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(7×1) reconstruction of the $(11\bar{2}0)$ surfaces of holmium and erbium

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We report the (7×1) reconstruction of the clean $(11\bar{2}0)$ surfaces of the lanthanide elements Ho and Er. For both elements low-energy electron diffraction showed a sharp sixfold symmetric pattern of spots, indicating a collapse of the ideal open surface to a close-packed structure very similar to a (0001) surface. The absence of any diffraction spots from the underlying ideal structure implies that the reconstruction is many layers deep. Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) data taken from the reconstructed Ho$(11\bar{2}0)$-(7×1) surface are found to be virtually indistinguishable from those taken from a Ho(0001) sample—minor discrepancies may be due to differing surface topographies of the samples. The stability of the ARUPS spectra with temperature implies that the Ho$(11\bar{2}0)$-(7×1) surface remains reconstructed at temperatures up to 1000 K. By contrast, the spectra from Er$(11\bar{2}0)$ change considerably in the temperature range 800–1000 K. It is not yet known whether this is due to a transformation of the reconstructed surface back to its ideal structure or simply a roughening of the surface.

I. INTRODUCTION

The surfaces of hexagonal-close-packed (hcp) metals have not been subjected to the same experimental scrutiny that cubic metals have benefited from over the past 25 years. Primarily, this has been due to the difficulties encountered in preparing and cleaning hcp crystals. Low-energy electron-diffraction (LEED) studies of the (0001) surfaces of a number of hcp metals [Be,[1] Re,[2] Zn,[3] Ti,[4] Cd,[5] Co,[6] and Sc (Ref. 7)] have shown that the clean surfaces do not differ substantially from the ideal (bulk termination) structure except for an interlayer relaxation perpendicular to the surface. A recent study of epitaxially grown Sm(0001) (Ref. 8) has shown a (5×5) reconstruction at low temperatures, driven by a valence change—trivalent bulk and divalent at the surface—causing a difference in the equilibrium atomic radius. Such a change of valence at the surface is a property peculiar to Sm. Other crystallographic surfaces of hcp metals have also been studied [Ti$(10\bar{1}1)$ (Ref. 9) and Re$(10\bar{1}0)$ (Ref. 10)] but they have not shown any surface reconstruction. Structural changes have been reported on the $(10\bar{1}2)$ and $(11\bar{2}0)$ surfaces of Co,[11,12] but these were at temperatures close to the hcp-bcc bulk phase transition. The report of the surface reconstruction of Ti$(10\bar{1}0)$ (Ref. 13) was based on reflection high-energy electron-diffraction (RHEED) data, which were shown subsequently to be misinterpreted. A LEED study[14] showed no evidence for a reconstruction and it was suggested that the earlier RHEED data could have been produced by surface contamination. The LEED and angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) study of clean Y$(11\bar{2}0)$ (Ref. 15) was the first to show a surface reconstruction of a hcp metal. Unlike the Sm(0001) reconstruction, in which the surface lattice is a simple conformal expansion of the bulk, the Y$(11\bar{2}0)$ reconstruction involves a change of symmetry; the twofold symmetric ideal $(11\bar{2}0)$ surface reconstructs to a close-packed structure with sixfold symmetry.

In an effort to gain a better understanding of the surface reconstruction observed on the $(11\bar{2}0)$ surface of Y we have carried out a LEED and ARUPS investigation of the same surface of Ho and Er. This work has reinforced the prediction[15] that similar reconstructions would occur on the $(11\bar{2}0)$ surfaces of all of the rare-earth elements. However, although the reconstructed surfaces of these three elements have a similar hexagonal structure, there are important differences between the reconstructions reported in this paper and that of Y. One of the most significant is the LEED pattern, being sixfold symmetric in the former case and twelvefold in the latter. Also, the rate at which the samples were cooled to room temperature after the cleaning cycle anneal had a considerable effect on the reconstruction of Y, but none on the reconstructions of Ho and Er. Both of these points will be discussed in a later section.

