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ABSTRACT

A dynamical LEED analysis is presented of the (√3X√3)R30°
superlattice on the (111) surface of an α-Cu-Al alloy single
crystal with a bulk Al concentration of 16 at. %. This surface
ordering contrasts with the lack of long-range order in the
bulk. In the ordered surface the Al atoms are found to be sub-
stitutionally arranged within the topmost layer with (√3X√3)R30°
symmetry. No evidence for the ordering of Al in deeper layers is
detected by this analysis. The fcc-(111) stacking sequence is
maintained at the surface, and the surface atoms occupy positions
within ±0.05Å of bulk Cu lattice positions, i.e. no appreciable
top-layer spacing change and no mixed-layer buckling are
detected.

I. INTRODUCTION

The structure of alloy surfaces has only recently begun to be investigated by low-energy electron diffraction (LEED), and very few results have been published. Several groups however are embarked on the structural determination of different alloy surfaces [1,3]. The most advanced study appears to be that of NiAl (110) [3]. Other LEED analyses in progress concern the (111) and (100) surfaces of Cu₃Au [1], the (111), (100) and (110) surfaces of Ni₃Al [1] and the (100) surface of Pt₃Ti [2]. However, in these alloys the surface superlattices are directly related to the long-range order of the bulk alloy. By contrast, we have investigated an alloy surface which exhibits long-range order at the surface in the absence of long-range order in the bulk [4], namely α-Cu-Al. This surface is also under LEED investigation by Berning and Coleman [5].

The (111) surfaces of α-Cu-Al alloys with a bulk Al concentration of more than 9 at. % Al have been known for many years to exhibit a (√3X√3)R30° superlattice [6,7]. This surface structure has been shown to undergo a reversible (√3X√3)R30° to (1X1) phase transformation at 570 K on the (111) surface of a Cu-12.5 at. % Al alloy [8]. It has been suggested, without supporting evidence, that this superlattice is due to an ordered overlayer of Al atoms above the alloy surface [6]. This model was subsequently used to account for the changes in the copper-like surface-state observed in ultraviolet photoemission experiments on this alloy [9]. Recently, a preliminary low-energy electron diffraction intensity

analysis using only integral-order beam intensities arrived at a surface structure consistent with this aluminum overlayer model [5].

However, the $(\sqrt{3}X\sqrt{3})R30°$ superlattice phase also admits to another description based on the known properties of bulk Cu-Al alloys. The α-phase of Cu-Al is a substitutional alloy in which Al atoms occupy sites on a copper-like lattice [10]. Also, Cu-Al is a compound-forming system in which the heat of formation of α-Cu-Al is about -2 Kcal/mole [11]. Thus one may propose that the alloy surface is also substitutional, with the Al atoms substituting for copper atoms in an ordered manner in the surface with $(\sqrt{3}X\sqrt{3})R30°$ symmetry. In such a surface each Al atom could have from six to nine Cu nearest neighbors as opposed to at most three in the overlayer model. Furthermore, such a substitutionally ordered surface is consistent with the short-range order observed in bulk α-Cu-Al. X-ray diffuse scattering measurements have shown that Al-Al nearest neighbors are virtually nonexistent in the bulk [12], and that the arrangement of three Al atoms in a triangle in the (111) plane about a Cu atom is seven times more prevalent than statistically predicted [13]. The substitutional surface in which one-third of a monolayer of Al atoms is arranged with $(\sqrt{3}X\sqrt{3})R30°$ symmetry fulfills both of these short-range order criteria, in that there are no Al-Al nearest neighbors, and every Cu atom is surrounded by three Al atoms in the (111) plane.

Given these two and possibly other surface structural models, it is important to determine the actual structure of the alloy surface ·to properly interpret the phase transformation and electronic structure results. Also, the determination of this alloy surface structure is of special interest, as it represents one of the first detailed structure determinations of an alloy surface by LEED or by any other technique.

