

## Shear Displacement of the K(110) Surface

B. S. Itchkawitz,<sup>(1)</sup> A. P. Baddorf,<sup>(2)</sup> H. L. Davis,<sup>(2)</sup> and E. W. Plummer<sup>(1)</sup>

<sup>(1)</sup>Physics Department, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6396

<sup>(2)</sup>Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6032

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A low-energy electron diffraction analysis of the clean K(110) surface has been performed at 25 K, providing a quantitative structural determination of a clean alkali-metal surface. The K(110) surface exhibits a novel surface phase consisting of a lateral shear displacement between the first two surface planes while preserving their two-dimensional periodicity. The atomistic description of this surface structure is related to that of the bulk martensitic phase transitions of the alkali metals.

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General interest in investigations of clean alkali-metal surfaces is motivated by their utility as experimental touchstones for theoretical descriptions of metal surface physics. Studies of these pristine surfaces promise to provide a basis for developing a fundamental understanding of the physical phenomena of metal surfaces. However, detailed structural examinations of these surfaces have been very limited. Besides a pair of limited low-energy electron diffraction (LEED) studies of the Na(110) surface [1], there have been no other structural determinations of alkali-metal surfaces. The study of the LEED spot intensities as functions of the incident electron energy (LEED  $I$ - $V$  profiles) described in this Letter is a detailed, quantitative structural determination of a clean alkali-metal surface which has surmounted the experimental constraints of high surface reactivity and low Debye temperature which have hindered previous studies.

Crystal terminations of close-packed metal surfaces have been previously found to induce two types of structural distortions: interplanar relaxations normal to the surface and lateral reconstructions which alter the two-dimensional periodicity of the surface. We have found that the clean K(110) surface exhibits a novel surface structure consisting of a lateral shear displacement between the first two surface planes while preserving their  $(1 \times 1)$  periodicity. This result is the first example of a lateral structural distortion of a clean low-index surface which leaves the two-dimensional periodicity of the surface plane unchanged. This surface shear displacement is similar to the atomistic description of the bulk martensitic phase transitions of the alkali metals and it pertains to the physics of the nucleation of these transitions.

Our study of the K(110) surface structure was motivated by the results of a previous angle-resolved photoemission study of the K(110) valence band [2]. An anomalously intense surface umklapp peak was observed, indicating the possible existence of a significant distortion of the surface structure from bulk termination. However, the LEED patterns observed from these crystals showed a  $(1 \times 1)$  bcc (110) structure, indicating that the two-dimensional periodicity of the bcc (110) planes is preserved. It was proposed that shear displacements might exist among the first few atomic planes of the K(110) surface [2]. The proposed surface shear displacement is

shown schematically in Fig. 1. The surface atoms (white) are all shifted laterally along the  $[1\bar{1}0]$  direction, preserving the two-dimensional periodicity of the bcc (110) planes. The surface atoms can be thought of as being displaced from the twofold bridge sites of the underlying layer toward the quasi-threefold hollow sites. Note that there are two equivalent directions,  $180^\circ$  apart, along which the shear displacement may occur, resulting in two directional surface domains with equal probabilities of formation.

Previous LEED  $I$ - $V$  profile investigations have concluded that this type of surface shear displacement does not exist for the clean bcc (110) surfaces of W, Mo, and Fe [3]. However, in a LEED study of the H/W(110) system, Chung, Ying, and Estrup [4] observed the loss of a mirror plane symmetry upon the adsorption of approximately a one-half monolayer of hydrogen while the two-dimensional periodicity of the LEED pattern remained unchanged. This was interpreted as evidence of one domain of a shear displacement along the  $[1\bar{1}0]$  direction among the W(110) surface planes, but no attempt was made to determine the magnitude of the shear displacement.