II. EXPERIMENTAL PROCEDURES AND INSTRUMENTATION

The Ho and Er samples were spark-machined from high-quality single-crystal boules grown by Dr. D. Fort (Department of Metallurgy and Materials, University of Birmingham, United Kingdom). Elemental analysis of the raw material indicated a total impurity content of ~ 0.1 at. %, with O and C the dominant impurities. The procedure used to clean the lanthanide elements Ho and Er was essentially the same as that previously described for Y.[15,16] A range of anneal temperatures was tested (900 ± 100 K) and this was found to make no difference to the structure of the reconstruction. At all times the samples were kept well below their hcp-bcc bulk phase transition temperatures of 1240 K (Ho) and 1190 K (Er). The cleaning cycles were repeated (typically ~ 25 cycles) until the photoemission spectra obtained were completely reproducible—this has been found to be the most critical test of surface cleanliness for rare earths. The LEED and photoemission experiments were carried out on beamline 6.2 of the Synchrotron Radiation Source at the Science and Engineering Research Council Daresbury Laboratory, United Kingdom. The base pressure of the chamber was $\sim 2\times10^{-10}$ mbar and the most abundant residual gases were Ar and CO. The chamber and instrumentation used for the Ho and Er experiments were the same as those used for Y, with the exception of different LEED optics in the case of Ho. Thus, LEED photographs from Ho are not directly comparable with those from the other elements.

III. LEED RESULTS

The LEED patterns obtained at room temperature from Ho and Er immediately after a cleaning cycle are shown in Fig. 1. The patterns, clearly sixfold symmetric, are very similar to those obtained from a (0001) surface; the threefold symmetry of a (0001) surface produces a sixfold symmetric LEED pattern due to equal probabilities of the two possible bulk terminations. There are no diffraction spots visible that can be attributed to the substrate [which would show a rectangular pattern with missing spots characteristic of the ideal $(11\bar{2}0)$ surface[15]]. Thus, as is the case for Y, the sixfold symmetry of the reconstruction must extend over many atomic layers; a LEED beam energy of 50 eV (mean free path ~ 0.7 nm) and a layer separation ~ 0.35 nm require a reconstruction depth of at least five layers so that substrate spots are not observed. A visual comparison between the Ho$(11\bar{2}0)$ diffraction pattern and that of Ho(0001) at the same beam energy indicates that the lattice parameter of the reconstructed surface is within a few percent of that of the (0001) surface, as was found for Y.[15]

Although the reconstructed surfaces of all the elements Y, Ho, and Er have been referred to as sixfold symmetric, there is an obvious difference between the LEED patterns obtained from Ho and Er compared with that from Y.[15] The twelvefold symmetric pattern exhibited by Y$(11\bar{2}0)$ was interpreted as being the superposition of two hexagonal patterns, one rotated by $\pi/2$ with respect to the other. Thus, it appears that the reconstructed surface comprises domains having internal hexagonal structure in two possible orientations with respect to the underlying (ideal) crystal structure. This implies that the collapse of the open $(11\bar{2}0)$ structure is equally probable along either of the two orthogonal directions [0001] and $[10\bar{1}0]$. The LEED patterns from Ho and Er do not show any sign of such a second set of hexagonal spots, suggesting that the collapse of the unit cell occurs exclusively along the [0001] direction for both samples. Figure 2 shows the orientation of the reconstructed surface lattice with respect to that of the ideal $(11\bar{2}0)$ surface lattice. It can be seen that the magnitudes of the lattice vectors of the two structures match in the $[10\bar{1}0]$ direction of the ideal lattice, and have the ratio c/a in the [0001] direction. For Y, Ho, and Er the c/a ratio is 1.570 ± 0.001, which we note is very close to the integer

