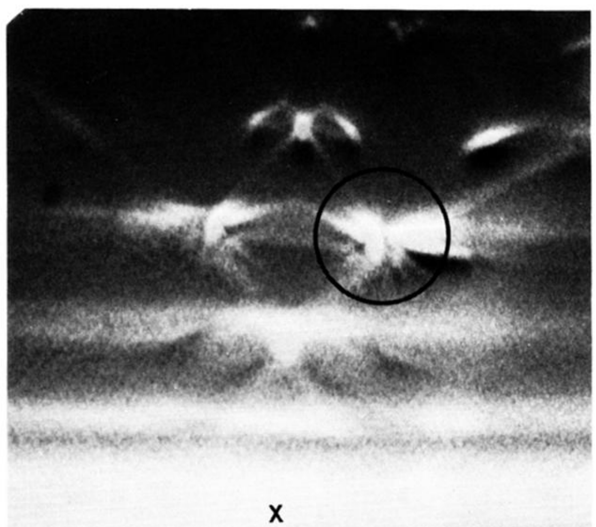

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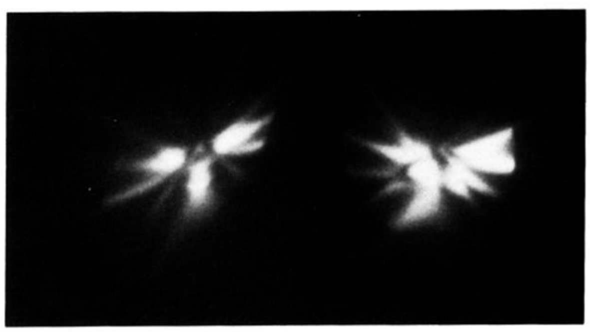

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