In this study of the K(110) surface, single-crystal K(110) samples were prepared *in situ* by evaporating potassium from a getter source onto a clean Ni(100) substrate kept at 160 K. The Ni substrate appeared slightly rippled, indicating the existence of steps. The clean Ni LEED spots were not split, so the step periodicity was greater than the coherence length of the incident electrons ( $\sim 100$  Å). The potassium films,  $\sim 1000$  Å thick,

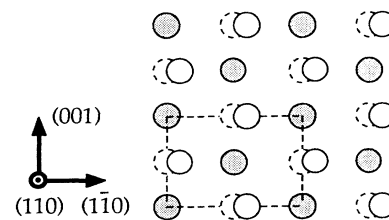


FIG. 1. Schematic of the proposed shear displacement structure of the K(110) surface. The surface atoms (white) are laterally displaced along the  $[1\bar{1}0]$  direction relative to the bulk.

were annealed to 270 K, then cooled to 25 K for the measurements. LEED patterns from these films showed no Ni spots and the K spots exhibited the twofold symmetric pattern of the bcc (110) structure. The lattice mismatch between the Ni substrate and the potassium is less than 1% along the potassium nearest-neighbor direction. Note that on a perfect fcc (100) substrate, there should be two equivalent orientations of bcc (110) layers with their  $[1\bar{1}0]$  directions aligned with the  $[010]$  and  $[001]$  directions of the substrate. Our observation of a single orientation of K(110) on the Ni(100) crystal is likely due to the steps on the Ni surface which break its fourfold symmetry and permit only one orientation to begin growing. Subsequent potassium layers formed epitaxially, producing the observed structure.

The experiment was performed in an ultrahigh-vacuum chamber with a base pressure of  $2.5 \times 10^{-11}$  mbar. Adsorption of contaminants on these K(110) films was characterized by high-resolution electron-energy-loss spectroscopy (HREELS) of the vibrational modes of the adsorbed species. A vibrational peak at 30 meV from atomic oxygen first appeared after approximately 45 min in ambient vacuum at 88 K. By exposing to  $O_2$ , this peak was equated with an exposure of less than 0.01 L of  $O_2$ . No other vibrational peaks were observed for energy losses of up to 480 meV. All of the LEED  $I$ - $V$  profiles used in this study were obtained during the first 40 min after film growth to minimize the effects of contamination.

To measure the diffraction spot intensities over a sufficient range of electron kinetic energies, the low Debye temperature of bulk potassium ( $\Theta_D = 100$  K) requires cooling the K(110) films with a liquid-helium cryostat. The LEED  $I$ - $V$  profiles were measured using reverse-view LEED optics controlled by a video data-acquisition system [5]. With this experimental apparatus and by cooling the K(110) sample to 25 K, the normal incidence  $I$ - $V$  profiles of 38 individual diffraction spots for the electron kinetic energy range 30 to 230 eV were measured. The  $I$ - $V$  profiles did not show any evidence (loss of a mirror plane symmetry) of the dominance of one directional domain of sheared structure. Therefore, the measured profiles of symmetrically equivalent spots were averaged to produce twelve profiles which were compared to calculations. This averaging of equivalent spot intensities improved the signal-to-noise ratio and reduced the effects of any small misalignments of the sample to normal incidence [6].

The atomic structure of the K(110) surface was determined by comparing the twelve experimental  $I$ - $V$  profiles with the results of dynamical LEED calculations for various structural models. The agreement between the experimental and calculated profiles was expressed in terms of the  $R_2$  reliability factor [7], which for perfect agreement equals zero. Thus, our structural determination of the K(110) surface is that specifically assumed structure which leads to the best agreement (smallest  $R_2$  value) be-

tween the experimental and calculated profiles.

The calculated LEED  $I$ - $V$  profiles were obtained using a dynamical multiple-scattering description of the electron scattering using computer codes based on the giant matrix inversion technique [8]. For each of the structural models investigated, the calculations were performed to full convergence using a sum of spatial lattice points within a circle of 50 Å for each atomic layer, eight atomic layers, and sixteen phase shifts at an incident electron energy of 220 eV.