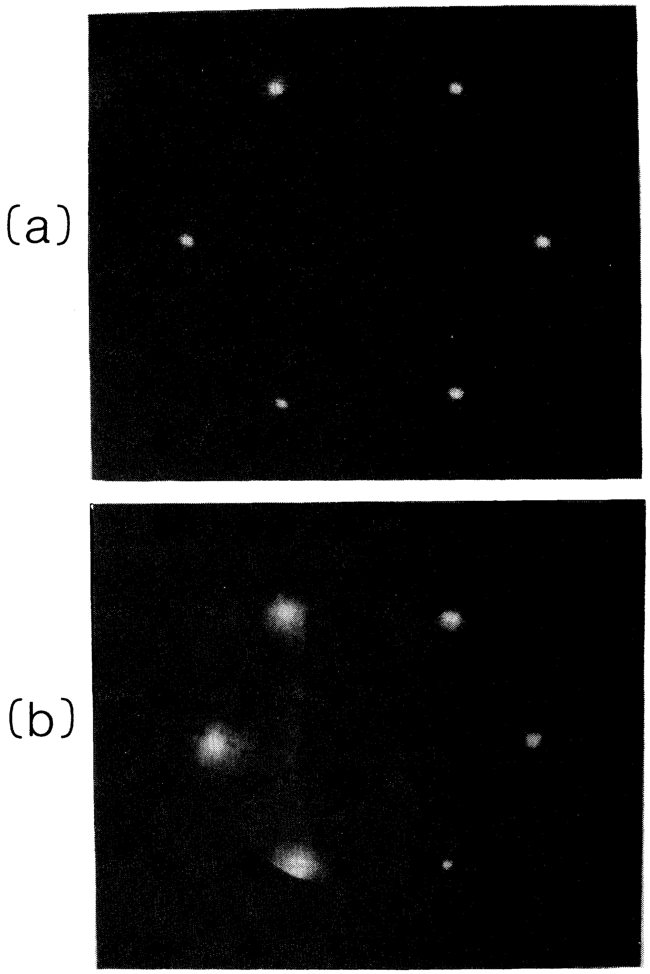


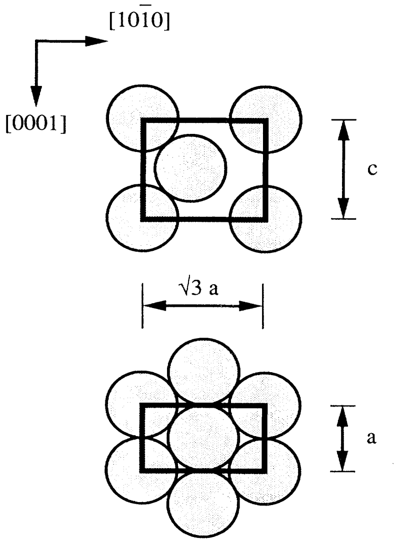
FIG. 1. LEED patterns from (a) Ho$(11\bar{2}0)$-(7×1) and (b) Er$(11\bar{2}0)$-(7×1). The photographs are not directly comparable as they were taken with different LEED optics.

ratio 11/7 (=1.571). Thus, for the reconstruction of the Ho and Er surfaces, 11 unit cells of the surface lattice match almost exactly to 7 unit cells of the ideal $(11\bar{2}0)$ structure beneath, giving the Wood notation $(11\bar{2}0)$-(7×1) for the reconstruction. For the other domain orientation seen in Y$(11\bar{2}0)$ the lattices are incommensurate and so no such notation can be applied to the Y reconstruction. It is presumably the incommensurate nature of this orientation that prohibits the surfaces of Ho and Er from exhibiting such a two-domain reconstruction. The behavior of Y in this respect has yet to be explained. Relating the surface structure to the underlying ideal structure has some meaning if the two are in close proximity, as is the case for all the surface reconstructions observed on cubic metals. However, for the reconstructions described here, the large increase ($\sim 60\%$) in atomic area density from the bulk to the surface means that it is likely that the reconstruction is accommodated over many atomic layers. Thus, the commensurate relationship between the surface lattice parameters and those of the bulk lattice, giving rise to the (7×1) notation, may be only coincidental.

Another substantial difference between the reconstructions reported here and that of Y concerns their time dependence. As has already been reported[15] the LEED patterns and ARUPS spectra observed from Y$(11\bar{2}0)$ were strongly dependent on the rate at which the sample was cooled to room temperature after the cleaning cycle anneal. If the sample was allowed to cool naturally (from 875 to 375 K in approximately 30 min) the surface was found to have the ideal $(11\bar{2}0)$ structure. Only if the sample was cooled slowly, over a time period of many hours, did the reconstruction occur. By constrast, the reconstructions of Ho and Er appear to be spontaneous; the observed structure is independent of the rate at which the samples are cooled. Although it has been argued that the reconstruction of Y$(11\bar{2}0)$ was induced by H contamination,[18] this has been refuted[19] and so there appears to be no explanation as to why the $(11\bar{2}0)$ surface of Y should behave any differently from those of Ho and Er.