II. EXPERIMENTAL

The LEED experiments were conducted in an ultrahigh-vacuum system with a base pressure of 5×10^{-10} torr. The system was equipped with a quadrupole mass spectrometer, an off-axis electron gun for Auger electron spectroscopy (AES), and four-grid LEED optics. There were no exposed insulators in the vicinity of the crystal so that electrostatic fields would not deflect the LEED beams. Also, the system was enclosed within Helmholtz coils to neutralize magnetic fields. These coils were adjusted so that the specularly reflected LEED beam was not deflected significantly over the 20 to 300 volt energy range used for the LEED intensity-voltage (I-V) measurements.

The preparation of the copper-aluminum single crystal used in these experiments has been described previously [7]. The crystal was mounted on 0.012" tungsten wires which passed through a pair of holes spark machined through the crystal parallel to the surface. The sample was heated by passing current through the tungsten wires, and the temperature was measured both with a

3

chromel-alumel thermocouple spot welded into a cavity in the crystal and with an optical pyrometer. In addition to heating to 1200 K, the crystal could be cooled to 130 K by conduction to a pair of liquid nitrogen reservoirs.

The sample was mounted on a manipulator capable of independent azimuthal and polar angle rotations. The crystal surface was initially oriented with the (111) face perpendicular to the azimuthal rotation axis as determined by laser reflection from the optical surface, and the alignment was later adjusted by LEED observations. Normal incidence was determined by visual comparison of the symmetry related LEED beams. It was possible to see deviations from normal incidence of less than ±0.2° with this method. The accuracy of the orientation was confirmed by the close agreement among symmetry-related LEED I-V curves as shown in Fig. 1a. The off-normal incidence angles were set by rotating the crystal away from the experimental normal-incidence position using a scale inscribed on the manipulator.

The copper-aluminum crystal was cleaned by Ar ion bombardment at 500 eV. Surface composition was monitored by AES. After ion bombardment the clean crystal surface exhibited a diffuse (1X1) LEED pattern. Upon annealing, the ($\sqrt{3}$X$\sqrt{3}$)R30° pattern appeared and the surface concentration of Al, as determined by the low energy Cu-*MVV* and Al-*LVV* Auger lines, increased. Once the ($\sqrt{3}$X$\sqrt{3}$)R30° pattern had formed, the low energy Auger peaks did not change as the crystal was heated. At 570 K the (111) α-Cu-Al surface undergoes a reversible order-disorder

4

phase transformation to (1X1) symmetry [8]. Before each LEED I-V measurement the crystal was heated well above the phase transition temperature and then cooled in stages at lower temperatures according to a fixed schedule to insure reproducible surface ordering. After this procedure a sharp superlattice pattern was observed. An attempt was made to quench in the (1X1) structure by rapidly cooling the crystal from above the transition temperature. At our maximum cooling rate of -10 K/sec a well ordered (√3X√3)R30° pattern was still observed.

LEED I-V curves were recorded for the (√3X√3)R30° superlattice between 20 and 300 volts with the crystal cooled to ~150 K. Data were collected with the incident electron beam at normal incidence and also with the incident beam inclined 10 and 15 degrees toward the [1$\bar{1}$0] direction. The data were collected using a high-sensitivity vidicon camera to record the pattern on video tape for later analysis. The entire diffraction pattern was analyzed using a video digitizer interfaced to an LSI-11 microcomputer. Sixteen consecutive video frames at a given primary beam energy were summed to improve the signal-to-noise ratio, then an image recorded at zero beam voltage was subtracted to correct for the camera dark current and for stray light from the LEED screen and the filament. I-V curves were generated by a data reduction program that located diffracted beams in the digitized image, made local background corrections, and integrated the beam intensity [14].

Two independent sets of I-V curves were collected at each electron beam incidence angle. The crystal was sputter cleaned, annealed, and reoriented between the independent data sets. There is close agreement between the independent data sets as illustrated in Fig. 1b.