In the structural models investigated, we considered shear displacements along the  $[1\bar{1}0]$  direction among the first three atomic planes of up to 0.8 Å, shear displacements along the  $[001]$  direction among the first two planes of up to 0.3 Å, and the interlayer relaxations normal to the surface among the first four atomic planes of up to  $\pm 10\%$  of the bulk value of 3.72 Å. Because of the observed symmetry in LEED, we only considered equal amounts of the directional domains of sheared structure.

Besides the structural parameters, the models included the customary nonstructural parameters: the scattering potential, the real and imaginary components of the optical potential, and the isotropic surface and bulk Debye temperatures. The nonstructural parameters were varied to determine the optimal values to use with the K(110) data. Variations of these parameters did not appreciably affect the values for the structural parameters.

Figure 2 shows the variation of the total  $R_2$  value versus  $\Delta s_{12}$ , the magnitude of the shear displacement between the first and second atomic K(110) planes. There is a clear and reasonably deep minimum of  $R_2 = 0.0411$  for a shear displacement of  $\Delta s_{12} = 0.23$  Å. This  $R_2$  minimum is on a par with that of other successful LEED studies of monatomic metal surfaces. With no shear displacements included, the minimum value of  $R_2$  reached was 25% higher than at the ultimate minimum. The

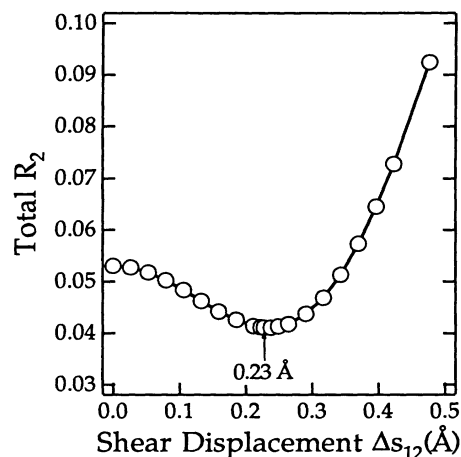


FIG. 2. Total  $R_2$  value vs the magnitude of the shear displacement  $\Delta s_{12}$  between the first and second K(110) surface planes along the  $[1\bar{1}0]$  direction.

TABLE I. Structural parameters for the optimum structure. The  $\Delta s_{ij}$  values correspond to shear displacements along the  $[1\bar{1}0]$  direction between adjacent layers. Negative values of the intraplanar relaxations  $\Delta d_{ij}$  correspond to contractions between adjacent surface planes.

$\Delta s_{12} = 0.23 \pm 0.04 \text{ \AA}$	$\Delta d_{12} = (-0.7 \pm 0.3)\%$
$\Delta s_{23} = 0.02 \pm 0.06 \text{ \AA}$	$\Delta d_{23} = (-0.7 \pm 0.4)\%$
	$\Delta d_{34} = (-0.5 \pm 0.6)\%$

shear displacement structure is further supported by the fact that the  $R_2$  values for each of the twelve individual profiles were reduced by including the shear displacement. The average of the shear displacements which minimized the individual  $R_2$  values was  $0.27 \pm 0.07 \text{ \AA}$ . Such consistency in the minima of the individual  $R_2$  values provides strong support for a shear displacement of the order of  $0.2 \text{ \AA}$  on the K(110) surface.

Four measured profiles are shown in Fig. 3 with the corresponding calculated profiles for the optimum structure which produced the minimum value of  $R_2$ . The calculated  $I$ - $V$  profiles of Fig. 3 correspond to a model surface structure with equal amounts of the two directional domains sheared in opposite directions. For each domain, the shear displacement between the first and second layers is  $\Delta s_{12} = 0.23 \pm 0.04 \text{ \AA}$  along  $[1\bar{1}0]$ , with a nearly zero shear in the same direction between the second and third layers. This value of  $\Delta s_{12}$  corresponds to 25% of the distance from the twofold bridge site to the quasi-threefold hollow site. The optimum structure also contains small interlayer relaxations normal to the surface among the first four atomic planes. Table I contains the structural parameters of the optimum structure. Investigations of deeper displacements or relaxations were prevented by the loss of sensitivity due to the short mean free path of the incident electrons. However, such deviations are expected to be quite small. The errors cited in Table I are based on judgements which take into account variations of  $R_2$  as the model parameters were adjusted.