IV. PHOTOEMISSION SPECTRA

As LEED indicated that the $(11\bar{2}0)$-(7×1) surface has a structure of the same symmetry and similar lattice constant as a (0001) surface, it is to be expected that the ARUPS spectra from these two surfaces are likely to have features in common. In fact the normal emission spectra from the Ho$(11\bar{2}0)$-(7×1) surface and a Ho(0001) surface are virtually indistinguishable, as can be seen from Fig. 3. Also shown is a spectrum from a third Ho sample with a $(10\bar{1}0)$ surface. Though not as close a match to the Ho(0001) spectrum as is the case for Ho$(11\bar{2}0)$-(7×1), the close correspondence between the spectra clearly suggests that the $(10\bar{1}0)$ surface too has reconstructed to a close-packed structure. This suggestion was strengthened by visual observation of a sixfold



	c	a	c/a
Y	0.573	0.365	1.571
Ho	0.562	0.358	1.570
Er	0.559	0.356	1.569

FIG. 2. The ideal (top) and reconstructed (bottom) $(11\bar{2}0)$ surface unit cells and tabulated values of their dimensions (in nm) (Ref. 17).

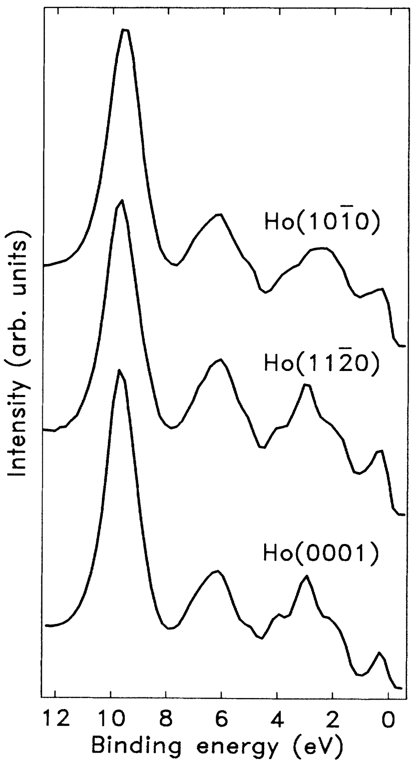


FIG. 3. Photoemission spectra from the three principal crystallographic surfaces of Ho; photon energy 40 eV, photon incidence angle 30°, normal emission.

symmetric LEED pattern from Ho($10\bar{1}0$), but the diffuse spots on a bright background were unsuitable for photography. [A full study of Ho($10\bar{1}0$) is in progress to establish the surface structure with more certainty.] As both the ($11\bar{2}0$) and ($10\bar{1}0$) surfaces appear to reconstruct to a structure similar to that of a (0001) surface, it seems probable that other surfaces of Ho will be found to be close packed. This may well be the case for the surfaces of other rare earths as well.

Interpretation of many of the features in the photoemission spectra from Ho in terms of the valence-band electronic structure is being carried out and will be published in a later paper. At present, we are only concerned with the large peak at a binding energy of 9.6 eV. This peak has been seen at approximately the same energy, and with similar intensity, in the spectra of every rare-earth surface we have studied to date that exhibits sixfold symmetry (Gd and Pr,[20] Y,[15,16,19] Ho, and Er). Although the first ARUPS study of Gd(0001) (Ref. 21) only showed valence-band spectra down to 3 eV binding energy, the text implies that a peak was observed at a higher binding energy than the 8.3 eV of the $4f$ peak. A spin-resolved photoemission study of epitaxially grown Gd(0001),[22] though not showing the peak explicitly, does show the high-intensity $4f$ peaks on a background that changes abruptly in the region of 9–10 eV binding energy. We have found[15,16,19] that this peak, which does not appear in one-electron photocurrent calculations, is very sensitive to the degree of hexagonal order on a surface—even the slightest disruption of surface order, which would tend to make the spots in the LEED pattern more diffuse, significantly reduces the intensity of this peak. Thus, although its origin is unclear, we are confident that this surface-order-dependent state can be used as an indicator of a well-ordered hexagonal surface.