III. THEORY

The atomic scattering properties used in the LEED intensity calculations were assumed to be equal to those of bulk Cu and bulk Al. The scattering phase shifts were derived from Burdick's and Snow's atomic potentials for Cu and Al, respectively [15,16]. Well-established multiple-scattering calculation schemes were chosen [17]. The mixed coplanar or near-coplanar Cu-Al layers were treated by matrix inversion (the Reverse Scattering Perturbation scheme also was tried [17], but failed to converge). Layer stacking was performed with Renormalized Forward Scattering. For nonstructural parameters we chose: an initial muffin-tin zero of 10 eV, *a posteriori* adjusted to 8 eV; an imaginary part of the inner potential of 3.8 eV at 90 eV, proportional to $E^{1/3}$; and Debye temperatures of 335 K and 514 K for Cu and Al, respectively.

We have applied the same R-factors that were used in previous work, namely the five R-factors ROS, R1, R2, RRZJ, and RPE, as well as their average [18]. The structural search was conducted on the basis of the average R-factor, while we also quote some individual R-factors (the Zanazzi-Jona and Pendry R-factors) for the preferred structure.

6

IV. RESULTS AND DISCUSSION

The following four structural models were tested for the ($\sqrt{3}$X$\sqrt{3}$)R30° surface structure of the α-Cu-Al alloy.

1. One-third of a monolayer of Al located in both fcc and hcp hollow sites on pure Cu(111), with Cu-Al layer spacings of 1.787Å to 2.237Å in steps of 0.05Å.

2. One-third of a monolayer of Al located substitutionally within the top layer of fcc-Cu(111) (using a bulk Cu lattice constant), cf Fig. 2. The mixed top layer was given bucklings of 0.0Å, ±0.1Å, and ±0.2Å (i.e. Al atoms depressed below or raised above the top copper layer by the amounts indicated). Also, the layer spacing between the mixed top layer and the next pure Cu layer was varied from 1.887Å to 2.287Å in steps of 0.1Å.

3. As model 2, but with hcp termination of the fcc substrate, i.e. an ABACBACB... layer stacking.

4. As model 2, but with Al substitutionally incorporated into every other layer (i.e. in the 1st, 3rd, 5th, etc. layers from the surface) in a ($\sqrt{3}$X$\sqrt{3}$)R30° arrangement. The layer registries were chosen such that the fcc stacking and the three-fold and mirror symmetries of the pure Cu lattice were maintained, even though many other mutual mixed layer registries are possible which produce a lower overall symmetry.

None of the models tested assumed Al to be located in the second layer, in keeping with the bulk short-range order result that Al tends to avoid Al nearest neighbors [12]. Also, Auger

measurements of the surface composition favor a concentration profile with the second layer depleted in Al [19].

Normal-incidence data were used to test all above-mentioned models. Off-normal incidence data were used only to investigate model 2. R-factor comparisons clearly rule out models 1 (overlayer) and 3 (hcp termination). An overlayer model was favored by Berning and Coleman, using tentative deductions based on simplified LEED calculations in which a (1X1) structure was postulated, and only the specular beam intensities were compared to experiment [5]. Model 2 is the most satisfactory in our work, and corresponding R-factor contour plots are presented in Fig. 3. The best results lie within ±0.05Å of the bulk Cu lattice positions, with a slight tendency toward a small expansion of the top layer spacing by +0.05Å and a small inward buckling of the Al atoms by -0.025Å. We do not consider these tendencies to be significant. The larger Al metallic radius of 1.43Å compared to the Cu value of 1.28Å might suggest a top layer expansion as calculated, but more plausibly it would suggest an outward buckling of the Al, contrary to the calculation. The best R-factor values (averaged over all of the data) are: 0.218, 0.300, and 0.514 for the five R-factor average, the Zanazzi-Jona R-factor and the Pendry R-factor respectively. Theoretical and experimental I-V curves are shown in Fig. 4 for a structure close to the R-factor minimum.