At various stages of the iterative process which led to the final values of the model parameters, the possibility of a shear displacement along the  $[001]$  direction was considered. Within the uncertainty of the LEED analysis, no evidence was found for a component of the shear displacement along this direction. Thus, the consideration of a shear displacement along the  $[001]$  direction has provided more confidence that the reduction of the total  $R_2$  value is significant, and that the large shear displacement along the  $[1\bar{1}0]$  direction is physically sound.

An analogy for this new surface phase can be drawn from the bulk martensitic phase transitions of the alkali metals. The light alkalis transform from the bcc structure to the 9R structure when cooled below their transition temperatures (75 K for Li, 35 K for Na) [9]. These transitions have been attributed to the larger vibrational entropy of the bcc phase which stabilizes it at higher temperatures [10]. The heavy alkalis transform from the bcc

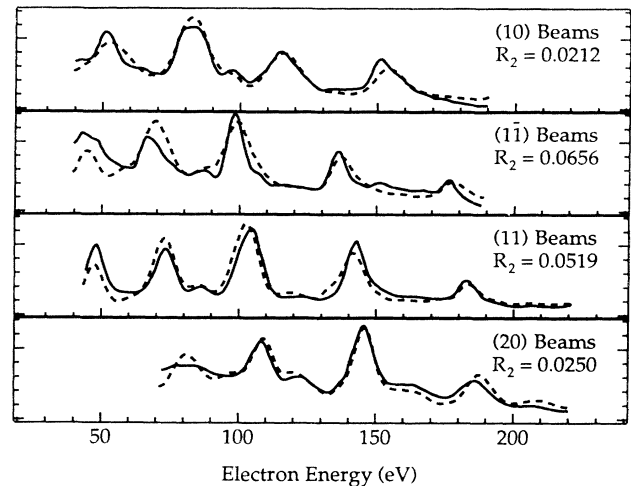


FIG. 3. Measured LEED  $I$ - $V$  profiles (solid lines) for four sets of diffraction spots and their corresponding calculated profiles (dashed lines) for the optimum structure. The labeling convention is such that the  $(n\bar{n})$  LEED beams are along the  $[1\bar{1}0]$  direction and the  $(nn)$  beams are along the  $[001]$  direction.

to the fcc structure when pressurized above their transition pressures (114 kbar for K, 70 kbar for Rb, 23 kbar for Cs) [11]. The driving forces of these transitions are less clear because they are dependent on the small energy differences at zero temperature between the various structures. But optical reflectivity measurements have found that these transitions are correlated with pressure-induced enhancements of the hybridization of the occupied  $s$  bands with the unoccupied  $d$  bands [11,12].

Although they originate from different physical processes, the atomistic motion descriptions of the bcc-to-9R transitions and the bcc-to-fcc transitions are quite similar. Both transitions can be described by shear displacements of the bcc (110) planes along the  $[1\bar{1}0]$  direction combined with intraplanar relaxations which change these planes into hexagonal-close-packed planes. The shear displacement of the surface K(110) plane detected in this work is analogous to these shear displacements of the bulk bcc (110) planes.

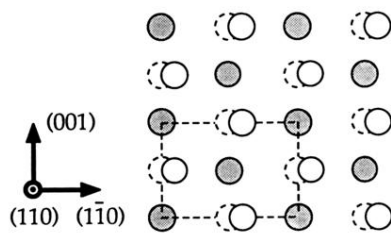
Although bulk potassium is not seen to transform for temperatures down to 5 K [9], Wilson and de Podesta have proposed that many of the low-temperature structural and electronic anomalies observed in potassium [13-15] may be due to formation of the martensitic phase in regions of the bulk under strain due to lattice defects [16]. The planar free surface of the K(110) crystal may provide the necessary defect strain fields or other changes of the free energy to nucleate the martensitic phase at the surface for conditions for which the bulk does not yet transform [17,18]. Such considerations led Clapp [17] in 1973 to suggest using LEED to detect the existence of martensitic precursors at crystal surfaces. The observation of the shear displacement of the K(110) surface has

relevance in determining the role of surfaces, grain boundaries, and defects in the nucleation of martensitic phases and in determining the important contributions to the free energy in driving these transitions.