The ARUPS spectra from Ho showed essentially no change (except for phonon broadening of the peaks) as the samples were heated from room temperature up to approximately 1000 K (the maximum attainable temperature of our resistive heating stage). This is in marked contrast to the temperature dependence of the spectra from Er shown in Fig. 4. The most obvious change with temperature is the disappearance of the surface-order-dependent state which, as has been shown with Y,[15] is indicative of the surface reverting to its ideal structure. However, in the case of Er, the disappearance of the surface-order-dependent state could also be interpreted as a roughening or "amorphising" of the surface, as this too would reduce the degree of hexagonal order. These two alternative explanations cannot be distinguished using LEED because of the elevated temperature of the reconstruction transition. For both Ho and Er, unlike the situation for Y, the LEED pattern of the ideal ($11\bar{2}0$) surface could not be observed as the diffraction pattern from the reconstructed surfaces persisted up to the point at which the pattern was rendered invisible due to the glow from the samples at $T \sim 800$ K. The ARUPS spectra from Er($11\bar{2}0$) at high temperature ($T > 1000$ K) have most of their intensity weighted close to the Fermi energy E_F (apart from the multiplet $4f$ peaks spread over the binding-energy range 5–11 eV) but this observation is insufficient to distinguish between an ideal ($11\bar{2}0$) and an amorphous (or polycrystalline) surface. As Er has the same crystal structure and analogous atomic outer-electron configuration to Y, we expect to see a close similarity between the electronic structures of these two elements. We have found for Y that the spectrum from an ideal ($11\bar{2}0$) surface has its most intense features within ~ 2 eV of E_F (Ref. 15) (due to a large contribution from electron states at the K and M points in the Brillouin zone) and that from a polycrystalline surface resembles a density-of-states curve, which peaks at E_F.[16] Thus, without further investigation, we cannot determine unambiguously the state of the Er($11\bar{2}0$) surface at high temperatures.

As the binding energy of the $4f$ electrons in Er covers the range 5–11 eV, some of the corresponding peaks overlap the surface-order-dependent state at 9.6 eV and so the intensity of the photoemission at that energy will not be a reliable indicator of the state of the surface reconstruction. [This was not a problem for Y (Ref. 15), which showed a flat background in the region of 10 eV binding energy at temperatures above the reconstruction temperature due to the total absence of f electrons.] For Er, a more representative quantity to use is the integrated photoemission intensity between suitable energy limits either side of the surface-order-dependent state. The integrated intensity of the $4f$ electron emission can be assumed to be independent of the surface structure and so will give rise to a contribution to this quantity that will vary only slightly with temperature due to phonon

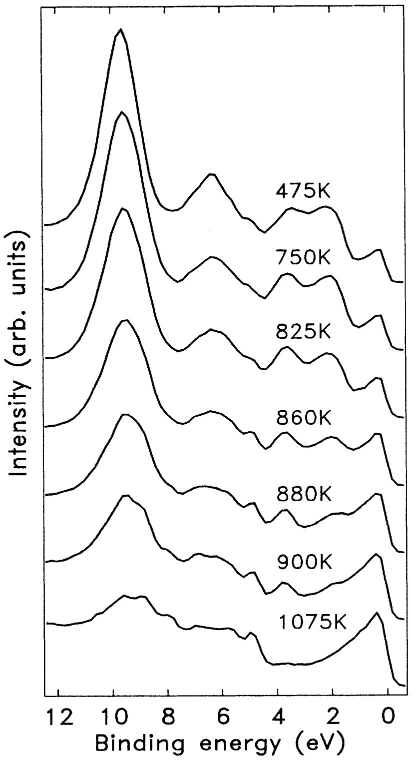


FIG. 4. Photoemission spectra from Er($11\bar{2}0$) as a function of temperature; photon energy 40 eV, photon incidence angle 30°, normal emission.