Model 4 (Al in alternate layers) performed reasonably well, but clearly not as well as model 2. The minimum R-factor in-

creases from 0.19 to 0.24 (for the normal incidence data) upon the addition of ordered subsurface Al. This result is consistent with the fact that α-Cu-Al has only short range order in the bulk. The random mixing of a certain amount of Al in the near-surface layers could account for some of the discrepancy between the calculated and experimental I-V curves shown in Fig. 4. It is however more likely that structural refinements with the (√3X√3) R30° periodicity are needed to remove the discrepancy. Many other structural models of lower overall symmetry are of course possible. One such model, which is under consideration, would permit the Cu atoms in the topmost layer to be non-coplanar. However, we feel that, in light of the clear minima in the R-factor plots for model 2, we have already established the nature of the surface structure in its most important aspects. Namely, the structure is substitutional and close to a simple fcc-Cu(111) termination; any more complex model will represent a refinement of this result.

V. CONCLUSIONS

The ordered (√3X√3)R30° surface phase that forms on the (111) crystal face of α-Cu-16 at. % Al has been analyzed by LEED surface crystallography. The ordering in the surface occurs while the bulk phase remains disordered. The Al atoms occupy substitutional positions in bulk-like lattice sites within the top layer with (√3X√3)R30° symmetry. There is no evidence for ordering of Al in the subsurface, and there is no evidence for a significant top-layer spacing change or for mixed-layer

buckling. This surface structure is consistent with the short-range order in bulk α-Cu-Al.

ACKNOWLEDGEMENT

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Figure 1. Experimental I-V curves from the Cu-Al (111) surface at normal incidence, with the crystal at 150 K (curves are vertically offset for clarity):

a) I-V curves for the symmetry related (1,0), (0,-1) and (-1,1) diffraction beams;

b) I-V curves averaged among symmetrical beams but from two different runs. The crystal surface was sputter cleaned, annealed and reoriented between runs. Averaged curves for the (1,0) and the (1/3,1/3) beam sets are shown.

Figure 2. Definition of the structural parameters for the geometry of model 2; outward expansion, relative to the bulk spacing, of the topmost (substitutional Cu-Al) layer from the second (pure Cu) layer, and outward displacement of the Al atoms relative to the plane of the top layer Cu atoms.

Figure 3. Contour plots of the five R-factor average as a function of the structural parameters for model 2. Contour plots for both normal incidence and 15° off normal are shown.

Figure 4. Comparison between theoretical and experimental I-V
curves at normal incidence for the near-optimum geom-
etries of model 1 (a 1/3 monolayer Al overlayer on
bulk Cu) and model 2 (1/3 of a monolayer of Al substi-
tuted in the top layer of bulk Cu). R-factor analysis
shows significantly better agreement between model 2
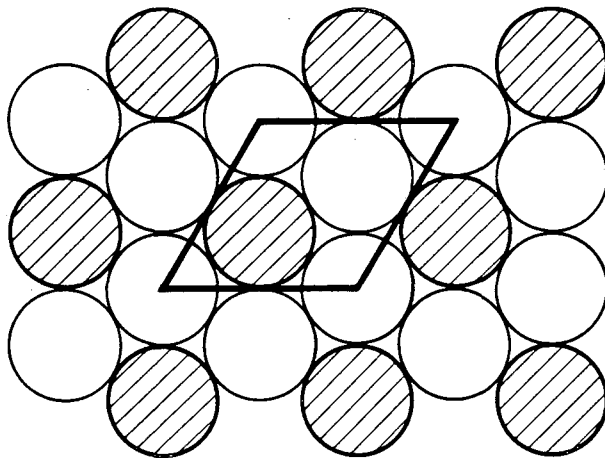and experiment.