In conclusion, a detailed LEED  $I$ - $V$  profile analysis has successfully determined that the clean K(110) surface exhibits a shear displacement structure. This surface shear displacement exhibits an atomistic similarity to the bulk martensitic phase transitions of the alkali metals. Future examinations of the clean K(110) surface using surface ion scattering at low temperatures would be most welcome as further proof of the shear displacement structure.

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- [1] S. Andersson, J. B. Pendry, and P. M. Echenique, *Surf. Sci.* **65**, 539 (1977); S. Å. Lindgren *et al.*, *J. Phys. C* **15**, 6285 (1982).
- [2] B. S. Itchkawitz, In-Whan Lyo, and E. W. Plummer, *Phys. Rev. B* **41**, 8075 (1990).
- [3] M. A. Van Hove and S. Y. Tong, *Surf. Sci.* **54**, 91 (1976); L. Morales de la Garza and L. J. Clark, *J. Phys. C* **14**, 5391 (1981); H. D. Shih *et al.*, *ibid.* **13**, 3801 (1980).
- [4] J. W. Chung, S. C. Ying, and P. J. Estrup, *Phys. Rev. Lett.* **56**, 749 (1986).
- [5] B. S. Itchkawitz, Ph.D. thesis, University of Pennsylvania, 1991 (unpublished).
- [6] H. L. Davis and J. R. Noonan, *Surf. Sci.* **115**, L75 (1982).
- [7] M. A. Van Hove, S. Y. Tong, and M. H. Elconin, *Surf. Sci.* **64**, 85 (1977).
- [8] J. B. Pendry, *Low Energy Electron Diffraction* (Academic, New York, 1974), p. 133.
- [9] H. G. Smith, *Phys. Rev. Lett.* **58**, 1228 (1987); R. Berliner *et al.*, *Phys. Rev. B* **40**, 12086 (1989).
- [10] S. Alexander and J. McTague, *Phys. Rev. Lett.* **41**, 702 (1978); J. R. Morris and R. J. Gooding, *ibid.* **65**, 1769 (1990); R. J. Gooding and J. A. Krumhansl, *Phys. Rev. B* **38**, 1695 (1988).
- [11] K. Takemura and K. Syassen, *Phys. Rev. B* **28**, 1193 (1983); K. Takemura, S. Minomura, and O. Shimomura, *Phys. Rev. Lett.* **49**, 1772 (1982); H. Tups, K. Takemura, and K. Syassen, *ibid.* **49**, 1776 (1982).
- [12] J. Yamashita, S. Wakoh, and S. Asano, *J. Phys. Soc. Jpn.* **27**, 1153 (1969); J. Yamashita and S. Asano, *ibid.* **29**, 264 (1970); S. G. Louie and M. L. Cohen, *Phys. Rev. B* **10**, 3237 (1974).
- [13] A. W. Overhauser, *Adv. Phys.* **27**, 343 (1978).
- [14] S. A. Werner, J. Eckert, and G. Shirane, *Phys. Rev. B* **21**, 581 (1980).
- [15] Q. Zhao *et al.* (to be published).
- [16] J. A. Wilson and M. de Podesta, *J. Phys. F* **16**, L121 (1986).
- [17] P. C. Clapp, *Phys. Status Solidi B* **57**, 561 (1973).
- [18] R. Stedman, *J. Phys. F* **6**, 2239 (1976).



**FIG. 1.** Schematic of the proposed shear displacement structure of the K(110) surface. The surface atoms (white) are laterally displaced along the  $[1\bar{1}0]$  direction relative to the bulk.