broadening. Reanalyzing the Y data[15] in a similar way allows direct comparison of the temperature dependence of the Y and Er reconstructions, as shown in Fig. 5. The reconstruction temperature T_R, defined as the temperature at which the integrated intensity has fallen by one-half of its total change, is found to be 875 ± 25 K for Er [cf., $T_R=610\pm10$ K for Y (Ref. 15)]. The larger uncertainty in the reconstruction temperature for Er is due to the increasing phonon broadening of the $4f$ peaks with temperature. The latter results in a decreasing contribution to the measured integrated intensity, which is evident in the Er curves of Fig. 5 as a nonzero gradient at high temperatures. Apart from the effects of the $4f$ emission in Er, the qualitative shape of the curves, including the dip in the curves for increasing (but not decreasing) temperature at $T\sim T_R-100$ K, is the same for both elements. Its presence in the Er data indicates that the surface is undergoing a transition similar to that of Y, i.e., a reconstruction rather than surface roughening. The fact that this dip is not apparent in the original presentation of the Y data (upper curve of Fig. 3 in Ref. 15) implies that the *peak* intensity is *not* an accurate indicator of the reconstruction. This must be due to the change in the line shape of the surface-order-dependent state which can be seen in the Y data but as yet cannot be explained [changes in the line shape of the surface-order-dependent state observed on Er(11$\bar{2}$0) are predominantly due to the underlying $4f$ emission].

V. VALENCE-BAND ELECTRONIC STRUCTURE

As already shown in Fig. 3, the normal emission spectra from Ho(11$\bar{2}$0)-(7×1) and Ho(0001) are virtually indistinguishable at a photon energy of 40 eV. A more critical test of the similarity between the structure of these two surfaces involves comparison of the valence-band (0–5 eV binding energy) spectra taken over a range of photon energies and emission angles in order to probe various regions of the Brillouin zone. No substantial differences between the two surfaces were found in the spectra taken at different photon energies. However, differences were found in the spectra taken at particular emission angles θ, as shown in Fig. 6. (As mentioned earlier, a full analysis of these spectra will be published in a later paper.) Although the overall correspondence between the spectra is very good, especially at small emission angles—$\theta<20°$ corresponds to electron k vectors with components parallel to the surface lying within the first Brillouin zone—there are clearly some discrepancies in relative intensities at larger angles. This is most notable in the peak just below E_F at $\theta\sim80°$, which for Ho(0001) corresponds to emission of electrons with $k_{\parallel}$ close to the M point of the Brillouin zone. Thus, the (11$\bar{2}$0)-(7×1) surface is not identical to the (0001) surface in all respects. However, the surface sensitivity at $\theta=80°$ is six times higher than at normal emission, and so such discrepancies may be due to differences in surface topography.

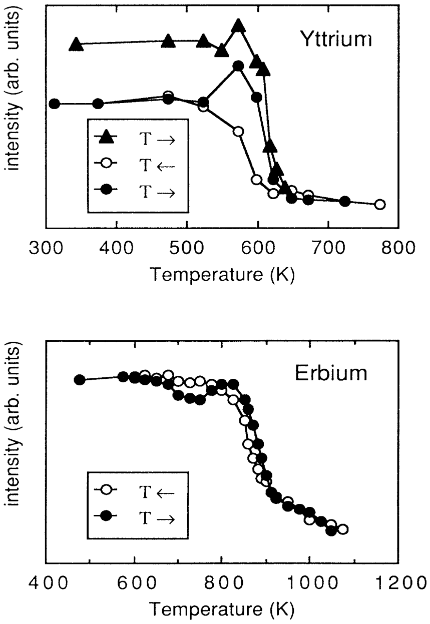


FIG. 5. Integrated surface-order-dependent state intensity as a function of temperature for Y(11$\bar{2}$0) and Er(11$\bar{2}$0). The legend denotes increasing or decreasing temperature.