α - Cu Al (III) - (√3 x √3) R30°
Experimental I-V Curves
θ = 0° T = 150°K

Beam voltage
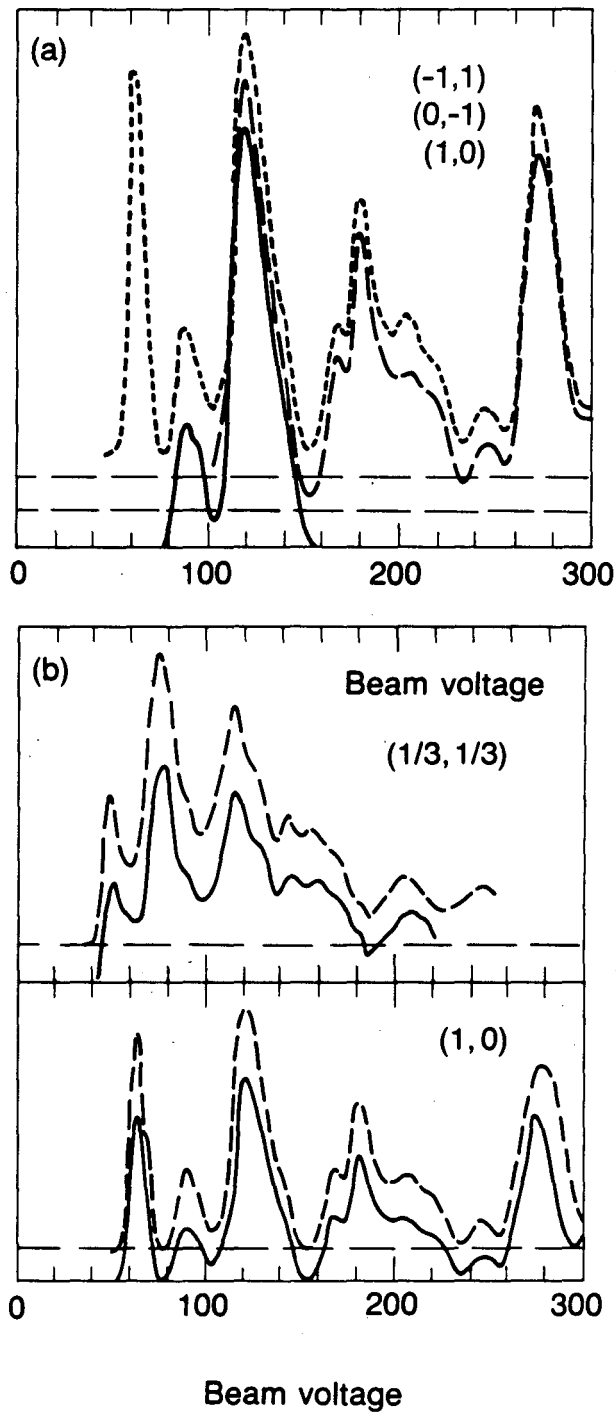
XBL 853-8026

Fig. 1

α - Cu Al (III) - ($\sqrt{3}$ x $\sqrt{3}$) R30°
Substitutional Al Model Parameters
Al Atom Shaded

Top view

Outward
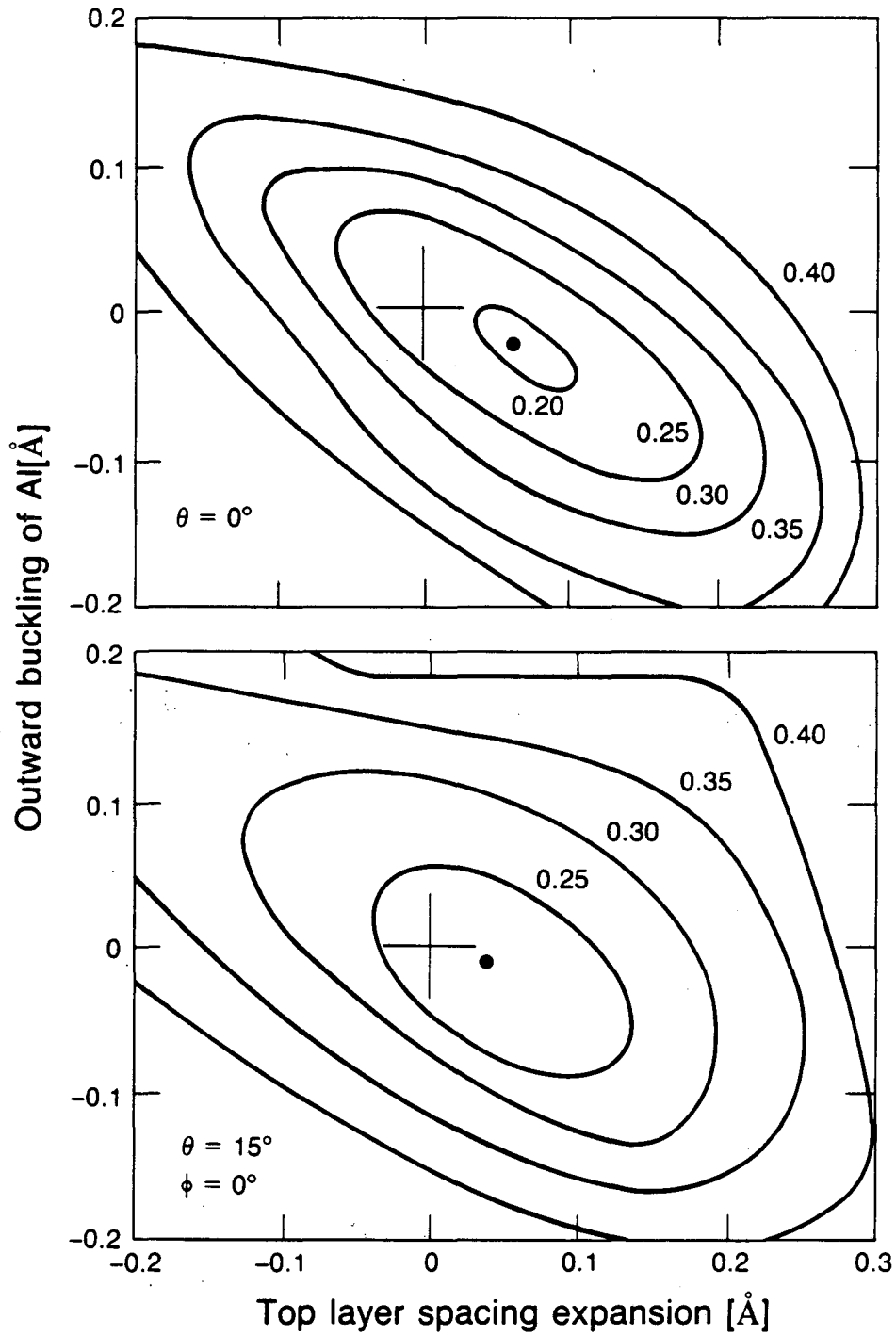displacement
of Al

Outward
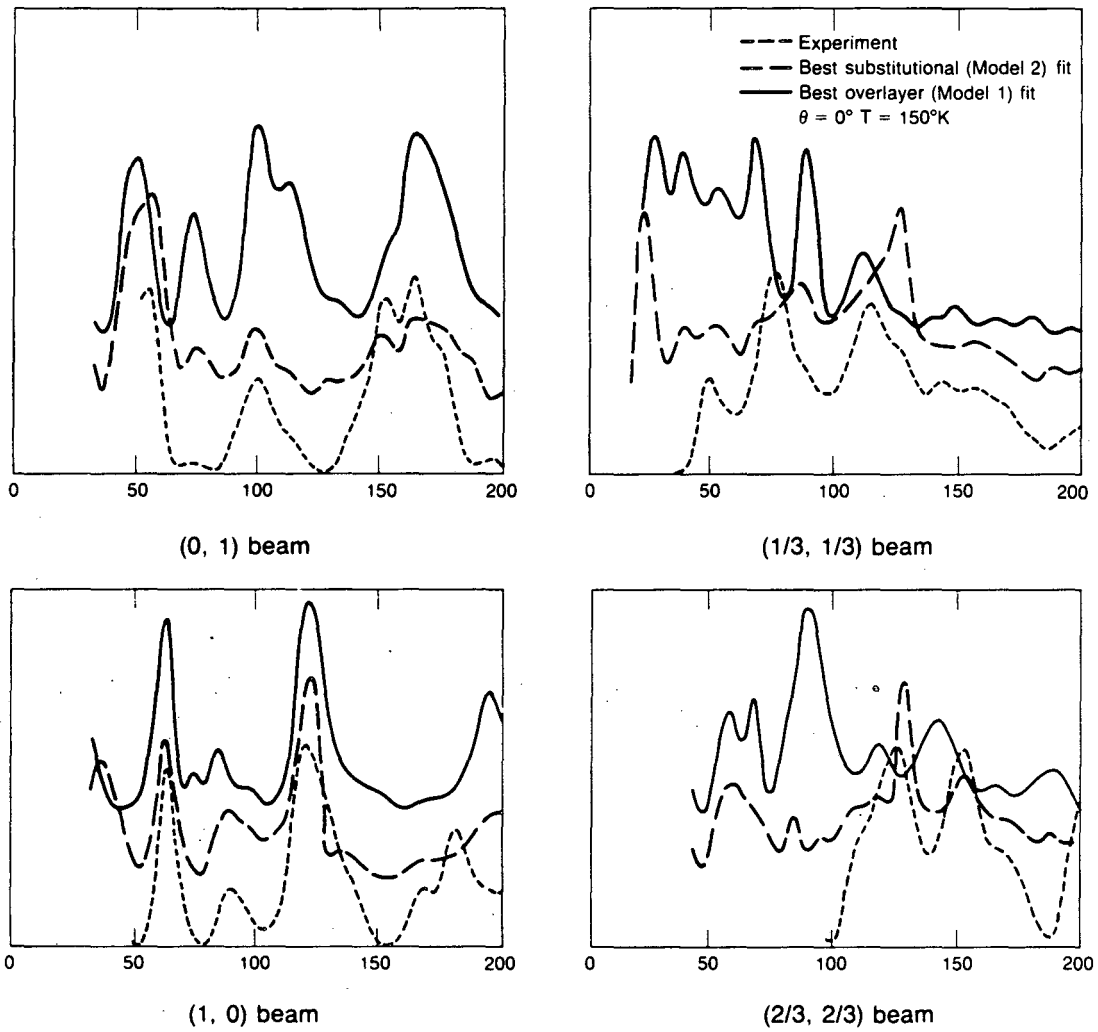expansion
of top layer
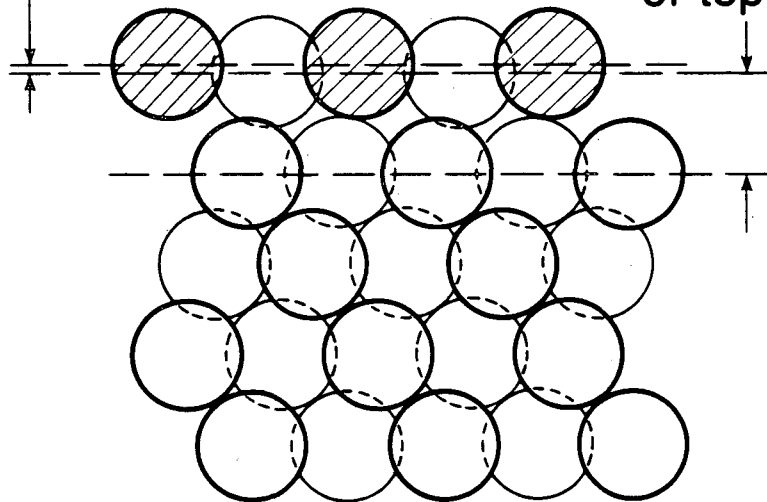
Side view

XBL 855-9971

Fig. 2

α - Cu Al (III) - ($\sqrt{3}$ x $\sqrt{3}$) R 30° Structure
R - factor contour plots

Fig. 3

XBL 853-8027

α - Cu Al (III) - ($\sqrt{3}$ x $\sqrt{3}$) R30° Structure
Comparison of Theory and Experiement

Legend:
- - - Experiment
— — Best substitutional (Model 2) fit
—— Best overlayer (Model 1) fit
θ = 0° T = 150°K

(0, 1) beam

(1/3, 1/3) beam

(1, 0) beam

(2/3, 2/3) beam

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Fig. 4

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