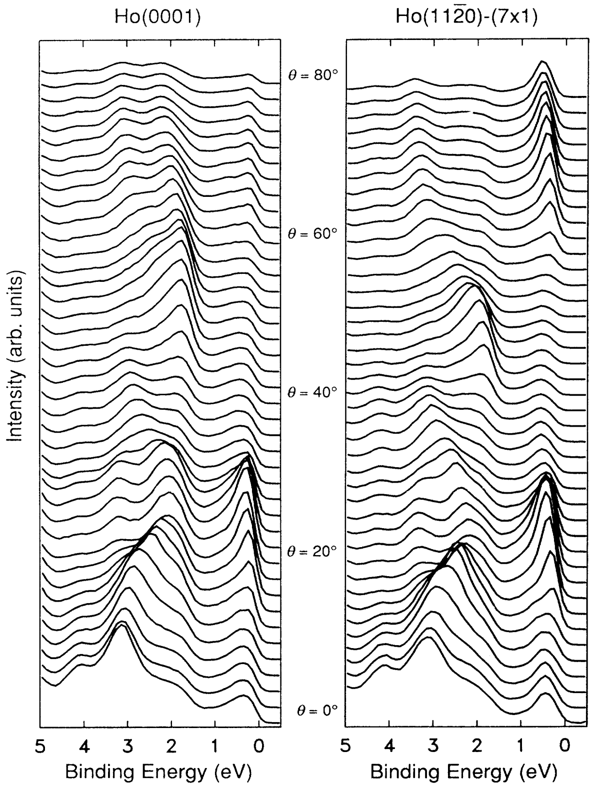


FIG. 6. Valence-band photoemission for Ho(0001) and Ho(11$\bar{2}$0)-(7×1) as a function of the photoelectron emission angle θ. For Ho(0001) the incidence-emission plane is (11$\bar{2}$0) and for Ho(11$\bar{2}$0) the incidence-emission plane is (0001).

VI. SUMMARY

We have observed a reconstruction of the $(11\bar{2}0)$ surfaces of Ho and Er involving a change from twofold to sixfold surface symmetry. The reconstructed surface of Ho$(11\bar{2}0)$ produces essentially the same LEED patterns and ARUPS spectra as a Ho(0001) sample, indicating that the reconstruction is at least as deep as the probe depth of these techniques. We have assigned the notation (7×1) to the reconstruction, although it is not yet clear if this reflects an underlying mechanism or is a numerical coincidence. The Ho$(11\bar{2}0)$-(7×1) surface was observed only in its reconstructed state, whereas Er$(11\bar{2}0)$ was observed to go through a transition at 875 K to, possibly, its ideal structure. Our investigations of clean rare-earth surfaces will continue with the $(10\bar{1}0)$ surfaces of Y, Ho, and Er, and the $(11\bar{2}0)$ surfaces of other elements. In an effort to quantify some of the unknown factors involved in the reconstructions of Y, Ho, and Er, we intend to perform some quantitative $(I-V)$ LEED experiments.

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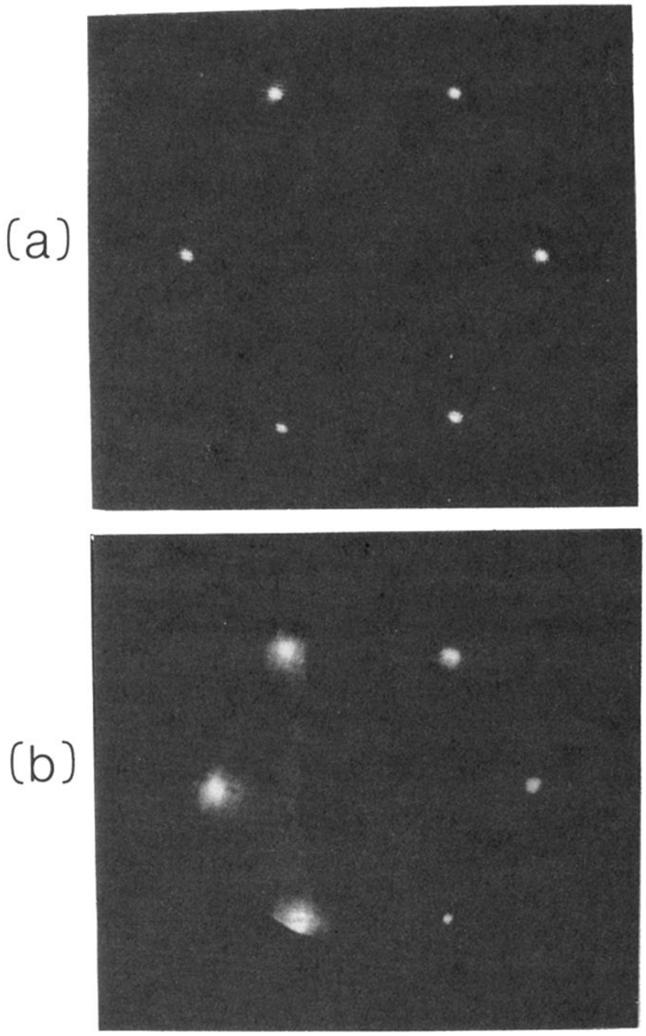

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